Electron probe microanalysis
of carbon containing steels
at a high spatial resolution

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Abstract

Whether it be inclusions, precipitates, segregation at grain boundaries, heterogeneous distribution of phases or constituents with complex morphologies, the development of new advanced high strength steels and manufacturing processes relies on the chemical characterization of their submicrometer features. More than any other alloying element, carbon plays a determining role, controlling the microstructure and the mechanical properties of these alloys. This work establishes acquisition and quantification strategies to measure the carbon concentration in low and high alloy steels by electron probe microanalysis at a high spatial resolution, circumventing many challenges associated with the measurement of this element. The optimal experimental conditions in terms of accuracy, precision and spatial resolution are determined using an optimization algorithm based on Monte Carlo simulations. Applications of the developed method for dual phase, transformation induced plasticity and twinning induced plasticity steels are presented.

Out of the challenges, the carbon contamination and the quantification using soft X-rays are further elaborated in order to better understand their factors and mechanisms. The influence of the sample preparation, anti-contamination devices and experimental parameters on the carbonaceous deposits produced by a focused electron beam is studied based on specifically designed experiments and numerical simulations. The results support the hypothesis of the sample as the predominant source of contaminants, the low absorption and desorption rate of organic molecules on/from the sample surface, and the existence of a diffusion limited regime under the typical experimental conditions of a modern electron microprobe equipped with oil-free vacuum pumps.

The quantification problems using soft X-rays, especially for the L3–M4,5 X-ray transition of first transition series metals, are investigated using Fe–Ni binary alloys. The effect of chemical bonding on the X-ray intensity is observed even for these metallic alloys. This work shows that the use of empirical mass attenuation coefficients and transition probability ratios, calculated from experimentally measured X-ray intensity vs. accelerating voltage curves, reduces the discrepancies between the experimental and calculated k-ratios, at least for this binary system.


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The submission of my doctoral thesis more or less coincides with the ten-year anniversary of my first scientific work, a poster presentation at the Microscopy & Microanalysis 2006 Meeting in Chicago entitled “Comparison of Monte Carlo simulated k-ratios using WinX-Ray and WinCasino with experimental results”. The following acknowledgements extend beyond those of this thesis and attempt to thank all people who helped, advised and supported me in the first decade of my scientific career.

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Abbreviations

AES  Auger electron spectroscopy
AFM  atom force microscope
AHS  advanced high strength
APF  area to peak factor
APT  atom probe tomography
BCC  body centred cubic
BCT  body centred tetragonal
BSE  backscatter electron
CBED  convergent electron beam diffraction
CCT  continuous cooling transformation
CDF  cumulative density function
CP   complex phase
DOI  digital object identifier
DP   dual phase
EBID  electron beam induced deposition
EBSID electron backscatter diffraction
ED   energy dispersive
EDS  energy dispersive spectroscopy
EELS electron energy loss spectroscopy
EPMA  electron probe microanalysis
FCC  face centred cubic
FIB  focused ion beam
FTIR  Fourier transform infrared spectroscopy
FWHM full width at half maximum
IQ   image quality
IUPAC  International Union of Pure and Applied Chemistry
KAM  kernel average misorientation
LOM  light optical microscope
MAC  mass attenuation coefficient
NEXAFS  near edge X-ray absorption fine structure
PDE  partial differential equation
PDF  probability density function
PE  primary electron
PHA  pulse height analyzer
RGA  residual gas analyzer
SDD  silicon drift detector
SE  secondary electron
SE1  secondary electron generated by backscatter electrons
SE2  secondary electron generated by primary electrons
SEM  scanning electron microscope
SFE  stacking fault energy
SIMS  secondary ion mass spectrometry
STEM  scanning transmission electron microscope
TEM  transmission electron microscope
TRIP  transformation induced plasticity
TTT  time temperature transformation
TWIP  twinning induced plasticity
UV  ultraviolet
WD  wavelength dispersive
WDS  wavelength dispersive spectroscopy
WEA  white etching area
WEC  white etching crack
XPS  X-ray photoelectron spectroscopy
# Contents

Abstract ii

Kurzfassung iii

Acknowledgements iv

Abbreviations vi

Contents viii

List of Tables x

List of Figures xi

1 Introduction 1

2 Literature review 3

2.1 Electron probe microanalysis 4

2.1.1 Electron optics 4

2.1.2 Electron- and photon-matter interactions 17

2.1.3 X-ray spectrometers 28

2.1.4 Quantification 38

2.2 Characterization of steel microstructure 44

2.2.1 Steel constituents 45

2.2.2 Quantification of carbon 49

2.3 Carbon contamination 53

2.3.1 Characteristics 54

2.3.2 Mechanisms 56

2.3.3 Factors 73

2.4 Quantification using soft X-rays 95

2.4.1 Problem statement 96

2.4.2 Challenges 98

2.4.3 Solutions 107

3 High resolution characterization of steel microstructure 109

3.1 Instrument characterization 110

3.1.1 Description of the instrument 110

3.1.2 Electron optics 112

3.1.3 Wavelength dispersive spectrometer 115

3.2 Acquisition and quantification strategies 126

3.2.1 Low alloy steels 127

3.2.2 High alloy steels 142

3.3 Validation 148
Contents

3.3.1 Accuracy ............................................. 148
3.3.2 Precision ............................................ 149
3.3.3 Spatial resolution .................................... 151
3.4 Optimization of analytical conditions .................. 153
3.4.1 Definition of quality metrics ......................... 155
3.4.2 Implementation ....................................... 168
3.4.3 Results ............................................... 169
3.4.4 Discussion ........................................... 174
3.5 Applications ............................................ 175
3.5.1 Low alloy steels ....................................... 175
3.5.2 High alloy steels ...................................... 181
3.5.3 Combination of EPMA and EBSD ..................... 191

4 Carbon contamination .................................... 199
4.1 Materials and methods .................................. 201
4.1.1 Instrument ........................................... 201
4.1.2 Material ............................................... 201
4.1.3 Sample preparation ................................... 202
4.1.4 Experiments .......................................... 203
4.1.5 Production of carbonaceous deposits ............... 203
4.1.6 Atom force microscope measurements ............... 204
4.1.7 Evaluation ............................................ 204
4.1.8 Simulations ........................................... 208
4.2 Results and discussion .................................. 212
4.2.1 Experiments .......................................... 212
4.2.2 Simulations ........................................... 222

5 Quantification using soft X-rays ......................... 237
5.1 Materials and methods .................................. 238
5.1.1 Sample preparation ................................... 238
5.1.2 Acquisition ........................................... 239
5.1.3 Fitting of wavelength dispersive spectra .......... 240
5.1.4 Evaluation ............................................ 241
5.1.5 Calculations of empirical mass attenuation coefficients 242
5.1.6 Oxidation measurements ............................... 243
5.2 Results and discussion .................................. 244
5.2.1 Experimental intensities ............................. 244
5.2.2 Area to peak factor ................................... 245
5.2.3 Experimental k-ratios ................................ 247
5.2.4 Calculated k-ratios ................................... 249
5.2.5 Quantification ........................................ 251
5.2.6 Calculation of empirical mass attenuation coefficients 252
5.2.7 Calculated k-ratios with the new mass attenuation coefficients 256
5.2.8 Calculated k-ratios with α factors ..................... 258
5.2.9 Oxidation ............................................. 261

6 Conclusion ............................................... 265

References .................................................... 275
# List of Tables

2.1 Notation of the atomic subshells .................................................. 21
2.2 Notation of common X-ray transitions ........................................... 22
2.3 Characteristics of steel constituents .............................................. 49
2.4 Identification criteria of steel constituents for EBSD, EPMA and LOM after nital etching. 50
2.5 Interfering high order X-ray reflections of major alloying elements in steel .......... 52
2.6 Summary of quantification results reported in the literature using a low accelerating voltage and the L$_3$–M$_4$–M$_5$ X-ray transitions ............................................ 97
2.7 Interfering X-ray reflections of major alloying elements in steel .................. 102
2.8 Summary of quantification results reported in the literature using a low accelerating voltage and the L$_3$–M$_1$–L$_2$–M$_1$ X-ray transitions ......................... 108

3.1 Configuration of the wavelength dispersive spectrometers .................... 111
3.2 Simulated lateral and depth resolution of different X-ray transitions ............ 133
3.3 Composition of four carbon containing reference steel alloys .................. 137
3.4 Influence of the mass attenuation coefficient on the carbon mass fraction ........ 139
3.5 Recipe for preparation of steel samples ............................................. 140
3.6 Composition of the steel samples used to construct the empirical equation ........ 144
3.7 Experimentally measured apparent carbon mass fractions and their uncertainty for the different reference steel alloys ........................................... 145
3.8 Proportionality constants calculated from the linear regression of the simulated and experimental net and background intensities .................................... 158
3.9 Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze only carbon ........................................... 170
3.10 Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze the alloying elements using their K–L$_{2,3}$ X-ray transition .................................................. 172
3.11 Accuracy, precision, depth resolution, lateral resolution and cost for the default experimental parameters .................................................. 173
3.12 Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze the alloying elements using their L$_3$–M$_{4,5}$ X-ray transition .................... 173
3.13 Average composition from the wet chemistry and EPMA measurements ........ 185

5.1 Mass attenuation coefficients for the Fe and Ni L$_3$–M$_{4,5}$ X-ray transitions in Fe and Ni from four MAC databases ........................................ 251
5.2 Empirically determined compound MACs for the Fe and Ni L$_3$–M$_{4,5}$ X-ray transitions based on both types of acquisition ........................................ 254
5.3 Elemental MACs for the Fe and Ni L$_3$–M$_{4,5}$ X-ray transitions in Fe and Ni from the two databases and newly determined MACs in this work ................................ 256
List of Figures

2.1 Calculated energy spread and emission current density as a function of the electric field strength and the emitter temperature. .................................................. 8
2.2 Electron traces in an electron column with an objective lens aperture, an objective lens, and a strong and weak condenser lens. .......................................................... 11
2.3 Electron traces after a weak and a strong objective lens. .................................................. 12
2.4 Chromatic aberration as a function of the accelerating voltage for different energy spreads. .... 14
2.5 Final beam diameter as a function of the divergence angle for different beam currents and accelerating voltages. .......................................................... 16
2.6 Optimal beam diameter as a function of the accelerating voltage for different beam currents. .... 17
2.7 Probability density function and cumulative distribution function for dice rolling. ............... 19
2.8 Sketches of electron interactions with matter: elastic scattering, inelastic scattering and Bremsstrahlung emission. .......................................................... 23
2.9 Sketch of the dominant photon interaction with matter, photoelectric absorption. ............... 27
2.10 Schematic representation of a silicon drift energy dispersive spectrometer. ....................... 31
2.11 Calculated $\phi(p_z)$ curve of the Mn K-L2,3 X-ray transition emitted from a pure Mn sample. .. 43
2.12 Iron-carbon phase diagram for a low alloy steel. .......................................................... 47
2.13 Time temperature transformation diagram for a low alloy steel. ..................................... 47
2.14 Different shapes of carbonaceous deposit obtained from a stationary focused electron beam. ... 56
2.15 Sticking coefficients as a function of the sample temperature. ......................................... 61
2.16 Calculated cracking cross sections for C2H2, C4H6, and C6H10 as a function of the electron energy and simulated electron energy distribution for tungsten. ....... 70
2.17 Contamination rate as a function of the atomic number, thermal conductivity and BSE yield as measured on pure substrates. .................................................. 75
2.18 Volume of carbonaceous deposits produced by scanning a beam over a area of 5μm x 5μm for one hour as a function of the pumping time. ............................................... 78
2.19 Thickness of a carbon thin film as a function of the temperature of the cold trap. ............... 80
2.20 Height of carbonaceous cones and thickness of carbonaceous films as a function of the irradiation time. .......................................................... 84
2.21 Height and volume of carbonaceous cones as a function of the irradiation time calculated for three reaction regimes. .................................................. 85
2.22 Profiles of contamination deposits calculated for different values of the replenishment parameter. 87
2.23 Profiles of contamination deposits calculated for different beam currents. ....................... 87
2.24 Shape of the contamination deposit as a function of the beam current density, beam current and beam area based on experimental measurements. ................... 90
2.25 Shape of the contamination deposit as a function of the beam current and beam area based on experimental measurements. ............................................... 90
2.26 Contamination rate as a function of the beam diameter and beam current. ....................... 91
2.27 Height, diameter and volume of conical contamination deposits produced by a focus beam as a function of the accelerating voltage. .................................................. 93
2.28 Depth resolution and net intensity of the Fe K-L2,3 and L3-M4,5 X-ray transition as a function of the accelerating voltage. .................................................. 96
2.29 Apparent Cr mass fraction as a function of the thickness of a carbon film deposited on a pure chromium substrate at an accelerating voltage of 5 kV. .................. 99
2.30 WD spectra acquired on pure reference materials of Cr, Mn, Fe, Co and Ni at 5 kV using a LDE1 and TAP dispersive element. .................................................. 101
2.31 Mass attenuation coefficient for Cr, Mn, Fe, Co and Ni samples as a function of the X-ray energy. 104
2.32 Mass attenuation coefficient for C, Si and Mo samples as a function of the X-ray energy. ....... 105

3.1 Assembly of the gas jet on the liquid nitrogen cold trap. .................................................. 112
3.2 Current stability over a period of 48 h. .......................................................... 113
3.3 Experimental procedure to determine the beam diameter from SE images. ....................... 114
3.4 Beam diameter as a function of the beam current and accelerating voltage. ....................... 116
3.5 WD spectra acquired around the C K-L2,3 X-ray transition on pure metallic samples of B, Si, Cr, Fe and Ni. .......................................................... 117
3.6 WD spectra acquired around the C K-L2,3 X-ray transition on Cr and Mn using different widths of the PHA window. .................................................. 119
3.7 ED Bremsstrahlung spectra simulated by Monte Carlo on different samples. ....................... 121
List of Figures

3.8 Calculated X-ray reflectivity distribution of the LDE2 multilayer and LiF dispersive element as a function of X-ray energy. .......................... 122
3.9 Theoretical WD spectra for B, Si, Cr, Fe and Ni samples. ............................................. 123
3.10 Experimental and simulated spectra around the K-L X-ray transitions obtained from pure Ni and 3 nickel silicides. ......................................................... 124
3.11 Relative error on the output count rate for different deviations of the time constant as a function of the output count rate. ............................. 125
3.12 Measured output count rate as a function of the output count rate for the C K-L3,2 X-rays. 126
3.13 Normalized output count rate as a function of the output count rate for the C K-L3,2 X-rays. 127
3.14 Simulated radial distributions of the BSE and the emitted C K-L3,2 X-rays. ................ 128
3.15 Experimental C K-L3,2 X-ray intensity along a 16-μm line scan across a DP steel sample. 129
3.16 Experimental C K-L3,2 X-ray intensity along 16-μm line scans measured on pure iron with and without anti-contamination device. ................................. 130
3.17 Experimental C K-L3,2 X-ray intensity along 16-μm line scans measured on pure iron with an oxygen jet. ................................................................. 135
3.18 Experimental C K-L3,2 X-ray intensity along 30-μm line scans measured on four reference steel alloys. 136
3.19 Simulated calibration curves using several reference materials with a carbon mass fraction less than 1%, and using only pure Fe and Fe3C. .............................. 137
3.20 Experimental C K-L3,2 X-ray intensity along 16-μm line scans measured on a flat polished and a nital etched sample. .................................................. 139
3.21 Comparison between the apparent and corrected carbon mass fractions as a function of the accelerating voltage and electron dose. ............................ 141
3.22 Comparison between the apparent and corrected carbon mass fractions as a function of the mean atomic number for the different reference steel alloys. ........ 142
3.23 Comparison between the apparent and corrected carbon mass fractions as a function of the carbon mass fraction along a 16-μm line scan acquired on a 0.64 mass % C reference steel sample. 143
3.24 Precision of carbon measurements for well-separated point and line scan acquisition. .... 151
3.25 Comparison between experimental and simulated line scan across a ferrite-martensite boundary. 152
3.26 Simulated ED spectrum around the Fe K-L3,2 peak for a pure iron sample. .................. 153
3.27 Simulated radial distributions of the BSE and the emitted C K-L3,2 X-rays. ................ 154
3.28 Comparison between experimental and simulated net and background intensities for Fe. .... 157
3.29 Relative precision of the C K-L3,2, Mn K-L3,2 and Mn L3-M4,5 X-ray transitions as a function of the accelerating voltage and electron dose. ............... 158
3.30 Comparison between experimental and simulated carbon distribution of a Mn–Mo DP steel sample. ........................................................................ 159
3.31 Depth resolution of the C K-L3,2, Fe K-L3,2, L3-M4,5 and L3-M1 X-ray transitions as a function of the accelerating voltage. ......................................... 160
3.32 Simulated depth and radial X-ray emission distribution of the C K-L2,3 X-ray transition at four accelerating voltages. ....................................... 161
3.33 Lateral resolution of the C K-L3,2, Fe K-L3,2 and Fe L3-M4,5 X-ray transitions as a function of the accelerating voltage for different beam currents. .... 162
3.34 Variation of the optimal experimental parameters and resulting quality metrics as a function of the carbon mass fraction. ........................................ 163
3.35 Comparison between experimental and simulated carbon distribution of a Mn–Mo DP steel sample. ........................................................................ 164
3.36 Simulated depth and radial X-ray emission distribution of the C K-L2,3 X-ray transition at four accelerating voltages. ....................................... 165
3.37 Variation of the optimal experimental parameters and resulting quality metrics as a function of the carbon mass fraction. ........................................ 166
3.38 Carbon, manganese, aluminum and silicon mass fraction along 30-μm line scan across TRIP steels produced with different holding periods in the bainite transformation stage. 167
3.39 Carbon, aluminum, manganese and iron mass fraction along a 2-mm line scan across an as-quenched TWIP steel before and after applying the corrections for high alloy steels. 168
3.40 Carbon, silicon and chromium mass fraction along a 16-μm line scan across three WEs. 169
3.41 Bright field STEM images of a low carbon content and high carbon content WEA. .......... 170
3.42 Example of the alignment and merging of EPMA and EBSD datasets. ......................... 171
3.43 Grain average IQ map for the separation between martensite and the other constituents. 172
3.44 KAM and C K-L3,2 X-ray intensity map of the remaining non-martensitic pixels. ........ 173
3.45 Identified steel constituents from the combination of EPMA and EBSD mappings. ........ 174
3.46 Precision of carbon measurements for mapping acquisition. ..................................... 175
3.47 Overlay of the ferrite-martensite boundary determined from the grain average IQ map on the C K-L3,2 X-ray intensity map of a martensite island. ............. 176
3.48 Sample holder used to hold the GaAs wafer pieces. ..................................................... 202
3.49 Profile of a typical AFM measurement of a carbonaceous ring. ................................ 203
3.50 Methodology to extract two-dimensional profiles from a carbonaceous ring and calculate critical dimensions. ................................................................. 204
3.51 Calculated cracking rate as a function of the radius. .................................................... 210
3.52 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces cleaned using different solutions. ......................................................... 211
List of Figures

4.6 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces with and without plasma cleaning...
4.7 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces after different pumping times inside the specimen chamber...
4.8 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces with and without a liquid nitrogen cold trap...
4.9 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces with and without a gas jet blowing O2 gas...
4.10 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces after different irradiation time...
4.11 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces using different beam currents...
4.12 Experimental C K–L2,3 intensity along 16µm line scans measured on GaAs at 15 kV and different beam currents.
4.13 Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces using different beam currents and accelerating voltages.
4.14 Simulated contamination profiles for different organic molecules as well as the corresponding cracking rate.
4.15 Critical dimensions of simulated contamination profiles as a function of the number of carbon atoms in the adsorbed organic molecules for different surface coverages.
4.16 Rate constant, extracted from simulated contamination profiles, as a function of the number of carbon atoms in the adsorbed organic molecules for different surface coverages.
4.17 Critical dimensions of simulated contamination profiles as a function of the surface coverage.
4.18 Critical dimensions of simulated contamination profiles as a function of the irradiation time.
4.19 Critical dimensions of simulated contamination profiles as a function of the irradiation time for different beam currents.
4.20 Simulated contamination profiles for different beam currents as well as the corresponding cracking rate.
4.21 Shape of the simulated contamination deposit as a function of the beam current and beam area.
4.22 Critical dimensions of simulated contamination profiles as a function of the beam current.
4.23 Critical dimensions of simulated contamination profiles as a function of the accelerating voltage for three beam currents.
4.24 Simulated contamination profiles for different accelerating voltages as well as the corresponding cracking rate.
4.25 Profile of the simulated beam of electrons.
4.26 Critical dimensions of simulated contamination profiles as a function of the accelerating voltage for three beam currents using a Gaussian beam profile with an exponential tail.

5.1 Fe–Ni phase diagram.
5.2 Example of the fitting procedure of a WD spectrum acquired on pure iron.
5.3 Experimental X-ray intensities as a function of the accelerating voltage acquired on Fe, Fe25Ni75, Fe50Ni50, Fe75Ni25 and Ni.
5.4 Area to peak factor as a function of the accelerating voltage for the Fe50Ni50 sample, and the Fe and Ni L3–M4,5 X-ray transitions.
5.5 Fitted Ni L3–M4,5, L2–M4 and satellite peaks from WD spectra.
5.6 Experimental k-ratios for the Fe and Ni L3–M4,5 X-ray transitions as a function of the accelerating voltage.
5.7 Experimental and calculated k-ratios for the Fe and Ni L3–M4,5 X-ray transitions as a function of the accelerating voltage comparing calculated k-ratios obtained from four intensity models.
5.8 Experimental and calculated k-ratios for the Fe and Ni L3–M4,5 X-ray transitions as a function of the accelerating voltage comparing calculated k-ratios obtained from four MAC databases.
5.9 Relative error on the Fe and Ni concentrations after quantification.
5.10 Experimental and calculated X-ray intensities as a function of the accelerating voltage acquired on Fe, Fe25Ni75, Fe50Ni50, Fe75Ni25 and Ni.
5.11 Experimental and calculated X-ray intensities as a function of the accelerating voltage for the Fe and Ni L3–M4,5 X-ray transition, and two MAC databases.
5.12 Empirically determined compound MACs for the Fe and Ni L3–M4,5 X-ray transitions as a function of Fe mass fraction.
5.13 Experimental and calculated k-ratios as a function of the accelerating voltage. Calculated intensities using different MACs, including those experimentally determined in this work.
5.14 Experimental and calculated k-ratios as a function of the accelerating voltage. Calculated intensities using the MACs and α factors experimentally determined in this work.
5.15 α factors for the Fe and Ni L3–M4,5 X-ray transitions and both acquisition methods as a function of the Fe mass fraction.
5.16 Thickness of the native oxide layer as a function of the Fe mass fraction.
Introduction

With a yearly production of over 1.6 Gt, steel represent 26% of the ferrous alloys (steel, iron and ferro-alloys), 25% of the metal, and 7% of the mineral world production in 2014 [27, 59]. It is the 5th most produced mineral commodity based on the British Geological Survey [59]. Besides historical and economical factors, it is the desirable, adaptable properties of steel, expressed in over 3500 different grades [18, 410], that explain its omnipresence in modern society, as elegantly articulated by the eponym of the steel constituent bainite, Edgar C. Bain [20]:

It is *allotropy* in iron, however, and its attendant circumstances, particularly with reference to carbon solubility, which makes possible the unparalleled range of properties which are encompassed by steels covering the usual range of carbon content; for allotropy is retained in the presence of considerable carbon and other elements, and thereby the capacity for advantageous heat-treatment comes into play.

There is no better example of this polymorphism than advanced high strength [AHS] steels with their complex, multiphase microstructure and superior combination of strength and ductility [352]. Since the 1970’s, advancements in material science and production technology have led to the development of carefully engineered thermomechanical processes and the invention of new steel grades tailored to specific applications [285, 325]. As the second largest market [7], the automotive industry has propelled the research and production of AHS steels, such as dual phase [DP], complex phase [CP] and transformation induced plasticity [TRIP] steels. They have replaced traditional steel grades in automobile chassis, from an average use of 9.5% in 2007 to 34.8% in 2015, on a per mass basis [186]. Behind this material revolution is the quest to curb carbon emissions from transportation vehicles by reducing their weight [117]. Parts manufactured with AHS steels can meet the same structural design criteria (strength, energy absorption, stiffness, etc.), while being thinner and consequently lighter.

These attractive properties of AHS steel come in large part from their heterogeneous microstructure, acting as a self-subsistent composite material. However, as noted by Rashid [285] for DP steels, it is not the heterogeneity alone that gives these properties, but the distribution, morphology, chemical composition of the constituting phases:

The various developments made it clear that a dual phase microstructure by itself did not automatically guarantee good formability, but that the objective of good formability with high strength can be accomplished by proper control of steel composition and process variables.
In other words, the development of AHS steels hinges on the ability to characterize their microstructure in order to understand their mechanical properties, better control their manufacturing processes and predict their life cycle. With the growing complexity of the microstructure consisting of more numerous and smaller phases, a detailed characterization necessitates a spatial resolution that only electron microscopy can achieve, and microstructural information beyond simple morphological descriptions, as referred in the preceding citation.

A well-established characterization technique for steels is electron probe microanalysis [EPMA], performed in a scanning electron microscope [SEM] or electron microprobe. It has the unique advantage to provide accurate, local, quantitative chemical information on the micrometer to nanometer scale, while allowing the investigation of a representative sampling area (millimeter range). This allows to directly relate the chemical information to the microstructure. With their improved electron optics and analytical potential, new generation electron microprobes satisfy the characterization requirements of AHS steels for accurate chemical measurements at a high spatial resolution.

Since their introduction, one decade ago, Schottky emitter electron microprobes have been used in a wide range of applications outside steel metallurgy from chemical characterization of micro-meteoroids captured on the International Space Station [240] to partitioning analysis of alloying elements in a cobalt-base superalloy [317]. A literature review on publications using this type of instrument [256] however concluded that very few papers reported quantitative analyses of sub-micrometer features or often neglected the challenges associated with this type of analyses [25, 35, 223, 235, 271].

It is the guiding line, ligne directrice, Leitlinie of this thesis to assess, study and overcome these challenges to extend the analytical capabilities of EPMA, with a profound focus on the characterization of modern steel alloys. Three topics are discussed, starting with high resolution characterization of steel microstructures in Chap. 3. A particular emphasis is conferred to the measurement of carbon, the element that "influences the properties of iron more profoundly than any other and often more usefully" according to Bain [20] and is arguably one of the most challenging element to measure by EPMA. Building on the scientific knowledge of the last three decades reviewed in §2.2, Chap. 3 presents, validates, optimizes and applies improved acquisition and quantification strategies to measure the elemental distribution of multiphase steels at a high spatial resolution. Chapters 4 and 5 explore two remaining challenges of EPMA characterization of steel, or more generally any material analyzed at low accelerating voltages: the carbon contamination and the quantification using soft X-rays. As an attempt to demystify their root causes, factors and mechanisms, fundamental experimental and analytical research on these topics was undertaken, starting with in-depth reviews of the literature in §2.3 and 2.4. Before diving into these three topics, §2.1 offers a contemporary description of the electron probe microanalysis technique, based on the latest electron emitter, spectrometers, and physical interaction simulation models.
In the early 1950’s, the combination of the groundbreaking work on electron microscopy by Ruska and Knoll [308], Ardenne [14] and Hillier [146], the discovery of X-ray radiations by Röntgen [307], the innovations in crystal diffraction spectrometers by Bragg and Bragg [52], Johann [172] and Johansson [173] and the advancement in X-ray spectroscopy by Moseley [231] and Siegbahn [328] resulted in the invention of the electron microprobe and a new analytical method by Castaing during his Ph.D. thesis under the supervision of Guinier [71, 143, 288]. As summarized by Heinrich [143], “Castaing’s brilliant contribution was the skillful combination of known principles in a device which fulfilled an entirely new function”. This new function is two-fold: “to qualitatively determine and quantitatively measure the elemental composition of solid materials [...] on a spatial scale of approximately one micrometer” using characteristic X-rays produced by a focused electron beam [165]. This definition, specified in the ISO 23833:2012(E) Microbeam analysis — electron probe microanalysis (EPMA) — vocabulary [165], describes the technique, nowadays known as EPMA. Although the principles were first described in a patent by Hillier [146], Castaing [70] “laid the foundations of the theory and practice” of EPMA, which are still used today [288]. Following the need to characterize increasingly more complex materials, instrumental and theoretical advancements have built on the idea of Castaing and improved the sensitivity, resolution and applicability of EPMA.

The term “electron probe microanalysis”, “electron microprobe analysis”, “microbeam analysis”, “electron probe X-ray microanalysis”, “electron microprobe analyzer” or “electron probe microanalyzer” are often interchangeably used in the literature. To avoid any confusion, in this work, EPMA always refers to the analytical technique defined above and its quantitative nature is implied, unless otherwise specified. As qualitative EPMA, the determination of which elements are present, is a prerequisite for quantitative EPMA, it is also implicitly discussed. EPMA can be equally employed in various electron microscopes (i.e. electron microprobes, SEM, transmission electron microscope [TEM]) and using various X-ray spectrometers (energy dispersive spectroscopy [EDS] and/or wavelength dispersive spectroscopy [WDS]). The literature review focuses on the experimental conditions typically found in electron microprobes and SEMs. Both X-ray spectrometers are reviewed.

Another source of confusion is the difference between electron microprobes and SEMs. As designed by Castaing and first commercialized in 1956 [71], the electron microprobe was a fixed (non-scanning) electron beam microscope dedicated for EPMA of solid samples using at least one wavelength dispersive [WD] spectrometer and typically equipped with an integrated optical microscope to adjust the focal point. Since the commercialization of the first SEM in 1965 (although initially developed by Ardenne [14] in 1938) and first scanning electron microprobes ( Cameca Camebax and JEOL JXA-3) [71], both types of instrument share many similarities: range of accelerating voltages (1 to 40 kV), type of electron emitters, vacuum conditions, sample
geometries (solid, 1 to 3 cm in size), stage control, etc. Historically, the determining difference was the type of X-ray spectrometers attached to the instrument: WD for electron microprobes and energy dispersive [ED] for SEM. This difference is visually assessed by the presence of a specially designed specimen chamber to accommodate up to five WD spectrometers. This distinction is however less clear nowadays with electron microprobes equipped with ED spectrometers and SEMs with parallel or focusing beam WD spectrometers. A more actual description of modern microprobes is probably summarized by the expression “dedicated for EPMA”, indicating a deliberated design of an instrument to achieve accurate and precision quantitative analyses.

Apart from the principles of EPMA (§2.1), this chapter reviews the current knowledge on three other topics which will be further elaborated in this thesis: (1) the characterization of steel microstructure by EPMA (§2.2), (2) the phenomenon of contamination (§2.3), and (3) the quantification using soft X-rays (§2.4).

2.1 Electron probe microanalysis

Dissecting the definition of EPMA as stated in ISO norm, this analytical technique consists in four key characteristics: (1) the irradiation of a sample by a focused electron beam, (2) the generation of characteristic X-rays inside the sample, (3) the detection of emitted X-rays and (4) the conversion of X-ray intensities to a composition. A section is dedicated to review each of these characteristics. The electron emitters, magnetic lenses and their aberrations are discussed in §2.1.1. §2.1.2 covers the electron-matter interactions leading to the emission of X-rays. The different types of spectrometer used in electron microscopy to detect X-rays are explained in §2.1.3. Finally, §2.1.4 details the quantification principles to transform X-ray intensities to a composition.

2.1.1 Electron optics

An electron column is designed to produce a beam of electrons and accelerate them towards the sample. This task can be divided into four sequential steps: (1) the emission of electrons in vacuum from a cathode, (2) the demagnification of the electron beam source by a series of convergent magnetic lenses (one to three condenser lenses and an objective lens) and apertures, (3) the correction of astigmatism by the stigmator, and (4) the deflection of the electron beam by the scan coils to produce an image or irradiated a specific point on the sample [124, 292]. Each electron microprobe or SEM has its own specific arrangement of these components, a closer attention is placed on the main electron microscope used in this work, an electron microprobe, JEOL JXA-8530F (JEOL Ltd., Akishima, Tokyo, Japan), installed in 2011. From top to bottom, it consists of a Schottky emitter (W(100) with a ZrO coating), a suppressor electrode, an extracting anode, an accelerating anode, two condenser lenses, a gun valve, an objective aperture, an aperture angle control lens, a Faraday cup, an integrated light optical microscope, a stigmator, scan coils and an objective lens. The main components are reviewed in this section.
2.1. Electron probe microanalysis

Emitter

Starting from the emitter, three main categories are currently available for electron microscopes: thermionic, Schottky and field emission [292]. They differ from the physical principle used to lower the potential barrier at the solid-vacuum interface in order for electrons to leave the solid surface into the vacuum. The magnitude of the potential barrier at 0 K is a characteristic material property known as the work function \( \phi_0 \). Thermionic emission rely on increasing the temperature of the emitter (e.g. W filament or LaB\(_6\) crystal), whereas field emission is achieved by electron tunnelling due to a strong electric field created from a sharp emitter tip (radius of \(0.1 \mu\text{m}\)) and an applied electrical potential between the tip and the first anode [292]. For thermionic emission, the emission current density \( j_C \) (in A m\(^{-2}\)) is defined by the Richardson law and depends on the cathode temperature \( T_C \) (in K) and its work function \( \phi_C \) (in J):

\[
j_C = \frac{4\pi e m_e k_B^2}{h^3} T_C^2 \exp \left( \frac{-\phi_C}{k_B T_C} \right), \tag{2.1}\]

where \( e \) is the elementary charge \((1.602 \times 10^{-19} \text{C})\), \( m_e \), the electron mass \((9.109 \times 10^{-31} \text{kg})\), \( k_B \), the Boltzmann constant \((1.38 \times 10^{-23} \text{JK}^{-1})\), and \( h \), the Planck constant \((6.626 \times 10^{-34} \text{Js}^{-1})\).

Popularized in the 1980’s for wafer inspection in the semiconductor industry [248], Schottky or field enhanced thermionic emission combines the principles of thermionic and field emission with additional reduction of the work function by a surface catalytic and crystallographic effect. Schottky emitters are made of a single crystal tungsten tip with a radius between 0.1 to 1.0 \( \mu\text{m} \) with a reservoir of ZrO\(_x\) approximately 500 \( \mu\text{m} \) away from the tip [58, 292, 349]. They can be operated between 300 to 1800 K, but typically around 1700 to 1800 K, in a vacuum of \(10^{-6}\) to \(10^{-7} \text{Pa} \) [58, 349, 404]. At 1800 K the thermal energy is not high enough to obtain an appreciable electron emission, 1 A m\(^{-2}\) using Eq. 2.1 and a work function of 4.5 eV. For comparison, at a normal operating temperature of 2700 K for thermionic emission [404], a tungsten filament generates a current density of \(3.5 \times 10^4 \text{A m}^{-2}\). Nonetheless, these high temperatures allow the surface diffusion of zirconium and oxygen from the reservoir towards the tip surfaces [58]. The atomic coverage preferentially reduces the work function of \{100\} crystallographic planes of the W tip from 4.5 to approximately 2.9 eV [58, 292, 349, 404]. To maximize the emission from the \{100\} planes, the tip is usually shaped as an octagonal pyramid with faces alternating between \{100\} and \{110\} planes [58]. Almost all electron emission occurs on the \{100\} planes, emission from other crystallographic planes is negligible [58]. Studies have determined “that both the Zr coverage and the Zr/O ratio are critical in establishing the minimum work function” [349]. Without any applied electrical field, the work function remains relatively high, still higher than the one of LaB\(_6\) (2.75 eV), and the emission current density low, \(3 \times 10^4 \text{A m}^{-2}\ (\phi = 2.9 \text{eV})\), still lower than a thermionic tungsten filament.

The Schottky effect is the further reduction of the work function by an applied electric field as defined by

\[
\phi_C = \phi_0 - \sqrt{\frac{e^3 F}{4\pi \epsilon_0}}, \tag{2.2}
\]
where $\phi_0$ is the initial work function of the cathode material, $F$, the electric field strength (in V m$^{-1}$), and $\epsilon_0$, the electric constant or vacuum permittivity ($8.854 \times 10^{-12}$ F m$^{-1}$). With a field strength of $5 \times 10^8$ V m$^{-1}$ [349], the work function is reduced to 2.05 eV and the emission current density jumps to $7 \times 10^6$ A m$^{-2}$ using Eq. 2.1, two orders of magnitude larger than without an electric field.

The use of Eq. 2.1 and 2.2 to calculate the emission current density is however not completely accurate for two reasons. First, the strength of the electric field observed on the emitter facets depends on the tip geometry and the distance between the emitter and the anode. Both quantities are usually unknown. Swanson and Schwind [349] and Bronsgeest [58] introduced a field factor ($\beta$) to express the field strength as a function of the measurable extraction voltage, $V_E$: $F = \beta V_E$. Secondly, the magnitude of the electric field used in Schottky emitter electron microscopes is high enough to cause tunnelling of electrons. This is referred to as the extended Schottky emission, where the electron emission based on the Schottky effect is further enhanced by field emission [58, 349, 360]. The contribution can be evaluated using a dimensionless parameter, $q$,

$$q = \left( \frac{h (4\pi\epsilon_0e)^{1/4}}{2\pi^2m_e^{1/2}k_B} \right) \left( \frac{F^{3/4}}{T} \right),$$

(2.3)

and the emission current density for the extended Schottky emission, $j'_C$, becomes

$$j'_C = j_C \frac{\pi q}{\sin(\pi q)},$$

(2.4)

where $j_C$ is calculated using Eq. 2.1 and 2.2 [58, 349]. Eq. 2.4 is only accurate up to $q = 0.7$ [58]. The effect of field emission are noticeable for $q > 0.3$. For the previous example with an electric field strength of $5 \times 10^8$ V m$^{-1}$, $q$ is equal to 0.31, and increases the emission current density by 17%.

To characterize an electron emitter, the emission current density is not directly used, but in relation with the cross-sectional area of the beam source and the angular spread of the electrons. This quantity, known as the brightness ($B$), is an important characteristic of an electron gun as it stays constant throughout an optical system, invariably of the electron lenses and apertures [124, 292, 369]. As point out by Kruit et al. [198], the electron beam can be accelerated or decelerated in the electron optics. The true immutable quantity is therefore the reduced brightness, $B_r$ (in A m$^{-2}$ sr$^{-1}$ V$^{-1}$), defined as the “current $I$ per unit area $\delta A$ into a solid angle unit $\delta \Omega$ divided by the electron acceleration voltage $E_0$” [198]:

$$B_r = \frac{(\delta I_p)}{(\delta A)(\delta \Omega)E_0}.$$

(2.5)

Two other distinctive parameters of an electron emitter are its energy spread, the energy distribution of the electrons in the beam, and its current stability, the variation of the beam current as a function of time. All three characteristics are reviewed in the next paragraphs.
2.1. Electron probe microanalysis

**Reduced brightness** As the reduced brightness is a constant value for an electron optics system, it can be calculated either at the emitter or at the sample. Experimentally, the reduced brightness is defined as:

\[
B_r = \frac{4I_p}{\pi^2\alpha^2 d^2 E_0}, \tag{2.6}
\]

where \(I_p\) and \(d\) are respectively the beam current and diameter measured after an aperture with a divergence angle \(\alpha\). \(E_0\) is the accelerating voltage of the electrons in the beam. In this equation, the solid angle \(\Omega\) was approximated using the small angle approximation: \(\Omega = 2\pi(1 - \cos \alpha) \approx \pi\alpha^2\).

As lens aberrations influence the diameter of the beam irradiating the sample (§2.1.1), the reduced brightness is usually evaluated using the current density and virtual source diameter of the emitter. Bronsgeest [58] derived an equation for the reduced brightness of Schottky emitters:

\[
B_r = \frac{e}{(\ln 2)\pi k_B} \frac{j_{C}'}{T_C}. \tag{2.7}
\]

This derivation gives the interesting result that the reduced brightness is independent of the virtual source diameter, the aperture angle and the tip radius. Using the emission current density previously calculated \((F = 5 \times 10^8 \text{V m}^{-1}, \phi_C = 2.9 \text{eV}, T_C = 1800 \text{K})\), a reduced brightness of \(2.4 \times 10^7 \text{A m}^{-2} \text{sr}^{-1} \text{V}^{-1}\) is obtained. This falls in the range of the expected reduced brightness for Schottky emitters, \(10^7\) to \(10^8 \text{A m}^{-2} \text{sr}^{-1} \text{V}^{-1}\) [124, 292, 349, 404].

**Energy spread** Ideally, all electrons in the electron beam should have the same energy. This is critical to minimize chromatic aberrations (§2.1.1). For all three types of emitters, the emission probability of an electron does not follow a Dirac delta function, but a distribution around the extraction voltage (and around the accelerating voltage after the accelerating anode). Generally, thermionic emission has the broadest energy distribution \((\Delta E_0 = 0.5 \text{ to } 3 \text{V [292, 404]})\), while one of the major advantages of field emission is its narrow energy spread \((\Delta E_0 = 0.2 \text{ to } 0.3 \text{V [292, 404]})\). As for the current density and reduced brightness, Schottky emission results in an intermediate energy spread \((\Delta E_0 = 0.4 \text{ to } 0.7 \text{V [292, 349, 404]})\), which also depends on the extraction voltage and the emitter temperature. Bronsgeest [58] explained the energy distribution as follow: “for energies below the barrier peak [i.e. the work function reduced by Schottky effect] the occupation of electron energy levels inside the metal is high, but the transmission probability low, while for energies above the barrier the escape probability is high, but the occupation of the energy levels inside the metal low.” Swanson and Schwind [349] reported an analytical equation to describe the extended Schottky emission current density, \(j_{C}'\), as a function of energy, \(E\):

\[
j_{C}'(E) = E_F + \phi_C - \frac{j_C q}{k_B T} \ln \left[ 1 + \exp \left( \frac{E}{qk_BT} \right) \right], \tag{2.8}
\]
where $E_F$ is the Fermi energy, and $j_C$, $\phi_C$ and $q$ are respectively calculated using Eq. 2.1, 2.2 and 2.3. The influence of the electric field strength and emitter temperature on the energy spread is illustrated in Fig. 2.1. The energy spread is calculated as the full width at half maximum [FWHM] of the energy distribution obtained from Eq. 2.8. The energy spread can be reduced by decreasing the electric field or temperature, but at the expense of the reduced brightness. As Eq. 2.4 and 2.8 are only valid for $q < 0.7$, calculations for the conditions used for field emission microscopes (a high electric field and a low temperature) are not possible.

**Current stability** With its highest reduced brightness and narrowest energy spread, the emitter based on field emission would appear to be the best type for electron microscopy. This technology has however one big downside: the current stability. Its emission current approximately fluctuates by 5 % h$^{-1}$ [124, 404], and even more before or after flashing, a required conditioning process to remove adsorbed contaminants ($O_2$, $H_2$, $H_2O$) on the emitter surface [124]. These contaminants also affect Schottky emitters, but to a lesser extent. The high emitter temperature in combination with high vacuum pumps (ion pumps) reduces the absorption of residual gases [349]. In general, the current stability of Schottky emitters, as well as thermionic emitters, is at least 5 times better than cold field emitters [124, 404]. At a low electric field strength, the phenomenon of plane collapse or collapsing rings causes large instabilities in the emission current ($\approx 70\%$) [58, 349]. Regardless of the electric field, over several months and years, driving forces towards an equilibrium crystal shape with the lowest total surface free energy progressively change the tip geometry. This effectively reduces the field factor ($\beta$) and consequently decreases the emission current density [58].

Figure 2.1: Calculated energy spread and emission current density as a function of (a) the electric field strength and (b) the emitter temperature. The energy spread is calculated as the FWHM of the emitted electron energy distribution as calculated by Eq. 2.8.
2.1. Electron probe microanalysis

Electromagnetic lenses

Lenses in an electron microscope are electromagnets where a magnetic field is created by passing an electrical current through a wire wound around a hollow, radially symmetrical magnetic core [292, 359, 404]. In order to obtain the focusing capability required for high resolution, the magnetic core is designed to concentrate the magnetic field. This is an essential characteristic of electromagnetic lenses used in electron microscopy [308, 359]. A yoke geometry is used where the magnetic field produced by the wound wire can only leak through a small gap. The specially shaped part of the magnetic core defining this gap is called the pole piece [167, 359, 404]. To minimize lens aberrations, different lens designs exist, especially for the objective lens (out-lens, pinhole, immersion, Snorkel, etc.) [124, 167, 359]. The yoke and the pole piece are usually made of pure iron with a well-controlled grain size (30 to 50 µm in diameter) to ensure high magnetic permeability [359]. The wire is made of copper to minimize resistive heating, although water cooling is usually required [404].

A parallel can be drawn between electromagnetic lenses in an electron microscope and convergent optical lenses in a light optical microscope [LOM] with a monochromatic light source. An object at distance $p$ from the lens will be demagnified onto an image plane at distance $q$ following Newton’s lens equation and the thin lens approximation:

$$\frac{1}{f} = \frac{1}{p} + \frac{1}{q},$$

where $f$ is the focal length ($f > 0$) [292, 404]. The demagnification ($D$), the reduction factor between the size of an object before and after a lens, is defined as:

$$D = \frac{p}{q} = \frac{p}{f} - 1.\tag{2.10}$$

In contrast to optical lenses in a LOM, the focal length of electromagnetic lenses can be adjusted by varying the current in the wire [167]. From the simplified Ampere’s Law for electromagnets ($B = NI\mu/L$), the magnetic field ($B$) is proportional to the current ($I$) passing through a wire of length $L$ wound $N$ times around a magnetic core with a permeability ($\mu$). As the strength of the magnetic field depends on the yoke and pole piece design, the exact relationship requires finite element modelling [359]. From the Lorentz force equation for electrons in a pure magnetic field ($\vec{F} = -e(\vec{v} \times \vec{B})$), varying the magnetic field changes the force exercised on the electrons and thus the focal length. For a symmetric electromagnetic lens with a normally distributed magnetic field, Reimer [292] derived a relationship between the focal length ($f$) and the magnetic field:

$$f = \frac{16m_eE_0}{\pi eB_0^2\sigma_B},$$

where $E_0$ is the beam energy of the electrons (in V), and $B_0$ and $\sigma_B$ are respectively the amplitude (in T) and the width (in m) of the magnetic field distribution. The equation shows that increasing the magnetic field decreases the focal length, decreases the image plane distance $p$ and increases the demagnification. This complements the introductory statement that strong lenses are required to achieve a small electron beam. Another deduction from Eq. 2.11 and from the presence of the electron velocity
(i) in the Lorentz force equation is that the electron energy \( E_0 \) influenced the focal length for a given magnetic field. To obtain the same focal length, or in other words to focus the beam on the same location, a stronger magnetic field is required at higher beam energy. Because of the intrinsic energy spread of the emitter, this also implies that the action of an electromagnetic lens on a non-monochromatic electron beam results in slightly different focal lengths. This is known as the chromatic aberration, which will be discussed in §2.1.1.

Depending on their purpose, electromagnetic lenses in a SEM or electron microscope are referred to as condenser or objective lens. In combination with the objective lens aperture, the aperture before the objective lens, the condenser lens controls the diameter and current of the beam entering the objective lens. There is usually one or two condenser lenses in an electron column. The final lens is the objective lens, which determines the focus and final diameter of the beam. It provides the largest demagnification of the electron beam [124, 167].

**Condenser lens(es)** The action of the condenser lens on the beam diameter and beam current can be geometrically explained (Fig. 2.2), where all electron traces are calculated based on Eq. 2.9. When the magnetic field in the condenser lens is increased, the focal length is decreased as well as the distance between the lens and the image plane \( q \). Most of the electrons hit the objective lens aperture and few reach the objective lens (Fig. 2.2a). On the other hand, if the magnetic field in the condenser lens is decreased, the crossover point between the condenser lens and the objective lens aperture is lower, and most of the electrons pass through the aperture (Fig. 2.2b). Therefore, the strength of the condenser lens with respect to the size of the objective lens aperture controls the number of electrons reaching the specimen, i.e. the beam current. It also plays a determining factor on the beam diameter. For a given divergence angle \( \alpha \) (same objective lens aperture and working distance), as the reduced brightness \( B_r \) is constant at any location along the electron column, an increase of the beam current necessitates an increase of the beam diameter as per Eq. 2.6. As noted by Goldstein et al. [124], “if there were no aberrations in the system, it would only be necessary to increase the [divergence] angle to increase the [beam] current at a constant [beam] diameter”.

The addition of a second condenser lens allows the collection of more electrons from the emitter which results in higher beam currents [170]. This is illustrated in Fig. 2.2c where the focal length of the second condenser lens (CL2) is identical as the one of the condenser lens (CL) in Fig. 2.2b. The additional condenser lens near the emitter captures and focuses the electrons down the column. As a result, more electrons pass through the objective lens aperture.

**Objective lens** The objective lens is responsible to focus electrons passing through the objective lens aperture on the specimen surface, usually to the smallest possible spot to achieve the best spatial resolution. The focus is expressed as a working distance, which is defined as the distance between the centre of the objective lens to the specimen plane [124]. As shown in Fig. 2.3, increasing the magnetic field of the objective lens decreases the focal length and the working distance. It also increases the divergence angle, which improves the achievable spatial resolution in two ways [179]. First, from the reduced brightness equation (Eq. 2.6), a large divergence angle
means a smaller beam diameter for a constant beam current. Secondly, resolution loss due to aperture diffraction is minimized (§2.1.1). This comes with the drawback of a reduced depth of focus, which limits the study of rough surfaces.

The advantages and disadvantage of small working distances are often not applicable for measurement conditions required for quantitative analysis, i.e. those in an electron microprobe. To maximize the X-rays collected, all X-ray spectrometers necessitate the specimen to be accurately positioned at a certain working distance, known as the analytical working distance. For a given beam current, the strength of the objective lens and the divergence angle are therefore fixed by the analytical working distance. As quantitative analysis must be performed on polished surface, any improvement or worsening of the depth of focus is irrelevant.

**Lens aberrations and aperture diffraction**

As mentioned several times in this review, electromagnetic lenses are not perfect, meaning that cannot simply be modelled using Eq. 2.9. In optics, deviations from this model are called aberrations [138]. They limit the demagnification capability of the electromagnetic lenses. Up to now, the dependence of the final beam diameter on the beam current and divergence aperture was demonstrated using Eq. 2.6. The relationship between the beam diameter and the analytical conditions is incomplete unless the lens aberrations and the aperture diffraction are included in the calculations. Three lens aberrations are of importance in a SEM: spherical, chromatic and astigmatism [292].
Figure 2.3: Electron traces after a weak (blue) and a strong (green) objective lens. The divergence angle ($\alpha$) is increased as the working distance decreases ($\alpha_2 > \alpha_1$). The aspect ratio is 1:22.

**Beam diameter**  The electrons inside the beam are spatially distributed following some profile, which is often expressed by a single quantity, the beam diameter. This reduction implies that the profile is known and can be represented by a mathematical function (Gaussian, Lorentzian, etc.). In the context of a SEM, these two assumptions are rarely satisfied. Nonetheless, the beam profile is generally assumed to be Gaussian, where the beam diameter is defined as the FWHM [124, 176, 292, 404], despite evidence of stronger tails especially at high beam currents [26, 58, 169]. This work makes the same assumption, especially for consistency with the Monte Carlo simulation programs later used in this thesis. The reader is referred to the work of Barth and Kruit [26] and Bronsgeest [58] for the derivation of the final beam diameter using their profile independent definition based on the full width containing 50% of the total current.

**Spherical aberration**  This aberration occurs due to the inhomogeneous magnetic field within a lens which deflects electrons differently depending on their distance from the optic axis. “If parallel rays are incident on an electron lens, those further from the optic axis are focused closer to the lens” [292]. The action of the lens no longer results in imaging a point at distance $p$ before the lens to a point at distance $q$ after the lens (Eq. 2.9). A disk is instead obtained, consisting of a “central high-intensity region surrounded by a halo of decreasing intensity” [404]. For a point source, the diameter of the disk ($d_s$) at distance $q$ from the lens (known as the Gaussian image plane) is expressed as a function of the divergence angle ($\alpha$) and a spherical aberration coefficient ($C_s$) [292, 404]:

$$d_s = 2C_s \alpha^3.$$  \hspace{1cm} (2.12)
The spherical aberration coefficient depends on the magnetic field of the lens. Reimer [292] estimated that it varies with the focal length \((f)\) and the width of the magnetic field distribution \((\sigma_B)\): \(C_s \approx 3f^3/4\sigma_B^2\). Spherical aberrations manifest themselves more at longer working distances since \(C_s\) increases with the focal length. The objective lens of a SEM has larger \(C_s\) than its counterpart of a TEM due to the requirement of longer working distances. Magnitudes in the range of 20 to 120 mm have been reported [124, 233, 292].

**Chromatic aberration** Chromatic aberration is the consequence of the energy spread of the emitter (§2.1.1). As shown in Eq. 2.11, for a given magnetic field, a more energetic electron is focused with a longer focal length by an electromagnetic lens. For a Gaussian distributed energy spread \((\mu = E_0\text{ and FWHM} = \Delta E_0)\), the variation in the focal length \((f)\) is equal to: \(\Delta f = f \Delta E_0/E_0\) [292]. As for spherical aberrations, a point source becomes a disk with a diameter \((d_c)\) defined as:

\[
d_c = C_c \frac{\Delta E_0}{E_0} \alpha ,
\]

where \(C_c\) is the chromatic aberration coefficient. The equation assumes that the energy spread is Gaussian distributed where \(\Delta E_0\) is equal to the FWHM. \(\Delta E_0\) can be calculated using Eq. 2.8.

Similarly to spherical aberrations, \(C_c\) increases at longer focal lengths [233]. Its magnitude is comparable to the focal length [124, 292]. In a SEM, Nakagawa [233] measured \(C_c\) values approximately 5 times smaller than \(C_s\) values, in the range of 10 to 50 mm. Chromatic aberrations especially limit the achievable spatial resolution at low accelerating voltages as the ratio \(\Delta E_0/E_0\) increases with decreasing accelerating voltage [124, 292, 361]. Fig. 2.4 shows this dependence for the three main electron emitter types, clearly demonstrating the limitation of thermionic emitters at low accelerating voltages.

**Astigmatism** Inhomogeneities in the magnetic field of an electromagnetic lens due to machining imprecision, charging effects, microstructural defects, etc. result in astigmatism [124, 288, 292, 404]. A lens suffering from astigmatism transforms a circular object into an elliptical image. This aberration can be corrected with a well-adjusted stigmator. This device consists in an octupole, a pair of small quadrupole electromagnetic lenses. It is located just above the lens to correct, which can either be a condenser or objective lens. It applies a weak supplement to the magnetic field of the lens to “make [it] appear symmetric to the electron beam” [124].

**Aperture diffraction** Any wave entering a small aperture suffers from aperture diffraction where a point is imaged as a Airy disk, a Fraunhofer diffraction pattern [124, 292, 404]. To evaluate the enlargement of a point source by aperture diffraction, the half-width of the first zero in the Airy disk intensity function \((r \text{ when } I_A(r) = 0)\) is usually taken as the effective aperture diffraction diameter assuming a Gaussian beam [124, 292, 318, 404].

\[
d_d = 0.61 \frac{\lambda}{\alpha} .
\]
Chapter 2. Literature review

Figure 2.4: Chromatic aberration as a function of the accelerating voltage for different energy spreads.

Aperture diffraction depends on the wavelength ($\lambda$) of the incident wave. For electrons, the wavelength can be expressed as a function of the accelerating voltage using de Broglie’s equation, relating the wavelength of a particle with its momentum [404]:

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m_e eE_0}},$$  \hspace{1cm} (2.15)

where $h$ is Planck constant ($6.626 \times 10^{-34}$ J s$^{-1}$), $m_e$, the electron mass ($9.109 \times 10^{-31}$ kg), and $E_0$, the accelerating voltage (in V). Relativistic effects are not included as the influence of relativity is negligible for accelerating voltages below 50 kV [292]. Writing Eq. 2.14 as a function of the accelerating voltage ($E_0$) gives

$$d_d = \frac{0.61h}{\sqrt{2m_e e}} \left( \frac{1}{\alpha \sqrt{E_0}} \right).$$ \hspace{1cm} (2.16)

In comparison to the spherical and chromatic aberrations, the effective diameter of the aperture diffraction inversely varies with the divergence angle. Increasing the latter decreases the broadening of a point source. As for chromatic aberrations, aperture diffraction dominates at low accelerating voltages.
2.1. Electron probe microanalysis

**Final beam diameter**  Coming full circle, the final beam diameter can now be calculated from the formulated equations. As previously stated, the reduced brightness is a constant quantity throughout the electron column. Ignoring for the moment lens aberrations and aperture diffraction, re-writing Eq. 2.6 gives the ideal beam diameter ($d_0$):

$$d_0 = \frac{4I_p}{\pi^2 \alpha^2 E_0 B_r} = \sqrt{\frac{4I_p}{\pi^2 E_0 B_r} \left( \frac{1}{\alpha} \right)},$$  \hspace{1cm} (2.17)

where $I_p$ is the beam current, $E_0$, the accelerating voltage, and $\alpha$, the divergence angle. For Schottky emitter, the reduced brightness can be calculated using Eq. 2.7 which incorporates the emitter intrinsic characteristics and operating conditions such as the cathode temperature, the electric field and the field factor.

The combination of the ideal beam diameter and effective beam diameters from lens aberrations and aperture diffraction gives the final beam diameter ($d_p$) [57, 58, 124, 292]:

$$d_p = \sqrt{d_c^2 + d_s^2 + d_c^2 + d_d^2}.$$  \hspace{1cm} (2.18)

As many factors influence the final beam diameter, not a single figure can summarized all the implications of Eq. 2.18. Fig. 2.5 shows the relationship between the final beam diameter ($d_p$) and the divergence angle for different accelerating voltages and beam currents. The other quantities were chosen as follows. As calculated in §2.1.1, a reduced brightness of $2.4 \times 10^7$ A m$^{-2}$ sr$^{-1}$ V$^{-1}$ was used. Values for $C_s$ (30 mm) and $C_c$ (15 mm) were taken from the measurements of Nakagawa [233] at their lowest working distance (15 mm). The energy spread was set to 0.5 V. Unless otherwise specified a beam current of 100 nA and an accelerating voltage of 15 kV were selected to reflect typical analytical conditions used in an electron microprobe.

Overall, lower beam currents and higher accelerating voltages require smaller divergence angles. This optimal divergence angle comes from the competing behaviours of the different effective diameters contributing to the final beam diameter. Aperture diffraction and the fixed reduced brightness are responsible for the increase of the final beam diameter at low divergence angles. The increase of the final beam diameter after the minimum is due to the chromatic aberration and especially the spherical aberration at higher divergence angles. In aberration corrected instruments, the reduction of the aberrations damps this increase allowing larger divergence angles to be used to minimize the effects of aperture diffraction [179].

Assuming that the objective aperture can produce the optimal divergence angle\(^1\), the beam current and accelerating voltage have also a large influence on the actual size of the final beam diameter. It increases with increasing beam current and decreasing accelerating voltage. This behaviour appears more clearly in Fig. 2.6, where the optimal final beam diameter is plotted as a function of the accelerating voltage for different beam currents. The optimal final beam diameter is defined as the diameter at the optimal divergence angle for each combination of beam current and accelerating voltage. Fig. 2.6 shows an exponential deterioration of the beam diameter at

\(^1\)by either changing the aperture diaphragm or using an aperture angle control lens (as in the JEOL JXA8530F), which optimizes the divergence angle. Positioned below the objective lens aperture, it has the ability to dynamically decrease the divergence angle and adjust it to minimize lens aberrations.
Figure 2.5: Final beam diameter as a function of the divergence angle for different (a) beam currents and (b) accelerating voltages. The diameters were calculated using Eq. 2.18. The arrows indicate the smallest beam diameter for a set of conditions.
2.1. Electron probe microanalysis

accelerating voltages below 5 kV. At 10 kV, increasing the beam current from 1 to 100 nA results in a 4-fold broadening of the optimal final beam diameter. In summary, the final beam diameter, or in other words the spatial resolution, largely depends on the selection of the accelerating voltage and beam current.

2.1.2 Electron- and photon-matter interactions

The expression “a sample is irradiated or bombarded by an electron beam” implies the transport and interaction of incident electrons with the atoms of the sample. Different mechanisms determine their trajectories, the interaction volume and the generation probabilities of secondary particles. One of these particles are X-ray photons, the cornerstone of EPMA.

In order to explain the evolution of incident electrons and generated secondary particles inside a sample, numerical models have been developed. They can be divided into two categories: deterministic modelling or Monte Carlo simulations. The former solves partial differential equations [PDEs] using numerical methods where the different electron-matter interactions are expressed in the form of the Boltzmann transport equation [315]. Up until recently [225, 299], the solution for such system of equations required several approximations and was limited to simple geometries. This led to the development of Monte Carlo based simulations where the trajectory and interactions of each incident electron or secondary particle are chronologically simulated until it either escape the sample or looses all its energy [95, 122, 155, 178, 213, 300, 315]. The probability of each interaction is sampled using random numbers, hence the name of this numerical method. At a large number of simulated trajectories, both modelling strategies yield the exact same solution.
This section describes the underlying physical principles behind electron-matter interactions following the structure of a pseudo Monte Carlo simulation program. Killing two birds with one stone, this practical approach aims at chronologically explaining the influence of each mechanism on the position, direction of movement and energy of each particle, namely the electrons and photons. These three quantities are also those tracked throughout a Monte Carlo simulation. As the field of electron- and photon-matter interactions is extensive, the scope of this discussion is limited to interactions occurring at energies below 30 keV. As each Monte Carlo program has its own particularities and algorithms, the discussion focuses on the general concepts applicable to any program, albeit a closer resemblance with the structure of the PENELOPE [213, 315] Monte Carlo code.

Basic concepts of Monte Carlo simulation

Probability An interaction is an event in time and space occurring between two species at a certain probability described by a probability density function [PDF]. The latter depends on the type of incident particle and its energy as well as the interacting specie. Concretely, in the context of electron microscopy context, the incident particles are either electrons or photons and the interacting species are the atoms of the sample. More specifically, there exists a probability for an electron or a photon with an energy \( E_1 \) to interact with an atom \( A \): \( p_A(E_1) \), where \( \int p(E) \, dE = 1.0 \). Expressing the PDF as a cumulative density function [CDF], the probability of an event to occur can be decided by a random number (\( \xi \)). This method is referred to as sampling and is mathematically expressed by:

\[
\xi = \int_{-\infty}^{x} p(x') \, dx'.
\]

For example, the PDF and CDF for dice rolling is illustrated in Fig. 2.7. The PDF is constant as there is an equal chance of rolling any face of the die. To randomly decide which face is obtained after a single role, a random number between 0.0 and 1.0 is generated and the corresponding face is extracted from the inverse CDF as shown in Fig. 2.7. This strategy can be applied to any probability and is at the core of Monte Carlo simulations.

Cross section Another representation of probabilities is the cross section, which is often used to represent interaction probabilities of particles [121, 315]. Figuratively, a cross section is equal to the area occupied by atoms inside a box of infinitesimal thickness [121]. As such, cross sections are expressed in units of area. Increasing the number of atoms in the box, i.e. increasing the mass density, or increasing the cross section increases the interaction probability of an incident particle. Mathematically, the probability of a given interaction (\( p \)) in a box full of atoms is given by

\[
p = \frac{\sigma}{A} \mathcal{N} = \frac{\sigma}{A} \frac{N_{AP\rho}A \Delta s}{M} = \frac{N_{AP\rho}}{M} \mathcal{N} \sigma \Delta s,
\]

(2.20)
2.1. Electron probe microanalysis

where $\sigma$ is the interaction cross section, $A$, the area of the box, and $N$, the number of atoms inside the box, $N_A$, Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$), $\rho$, the mass density of the sample, $M$, the molar mass of atom, and $\Delta s$, the thickness of the box. From the abstract concept of a box of atoms, the area of the box ($A$) is removed from the simplification, but the thickness ($\Delta s$) remains. Eq. 2.20 also shows the dependence of the interaction probability on the cross section ($\sigma$) and the number of atoms per unit volume ($N'''' = N_A \rho / M$).

Mean free path To remove the thickness dependence from Eq. 2.20, the probability ($p$) can be expressed as a linear probability, the probability of an interaction occurring over a distance $\Delta s$, or inversely the average distance a particle travels between interactions. This distance, known as the mean free path ($\lambda$), is defined as

$$\lambda^{-1} = N'''' \sigma = \frac{N_A \rho}{M} \sigma .$$

(2.21)

This concept is extensively used in Monte Carlo simulations to calculate the location of an interaction. A particle is said to travel in straight line in the direction of movement until the next interaction, where its energy and direction can change based on other interaction probabilities. The mean free path is an average distance, meaning that over its trajectory a particle may travel shorter and longer distances between interactions. The associated PDF to this process is $p(s) = \lambda^{-1} \exp \left(-s/\lambda\right)$, and from Eq. 2.19 the sampling formula using a random number $\xi_1$ is

$$s = -\lambda \ln \left(1 - \xi_1\right) ,$$

(2.22)

where $s$ is a randomized distance travelled by a particle between two interactions. Overall the trajectory of a particle therefore resembles a tree structure composed of segments with lengths determined by Eq. 2.22, nodes corresponding to interactions and new branches analogous to the generation of secondary particles.
Multiple interactions and atoms  Eq. 2.20 and 2.22 described a system where only one type of interactions is possible and all atoms are identical, i.e. a pure sample. This situation is obviously far from the reality. As it will be described in §2.1.2 and 2.1.2.1, a particle has multiple ways to interact with an atom. Following the addition rule of probabilities, the probability of having one type of interaction is simply the sum of all probabilities, the sum of the cross section for each interaction \( \sigma_j \) \[121, 315\]. In a homogeneous compound sample, the probability of interacting with one atom depends on both its interaction probability, i.e. its cross section \( \sigma_i \), and its relative amount with respect to the other atoms, i.e. the number of this atom per unit volume \( (N_i') \) \[86, 121\]. Therefore, the total interaction cross section \( (\sigma_T) \) for a particle having \( N^j \) types of interaction while travelling in a sample containing \( N^i \) elements is

\[
\sigma_T = \sum_i^{N^i} \sum_j^{N^j} N_i'' \sigma_{i,j},
\]

where \( \sigma_{i,j} \) is the cross section of interaction \( j \) with atom \( i \). The number of atom \( i \) per unit volume \( (N_i'') \) is usually expressed using the mass fraction of atom \( i \) \((w_i)\) and the sample mass density \( \rho \), both macroscopically measurable quantities: \( N_i'' = N_A w_i / M_i \) \[121\]. From the total interaction cross section, the probability of an interaction \( j \) with atom \( i \) \( (p_{i,j}) \) is simply

\[
p_{i,j} = \sigma_{i,j} / \sigma_T.
\]

Combining Eq. 2.22 and 2.23, a randomized distance between any two interactions of a particle travelling in a compound can be calculated, taking \( \lambda \) as \( \lambda_T = 1/(N'' \sigma_T) \) per Eq. 2.21. After travelling this distance, the interacting atom \( (i) \) and the type of interaction \( (j) \) can be decided by sampling the probabilities defined by Eq. 2.24 using a random number \( (\xi_2) \) as expressed by Eq. 2.19 and shown in Fig. 2.7.

Terminology in solid-state physics

Before diving in the description of the different interactions, the terminology used to describe atomic structure, electronic configurations and X-ray transitions is first clarified. An atom is said to be in an excited state when its energy is greater than the ground state. At the ground state, an atom has the same number of protons and electrons, equal to the atomic number. Based on quantum mechanics and Pauli exclusion principle, each electron is characterized by four quantum numbers: principal \((n = \{1, 2, \ldots\})\), azimuthal \((\ell = \{0, 1, \ldots n - 1\} \text{ or } \{s, p, d, f\})\), magnetic \((m_\ell = [\ell, \ell])\) and spin \((m_s = [-s, s], \text{ where } s = 1/2 \text{ for electrons})\) \[402\]. Among other things, these numbers describe the discrete energy levels occupied by the electrons, their respective binding energies \[391\]. In other words, the energy of an electron is equal to the energy required to remove it from the atom \[391\]. By convention, the energy input required to overcome the binding energy is positive and therefore the energy levels take negative values. As each element in the periodic table has a different electronic configuration, the energy levels are characteristic to each element.

The solution of the Schrödinger equation states that the energy of an electron depends on its principal quantum number. Electrons with the same principal quantum number are said to share the same atomic shell \[293, 391\]. Atomic shells are often
2.1. Electron probe microanalysis

Table 2.1: Notation of the atomic subshells

<table>
<thead>
<tr>
<th>n</th>
<th>ℓ</th>
<th>j</th>
<th>orbital</th>
<th>Siegbahn</th>
<th>IUPAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1/2</td>
<td>1s₁/₂</td>
<td>K</td>
<td>K</td>
</tr>
<tr>
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<td>0</td>
<td>1/2</td>
<td>2s₁/₂</td>
<td>LI</td>
<td>L₁</td>
</tr>
<tr>
<td>2</td>
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<td>1/2</td>
<td>2p₁/₂</td>
<td>LII</td>
<td>L₂</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3/2</td>
<td>2p₃/₂</td>
<td>LIII</td>
<td>L₃</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1/2</td>
<td>3s₁/₂</td>
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<td>1</td>
<td>1/2</td>
<td>3p₁/₂</td>
<td>MII</td>
<td>M₂</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3/2</td>
<td>3p₃/₂</td>
<td>MIII</td>
<td>M₃</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3/2</td>
<td>3d₃/₂</td>
<td>MIV</td>
<td>M₄</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5/2</td>
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<td>MV</td>
<td>M₅</td>
</tr>
<tr>
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<td>4s₁/₂</td>
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<tr>
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<tr>
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<td>NIII</td>
<td>N₃</td>
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<tr>
<td>4</td>
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<td>4d₃/₂</td>
<td>NIV</td>
<td>N₄</td>
</tr>
<tr>
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<td>5/2</td>
<td>4d₅/₂</td>
<td>NV</td>
<td>N₅</td>
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<td>NVI</td>
<td>N₆</td>
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<td>7/2</td>
<td>4f₇/₂</td>
<td>NVII</td>
<td>N₇</td>
</tr>
</tbody>
</table>

Table 2.1: Notation of the atomic subshells labelled K, L, M, . . . Q from the notation used by Barkla and Moseley [391]. The occupancy of an atomic shell is equal to \(2n^2\) [391]. The first atomic shell (K or \(n = 1\)) is the closest to the nucleus and has the largest binding energy.

For heavier elements than boron, interactions between the electrons of an atom split the energy levels defined by the principal quantum number into sublevels. More specifically, an angular momentum is generated between electrons of an atomic shell from the interaction of their spin magnetic moment and their orbital angular momentum defined by their spin and azimuthal quantum number, respectively [234]. Referred to as the total angular momentum, it can be expressed as a derived quantum number (\(j\)), which is equal to \(|\ell \pm s|\) [234, 293, 391]. This phenomenon is known as the spin-orbit interaction and becomes more significant for high atomic number element [234]. Consequently, each atomic shell is subdivided into \((2n - 1)\) subshells, known as atomic subshells or as X-ray levels in X-ray spectroscopy [166].

Three nomenclatures are typically used to represent the subshells: orbital, Siegbahn or from the International Union of Pure and Applied Chemistry [IUPAC] [166]. The orbital representation expresses a subshell using the principal quantum number, the azimuthal quantum number (as letter) and angular momentum in the form of \(n\ell j\), e.g. \(2p₃/₂\). The Siegbahn notation and the one from the IUPAC use the capital letter notation of the atomic shell (K, L, M, . . . , Q) in combination of an integer for each subshell, expressed in Roman numeral in the former notation and in Hindu-Arabic numeral in the latter. Tab. 2.1 gives the equivalence between the different notations up to \(n = 4\).

The highest filled subshells, i.e. subshells with the lowest binding energy, contain the valence electrons, which are involved in chemical bonding. In a solid, the interaction between the electrons of the different atoms enlarges the energy levels to form continuous energy bands, both for the filled and unfilled subshells. The highest
filled band, which contains the valence electrons, is called the valence band, whereas conduction band corresponds to the lowest unfilled band. In metals, the highest filled band is partially filled and serves both as the valence and conduction band. For semiconductors and insulators, a band gap, an energy difference, exists between the two bands.

As it will be discussed in §2.1.2.0.2, inelastic scattering may eject an electron located in a subshell of an atom. From this excited state, an electron from an outer shell or subshell will almost instantly fill the vacancy. This cascading phenomenon allows the atom to recover its ground, lowest energy state. Through this relaxation process, the electron undergoes a transition, a change of its quantum state, leading to the release of energy either as a radiative or non-radiative transition. The physical description of the processes are left for §2.1.2.0.2 and only the terminology is presented here.

A transition is said to be radiative when the excess energy is released in the form of a characteristic photon, or more precisely a characteristic X-ray as the energy difference between the atomic subshells falls inside the range of X-ray radiations (0.1 to 100 keV). Two nomenclatures exist to identify X-ray transitions: Siegbahn or from the IUPAC. The latter explicitly labels the X-ray using the protagonist subshells: the inner subshell with the electron vacancy and the outer subshell of the relaxing electron. The Siegbahn notation only specifies the inner shell (note shell and not subshell) with the electron vacancy and assigns a letter (Greek) to the transition. Depending on the spectrometer resolution, the energy levels within one shell can be too small to be resolved and groups of subshells are used to express this set of transitions. Tab. 2.2 lists common X-ray transitions expressed in both nomenclatures.

There are two types of non-radiative transition: Auger [17] and Coster-Kronig [81]. In the former, the excess energy of the relaxation process is transferred to another electron, which gets ejected from the atom. This Auger electron is typically located in the same atomic shell as the electron relaxing to fill the vacancy in an inner subshell of the atom. For example, the excess energy from an electron relaxing from the L$_1$ to the K causes the emission of an Auger electron from the L$_2$ [384]. This transition is expressed using the IUPAC notation as K–L$_1$L$_2$. Coster-Kronig transitions are relaxation transitions occurring within the same shell. The same notation as radiative transitions from the IUPAC is used. For example, the Coster-Kronig transitions for the L shell are L$_1$–L$_2$, L$_1$–L$_3$, and L$_2$–L$_3$.

<table>
<thead>
<tr>
<th>Siegbahn</th>
<th>IUPAC</th>
<th>Siegbahn</th>
<th>IUPAC</th>
</tr>
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<tr>
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<td>K–L$_3$</td>
<td>Kα$_2$</td>
<td>K–L$_2$</td>
</tr>
<tr>
<td>Kα</td>
<td>K–L$_{2,3}$</td>
<td>Kβ</td>
<td>K – M$<em>{2–5}$N$</em>{2–5}$</td>
</tr>
<tr>
<td>Lα$_1$</td>
<td>L$_3$–M$_5$</td>
<td>Lα$_2$</td>
<td>L$_3$–M$_4$</td>
</tr>
<tr>
<td>Lα</td>
<td>L$<em>3$–M$</em>{4,5}$</td>
<td>Lβ$_1$</td>
<td>L$_2$–M$_4$</td>
</tr>
<tr>
<td>Lγ</td>
<td>L$<em>{1,2}$–N$</em>{1–6}$O$_{1–3}$</td>
<td>Lℓ</td>
<td>L$_3$–M$_1$</td>
</tr>
<tr>
<td>Lη</td>
<td>L$_2$–M$_1$</td>
<td>Mα</td>
<td>M$<em>5$–N$</em>{6,7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mγ</td>
<td>M$_3$–N$_5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mβ</td>
<td>M$_4$–N$_6$</td>
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<tr>
<td></td>
<td></td>
<td>Mζ</td>
<td>M$<em>{4,5}$–N$</em>{2,3}$</td>
</tr>
</tbody>
</table>

Table 2.2: Notation of common X-ray transitions
2.1. Electron probe microanalysis

Electrons interact with atoms of a sample through three interactions: (1) elastic scattering, (2) inelastic scattering and (3) Bremsstrahlung emission [315]. Fig. 2.8 schematically shows these interactions where an incident electron with energy $E_{\text{in}}$ interacts with an atom. The variable $E'$ indicates the energy of the incident electron after the interaction. In the case of the generation of a secondary particle, its energy and scattering angle are represented by $E_s$ and $\theta_s$ respectively.

2.1.2.0.1 Elastic scattering When an electron approaches an isolated atom, it is attracted by the positive charge of the nucleus and repulsed by the negative charge of the electron cloud [292]. As the distance between the electron and the nucleus decreases, the Coulomb forces increases and have a large influence on the electron trajectory [292, 404]. The scattering angle, the angle between the incident and outgoing trajectories ($\theta$ in Fig. 2.8a), can be as large as 180° [292]. The incident electron is less affected by the electron cloud of the atom, which only reduces the Coulomb forces exerted by the nucleus. The electron cloud is said to “screen” the nuclear charge [292].

The characterization of this type of interactions as “elastic” signifies that the incident electron preserves its energy; only its direction of movement is altered. Strictly speaking this statement is not completely accurate since the electron causes some recoil of the nucleus, implying some energy loss. However, the latter corresponds to only a few meV as the nucleus is significantly more massive than the electron, which explains the omission of the recoil phenomenon [315].

For bulk samples, elastic scattering is responsible for electron backscattering. Over a series of elastic interactions, the electron trajectory is reverted; an electron exits the sample through the same surface it entered [124, 292]. With their higher nuclear charge, higher atomic number ($Z$) elements lead both to higher scattering probabilities, i.e. a shorter mean free path between elastic interactions, and larger scattering angles. This combined effect results in a decrease of the electron irradiated volume, the interaction volume, as the mean atomic number of a sample ($\bar{Z} = \sum w_i Z_i$) increases [124]. Lowering the accelerating voltage, the energy of the incident electrons, has a similar effect than increasing the mean atomic number.

Figure 2.8: Sketches of electron interactions with matter: (a) elastic scattering, (b) inelastic scattering and (c) Bremsstrahlung emission. Sketches were inspired from [315].
Simulation  In modern Monte Carlo programs, the simplistic, analytical Rutherford scattering cross sections have been replaced by more accurate, computationally faster, tabulated cross sections from Mott [82] or ELSEPA [316]. Elastic cross sections are reported as differential cross sections as a function of the scattering solid angle \((d\sigma/d\Omega)\). The integration over the unit sphere gives the total elastic scattering cross section \((\sigma_{el,T} = \int_0^{4\pi} (d\sigma/d\Omega) d\Omega)\) and the integration to a specific angle \((\theta)\) gives its scattering probability \((\sigma_{el,\theta} = \int_0^\theta (d\sigma/d\Omega) d\Omega)\). From this PDF, Eq. 2.19 and a random number \(\xi_3\), a randomized scattering angle can be determined for each elastic interaction [121, 315]. This angle corresponds to the polar angle, the deflection angle from the incident direction of movement. As elastic scattering is axially symmetric, the azimuthal angle \((\phi)\), the angle around the new direction of movement, is sampled by \(2\pi\xi_4\) [121].

2.1.2.0.2 Inelastic scattering  As the name suggests, inelastic scattering involves energy losses. This type of interaction is the “dominant energy loss mechanism for electrons” [315]. In comparison to elastic scattering where the atom indirectly interacts with the incident electron via Coulomb forces, inelastic scattering involves the direct collision between the incident electron and one electron from the atom. From the conservation of momentum law, a part of the incident electron energy is transferred to the impacted electron (Fig. 2.8b). The amount of energy transferred \((\Delta E_{in})\) depends on the incident energy, the atomic structure and the inelastic scattering cross sections, which defines the Bethe curve [315]. If this energy is greater than the energy level (i.e. binding energy, \(E_{n\ell j}\)) of the atomic subshell \(n\ell j\) where the impacted electron resides, it is ejected from the atom (Fig. 2.8b) [124, 292]. The energy of the ejected electron is then equal to \(\Delta E_{in} - E_{n\ell j}\), which can range from a few eV to several keV [124]. Conversely, if the energy transferred to the impacted electron is less than its binding energy, inelastic scattering induce plasma oscillations, where electrons in the valence and conduction band oscillate following a “collective longitudinal charge-density wave” [292]. After the impact, the incident electron continues its trajectory, roughly along the same direction of movement. The inelastic scattering angle is much smaller than for elastic scattering [121].

To clarify, ejected electrons are particles of second generation, but are not necessarily secondary electrons [SEs]. Per definition, SEs have an energy lower than 50 eV. Their emission is a special type of inelastic interaction where the impacted electrons are from the outer shells, i.e. the valence or conduction band. With their low binding energy \((E_{n\ell j})\), their ejection requires a small \(\Delta E_{in}\), resulting in ejected electrons with a small energy \((E_s)\) [124, 404]. Because of their low energy, SEs have a small (elastic) mean free path and only those generated near the sample surface can escape [404].

An inelastic interaction leaves the atom in an excited state, one electron is missing. Different outcomes result from this disequilibrium: characteristic, resonance and satellite X-ray emission, Auger electron emission, Coster-Kronig transitions and cathodoluminescence [47, 292]. There are probabilities associated to each outcome, which depends on (1) the subshell with a missing electron, (2) the electronic configuration of the atom in the excited state and (3) the relaxation process of the atom to recover its ground state.
Radiative and non-radiative emission  From an excited atom with one electron hole in the atomic subshell $A$, one relaxation process involves the transition of an electron from an outer subshell $B$ to fill this vacancy ($B \rightarrow A$). The emission of X-rays or Auger electrons is produced if the subshell $A$ is an inner subshell, i.e. not in the valence band, and if the shell of $B$ is different and above the one of $A$. In terms of the principal quantum number $n$, $n_A$ must be less than the maximum principal quantum number and $n_B$ must be greater than $n_A$. The energy difference between the subshells $A$ and $B$, $\Delta E_{BA} = E_B - E_A$, is either released either in the form of an X-ray or an Auger electron. By convention $E_A$ and $E_B$ are negative values and $E_A < E_B$, giving $\Delta E_{BA} > 0$. For X-ray emission, the excess energy is completely transferred to the photon and the X-ray energy is equal to $\Delta E_{BA}$. For Auger emission, the excess energy is transferred to another electron located on an other outer subshell $C$, generally on the same shell as $B$. The electron, now called Auger electron, leaves the atom with a kinetic energy equal to $\Delta E_{BA} - E'_C$, where $E'_C$ is the binding energy of subshell $C$ in the excited state [292]. From this equation, the subshell $C$ must have a binding energy ($E'_C$) lower than the $\Delta E_{BA}$ for Auger electron emission to be possible.

Coster-Kronig transitions  In the case that the relaxation process occurs between two subshells ($A' \rightarrow A$) within the same shell ($n_{A'} = n_A$), this transition is called a Coster-Kronig transition [81]. Coster-Kronig transitions are obviously impossible in the first shell (K, $n = 1$). The excess energy also leads to emission of Auger electron from an outer shell, generally from the valence band due to the small value of $\Delta E_{AA'}$ [292, 315].

Satellite emission  After the emission of an Auger electron, the atom remains in an excited state as two subshells are empty (from the notation above, subshell $B$ and $C$). Multiple vacancies can also occur due to “shake-off and shake-up” processes where two electrons are ejected by a single inelastic interaction [47]. The relaxation from this doubly excited state results in the emission of a satellite X-ray or satellite Auger electron. The emitted particle has a slightly larger energy than the one of an equivalent transition from the single excited state.

Resonance emission  Another relaxation process is the X-ray resonance emission [46, 47]. As for “normal” X-ray or Auger emission, an inelastic interaction leaves the atom in an excited state with one electron missing in an inner subshell. However, instead of an other, outer electron relaxing to fill this vacancy, resonance emission occurs when the impacted electron itself directly returns to its subshell. This leads to the emission of an X-ray with an energy equal to the energy level of this subshell. The probability of this phenomenon depends on whether the impacted electron can preserve its quantum state long enough to allow the return to its initial subshell before any other relaxation process occurs [47]. Theoretically improbable in solids due to strong atom interactions, X-ray resonance emission was experimentally observed for rare-earth metals and transition metals in the first row of the periodic table [45, 46]. Bonnelle [46] observed a decrease of the X-ray resonance emission for rare-earth metals (La, Ce, Gd and Dy) as the accelerating voltage is increased. She explained her findings based on the fact that the resonant X-ray energy coincide with the self absorption edge and absorption increases with the accelerating voltage (see §2.1.2.1).
Cathodoluminescence  In semi-conductors and insulators, inelastic scattering with a valence electron may cause it to move to one of the unfilled energy bands of the conduction band. The recombination process, where the electron in the conduction band recombines with the hole in the valence band, may be radiative or non-radiative. In the former case, a photon is emitted with an energy in the infrared to ultraviolet range, a phenomenon known as cathodoluminescence [292].

Simulation  There exist two schemes to simulate inelastic scattering in modern Monte Carlo programs. The first, used in the Monte Carlo programs CASINO 2 [95, 155], WIN X-RAY [122], NISTMONTE [300] and MONACO [10], approximate all types of inelastic scattering as a single, continuous energy loss process, governed by the stopping power or Bethe-loss equation. This is known as the continuous slowing down approximation. The other approach, the one of the Monte Carlo program PENEOPE [213, 315], consists in simulating every inelastic interactions, as it is done for elastic interactions. With the large number of interactions in each trajectory, this methodology is considerably slower than the former. To speed up the simulations, PENEOPE [213, 315] allows a mixture of the two approaches, where only inelastic interactions with large energy losses and/or large angular deflections are simulated [315].

Concentrating on the main analyzed signal in this work, characteristic X-rays, the probability of generating a specific X-ray transition, for instance between subshell B and A, depends on three separate probabilities: (1) the ionization cross section, (2) the relative transition probability and (3) the fluorescence yield [120]. Sequentially, the ionization cross section defines the probability of an incident electron with energy E to remove an electron from subshell A. Equations from Casnati et al. [68] and Bote and Salvat [50] are commonly used to calculate ionization cross sections. Then the relative transition probability, also known as the characteristic line weight, determines the subshell of electron B which will relax to fill the vacancy in subshell A. Finally, the fluorescence yield is the probability of having a radiative transition, the probability of generating an X-ray. To include Auger electron emission and Coster-Kronig transitions, the relative transition probability and the fluorescence yield (or its complement for non-radiative transitions) can be combined to give a single list of all transition probabilities [292, 315]. The tabulation from the LLNL Evaluated Atomic Data Library [252] is one source of transition probabilities. Resonance and satellite X-ray emissions are usually not simulated by Monte Carlo programs, whereas special programs have been developed for simulating SEs [370, 371] and cathodoluminescence [87].

2.1.2.0.3 Bremsstrahlung emission  When an accelerated electron, i.e. incident electron, travels near an atom, it may be elastically scattered due to the Coulomb force with the nucleus (§2.1.2.0.1) or it may be decelerated by the electrostatic field of the atom [124]. In Monte Carlo simulations, the two interactions are independently handled due to their different probabilities and opposite effects on the trajectory and energy of the incident electron [315]. While the electron trajectory is conserved (Fig. 2.8c), deceleration may imply a significant loss of energy, which ranges from a few eV to complete annihilation [292]. As for characteristic X-ray emission, the excess energy is released in the form of an X-ray, known as Bremsstrahlung (braking
2.1. Electron probe microanalysis

![Photoelectric Absorption Diagram]

Figure 2.9: Sketch of the dominant photon interaction with matter, photoelectric absorption. Sketch was inspired from [315].

radiation), but with the difference that its energy can take any value up to the accelerating voltage. Another difference is that Bremsstrahlung X-rays have an angular distribution, predominantly in the same direction as the incident electron, instead of being anisotropically generated as characteristic X-rays [292, 315]. Bremsstrahlung emission creates a continuous energy distribution of X-rays. In the context of EPMA an X-ray spectrum is therefore the combination of characteristic X-ray peaks from inelastic scattering and a background signal from Bremsstrahlung emission. As elastic scattering, this interaction also depends on the mean atomic number of a sample [292]. In Monte Carlo programs, partial cross sections [2] or analytical equations [197] define the energy and angular distribution of Bremsstrahlung emission.

2.1.2.1 Photon interactions

Photons or more specifically X-rays interact less with matter than electrons. For instance, photons can be generally assume that they travel in straight line, without any elastic (Rayleigh) or inelastic (Compton) scattering [122, 155, 300]. The dominant interaction is photoelectric absorption where the photon is completely absorbed by an atom (Fig. 2.9) [292]. This interaction may lead to the re-emission of a photon, a phenomenon known as fluorescence [315].

**Photoelectric absorption** In many aspects, the processes involved in photoelectric absorption are similar to those of electron inelastic scattering, except that the energy transferred to the atom comes from a photon and that all its energy is transferred. In details, under certain probabilities, a photon collides with one electron of an atom. If the energy of this photon \( E \) is greater than the energy level (i.e. the binding energy, \( E_{n\ell j} \)) of the electron, the latter, known as a photo-electron, is ejected from the atom with a kinetic energy equal to \( E_k = E - E_{n\ell j} \) [315]. This phenomenon is the basis of photoelectric devices such as solar panels. In EPMA it applies to both background and characteristic X-rays, and is predominant in the soft X-ray range \( (E < 1 \text{ keV}) \).

The probabilities of this interaction are expressed as photoelectric absorption cross sections \( \sigma_{i,\text{ph}}(E) \), which specify the probability of an X-ray of energy \( E \) to be absorb by an element \( i \) [315]. Unlike ionization cross sections, the shape of the photoelectric absorption cross sections is characterized by sharp edges located at the energy level \( (E_{n\ell j}) \) of each subshell. The abrupt change in the absorption behaviour comes from the fact that “photoionisation of a given shell is only possible when the photon energy
Chapter 2. Literature review

Chapter 2. Literature review

exceeds the corresponding [binding] energy" [315]. For characteristic X-rays, the cross sections are usually reported as mass attenuation coefficient [MAC] or mass absorption coefficients \((\mu/\rho)|^j_i = N_A \sigma_{\text{ph}}(E_j)/M_i\), which gives the absorption probability of a characteristic X-ray from a emitter element \(j\) in an absorbed element \(i\) [288, 315].

Resonance absorption The phenomenon behind X-ray resonance emission from electron inelastic scattering is also possible from photon excitation. It has the consequence of enhancing absorption in atoms with unfilled subshells such as rare-earth elements and transition metals in the first row of the periodic table [47]. In an absorption spectrum, this “anomalous” absorption is observed as a sharp peak above the absorption edge, often described as a “white line” [200, 218]. As it depends on different factors such as chemical bonding, this phenomenon is generally excluded from available photoelectric absorption cross sections.

Fluorescence Photoelectric absorption leaves the atom in an excited state. As they are no physical difference between an atom excited by an electron or a photon, the different outcomes from the relaxation of the atom to its ground state presented in §2.1.2.0.2 are also applicable after a photoelectric absorption interaction [315]. The emission of second generation X-rays or Auger electrons is called fluorescence or secondary fluorescence [124]. X-ray fluorescence is the combination of three interactions: (1) the emission of a characteristic or Bremsstrahlung X-ray by an electron, (2) the photoelectric absorption of this X-ray and (3) the radiative relaxation of this ionized atom. All three phenomena are associated with low probabilities. From a probability standpoint, the emission of an X-ray by an X-ray is less likely than the one from an electron as electrons generally interact more with matter than X-rays and can do so with several atoms along their trajectory [315]. The lower interaction probability of X-rays also means that fluorescence effects can be observed over a larger volume than the electron interaction volume, which may lead to interpretation problems in heterogeneous samples [111, 113, 215].

Simulation In Monte Carlo programs, the photoelectric absorption is implemented either as a interaction probability along the X-ray path (PENELOPE [213, 315]) or as an X-ray with an attenuated intensity, \(I_j = I_{j,0} \exp\left[-\frac{\mu}{\rho}\right]|^j_i \rho_i s_i\), where \(\rho_i\) and \(s_i\) are respectively the density and distance travelled in element or sample \(i\) (CASINO 2 [95, 155], WIN X-RAY [122], NISTMONTE [300], MONACO [10]).

2.1.3 X-ray spectrometers

The third ingredient of EPMA is the detection of the X-rays emitted from the sample. From quantum mechanics, an X-ray photon behaves like a particle with a certain energy and an electromagnetic wave with a specific wavelength. As for electrons inside the column (§2.1.1), de Broglie’s equation (Eq. 2.15) relate the two quantities. This duality implies that X-rays can be detected either using their energy by an energy dispersive spectrometer or their wavelength by a wavelength dispersive spectrometer. EPMA is a spectroscopy method, thus X-ray detectors should more rigorously be referred to as “dispersive spectrometers” as they both count the number of X-rays
entering them and determine their energy or wavelength through a dispersion process. The result is a spectrum, where X-ray intensities are measured as a function of the energy or wavelength. §2.1.3.1 and 2.1.3.2 summarizes (1) the principles of operation, (2) the resolution, (3) the efficiency, and (4) the artifacts of both technologies. The principles of operation cover how X-rays are converted into an intensity. The resolution discusses the resolving power of a detector, its ability to differentiate between different characteristic X-rays. The efficiency, defined as “the probability that an incoming photon is detected as a pulse by the spectrometer” [6], explains the factors influencing the capability of the detector to detect the incoming X-rays. Finally, the detection of X-rays is not always perfect and may result in artifacts. The most common ones of each spectroscopy technique are described.

### 2.1.3.1 Energy dispersive spectrometer

The technology of EDS designed for EPMA drastically changed in 1996 with the first commercial silicon drift detector [SDD] [204] based on the groundbreaking work of Gatti and Rehak [119] in 1984. In comparison to the preceding technology, lithium-drifted silicon crystal detector, SDDs improves almost all aspects of X-ray detection: better energy resolution, higher count rate, larger active area and ease of use. Although the two technologies share many components and involve similar physical processes, this section focuses on the newest technology.

The spectrometer assembly consists of (1) a detector, (2) a heat sink and (3) a pulse processor. The detector itself is made of (1) a collimator, (2) an electron trap, (3) a window, (4) a sensor, (5) a field effect transistor, and (6) a Peltier element. The collimator blocks stray X-rays produced by electrons hitting the microscope chamber. The electron trap prevents SEs and backscatter electrons [BSEs] to enter the detector. The window protects the sensor and serves as a vacuum barrier when the microscope chamber is vented. The window is generally made of a polymer-based thin film deposited on a supporting grid. The sensor is the active device where X-rays are converted into an electrical current. The field effect transistor amplifies the signal before sending it to the pulse processor. It is positioned as close as possible to the sensor to reduce noise. The Peltier element cools the sensor and field effect transistor to also reduce electrical noise. The heat produced by the Peltier element is dissipated by the heat sink [246, 292].

**Principles of operation** The conversion of an X-ray into an electrical current is based on the photoelectric absorption effect described in §2.1.2.1 and properties of semi-conductors, in occurrence silicon. When an incoming X-ray with energy $E_x$ travels or “disperses” through a silicon sensor, it is progressively absorbed by photoelectric absorption interactions, mainly with the valence electrons. Their ionization over the energy gap ($E_g \approx 3.8 \text{ eV}$) into the conduction band creates ($E_x/E_g$) electron-hole pairs [292]. As $E_g$ is constant for pure silicon, the number of electron-hole pairs created is directly proportional to the energy of the incoming X-ray.

In order to satisfy this proportionality the silicon sensor must be a very high purity, free of impurities and mobile charge carriers. In the former lithium drifted silicon sensors, lithium, a n-type dopant (electrons $>$ holes), was diffused through a p-doped silicon crystal (holes $>$ electrons) to nullify the mobile hole carriers and create an intrinsic semiconductor [124]. To prevent subsequent diffusion of lithium,
these detectors had to be operated at liquid nitrogen temperature [244]. Another method to generate an intrinsic semiconductor is by joining a p-type and a n-type silicon semiconductor, known as a p-n junction [400]. At the boundary, the holes from the p-type semiconductor and the electrons from the n-type semiconductor recombine and form a zone depleted of any charge equivalent to an intrinsic semiconductor [119]. When a reverse bias is applied (negative voltage applied on the p-type semiconductor and positive voltage on the n-type semiconductor), the size of the depleted zone increases [119].

The major advancement of SDD comes from the application of this physical concept to a special detector geometry allowing the detection of X-rays [119, 204]. In comparison to the lithium-drifted detector, the SDD technology offers improved capabilities by reducing the size of the anode and adding an additional radial drift electric field created by a series of concentric electrodes. A smaller anode decreases the capacitance of the sensor, reduces noise in the voltage signal, allows high frequencies for the saw-tooth pulsing voltage, results in a more rapid response and ultimately higher count rates can be achieved [246, 392]. Geometrically, the design of SDD decouples the size of the sensor’s active area and the size of the anode, allowing a larger collection angle.

The cross section of an SDD is sketched in Fig. 2.10. In this radial detector geometry, the anode, made of n-type semiconductor, is the centre of symmetry, located on the front side of the sensor. The cathodes, made of p-type semiconductor, are located on front and back side of the sensor. The X-rays enter through the back side and get absorbed in the large depleted zone created by the voltage applied between the anode and cathodes. A sensor with an insufficient applied voltage is shown in Fig. 2.10a with an approximated undepleted zone. Each X-ray generates a proportional amount of electron-hole pairs. The cathodes on the front side have slightly different voltages to force the electrons to drift towards the anode (Fig. 2.10b) and the holes (not shown) towards the cathodes.

To measure the charge collected at the anode, the applied voltage is pulsed following a saw-tooth function, a linear increase followed by sharp restoration. The charge build-up from the absorption of an incoming X-ray causes a sudden voltage jump proportional to the X-ray energy, which is then analyzed by a pulse processor after amplification. The limitation of this process is that each voltage jump, i.e. each incoming X-ray, must be separated by a certain time interval, known as the processing time, in order for the energy to be accurately determined [246, 292]. As each X-ray is processed, the number of counts in each energy bin of the spectrum increases and the spectrum takes shape.

Increasing the processing time improves the resolution as the height of the voltage jump can be more precisely measured, but decreases the detection rate of X-rays. When two or more X-rays enter the detector within a time interval less than the processing time, the detector cannot process these X-rays and is said to be “dead”. The time fraction when the detector cannot measure X-rays is called the dead time, as opposed to the live time when the detector is active. In terms of incoming X-ray count rate ($n$) and detected X-ray count rate ($n'$), the dead time is:

$$\text{dead time} = 1 - \frac{n'}{n}.$$  \hspace{1cm} (2.25)
Figure 2.10: Schematic representation of a silicon drift energy dispersive spectrometer. (a) SDD with an insufficient applied voltage to have a complete depleted zone. (b) drift direction of electron-hole pairs created by two X-rays. Adapted from [246].
From a spectrum, the intensity of a characteristic X-ray transition is determined by the area underneath its corresponding peak. Because of the limited resolution of EDS, which will be explained in more details in the following paragraph, the peaks of X-ray transitions with similar energies overlap. Filtering, deconvolution and fitting procedures are then used to resolve every peak and extract their net intensity, i.e. their characteristic intensity.

**Resolution** The energy resolution is the resolving power of a detector, which defines the width of a characteristic peak located at a certain X-ray energy. There are three main factors controlling the energy resolution: (1) the material of the sensor ($\sigma_m$), (2) the electronic noise ($\sigma_n$) and (3) the extent of incomplete charge collection ($\sigma_{icc}$) [246]. The energy resolution is equal to the quadrature addition of these factors [124, 292, 404]:

$$\sigma(E) = \sqrt{\sigma_m^2(E) + \sigma_n^2 + \sigma_{icc}^2(E)}, \quad (2.26)$$

usually expressed as the FWHM: $FWHM(E) = (2\sqrt{2\ln 2})\sigma(E)$.

First, the semi-conducting material inside the sensor (e.g. silicon or germanium) and its purity influence the uncertainty in the formation of electron-hole pairs. This uncertainty also depends on the X-ray energy. It can be expressed as $\sigma_m(E) = (\sqrt{FE_g})\sqrt{E}$, where $F$ is a material’s constant known as the Fano factor ($\approx 0.1$ for Si) and $E_g$ is the band gap energy [124, 246, 302]. Secondly, the quality of the electronics to amplify the charge collected at the anode while maintaining a low electronic noise has a large influence of the energy resolution. By selecting a longer processing time, the noise is averaged over a longer period of time and the resolution improves at the detriment of detection rate of X-rays. This uncertainty is independent of the X-ray energy and is a constant for a given electronic system. This is the fundamental compromise of EDS between resolution and counting statistics [124]. The last factor modifying the energy resolution is the phenomenon of incomplete charge collection, which arises when not all electron-hole pairs are collected by the anode and cathodes. This effect is more pronounced for low energy X-rays as the electron-hole pairs are produced closer to the back side cathode due to their shallow depth of penetration. In the spectrum this phenomenon appears as asymmetric peaks with a longer tail on the low energy side [246, 404].

In order to consider all these effects, the energy resolution of a given EDS system is usually reported for both the Mn K–L$_{2,3}$ and C K–L$_{2,3}$ [163]. Ignoring the incomplete charge collection, the resolution of an X-ray with energy $E$ ($FWHM(E)$) can be calculated using the measured resolution ($FWHM(E_0)$) at another X-ray energy $E_0$ [124, 302]:

$$FWHM(E) = \sqrt{k(E - E_0) + (FWHM(E_0))^2} \quad . \quad (2.27)$$

**Efficiency** The efficiency of an ED spectrometer depends on the composition and thickness of the window, the geometrical transparency of the supporting grid, the thickness of the cathode on the back side of the detector and the thickness of the sensor [6, 124]. The thickness of the cathode is also referred to as the dead layer since X-rays absorbed or partially absorbed in this zone of the sensor will not be properly detected, i.e. lower efficiency and higher incomplete charge collection [6,
The thickness of the sensor becomes important for high energy X-rays which may traverse completely the sensor without being absorbed. The efficiency curve is therefore the inverse product of the absorption curve for each layer crossed by the incoming X-rays before being absorbed in the sensor [6]. A SDD is 100% efficient between 3 to 11 keV [11].

**Artifacts** Apart from the peak shape alteration from incomplete charge collection, ED spectra may contain two other artifacts: escape and sum peaks. Both can lead to misidentification of the elements present in a sample and to underestimation of their concentrations.

Escape peaks, or internal fluorescence peaks, originate from the fluorescence of silicon by an incoming X-ray. As discussed in §2.1.2.1, one outcome of photoelectric absorption is the re-emission of an X-ray from the absorber, in occurrence here, the silicon sensor. If the fluorescent X-ray, Si K–L$_{2,3}$, is then re-absorbed inside the sensor, the number of electron-hole pairs created will still be proportional to the energy of the incoming X-ray. However, if the X-ray exits the sensor, the energy transferred to this X-ray is not counted, the proportionality is lost, and an artificial peak appears at the energy equal to $E - 1.74$ keV, where $E$ is the energy of the incoming X-ray and 1.74 keV, the energy of a Si K–L$_{2,3}$ X-ray. Although multiple fluorescent X-rays can theoretically escape, fluorescence of other silicon X-ray transitions (e.g. Si K–M$_{3,1}$, Si L$_{3}$–M$_{1}$ and Si L$_{2}$–M$_{1}$) can occur and a fluorescent Auger electron can be emitted, the escape peak caused by the fluorescence of the Si K–L$_{2,3}$ is the most probable. Escape peaks are an unavoidable artifact [124, 404].

A sum peak, or a pile-up peak, comes from the detection of two or more incoming X-rays as a single X-ray by the detector [404]. Normally, if two or more X-rays get absorbed inside the sensor within a time interval less than the processing time, these X-rays are rejected by the pulse processor and the dead time increases. If this time interval is however extremely short, this process fails; a single voltage jump is measured at the anode with a height proportional to the sum of the energy of each incoming X-ray. In a spectrum acquired at a high input count rate, several sum peaks are detectable, practically for each combination of characteristic peaks. For example, in a Fe–Ni alloy, possible sum peaks are $2 \times$ Fe K$_{\alpha}$, $2 \times$ Ni K$_{\alpha}$, Fe K$_{\alpha}$ + Ni K$_{\alpha}$, $2 \times$ Fe L$_{\alpha}$, $2 \times$ Ni L$_{\alpha}$, Fe L$_{\alpha}$ + Ni L$_{\alpha}$, etc. The height of a sum peak depends on the input count rate and the height of the original characteristic peaks. With the higher input count rates achievable with an SDD, the magnitude and implications of sum peaks in an ED spectrum have grown. For instance, this artifact is barely discussed or overlooked in the literature on lithium-drifted detectors [124, 288, 292]. Fortunately, it had been minimized by improvements in the pulse processor and post-acquisition correction routines [340]. Nevertheless, for accurate EPMA measurements, it is recommended to keep the dead time below 10% [236, 238].

**2.1.3.2 Wavelength dispersive spectrometer**

In the early years of EPMA, Castaing used a single, manually operated WD spectrometer to measure diffusion in a copper-zinc alloy [70]. Although the spectrometer operation is now fully automated and up to 5 spectrometers are installed on modern
Chapter 2. Literature review

microprobes, their principle of operation remain the same: a dispersive element (e.g. a single crystal) filters the incoming X-rays from an electron irradiated sample based on their wavelength and a detector counts the filtered X-rays [288].

The spectrometer assembly consists of (1) a dispersive element, (2) a detector, (3) a mechanical system and (4) a pulse processor. The dispersive element refers to any periodically structured material, such as a natural single crystal oriented in a particular crystallographic orientation or a synthetic layered element produced by sputtering alternating layers to form a periodic structure. The detector is a gas proportional counter, where a cylindrical chamber is filled with a noble gas, normally a mixture of argon and methane, or xenon. The mechanical system holds and moves the dispersive element and detector. The pulse processor, also known as pulse height analyzer [PHA], amplifies the signal from the detector and counts the number of X-ray detected.

Principles of operation The filtering process follows Bragg’s law, which gives the scattering angle ($\theta$) with the strongest constructive interference between a monochromatic incoming wave and a dispersive element:

$$n\lambda = 2d \sin \theta , \quad (2.28)$$

where $\lambda$ is the wavelength of the incoming wave, $d$ is the inter-planar spacing of the dispersive element and $n$ the order of the constructive interference ($n \in \mathbb{N}^+$). A wave impinging on a dispersive element is elastically reflected by the atoms of a crystal lattice or by the layers of a multilayer structure. Constructive interference between the incoming wave and the reflected waves occurs when the incident angle, angle between the incoming wave vector and the dispersive element surface, is equal to the scattering angle, angle between the reflected wave vectors and the dispersive element surface. This condition is satisfied only if the wavelength is an integer multiple of $2d \sin \theta$ as stipulated by Bragg’s law [124, 288, 385].

In a spectrometer, the condition of equal incident and scattering angles translates in having the source (i.e. the sample), the crystal and the detector lying on the circumference of a circle, known as the Rowland circle [288]. To change the incident angle, the mechanical system of the spectrometer moves both the dispersive element and detector. The possible incident angles vary between 10 and 60° depending on the dimension of the Rowland circle (100 to 160 mm). To ensure that the sample also respect the geometrical requirement, the shallow depth of focus of a LOM is used in the electron microprobes for the precise alignment of the z-position [143, 167].

The X-rays produced by inelastic scattering and by Bremsstrahlung emission are polychromatic (§2.1.2). For a given dispersive element (i.e. fixed inter-planar spacing, $d$) and given position of the dispersive element on the Rowland circle (i.e. incident angle, $\theta$), only the X-rays fulfilling Bragg’s law will diffract into the detector. In other words, the dispersive element filters out all incoming X-rays, except those with a wavelength equal to $2d \sin \theta/n$. This is a highly efficient filtering process, except for the presence of high order reflections ($n > 1$). The selective filtering implies that different dispersive elements and incident angles are required to detect the characteristic X-rays of all elements in the periodic table. In contrast to EDS where X-rays of all energies are acquired in parallel without any modification to the spectrometer, WDS acquires each X-ray serially.
Apart from being polychromatic, X-rays produced by an electron beam are isotropically emitted, i.e. the sample can be considered as a point source [288]. The distance between the sample and the dispersive element is usually however too short to assume parallel illumination. Each incoming X-ray has a slightly different incident angle, and consequently a different scattering angle with the dispersive element. To improve the focusing of the reflected X-rays onto the detector, the dispersive element is either ground and/or bent to increase the radius of curvature. The best focusing is obtained from the Johansson geometry where the dispersive element is bent to a radius equal to twice the Rowland circle and then ground to perfectly match the Rowland circle. Since grinding is not possible for all crystals, often only the bending step is taken, known as the Johann geometry [288, 408].

The physical processes responsible for converting the reflected X-rays into an electrical current in a gas proportional counter resemble those described for an ED spectrometer. Instead of creating electron-hole pairs, the incoming X-ray ionize the inert gas creating electron-ion pairs. A voltage is applied between a central anodic wire and a cathodic back plate. The electrons are attracted to the anode and the ions to the cathode. The amplitude of the pulse between them is proportional to the X-ray energy. For an X-ray with the same energy, less electron-ion pairs are produced as electron-hole pairs because the ionization energy of argon is 7 times larger than the energy gap of silicon (26.4 vs. 3.8 eV). To increase the number of electron-ion pairs produced, the applied voltage is increased to accelerate the free electrons causing further ionization inside the gas. The selection of the optimal voltage depends on the X-ray energy [143, 245, 288, 408].

As the ED detectors, fluorescence of Ar or Xe atoms by an incoming X-ray may create an escape peak if the fluorescent X-ray leaves the detector. For WDS the escape peak is not considered an artifact since all the detected counts are summed up regardless of their energy in the final intensity. The ionization of argon atoms also generates ultraviolet [UV] radiations, which may produce electrons as they interact with the walls of the counter. This problem does not occur in xenon filled gas proportional counters. To absorb these radiations, between 10 to 25% of methane (CH$_4$) is added to the gas mixture [143, 288].

As for ED spectrometers, gas proportional counters require a certain amount of time to absorb and process each X-ray, and are characterized by a dead time. The rate-limiting step is the movement of Ar ions to the cathode. Here as well, methane improves the detector operation by neutralizing the Ar ions before they reach the cathode [408]. The dead time constant for gas proportional counter is usually reported in µs and ranges between 1 to 4µs [67]. At low count rates, the incoming X-ray count rate ($n$) can be calculated from the detected X-ray count rate ($n'$) if the dead time constant $\tau$ is known [288]:

$$n = \frac{n'}{1 - n'\tau}.$$  \hspace{1cm} (2.29)

It is recommended to keep the count rate below 50 000 count/s to avoid dead time related effects [168]. Assuming a dead time constant of 2µs, and combining Eq. 2.25 and 2.29, this recommendation is approximately equivalent to the one for EDS to keep the dead time below 10%.
Although the area underneath a characteristic peak could be used like in EDS, the X-ray intensity in WDS is typically determined by measuring the height of the peak (i.e. the maximal intensity) and two background intensities on either side of the peak. The background intensity underneath the peak is then calculated by interpolation and subtracted to the peak intensity to obtain the net intensity. Another method is to estimate the background intensity using the mean atomic number technique [92]. Background intensities are measured on different reference samples that do not contain the element of interest, recorded as a function of the mean atomic number ($\bar{Z}$) of the reference samples and interpolated to found the background intensity of the element of interest in a sample with an unknown composition.

**Resolution** WDS is characterized by two resolutions: a wavelength resolution from the dispersive element and an energy resolution from the detector.

The former refers to the focusing and filtering capability of the dispersive element. If a spectrum is acquired by changing the incident angle, the wavelength resolution becomes analogous to the energy resolution of an ED detector as it controls the FWHM of the peaks. The focusing inaccuracies come from the fact that the incident angle is not constant over the whole surface of the dispersive element. Even in the Johansson geometry, the incident angle is only constant in the plane of the Rowland circle, but not along the perpendicular direction. From Reed [288], the wavelength resolution of a dispersive element following the Johansson geometry is given by:

$$\sigma_\lambda = \left(\frac{a}{r}\right)^2 \frac{d}{4n \sin \theta},$$

(2.30)

where $a$ is the half-width of the crystal, $r$ is the radius of the Rowland circle and $d$, $n$ and $\theta$ are taken from the Bragg’s law (Eq. 2.28). Reed [288] concluded that the “wavelength resolution is thus quite strongly dependent on $\theta$ and is relatively independent of the properties of the [dispersive element]”. In general, after converting the wavelength resolution into an energy resolution (Eq. 2.15), the resolution of WDS is approximately 30 times better than the one of EDS [124].

In contrast to the ED detector, the task of the gas proportional counter is mainly to count the number of incoming X-rays and has no influence on the width of the peaks. It does not need to accurately determine the energy of the X-rays, as the dispersive element has already filtered the incoming X-rays based on their wavelength. Its capability to filter the incoming X-rays based on their energy nonetheless becomes important in the case of high order reflections. High order reflections are multiples of a wavelength, or from an energy perspective, inverse multiples of an energy. While the dispersive element cannot differentiate these X-rays based on their wavelength, the gas proportional counter complements the dispersive element and acts as a second filter based on their energy. The energy resolution of a gas proportional counter is however at least 6 times worst than the one of an ED detector, owing to larger uncertainties in the formation of electron-ion pairs ($\sigma_m^{\text{EDS}} \approx 0.62\sqrt{E}$ vs. $\sigma_m^{\text{WDS}} \approx 4.56\sqrt{E}$).

**Efficiency** The efficiency of a WD spectrometer depends on the dispersive element reflectivity, the composition and thickness of the window in front of the detector, the geometrical transparency of the supporting grid and the type of gas inside the gas proportional counter [288]. Bragg’s law (Eq. 2.28) defines the conditions for diffraction, but gives no information regarding the efficiency of this process, known as the
reflectivity or reflectance and defined as the ratio between the intensity of the incoming and reflected waves [403]. For pure crystal, the reflectivity is influenced by the composition and surface roughness of the dispersive element, and by the composition, surface roughness, periodicity and interdiffusion of the layers for multilayer dispersive element [129]. The reflectivity also varies as a function of the incident angle and energy of the incoming X-rays [129, 288]. The window seals the gas inside the detector, but not all windows offer a leak-tight seal. For instance, thin polymeric windows typically used in argon/methane counters minimize the absorption of soft X-rays, but slightly leak inside the vacuum chamber. On the other hand, beryllium windows used in xenon counters are completely impermeable, but prevent the detection of soft X-rays [288]. The supporting grid is usually 70 to 80% transparent [288]. The absorption behaviour between Ar and Xe is critical for high energy X-rays (> 4 keV), which may not be completely absorbed in Ar [124, 288]. Overall, the efficiency of a WD spectrometer is usually more than 30% [124]. Albeit this limitation, because of the effective filtering of the dispersive element, high beam currents can be used without saturating the detector with X-rays. This is not possible with an ED spectrometer as the dead time would become overwhelmingly high [124].

Artifacts WDS suffers from three artifacts: (1) defocusing, (2) background “holes” and (3) total internal reflection. They can however be prevented by a well-designed experimental procedure and careful measurements.

Defocusing relates to the deviation of the position where the electron beam intersects the sample from the Rowland circle. Any deviation from this optimal analytical position results in a decrease of the measured intensity. In the z-direction, the direction along the optical axis, the sample position is adjusted using the LOM to avoid any defocusing. At low magnification or at large beam shifts, the incident angle of the incoming X-rays with the dispersive element changes and the conditions for diffraction are no longer satisfied. The resultant intensity loss is more noticeable for shifts along the spectrometer plane. The largest allowable shift without significant effects is roughly 20 to 40μm depending on the incident angle and the spectrometer geometry [288], limiting the length of line scan acquisitions using beam deflection.

Background “holes” are anomalous depressions in the background signal due to multiple reflections of Bremsstrahlung X-rays on differently oriented crystallographic planes of the dispersive crystal [295, 326]. As explained by Self et al. [326], an incoming X-ray may be diffracted by multiple planes if the Bragg condition is satisfied, i.e. \( 2d(hkl)\sin\theta = 2d(h'k'l')\sin\theta' \), where \( \theta' \) is the angle between the incoming X-ray and the normal of plane \( \{h'k'l'\} \). A notable case is the background “hole” near the Au L\(_3\)–M\(_{4,5}\) peak measured on the LiF crystal [112, 295, 326]. Although the magnitude of this artifact is relatively low, it may a large influence in the measurement of trace elements [295].

As the setting sun on a clear lake or light in a fibre optic cable, the total internal reflection of X-rays on the dispersive element is also possible under certain conditions, namely the energy of the incoming X-ray and the incident angle [290]. There is a critical incident angle for total internal reflection to occur, which can be calculated from solving Snell’s law, \( n_1 \cos\theta_1 = n_2 \cos\theta_2 \), for \( \theta_2 = 0 \) (n.b. “cos” is used instead of “sin” to follow the angle definition of Bragg’s law). The refractive index \( n_2 \) of a dispersive element depends on its composition and on the energy of the incoming X-rays. Most X-rays will not have a critical angle large enough for total internal
reflection to occur inside the incident angle range of a normal WD spectrometer. As demonstrated by Rehbach and Karduck [290], there however exist exceptions which have a noticeable influence on the shape of the background at low incident angles (e.g. Si L$_3$–M$_1$, Si L$_2$–M$_1$, Al L$_3$–M$_1$, Al L$_2$–M$_1$, etc.). This overall increase of the background intensity can be understood by the fact that, in reflection, the reflected angle is equal to the incident angle; X-rays are directly reflected in the gas proportional counter at all incident angles below the critical angle. As for the background “holes”, total internal reflection does not affect the characteristic X-ray intensities, but requires special attention in order to properly measure the background.

### 2.1.4 Quantification

From electrons to X-rays and from X-rays to intensities, the last step in EPMA is the conversion of X-ray intensities to a composition, i.e. the quantification. From the early days of EPMA [70], it was found that the mass fraction of an element $i$ ($w_i$) inside a sample is proportional to its X-ray intensity ($I_i$). It is however not directly proportional and there is no direct method to obtain the mass fractions from the measured X-ray intensities [124, 292]. The quantification is an inverse problem, where the composition is determined by an iterative procedure comparing experimental intensities with intensities calculated by a model for a given geometry (denoted as $g$) and estimate of the mass fractions ($\hat{w}_i$). Mathematically, it becomes an optimization problem where the cost function is the difference between the experimental intensity ($I_{\text{exp}}$) and calculated intensity ($I_{\text{calc}}$) for each element $i$ in a sample with $N^i$ elements [256]:

$$
\min_{\hat{w}_i} \sum_{i=1}^{N^i} \left( I_{i,\text{exp}} - I_{i,\text{calc}}(g, \hat{w}_1, \ldots, \hat{w}_i, \ldots, \hat{w}_{N^i}) \right)^2.
$$

(2.31)

Three key points can be drawn from Eq. 2.31. First, the X-ray intensity of element $i$ refers either to the intensity of one characteristic X-ray transition or the sum of the intensities of several characteristic X-ray transitions [238]:

$$
I_i = \sum_{k=1}^{N^{i,k}} I_{i,k},
$$

(2.32)

where $I_{i,k}$ is the net intensity of the X-ray transition $k$ of element $i$ and $N^{i,k}$ is the number of X-ray transitions considered in the intensity. Eq. 2.31 stands as long as the X-ray transitions used in the calculations correspond to those experimentally measured. Secondly, in order to calculate an intensity, the geometry of the sample must be known. The term “geometry” refers to the microstructural arrangement of the atoms within the X-ray interaction volume. For example, positioning an electron beam at a phase boundary or on a rough surface will yield a different X-ray intensity than inside a single phase, polished sample. With the diversity of geometries comes the complexity of the intensity models. Although Monte Carlo programs could theoretically simulate any geometry [225], practically and classically EPMA relies on analytical models, models based on physical equations without any random number, and requires a flat polished surface and homogeneity with the X-ray interaction volume [124]. The latter is defined by the volume inside the sample where X-rays are
emitted, either by inelastic scattering of electrons or by fluorescence of other X-rays. The third deduction is the requirement to either measure the intensity or to \textit{a priori} know the mass fraction of all elements present in the X-ray interaction volume in order for the model to calculate the intensity. Prior knowledge can come from other analytical techniques or from assumptions, like in the case of oxides where oxygen content can be estimated based on the charge balance between the cations and anions [288]. In other cases, the identification of all elements by a careful qualitative analysis and the measurement of their X-ray intensity is crucial to obtain accurate mass fractions.

Another determining factor for the accuracy is unquestionably the model and physical parameters used in the calculation of the intensities. As described in §2.1.2, electron-photon-matter interactions are complex phenomena, which can only be modelled by making some assumptions and compromises. Without enumerating and dissecting every model developed in the last 65 years, §2.1.4.2 explains common working principles shared by several models, but first §2.1.4.1 formulates the fundamental intensity equation and elaborates on the physical parameters involved in this equation. Finally, §2.1.4.3 describes the experimental strategy used in EPMA to further simplify the fundamental intensity equation.

### 2.1.4.1 Fundamental intensity equation

Let an incident beam of electrons with an accelerating voltage of $E_0$ perpendicularly impact a flat polished sample. Let the X-ray interaction volume $\mathcal{V}$ resulting from electron-photon-matter interactions be chemically homogeneous. Let the volume consist of $N$ elements with a mass fraction $w_i$ for each element $i$, where the composition is expressed as $\vec{w} = \{w_1, \ldots, w_i, \ldots, w_N\}$ and where $\|\vec{w}\| = \sum_{i=1}^{N} w_i = 1$. The measured intensity, $I_{i,k}$ (unitless), of the characteristic X-ray transition $k$ of element $i$ by a spectrometer is therefore defined as [120]:

$$I_{i,k}(E_0, \vec{w}) = \frac{N_A w_i}{M_i} \frac{I_{p\tau}}{e} \left( \frac{\Omega}{4\pi} \right) \epsilon(E_{i,k}) p_{i,k} \gamma_{i,k}(E_0, \vec{w}) f_{i,k}(\vec{w}) , \tag{2.33}$$

where $\gamma_{i,k}$ is the emission probability of X-rays by electrons:

$$\gamma_{i,k}(E_0, \vec{w}) \approx \int_{\rho z = 0}^{\infty} \int_{E = E_{i,k'}} \sigma_{\text{ion},i,k}(E) n_e(\rho z, E, \vec{w}) \exp (-\chi_{i,k}(\vec{w}) \rho z) \, dE \, d\rho z , \tag{2.34}$$

and $f_{i,k}$ is the contribution of fluorescence to the intensity:

$$f_{i,k}(\vec{w}) = 1 + \sum_{i' = 1}^{N} \sum_{k' = 1}^{N} f_{\text{ch},i,k,i',k'} + f_{\text{Br},i,k}(\vec{w}) . \tag{2.35}$$

Eq. 2.33 is divided in four groups. The first group confirms the proportionality between the mass fraction ($w_i$) and the intensity, or more precisely the number of atoms $i$ per mass inside an X-ray interaction volume ($\mathcal{V}$). $N_A$ is Avogadro’s number.
(6.022 \times 10^{23} \, \text{mol}^{-1}) \text{ and } M_i, \text{ the molar mass of element } i \, (\text{kg mol}^{-1}), \text{ giving the unit of kg}^{-1} \text{ to the first group. Evidently, the presence of the composition in the emission probability, } \gamma_{i,k} \text{ and fluorescence contribution, } f_{i,k}, \text{ proves the absence of direct proportionality with the intensity.}

The second group represents the number of electrons hitting the sample from the incident electron beam, which can be calculated from the beam current, \( I_p \) (in A), the acquisition time, \( \tau \) (in s) and the elementary charge, \( e \ (1.602 \times 10^{-19} \, \text{C}) \). The second group is unitless.

The third group is related to the spectrometer, which is characterized by a solid angle, \( \Omega \) (in sr) and an efficiency, \( e \) (unitless). The solid angle is the area occupied by the spectrometer on the unit sphere, see Zaluzec [421] for EDS and Reed [288] for WDS. The efficiency, as discussed in §2.1.3, depends on the energy of the incoming X-ray, expressed here as \( E_{i,k} \). The third group is also unitless.

All the electron-photon-matter interactions discussed in §2.1.2 determine the value of the terms in the last group and in Eq. 2.34 and 2.35. Elastic and inelastic scattering of electrons are represented by the electron density function, \( n_e \) (unitless), which gives the probability of finding an electron with an energy \( E \) inside a layer buried at a depth \( \rho z \) with a mass thickness \( d_pz \) and a composition \( \vec{w} \). In other words, it is the local energy distribution of electrons inside a layer [10]. The probability of an electron of energy \( E \) ionizing the atomic subshell \( k' \) of atom \( i \) is given by the ionization cross section for the atomic subshell \( k' \), \( \sigma_{\text{ion},i,k'} \) (in m\(^2\)). The subscript \( k' \) is used to represent the ionized atomic subshell of the X-ray transition \( k \). After ionization, the probability that the relaxation of atom \( i \) produces a radiative transition \( k \) is given by the transition probability, \( p_{i,k} \) (unitless). This probability includes other outcomes of the relaxation, i.e. Auger emission and Coster-Kronig transitions. The exponential term in Eq. 2.34 describes the photoelectric absorption of X-rays. The absorption function, \( \chi_{i,k} \) (in m\(^2\)kg\(^{-1}\)), is defined as:

\[
\chi_{i,k}(\vec{w}) = \text{cosec } \psi \sum_{ii=0}^{N(\vec{w})} \sigma_{\text{ph},ii}(E_{i,k}) \frac{N_A w_{ii}}{M_{ii}},
\]

(2.36)

where \( \sigma_{\text{ph},ii}(E_{i,k}) \) is the photoelectric absorption cross section for an X-ray with an energy \( E_{i,k} \) interacting with an atom \( ii \) (in m\(^2\)), and \( \psi \), the take-off angle, the angle between the sample surface and the spectrometer (in rad). Instead of the photoelectric absorption cross section, the absorption probability of an atom \( ii \) is usually reported as a mass absorption coefficient, \( (\mu/\rho)_{ii} \) (in m\(^2\)kg\(^{-1}\)), which is defined as: \( (\mu/\rho)_{ii}(E_{i,k}) = \sigma_{\text{ph},ii}(E_{i,k})N_A/M_{ii} \). Essentially, the photoelectric absorption of an X-ray is calculated from the product of its absorption probability and the distance it travels inside volume \( V \) towards the spectrometer. This distance is approximated from the take-off angle of the spectrometer (\( \psi \)) and the mass depth of X-ray emission (\( \rho z \)). Removing the exponential term from Eq. 2.34 would yield the generation probability of X-rays by electrons. \( f_{i,k} \) takes care of the fluorescence contribution to the intensity, i.e. the re-emission of an X-ray after photoelectric absorption. Another way to look at the last group of Eq. 2.33 is that the emission of X-rays inside the X-ray interaction volume is divided into two quantities, \( \gamma_{i,k} \) (in kg) and \( f_{i,k} \) (unitless), based on whether an electron or an X-ray ionizes the atom.
2.1. Electron probe microanalysis

Eq. 2.34 is a double integral as it depends on both the energy and depth distribution of the electrons inside the X-ray interaction volume. The first integral is performed over the X-ray interaction volume from the surface ($\rho z = 0$) to an infinite depth where no X-ray are emitted. The second integral is bound between the ionization energy of the X-ray transition ($E_{i,k'}$) and the beam energy ($E_0$) as only those electrons can produce the X-ray transition of interest. The electron density function and exponential term for the photoelectric absorption are spatially dependent. The ionization cross section and the electron density function depends on the energy of the electrons (second integral), whereas the photoelectric absorption cross section is a constant for a given X-ray transition and composition.

The fluorescence phenomenon can intensify the emission of an X-ray transition $k$ if the photoelectric absorption of other, more energetic X-rays results in the emission of more of $k$ X-rays. Theoretically any X-ray with an energy above the ionization energy of the atomic subshell $k'$ of atom $i$, $E > E_{i,k'}$, can be absorbed by an atom $i^*$ and produce a fluorescent X-ray from the relaxation transition $k^*$. Generally, as characteristic X-rays outnumber Bremsstrahlung X-rays, fluorescence from characteristic X-rays is more probable [120, 288]. Eq. 2.35 considers separately the contribution of characteristic and Bremsstrahlung X-ray fluorescence to the intensity. To account for all different combinations and individual probabilities, the total probability of fluorescence by characteristic X-rays, $f_{ch}$, is calculated from a double summation over all elements in the X-ray interaction volume, $N^i(\vec{w})$ and all possible X-ray transitions, $N^i\star,k$. The contribution from Bremsstrahlung X-rays is represented by a single factor, $f_{Br}$. A more complete description of the contribution of fluorescence to the intensity is given by Llovet et al. [215].

2.1.4.2 $\phi(\rho z)$ models

In order to calculate the emission probability of X-rays by electrons, $\gamma_{i,k}$, the critical term is the electron density function, $n_e$, as the other quantities, such as the cross sections, can either be calculated or obtained from tabulations. Three methods have been used to approximate the electron density function: (1) Monte Carlo simulations [10], (2) solutions of the electron transport equation [225] or (3) $\phi(\rho z)$-based models [28, 33, 70, 273]. The later solution indirectly calculates the electron density function by defining a new function, $\phi(\rho z)$, as “the ratio between the [generated X-ray] intensity of a [...] layer of mass thickness $d\rho z$ at mass depth $\rho z$ and that of an identical but unsupported layer” [273]. In other words, the $\phi(\rho z)$ function represents the depth distribution of X-ray emission by electrons, normalized by an unsupported layer.

In an unsupported layer of infinitesimal thickness, single scattering is assumed; an incident electron interacts at most once inside the layer. In Eq. 2.34, the second integral disappears as the energy distribution is equal to a Dirac delta function centred at the beam energy ($E_0$), the electron density function goes to unity in the absence of scattering and the exponential term vanishes as there is no photoelectric absorption. $\gamma_{i,k}$ becomes a constant, equal to $\sigma_{ion,i,k'}(E_0)$. From the definition of the $\phi(\rho z)$, all
terms in Eq. 2.33 cancel out in the intensity ratio except the emission probability of X-rays by electrons. Based on the quantities defined for Eq. 2.34, the $\phi(\rho z)$ function is formulated as:

$$\phi_{i,k'}(\rho z, E_0, \vec{w}) = \frac{1}{\sigma_{\text{ion},i,k'}(E_0)} \int_{E=E_{i,k'}}^{E_0} \sigma_{\text{ion},i,k'}(E)n_e(\rho z, E, \vec{w}) \, dE,$$

(2.37)

and the emission probability simplifies to:

$$\gamma_{i,k}(E_0, \vec{w}) \approx \sigma_{\text{ion},i,k'}(E_0) \int_{\rho z=0}^{\infty} \phi_{i,k'}(\rho z, E_0, \vec{w}) \exp (-\chi_{i,k}(\vec{w})\rho z) \, d\rho z.$$

(2.38)

Fig. 2.11 shows a typical $\phi(\rho z)$ curve of the Mn K–L$_{2,3}$ X-ray transition emitted from a pure Mn sample irradiated with a 15 kV electron beam, calculated using the XPP [273] analytical model. The curve is characterized by (1) a initial value greater than unity ($\phi(\rho z = 0)$), (2) a maximum value at a certain mass depth ($\phi(\rho z_m) = \text{max}$), and (3) a maximal mass depth of ionization ($\phi(\rho z \to \infty) = 0$) [273]. The initial value, also known as the surface ionization, primarily depends on the level of electron backscattering. As elastic scattering may revert the trajectory of incident electrons, these BSEs also undergo inelastic scattering on their way out of the sample producing more X-rays than in the idealized case of an unsupported infinitesimal layer where electron backscattering is nonexistent. The overvoltage ratio, the ratio between the beam energy and the ionization energy ($U_{0,i,k} = E_0/E_{i,k}$), the energy loss function of the incident electrons, and the ionization cross section influence the other two characteristic features of the $\phi(\rho z)$ curve [273]. To analytically calculate the $\phi(\rho z)$ function at any mass depth, different mathematical functions have been used to approximate the exact shape of the distribution: two quadratic functions in PAP [273], two exponential functions in XPP [273] and two Gaussian functions in PROZA [28]. The fitting parameters of these functions are calculated based on other physical parameters, such as cross sections, stopping power, etc. The models were verified using experimental intensity measurements using tracers [184, 289] and Monte Carlo simulations.

2.1.4.3 k-ratio

With $\phi(\rho z)$ models to calculate the emission probability of X-rays by electrons, all the terms related to electron-photon-matter interactions in Eq. 2.33 (fourth group) can be calculated or obtained from databases. The remaining terms need to be measured, determined or a priori known. While the beam current and acquisition time can be experimentally measured, the solid angle and efficiency of the spectrometer are either unknown, unpredictable or difficult to determine.

This led Castaing in the early days of EPMA to design his quantification procedure based on intensities normalized to reference samples with known compositions [70]. Experimentally, the net intensity of an X-ray transition is acquired using the same instrument, spectrometer and accelerating voltage on both the sample with an unknown composition $\vec{w}^{\text{unk}}$ ($I_i^{\text{exp,unk}}$) and on a reference sample containing element
2.1. Electron probe microanalysis

Figure 2.11: Calculated $\phi(\rho z)$ curve of the Mn K–L\textsubscript{2,3} X-ray transition emitted from a pure Mn sample irradiated with a 15 kV electron beam using the XPP [273] analytical model as implemented in [302]

$i$, but where the composition $\vec{w}^\text{ref}$ is known ($I_{i}^{\text{exp,ref}}$). To additionally remove the electron beam dependency, the experimental intensities are also normalized by the beam current and acquisition time. The ratio of these intensities is known as the experimental k-ratio, $k_{i,k}^{\text{exp}}$:

$$k_{i,k}^{\text{exp}} = \frac{I_{i,k}^{\text{exp,unk}}/(I_{p}^{\text{unk}})}{I_{i,k}^{\text{exp,ref}}/(I_{p}^{\text{ref}})}.$$  \hspace{1cm} (2.39)

Mathematically, the equivalent k-ratio between the intensities calculated per Eq. 2.33 and 2.38 cancels out several terms, including the third group related to the spectrometer:

$$k_{i,k}^{\text{calc}}(E_{0}, \vec{w}^{\text{unk}}, \vec{w}^{\text{ref}}) = \frac{\int_{0}^{\infty} \phi_{i,k}(\rho z, E_{0}, \vec{w}^{\text{unk}}) \exp\left(-\chi_{i,k}(\vec{w}^{\text{unk}})\rho z\right) d\rho z}{\int_{0}^{\infty} \phi_{i,k}(\rho z, E_{0}, \vec{w}^{\text{ref}}) \exp\left(-\chi_{i,k}(\vec{w}^{\text{ref}})\rho z\right) d\rho z} f_{i,k}(\vec{w}^{\text{ref}}).$$  \hspace{1cm} (2.40)

The quantification equation (Eq. 2.31) then reformulates into the optimization between the experimental and calculated k-ratios for all elements in the sample with an unknown composition:

$$\min \sum_{i=1}^{N} \left(k_{i}^{\text{exp}} - k_{i}^{\text{calc}}(\vec{w}_{1}, \ldots, \vec{w}_{i}, \ldots, \vec{w}_{N})\right)^{2}. \hspace{1cm} (2.41)$$

Apart from the points raised for the quantification equation based on intensities (Eq. 2.31), four additional conclusions can be drawn from the use of k-ratios. First, the simplification of physical terms, such as the transition probability ($p_{i,k}$) and the ionization cross section ($\sigma_{\text{ion},i,k}(E_{0})$), in Eq. 2.33 eliminates potential sources of uncertainties. Secondly, when $\vec{w}^{\text{ref}}$ approaches $\vec{w}^{\text{unk}}$, $k_{i}^{\text{exp}}$ and $k_{i}^{\text{calc}}$ tend towards unity.
and the influence of any inaccuracy in the physical model and parameters are reduced.
Thirdly, from Eq. 2.40, the same accelerating voltage ($E_0$) must be used to acquire the intensities of element $i$ on the unknown and reference sample. Deceleration of the incident electron beam in a conductive coating or charging of one of the samples would invalidate this assumption. As per Eq. 2.41, the accelerating voltage can however be changed to measure different elements. Finally, similarly to the accelerating voltage, the settings of the spectrometer used to acquire the intensities must be kept constant.

The explications and derivations presented in this section differ from the conventional approach used to explain the quantification in EPMA based on the matrix corrections, or familiarly $ZAF$ for the atomic number ($Z$), absorption ($A$) and fluorescence ($F$) correction [124, 143, 288, 292]. The classical quantification equation [124],

$$\frac{w_i^{\text{unk}}}{w_i^{\text{ref}}} = \frac{ZAF_{i,k}(E_0, \vec{w}_i^{\text{unk}}, \vec{w}_i^{\text{ref}})k_i^{\text{exp}}}{k_i^{\text{calc}}}$$

(2.42)

can be rewritten using Eq. 2.40 as the ideal case of Eq. 2.41 where $k_i^{\text{exp}}$ is equal to $k_i^{\text{calc}}$ and $ZAF_{i,k}$ is defined as:

$$ZAF_{i,k}(E_0, \vec{w}_i^{\text{unk}}, \vec{w}_i^{\text{ref}}) = \frac{\int_0^{\infty} \phi_{i,k'}(\rho z, E_0, \vec{w}_i^{\text{ref}}) \exp \left(-\chi_{i,k}(\vec{w}_i^{\text{ref}})\rho z\right) d\rho z}{\int_0^{\infty} \phi_{i,k'}(\rho z, E_0, \vec{w}_i^{\text{unk}}) \exp \left(-\chi_{i,k}(\vec{w}_i^{\text{unk}})\rho z\right) d\rho z} f_{i,k}(\vec{w}_i^{\text{ref}}).$$

(2.43)

**Summary**

Concluding on the principles of EPMA, Eq. 2.39 to 2.41 offer a perfect synthesis all the physical concepts described in this section. The measurement of an experimental k-ratio (Eq. 2.39) depends on the ability to form a focused, monoenergetic electron beam inside the electron column (§2.1.1), irradiate a sample and collect the emitted X-ray in a spectrometer (§2.1.3). The calculation of a theoretical k-ratio (Eq. 2.40) relies on the understanding and modelling of the electron-photon-matter interactions inside the sample as explained in §2.1.2. Finally, the quantification (Eq. 2.41) bridges the experimental and theoretical concepts to determine the chemical composition of a sample. EPMA is an analytical technique used in several fields of science and engineering: geology, petrology, material science, and as the next section will discuss steel.

**2.2 Characterization of steel microstructure**

Broadly speaking, steel can be defined as a metallic alloy primarily composed of iron [16, 41]. Around 80 other elements may be alloyed with iron to form steel [41]. The most common alloying element is carbon, which can present up to a mass fraction of approximately 2% (ferrous alloys with a higher carbon content are classified as cast irons) [16, 41, 64]. Other alloying elements can act as phase stabilizers, accelerate or delay phase transformations, and strength the steel by substituting iron atoms, occupying interstitial sites or forcing the precipitation of a second phase [16, 41].
Apart from their composition, “the performance of steels depends on the properties associated with their microstructures, that is, on the arrangements, volume fractions, sizes, and morphologies of the various phases constituting a macroscopic section of steel” [16]. The engineering of complex microstructures with several components by carefully designed heat treatments and manufacturing processes has led to the development of AHS steels such as DP, CP, TRIP, twinning induced plasticity [TWIP] steels [187]. It is an ongoing research area which aims at designing steel grades with a strength, ductility and toughness for a particular application [187].

Due to the complexity and heterogeneity of modern steel alloys, knowing their chemical composition and grain size is no longer sufficient to understand their mechanical properties and behaviour under deformation. The volume fraction, chemical composition and crystallographic structure of each microstructural constituent must be determined with high accuracy. These information become the input parameters for different modelling approaches (phase field [346, 348], representative volume element [277, 281], etc.), which can study the evolution of the microstructure during the manufacturing and predict the final mechanical properties. The decrease of the crystallite size in modern steels makes the characterization even more challenging.

This work focuses on the determination of the chemical composition of steel constituents in AHS steels by EPMA, a common technique used in the industry and research laboratories to study steels [4, 23, 32, 96, 108, 211, 250, 277, 281, 283, 309, 321, 322, 345, 357, 362, 413, 422, 423]. From all the possible alloying elements, the quantification of carbon is the most challenging, yet the most important as it has a large influence on the phase transformation and steel properties. After summarizing the common constituents found in AHS steels and their characteristics (§2.2.1), a review of the current strategies used in EPMA to measure this element is given in §2.2.2.

### 2.2.1 Steel constituents

The term “constituent” regroups all equilibrium phases (present in phase diagrams), metastable and common mixtures of phases present in modern steels. Smirnov et al. [333] denoted over forty different constituents in the literature for low carbon steels alone. The description is here limited to the constituents typically found in DP, TRIP, and CP steels, which will be studied in this work, namely ferrite, austenite, cementite, martensite, pearlite and bainite. The constituents are described and compared in the next paragraphs on the basis of their chemical composition, their crystallography and their characteristic identifiable features by chemical etching, EPMA and electron backscatter diffraction [EBSD] techniques. Summary tables are given at the end (Tab. 2.3 and 2.4).

#### 2.2.1.1 Equilibrium phases

Fig. 2.12 shows a typical iron-carbon phase diagram for a low alloy steel [382]. Neglecting the high temperature delta ferrite (δ), there are three other equilibrium phases: ferrite (α), austenite (γ) and cementite (Fe₃C). At room temperature, ferrite has a low solubility for carbon and contains less than 0.0002% [41]. All the remaining carbon forms cementite, a line compound with a fixed carbon mass fraction of 6.689%. The iron atoms follow a body centred cubic [BCC] crystal structure
in ferrite \((a = 0.286 \text{ nm} \ [41])\), whereas they have an orthorhombic crystal structure in cementite \((a = 0.509 \text{ nm}, b = 0.674 \text{ nm}, c = 0.453 \text{ nm} \ [116])\). The addition of Si, Cr and Mo promotes the formation of ferrite \([41, 277]\). As a substitutional atom, silicon also provides solid solution strengthening of ferrite \([320]\).

Austenite is an intermediate phase for any steel where the carbon atoms occupy the octahedral and tetragonal interstitial sites of the face centred cubic [FCC] crystal-structured iron atoms \((a = 0.364 \text{ nm} \ [41]) \ [41, 64]\). The larger interstitial sites in the FCC lattice in comparison to those in the BCC lattice increase the carbon solubility in austenite \([16]\). Under equilibrium conditions, austenite does not exist at room temperature unless other alloying elements are introduced such as Ni in stainless steels or Mn in TWIP steels. Under non-equilibrium conditions, elements such as C and Mn can stabilize the austenite resulting in a metastable phase known as retained austenite (e.g. TRIP and CP steels) \([41]\).

Chemical etching followed by LOM investigation is the traditional method to identify steel phases. It either preferentially etches one phase or electrolytically deposits a layer over a phase \([13]\). Nital etchant, a solution of 1 to 3% nitric acid and ethanol, reacts more strongly with low carbon phases, in occurrence ferrite. Coloured etchants, Le Pera and Klemm (see \([13]\) for solution), selectively colours ferrite grains. Under a LOM, cementite and retained austenite respectively appear elevated or white after nital and coloured etching. The differentiation between these two phases is usually done based on their morphology, rather than clear characteristic features. This is not the case in EBSD as each phase has a distinct crystal structure, which can be determined from the collected diffraction patterns. For further explanations on EBSD, the reader is referred to Schwartz et al. \([324]\) and the Master’s thesis of this author \([257]\).

For EPMA, authors have reported different precisions on the quantification of the carbon mass fraction in steel: \(< 0.1 \% \) by Duerr and Ogilvie \([96]\), 0.04 % by Almagro et al. \([4]\), 0.05 % by Turpin et al. \([362]\), 0.03 % by Liu et al. \([211]\), and \(< 0.1 \% \) by Zhu et al. \([423]\). It is therefore not possible with EPMA to measure the carbon content inside ferrite. However, this technique can differentiate between ferrite and retained austenite as shown by Liu et al. \([211]\), and theoretically between retained austenite and cementite as the carbon content in retained austenite falls in between the one of ferrite and cementite.

### 2.2.1.2 Metastable phases

Metastable phases are formed by specific heat treatments where the final step is a rapid cooling, quenching, in water, oil, salt bath or liquid gas \([16]\). This leaves little to no time for the atoms to diffuse or reorganize, as they would normally do under slow cooling to reach their equilibrium structure. The influence of the holding time and cooling rate is captured by time temperature transformation [TTT] or continuous cooling transformation [CCT] diagrams. An example of a TTT diagram for a low alloy steel is shown in Fig. 2.13 \([382]\).

Quenching of steel causes an athermal transformation, where “single atoms do not exchange places, [but] only clusters of atoms exchange places in a coordinated, coupled movement” \([41]\). Martensite is a highly distorted and strained structure, organized in plates for high carbon steels (carbon mass fraction > 1.4%), blocks of small laths for low carbon steels (< 0.5 %) and a mixture of both for medium carbon steels \([41]\). Since carbon could not diffuse out of the lattice, martensite has a distorted
2.2. Characterization of steel microstructure

Figure 2.12: Iron-carbon phase diagram for a low alloy steel. Modified from [382].

Figure 2.13: Time temperature transformation diagram for a low alloy steel. Modified from [382].
BCC lattice, a body centred tetragonal [BCT] crystal structure, where the elongation along the c-axis depends on the carbon content [41, 64]. Another consequence of the diffusionless transformation is the larger unit cell volume of martensite in comparison to the more closely-packed austenite, which further strain the steel creating large amounts of dislocations. The combination of these two factors procures high hardness and strength to martensite in comparison to ferrite and austenite [16, 41].

The martensitic transformation starts and ends at specific temperatures (Fig. 2.13), which depends on the steel composition, especially the carbon content. “At any carbon content larger than 0.5% the martensite formation is incomplete when room temperature is reached and [...] retained austenite appears.” [41] Since Si is insoluble in cementite, its addition prevents the formation of cementite and consequently helps the retention of austenite [41, 43, 277].

Thermodynamically, martensite and retained austenite are metastable as heating will cause carbon atoms to diffuse and form carbides (i.e. cementite) [16]. This process, known as tempering, reduces the hardness, but to the advantage of improved ductility and toughness. Retained austenite is also mechanically unstable, as it transforms into martensite under plastic deformation, providing additional strength to the steel [16].

Martensite is recognized after nital etching from its brownish, dark colour under a LOM and rough, textured appearance in a SEM. In EBSD, martensite cannot be differentiated from ferrite due to the low tetragonality (c/a ratio) of its crystal structure. Usually, its segmentation is performed based on the quality of its diffraction patterns [253, 257, 259, 310, 351, 353, 411, 412, 418]. The higher strain and dislocation density in martensite distort the lattice, resulting in more diffuse diffraction and the deterioration of the acquired patterns [257]. In EPMA, martensite can be identified by its higher amount of carbon than ferrite, but depending on the carbon content the differentiation from retained austenite may be more difficult.

### 2.2.1.3 Mixture of phases

Slow cooling a steel below the eutectoid temperature (723°C in Fig. 2.12) results in a microstructure consisting of ferrite, cementite and a particular periodic arrangement of these two phases known as pearlite. As the carbon atoms diffuse out of ferrite into austenite, a lamellar structure of alternating layers of ferrite and cementite forms [41]. It can easily be identified after nital etching, but the lamellar spacing is normally too small (< 200 nm) to be measured by EBSD or EPMA.

As shown in Fig. 2.13, another constituent forms by cooling a steel using an intermediate cooling rate: bainite. The result is an unordered two-phase microstructure consisting of dislocation-rich ferrite and either cementite or retained austenite, depending on the alloying element (e.g. Si) [39]. The slower cooling rate in comparison to the one to form martensite allows the diffusion of carbon atoms, but not to the extent required to form pearlite [41]. At high temperatures, the diffusion progresses more quickly and a carbon-free ferrite is formed inside the bainitic microstructure, referred to as upper bainite. Oppositely at low temperatures, the microstructure of the lower bainite is characterized by the presence of carbon atoms and precipitated cementite inside its ferrite grains [41, 254]. Based on atom probe tomography [APT] and convergent electron beam diffraction [CBED], Bhadeshia [39] reported a higher carbon concentration in the bainitic ferrite than in equilibrium ferrite, corroborating the incomplete diffusion of the carbon atoms.
2.2. Characterization of steel microstructure

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Crystal structure</th>
<th>Approx. carbon mass fraction (%)</th>
<th>Other alloying elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>BCC</td>
<td>0.0002</td>
<td>Si, Cr, Mo</td>
</tr>
<tr>
<td>Cementite</td>
<td>Orthorhombic</td>
<td>6.689</td>
<td>Cr</td>
</tr>
<tr>
<td>(Retained) austenite</td>
<td>FCC</td>
<td>0.5 to 2</td>
<td>Mn, Ni</td>
</tr>
<tr>
<td>Martensite</td>
<td>BCT</td>
<td>0.1 to 1.0</td>
<td>Mn</td>
</tr>
</tbody>
</table>

Table 2.3: Characteristics of steel constituents.

In DP and TRIP steels, the presence of pearlite and bainite is detrimental to the overall toughness. The addition of Mn, Mo, Ni and Cr delays the formation of these constituents, allowing the carbon enrichment of austenite and therefore promoting the formation of martensite and retained austenite [41, 43, 277].

Although the limited resolution of EBSD and EPMA does not allow the measurement of the individual components of bainite in a SEM, bainitic regions can be indirectly identified. In EPMA, it is expected that the carbon content of bainite, being determined from the volume fraction of bainitic ferrite and cementite/martensite, falls between the one of ferrite and martensite. In EBSD, the diffraction patterns of bainite are also diffused, but the reduction in quality is less pronounced than in martensite. Instead of the diffraction quality, Zaefferer et al. [418] used the kernel average misorientation [KAM], calculated as the average misorientation around each given pixel, to segment out the bainite from ferrite in TRIP steels. The higher dislocation density in bainite leads to higher KAM values. The combination of the diffraction quality to segment martensite and the KAM to segment bainite is the strategy recommended by European report on the *Microstructural quantification of multi phase steels (Micro-Quant)* [1] for the phase identification in CP and TRIP steels. Under a LOM, bainite has a broken morphology which can be observed after nital etching [304].

Summary

Tab. 2.3 summarizes the characteristics of the aforementioned steel constituents, whereas Tab. 2.4 gives the strategy for their identification using either EBSD, EPMA or LOM after nital etching.

2.2.2 Quantification of carbon

There are five main challenges with the quantification of carbon by EPMA: (1) carbon contamination, (2) low X-ray intensity, (3) interferences of high order X-ray reflections, (4) determination of the background, and (5) selection of reference materials. All these challenges also generally apply to the quantification of any soft X-ray, for example boron [34], oxygen [31], nitrogen [30] and L X-ray transitions of transition metals [125, 214, 235, 295, 405] (see §2.4.2). The next paragraphs explain these difficulties and review the solutions and strategies found in the literature to circumvent them.
Chapter 2. Literature review

<table>
<thead>
<tr>
<th>Constituent</th>
<th>EBSD</th>
<th>EPMA</th>
<th>LOM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystal structure</td>
<td>Diffraction quality</td>
<td>KAM</td>
</tr>
<tr>
<td>Ferrite</td>
<td>BCC</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Cementite</td>
<td>Ortho.</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>(Retained) austenite</td>
<td>FCC</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Martensite</td>
<td>BCC</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Pearlite</td>
<td>BCC</td>
<td>medium-high</td>
<td>medium</td>
</tr>
<tr>
<td>Bainite</td>
<td>BCC</td>
<td>medium-high</td>
<td>high</td>
</tr>
</tbody>
</table>

Table 2.4: Identification criteria of steel constituents for EBSD, EPMA and LOM after nital etching. Inspired by [1]

2.2.2.1 Carbon contamination

The phenomenon of carbon contamination consists in the cracking of organic molecules by the electron beam resulting in the deposition of a carbonaceous material on the specimen surface. The magnitude of this phenomenon depends on many factors and several mitigating strategies have been proposed. §2.3 is dedicated to the explanation and review of this phenomenon. For the moment, it goes without saying that it becomes impossible to obtain accurate quantitative measurements if irradiating the sample with an electron beam is continuously producing the same element one tries to measure.

For the measurement of carbon in steels, the most common anti-contamination devices used are the gas jet [4, 32, 96, 108, 164, 266, 303, 309] or a liquid nitrogen cold trap [96, 164, 309]. The former creates a protective or reactive, local atmosphere around the measurement position depending on the injected gas, whereas the latter locally improves the vacuum by capturing volatile organic molecules. In combination with the gas jet, a decontamination time from 1 to 60 min was used by several authors to clean the surface prior to a measurement or to remove previously deposited carbonaceous deposits [4, 32, 96, 108, 303]. As crucial as it is for accurate carbon measurements, many authors [23, 211, 250, 422, 423] neglected to mention the strategy used to minimize contamination during their experiment.

Even with a decontamination time, many authors [4, 32, 96] warned against using too small step sizes between the measurement locations: “It is definitely not advisable to perform a series of carbon measurements on closely located spots or areas because
the next measurement might be performed right in the halo produced by the previous one.” [32]. Duerr and Ogilvie [96] recommended a step size greater than 10μm and Almagro et al. [4] greater than 2μm.

2.2.2.2 Low X-ray intensity

Physically, there is a low probability that an ionization interaction with a carbon atom results in the emission of a C K-L₂,₃ X-ray (i.e. low fluorescence yield) and a high probability that this X-ray is photoelectrically absorbed by the steel matrix (i.e. high MAC in Fe, Cr and Ni). Additionally, the carbon mass fraction in steel constituents is typically below 1 %, which further reduces the number of emitted X-rays. Because of their better detection efficiency and energy resolution below 1 keV, WD spectrometers are the most appropriate spectrometers for the measurements of carbon in steel. Only qualitative carbon measurements were published using EDS [23].

In order to detect a statistically relevant intensity to precisely determine the carbon content, authors suggested to use long acquisition times and/or higher beam currents [4, 96, 303], to use multilayer dispersive elements with higher reflectivity [4, 164, 309] or to change the gas mixture inside the proportional counter [96]. Almagro et al. [4] and Robaut et al. [303] recommended a beam current between 100 to 300 nA and a counting time of at least 10 s. Multilayer dispersive elements made of alternating layers of W and Si (d = 2.97 nm) or Ni and C (d = 4.96 nm) have the advantages of having a higher reflectivity than natural crystals such lead stearate, and lowering the intensity of high order lines (discussed in §2.2.2.3) [4, 164, 309]. Soft X-ray peaks in a spectrum are also known to change shape and shift in energy depending on the chemical bonding [30–32, 34]. Another benefit of multilayer dispersive elements is that their worst energy resolution masks most of these effects [32]. Finally, Duerr and Ogilvie [96] increased the methane to argon ratio from 10/90 to 75/25 to allow a longer mean free path of soft X-rays inside the detector. The exact intensity gain was not reported.

In conclusion, the carbon contamination aggravates the low X-ray intensity problem. Unless the contamination is controlled and minimized, increasing the acquisition time inevitably leads to higher contamination and inaccurate measurements. Another option is to increase the beam current, but this will worsen the spatial resolution as the beam diameter increases with the beam current (see §2.1.1).

2.2.2.3 Interferences of high order X-ray reflections

One consequence of Bragg diffraction is the presence of high order X-ray reflections in a WD spectrum (§2.1.3.2). This is particularly problematic for steels, where the high order X-ray reflections of the major alloying elements (Cr, Mn, Fe and Ni) appear in the vicinity of the C K-L₂,₃ peak [4, 32, 96, 164, 309]. Examples are given in Tab. 2.5. A solution to minimize the influence of high order reflections is to use the gas proportional counter as an ED spectrometer. The PHA is operated in differential mode, which allows to partially filter out high order reflections based on their higher energy [4, 32, 96, 164].
### 2.2.2.4 Determination of the background

As the limited energy resolution of the gas proportional counter prevents the complete removal of high order X-ray reflections, the spectrometer positions to measure the background intensities must be carefully selected [32, 309]. Another problem is that the background of multilayer dispersive elements is highly curved and this curvature is sensitive to the specimen analyzed [32]. In steels, the presence of silicon as an alloying element changes the background shape due to the total internal reflection effect, as described in §2.1.3.2 [290]. Almagro et al. [4] also discussed irregularities in the background from absorption edges.

Nonetheless, Fisher and Farningham [108] (and most likely Duerr and Ogilvie [96]) used the traditional low and high background measurements and reported reasonable carbon concentration values for several steel compositions. Almagro et al. [4], Ruste [309] and Bastin and Heijligers [32] proposed another solution which consists in the measurement of the background intensity at the C K–L\textsubscript{2,3} peak position on a reference sample with a similar composition as the unknown but without carbon. This removes the challenging task of finding appropriate background positions and a suitable fitting function. It also subtracts the contribution of the carbon contamination to the background intensity, assuming similar contamination behaviours on the unknown and this reference sample. For low alloy steels, this sample could be pure iron as the steel are mainly composed of iron [4]. For high alloy steels containing large amount of Cr, Mn or Ni, it is less clear which sample or procedure to use to obtain the background intensity. Almagro et al. [4] described a methodology where the background intensity of the unknown is calculated by the sum of the background intensities measured on pure samples for each alloying element weighted by their mass content. This method approaches the mean atomic number background technique proposed by Donovan and Tingle [92].

<table>
<thead>
<tr>
<th>X-ray transition</th>
<th>Order</th>
<th>( E ) (eV)</th>
<th>( E' ) (eV)</th>
<th>( \Delta E ) (eV)</th>
<th>( \lambda' ) (nm)</th>
<th>( \Delta\lambda ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K–L\textsubscript{2,3}</td>
<td>1st</td>
<td>282.03</td>
<td>282.03</td>
<td>–</td>
<td>4.396</td>
<td>–</td>
</tr>
<tr>
<td>Fe L\textsubscript{1}–M\textsubscript{5}</td>
<td>3rd</td>
<td>845.44</td>
<td>281.81</td>
<td>–0.217</td>
<td>4.400</td>
<td>0.0034</td>
</tr>
<tr>
<td>Fe L\textsubscript{1}–M\textsubscript{4}</td>
<td>3rd</td>
<td>844.52</td>
<td>281.51</td>
<td>–0.523</td>
<td>4.400</td>
<td>0.0082</td>
</tr>
<tr>
<td>Mn L\textsubscript{2}–M\textsubscript{1}</td>
<td>2nd</td>
<td>567.42</td>
<td>283.71</td>
<td>1.680</td>
<td>4.370</td>
<td>–0.0260</td>
</tr>
<tr>
<td>Ni L\textsubscript{3}–M\textsubscript{4,5}</td>
<td>3rd</td>
<td>851.47</td>
<td>283.82</td>
<td>1.793</td>
<td>4.368</td>
<td>–0.0278</td>
</tr>
<tr>
<td>Mn L\textsubscript{3}–M\textsubscript{1}</td>
<td>2nd</td>
<td>556.22</td>
<td>278.11</td>
<td>–3.920</td>
<td>4.458</td>
<td>0.0620</td>
</tr>
<tr>
<td>Cr L\textsubscript{3}–M\textsubscript{4,5}</td>
<td>2nd</td>
<td>572.90</td>
<td>286.45</td>
<td>4.328</td>
<td>4.328</td>
<td>–0.0678</td>
</tr>
<tr>
<td>Fe L\textsubscript{3}–M\textsubscript{1}</td>
<td>2nd</td>
<td>615.30</td>
<td>307.65</td>
<td>25.620</td>
<td>4.030</td>
<td>–0.3661</td>
</tr>
<tr>
<td>Cr L\textsubscript{2}–M\textsubscript{1}</td>
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<td>510.22</td>
<td>255.11</td>
<td>–26.920</td>
<td>4.860</td>
<td>0.4639</td>
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<td>Cr L\textsubscript{3}–M\textsubscript{1}</td>
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<td>250.16</td>
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<td>0.5600</td>
</tr>
<tr>
<td>Fe L\textsubscript{2}–M\textsubscript{1}</td>
<td>2nd</td>
<td>627.80</td>
<td>313.90</td>
<td>31.870</td>
<td>3.950</td>
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<tr>
<td>Mn L\textsubscript{3}–M\textsubscript{4,5}</td>
<td>2nd</td>
<td>637.44</td>
<td>318.72</td>
<td>36.690</td>
<td>3.890</td>
<td>–0.5061</td>
</tr>
<tr>
<td>Fe L\textsubscript{3}–M\textsubscript{4,5}</td>
<td>2nd</td>
<td>704.80</td>
<td>352.40</td>
<td>70.370</td>
<td>3.518</td>
<td>–0.8779</td>
</tr>
</tbody>
</table>

Table 2.5: Interfering high order X-ray reflections of major alloying elements in steel. Their energy (\( E' \)) and wavelength (\( \lambda' \)) are expressed as the equivalent value for the given interfering order. The difference in energy and wavelength to C K–L\textsubscript{2,3} peak is also given. Energy of primary X-rays were obtained from [315].
2.2.2.5 Selection of reference materials

The last, but not least, challenge for carbon quantification is the selection of the reference material to calculate the experimental k-ratio of the C K–L$_{2,3}$ X-ray transition (Eq. 2.39). As any microanalysis reference material it must be homogeneous, stable, well-characterized. Different reference materials were used over the years: diamond [96, 309], Cr$_3$Cr$_2$ [108], cementite (Fe$_3$C) [4, 32], or a series of carbon-containing steels [164, 211, 250, 303, 413, 423]. The choice of diamond is questionable since there is a large difference in the absorption behaviour of C K–L$_{2,3}$ X-rays in pure carbon and steels. As there exist large inaccuracies in the MACs of soft X-rays, it is more advisable to select a reference material with a composition closer to the unknown [32]. Potential errors in the intensity calculations are minimized by the k-ratio (Eq. 2.40).

Expanding on this idea, many authors [164, 211, 250, 266, 303, 413, 423] resorted to a calibration curve to quantify carbon in steels. This strategy removes the need of accurate models and MACs, but adds the burden to find and measure carbon-containing, certified steel samples. The C K–L$_{2,3}$ X-ray intensity is assumed to be directly proportional to the carbon content for mass fractions below 1%, giving the equation:

$$I_{exp}^{C K–L_{2,3}} = mw_C + b,$$

where $m$ and $b$ are respectively the slope and intercept of the calibration curve obtained from the measurement of the C K–L$_{2,3}$ X-ray intensity ($I_{exp}^{C K–L_{2,3}}$) on reference steel samples with different carbon contents ($w_C$). Typically, 4 to 5 fully martensitic steels of various compositions are used to calculate $m$ and $b$ [164, 211, 250, 303]. Almagro et al. [4] however pointed out that alloying elements (e.g. Ni and Cr) have an influence on the slope of the calibration curve due to their different absorption behaviour. They suggested to either correct the measured intensities using a $\phi(\rho z)$ model or to only use Fe$_3$C as a reference material.

Summary

The development of analytical techniques in electron microscopy, such as EPMA and EBSD, is not accidental or purposeless, but emerges from the need to characterize increasingly more complex materials. AHS steels are good examples with their chemically and crystallographically heterogeneous microstructure. The unambiguous identification of all the constituents is challenging as assessed by Tab. 2.4 and may often require the synthesis of different measurements. By measuring the local chemical composition, and especially the carbon content, EPMA offers a discriminating criterion for many constituents and provides a final portrait of the preceding heat treatment processes. As detailed in §2.2.2, the quantification of this element faces several obstacles, none more significant than the carbon contamination, which is the topic of the next section.

2.3 Carbon contamination

The term “contamination” refers to an undesirable process that pollutes, infects, renders unfit the use of an object or substance [224]. In the context of electron microscope, although there could be other contamination processes involved, contamination
generally refers to the formation of a carbonaceous material on the specimen surface as a result of cracking of complex organic molecules by electron bombardment. This process is defined as undesirable as it deteriorates the quality and accuracy of the measurements. As mentioned in the last section, it is particularly detrimental for the quantification of light elements and the quantification using soft X-rays at high resolution, i.e. the objectives of this work. It is however not always the case, as in electron beam induced deposition [EBID], the same phenomenon becomes advantageous and provides a tool to fabricate nano-structures inside an electron microscope. The knowledge gained through the optimization of the cracking process can be reversibly applied to help understand and prevent contamination.

Since it was first reported in an electron microscope by Watson [377] in 1947, over 100 publications have directly or indirectly discussed and studied the phenomenon of contamination, or more generally electron beam induced formation of carbonaceous material. This section offers both a historical and dialectical review of the available literature on this topic, with a strong inclination towards contamination occurring under normal EPMA conditions in a SEM and electron microprobe.

First, the characteristics of the deposited carbonaceous material as measured by different analytical techniques will be summarized. Secondly, the different theories regarding the physical mechanisms involved in contamination will be described and compared to establish its causes and factors. Finally a systematic description of the influence of the different instrumental, analytical and sample-specific factors on the contamination will be given. Experimental measurements from the literature will be reviewed and explained based on the current understanding of the contamination mechanisms. Proposed solutions to mitigate contamination will also be covered.

2.3.1 Characteristics

When observed under the LOM, the deposit resulting from electron bombardment in an electron microscope or simply from an electron beam has a brownish to black colour [44, 267, 286, 376, 377]. The opacity increases as a function of the acquisition time [147]. Based on light absorption spectrum, Christy [76] determined that the carbonaceous deposit has a refractive index between 1.6 to 2.0.

The atomic structure and chemistry of the deposit were studied by many authors. Electron diffraction [147, 363] and Raman spectroscopy [54, 55, 89, 91, 202, 229] confirm the amorphous nature of the deposit. More specifically, authors reported Raman spectra showing peaks at 1350 and 1580 cm$^{-1}$. For Miura et al. [227] and Djenizian et al. [91] these peaks are an indicator for a diamond-like carbon structure, whereas they correspond to a disordered, graphite-like carbon structure for Sieber et al. [327], Bret et al. [55], Ding et al. [89] and Lau et al. [202]. The broadness of the peaks indicates that the carbonaceous deposit is highly disordered [89, 202]. Lau et al. [202] estimated the crystallite size to be 12.5 nm.

From electron energy loss spectroscopy [EELS] [147, 274], EDS [55, 147, 199, 306, 323, 363, 376, 379], Fourier transform infrared spectroscopy [FTIR] [55, 199] and near edge X-ray absorption fine structure [NEXAFS] [205], it is clear that the deposit are mainly composed of carbon. Bret et al. [55], Roediger et al. [306] and Wanzenboeck et al. [376] independently obtained using EDS a carbon to oxygen ratio of 9:1. Schiffmann [323] only detected trace amounts of oxygen. Wendt [379] measured a higher oxygen fraction and detected silicon in the EDS spectrum. Using
2.3. Carbon contamination

FTIR, Kumao et al. [199] also identified silicon in the contamination deposit as a Si−C bond. In both cases, the presence of Si in the deposit was attributed to the silicon containing oil used in the diffusion pumps of the microscopes. The oxygen is preferentially bonded to carbon by a double bond [55, 199, 205]. The presence of nitrogen was only reported by Kumao et al. [199]. Furthermore the FTIR spectra proved the presence of hydrogen bonded to carbon in the deposit [55, 199], which was anticipated by many authors who only measured the composition of the deposit using X-rays [323, 379]. The presence of hydrogen was further confirmed by secondary ion mass spectrometry [SIMS] where a deuterated paraffin precursor (C_{24}D_{50}) was deposited by EBID [89]. Deuterium was used to ensure that the measured hydrogen was coming from the precursor and not from residual hydrogen in the vacuum. The amount of hydrogen/deuterium was not quantified by Ding et al. [89] nor was any other element (e.g. oxygen) in the deposit reported.

An interesting result from Bret et al. [55] is that the composition of the deposit is almost independent on the composition of organic precursors injected in the vicinity of the electron beam as measured by EDS and FTIR. Styrene (C_8H_8), acrylic acid (C_3H_4O_2), propionic acid (C_3H_6O_2), acetic acid (C_2H_4O_2) and formic acid (CH_2O_2) all formed, on a naturally oxidized Si substrate, a deposit with a composition close to C_9H_2O. The X-ray quantification was verified using a C_{10}H_{16}O reference material. The high concentration of oxygen cannot be explained by the natural oxide of the Si substrate although a peak for the Si−O bond was identified in the FTIR spectra. This result implies that the oxygen-containing precursors loose most of their oxygen atoms and oxygen-free precursors gain oxygen atoms, probably from the residual oxygen gas molecules present in the vacuum. As no silicon-containing precursor was used the results from Wendt [379] and Schifflmann [323] can not be verified. The precursor independence was also noted by Leontowich and Hitchcock [205], although with less experimental verifications as Bret et al. [55]. Surprisingly Ueda and Yoshimura [363] measured using EDS the presence of substrate elements inside the carbonaceous deposit and concluded that diffusion of these elements may occur. Although the details of their measurements are missing it seems more likely that the effect observed is due to either improper background correction or X-ray production from scattered electrons. A composition close to C_9H_2O as measured by [55, 306, 376] appears to be the most probable chemistry of the deposit in a silicon-free vacuum environment.

The carbonaceous deposit is chemically stable. At room temperature, it is insoluble in any common solvents [102, 147, 343], unaffected by strong acids and alkalies [60, 91, 99, 147, 327] and inert to electron beam etching in oxygen or water atmosphere [60]. It also has a low vapour pressure [99]. The deposit however disappears after heating above 450°C in air [147, 267, 343]. Electron beam etching can be performed if the sample is cooled below approximately −80°C as there is a high concentration of adsorbed water molecules on the specimen surface [139, 157].

The mechanical properties of the deposit formed by a paraffin precursor were measured by Ding et al. [89] using nanoindentation. Both the hardness (3.6 to 4.0 GPa) and elastic modulus (34.3 to 59.5 GPa) were found to increase with the accelerating voltage (3 to 20kV) used for the deposition. The values are in agreement with other reported values for hydrogenerated amorphous carbon films. The increase seems to be proportionally correlated to the amount of sp^3-bonded carbon atoms, as measured by EELS.
The electrical properties of the deposit are unclear. Poole [267] and Christy [76] reported high specific resistivity values for the deposit, greater than $10^9 \Omega \text{cm}$, whereas Hübner et al. [160] estimated the deposit to have a good conductivity with specific resistivity lower than $400 \Omega \text{cm}$. The difference between the shape of the deposit measured, film over a large area for [76, 267] and a sharp atom force microscope [AFM] tip for [160], may explain the disagreement between these experiments. More generally, Iřen [156] and Lau et al. [202] described carbonaceous deposit as a dielectric material.

The last and most critical characteristic for quantitative EPMA is the geometrical shape of the deposit. For instance, it determines how the contamination influences the deceleration of the primary electron [PE] beam and the emission of SEs, BSEs and X-rays. Various shapes have been observed depending on the observation mode (spot, line raster, area raster) and analytical conditions used. For a stationary focused electron beam the carbonaceous deposit takes the shape of either a cone/pillar [9, 80, 91, 156, 160, 181, 182, 189, 228, 323, 363, 416], a ring/annulus [32, 69, 156, 158, 159, 283, 284, 291] or the combination of both [216, 312, 358] (Fig. 2.14). Many authors have concluded that the shape is dependent on the electron beam size [69, 99, 109, 156, 158, 181, 182] and other factors such as the irradiation time and the BSE distribution [9, 158]. Discussions about the correlation between the deposit shape and different instrumental and analytical parameters will however be postponed to the following sections to concentrate on the physical processes involved in the formation of carbonaceous deposits.

### 2.3.2 Mechanisms

The first hypothesis regarding the contamination mechanisms in an electron microscope was given by Watson [377]. In his paper on “An effect of electron bombardment upon carbon black”, he observed differences in the shape of the carbon black specimen while he was characterizing it using an electron microscope. Based on other results from Stewart [343], he explained his observations by the “well-known phenomenon of polymerization and condensation of organic vapours and gases, and certain other gaseous products, under electron or other charged-particle bombardment”
2.3. Carbon contamination

From his explanations, the contamination mechanism can be summarized as a reaction (Rxn. 2.1) where the reactants are organic molecules and electrons, and the product is the carbonaceous deposit, as described in the previous section.

\[
\text{organic molecules + electrons} \xrightarrow{\text{contamination}} \text{carbonaceous deposit} \quad (2.1)
\]

Since 1947, several experiments have been performed to understand the contamination phenomenon, but the concepts put forward by Watson remain. The knowledge about the individual reaction steps involved, the sources of organic molecules and the interaction between them and electrons has however improved since. In this section, the events leading to contamination is explained in sequential order starting from the sources of organic molecules up to the polymerization and formation of the carbonaceous deposit.

2.3.2.1 Sources of reactants

Overwhelmingly in the literature, vapours emanating from diffusion pump oil [37, 60, 61, 76, 80, 96, 103, 109, 150, 156–158, 162, 190, 199, 210, 217, 247, 267, 303, 350, 354, 356, 368, 376, 378], vacuum sealant grease [61, 76, 103, 147, 190, 199, 210, 217, 247, 267, 303, 306, 350, 354, 356, 377, 378] and rubber gaskets [36, 60, 76, 103, 210, 247, 350] have been considered the main sources of contaminants in the microscope chamber. Ennos [103] tested different materials used in the microscope chamber in a separate, specially designed apparatus. His conclusion was that the most contaminating substance is the diffusion pump oil followed by vacuum grease and rubber gaskets. He also suggested to eliminate as much as possible all high-vacuum grease and rubber gaskets as even the smallest amount can significantly increase the contamination level. A similar conclusion was obtained by Komoda and Morito [190] who measured an increase of the contamination rate on carbon black particles in a TEM if diffusion pump oil or vacuum grease are placed near the specimen. The apparent influence of the diffusion pump oil on the contamination lead some researchers to replace the mineral oil by silicon [151, 221] or perfluoropolyether [21, 152] oils. Silicon oils, also commercially known as Dow Corning 704 or 705, has the advantage of having a lower vapour pressure than mineral oil, which “help to decrease the partial pressure of organic contaminants in a vacuum atmosphere” [151]. However Mayer [221] reported no major differences in the contamination when replacing the mineral oil from his diffusion pump with Dow Corning 704 silicon oil. The perfluoropolyether, also known as fluorocarbon, Fomblin or Apiezon, has the property to be resistant to polymerization under electron bombardment [21, 24, 217]. It was hypothesized by Baker et al. [21] that the stable C–F bond suppresses the polymerization of species fragmented by the electrons. He observed no deposit after bombarding a target covered with Apiezon C oil for 5 h (1 kV, 10 mA). Although still present, a reduced amount of contamination was also measured by Holland et al. [152], Conru and Laberge [80] and Tomita et al. [356] using this type of oil. The large beam current used by Baker et al. [21] might have also contributed to the contamination prevention.

Instead of replacing the oil, other researchers opted to replace the diffusion and rotary pumps by oil free, dry pumps such as ion, scroll and turbomolecular pumps. Vacuum system with diffusion and/or rotary pumps suffer from backstreaming of oil vapour [24, 40, 217]. On the other hand, scroll pumps use solid sliding lubricant
instead of sealing fluids in between its rotating spiral metal strips [206]. Although small backstreaming have been reported for turbomolecular pumps with oil bearings [24], modern pumps are usually equipped with magnetically levitated bearings [206]. Ion pumps have no moving parts and require no lubricant [206]. Taylor et al. [354] observed a large decrease in contamination after replacing the oil diffusion pump of their TEM by a turbomolecular pump. Two months after the pump exchange the contamination rate dropped from 0.5 to 0.0006 nm s\(^{-1}\) (the methodology used to measure the contamination rate is unfortunately missing from the paper). Contamination reduction was also measured by Konuma [192] who replaced the oil diffusion pump of an electron microscope by an ion pump. Contamination was evaluated by measuring the C K–L\(_{2,3}\) integrated intensity of an aluminum target irradiated for 10 h at an accelerating voltage of 3 kV and a beam current of 2 mA (current density of 6 mA cm\(^{-2}\)). The change to the ion pump reduced by one order of magnitude the intensity. As Taylor et al. [354], Bastin and Heijligers [32] replaced the oil diffusion pump of their electron microprobe by a turbomolecular pump, but obtained contradictory results. No noticeable reduction of contamination was observed which led the authors to conclude that “there are sufficient sources for carbon contamination left” [32]. Love et al. [217] are reluctant to the advantage of turbomolecular pumps as in their opinion the contribution of seals and gaskets to contamination outweighs the advantage of such pump. The results of Bauer and Speidel [36] substantiates this idea as the replacement of rubber gaskets by Ag–In gaskets in their TEM resulted in a 33\% reduction of the contamination rate.

One often cited other source of contamination is the specimen itself [32, 60, 96, 98, 99, 110, 156, 158, 162, 201, 217, 249, 303, 368, 372, 376]. In modern vacuum systems, the specimen becomes the main source of contamination as all other sources have been eliminated by oil free pumps and vacuum resistant greases [24, 98, 156, 303, 368, 376]. Outgassing of mounting materials [32, 96, 147] as well as adhesives, paint and solvents [32, 162, 201] used during the sample preparation adds to the quantity of organic molecules present in the vacuum chamber. But even if the use of outgassing substances are minimized, an non-negligible source of organic molecules is the room air as it contains trace amounts of organic vapour from plants, animals and synthetic sources [56, 99, 368]. As the specimen, the surrounding mounting material and the specimen holder offer a large surface area for adsorbed molecules, a significant amount is introduced in the vacuum chamber by each sample exchange [110, 156, 217, 247].

Similarly the walls of the microscope chamber and column also offer a large surface area for adsorbed contaminants [61, 103, 147, 306, 376]. As put by Lesker [206], “an oil-free system is never achieved by simply replacing existing oil-sealed pumps with dry pumps; all surfaces in the chamber and pumping lines will be contaminated with an oil film.” According to Wanzenboeck et al. [376] the desorption of organic molecules adsorbed on chamber walls by the instrument’s pumps “can take months up to several years depending on the level of contamination”. This statement appeared to be verified by the experiment of Roediger et al. [306]. The contamination in an SEM was carefully monitored after a prolonged exposure of the chamber to air (several hours). The variation of the contamination was evaluated by the volume of the carbonaceous deposit leftover by a rastered electron beam over a area of 5 \(\mu\)m \(\times\) 5 \(\mu\)m (accelerating voltage of 1 kV, beam current of 300 pA and total irradiation time of 1 h) measured using an AFM. The initial contamination level before opening the chamber was only recovered after two months of pumping. Using the same methodology the
2.3. Carbon contamination

authors also showed lower contamination in an instrument equipped with an air-lock sample exchange system. The slow desorption of organic molecules inside the instrument led to the introduction of in-situ cleaning devices such as plasma cleaner [162, 207, 368, 419, 420] and UV light [338, 376].

In summary, reactants in the contamination process comes from different sources, mainly pumps and sealants, chamber walls, specimen holder and specimen. As it will be described later the contribution of each source to the overall contamination can be reduced, but organic molecules will always be present in any vacuum system. There is also a compromise to be found between the ease of sample evaluation (e.g. pumping time, cleaning time, sample preparation method) and the tolerable level of contamination.

One point not discussed in this section is the nature and type of the organic molecules present inside the vacuum involved in the contamination phenomenon as few measurements have been published. Residual gas analysis based on mass spectroscopy can only provide a partial answer as the ionization process involved in this technique fragments the original organic molecules preventing their identification [376]. Ignoring this fact, Hart et al. [136] reported methane (CH\textsubscript{4}), ethane (C\textsubscript{2}H\textsubscript{6}), diethyl ether ((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O), butene (C\textsubscript{4}H\textsubscript{8}), acetone (C\textsubscript{3}H\textsubscript{6}O), butane (C\textsubscript{4}H\textsubscript{10}) and pentene (C\textsubscript{5}H\textsubscript{10}) as potential contaminants. In a TEM equipped with a temperature-controlled specimen holder Mitchell [226] determined the contamination kinetics as a function of temperature by scanning the beam over an area of 170 nm × 170 nm (200 kV, 0.155 nA, scanning transmission electron microscope [STEM] operation conditions) on PtNi nanoparticles deposited on holey carbon film and measuring the thickness of the formed deposit by EELS. Based on the assumption that the observed differences are due to changes in the diffusion of organic molecules on the specimen surface he calculated an activation energy for diffusion of 76 kJ mol\textsuperscript{−1}. Comparing this value with other activation energies of organic molecules, he concluded that long chain hydrocarbons, aromatics and/or plasticizers are likely responsible for contamination, without specifying any chemical formula. Rykaczewski et al. [312] assumed C\textsubscript{4}H\textsubscript{6} as a representative residual hydrocarbon in their simulations, Silvis-Cividjian et al. [330], C\textsubscript{2}H\textsubscript{5}, Toth et al. [358], C\textsubscript{4}H\textsubscript{11}, and Lobo et al. [216], C\textsubscript{9}H\textsubscript{20}

2.3.2.2 Adsorption and desorption

Before describing the underlying reaction steps of the overall contamination reaction (Rxn. 2.1), the location where the reaction occurs will be discussed. The key question as posed by Li and Joy [208] is whether the reaction “occurs in the gas phase or on the substrate surface”. Three main experiments are found in the literature which all lead to the conclusion that the surface acts as a catalyst for the contamination process. First Hillier [147] compared the contamination rate when a negative and positive voltage (1 kV) is applied to the sample. The reasoning behind this experiment was that if the organic molecules are ionized in the gas phase, they would be attracted by the applied potential and the contamination rate would increase. No difference between the neutral and charged sample state was measured (methodology not given) which made him conclude that the surface must act as a catalyst. He further stated that “while the observations do not exclude the possibility that the material is formed in the gas phase, they do show that if this is so the material produced is not responsible for the contamination observed” [147]. Using the same concept as Hillier [147],
Kumao et al. [199] designed a slightly different experiment. In a TEM two electrodes (one positively and one negatively charged) supporting ZnO smoke crystals were set apart by 25\,\mu m in the specimen chamber. The applied voltage (50 V) was selected so that a tilted beam is deflected and illuminated both electrodes equally. If organic molecules are ionized in the gas by the electron beam different amounts of contamination should be measured on the ZnO crystals protruding from both electrodes. Similarly to Hillier [147] no difference was observed. A third experiment by Li and Joy [208] evaluated the contamination rate as a function of the substrate temperature. Their measurements showed an Arrhenius relationship between the contamination rate and substrate temperature. This indicates a temperature dependent residence time of the organic molecules on the substrate surface, therefore proving that contamination reaction occurs on the surface. Without experimental evidence, Ennos [102], Hart et al. [136] and Hollenshead and Klebanoff [153] also formulated the same hypothesis based on the fact that there is a higher concentration of organic molecules on the surface than in the vacuum, thus a higher cracking probability.

Consequently, the adsorption of organic molecules on the surface of the sample is the first step of the contamination process [76, 136, 150, 157, 191, 210, 217, 232, 365, 416]. Two types of adsorption can occur depending on the bonds between the molecules and the surface: (1) physisorption with weak bonds from dipole interactions and (2) chemisorption with strong and non-reversible chemical bonds [100, 364]. Physisorption is generally the accepted type of adsorption for organic molecules involved in contamination [60, 157, 364]. This implies that, in vacuum, the reverse process of adsorption, desorption, also takes place. In other words, the adsorbed molecules have a finite residence time on the sample surface. There is a dynamic equilibrium between the adsorption and desorption process [364]:

\[
\text{(organic molecules)}(\text{g}) \xrightarrow{\text{adsorption}} \text{(organic molecules)}(\text{ads}) \quad (2.2)
\]

Many authors have proposed and used equations to describe this equilibrium. Adsorption depends on the flux of organic molecules from the vacuum impinging the surface \((F)\) and the sticking probability or sticking coefficient of these molecules \((S)\) [76, 136]. As different types of organic molecule may impinge the surface at different rate the subscript \(i\) is used in the following equations. The equations in this section were written to be as general as possible and to show the factors influencing each quantity as well as their interdependence. The impinging flux (molecule m\(^{-2}\)s\(^{-1}\)) is described by Eq. 2.45 [150, 182, 210, 232] from the kinetic theory of gases:

\[
F_i(p_i, T_g) = \frac{p_i}{\sqrt{2\pi m_i k T_g}}, \quad (2.45)
\]

where \(p_i\) and \(m_i\) are respectively the partial pressure (Pa) and mass (kg molecule\(^{-1}\)) of the organic molecule \(i\), \(k\) the Boltzmann constant (J K\(^{-1}\)) and \(T_g\) the temperature of the gas (K).

The sticking coefficient (unitless) decreases as the sample temperature increases [136, 217, 323, 381] as measured by Wetterer et al. [381] for different hydrocarbons on gold (Fig. 2.15). At low temperature (\(<\,100\text{K}\)) the sticking coefficient approaches unity [355, 381]. Based on experimental results, Hart et al. [136] proposed an equation for the sticking coefficient which varies with the sample temperature \(T_s\) in the form: \(S(T_s) \propto a \exp (b/T_s)\). Other authors have also implied a dependence to the type
of bonding between the organic molecules and the sample [55]. Utke et al. [364] generalized that “when the precursor molecules are polar or easily polarizable, the adhesion forces are high […] and the sticking probability too”. To illustrate the potential combined influence of the type of organic molecules $i$ and the sample $s$, the sticking coefficient is expressed with both subscripts $S_{i,s}$. Generally in all the following equations, the subscript $s$ encompasses all properties of the sample: electrical and thermal conductivity, lattice spacing, atomic bonding, etc.

The evolution of the number of adsorbed molecules $n$ at position $\vec{r}$ as a function time $t$ can be expressed as a set of partial differential equation [PDE]. For each mechanism an equation will be formulated to demonstrate the different factors involved in the contamination phenomenon and their interactions. Adsorption is either described as a zeroth order reaction (Eq. 2.46) [76, 149, 181, 182, 232] or a first order reaction using Langmuir law for adsorption (Eq. 2.47) [153, 210, 216, 365].

$$\left(\frac{\partial n_i(\vec{r}, t)}{\partial t}\right)_{\text{ads}} = S_{i,s}(T_s) F_i(p_i, T_g) \quad \text{,}$$ \hspace{1cm} (2.46)

$$\left(\frac{\partial n_i(\vec{r}, t)}{\partial t}\right)_{\text{ads}} = S_{i,s}(T_s) F_i(p_i, T_g) \left(1 - \sum \frac{A_i n_i(\vec{r}, t)}{A_0}\right) \quad \text{,}$$ \hspace{1cm} (2.47)

where $A_i$ is the area occupied by molecule $i$ on the surface with a total area $A_0$. The ratio $\sum A_i n_i(\vec{r}, t)/A_0$ represents the fraction of sites occupied by adsorbed molecules. Note that Eq. 2.46 is a special case of Eq. 2.47 when the number of adsorbed molecules tends to zero. It is generally accepted that no more than a monolayer of molecules can be adsorbed on any surface [149, 153, 311, 365]. Eq. 2.47 therefore accounts for surface sites already occupied and limits the coverage.

In the context of contamination inside an electron microscope, two types of desorption are occurring: thermal and electron stimulated desorption. Thermal desorption is represented by a mean residence time ($\tau$) which follows an Arrhenius relationship (Eq. 2.48) [76, 94, 107, 181, 210].
\[
\left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right)_{\text{des}} = -n_i(\vec{r}, t) \frac{1}{\tau_{i,s}(T_s)}, \text{ where}
\]

\[
\tau_{i,s}(T_s) = \frac{1}{\nu_{i,s,0}} \exp \left( \frac{E_{i,s,\text{des}}}{kT_s} \right), \quad (2.48)
\]

\(\nu_{i,s,0}\) and \(E_{i,s,\text{des}}\) are respectively the vibrational frequency (s\(^{-1}\)) and the desorption energy (J) of an adsorbed molecule \(i\) on sample \(s\), Boltzmann constant (JK\(^{-1}\)), and \(T_s\), the temperature of the sample surface (K). Again here, the mean residence time depends on both the type of adsorbed molecules \(i\) and the sample itself \(s\).

Electron irradiation can force desorption of adsorbed organic molecules [149, 150, 208, 276, 364]. In contrast to cracking, which will be subsequently discussed, this process does not leave any deposit on the surface. This was observed by Li and Joy [208] who measured different desorption energies for WF\(_6\) molecules at different accelerating voltages and beam currents. They explained their results by the fact that increasing the SE yield (lower voltage or higher current) enhances electron stimulated desorption. Hirsch [149] modified Eq. 2.48 to include another term for the electron stimulated desorption (Eq. 2.49).

\[
\left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right)_{\text{des}} = -n_i(\vec{r}, t) \left( \frac{1}{\tau_{i,s}(T_s)} + \int_0^{E_0} \sigma_{i,s,\text{des}}(E) \left( \frac{j_s(E, \vec{r})}{e} \right) dE \right), \quad (2.49)
\]

where \(E_0\) is the energy of the PEs, \(\sigma_{i,s,\text{des}}(E)\), the desorption cross section (m\(^2\) electron\(^{-1}\)) for organic molecule \(i\) on sample \(s\) as a function of the electron energy \(E\), \(j_s(E, \vec{r})\), the electron current density (Am\(^{-2}\)) at a given electron energy \(E\) and position \(\vec{r}\), and \(e\), the electron charge (1.602 \times 10^{-19} C). The dependence of the current density on the sample \(s\) is discussed in §2.3.2.4.

Without electron irradiation and under stable conditions, adsorption and desorption processes will reach an equilibrium. The steady-state concentration of adsorbed organic molecules on the sample surface depends on several parameters as shown in Eq. 2.47 and 2.49. Another important parameter is the initial concentration of adsorbed organic molecule before the insertion of the sample inside the microscope chamber. Yoshimura et al. [416] observed higher contamination if the sample is left inside the vacuum over an extended period of time whereas Bastin and Heijligers [32] advised to leave the sample inside the microscope overnight before starting any analysis. Ignoring the dynamic nature of adsorption and desorption under electron irradiation, Rykaczewski et al. [311] and Amman et al. [9] have neglected these processes in their calculations and only considered the influence of surface diffusion. Both were able to explain their experimental results while excluding the phenomena of adsorption and desorption.

### 2.3.2.3 Surface diffusion

The assumption used by Rykaczewski et al. [311] and Amman et al. [9] to ignore adsorption of organic molecules from the vacuum to the specimen surface (and also their desorption) stems from several published investigations where surface diffusion
2.3. Carbon contamination

plays an important role in the contamination process. As exposed in the previous section, the contamination reaction occurs on the specimen surface and depends on the concentration of organic molecules adsorbed on this surface. Surface diffusion where molecules move due to external forces on the surface towards the electron irradiated area is also a potential source of organic molecules involved in the contamination process. Different experiments have been performed to study surface diffusion and confirmed the importance of this process on contamination. The basis of these conclusions can be divided into four categories: temperature dependence, time dependence, influence of anti-contamination devices and shape of carbonaceous deposits.

Authors have varied the surface temperature by different methods. Castaing and Descamps [69] increased the temperature by increasing the beam diameter (and beam current) of their electron microprobe while keeping the current density constant \(2.5 \times 10^4 \text{ A m}^{-2}\). As the temperature increased, higher amount of contamination was observed inside the original contamination-free ring. This observation led the authors to conclude that the migration speed of the organic molecules (diffusion coefficient) is increased with temperature, allowing more time for the molecules to diffuse further to the centre of the beam. Hart et al. [136], Rackham and Eades [276] and Mitchell [226] used an \textit{in situ} heating and/or cooling stage to control the temperature of the specimen in a TEM condition. Hart et al. [136] measured the highest contamination rate at \(-20^\circ\text{C}\) on a holey carbon film for the temperature range of \(-85\) to \(200^\circ\text{C}\). Mitchell [226] cooled down a carbon support up to \(-0.3^\circ\text{C}\) and observed a decrease by over an order of magnitude of the contamination rate. The observed kinetics follows an Arrhenius plot where the surface diffusion is a thermally activated process. Without reporting their experiments in detail, Rackham and Eades [276] also concluded cooling the specimen reduces the mobility of organic molecules. From these experiments, one must however remember that the sample temperature does not only influence the surface diffusion but also the desorption as shown in Eq. 2.48. “Heating accelerates the desorption of molecules but increases the diffusion of molecules on the surface, \[\text{whereas}\] cooling slows down molecule diffusion but increases adsorption of molecules from the vacuum.” [156] Nonetheless, as pointed out by Hart et al. [136], these results “cannot only be explained by the theory that contamination is produced by the adsorption [and desorption] of gas molecules on the specimen surface”, notably the decrease of contamination at lower sample temperature despite lower desorption.

Another proof of the surface diffusion is to look at the variation of the contamination as a function of time. Many authors have reported a “saturation” of the contamination as a function of time [9, 44, 80, 148, 189, 194, 350, 416]. Knox [189] argued that this decrease of the contamination rate after a long exposure time happens when the height of the contamination deposit is equal to the mean path length of adsorbed hydrocarbons calculated based on the average distance a molecule can travel before being desorbed. He estimated this distance to be approximately 1\textmu m. More generally, Mitchell [226] found that the contamination build-up over a scanned area in STEM follows a parabolic rate equation:

\[h = K_p \sqrt{t} + c,\]  

(2.50)

where \(h\) is the deposit thickness, \(t\) the time, \(K_p\) the rate constant and \(c\) a constant. As this type of kinetics is typically associated to diffusion limited processes, he concluded that the contamination rate is dependent on the diffusion of organic molecules across the surface. As previously mentioned, Rykaczewski et al. [311] and Amman et
al. [9] were able to predict the contamination behaviour observed in their experimental results solely by including surface diffusion in their model. Looking at the contamination kinetics as a function of the beam current density, Reimer and Wächter [291] and Wendt [379] also observed that the contamination does not scale proportionally with this quantity. They explained the saturation effect by the limited offer of new organic molecules at the impact point by surface diffusion.

Reimer and Wächter [291] and Yoshimura et al. [416] arrived to the same conclusion from their experiment using a liquid nitrogen cold trap. Using this anti-contamination device contamination was reduced but not eliminated. Since a cold trap effectively decreases the partial pressure of organic molecule gases around the sample, the authors interpreted the results as a decrease of contamination coming from direct adsorption. On the other hand, since the sample temperature was not changed surface diffusion then became the dominant source of contaminants. Flood- ing a large area using a largely defocused electron beam prior to any measurement is an anti-contamination technique used by many authors [24, 60, 99, 110, 156, 157, 201, 217, 226, 276, 291, 373, 416]. Love et al. [217] explained the observed delay before the start of contamination build-up by the larger distance required for organic molecules to diffuse before reaching the electron beam irradiated area.

Finally, the shape of the carbonaceous deposit formed under different beam irradiation strategies was an indication for several authors of the importance of surface diffusion, especially in the case of a ring-shaped deposit [69, 99, 291, 365]. Reimer and Wächter [291] showed contamination rings where the rings broadens (smaller inner diameter) with decreasing beam current densities. Assuming organic molecules are replenished by surface diffusion, at high current density, cracking immediately occurs when they enter the electron irradiated area, thus forming a sharp carbonaceous ring. At low current density, the molecules have slightly more time to travel towards the centre of the irradiated area and the deposit width broadens. Instead of studying contamination produced by a stationary focused beam, an area [89, 150] or a line [9] was irradiated by a continuously scanning beam. Hirsch et al. [150] and Ding et al. [89] observed ticker carbonaceous deposits at the edges and corners of a scanned area. They explained the observed structure by the “greater supply of unreacted molecules” at the edges. In the case of Ding et al. [89] their experiment was performed in the presence of a paraffin precursor source which increases the partial pressure of contaminant in the vacuum and should favour higher adsorption as per Eq. 2.45 and 2.47. Amman et al. [9] measured higher contamination at the end of 65μm-long line which they also associated to “greater source of hydrocarbons”. Furthermore, this paper presents an interesting experiment to illustrate the dependence of contamination on the supply of organic molecules available by surface diffusion. First, a series of concentric squares were produced by beam irradiation. Then the beam was focused in the centre to produce a single dot. Its height was compared with the one of an isolated dot. The experiment was repeated for different substrates (GaAs and Si) as well as different square sizes. In all cases the height was reduced by more than 30%, the greatest reduction was obtained for the smaller squares (≈ 40μm x 40μm).

All these experiments clearly show that surface diffusion plays an important, if not the most dominant role [150, 157], in controlling the contamination process. From the literature review on this topic, only one reference was found where the hypothesis of surface diffusion was refuted. Kumao et al. [199] based their contradictory opinion on two experiments. First ZnO crystals were suspended over a formvar film
2.3. Carbon contamination

and characterized in a TEM. The crystals were partially shadowing the film, leaving areas where the beam only irradiated the crystals and not the film. After a 30 min exposure, the authors expected to observe higher contamination at the edges of the shadowed areas due to migration of adsorbed organic molecules to replenish exposed areas of the film. The absence of contrast differences led to the conclusion that surface diffusion has little influence on the contamination. One can however argue that it is unclear whether the additional carbonaceous deposits at the edges of the shadowed areas would be visible under these experimental conditions as the formvar film \((C_3H_7)\) is already largely composed of carbon and a relatively large accelerating voltage was used 100 kV. In a second experiment, an aluminum film was irradiated at 500 kV. At a high beam current density \((1.1 \text{ A cm}^{-2})\) the carbonaceous deposit formed a ring, whereas at a lower beam current density \((1 \times 10^{-3} \text{ A cm}^{-2})\) a flat top cone was produced. These results were attributed to a temperature gradient created by the electron beam. According to them, the electron beam locally increases the specimen temperature, favouring desorption and leading to lower contamination. On the other hand, at the perimeter of the electron beam, the temperature is lower, providing a higher concentration of organic molecules and thus higher contamination. A steeper temperature gradient is therefore produces at higher beam current densities, explaining the formation of a ring due to higher contamination at the edges of the irradiated area. Again this theory seems unlikely since it would require a unrealistic steep temperature gradient \([358]\) and, as it will be discussed later, the electron beam has only a moderate influence on the sample temperature.

To complete this section on surface diffusion, three potential driving forces behind the migration of the adsorbed organic molecules will be discussed, namely the chemical, thermal and electrical gradients \([157, 162]\). When the electron beam irradiates a sample, cracking locally and temporarily depletes the amount of organic molecules underneath the beam. This creates a gradient between the equilibrium concentration of organic molecules adsorbed on a given surface, determined by the adsorption and desorption rates, and the concentration under the irradiated area. This chemical gradient drives molecules towards the irradiated area to establish a new equilibrium. This is the underlying mechanism implied by Reimer and Wächter \([291]\), Amman et al. \([9]\) and others in their explications of the contamination phenomenon. Mathematically, it can be expressed as a PDE:

\[
\left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right)_{\text{diff}} = D_{i,s} \nabla^2 n_i(\vec{r}, t),
\]

where \(D_{i,s}\) is the diffusion coefficient \((\text{m}^2 \text{s}^{-1})\) for the organic molecule \(i\) on sample \(s\), and \(\nabla^2\) represents the spatial gradient between two positions \(\vec{r}\) on the sample surface.

As aforementioned, many authors have explained differences in the contamination observed at different sample temperatures by the thermally active nature of surface diffusion \([69, 136, 226, 276]\). At higher sample temperatures more energy is transferred to an adsorbed molecule in the form of vibrations. The molecule can then overcome the binding energy and be displaced to a new adsorption site. Similarly to the mean residence time for desorption, the diffusion coefficient \(D_i\) of a organic molecule \(i\) depends on the sample temperature \(T_s\) and an activation energy \(E_{i,diff}\) \([364]\):

\[
D_{i,s}(T_s) = D_{i,s,0} \exp \left( \frac{-E_{i,s,diff}}{kT_s} \right),
\]

(2.52)
where \( D_{i,s,0} \) is the maximum diffusion coefficient at infinite temperature. As both surface diffusion and desorption require the bond between a molecule and the surface to be broken, their activation energies \( E_{i,s,\text{diff}} \) and \( E_{i,s,\text{des}} \) were experimentally found to be related, although only under ideal conditions. The ratio \( E_{i,s,\text{des}}/E_{i,s,\text{diff}} \) should be in the range of 3 to 10 [364].

From Eq. 2.52, one question is therefore how much heat is produced by electron irradiation in a system where the sample temperature is not controlled. Inelastic collisions between electrons and matter transfer energy to the sample mostly in the form of heat [51, 99]. Calculations of the extent of specimen heating have been performed using heat balance equations [99, 226, 292] or more advanced combination of Monte Carlo simulations and finite element modelling [77, 208, 282]. Reimer [292] proposed the following equation to calculate the increase of temperature in a bulk sample:

\[
\Delta T_s = \frac{3fE_0I}{2\pi\kappa R_s},
\]

where \( f \) is the fraction of the electrons not leaving the sample as BSE or SE, \( E_0 \), the accelerating voltage (V), \( I \), the electron beam current (A), \( \kappa \) the thermal conductivity (W m\(^{-1}\)K), and \( R_s \), the electron range radius (m) in sample \( s \). For copper (\( f = 70\% \) and \( \kappa = 420 \text{W m}^{-1}\text{K} \)) and a current of 1 nA, the temperature increase would be in the order of 0.02 K. Using the same equation, Mitchell [226] estimated the specimen heating in his carbon thin film to be 5 K at 200 kV, 23.3 nA. Using simulations Li and Joy [208] reported a 1 K increase in tungsten at 20 kV, 1.42 nA and Randolph et al. [282] a 30 K increase in SiO\(_2\) at 1.5 kV, 0.5 nA. Fewer experimental measurements have been reported. Chu et al. [77] fabricated a thin film thermocouple on a 1 \( \mu \)m SiO\(_2\) film on silicon. They measured a peak temperature increase of 70 K at 15 kV, 600 nA and a beam diameter of 2 \( \mu \)m. Using Kossel microdiffraction technique, Bouscaud et al. [51] measured the lattice dilatation of copper and germanium single crystals at 30 kV between 100, 500 and 1000 nA and converted the change in lattice parameters to a temperature increase using the thermal coefficient. At 100 nA, the temperature rise for copper and germanium was respectively 0.3 and 1.8 K. Overall, the temperature increase due to specimen heating is relatively small, especially in the case of good thermal conductors (e.g. copper, carbon, tungsten). This led authors to conclude that specimen heating is a negligible factor for electron beam induced processes such as contamination [99, 208, 358].

Finally, adsorbed organic molecules can be polarized by the electric field resulting from incomplete charge neutralization due to SE emission. This electric field enhances surface diffusion [110, 157, 159, 162]. To evaluate this effect Fourie [110] performed an experiment where a stationary beam irradiated a thin foil made of an insulating material (not specified in the paper) at different distances from the conductive supporting grid. When the beam was far or slightly overlapping the grid, a carbonaceous deposit was observed. Oppositely, when the beam was mostly irradiating the grid (> 50%), no deposit was detected after a 5 min exposure. According to the author,
the absence of contamination in the later case results from the elimination of the electric field due to complete charge neutralization by the supporting grid. He added a term to Eq. 2.51 to take into account the electric field enhanced surface diffusion.

\[
\left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right)_{\text{dif}} = D_{i,s} \left( \nabla^2 n_i(\vec{r}, t) + \frac{\alpha_i}{kT_s} \nabla E_{s,f} n_i(\vec{r}, t) \right),
\]

where \(\alpha_i\) is the polarizability of molecule \(i\) and \(E_{s,f}\), the electric field generated by sample \(s\). The additional dependence on the sample temperature \((T_s)\) in the second term is not discussed in the paper. Hristu et al. [158] attributed the obtained ring-shaped carbonaceous deposits to the charge implementation distribution within their hydroxyapatite samples. They observed carbonaceous rings with significantly larger diameter than the BSE escape area. The trapped charges have the effect of defocusing the electron beam thus enlarging the electron distribution. Cautiousness should be exercised in the interpretation of these results since the studied samples are insulators and have a low thermal conductivity; thermal effects could also enhance surface diffusion [291].

In summary, under high vacuum conditions in the electron microscope, surface diffusion can be the limiting step of the contamination rate [311, 365]. In other words, the contamination rate is governed by the concentration of adsorbed organic molecules in the electron irradiated area.

### 2.3.2.4 Cracking

Until now the discussion mainly concentrated on the first reactant, the organic molecules, of the contamination reaction (Rxn. 2.1). To produce a carbonaceous deposit, electrons, the second reactant, must interact with the organic molecules. Cracking is defined as “the process whereby complex organic molecules [...] are broken down into simpler molecules” [389]. In the case of electron induced cracking two main reactions are involved: electron impact ionization and electron impact dissociation [5, 102, 329]. The free radicals produced are either neutral atoms (e.g. C, C\(_2\), H), ions (e.g. C\(^+\), C\(_x\)H\(_y^+\)) or simple molecules (e.g. C\(_x\)H\(_y\)) [5, 135].

\[
(\text{organic molecules})(\text{ads}) + \text{electrons} \xrightarrow{\text{ionization}} (\text{organic radicals}) \quad \xrightarrow{\text{dissociation}} \quad (2.3)
\]

As for other electron interactions and electron stimulated desorption (Eq. 2.49), these reactions can be expressed as cross sections which depend on the electron energy \(E\) and the type of organic molecule \(i\). Combining this with the energy and spatial dependent electron current density \(j_s(E, \vec{r})\), the cracking rate is therefore:

\[
\left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right)_{\text{c}} = -n_i(\vec{r}, t) \int_0^{E_0} \sigma_{i,c}(E) \frac{j_s(E, \vec{r})}{e} \, dE , \quad \text{where}
\]

\[
\sigma_{i,c}(E) = \sigma_{i,\text{ion}}(E) + \sigma_{i,\text{diss}}(E) , \quad \text{and}
\]

\[
(\text{organic molecules})(\text{ads}) + \text{electrons} \xrightarrow{\text{ionization}} (\text{organic radicals}) \quad (2.3)
\]
\( \sigma_{i,\text{ion}}(E) \) and \( \sigma_{i,\text{diss}}(E) \) are respectively the cross sections for electron impact ionization and dissociation, and \( E_0 \), the energy of the PEs. As in Eq. 2.49, the electron current density \( j_s(E, \vec{r}) \) represents the total current density including all sources of electrons traversing the sample surface, PE, SE, BSE and Auger electrons:

\[
  j = j_{\text{PE}} + j_{\text{SE}} + j_{\text{BSE}} + j_{\text{Auger}}.
\]  

(2.56)

Note that the last three terms are sample and accelerating voltage dependent as these emitted electrons derived from the electron scattering behaviour. The energy and the spatial distribution of each electron source in relation with the cracking cross section is therefore critical in determining the cracking probability.

Experimental evidence that SEs with energies around 5 eV can crack organic molecules has been reported as early as 1953 by Poole [267] and Ennos [102]. The latter reached this conclusion after measuring no change in the contamination rate from experiments performed with accelerating voltages between 0.8 to 75 kV [102]. Hirsch [148] hypothesized that the threshold energy for dissociation of organic molecules must be below 5 eV since contamination was observed with an electron beam at this energy. Mayer [221] reached the same conclusion. After correcting for the influence of BSEs, Ranzetta and Scott [284] obtained similar contamination rates on Al, Fe, Ni, Cu and Au. Hren [156] attributed the higher contamination observed near the edges of a scanned area to higher SE yield. The surface diffusion was not considered to justify this result. In other fields where photons are the primary particles, contamination also occurs on irradiated surfaces [44, 153, 205]. Leontowich and Hitchcock [205] obtained a strong correlation between the contamination rate (measured as the height of the carbonaceous deposit by AFM) and the carbon 1s X-ray absorption (directly obtained from the measurement) measured at different photon beam energies (282 to 300 eV). As the number of emitted SEs is proportional to the X-ray absorption, the results suggest that the cracking process primarily involves SEs. The same conclusion was given by Boller et al. [44], but refuted by Hollenshead and Klebanoff [153] based on the fact that the SE emission cannot explain the decrease in the contamination rate over time. Surface diffusion was estimated to play an insignificant role in their model.

The electron energy dependence of the cracking process is unequivocally confirmed by evaluating the cross sections of 16 organic molecules tabulated and fitted by Alman et al. [5]. They found that generally the cross section of an organic molecule \( i \) quadratically varies from an energy threshold \( E_{i,\text{th}} \) to an energy \( E_{i,\text{max}} \) with the maximum probability of ionization or dissociation \( \sigma_{i,\text{max}} \), and then exponentially decays with a constant \( \lambda_i \). In other words, the cross section can be expressed as

\[
  \sigma_i(E) = \begin{cases} 
    0 & E \leq E_{i,\text{th}}, \\
    \sigma_{i,\text{max}} \left( 1 - \left( \frac{E_{i,\text{max}} - E}{E_{i,\text{max}} - E_{i,\text{th}}} \right)^2 \right) & E_{i,\text{th}} < E < E_{i,\text{max}}, \\
    \sigma_{i,\text{max}} \exp \left( - \frac{(E - E_{i,\text{max}})}{\lambda_i} \right) & E \geq E_{i,\text{max}}.
  \end{cases}
\]

(2.57)

They noted a relationship between the fitting parameters and the number of hydrogen (H) and carbon (C) atoms in the molecule.
2.3. Carbon contamination

\[ E_{i,\text{ion,th}} = E_{i,\text{diss,th}} \approx 10 \quad \text{eV} \]
\[ E_{i,\text{ion,max}} = E_{i,\text{diss,max}} = 7.71(\text{C}) + 1.31(\text{H}) + 67.0 \quad \text{eV} \]
\[ \lambda_{i,\text{ion}} = \lambda_{i,\text{diss}} = -64.37(\text{C}) + 35.40(\text{H}) + 668.36 \quad \text{eV} \]
\[ \sigma_{i,\text{ion,max}} = (2.36(\text{C}) + 0.413(\text{H}) - 0.631) \times 10^{-20} \quad \text{m}^2 \]
\[ \sigma_{i,\text{diss,max}} = (1.89(\text{C}) + 0.33(\text{H}) - 0.51) \times 10^{-20} \quad \text{m}^2 \] (2.58)

Using these equations, the variation of the cracking cross sections as a function of energy for C$_2$H$_5$, C$_4$H$_6$ and C$_5$H$_{10}$ is plotted in Fig. 2.16a. Using their Monte Carlo simulation program, Smith [335] simulated the electron energy distribution of emitted (SEs and BSEs) for 100 000 PEs bombarding a tungsten substrate (Fig. 2.16b). Comparing the cracking probability with the electron energy distribution, despite a large number of high energy BSEs and PEs, SEs predominantly have the highest cracking probability. Furthermore, Wendt [379] argued that electrons with a grazing angle to the surface crack more organic molecules, thus favouring cracking by SEs and BSEs. However, as noted by Schiffmann [323] and shown in Fig. 2.16, the energy distribution of SEs peaks below the cracking energy threshold of organic molecules (≈ 10 eV [5]). The contribution of all electrons must therefore be considered [323] as it can differ from case to case [364]. With the exception of recent works by Silvis-Cividjian et al. [330], Rykaczewski et al. [311] and Smith [335], the electron energy dependence of the cracking process was ignored and a constant value was typically used for the cross section [9, 76, 136, 149, 150, 153, 181, 210, 216, 232, 358, 365].

Apart from the energy distribution, cracking also depends on the spatial distribution of the electrons, both PEs, defined by the electron beam profile, and the emitted electrons (SEs and BSEs), defined by the accelerating voltage of the PEs and electron scattering inside the sample. The electron beam profile is often assumed to be Gaussian [216, 364]. Wendt [379] attributed the formation of a ring-shaped deposit to the stray electrons (scattered electrons in the microscope column) which hit the sample outside the normally assumed beam profile. Knox [189] observed cone-shaped carbonaceous deposits 20 times larger than the estimated beam diameter of his TEM (focused beam) on a carbon thin film. His explanation for these findings was that the organic radicals migrate away from the beam before polymerizing. The influence of stray electrons, the electron beam profile or the additional gold coating used to image the deposits was not considered. More recently, to evaluate the spatial distribution of emitted electrons, Monte Carlo simulations have been used to take into account the BSEs and both the SEs produced by the PEs (SE1) and by the BSEs (SE2) [311, 312, 330, 335]. In the case of large deposits, forward scattered SEs produced by electron scattering inside the deposits also contribute to cracking [311, 330, 335]. Simulations were successfully used to explain the shapes obtained by EBID: cone [330, 335] and ring/pillar [312].

2.3.2.5 Polymerization

The final reaction step is the polymerization of the organic radicals produced by electron cracking followed by cross-linking to form a stable carbonaceous deposit [60, 69, 76, 90, 102, 136, 139, 147, 151, 153, 156, 157, 191, 210, 217, 232, 267, 276, 284,
Figure 2.16: (a) Calculated cracking cross sections for $\text{C}_2\text{H}_5$, $\text{C}_4\text{H}_6$ and $\text{C}_6\text{H}_{10}$ as a function of the electron energy [5]. The electron impact and dissociation cross sections for $\text{C}_2\text{H}_5$ are explicitly shown. (b) Simulated electron energy distribution for tungsten (100,000 electrons, accelerating voltage of 1 kV). Reproduced from [335].
2.3. Carbon contamination

Polymerization is the process where shorter molecule chains react together to form longer polymeric chains, whereas cross-linking is the process where bonds are formed between polymeric chains [390, 401].

\[ \text{(organic radicals)} \xrightarrow{\text{polymerization}} \text{(carbonaceous deposit)(s)} \quad (2.4) \]

As previously reported in the characteristics of the carbonaceous deposit, the evidence of these processes is the presence of bonds between C, O and H [55, 89, 199], especially double bonds between C=O [55, 199, 205] and C−C [205]. Furthermore, X-ray photoelectron spectroscopy [XPS] and Auger electron spectroscopy [AES] measurements from Guise et al. [128] suggest a “greater fraction of higher order carbon-carbon bonds (C=C and C≡C)” in deposits formed by electron irradiation than in those formed by thermal processes. Harkins [135] observed, in different electrical discharge experiments (but not using an electron beam), a high reactivity of the organic radicals which rapidly react to form longer polymeric chains. In other words, the time between the ionization or dissociation of an adsorbed organic molecule by an electron and the polymerization of the free radicals produced is short.

Mathematically, the growth rate of the carbonaceous deposit \(N(\vec{r}, t)\) is the additive inverse of the cracking rate of each adsorbed molecule \(i\) (Eq. 2.55):

\[
\left( \frac{\partial N(\vec{r}, t)}{\partial t} \right) = \sum \left\{ - \left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right) \right\}. \quad (2.59)
\]

2.3.2.6 Etching

Concurrently and competitively from contamination, another process also takes place inside the vacuum chamber of an electron microscope: etching. It is the reverse process of contamination; a carbonaceous deposit is removed by the combined action of etching molecules and electrons.

\[ \text{(deposit)(s)} + \text{(etching molecules)(ads)} + \text{electrons} \longrightarrow \text{(volatile products)(g)} \quad (2.5) \]

In the case of contamination in an electron microscope, the most likely etching molecules are residual gas vapours of O₂, H₂ and H₂O [157]. The latter appears to be the principal etching reactant in the literature [98, 157, 339], unless oxygen is intentionally introduced in the specimen chamber [98, 190]. As the organic molecules in contamination, the amount of etching molecules adsorbed on the surface depends on the adsorption, desorption and surface diffusion [216]. Eq. 2.47, 2.49 and 2.54 derived for organic molecules also apply where the subscript \(i\) would refer to an etching molecule involved in the etching process.

Two main mechanisms have been proposed to explain the etching process of carbonaceous deposit: (1) activation of carbon atoms by the electrons followed by reaction with the etching molecules, or (2) activation of the etching molecules by the electrons followed by reaction with the deposit [98, 139, 339]. In other words, the main difference between the two mechanisms is which species are activated by the electrons. Heide [139] and Spinney et al. [339] concluded that the second mechanism is more dominant, whereas Egerton and Rossouw [98] claimed that the first mechanism could predominate “if the ionization cross sections of the etching molecules
are less than that of carbon”. Spinney et al. [339] calculated the energy required to activate, i.e., to displace a carbon atom, to be 39 keV. As etching was observed with an electron beam of lower energy it is unlikely that the activation of carbon atoms by electrons is the main etching mechanism. The calculations of Egerton and Rossouw [98] considered a 80 kV incident electron beam, which may explain their conclusion. Privileging the second mechanism, Eq. 2.55 can also describe the activation of etching molecules. As for cracking of the organic molecules, the energy and spatial distribution of the electrons will influence the etching process. Following their activation, the etching radicals must react with atoms from the carbonaceous deposit for etching to take place. The efficiency of this reaction is unclear. Lobo et al. [216] approximated this probability by the area occupied by an adsorbed organic molecule on the surface. Including etching, Eq. 2.59 becomes

$$\left( \frac{\partial N(\vec{r}, t)}{\partial t} \right) = \sum \left\{ - \left( \frac{\partial n_i(\vec{r}, t)}{\partial t} \right) \right\} - N(\vec{r}, t) \sum \left\{ -\beta_{ii} \left( \frac{\partial n_{ii}(\vec{r}, t)}{\partial t} \right) \right\}, \quad (2.60)$$

where the subscript $ii$ is introduced to differentiate between the number of adsorbed organic molecules $i$ and etching molecules $ii$ at position $\vec{r}$ and time $t$, and $\beta_{ii}$ corresponds to the probability of the etching reaction between the carbonaceous deposit and etching molecule $ii$. Lobo et al. [216] also considered in their derivation the plausible reaction between the organic radicals (product of Rxn. 2.3) and the etching radicals. This adds an additional factor influencing the number of adsorbed organic molecules $n_i(\vec{r}, t)$ and limits the number of etching molecules $n_{ii}(\vec{r}, t)$ available to react with the carbonaceous deposit $N(\vec{r}, t)$.

The actual nature of the volatile products was not studied in the literature. Spinney et al. [339] mentioned CO$_x$ as an example by-product. It is however clear that they are gases and they are pumped away from the surface by the vacuum system of the microscope [157, 216, 339, 358].

Evidences of etching of the carbonaceous deposit have been reported by different authors. Castaing and Descamps [69] and Ranzetta and Scott [284] reported that electron irradiation can clean a contaminated area. Egerton and Rossouw [98] observed that not only contamination was stopped by leaking air into the specimen chamber but that the thickness of the analyzed carbon thin film was reduced, or more generally the film was etched. This transition between the contamination to the etching regime appear to depend on the experimental parameters, notably on the sample temperature [139, 358], the concentration of adsorbed organic molecules [9, 216], the partial pressure of etching molecules [98, 339, 358] and the electron current density [216, 358]. In the model developed by Toth et al. [358] and improved by Lobo et al. [216], the coexistence and dissimilar efficiency of the contamination and etching processes were clearly demonstrated. Although their experimental results showed an extreme case where the electron beam induced deposition is performed in an environmental SEM with a water pressure of 100 Pa (excess of etching molecules), the potential influence of etching on contamination under normal operating conditions can not be neglected, especially in the situation where the cracking reaction is limited by the number of adsorbed organic molecules.
2.3.3 Factors

In the previous section, contamination mechanisms were described by PDEs containing different variables and quantities. They can be divided into five categories of principal factors influencing contamination. The first factor regroups the chemical substances involved in the reactions: the organic molecules, the etching molecules and the sample itself. The large amount of quantities with subscripts $i$ and/or $s$ in the equations shows their importance in controlling the contamination process as well as their interdependence. The nature of these substances defines the magnitude of these quantities, the amount of adsorbed organic and etching molecules, the cracking and etching probabilities, and thus the contamination rate. The second factor regroups any preparation step or process influencing the amount of adsorbed organic and etching molecules before electron irradiation. It includes the influence of cleaning, vacuum system, anti-contamination devices and sample temperature. Thirdly, in all the formulated PDEs the independent variable is always the irradiation time $t$. Contamination is a dynamical process where molecules change chemical states and nature. Regardless of the kinetics of each process, different irradiation times will yield different solutions and snapshots of the contamination behaviour. Fourthly, the electron current density is another critical factor as it directly governs the cracking and etching rates. Its energy distribution in combination with the one of the cracking cross sections and its spatial distribution in combination with the transport of organic molecules to the electron irradiated area by adsorption and/or surface diffusion define the amount of contamination and the resulting shape of the carbonaceous deposit. Finally, the accelerating voltage indirectly impacts the contamination process by changing the current density of emitted SEs and BSEs, and the sample temperature.

2.3.3.1 Chemical substances

The literature on the type of organic molecules present in a modern high vacuum is sparse. As shown in §2.3.2.1, the replacement of oil diffusion pumps and outgassing seals as well as the use of anti-contamination devices lead to the current reality that the specimen and specimen holder are the main sources of contaminants [24, 98, 156, 303, 368, 376]. The chemistry of the organic molecules adsorbed on the sample no longer corresponds to the one of the oil used. There is no clear consensus on the chemical formula of organic molecules involved in contamination. It is however probably safe to say that the organic molecules are long chain hydrocarbons [136, 226, 312, 330] and that more than one type is present on the sample surface [136]. As for the etching molecules, water was often cited as the principal reactant [98, 157, 339].

Even if it is clear that contamination occurs on all materials, conflicting results and explanations have been reported about the influence of the substrate on contamination. Hillier [147] and Poole [267] observed no variation of the contamination rate as a function of the substrate used. Copper, nickel, copper-nickel alloy, silver and stainless steel were studied by the latter author. However since 1953 all papers reporting on this topic have shown differences in the contamination behaviour depending on the substrate, which were either explained by the thermal conductivity [32, 69, 242], electron backscattering [9, 284], sticking coefficient [162, 377] and
atomic number [363]. As an attempt to quantify these explanations, the contamination rates measured by Ong [242], Ranzetta and Scott [284], Konuma [193] and Ueda and Yoshimura [363] on pure substrates were compiled. These are the only contamination experiments found in the literature where more than two substrates were studied by the same research groups. Fig. 2.17 shows these results as a function of different sample properties: atomic number, thermal conductivity [407] and BSE yield [180]. Ong [242], Ranzetta and Scott [284] and Konuma [193] measured the contamination rate by recording the C K–L\(^{2.3}\) X-ray intensity as a function of time in their electron microprobe. Ranzetta and Scott [284] and Konuma [193] reported the contamination rates as a percentage of the X-ray intensity measured on pure carbon whereas Ong [242] used count/s. Ong [242] used a stationary beam of 10 kV (current not reported), Ranzetta and Scott [284] scanned a 100\(\mu\)m \(\times\) 100\(\mu\)m area at 4 kV and 600 nA, and Konuma [193] a 25\(\mu\)m defocused beam of 10 kV and 20 nA. Ueda and Yoshimura [363] used a different experimental setup where “a free-standing nanowire was grown from the protrusion by moving the beam manually toward the vacuum”. For this comparison, the reported growth rate (in \(\mu\)m min\(^{-1}\)) at 5 kV was taken as the contamination rate.

No clear relationship can be found between the contamination rates and the sample properties, except for the results of Ranzetta and Scott [284] which show an increase of the contamination rate with the atomic number and BSE yield. This matches the hypothesis where for a given accelerating voltage more SEs and BSEs are produced in a high atomic number substrate which leads to a higher emitted current and more contamination. From the results of Ueda and Yoshimura [363], if the contamination rate for copper is excluded, the contamination rate appears to decrease with increasing thermal conductivity. In all the contamination equations the thermal conductivity only appears in the calculation of the beam induced heating of the sample (Eq. 2.53). Consequently, a low thermal conductivity equals higher sample heating by electron irradiation, higher desorption rates and lower contamination. The reverse tendency is observed in the results of Ueda and Yoshimura [363]. Besides, sample heating should be minimal in their experimental setup as the beam does not directly impact the substrate. Qualitatively, Bastin and Heijligers [32] and Wendt [379] also hypothesized a dependence on the thermal conductivity. Bastin and Heijligers [32] observed almost no contamination on B and Si in comparison to Cu. However, they also noted generally higher contamination on all transition metals from the first row of the periodic table, which they explained as a “some kind of catalytic action of metal” on the cracking process. Wendt [379] described lower contamination rate on Pb than Au.

As mentioned earlier the sticking coefficient is also sample dependent, and could influence the number of adsorbed organic molecules. Equations and some calculated sticking coefficient values have been reported by German and Sheintuch [123] for methane (CH\(_4\)) molecules adsorbed on Ni, Cu and Pt substrate at 500 K. Even after recalculating their sticking coefficients for a substrate at room temperature, the values remain very small (< 10\(^{-6}\)) and those of Ni and Pt are six order of magnitude bigger than the one of Cu. As shown in Fig. 2.15 the sticking coefficient depends on the hydrocarbon chain length, and it is very likely that the organic molecules involved in the contamination process have longer chains than methane. It is therefore impossible without more appropriate values to validate the influence of the sticking coefficient on the contamination.
2.3. Carbon contamination

![Contamination rate graphs](image)

(a) Atomic number  
(b) Thermal conductivity  
(c) BSE yield

Figure 2.17: Contamination rate as a function of the (a) atomic number, (b) thermal conductivity and (c) BSE yield as measured on pure substrates [193, 242, 284, 363]
In summary, the sample affinity for adsorption of organic molecules is an uncontrollable parameter as samples of all natures are analyzed in an electron microscope. Although the results presented in Fig. 2.17 confirm that the sample’s role in determining the contamination behaviour, no clear explanation for this dependence can be demonstrated. This may be due to the fact that other factors are influencing the contamination behaviour, which should be carefully measured, controlled and understood to properly establish the sample dependence on the contamination. This interpretation arises from the large differences between the results of the three research groups.

2.3.3.2 Initial condition

The initial condition is synonym to the amount of organic (and etching) molecules adsorbed on the sample surface before electron irradiation. The concentration of molecules depends on the history of the sample. From the native amount present on the sample prior to the insertion in the specimen chamber, the vacuum system (airlock, pumps, etc.), anti-contamination devices (e.g. plasma cleaner) and in situ accessories (e.g. heating or cooling stage, gas jet) influence the state of the sample surface.

**Cleaning** Starting from the beginning, samples are usually cleaned before being inserted in the instrument to remove dusts, greases, polishing solution residues, etc. [32, 73]. Systematic cleaning also aims at obtaining reproducible results [260, 303]. The goal of any cleaning method is to overcome the adhesive forces, mainly physisorption (van der Waals forces) between the organic molecules and the sample surface.

Liquid solvents remove contaminants adsorbed on the sample surface by decreasing the magnitude of the attractive forces and increasing electrostatic repulsion forces [73]. Distilled water [73, 91, 306, 327], ethanol [32, 73, 150, 327], methanol [91, 150, 291], isopropanol [91, 306], acetone [73, 91, 148, 226, 306] and trichloroethylene [101] are commonly used solvents, in combination with an ultrasonic bath, which increases the desorption forces by its cavitation action [32, 73, 303, 306]. The influence of cleaning on contamination is however debated by Roediger et al. [306]. They observed no difference in the volume of the carbonaceous deposits produced from a as-received silicon wafer sample or one cleaned with acetone, isopropanol and distilled water. Higher contamination was only observed if a sample was deliberately made dirty by human fingerprints. As silicon wafers are usually sold in a cleaned state, this observation may not apply to other samples which have been prepared through sectioning, mounting, grinding and polishing.

Apart from liquid based cleaning, plasma cleaning is a well-established technique in electron microscopy [162, 207, 368, 419, 420]. It consists in creating a low temperature plasma from a strong electromagnetic field usually produced by a high frequency generator or a direct current potential [162, 420]. Organic molecules are removed from the sample surface by three mechanisms: (1) activation by UV radiation to create free radicals, (2) energy transfer from neutral particles to the surface, and (3) formation of free radicals by charged particles impacting and chemically reacting with the adsorbed molecules [420]. While plasma cleaning can be effective with only inert gas such as Ar [420], higher cleaning efficiency has been reported with the addition of reactive gases such as O₂ in the chamber of the plasma cleaner [162, 207, 380, 420]. O₂ was said to help the conversion of organic radicals to gaseous components [420]. Levesque
and Leckenby [207] argued that room air is a good gas mixture for plasma cleaning, whereas Isabell et al. [162], Zaluzev [420] and Griffiths and Walther [127] obtained good contamination reduction with 25% oxygen and 75% argon. Zaluzev [420] showed that a two-step process with first argon followed by oxygen is a more efficient cleaning strategy [420], but Isabell et al. [162] refuted this affirmation. The disadvantages of oxygen are the oxidation of the sample surface [380] and etching of carbon containing samples or supporting films [127]. These downsides appear to depend on the operating conditions (power and cleaning time) as they were not observed by Isabell et al. [162] and Mitchell [226]. Although some authors claimed that plasma cleaning completely prevents contamination [162, 368], most results reveal a significant decrease of the contamination rate (approximately 95% [127, 420]) and a dependence on the sample [226]. Even after cleaning for 2 h, Mitchell [226] still measured contamination on a carbon support film, while no sign of contamination was observed on a gold on carbon specimen after cleaning for 60 min.

A related cleaning method is based on UV radiation and ozone (O₃) [338, 376]. A lamp emits UV light with different wavelengths to (1) form ozone from an oxygen atmosphere (50 kPa) and (2) dissociate organic molecules adsorbed on the sample. Ozone molecules then react with the free radicals. Soong et al. [338] mentioned that UV light causes “less damage to various carbon structures such as graphite and graphene”. Wanzenboeck et al. [376] measured a 90% reduction of the height of carbonaceous deposits (5µm × 5µm area under a 1 kV, 300 pA beam for 1 h) produced before and after in situ cleaning using UV radiation and ozone.

Other cleaning techniques have been proposed. Singh et al. [332] used a Nd:YAG laser to remove organic molecules from a gold sample. At this infrared wavelength (1064 nm), light is highly absorbed in carbon (50%) resulting in the excitation of the organic molecules without damaging the gold substrate [332]. Love et al. [217], Kanaya et al. [181] and Hirsch et al. [150] suggested bombarding the sample with an argon ion beam to clean the sample. The contamination reduction of these techniques was however not quantified by the authors.

**Vacuum system** Another debated topic is whether the vacuum has a positive or negative influence on the contamination, or more precisely whether the vacuum system reduces or increases the amount of adsorbed organic molecules. As discussed in §2.3.2.1, oil from pumps, various seals and any surface inside the vacuum chamber, etc. are potential sources of contaminants. Mixed responses have been reported by replacing or improving the quality of these components. It should however be noted that each instrument have a different vacuum system with different pump arrangements, pump specifications, sizes of specimen chamber, construction materials, lengths of pumping lines, etc. [24] These details are obviously not mentioned in scientific publications and the operating pressure of the vacuum system is seldom provided along the type of pumps used. The impact on the instrument history (samples analyzed, number of repairs, etc.) is also difficult to evaluate. Roediger et al. [306] showed that a prolonged exposure of the SEM chamber to air for maintenance worsened the contamination inside this instrument for nearly two months. Other authors have also attributed changes in the contamination level between separate sessions due to different vacuum conditions [284, 323]. The limited availability of residual gas analyzers...
Figure 2.18: Volume of carbonaceous deposits produced by scanning a beam over a area of $5\mu m \times 5\mu m$ for one hour (1 kV, 300 pA) as a function of the pumping time. Reproduced from [306] with modifications to remove data unnecessary to the discussion.

[RGAs] attached to electron microscopes as well as their limitation to measure the partial pressure of all residual gases [376] prevents more quantitative understanding of the vacuum system.

Despite these difficulties, the following trend can be discerned from the literature: with the overall improvements in modern electron microscopes the vacuum system is no longer a predominant source of a contamination. The term “overall” was selected as it is not possible to identify an ambiguous reason for this change. In 1983, 1994 and 2000 Yoshimura et al. [416], Hirsch et al. [150] and Wendt [380] respectively recommended to minimize the amount of time a sample is left inside the specimen chamber. In a SEM with a dry pumping system, the latter author measured comparable contamination rates between a dirty silicon sample and one left in vacuum for 72 h. Approximately ten and fifteen years later Roediger et al. [306] and Buse and Kearns [62] observed the reverse behaviour in their instrument, also equipped with a dry vacuum system (i.e. turbomolecular and scroll pumps) as Wendt [380]. The results of Roediger et al. [306] are reproduced in Fig. 2.18, where the volume of carbonaceous deposits is plotted as a function of the pumping time. Each deposit was produced by scanning a beam over a area of $5\mu m \times 5\mu m$ for one hour and measured by AFM. The deposit volume was reduced by approximately 20% after one hour and stabilized after 5 to 7 h of pumping. Buse and Kearns [62] observed a stabilization of the contamination after 4 h.

**Cold trap** Another approach to improve the vacuum inside the specimen chamber is to use a cooling block, cooling plate, cooled trap, cold trap, cold finger, liquid nitrogen trap, cryoshield, etc. To prevent confusion in the terminology, the expression “cold trap” is selected in this work to describe any metallic part cooled to a temperature below room temperature inside the specimen chamber. From Eq. 2.47 and 2.48,
2.3. Carbon contamination

lowering the temperature increases the sticking coefficient and the mean residence
time of any molecule inside the vacuum. This dual effect increases adsorption and
decreases desorption, resulting in the capture of gaseous molecules and the reduction
of their partial pressure in the vicinity of the cold trap [24, 80, 96, 156, 416]. A
higher vacuum is effectively created, which Hren [156] and Heide [139] independently
estimated to be in the order of $10^{-6}$ Pa at temperatures below $-130 \, ^\circ$C, two orders of
magnitude lower than the typical pressure inside a specimen chamber. The efficiency
of this anti-contamination device depends primarily on its location with respect to the
sample and its temperature. Although authors have observed reduced contamination
rates by simply having a cold trap in the specimen chamber [76, 151, 190, 415], a
large cold trap as close as possible to the sample appears to be the most efficient
location to minimize contamination [24, 96, 150, 156, 242, 247, 284, 356, 416]. Reduc-
tion of the contamination rate between 2 to 25 times were reported with a
cold trap above the sample [147, 242, 284, 415]. The influence of the temperature was
studied by Heide [139], Ranzetta and Scott [284] and Hirsch et al. [150]. Heide [139]
measured thickness variations of a carbon thin film under a 60 kV electron beam
beam diameter of $\approx 2 \mu m$ and a current density of $\approx 0.4 \, A\, cm^{-2}$ at different cold
trap temperatures. His results are reproduced in Fig. 2.19. Lowering the temperature
reduced the contamination, but between $-35$ to $-110 \, ^\circ$C etching dominated. He
explained this observation by the fact that at temperatures below $-60 \, ^\circ$C most organic
molecules are adsorbed on the cold trap while etching molecules such as H$_2$O remain
on the sample surface. Water would only condensate on the cold trap at temperatures
below $-130 \, ^\circ$C. More mathematically, organic and etching molecules have different
sticking coefficients and desorption energies, thus their adsorption and desorption
rates will vary differently as a function of the temperature. The etching regime was
not observed by Hirsch et al. [150] who only observed a decrease of the carbonaceous
deposit thickness leftover by scanning a $5 \mu m \times 15 \mu m$ area of a silicon sample at
1 kV. The contamination was reduced by 70 % using a cold trap at $-20 \, ^\circ$C, but no
further improvement was noted at lower temperatures. Ranzetta and Scott [284]
reached the same conclusion and recorded no change in the contamination behaviour
below $-35 \, ^\circ$C. The differences between these results and those of Heide [139] may
be explained by the different accelerating voltages (1[150] and 4[284] vs. 60 kV[139]),
specimen types (bulk[150, 284] vs. lamella[139]) and current densities (0.0001[150,
284] vs. 0.4 A cm$^{-2}$[139]). The latter seems a reasonable explanation based on the
work of Toth et al. [358], where etching was proven to predominate at higher electron
current densities. The experiments of Heide [139] were therefore performed under
more favourable conditions for etching.

Despite being an efficient anti-contamination device, the cold trap does not com-
pletely prevent the formation of a carbonaceous deposit on the sample surface [32, 96,
150, 276, 350]. Some authors have combined the cold trap with other in situ devices
to further reduce the contamination such as a gas jet [80, 303, 350], a heating stage
[276] or a cooling stage [139, 150]. The next paragraphs look at the influence of the
gas jet and sample temperature on the contamination, independently of the cold trap.

**Gas jet** A gas jet is a in situ gas injection nozzle that increases the partial pressure
of a gas locally near the measurement position on the sample [24]. Different gases
have been blown onto the sample: H$_2$ [140, 193], He [32, 140, 193, 350], N$_2$ [36, 60,
140, 193], O$_2$ [32, 36, 60, 97, 140, 193, 247, 303], Ne [32], Ar [60, 140], air [32, 69, 96,
Figure 2.19: Thickness of a carbon thin film as a function of the temperature of the cold trap. “Verschmutzung” translates to contamination and “Abbau” to etching. Reproduction from [139].

97, 140, 193, 303], HCl [60], H₂O [60, 190], CO₂ [140, 190], C₃H₈ [140, 190] and CH₄ [193]. Except for those consisting of organic molecules (CO₂, C₃H₈, CH₄), contamination reduction was reported by the authors for all gases. From Eq. 2.45 and 2.47, the gas jet increases the partial pressure \( p_i \) of the injected molecules, which initially increases their adsorption rate and the total number of those molecules adsorbed on the sample surface. Due to the high partial pressure, the adsorption of these molecules is preferential over the one of organic molecules. As the ratio \( \sum A_i n_i(\vec{r}, t)/A_0 \) tends toward unity, the adsorption of all molecules decreases, including the adsorption of organic molecules involved in contamination. In sum, the injected gas molecules occupy adsorption sites on the sample surface, thus limiting the adsorption and diffusion of organic molecules [24, 60]. This explanation is reinforced by the observations of Konuma [193] and Bruenger et al. [60] where similar contamination rates were measured in the presence of H₂, He and N₂, and N₂, O₂, Ar and H₂O respectively. As the area occupied on the surface by these molecules \( A_i \) can be assumed to be relatively comparable, the nature of the injected molecules has little influence on the contamination reduction mechanism. However, in contradiction to the results of Bruenger et al. [60], Bastin and Heijligers [32] and Konuma [193] reported lower contamination rates in the presence of oxygen, either from the injection of O₂ or air. This additional contamination reduction was explained by higher etching rates of the carbonaceous deposits by the adsorbed oxygen molecules [4, 32, 96, 303]. To take advantage of the etching process, these authors recommended to use a decontamination time between 30 to 100 s before starting a measurement on a new location. During this decontamination time the beam is irradiating the sample, allowing the adsorption, cracking and etching processes to take place as described in §2.3.2.6. It is difficult to understand why Bruenger et al. [60] did not observe the dual action of oxygen on the contamination. As in the case of the cold trap results, the differences in the current density may give some clarifications. The current density used by Bruenger et al. [60] \( (2 \times 10^{-5} \text{ A cm}^{-2}) \) is at least two order of magnitude smaller than the one used by Konuma [193] \( (4 \times 10^{-3} \text{ A cm}^{-2}) \) and Bastin and Heijligers [32] \( (0.127 \text{ A cm}^{-2}) \). Again this fits with the postulate that low current densities lead to lower etching rates.
2.3. Carbon contamination

According to Almagro et al. [4], the highest efficiency is achieved when the gas jet nozzle is as close as possible to the sample pointing at the measurement location and when the gas flow is as high as possible “while maintaining a workable vacuum in the sample chamber” [4] and preserving a reasonable lifetime of the filament (especially applicable for tungsten filament microscopes) [32]. Generally, authors have reported a deterioration of the vacuum by one order of magnitude when the gas jet is used.

Sample temperature Continuing his experiments on the cold trap, Heide [139] measured the effect of the sample temperature on the thickness of a carbon thin film. Whereas etching stops at temperatures lower than \(-110^\circ C\) when a cold trap is used, the etching rate increases if the sample is also cooled. In comparison to the original measurement at \(20^\circ C\), contamination is almost non-existent at temperature below \(-35^\circ C\). Likewise Hart et al. [136], Hirsch et al. [150] and Mitchell [226] attested the efficiency of this experimental setup. Hart et al. [136] and Mitchell [226] also used a carbon thin film in a TEM to study the influence of the sample temperature. Hart et al. [136] reported an exponential decrease of the carbonaceous film growth below \(20^\circ C\). By cooling from 20 to \(-0.3^\circ C\) a carbon thin film, Mitchell [226] determined that the contamination rate varies as a function of the sample temperature following an Arrhenius relationship and that it would become negligible below \(-20^\circ C\). He observed no contamination when the sample was cooled to liquid nitrogen temperature as well as no etching, despite a large current density \((1.41 \times 10^5 \text{ A cm}^{-2})\). For a bulk copper sample, the results of Hirsch et al. [150] show almost no contamination buildup when the sample and the cold trap is cooled below \(-10^\circ C\). Cooling the sample along the cold trap was more effective in reducing the contamination than the cold trap alone. Throughout this literature review, only two references were found where the sample was cooled without using a cold trap. Ennos [102] found an increase of the contamination rate at a sample temperature of \(-50^\circ C\). On the contrary, the contamination rate decreased with decreasing temperature in the experiments of Egerton and Rossouw [98] up to \(-60^\circ C\) after which thinning of the carbon thin film sample was observed.

Lowering the temperature has therefore two effects on the contamination behaviour. First, it increases the number of molecules adsorbed on the sample surface, providing more reactants for the cracking and etching reactions [139, 156]. Secondly, it reduces surface diffusion as per Eq. 2.52, limiting the number of organic molecules available for cracking near the electron-irradiated area [136, 150, 156, 226]. These mechanisms explain the differences between the results. From the results of Heide [139], organic molecules are preferentially adsorbed over etching molecules on a surface with a temperature above \(-100^\circ C\). If the sample is cooled without a cold trap, the number of organic molecules adsorbed on the sample surface will increase and lead to higher contamination as observed by Ennos [102]. Presumably in a cleaner vacuum as for Egerton and Rossouw [98], the rate limiting process is surface diffusion. Etching starts at lower temperatures, as only then etching molecules are adsorbed on the sample surface. A similar effect happens when the cold trap and sample are at the same temperature. The key to understand these results is the different adsorption behaviour of organic and etching molecules as a function of temperature [139]. In the other situation where a cold trap is used and maintained at a temperature lower than \(-130^\circ C\) (e.g. liquid nitrogen temperature), both organic and etching molecules get adsorbed on the cold trap, eliminating any adsorption on the sample surface. Under
these conditions, lowering the sample temperature now only affects the surface diffusion, which slows down following a thermally activated process as described by Hart et al. [136] and Mitchell [226]. Etching does not occur as there is no influx of etching molecules on the sample surface.

Curiously, contamination in an electron microscope turns out to be only a room temperature phenomenon as both cooling or heating the sample reduce its effects. Authors have reported minimization up to elimination of any sign of contamination when the sample is heated inside vacuum both with [136, 226, 242, 276] and without the presence of a cold trap [24, 96, 102, 148, 199, 267, 274, 291]. The critical temperature seems to be around 250°C, although each author has proposed their ideal temperature ranging from 50 to 400°C. As pointed out by Mitchell [226], the temperature should depend on the boiling point of the adsorbed organic molecules, and may need to be increased up to 450°C for oil-contaminated samples. Except for heat sensitive samples [284], baking the sample under vacuum is an efficient anti-contamination method. This process should however be performed in situ in a cleaned vacuum environment. Mitchell [226] related his experience with an external baking system where the contamination rate was found to increase with baking time because of pre-existing contamination inside his apparatus.

Flooding Flooding, pre-irradiation or beam showering describe the technique where a large area of the sample is bombarded by electrons either by defocusing the beam or fast scanning prior to the actual measurement. The method was first published by Rackham and Eades [276] who observed no contamination for a period of 10 min after flooding the sample for 5 min. They hypothesized three mechanisms to explain their results: (1) cracking of adsorbed organic molecules creating a uniform carbonaceous layer, eliminating subsequent surface diffusion, (2) electron stimulated desorption, and (3) electron beam induced heating. Since then, the effectiveness of flooding has been reported by many authors [24, 60, 156, 157, 201, 226, 373, 416]. The suggested flooding time is usually from 2 to 20 min with a large beam diameter (10 to 20 μm [226, 373], 1 to 2 mm [156, 416]) and a large beam current (largest condenser aperture [201, 276, 373], 23.3 to 153.4 nA [226]). This is equivalent to a small current density (2 × 10⁻⁵ A cm⁻² [416], ≈ 3.2 × 10⁻² A cm⁻² [226]). Only Bruenger et al. [60] used flooding in a SEM by alternatively scanning a small and large area. They noted that a high repetition rate (≈ 25 Hz) is required to avoid contamination in the small area. In comparison to the method used by other authors, the ratio between the flooded and measured area is much smaller (approximately 4) in the experiment of Bruenger et al. [60]. This may explain the need for this high repetition frequency.

From the mechanisms put forward by Rackham and Eades [276], electron beam induced heating seems unlikely. As demonstrated previously in §2.3.2.3, the temperature increase due to electron irradiation is relatively small even at high beam currents. The hypothesis of electron stimulated desorption was selected by Bance et al. [24] and Lábár et al. [201], where the former justified their position based on the fact that the beam current is too low to polymerize the organic molecules on the surface. Hren [156] and Mitchell [226] supported the other mechanism where flooding immobilizes the adsorbed organic molecules. In an unrelated work Christy [76] used a large defocused beam of 2 mm (∼ 3.2 × 10⁻⁴ A cm⁻²) to study the formation of continuous carbonaceous films on Sn thin films. His observations confirm that cracking occurs under low current density conditions and substantiate the flooding mecha-
2.3. Carbon contamination

nism involving the fixation of mobile organic molecules. It however does not exclude the possibility of electron stimulated desorption, but justifies the recommendation of Reimer and Wächter [291] and Mitchell [226] to first reduce the amount of adsorbed organic molecules by an effective cleaning method and thus prevent the deposition of a thick contamination layer during flooding. Furthermore, as flooding only prevents contamination by surface diffusion, adsorption should also be minimized during the measurement by using, for example, a cold trap or a gas jet.

2.3.3.3 Irradiation time

Since the first observation of contamination in an electron microscope by Watson [377], it is generally accepted that contamination increases with irradiation time. This relationship has been stated and confirmed in several publications. This statement however hides the dynamic and spatial nature of contamination where processes with different reaction rates and spatial distributions are involved as detailed in §2.3.2. Mathematically, the contamination rate (Eq. 2.59) is not necessarily equal to a constant and the contamination rate at position \( \vec{r}_1 \) is not necessarily equal to the one at position \( \vec{r}_2 \). Consequently, in order to further understand the contamination mechanisms, authors have measured and modelled the evolution of the carbonaceous deposits as a function of the irradiation time.

Experimentally, two relationships between the contamination and the irradiation time have been reported, either a linear increase [80, 98, 102, 150, 192, 193, 199, 242, 356] or a steep increase followed by a saturation [32, 44, 80, 150, 189, 226, 323, 350, 356, 416]. The type of relationship depends on the irradiation pattern of the electron beam (focused spot, defocused beam or rastered area), but also on how the contamination is measured. For instance, Conru and Laberge [80] and Tomita et al. [356] obtained cones as carbonaceous deposits from a focused beam in their SEM (25 kV, 5 pA) and TEM (100 kV, 200 pA) respectively. They observed a linear increase of the cone volume but a saturation of the cone height after approximately 100 s. For the same geometry, the saturation of the height and diameter was also measured by Knox [189] and Schiffmann [323].

For carbonaceous deposits shaped as rings, Bastin and Heijligers [32] measured the contamination as a function of time using the C K–L\(_{2,3}\) X-ray intensity on a copper substrate (10 kV, 100 nA). They reported a faster saturation of the X-ray signal when a cold trap is used, and no contamination with an air jet. These behaviours most likely correspond to the variation of the contamination in the centre of the carbonaceous ring and do not describe the contamination constituting the ring itself. On a non-conductive substrate made of a hydroxyapatite film on silicon using a focused beam of 20 kV, 1.4 nA, Hristu et al. described in [158] an increase of the ring (outer) diameter and ring width with increasing irradiation time, but reported in a later publication [159] no change in the ring diameter and a decrease of the ring width. Potentially changing charging effects may explain these conflicting results. No information about the height was given in their papers. Ong [242] showed a linear increase of the contamination on different substrates over a period of 5 min. The shape of the carbonaceous deposit was not specified, although based on the experimental conditions (focused beam, bulk substrate, 10 and 30 kV) could be assumed to be ring-shaped.
Figure 2.20: Contamination as a function of the irradiation time measured as (a) the height of the carbonaceous cones produced by a focused beam and (b) the thickness of the carbonaceous film produced by a rastered area. Experimental data were extracted from [80, 150, 189, 323, 356]

From deposits produced by a rastered beam over a 5 μm × 15 μm at 1 kV in a SEM, Hirsch et al. [150] observed both time–contamination relationships. Without a cold trap, the contamination increases linearly, whereas it saturates when the cold trap is used. With a cold trap, all the contamination experiments of Mitchell [226] in a STEM (200 kV) resulted in the saturation of the contamination with the irradiation time, regardless of the sample temperature, beam current or cleaning procedure. Both authors used the thickness variation of the deposited carbonaceous film to estimate the contamination.

To quantify the observed saturation, Mitchell [226] proposed a square root relationship (Eq. 2.50) based on the fact that “such kinetics are typical of a diffusion-limited process”. To verify the applicability of this equation to other contamination experiments, results were extracted from the published figures showing a saturation of the contamination [80, 150, 189, 323, 356]. Eq. 2.50 was fitted to the results using a least squares fitting method. Fig. 2.20 shows the variation of the contamination as a function of the irradiation time measured as the height of the carbonaceous cones produced by a focused beam and the thickness of the carbonaceous film produced by a rastered area. In all cases, the square root relation matches the experimental results. The difference in the experimental conditions may explain the different rate constants and intercept values.

Mitchell [226] suggested that the saturation of the contamination with irradiation time is an indication of a diffusion limited process. The concept of a rate limiting step have been used by many authors to explain their results [69, 216, 226, 291, 306, 311, 323, 358, 364]. One or more mechanisms controls the overall contamination rate as the other reaction rates are much faster. Rykaczewski et al. [311] identified three growth regimes whether there is an excess or deficiency of organic molecules available to be cracked by the electron beam. If there is an excess, the formation of a carbonaceous deposit is limited by the cracking process, reaction limited. If not enough molecules can reach the electron irradiated area, the regime is diffusion limited. The third regime is a mixture of the other two, a mixed growth regime.
Using these concepts, Rykaczewski et al. [311] numerically solved the contamination equations (neglecting etching) using different values for the quantities to simulate the three regimes. Their results, showing the variation of the height and volume of a contamination cone, are reproduced in Fig. 2.21. Assuming a mixed regime, which is slightly more reaction limited, similar trends are observed between these calculated results and the experimental ones from Conru and Laberge [80] and Tomita et al. [356] for the same geometry, i.e. a linear increase of the cone volume and a saturation of the height. The comparison is however difficult since calculations were only performed for a short time scale (< 2 s). Furthermore, the results of Rykaczewski et al. [311] suggest that the departure from a linear behaviour of the contamination as a function of the irradiation time is due to some extent to a limited diffusion of organic molecules. This could explain the results of Hirsch et al. [150]. The cold trap reduces the number of adsorbed organic molecules by limiting/eliminating adsorption. This creates a situation where surface diffusion controls the number of available organic molecules for cracking.

The influence of surface diffusion on the contamination behaviour is further evidenced in the experiment of Amman et al. [9] where a time delay was added in between the electron irradiation. During this time, the beam does not hit the sample. Using a focused electron beam (40 kV) and while keeping the total electron dose constant, the deposition was interrupted 40 times by a delay ranging from 22 ms to 100 s. The height of the produced carbonaceous dot increased with the time delay, up to approximately 20 s where no difference in the height was then observed. They explained these results by the fact that there is a critical transport time required to replenish, by surface diffusion, areas depleted in organic molecules. On a shorter time and spatial scale, this experiment is similar to the flooding method, described previously.
Swaroop [350] and Mitchell [226] noted an incubation period where the contamination rate is much slower in the first seconds after the sample is irradiated by electrons. Using a focused beam of 15 kV, 376 pA, Rykaczewski et al. [312] produced a carbonaceous deposit consisting of a cone surrounded by a ring on a silicon wafer. They measured the evolution of the cone and ring height over 25 min. They observed that the cone grew faster than the ring at the beginning but the growth rate of the ring increased after approximately 15 min.

Overall, these examples show that the contamination cannot be assumed to be constant in time and space. The deposits produced take different shapes and evolve differently with the irradiation time. The total volume of the carbonaceous deposit was suggested to be the most stable and more representative criterion to quantify contamination by Roediger et al. [306] and Rykaczewski et al. [311]. Despite the difficulty to obtain reliable physical quantities [364], simulations appear to be the best method to understand the contamination behaviour as a function of time for different experimental conditions.

### 2.3.3.4 Beam current density / beam current

Apart from the changes in the contamination rates, one evident outcome of different experimental conditions is the shape of the carbonaceous deposits even for a well-focused electron beam (Fig. 2.14). As aforementioned, authors have attributed the change from a cone to a ring structure to the relationship between the current density and surface diffusion [216, 291, 364]. In solving the contamination equations for the steady-state condition ($\frac{\partial n_i(\vec{r},t)}{\partial t} = 0$), Utke et al. [364] defined a dimensionless parameter ($\tilde{\rho}$) to represent the replenishment of organic molecules by surface diffusion inside the irradiated area. This parameter regroups the physical quantities for the sticking coefficient, impinging flux, residence time, diffusion coefficient, cracking cross section and current density. Essentially, increasing the current density decreases $\tilde{\rho}$. Calculated profiles of contamination deposits with different values of $\tilde{\rho}$ are shown in Fig. 2.22. Decreasing $\tilde{\rho}$ or increasing the current density results in the formation of a contamination ring because adsorbed molecules travel less before being cracked [365].

In their solution of the contamination equations Utke et al. [364] neglected the contribution of emitted electrons to the current density distribution. The influence of etching was also disregarded. Lobo et al. [216] included these omissions in their solution. This led them to a different explanation for the formation of a contamination ring. In their model, a high pressure of etching molecules was however selected ($10^2$ Pa), which implies a high impinging flux and high adsorption of water molecules on the sample surface (Eq. 2.45). Despite describing mainly variable pressure SEM conditions, their results showed an abrupt change from deposition to etching when the beam current density or beam current is increased (the beam profile was kept constant in their calculations). By removing both cracked and adsorbed organic molecules, etching reduces the number of molecules available for cracking and thus amplifies the diffusion limited regime depicted by Rykaczewski et al. [311]. At any given time, deposition and etching conditions coexist across the sample surface. Etching dominates under the electron beam due to the significantly high current density. Both primary and emitted electrons contribute to the current density. Deposition is favoured at the edges due to the lower current density and higher surface diffusion from the outside. According to Lobo et al. [216] this gives rise to the formation of a
2.3. Carbon contamination

Figure 2.22: Profiles of contamination deposits calculated for different values of the replenishment parameter $\tilde{\rho}$ assuming a Gaussian beam. Reproduced from [364].

Figure 2.23: Profiles of contamination deposits calculated for different beam currents. Reproduced from [216].

contamination ring as illustrated in Fig. 2.23. The energy distribution of the beam current was not accounted by the authors. By varying the values used for the cracking cross sections of organic and etching molecules, they concluded that the energy distribution has an influence on the shape of the contamination deposit, but it does not invalidate the contamination model presented in their paper.

Regardless of the explanations, the conclusion from the models of Utke et al. [364] and Lobo et al. [216] is that a contamination ring is formed at higher current densities. In order to support this statement with experimental measurements, the results from 14 publications, where the shape of contamination deposit and the beam current density, current or diameter were given, were compiled [32, 69, 159, 160, 181, 182, 189, 228, 260, 291, 312, 323, 358, 416]. This was done independently of other experimental parameters such as the accelerating voltage, type of sample, etc. and potential ambiguities in the determination of the current density or beam diameter. The actual size of the cone or ring is also not considered. In some instances, when only the beam current was given, the beam diameter as stated in the specifications
of that instrument was used to calculate the current density. The different observed shapes as a function of the beam current density, current and area (n.b. logarithmic scale) are graphically represented in Fig. 2.24.

In general, the relationship between the contamination shape and the current density was not demonstrated. Contamination rings were observed at low current densities and cones at high current densities. The reverse was expected based on the calculations from the contamination equations. One potential reason is the large differences between the beam areas used for the measurements (diameters from 0.002 to 10 μm). Most contamination rings were produced by large electron beams, except the dual structure observed by Toth et al. [358] and Rykaczewski et al. [312] using SEM with high resolution capabilities. A relationship is more clearly distinguishable using the beam current. Low currents create cone structure and high currents, rings. The dual structure seems an intermediate state, although the cone shape has been observed by Yoshimura et al. [416] at a higher beam current than the dual structure observed by Rykaczewski et al. [312]. The former research group used carbon thin films in a TEM (200 kV) for their measurements, whereas the experiments of the later were done in SEM (15 kV) on a bulk silicon sample. The low level of electron backscattering may prevent the formation of a contamination ring in the experimental setup of Yoshimura et al. [416]. As Reimer and Wächter [291] observed contamination rings on thin film samples (100 kV), the low beam current was nevertheless a determining factor. Based on the available results, the beam current, instead of the beam current density, appears to be the differentiating factor for the shape of the contamination deposit, with a critical value around 0.1 to 1 nA.

Relating back this finding with the theoretical contamination model and numerical solutions, a distinction should be made between the beam current, beam diameter and beam current density, although only the later directly appears in the cracking equation (Eq. 2.55). The beam current density is not a constant value as the number of electrons (primary and emitted) crossing the sample surface follows a distribution giving by the beam profile and scattering behaviour. Although the actual shape of the distribution is usually unknown, the beam is usually assumed to be Gaussian with an extended tail [216, 364]. Increasing the beam current increases the number of electrons available to crack adsorbed organic molecules, but also enlarges the beam profile as these two quantities are linked by the reduced brightness of the electron emitter (Eq. 2.6). This dependence is illustrated in Fig. 2.25 where the results from Fig. 2.24 are plotted as a function of the beam current and beam area. The theories of Utke et al. [364] and Lobo et al. [216] fit with this combined increase of the beam current and enlargement of the beam profile. For Lobo et al. [216], this gives rise to a larger gradient between the current in the centre of the beam and the one at the outside, and consequently to the coexistence of etching and deposition regimes. For Utke et al. [364], high currents leads to a rapid depletion of organic molecules in the irradiated area and a diffusion limited regime, where organic molecules must migrate over a larger distance due to the enlargement of the beam. Whether or not etching plays a decisive role in the contamination process, both theories agree that high beam currents favour a diffusion limited regime and the formation of contamination ring. A series of experiment where either the beam current or beam diameter would be kept constant while the other quantity is varied would certainly help understand the contamination behaviour. This especially applies to conditions of low beam currents and high defocus (lower right corner of Fig. 2.25) where no experimental measurements currently exist.
2.3. Carbon contamination

(a) Beam current density

(b) Beam current
Figure 2.24: Shape of the contamination deposit as a function of the (a) beam current density, (b) beam current and (c) beam area based on experimental measurements of [32, 69, 159, 160, 181, 182, 189, 228, 260, 291, 312, 323, 358, 416]. The symbol † and ‡ indicates a calculated or estimated value, respectively.

Figure 2.25: Shape of the contamination deposit as a function of the beam current and beam area based on experimental measurements of [32, 69, 159, 160, 181, 182, 189, 228, 260, 291, 312, 323, 358, 416].
2.3. Carbon contamination

![Graphs](a) Beam diameter (b) Beam current

Figure 2.26: Contamination rate as a function of (a) the beam diameter and (b) beam current. Data extracted from [232].

Apart from the shape of the contamination deposit, the beam current influences the contamination rate. Experimentally, different relationships between the contamination rate and beam current (or beam current density) have been reported: independent [232, 415], linear increase [147], linear increase followed by a saturation at higher currents [76, 102, 199, 379], decrease [150] or increase followed by decrease with maximum contamination rate at a specific beam current [80, 226, 306, 379]. The interpretation of these different behaviours is not straightforward because of the different irradiation methods (focus beam, rastered area), irradiation times (electron dose), measurement strategies (volume, height, thickness of deposit) and instruments (beam profile) used by the authors. In addition, some publications only contain qualitative statements [102, 147, 379, 415]. From his experiments where he varied the current density and the beam diameter (thin carbon film measured at 80 kV), Müller [232] concluded that the contamination rate is independent of the current density but decreases with larger beam diameters. Extracting the contamination rates from the figures and calculating the beam currents from the specified current densities and beam diameters reveal that the contamination rate also decreases with increasing beam current. The trend is however more ambiguous than the one with respect to the beam diameter reported by Müller [232] which showed perfect linearity (Fig. 2.26). More information about how the beam current density and beam diameter were measured would be required to better understand these findings.

All the results based on a rastered area [150, 226, 306] point to the existence of a maximum contamination rate at a specific beam current. Roediger et al. [306] reported a maximum at 60 pA and Mitchell [226] at 155 pA. The fact that Hirsch et al. [150] only reported a decrease of the deposit thickness may be explained by the higher currents used in their measurements (> 100 pA). The decrease of the contamination rate at higher beam current fits with the diffusion limited regime or etching enhanced regime previously described, especially when analyzing the results of Roediger et al. [306]. They measured a larger decrease when the contamination is evaluated using the height of the contamination deposit (measured in the centre) than the total volume. For a focused beam producing a cone, Conru and Laberge [80] also observed a maximum contamination rate at 25 pA. Although they explained
their results by the “the increase in backscatter electrons that hit the lens plate and create contamination there instead than on the sample”, their results could equally be interpreted based on the aforementioned theories. Oppositely to Hirsch et al. [150] the saturation observed by Christy [76] could potentially be explained by the low currents used (≈ 1 to 15 pA). No relationship between the contamination rate and the beam current was reported for contamination rings.

2.3.3.5 Accelerating voltage

Although the accelerating voltage does not appear in any of the contamination equations, it has a large influence on the cracking process by changing the energy and spatial distribution of the electron current density (§2.3.3.1). The accelerating voltages used in SEM or TEM are orders of magnitude larger than the threshold energy for cracking, which was estimated by Hirsch [148] and Mayer [221] to be less than 5 eV and calculated by Alman et al. [5] to be around 10 eV (Eq. 2.57). This led Hirsch [148] to conclude that the contamination process is independent of the accelerating voltage. The same conclusion was reached by Ennos [102], Hirsch et al. [150] and Ueda and Yoshimura [363] for voltages between 40 to 75 kV, 1 to 25 kV and 5 to 15 kV, respectively. The results of Hirsch et al. [150] however require more explanations as the beam current density was adjusted to keep the product of the cracking cross section and current density constant at each accelerating voltage. They approximated the cracking cross section to be proportional to $E_0^{-0.8}$. If the contamination results are instead corrected for a constant current density, the contamination produced by rastering the electron beam over a $5\mu m \times 15\mu m$ area on silicon decreases with increasing accelerating voltage. This relationship was also reported by Bahr et al. [19] and Kumao et al. [199] at higher accelerating voltages ($\geq 50$ kV) in their TEM. In the range between 50 to 2000 kV, Kumao et al. [199] estimated the decrease of the contamination rate as a function of the accelerating voltage to be proportional to $1/v^2$, where $v$ is the electron velocity. Expressing the electron velocity in terms of kinetic energy, this proportionality approaches the one proposed by Hirsch et al. [150] ($E_0^{-1}$ vs. $E_0^{-0.8}$). Under similar experimental conditions as Hirsch et al. [150], Roediger et al. [306] also found a decrease of the contamination deposited by a rastered beam ($7\mu m \times 7\mu m$) with increasing accelerating voltage (0.7 to 25 kV, 300 pA), but only in the centre of the irradiated area. Oppositely, the total volume, as measured by AFM, increases at high accelerating voltages. Hirsch et al. [150] did not evaluate the volume of their carbonaceous deposits; only the BSE intensity profiles across the deposits were reported. As shown by Roediger et al. [306], a rastered beam produces a complex structure with uneven contamination at the edges and in the interior, which may explain the discrepancies between the contamination at the centre height and over the total volume.

For a focused beam producing a cone structure, Hübner et al. [160] and Schiffmann [323] observed an analogous behaviour, where the cone height increases with increasing accelerating voltage (1 to 30 kV), while the cone diameter or opening angle decreases. The total volume was not studied by the authors. Using the reported values of Schiffmann [323] (3 pA, irradiation time of 12 min), the volume was calculated assuming the deposit to be a perfect cylinder (assumption based on the geometrical description of Schiffmann [323]). As shown in Fig. 2.27, the volume is significantly
2.3. Carbon contamination

Figure 2.27: Height, diameter and volume of conical contamination deposits produced by a focus beam as a function of the accelerating voltage (3 pA, irradiation time of 12 min). Height and diameter values reproduced from [323]. Volume calculated assuming a perfect cylinder as $\pi (\text{radius})^2 (\text{height})$.

larger at 1 kV due to the large diameter. This abnormal increase was explained by the “broadening of the electron beam at low energies” in their instrument [323]. Excluding this value, the volume reaches a maximum at 25 kV.

The increase of the contamination volume as a function of the accelerating voltage was also observed by Miura et al. [228] for a different contamination structure. Deposits were produced using the linear scanning mode of a SEM on a silicon sample at a magnification of 50 000 x (10 to 30 kV, 20 pA). Their results show an increase of the height, a decrease of the width, and an increase of the volume, assuming a cylindrical shape. The authors attributed the increased contamination rate to the “production of high-energy electrons by the high acceleration voltages” [228]. Although this explanation seems doubtful based on the present-day knowledge of the cracking cross sections (§2.3.2.4), these results reinforce those of Roediger et al. [306] and Schiffmann [323] which demonstrate an increase of the overall deposited contamination with the accelerating voltage. As pointed out by Roediger et al. [306], they also contradict the traditional belief based on visual assessment of SE images that contamination is worst at low accelerating voltages.

For the contamination ring geometry, Rykaczewski et al. [312] and Hristu et al. [159] observed an increase of the ring diameter with the accelerating voltage, but did not report on the height or total contamination volume. The former presented a linear increase of the ring diameter with the accelerating voltage from 3.5 $\mu$m at 10 kV to 8 $\mu$m at 30 kV (silicon substrate, $\approx$ 400 pA), whereas the later measured ring diameters of 9.35 and 15.04 $\mu$m at 20 and 30 kV, respectively (hydroxyapatite substrate, 14 nA, irradiation time of 7 s). The larger diameters in the experiments of Hristu et al. [159] was explained by the “effective defocusing of the incident beam” due to charging of the sample. Assuming that this effect produces an effective beam...
diameter of 2μm, the authors simulated the BSE radial distribution using a Monte
Carlo program. They found that the extent of the radial distribution matches the
observed ring diameters at both accelerating voltages. Furthermore, they attributed
the formation of contamination rings in their experiment to the shape of the radial
distribution, which changes from a pillar to ring with increasing beam defocusing.
Rykaczewski et al. [312] combined Monte Carlo simulations with the cracking rate
equation (Eq. 2.55). The observed linear relationship between the ring diameter and
the accelerating voltage was confirmed by the simulations.

Comparing the cone and ring geometries, it is interesting to note that increasing
the accelerating voltage has an opposite effect of the structure diameter. The cone di-
ameter decreases at higher accelerating voltages whereas the ring diameter increases.
All else being equal, increasing the accelerating voltage increases the electron inter-
action volume. SEs and BSEs are emitted further away from the beam centre. In
a diffusion limited regime, adsorbed organic molecules migrating on the sample sur-
face will be cracked as soon as they enter the electron irradiated area. This explains
the enlargement of the contamination ring diameter with the accelerating voltage.
At the same time, increasing the accelerating voltage improves the focusing of the
PEs resulting in a sharper beam profile (Fig. 2.6). In a reaction limited regime, the
contamination deposit resembles the beam profile [364]. Although BSEs and SE2s
are emitted outside the primary beam, their proportion in the overall electron dis-
tribution is less than the one of PEs and SE1s. As a consequence, sharpening of
the electron beam at higher accelerating voltages results in smaller cone diameters.
The influence of the accelerating voltage as well as the beam current (§2.3.3.4) on
the electron distribution, its magnitude and profile, is therefore a crucial element to
understand the contamination behaviour.

Summary

From the literature review on the topic of carbon contamination in electron mi-
croscopy, six mechanisms and five categories of dominant factors were identified. The
electron beam induced deposition of carbonaceous deposits on the sample surface in-
volves organic molecules, etching molecules and electrons (Rxn. 2.1 and 2.5) dynami-
cally interacting through adsorption, desorption, surface diffusion, cracking, polymer-
ization and etching processes. The deposition rate (Eq. 2.59) and the characteristics
of the carbonaceous deposits (e.g. shape, dimensions, etc.) depend on several factors,
which were grouped in five categories: chemical substances, initial conditions, irradiation
time, beam current / beam current density and accelerating voltage. Although
there is no magic mitigation solution for carbon contamination, the identification of
the underlying mechanisms and the classification of the factors allow to fundamen-
tally explain the experimentally observed behaviours and help understand existing
anti-contamination strategies. Knowing the influence of the irradiation time, beam
current and accelerating voltage on the carbon contamination can certainly assist the
selection of the optimal experimental parameters for a measurement. A shortcoming
of the literature review is the lack of experiments and simulations at typical analytical
conditions for EPMA, or in other words, at conditions where a well-focused electron
beam produces a ring-shaped carbonaceous deposit. This will be addressed in relation
with the carbon quantification of steels in Chap. 3 and more generally in Chap. 4.
2.4 Quantification using soft X-rays

As the accelerating voltage decreases, the mean free path between elastic and inelastic interactions decreases resulting in a smaller electron irradiated volume, and consequently a smaller X-ray emission volume. This fundamental concept is illustrated in Fig. 2.28. For a pure iron sample, the size of the X-ray emission volume is estimated as the depth where 95% of the X-rays are emitted based on Monte Carlo simulations (NISTMonte [300]). Lowering the accelerating voltage improves the resolution of both Fe K–L\textsubscript{2,3} and L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions. This improvement also comes from the decrease of the overvoltage ratio, the ratio between the accelerating voltage and the ionization energy of a particular X-ray transition (i.e. the binding energy of the corresponding atomic subshell, see §2.1.2). At a low overvoltage ratio, only the electrons that travelled a short distance inside the sample can excite the atoms as their energy remains above the ionization energy. The X-ray emission volume is confined below the surface near the impact point of the electron beam and is therefore much smaller than the electron irradiated volume. Besides improving the resolution, a low overvoltage ratio also entails a lower X-ray intensity as fewer electrons have the energy required to excite the atoms. From Fig. 2.28, both the resolution and intensity of the Fe K–L\textsubscript{2,3} X-ray transition decreases with the accelerating voltage.

At one point, the worsening in the precision due to low X-ray intensities neutralizes any gain in resolution. Practically, below a certain accelerating voltage, it becomes more advantageous to use an X-ray transition with a lower excitation energy. In the current example, better depth resolution and precision are achieved at an accelerating voltage of 9 kV using the Fe L\textsubscript{3}–M\textsubscript{4,5} than at 12 kV using the Fe K–L\textsubscript{2,3} X-ray transition. As the accelerating voltage is decreased, further improvements of the resolution are possible with the Fe L\textsubscript{3}–M\textsubscript{4,5} X-ray transition without the exponential drop of the X-ray intensity observed with the Fe K–L\textsubscript{2,3} X-ray transition. Pouchou [271] reached the same conclusion for a pure copper sample.

In theory, there is an undeniable advantage to perform EPMA at lower accelerating voltages using X-ray transitions with lower excitation energies: better spatial resolution with comparable precision. A lower contribution of fluorescence to the intensity [271], depth profiling of multilayer samples [297, 298] and charge neutralization of insulating materials [203] are other benefits of low accelerating voltage analyses [223]. Accuracy is however the Achilles heel of the quantification at low accelerating voltages. Many authors reported large inaccuracies when soft X-rays (X-rays with an energy less than 1 keV) are used for the quantification. A prime example is the carbon quantification using the C K–L\textsubscript{2,3} X-ray transition as discussed in §2.2.2, but this problem also applies to the K–L\textsubscript{2,3} X-ray transition of other ultra-light elements (e.g. B, N and O) [29–32, 34, 35], L\textsubscript{3}–M\textsubscript{4,5} X-ray transition of transition metals in the first row of the periodic table [125, 175, 214, 261, 271, 342], and M\textsubscript{5}–N\textsubscript{6,7} X-ray transition of rare earth elements [200].

This led Pouchou in 1996 to conclude: “The fact that the 3d-2p transition rate and the L self-absorption coefficient vary with the chemical state in the 3d transition elements is a strong limitation for the use of their L lines in routine applications of quantitative microanalysis” [271]. The relevance of this problem is however contem- porized by the advancement in the electron optics of modern electron microscopes. In comparison to thermionic emitters, Schottky and cold field emitters deliver small beam diameters at low accelerating voltages, making them attractive for the charac-
Chapter 2. Literature review

Figure 2.28: Depth resolution and net intensity of the Fe K–L$_{2,3}$ and L$_{3}$–M$_{4,5}$ X-ray transition as a function of the accelerating voltage. Using the Monte Carlo program NISTMonte [300], the resolution was calculated as the depth where 95% of the X-rays are emitted. The vertical dash lines indicated the ionization energy (E) of each X-ray transition.

terization of small microstructural features. The large inaccuracies in the quantification prevent modern microscopists to take advantage of these improved analytical capabilities for EPMA. As a testament, a review of the literature published in the last decade by this author [256] revealed limited use of electron microscopes equipped with such emitters for quantitative analyses at a high spatial resolution [130, 134, 241].

In the perspective of this work, this section concentrates on the quantification challenges using the L$_{3}$–M$_{4,5}$ lines of common steel alloying elements, such as Cr, Mn, Fe and Ni. An overview of the problem is given in §2.4.1 based on the results found in the literature. From the previous section (§2.2.2), many of the aforementioned challenges associated with the carbon quantification equally affect the quantification using the L$_{3}$–M$_{4,5}$ of the transition metals. The similitudes and differences are discussed in §2.4.2. Finally, potential solutions will be presented in §2.4.3.

2.4.1 Problem statement

The quantification problem of the first transition series metals has been investigated by many authors for different compounds: three Ni aluminides by Pouchou and Pichoir [272] (also in [271]), six Fe silicides by Gopon et al. [125], three Ni silicides by Heikinheimo et al. [142], three stainless steels by Llovet et al. [214], a stainless steel by Statham and Holland [341], and a metallic glass by Jonnard et al. [175]. All samples were analyzed with an accelerating voltage of 5 kV [125, 175, 214, 341] or 6 kV [142,
2.4. Quantification using soft X-rays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal (mass %)</th>
<th>Measured (mass %)</th>
<th>Relative error (%)</th>
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</table>

Table 2.6: Summary of quantification results reported in the literature using a low accelerating voltage and the L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions \[125, 142, 175, 214, 341\]. When available, the nominal mass fractions measured by EPMA at a higher accelerating voltage and using the K–L\textsubscript{2,3} X-ray transitions is tabulated. From \[125\], the nominal and measured mass fractions were calculated using the Chantler et al. \[72\] MAC database. From the round robins, results of all the participants were averaged.

meaning that the concentrations of Cr, Fe and Ni were measured using their L\textsubscript{3}–M\textsubscript{4,5} X-rays. Tab. 2.6 compares the nominal and measured mass fractions reported by the authors for the different samples. The results from Pouchou and Pichoir \[272\] are excluded since only k-ratios were disclosed. The nominal mass fractions were either measured by EPMA at higher accelerating voltages using the K–L\textsubscript{2,3} X-ray transitions \[125, 142, 175, 214\], or by other analytical techniques (e.g. optical mass spectroscopy) \[175, 214, 341\]. The results from Llovet et al. \[214\] and Jonnard et al. \[175\] came from round robins where 6 and 10 laboratories measured each sample, respectively. In all cases, the X-ray intensities were acquired using WD spectrometers and the quantification was performed with k-ratios based on pure reference materials.

The results tabulated in Tab. 2.6 certainly confirm the large errors on the Cr, Mn and Fe concentrations when the quantification is performed using the L\textsubscript{3}–M\textsubscript{4,5} X-rays. This level of inaccuracy is undoubtedly unexpected for EPMA, especially since Cr, Mn and Fe can all be considered as major elements with a mass fraction above 5\%. Although the measurement of L\textsubscript{3}–M\textsubscript{4,5} X-ray intensities is more challenging \[223\], the observed discrepancies cannot only be attributed to experimental errors, such as background subtraction, contamination, oxidation, etc. \[214\]. The fact that large errors were obtained on different samples by different participants and instruments reinforces this statement and confirms a systematic problem with the quantification of first transition series metals using the L\textsubscript{3}–M\textsubscript{4,5} X-rays.
In terms of relative errors, all the results point to an overestimation of the Fe and Ni content and an underestimation of the Cr content. The only exceptions are the SS63 and Ni glass samples, where the Fe content was underestimated. From the results of Gopon et al. [125], Heikinheimo et al. [142] and Llovet et al. [214], the relative error appears to increase as the concentration of an element decreases, or in other words as the difference between the composition of the unknown and the reference material (pure samples) increases. More results would be needed to unambiguously verify this trend. As the quantification hinges on the comparison of k-ratios, this tendency nonetheless denotes potential fundamental differences between the X-ray intensity emitted from the unknowns and reference materials. From Eq. 2.33, and more precisely from Eq. 2.34, it is not surprising that the composition influences the emission probability of X-rays. The results of Tab. 2.6 however attest that the intensity models and the fundamental parameters used in these models do not properly evaluate this influence.

Most authors have shown improved quantification results after modifying the MACs, either manually [341] or by empirically determining them [125, 142, 214, 271, 272]. Although large errors (> 5%) remain in almost all cases, the improvement demonstrates that the absorption of L$_3$–M$_{4,5}$ X-rays in these samples cannot be calculated from the traditional concentration-weighted summation of pure element MACs as in Eq. 2.36. The correction, or the determination of compound specific MACs, only offers a partial solution, as summarized by Statham and Holland [341]: “it is difficult to see how the analysis can be improved by any further improvement of the MACs”. Other potential root causes identified by the authors revolve around the effects of chemical bonding on the electronic structure of the atoms, e.g. presence and magnitude of satellite peaks, changes in the transition probabilities, and anomalous absorption. These are discussed in the following section.

### 2.4.2 Challenges

#### 2.4.2.1 Carbon contamination

Unfortunately, “it should not be forgotten that the contamination by carbon is a problem not only in the case of the carbon measurement, but also for the measurement of other soft X-rays” as mentioned by Pouchou [271]. Aside from the C K–L$_{2,3}$ X-rays, the carbon contamination has two indirect effects on the measured intensity of all soft X-rays at low accelerating voltages. First, since the electrons have a lower energy, they more strongly interact with the carbonaceous deposit, as they would do at higher accelerating voltages. The increase in the number of inelastic interactions effectively decreases the landing energy of the incident electrons, reducing the overvoltage ratio and the X-ray emission [287]. Secondly, most soft X-rays have a high absorption probability in carbon. From the MAC database of Chantler et al. [72], the MACs for Cr, Fe and Ni L$_3$–M$_{4,5}$ X-rays are respectively 935.8, 539.5 and 323.2 m$^2$ kg$^{-1}$, two orders of magnitude greater than those for the K–L$_3$, 1.5, 0.9 and 0.5 m$^2$ kg$^{-1}$.

To illustrate both effects of the carbon contamination, the apparent reduction of the Cr concentration due to contamination was simulated by Monte Carlo simulations (CASINO 2 [95, 155]) at an accelerating voltage of 5 kV using the Cr L$_3$–M$_{4,5}$ X-ray transition. The carbonaceous deposit was taken as a pure carbon film deposited on top of a pure chromium substrate. Fig. 2.29 shows the results for different carbon
Figure 2.29: Apparent Cr mass fraction as a function of the thickness of a carbon film deposited on a pure chromium substrate at an accelerating voltage of 5 kV. Cr L₃–M₄,5 k-ratios were obtained by Monte Carlo simulations (CASINO 2 [95, 155]) and then quantified using DTSA-II [302].
for each pure substrate. This strategy is identical to the aforementioned correction of the carbon contamination. The following thickness values were respectively obtained for Ti, Fe, Ni and Cu directly after polishing: 6.8, 3.2, 1.6 and 3.9 nm. Longer exposure to ambient air resulted in an increase of the TiO$_2$ thickness, but had no effect on the native oxide layer of the other elements. From these values, they reported that the calculated intensity loss would be from 5 to 8% at 2 kV for Fe, Ni and Cu, and up to 30% for Ti [141]. Similarly to Fig. 2.29, a Monte Carlo simulation at 5 kV with a 2-nm-thick Cr$_2$O$_3$ layer on top of pure chromium gave a 1% reduction in the Cr L$_{3-M_{4.5}}$ intensity.

Like contamination, and as shown by Heikinheimo and Llovet [141], the influence of oxidation on the X-ray intensity can be corrected with a thin-film correction program, if no oxygen is present in the sample [223]. Ideally, the correction should be independently applied to the unknowns and reference materials as the level of carbon contamination and oxidation is likely to change from sample to sample, especially from pure metallic reference materials to unknown alloys.

2.4.2.3 Interferences of X-ray transitions

In comparison to the C K–L$_{2,3}$, the interferences with the L X-ray peaks of first transition series metals mostly originate from other first order X-ray reflections ($n = 1$). In this range of photon energies, the energy separation between soft X-ray transitions is significantly reduced, overlapping and interference problems between adjacent X-ray peaks are therefore common, even for WDS. As expressed by Merlet and Llovet [223], “low-voltage EPMA will require the use of high resolution X-ray spectrometers”. Unfortunately, the available dispersive element are typically optimized for high reflectivity (high intensity), at the expense of the spectral resolution. Fig. 2.30a shows an overlay of five WD spectra acquired on pure reference materials of Cr, Mn, Fe, Co and Ni on a LDE1 dispersive element. These elements which are very common in different steel grades would all require interference corrections. The measurement of Fe and Co X-rays on a TAP dispersive element partially solves the interference problem with its better spectral resolution (Fig. 2.30b), but its lower reflectivity reduces the precision and the interference of the Fe L$_{3-M_{4.5}}$ with the Cr L$_{3-M_{4.5}}$ remains.

Besides the interferences between the different elements, Fig. 2.30a also evinces the interferences between the X-ray transitions of the same element, for instance the L$_2$–M$_4$ with the L$_{3-M_{4.5}}$, and L$_2$–M$_1$ with the L$_3$–M$_1$. The presence of the L$_3$ and L$_2$ absorption edges below the L$_{3-M_{4.5}}$ and L$_2$–M$_4$ peaks respectively further complicates the situation as the intensity ratio between the interfering lines changes with the sample composition. For this reason and the lack of reliable transition probabilities, it is difficult to foresee an accurate correction for this type of interference, unless a deconvolution algorithm is used to separate the peaks and determined the X-ray intensity from their area [294, 295]. Although no participant of Llovet et al. [214]’s round robin measured the X-ray intensity from the peak area, participants that used a TAP dispersive element to measure the Fe L$_{3-M_{4.5}}$ peak intensity did not obtain better quantitative results than those that used a LDE1 dispersive element (or equivalent).

Among the typical alloying elements in steel (C, Si, Cr, Mn, Fe, Co, Ni and Mo), only high order X-ray reflections of Mo and Si interfere in the spectral range shown in Fig. 2.30. Care should be taken in high alloyed steels containing these elements in large concentrations. As in §2.2.2.3, the interfering lines are listed in Tab. 2.7.
2.4. Quantification using soft X-rays

Figure 2.30: WD spectra acquired on pure reference materials of Cr, Mn, Fe, Co and Ni at 5 kV, \( \approx 50 \text{nA} \) using (a) a LDE1 and (b) TAP dispersive element (adapted from [255]).
Chapter 2. Literature review

<table>
<thead>
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<th>X-ray transition</th>
<th>Order</th>
<th>E (eV)</th>
<th>E′ (eV)</th>
<th>λ′ (nm)</th>
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<td>2.339</td>
</tr>
</tbody>
</table>

Table 2.7: Interfering X-ray reflections of major alloying elements in steel. Their energy (E′) and wavelength (λ′) are expressed as the equivalent value for the given interfering order.

2.4.2.4 Satellite emission

From Fig. 2.30b, a meticulous observation of the Ni L₃-M₄,₅ and L₂-M₄ peaks reveals that both peaks have an asymmetrical shape, with a longer tail on the high energy side. This peak broadening is caused by X-ray satellite emission, as several authors with higher resolution spectrometers reported [75, 294, 334].

Rémond et al. [294] distinguishes two categories of satellites. The first, on the high energy side of a given peak, originates from the multiple ionization of an atom, more than one electron is missing, which increases the energy difference between subshells [143, 294]. The relaxation of the ionized atom leads to the emission of a more energetic X-ray. According to Rémond et al. [294], this multi-ionized state “arise primarily from Coster-Kronig transitions”. The second category of satellites is visible on the low energy side of the peak, and occurs due to the “simultaneous emission of an X-ray photon, and a plasmon or an electron” [294]. Based on Fig. 2.30b and the results of Chopra [75], this category of satellites was not observed for the Ni L₃-M₄,₅.

As pointed out by Rémond et al. [294], satellites “are in some instances hidden by spectral distortions resulting from instrumental effects”.

The influence of satellite lines on the measured X-ray intensity and consequently on the quantification entirely depends on whether their magnitude varies as a function of the sample composition. For instance, if the ratio between a peak and satellite intensities is constant, the k-ratio nullifies the effect of this satellite line. On the other hand, if chemical bonding changes the emission probability of a satellite line, this induces a systematic error in the quantification results. From the literature, variations of the satellite intensity with the sample composition, as well as with the accelerating voltage, are likely explained by changes in the absorption behaviour [75, 294, 334]. As it will be discussed in the next section, the presence of the L₃ absorption edge below the L₃-M₄,₅ peak signifies that the high energy side satellites are more strongly absorbed than the parent peak. Their magnitude decreases as the overvoltage
increases. For the Cu L₃–M₄,₅, Rédond et al. [294] reported a decrease of the peak to satellite intensity ratio from 17.5 to 5.9 as the accelerating voltage is increased from 5 to 15 kV.

2.4.2.5 Absorption

As experimentally noted by several authors, the position and shape of the L₃–M₄,₅ X-ray peak of first transition series metals change as a function of the accelerating voltage. This was attributed to the phenomenon of self-absorption, which is defined as the photoelectric absorption of a characteristic X-ray by the same kind of atom it was emitted from [214, 334, 341].

Recalling the explanations from §2.1.2.1, photoelectric absorption occurs when an X-ray transfers all its energy to a bound electron of an atom. It is only possible if the energy of the X-ray is greater than the binding energy of this electron. This minimum energy criterion creates sharp changes in the absorption behaviour, referred to as absorption edges [46]. They are schematically shown in Fig. 2.31, where the value of the MACs [72] for Cr, Mn, Fe, Co and Ni is plotted as a function of the X-ray energy over the same range as Fig. 2.30.

One particularity of the first transition series metals is the overlap of their absorption edges and X-ray transitions; the L₃ absorption edge overlaps with the L₃–M₄,₅ X-ray peak and the L₂ absorption edge, with the L₂–M₄ X-ray peak [125, 214, 223, 334, 341]. This special situation leads to self-absorption [46, 106]. Concretely, the emission of L₃–M₄,₅ X-rays occurs due to the ejection of an electron in the L₃ subshell (2p³/₂) and the relaxation of an electron from the M₄ or M₅ subshell (3d³/₂ or 3d⁵/₂). For an X-ray with an energy above the L₃ edge, the photoelectric absorption may involve the ejection from an electron in the L₃ subshell (2p³/₂) to the conduction band. Since the 3d orbitals are partially filled for the first transition series metals, the ejected electron may land in one of the unoccupied 3d orbitals or other higher orbitals (e.g. 4sp) [106]. In reality, the former destination dominates. This explains the proximity of an absorption edge with its analogous X-ray transition. Approximately the same amount of energy is required for an X-ray to excite an atom than is released by the relaxation of an atom from this ionized state.

Generally, self-absorption of an X-ray transition occurs when the electron relaxing to fill the inner vacancy left by the inelastic interaction comes from the valence band. The concept is therefore not exclusive to L₃–M₄,₅ X-rays from first transition series metals. For example, the K–L₂,₃ X-ray transition of elements from B to F also exhibits self-absorption. The overlap of the K absorption edge and the C K–L₂,₃ is shown in Fig. 2.32a. On the other hand, self-absorption of Si K–L₂,₃ and Mo L₃–M₄,₅ X-rays does not exist, as visually demonstrated by Fig. 2.32b.

However, in contrast to carbon and other elements susceptible to self-absorption, the first transition series metals additionally encounter resonance absorption, also known as “anomalous absorption” or “white line” [46, 47, 200, 218]. As explained in §2.1.2.1, the resonance effect is the immediate return of an electron to its original state after its excitation from an X-ray. Here again, this phenomenon appears to be linked to the presence of empty orbitals in the valence band, and by the same token enhances X-ray absorption [46, 47].
Figure 2.31: Mass attenuation coefficient for Cr, Mn, Fe, Co and Ni samples as a function of the X-ray energy over the same range as Fig. 2.30. The values are obtained from the MAC database of Chantler et al. [72]. The $L_3-M_{4,5}$, $L_2-M_4$ and $L_3-M_1$ X-ray transitions are indicated by vertical lines.
Figure 2.32: Mass attenuation coefficient for C, Si and Mo samples as a function of the X-ray energy. The values are obtained from the MAC database of Chantler et al. [72]. The K–L$^{2,3}$ and L$^{3-5}$ X-ray transitions are indicated by vertical lines.
Consequently, the empty orbitals in the valence band of the first transition series metals are the key factor for self- and resonance absorption. Intuitively and from Eq. 2.36, any absorption phenomenon depends on the sample composition; higher the concentration of an atom is, larger will be its contribution to absorption. Moreover, in the case of self and resonance absorption, any change in the density of state of the valence band will influence the absorption behaviour, thus the presumption of the influence of chemical bonding on the X-ray intensities and the quantification [125, 214, 341]. Whether two or more elements are bounded by ionic, covalent, metallic or mixed bonding, the valence band of a compound or alloy will have a different configuration than the one of pure sample or even another compound or alloy. In metal oxides and intermetallic alloy such as FeSi and NiAl, chemical bonding increases the population of electrons in the valence bands, thus lowering the probability of self and resonance absorption [106, 271, 334]. Even for metallic bonded Fe−Ni alloys, Chun and Klein [78] interpreted the shift of the Fe L3 absorption edge measured by characteristic isochromat spectroscopy as “a transfer of 3d electrons from nickel to iron with alloying”, conceivably lowering the self-absorption of Fe L3–M4,5 X-rays, and enhancing the one of Ni L3–M4,5 X-rays.

In sum, both the number of atoms and the configuration of their valence band determine the photoelectric absorption by the first transition series metals. Only the former is considered in Eq. 2.36 and in all databases reporting MAC values. This led, for instance, Pouchou and Pichoir [269] to calculate empirical MACs based on X-ray intensities collected by an electron microprobe. For nickel alumines, the authors identified differences between the empirical MACs for pure Ni (3300 cm² g⁻¹), NiAl (2304 cm² g⁻¹) and Ni₃Al (2850 cm² g⁻¹) [271]. They attributed to the inverse dependence of the resonance absorption on the Al concentration, as the number of Al atoms increases, the resonance absorption of the Ni L3–M4,5 X-rays decreases. On the one hand, these results may explain the large inaccuracies in Tab. 2.6, and on the other expose the uncertain success of modifying the MACs. Empirically determined MACs may only be applicable for a particular alloy, rendering them nearly impractical for the quantification of unknown samples.

2.4.2.6 Transition probability

The occupancy of the valence band due to chemical bonding may also influence the radiative transition probabilities, the probability that a particular characteristic X-ray is produced by the relaxation of an atom from its excited state (§2.1.2) [125, 271, 341]. For the first transition series metals, increasing the number of valence electrons increases the probability that the atom relaxation results in the emission of L3–M4,5, L2–M4, L1–M5 and L1–M3 X-rays, all X-ray transitions originating from the M4 or M5 subshell, instead of other radiative and non-radiative transitions. For instance, the higher occupancy reduces the probability of Coster-Kronig transitions in the M shell.

In compounds and alloys with a more filled valance band, the combination of a higher emission probability and a lower photoelectric absorption may therefore significantly increase the measured L3–M4,5 X-ray intensity in comparison to the one measured on pure sample. This deduction appears to partially explain the results presented in Tab. 2.6. In most samples, higher Fe and Ni content were measured, implying higher k-ratios, and thus higher Fe L3–M4,5 and Ni L3–M4,5 intensities mea-
2.4. Quantification using soft X-rays

...ured on the samples than on pure iron and nickel. The lower Cr content in the steel samples may indicate a transfer of valence electrons from Cr to Fe and Ni atoms, effectively lowering the Cr L₃–M₄,₅ transition probability and increasing its absorption. Without a detailed knowledge of the electronic structure of these samples, it is however impossible to completely elucidate the phenomena behind the large inaccuracies of Tab. 2.6.

2.4.3 Solutions

In the perspective of EPMA, there currently exists no generic solution to the quantification problem using the L₃–M₄,₅ X-ray transitions of first transition series metals. Suggestions such as using empirical MACs or reference materials with a similar composition as the unknown only procure improvements over a limited scope. A promising solution based on the results of Gopon et al. [125], Statham and Holland [341], Pinard et al. [261] and Heikinheimo et al. [142] is the quantification using the L₃–M₁/L₂–M₁ X-ray transitions, L₃–M₁ being the most intense X-ray transition.

As stated by the authors, this X-ray transition has the advantages of being (1) far from absorption edges as shown in Fig. 2.31, and (2) unaffected by chemical bonding. The latter is explained by the fact that the relaxing electron in the L₃–M₁ and L₂–M₁ transitions comes from the M₁ subshell (3s₁/₂), an inner subshell for the first transition series metals. In that regard, there are more similarities between the L₃–M₁, L₂–M₁ and K–L₂,₃ transitions, than with the L₃–M₄,₅ transition. Although the other challenges at low accelerating voltages remain, those influenced by chemical bonding, namely the absorption and transition probability, disappear. Furthermore, the X-ray emission volume of L₃–M₁ X-rays is comparable to the one of the L₃–M₄,₅ X-rays as both transitions result from the ionization of the L₃ subshell [341]. The achievable spatial resolution is therefore similar. For example, at 6 kV, the depth resolution of the Fe L₃–M₄,₅ and L₃–M₁ in pure iron is 106.7 and 105.6 nm, respectively.

The principal downside of the L₃–M₁/L₂–M₁ X-ray transitions is their low intensity [125, 142, 261, 341]. Longer counting times, and or higher beam currents, are required to achieve the same precision, which unavoidably bring bigger concerns about carbon contamination. From the results of Pinard et al. [261], using the L₃–M₁/L₂–M₁ X-rays to quantify minor elements also seems uncertain. Besides its low intensity, the poor spectral resolution of WD spectrometers equipped with a multilayer dispersive element leads to several interferences as shown in Fig. 2.30a. This situation is particularly challenging for steels which normally contain all the elements measured in Fig. 2.30. Some quantification results from the literature using the L₃–M₁/L₂–M₁ X-rays are summarized in Tab. 2.8. In comparison to Tab. 2.6, there is a significant improvement for all the iron silicides reported by Gopon et al. [125]. For the steel samples, the deviations are still large, but at least one order of magnitude smaller.

Summary

As shown in this section as well as more specifically in §2.2.2 for the C K–L₂,₃ X-ray transition, the quantification at low accelerating voltages using soft X-rays entails several challenges, both in the acquisition and calculation of the X-ray intensities. Experimentally, the reduction of the interaction volume amplifies the influence of the carbon contamination and native oxidation on the measured X-ray intensities. The
Table 2.8: Summary of quantification results reported in the literature using a low accelerating voltage and the L$_3$–M$_{1,5}$ X-ray transitions [125, 261, 341]. Pinard et al. [261] used the same P11, P13 and P15 samples from Llovet et al. [214]. From [125] and Pinard et al. [261], the MACs were taken from the Chantler et al. [72] MAC database.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal (mass %)</th>
<th>Measured (mass %)</th>
<th>Relative error (%)</th>
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</thead>
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<td>Cr</td>
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low fluorescence yield and high photoelectric absorption cross sections of soft X-rays point to dispersive elements with a high reflectivity to measure their low X-ray intensity, while the quantity and proximity of soft X-ray peaks below 1 keV infer dispersive elements with a high spectral resolution to avoid interferences (Fig. 2.30). In the absence of a perfect dispersive element, the acquisition of soft X-ray intensities always become a compromise between a good precision (high intensity) and a good accuracy (no interference). Besides these experimental difficulties, the largest problem is however the inaccuracy of the analytical models. Their incomplete or nonexistent description of chemical bonding effects (i.e. satellite X-ray emission, anomalous absorption, occupancy of the valence band) prevents the quantification of the first transition series metals using their L$_3$–M$_{4,5}$ X-ray transitions (Tab. 2.6) and rare earth elements using their M$_{5–7}$ X-ray transitions. One way to eliminate the theoretical limitations is to use the L$_3$–M$_{1}$/L$_2$–M$_{1}$ X-ray transitions (Tab. 2.8), but this solution also accentuates the experimental challenges, especially the need for better dispersive elements, as it will be further elaborated in §3.4 of the following chapter. The topic of quantification using the L$_3$–M$_{4,5}$ X-ray transitions continues in Chap. 5. Following the objective of other experimental works summarized in this section, X-ray intensities were systematically and methodologically acquired on three Fe–Ni alloys in order to shed light on the quantification problem.
Chapter 3

High resolution characterization of steel microstructure

Whether it be inclusions, precipitates, segregation at grain boundaries or heterogeneously distributed constituents, the development of new steel alloys and manufacturing processes hinges on the chemical quantification of these submicrometer features. Undoubtedly a critical element to measure is carbon. From the literature review on its quantification (§2.2.2) two main conclusions can be drawn. First, since the first attempt in 1964 by Ranzetta and Scott [283], many advancements have been made to improve the accuracy and precision of carbon measurements in steels. The development of anti-contamination devices, more reflective dispersive elements and well-characterized reference samples are only a few examples. All this work is highlighted in three publications: (1) the European report “Electron-probe microanalysis of light elements; Measurements methods and certified reference materials (MICRO-LITE)” [4], (2) the ISO standard “ISO 16592:2012(E) Microbeam analysis — electron probe microanalysis (EPMA) — guidelines for determining the carbon content of steels using a calibration curve method” [164] and (3) the technical report of Bastin and Heijligers [32]. However, all these references clearly advice against decreasing the distance between the measurements below 2 µm, in the best case scenario. In other words, a smaller step size lowers the accuracy and precision, and prevents the quantification of steel constituents with a small carbon content. The second conclusion is therefore that the quantification of microstructural features at a high spatial resolution is not possible with the currently available experimental procedures. Historically, this limitation was not an issue. The instrument, in occurrence the electron microprobe equipped with a thermionic tungsten emitter, could only provide a beam diameter around 0.5 nm at the high beam currents required for the quantification of carbon [222]. Consequently, the instrument was the main limiting factor for the spatial resolution. With the greater availability of Schottky emitter electron microprobes in the last decade, the situation has changed. These instruments have significantly improved focusing optics, where smaller beam diameters can be achieved even at high beam currents.

The objective of this work is to harness the analytical potential of new-generation electron microprobes, and develop an acquisition and quantification strategy for the measurement of carbon in steels at a high spatial resolution, while maintaining the accuracy and precision of the currently available, state-of-the-art strategies. The definitions of the accuracy and precision are taken from Marinenko and Leigh [220] where the accuracy is “a measure of correctness or how close a result or measurand may be to the true value” and the precision “a measure of statistical repeatability or reproducibility”. Numerically, the objective translates into the measurement of carbon mass fraction below 1 % at an accuracy and precision better than 0.05 mass % C, based on the ISO standard [4]. As carbon is not the only alloying element of interest,
even in low alloy steels, the developed method should also allow the quantification of all alloying elements such as Mn, Si, Cr and Al. Finally, from an operator’s point of view, the method should practical, time-efficient and easy to perform.

Before describing, validating and applying the developed method, the results of a detailed characterization of the electron microprobe used for all the measurements is first presented (§3.1). Two aspects are of particular interest: the potential of the Schottky emitter electron optics and the efficiency of the WD spectrometer. Specifically, the spatial resolution depends on the achievable beam diameter, the precision, on the dispersive element reflectivity and beam current stability, and the accuracy, on the background determination and dead time correction of the gas proportional counter. Afterwards, the acquisition and quantification strategies developed for the measurement of carbon and other alloying elements are explained in details in §3.2, first for low alloy steels and then after appropriate modifications for high alloy steels. The accuracy, precision and spatial resolution attainable with these strategies are experimentally determined and compared with those of the currently available, state-of-the-art strategies (§3.3). Regardless of the strategy, the choice of accelerating voltage, beam current, measuring time for an acquisition has also a large influence on the accuracy, precision and spatial resolution. §3.4 describes an optimization procedure of these experimental parameters based on Monte Carlo simulations. Finally, applications of the developed acquisition method for steel research are presented in §3.5.

### 3.1 Instrument characterization

This section studies six aspects of an electron microprobe in order to better assess its capabilities for high resolution carbon measurements. These information are also prerequisites for the optimization procedure of §3.4. After a description of the instrument used (§3.1.1), the characterization of the electron optics (beam diameter and beam current stability) and of the WD spectrometer (energy filtration, reflectivity of dispersive elements, total internal reflection and dead time correction) are respectively given in §3.1.2 and 3.1.3.

#### 3.1.1 Description of the instrument

The electron microprobe used in this work is a JXA-8530F (JEOL Ltd., Akishima, Tokyo, Japan), equipped with a Schottky emitter. As per the specifications [168], it produces an electron beam with an accelerating voltage from 1 to 30 kV and a beam current from 0.01 to 500 nA. The best resolution, measured from a SE image is 3 nm, achieved at 30 kV and 0.01 nA. At more applicable conditions for EPMA, the resolution at 10 kV is 40 nm and 100 nm with a beam current of 10 nA and 100 nA, respectively.

Seven spectrometers are attached to the microscope chamber: five WD and two ED spectrometers. All sustain a take-off angle of 40° above the specimen surface plane with an analytical working distance of 11 mm. The WD spectrometers, manufacturer by JEOL, are equipped with different dispersive elements and gas proportional counters. Tab. 3.1 summarizes their configuration, which includes the lattice spacing \(d\) and chemistry of the dispersive elements (see §2.1.3.2 for more information). The
### 3.1 Instrument characterization

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>(d) (nm)</th>
<th>Type</th>
<th>Chemistry</th>
<th>Counter</th>
<th>Gas</th>
<th>Window</th>
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<td>LDE1</td>
<td>2.970</td>
<td>ML</td>
<td>W/Si</td>
<td>P10</td>
<td>PP</td>
<td></td>
</tr>
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<td>Pure</td>
<td>LiF</td>
<td>P10</td>
<td>PP</td>
<td></td>
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<td>7.290</td>
<td>ML</td>
<td>Mo/B(_2)C</td>
<td>P10</td>
<td>PP</td>
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<tr>
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<td>Pure</td>
<td>TlH(_2)C(_4)(_4)</td>
<td>P10</td>
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</tr>
<tr>
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<td>Ni/C</td>
<td>P10</td>
<td>PP</td>
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</tr>
<tr>
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<td>C(CH(_2)OH)(_4)</td>
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<td>PP</td>
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<td>Pure</td>
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<td>?</td>
<td>P10</td>
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<td></td>
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</tbody>
</table>

Table 3.1: Configuration of the wavelength dispersive spectrometers. The abbreviations used are: ML for multilayer, P10 for a gas mixture of 10% CH\(_4\) in argon, and PP for polypropylene. Information from \([49, 93, 112, 168]\).

The nominal dead time for all gas proportional counters is 1.1\(\mu\)s \([168]\). Of interest for the quantification of steel, the detection of carbon X-rays can be performed by spectrometers \#2 and/or \#5, while the X-rays of other alloying elements can be detected by the other spectrometers. A typical element arrangement of the spectrometers to measure low alloy steels is Si on \#1, Mo on \#2, Cr on \#3, Mn on \#4 and C on \#5.

The two ED spectrometers come from different manufacturers: JEOL Ltd. and Bruker Nano GmbH. Both are SDDs with a nominal surface area of 10\(\text{mm}^2\) and an energy resolution at the Mn K–L\(_{2,3}\) X-ray peak better than 125 eV.

The pumping system is completely oil free. Two scroll pumps (ULVAC, Methuen, MA, USA) are respectively used for the evacuation of the exchange chamber and for backing the turbomolecular pumps. The vacuum inside the specimen chamber and the electron column is produced by two turbomolecular pumps (Leybold Oerlikon, Pfäffikon, Switzerland). Finally, two ion pumps (JEOL, Akishima, Tokyo, Japan) are installed in the electron column to achieve the high vacuum required by the Schottky emitter.

Three anti-contamination devices are attached to the instrument: a plasma cleaner (XEI Scientific, Redwood City, CA, USA), a liquid nitrogen cold trap (JEOL, Akishima, Tokyo, Japan) and a gas jet (RWTH Aachen University, Aachen, Germany and Börder Elektronik, Melsbach, Germany). The plasma cleaner is mounted on the exchange chamber, allowing the direct cleaning of the samples prior to their insertion in the specimen chamber. The gas jet is installed on the cold trap and connected to a pure oxygen gas bottle. The oxygen flow is manually controlled by a needle valve (Swagelok, Solon, OH, USA). A picture of this assembly is shown in Fig. 3.1.
3.1.2 Electron optics

The physics and characteristics of Schottky emitter were introduced in §2.1.1 of the literature review. Two important characteristics are the beam current stability and the diameter of the electron beam irradiating the sample.

3.1.2.1 Beam current stability

Because of the low carbon content in steel and the intrinsically low intensity of the C K–L\textsubscript{2,3} X-rays, longer acquisition time may be necessary to improve the precision. On the other hand, as the X-ray intensity is direct proportional to the beam current (Eq. 2.33), any fluctuation of the beam current during this acquisition time would prevent the improvement of the precision. In order to measure the current stability, the beam current was recorded by the Faraday cup every 30 s for 48 h from an initial current of 50 nA and an accelerating voltage of 10 kV. The temperature of the room was also recorded using a thermocouple during the experiment at the same interval.

Results are shown in Fig. 3.2, where the relative deviation from the nominal beam current of 50 nA and temperature of 25°C are plotted as a function of time. The beam current appears to follow a cyclic, but irregular variation of small amplitude, less than 0.5 nA in absolute value. As shown in the inset in the top-right corner, this oscillation is negligible over the typical time scale used for an acquisition (< 300 s). It is not clear whether the absorption and desorption of gases on the emitter tip or changes of the tip geometry as presented in §2.1.1 can explain the current stability results.

3.1.2.2 Beam diameter

One advantage of a Schottky emitter in comparison to the thermionic emitters is the smaller beam diameter [188]. However, the final beam diameter depends on the column design and properties (lens aberrations and aperture diffraction), and on the analytical conditions (accelerating voltage and beam current) as described in §2.1.1. Unfortunately, the analytical conditions required for EPMA, accelerating voltage from
3.1. Instrument characterization

1 to 20 kV and a beam current from 1 to 200 nA, are far from the optimal ones to achieve the smallest beam diameter, a high accelerating voltage and small beam current.

In electron microscopy, the spatial resolution depends on the signal used for a measurement (e.g. SE, BSE, X-ray). In the case of EPMA, the X-ray interaction volume defines the spatial resolution (§2.1.2). The composition of the sample analyzed, the accelerating voltage selected, the X-ray transition measured and the beam diameter have therefore an influence on the spatial resolution. At low accelerating voltages and low overvoltages, the size of X-ray interaction volume decreases and the beam diameter becomes a critical parameter in determining the spatial resolution.

To study this effect and obtain quantitative values for the beam diameter, SE images of gold flakes on a carbon substrate were taken at different accelerating voltages and beam currents typically used for EPMA. Since the interaction volume of SEs is small in comparison to the measured resolutions (< 5 nm), the final beam diameter (Eq. 2.18) can be assumed to be equal to the resolution of an image. The latter was measured using the method developed by Joy [176], where it is defined as the extent of the low frequency region of an image. In the frequency domain, the high frequencies correspond to the noise of the image, whereas the low frequencies would be the signal.

Specifically, images (1280 px × 960 px) were acquired for different combinations of accelerating voltages (3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 20 and 25 kV) and beam currents (1, 10, 25, 50, 75 and 100 nA). Each image was divided in five regions of interest of 512 px × 512 px (Fig. 3.3a). For each region of interest, an Hanning window filter was applied as suggested by Joy [176] (Fig. 3.3b), and the Fourier transform was calculated. From the resulting power spectrum image of the Fourier transformation
Chapter 3. High resolution characterization of steel microstructure

Figure 3.3: Experimental procedure to determine the beam diameter from SE images based on their Fourier transform and the method of Joy [176]. Examples of the steps for an image acquired at 25 kV and 10 nA at a magnification of 40,000x. (a) Definition of the five regions of interests. (b) One region of interest after Hanning window filtering. (c) Power spectrum after Fourier transform. (d) Threshold of the low frequency region.

(Fig. 3.3c), the threshold of the low frequency region was manually selected following the instructions from Joy [176] and Probst et al. [275] (Fig. 3.3d). After performing a binary opening operation, the largest ellipse inscribing all the pixels of the threshold region was found. The diameter of the region was taken as the average length \( L_i \) of the two ellipse axes. The resolution, and equivalently the final beam diameter \( d_{p,i} \) for the region of interest \( i \), was determined from the relationship given by [176]:

\[
d_{p,i} = \frac{(D)(\Delta x)}{(L_i)},
\]

where \( D \) is the width of the region of interest (in px), in occurrence 512, and \( \Delta x \) is the resolution of a pixel in the original image (in m px\(^{-1}\)). Finally, the beam diameter is the average of the beam diameters determined for each region of interest. The standard deviation can be seen as the uncertainty of this method.
The results are shown in Fig. 3.4 as a function of the accelerating voltage and beam current. For all accelerating voltages, the beam diameter increases with the beam current (Fig. 3.4a). With an accelerating voltage of 3 kV the beam diameter is 79% larger at 100 nA than at 1 nA. For a fixed beam current, the beam diameter decreases with the accelerating voltage (Fig. 3.4b). There is a steep increase of the beam diameter for accelerating voltages below 10 kV.

At 10 kV, a beam diameter of 52 and 107 nm was respectively measured at 10 and 100 nA, matching the specifications from the manufacturer. The slightly higher values might originate from the different measurement methodologies. The smallest beam diameter was therefore obtained at the highest accelerating voltage (25 keV) and the lowest beam current (1 nA). This result and the trends observed in Fig. 3.4b are comparable to the final beam diameters calculated by Eq. 2.18 and shown in Fig. 2.6 (§2.1.1). At low accelerating voltages, chromatic aberrations and aperture diffraction dominate and increase the beam diameter. The beam diameter increases at high beam currents due the limited reduced brightness (Eq. 2.6). The combination of these factors explain the trends observed in Fig. 3.4. As the exact values for the spherical and chromatic aberration coefficients are unknown, the comparison between the calculated and experimental beam diameters can only be qualitative.

In summary, the significant increase of the beam diameter at accelerating voltages below 10 kV opposes the rule of thumb in scanning electron microscopy to lower the accelerating voltage to improve the spatial resolution. The axiom only applies at low beam currents. Although the X-ray interaction volume is reduced, which unequivocally reduces the penetration depth, the enlargement of the beam diameter worsens the lateral spatial resolution. Nonetheless, the results confirm the advantages of Schottky emitter over thermionic emitters [188]: a reduction of the beam diameter while maintaining a good beam current stability.

### 3.1.3 Wavelength dispersive spectrometer

In comparison to ED spectrometers, WD spectrometers have more user-adjustable parameters (e.g. choice of dispersive element, gas mixture in proportional counter, PHA settings, etc.) and require some optimization by the users to achieve the optimal detection of each X-ray transition. This is particularly relevant for the detection of the C K–L$_{2,3}$ X-rays due to the challenges presented in §2.2.2, namely the low X-ray intensity, the abnormal background and the presence of high order lines.

Since a picture is worth a thousand words, Fig. 3.5 shows spectra acquired around the C K–L$_{2,3}$ X-ray transition on pure metallic samples of B, Si, Cr, Fe and Ni using a WD spectrometer (#2, LDE2 dispersive element, gas proportional counter with P10 gas, differential mode of the PHA with an energy cutoff at 5 V). The acquisition conditions were an accelerating voltage of 8 kV and a beam current of approx. 300 nA. The spectrometer was moved in steps of 0.2 mm$^1$ with a dwell time of 5 s. The liquid nitrogen cold trap was used throughout the measurements to minimize the carbon contamination.

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$^1$The step size is expressed in JEOL units, also known as the spectrometer position. It corresponds to the distance moved by the dispersive element along the worm drive of the spectrometer. It is equal to $\lambda R/d$, where $\lambda$ is the X-ray wavelength, $R$, the diameter of the Rowland circle (always takes as 140 mm) and $d$, the inter-planar spacing.
Figure 3.4: Beam diameter as a function of (a) the beam current and (b) accelerating voltage.
3.1. Instrument characterization

Figure 3.5: WD spectra acquired around the C K–L\textsubscript{2,3} X-ray transition (vertical dashed line) on pure metallic samples of B, Si, Cr, Fe and Ni. The following experimental conditions were used: 8 kV, \( \approx 300 \) nA, LDE2 dispersive element, P10 filled gas proportional counter, 0.2 mm step, 5 s dwell time.

The first observation from Fig. 3.5 is that several peaks and features are observed in the spectra even though none of the sample contain carbon. Apart from the step exactly located at the C K–L\textsubscript{2,3}, all the other peaks correspond to high order X-ray reflections, as tabulated in Tab. 2.5. Notable interferences are the two peaks located on either side of the carbon peak in the chromium spectrum: the 2nd order reflection of the Cr L\textsubscript{3}–M\textsubscript{4,5} and L\textsubscript{4}–M\textsubscript{1} X-ray transitions located at 286.45 and 307.65 eV respectively. Even more problematic for the quantification of carbon in steel, the 3rd order reflection of the Fe L\textsubscript{1}–M\textsubscript{5} and L\textsubscript{1}–M\textsubscript{4} X-ray transitions (283.81 and 281.51 eV) almost perfectly superimpose over the carbon peak. Although their intensity is naturally lower as they are 3rd order reflections, the high concentration of iron in steels makes them unavoidable interferences, as seen in Fig. 3.5. The same conclusion applies to the 2nd order reflection of Mn L\textsubscript{3}–M\textsubscript{1} and L\textsubscript{2}–M\textsubscript{1} X-ray transitions (not shown) in high manganese containing steels such as TWIP steels. A final point about high order X-ray reflections is that most of the interferences tabulated in Tab. 2.5 are clearly visible in the spectra, despite using the solution of energy filtration by the PHA proposed by many authors [4, 32, 96, 164]. The usefulness of this method to minimize high-order X-ray reflections will be further discussed in §3.1.3.1.

A second observation from Fig. 3.5 is the step in the background intensity around the carbon peak. This sudden intensity decrease seems independent of the substrate, as it systematically appears in each spectrum at the same energy. While one can, at first sight, mistakenly identify this spectral feature as the C K–L\textsubscript{2,3} peak, its step-like shape, substrate independence and fixed position infer otherwise. Almagro et al. [4]
attributed this irregularity to the carbon K absorption edge, without further explanations. §3.1.3.2 shows that the changes in the reflectivity of multilayer dispersive elements could also be one possible explanation.

Thirdly, the use of a logarithmic scale for the ordinate axis points to large differences in the background intensity between the substrates. Whereas Cr, Fe and Ni have similar background magnitudes, much high background intensities are measured on B, and especially Si. As demonstrated by Rehbach and Karduck [290] and explained as an artifact of WDS in §2.1.3.2, this increase is caused by the total internal reflection of the B K–L$_{2,3}$, Si L$_3$–M$_1$ and Si L$_2$–M$_1$ X-rays on the surface of the dispersive element. Further proofs and explanations are given in §3.1.3.3.

Finally, a last aspect of X-ray detection by a WD spectrometer, not shown in Fig. 3.5, is the dead time. Its correction is performed using Eq. 2.29, provided that the dead time constant is known. Instead of relying on the generic value provided by the manufacturer, the dead time constant was experimentally determined for each gas proportional counter, i.e. each spectrometer. The methodology and results are presented in §3.1.3.4

3.1.3.1 Energy filtration

Normally, the presence of high order X-ray reflections complicates the selection of appropriate spectrometer positions to measure the background intensity. In the case of the C K–L$_{2,3}$, they also complicate the accurate determination of the peak intensity. If the method of measuring the background intensity on reference samples instead than on the unknown sample is used [4, 32, 309], high order X-ray reflections influence both the measurement of the peak and background intensities. The magnitude of these interferences depends on the sample composition, the worst situation being for pure samples, as shown in Fig. 3.5 where the high order X-ray reflections are easily distinguishable.

As mentioned previously, one solution is to use the gas proportional counter as an energy filter. The PHA is configured to only count X-rays within a certain energy window. To test this method, spectra on pure chromium and pure manganese were acquired under the same conditions as those of Fig. 3.5 using different PHA windows (Fig. 3.6). The lower limit of the window was kept at 0.5 V, while the width was changed from 1 to 5 V$^2$. Another spectrum was acquired without an upper limit for comparison.

For both samples, reducing the width of the PHA window from 5 to 1 V decreases the intensity of the high order X-ray reflections (Cr L$_3$–M$_1$, L$_2$–M$_1$, L$_3$–M$_{4,5}$, and Mn L$_3$–M$_1$, L$_2$–M$_1$ and L$_3$–M$_{4,5}$), but also the overall intensity detected by the gas proportional counter. The latter is the main drawback of the energy filtration. Selecting the appropriate window becomes a compromise between an accurate measurement with no interference and a precise measurement with higher intensities.

Another factor to consider is that the voltage distribution of PHA varies with the input count rate, the number of incoming X-rays per unit of time [287]. As the input count rate decreases, the distribution shifts to higher voltages [112]. With a narrow window the main pulse of the PHA distribution may be truncated at low input count rates, further decreasing the detected intensity. Although a width of 2 V would be

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$^2$The limits of the PHA window are expressed as V, but the values are not related to the actual energy of the X-rays (in eV). They only correspond to PHA settings.
Figure 3.6: WD spectra acquired around the C K–L$_{2,3}$ X-ray transition (vertical dashed line) on pure metallic samples of (a) Cr and (b) Mn using different widths of the PHA window.
ideal based on the results of Fig. 3.6, practically a wider window should be used to avoid any influence of the input count rate. Most of the carbon measurements reported in this work were acquired with a window of 4 V.

### 3.1.3.2 Reflectivity of dispersive elements

The concept and operation of a WD spectrometer revolve around Bragg’s law (Eq. 2.28): for a given incident angle and lattice parameter of the dispersive element, diffraction only occurs for X-rays with a specific wavelength, or multiple of this wavelength for high order reflections. While Bragg’s law stipulates the conditions for diffraction, it however does not provide any information on its efficiency, i.e. the ratio between the intensity of the diffracted and incident X-rays. This physical property of a dispersive element is called the X-ray reflectance or reflectivity. It depends on both the incident angle of the incoming X-ray and its energy [129, 288, 403].

The long wavelength of soft X-rays requires synthetic dispersive elements as no natural crystal exists with a large enough inter-planar spacing to satisfy Bragg’s law. Multilayer structures are fabricated by periodically interlacing layers with low and high indices of refraction. Instead of being diffracted on the atomic planes of a lattice, X-rays entering such multilayer dispersive element are reflected by the layers with a high index of refraction. The same constructive interferences formulated by Bragg’s law still occur between the reflected X-rays due to the periodicity of the multilayer structure. Apart from the indices of refraction, the reflectivity is also influenced by the X-ray photoelectric absorption inside the dispersive element [129]. Analytical models based on Fresnel equations have been developed to calculate the reflectivity of multilayer dispersive elements [129, 406].

This excursion about the X-ray reflectivity aims at evaluating whether it may explain the step in the background intensity around the carbon peak observed in all WD spectra presented so far. In other words, the goal is to calculate theoretical WD spectra using the same conditions as those from Fig. 3.5. For this qualitative comparison, the influence of the solid angle, focusing geometry, efficiency of gas proportional counter and high order reflections are ignored. A simple model is constructed where the reflected X-ray intensity for a given incident angle $\theta$ ($I'(\theta)$) is equal to the incident X-ray intensity $I(E)$ times the reflectivity ($R(\theta, E)$):

$$I'(\theta) = R(\theta, E)I(E). \quad (3.2)$$

The dependence of the reflected intensity on the incident angle $\theta$, of the incident intensity on the X-ray energy $E$ and of the reflectivity on both is carefully noted in Eq. 3.2.

The incident X-ray intensity distributions as a function of the X-ray energy were obtained from Monte Carlo simulations (NISTMONTE [300]), where they correspond to ED spectra of collected by an ideal spectrometer with a 100 % detection efficiency. Only Bremsstrahlung X-rays are recorded since this comparison focuses on the background intensity. Fig. 3.7 shows the simulated Bremsstrahlung spectra from B, Si, Cr, Fe and Ni samples irradiated by an incident electron beam with an accelerating voltage of 8 kV. Within the energy range of interest, 200 to 400 eV, no sudden change in the background intensity is observed.
3.1. Instrument characterization

The reflectivity was calculated using the online service offered by the Lawrence Berkeley National Laboratory [129]. As the exact structure of the multilayer dispersive element (LDE2) used experimentally to acquire the WD spectra is unknown, the input parameters for the reflectivity calculations were selected as follows: top layer of Ni, bottom layer of C, a infinite period of 4.96 nm, no interdiffusion, a ratio of the bottom layer thickness with the period of 0.4. The incident X-rays are also assumed to be unpolarized. The calculations were repeated for X-ray energies from 0 to 8000 eV and incident angles from 16 to 40°, approximately the angular range covered by the WD spectra in Fig. 3.5. An example of the reflectivity distribution as a function of X-ray energy for an incident angle of 30° is shown in Fig. 3.8. The distribution is characterized by an exponential decreasing reflectivity as a function of the X-ray energy, and by the presence of several peaks, corresponding to an enhanced reflectivity when Bragg’s law is satisfied by the periodic structure of the dispersive element. For comparison, the X-ray reflectivity distribution of a natural, pure crystal of LiF was also calculated and plotted in Fig. 3.8. The absence of major peaks highlights the different reflectivity behaviour between natural crystals and multilayer dispersive elements.

Applying Eq. 3.2 over the simulated X-ray intensities for B, Si, Cr, Fe and Ni samples and calculated reflectivities yields the theoretical WD spectra shown in Fig. 3.9. The incident angles were converted to corresponding X-ray energies and wavelengths for a direct comparison with Fig. 3.5. Except for boron, the simulated spectra for all substrates exhibit the step in the background intensity as experimentally observed. There is no clear explanation for the inconsistency of the boron spectrum. As aforementioned the background intensities of B and Si are affected by total internal reflection, which was not taken into consideration in the calculations. The significantly
lower simulated intensities for these two elements in comparison to the experimental ones confirm the large contribution of this physical process to the background intensity. Its role on the shape of the background and the presence of the step around the carbon peak is unknown. Furthermore, the X-ray absorption inside the window of the gas proportional counter was not considered in the calculations.

Another observation from Fig. 3.9 is that the step in the simulated spectra occurs before the C K–L\textsubscript{2,3}, whereas it approximately coincide with the C K–L\textsubscript{2,3} in the experimental spectra. Any misalignment of the spectrometer will cause errors in the conversion of the spectrometer position to X-ray energy, shifting the WD spectra to higher or lower X-ray energies. The same goes with any inaccuracy in the physical values used to calculate the reflectivity. Nonetheless, this simple model based on the calculations of the reflectivity demonstrates the influence of the dispersive element on the shape of the background.

### 3.1.3.3 Total internal reflection

To further assess the effect of total internal reflection, WD spectra were acquired on different nickel silicides under the same conditions. The nickel silicides are part of the same diffusion couple produced by Erkki Heikinheimo (Aalto University, Espoo, Finland) [142]. Two observations can be made from Fig. 3.10a. For X-ray energies below the step (≈ 300 eV), the background intensity slightly decreases with the Si content. The reverse behaviour occurs above the step where the background intensity significantly increases with the Si content.

The first observation can be interpreted by the change in the emission of Bremsstrahlung X-rays with the sample composition. As for Fig. 3.7, ED spectra containing only Bremsstrahlung X-rays were obtained by Monte Carlo simulations (Fig. 3.10b).
3.1. Instrument characterization

![Figure 3.9: Theoretical WD spectra for B, Si, Cr, Fe and Ni samples irradiated with a 8 kV electron beam and analyzed with a LDE2 multilayer dispersive element.](image)

Over this X-ray energy range, the background intensity decreases with the Si content, giving a physical explanation to the intensity decrease in the experimental spectra below \( \approx 300 \) eV.

As proposed by Rehbach and Karduck [290], total internal reflection of Si L\(_3\)–M\(_1\) and L\(_2\)–M\(_1\) X-ray transitions may artificially increase the background intensity and explain the inverse trend observed above \( \approx 300 \) eV. They calculated a critical angle of total internal reflection for these X-ray transitions to be 18.05°, meaning that this physical process only occurs for incident angles below 18.05° or in terms of X-ray energy above 403 eV. As the critical angle or energy depends on the index of refraction of the dispersive element, it is conceivable that the actual value for the LDE2 dispersive element lies around 300 eV or 24.6°.

3.1.3.4 Dead time correction

For WD acquisitions, the dead time of a gas proportional counter is corrected using Eq. 2.29, where the time constant \((\tau)\) is the critical parameter to accurately correct for the dead time. This correction becomes more important as the input count rate increases, or analogously as the concentration of an element or the beam current increases. To illustrate the importance of an accurate time constant, Fig. 3.11 shows the relative error on the output count rate for different deviations of the time constant from a nominal value of 1.1\(\mu\)s. For example, a deviation of 0.5\(\mu\)s of the time constant used to correct for the dead time \((\tau = 1.6\mu s)\) results in an error of 2.1% at an output count rate of 40 000 count s\(^{-1}\), i.e. 2.1% error on the measured intensity.
Figure 3.10: Experimental (a) and simulated (b) spectra around the C K–L$_{2,3}$ X-ray transition (vertical dashed line) obtained from pure Ni and 3 nickel silicides at 8 kV. The silicon content of each silicide is given in parenthesis. The experimental parameters for the spectra in (a) are 150 nA, LDE2 dispersive element, P10 filled gas proportional counter, 0.2 mm step, 5 s dwell time. The Monte Carlo program NISTMONTE [300] was used to calculate the simulated spectra in (b).
3.1. Instrument characterization

In order to experimentally determine the time constant, the incoming X-ray count rate \( (n) \) is expressed as \( kI_p \), as it is directly proportional to the beam current \( (I_p) \). Rewriting Eq. 2.29 yields a linear relationship between the output count rate normalized by the beam current and the output count rate \( (n') \) [67, 287]:

\[
\frac{n'}{I_p} = (-k\tau)n' + k,
\]

where \( k \) is a proportionality constant. By recording the output count rate \( (n') \) at different beam currents \( (I_p) \), the time constant can be calculated from the slope \( (-k\tau) \) and intercept \( (k) \) of the distribution.

Using this method, the time constant was measured for all spectrometers using different X-ray transitions and dispersive elements. The output count rate was varied from 1000 to 80 000 \( \text{count s}^{-1} \). Depending on the X-ray transition and dispersive element analyzed, the beam currents were accordingly adjusted to obtain this range of output count rates. The acquisition time was also modified to collect at least 100 000 counts. An example of the experimentally measured distribution is shown in Fig. 3.12 for the C K–L\(_{2,3}\) measured on the 2nd spectrometer with the LDE2 dispersive element at 15 kV. The linear regression fit performed with the numerical library NUMPY [174] gave a time constant of 2 \( \mu s \).

The results for all the measured X-ray transitions, dispersive elements and spectrometers are shown in Fig. 3.13. All measurements were performed with an accelerating voltage of 15 kV. Several data points are the average of two or more acquisitions. Interestingly, for a given spectrometer, different time constants were obtained depending on the X-ray transition. For instance on the 1st spectrometer, the time constant was measured for all X-ray transitions and dispersive elements. The output count rate was varied from 1000 to 80 000 \( \text{count s}^{-1} \). Depending on the X-ray transition and dispersive element analyzed, the beam currents were accordingly adjusted to obtain this range of output count rates. The acquisition time was also modified to collect at least 100 000 counts. An example of the experimentally measured distribution is shown in Fig. 3.12 for the C K–L\(_{2,3}\) measured on the 2nd spectrometer with the LDE2 dispersive element at 15 kV. The linear regression fit performed with the numerical library NUMPY [174] gave a time constant of 2 \( \mu s \).
constant for the O K–L\textsubscript{2,3} is 1.1\,µs (LDE1) while it is 2.3\,µs for the Fe K–L\textsubscript{2,3} (LIF). Generally, Xenon filled gas proportional counters (spectrometers #3 and #4) have lower time constants than P10 ones. It is adventurous to provide an explanation for the observed differences without a further understanding of the physical processes inside a gas proportional counter. Leaving this for future work, these experimental results however procure more accurate time constants than those provided by the manufacturer, preventing potentially large errors in the measured X-ray intensities.

### 3.2 Acquisition and quantification strategies

Going back to the objective of this work, this section presents the strategies used to quantify the alloying elements in steel at a high accuracy, precision and spatial resolution. For simplicity and practicality, a strategy applicable for low alloy steels was first developed (§3.2.1). In this work, a low alloy steel is roughly defined as a steel with no alloying element in larger concentration than 2 mass %. This restriction on the mass content applies to both the overall chemical composition of the steel and to any microstructural feature (e.g. martensite island, carbide, etc.). Per this definition, most grades of DP, CP and TRIP steels can be considered as low alloy steels. From a quantification point of view, the larger mass content of iron in comparison to the one of other alloying elements allows to stipulate further assumptions and make additional simplifications. Once the principles and methodology of this strategy are well established, the required modifications to apply it to high alloy steels (e.g. TWIP and bearing steels) is then presented in §3.2.2. The validation and the discussions about the optimization of these strategies are left for §3.3 and 3.4.
3.2. Acquisition and quantification strategies

3.2.1 Low alloy steels

Following the order in the literature review, the assumptions and solutions for the five main challenges of carbon quantification, with the addition of the spatial resolution, are first described and justified based on the conclusions from the previous section on the instrument characterization (§3.1). This is followed by a detailed description of the elaborated experimental steps to quantify carbon in steels.

3.2.1.1 Assumptions and solutions

Carbon contamination For the typical analytical conditions used in EPMA, the carbonaceous deposit produced by irradiating a flat, polished surface with a focused electron beam is a ring/annulus [10, 292, 329]. In other words, the highest contaminated area is located at a certain distance from the incident beam, which depends on the different factors such as the substrate and accelerating voltage [264]. Note that a carbonaceous ring was always observed regardless of the anti-contamination devices used (oxygen jet, liquid nitrogen cold trap, plasma cleaner) as presented in
Figure 3.14: Simulated radial distributions of the BSE and the emitted C K–L$_{2,3}$ X-rays. Sample contains 1 mass% of C, Si, Cr and Mn, balance Fe. An accelerating voltage of 15 kV, a beam current of 100 nA (beam diameter of 78 nm), 50 000 electrons were used in the simulation with NIST-MONTE [300]. The dash lines indicate the distance where 95% of the BSE and X-rays have been emitted.

Chap. 4. At 15 kV and 100 nA the ring formed on pure iron has approximately a diameter of 2 μm, with an approximate inner and outer diameter of 1.6 and 2.4 μm respectively. The influence of the carbonaceous deposit on the measurement depends whether the incident electrons or the generated X-rays traverse this structure and the magnitude of their interaction. With a beam diameter of less than 200 nm, it is clear that most of the incident electrons do not interact with the deposit. As for the BSE and X-rays, their spatial resolution can be simulated by Monte Carlo simulations. For this simulation and the subsequent ones in this section, an hypothetical steel sample containing C, Si, Cr and Mn, each with a mass fraction of 1%, is used. As shown in Fig. 3.14, the simulated radial distributions of BSE with an energy greater than the C K–L$_{2,3}$ ionization energy (288 eV) and of the emitted C K–L$_{2,3}$ X-rays fall well inside the carbonaceous ring under these analytical conditions. Considering 95% of the BSE and emitted X-rays, their radial resolution is approximately 361 nm and 244 nm, respectively. It can be safely concluded that most of the contamination produced by a single spot, i.e. the one forming the ring, has no influence on the measurement. Only the cracked organic molecules inside the ring affect the measured C K–L$_{2,3}$ X-ray intensity, justifying the advise of many authors to use a large step size (> 2 μm) for carbon measurements [4, 32, 96].

In a SEM or electron microprobe, performing measurements at a high spatial resolution automatically translates into reducing the distance between the measurement points, i.e. the step size. Consequently, as the step size is reduced, the contamination has a larger influence on the measurement due to the overlap of the carbonaceous
3.2. Acquisition and quantification strategies

Figure 3.15: Calculated C K–L$_{2,3}$ X-ray intensity along a 16-µm line scan (40 nm step size) showing the influence of the overlapping carbonaceous rings. The carbonaceous ring was assumed to a Gaussian distributed profiled centred on the ring diameter (2.7 µm) with a $\sigma$ equal to 0.4 µm.

rings. When the electron beam irradiates the carbonaceous deposits leftover by the previous neighbouring measurements, the electrons inelastically scatter inside the deposit generating C K–L$_{2,3}$ X-rays and increasing the measured X-ray intensity. This effect is schematically shown in Fig. 3.15 for an acquisition where the beam is scanned along a line, a line scan, over a distance of 16 µm with a step size of 40 nm. The X-ray intensity was approximated to be proportional to the height of the carbonaceous deposit underneath the electron beam. In turn, the height was calculated by the summation of Gaussian peaks representing the one-dimensional profile of the carbonaceous ring left at every measurement point. As soon as the electron beam interacts with the carbonaceous ring left by the first measurement point, the X-ray intensity sharply increases and reaches a plateau after a certain distance.

Experimentally, a similar behaviour is observed in Fig. 3.16 which shows three line scans acquired on pure iron over a distance of 16 µm with a step size of 40 nm and a dwell time of 5 s. The X-ray intensity corresponds to the intensity measured by the spectrometers at the C K–L$_{2,3}$ peak position without any background removal; only the dead time was corrected using the experimentally determined time constants reported in §3.1.3.4. The use of an oxygen jet or liquid nitrogen cold trap drastically changes the evolution of the C K–L$_{2,3}$ X-ray intensity over the line scan. The contamination mechanisms described in §2.3.2 can, to a certain extent, elucidate the differences between the X-ray intensity profiles.

Starting with the line scan acquired without an anti-contamination device, there are three dissimilarities between the experimental and calculated X-ray intensity profiles: (1) a small decrease of the intensity in the first micrometer, (2) a smoother
increase of the intensity after 2 μm, and (3) a gradual decrease of the intensity after 8 μm. As soon as the electron beam irradiates the sample, at 0 μm, contamination occurs and the X-ray intensity increases. The measured X-ray intensity of approximately 12 count s⁻¹ nA⁻¹ is therefore higher than the background intensity of pure iron free of contamination. As shown theoretically in Fig. 3.15, in the first micrometer, the beam is entirely confined inside the carbonaceous ring of this first point. One explanation for the decrease of the intensity within this distance is the development of a diffusion limited regime. As organic molecules initially adsorb on the sample surface are cracked in the first few steps of the line scan, surface diffusion becomes the main replenishment mechanism and the rate limiting step of the contamination process. The C K–L₂,₃ X-ray intensity drops since there are fewer organic molecules cracked underneath the electron beam. The absence of this decrease in the X-ray intensity profiles with an anti-contamination device suggests that the carbonaceous ring acts as a physical barrier against surface diffusion. Although their mechanisms differ, the result achieved by the oxygen jet and the liquid nitrogen cold trap is the same, a reduction of the contamination. As such, they prevent the formation of a tall carbonaceous deposit. The surface diffusion of organic molecules is not hindered. The second dissimilarity is most likely due to oversimplifications in the calculations of Fig. 3.15, which disregarded the electron beam diameter and the spatial distribution of BSEs. Considering all these factors would result in a smoother increase of the X-ray intensity. Thirdly, the decrease of the intensity after 8 μm may also arise from a surface diffusion limited regime as in the first micrometers. Assuming a initial uniform coverage, as the line scan progresses, the only available organic molecules are located
3.2. Acquisition and quantification strategies

ahead of the line scan direction, as those downstream were already cracked. This reduction in the supply of organic molecules, in combination with the limited surface diffusion, leads to a decrease of the contamination. A complementary explanation is related to etching, the competing reaction of contamination. Through the reaction between \( \text{O}_2, \text{H}_2 \) and \( \text{H}_2\text{O} \) molecules present in residual gas vapours inside the specimen chamber, the electrons (incident, SEs and BSEs) and the polymerized organic molecules inside the carbonaceous deposit, the latter is slowly etched away as volatile products. The magnitude of this process depends on several factors, including the availability of etching molecules on the sample surface. This effect can be observed in Fig. 3.16, where the decrease of the intensity is observed for the line scans without anti-contamination device and with the oxygen jet, but is absent in the line scan with the liquid nitrogen cold trap. As discussed in §2.3.3.2, a cold trap cooled at liquid nitrogen temperature forces the desorption of both organic and etching molecules from the sample surface. While decreasing the concentration of adsorbed organic molecules reduces the contamination, the removal of etching molecules prevents the volatilization of already cracked molecules.

Continuing with the line scan where a gas jet was continuously blowing oxygen at the measurement location, the significant decrease of the C K–L\(_{2,3}\) X-ray intensity along the whole distance proves the efficiency of this anti-contamination device. The action of the oxygen jet on the contamination is two-fold. First, the immediate reaction of the \( \text{O}_2 \) molecules with the cracked organic molecules prevents their deposition and polymerization on the sample surface. The experimental evidence is the absolute decrease of the X-ray intensity along the whole length of the line scan, indicating a contamination reduction both inside the carbonaceous ring over the first two micrometers and afterwards. Secondly, the higher partial pressure of oxygen promotes the adsorption of \( \text{O}_2 \) molecules on the sample surface. On the one hand, this promotes etching of the carbonaceous deposits, and on the other, the higher number of adsorbed molecules effectively creates obstacles for the diffusion of organic molecules towards the electron irradiated area. As for the line scan without anti-contamination device, the intensity decrease after \( \approx 8\mu\text{m} \) probably arises from a combination of factors: etching, limited surface diffusion and depletion of organic molecules.

All things considered, the line scan acquired with an oxygen jet have many similarities to the one without anti-contamination device, with the noteworthy exception to have a much lower contamination rate. This contrasts with the line scan acquired with a liquid nitrogen cold trap. Its overall higher X-ray intensity than its counterpart with an oxygen jet points to the subsistence of some organic molecules on the sample surface despite the driving force towards desorption. Their concentration is nonetheless reduced in comparison with the line scan without anti-contamination device, as shown by the lower X-ray intensity at \( 0\mu\text{m} \) (\( \approx 11\) count s\(^{-1}\) nA\(^{-1}\)) and throughout the line scan. The impediment of the etching reaction from the desorption of etching molecules may also explain the higher contamination. The striking feature of the line scan is however the longer initial plateau, which extends up to \( \approx 4\mu\text{m} \). It is not clear whether the cold trap delays the formation of carbonaceous rings or increases their diameter, postponing the intersection of the electron beam with the first ring. Repeating the same line scan acquisition gave every time the same intensity profile, but with slightly different intensity values. This demonstrates that contamination depends on many factors, which cannot be eliminated with the use of an anti-contamination device.
For accurate carbon quantification, the measurements should obviously be free of any contamination. As this is not possible, the next best case scenario would be a marginal, structureless and constant contamination. Unfortunately, under the analytical conditions for EPMA, the reality is otherwise: contamination is not negligible even with an anti-contamination device, a focus electron beam produces a carbonaceous ring, and the influence of contamination on the measurements changes along the line scan. Based on the results in Fig. 3.16, the most viable solution against contamination for the current experimental setup is the oxygen jet. As previously noted by many authors [32, 96, 288] it is the most effective method to reduce the contamination for well separated measurement locations. From the line scan results, this statement applies to the contamination inside the carbonaceous ring, as reported in the literature, but also to the total volume of contamination produced. Regarding the uniformity, the measured C K–L\textsubscript{2,3} X-ray intensity becomes relatively constant after the first 4\textmu m. This additional contribution can therefore be theoretically removed to obtain the true C K–L\textsubscript{2,3} X-ray intensity emitted from the sample. A final advantage of the oxygen jet in comparison to the liquid nitrogen cold trap is its practicality. It starts working as soon as the valve is open and runs indefinitely with a steady flow of oxygen.

The topic of contamination will be further elaborated in the next chapter (Chap. 4), where the factors and mechanisms will be studied in more details. For this fundamental work and the general acquired experience, a few key experimental considerations were found to play a significant role in order to obtain reliable results. Although unavoidable, variations in the contamination behaviour between samples, and especially between unknown and reference samples, should be minimized. As the composition of low alloy steels resembles the one of pure iron, the assumption is made that the contamination behaviour is identical on all samples. The strategy adopted to guarantee this equivalence is to mount all the samples using the same resin, prepare them with the same polishing steps, and clean them together using distilled water and high-purity ethanol. The goal is to have a similar concentration of organic molecules on all samples. Once cleaned, the samples are handled with gloves and immediately inserted inside the microscope, minimizing their exposure to ambient air. Leaving the samples overnight inside the specimen chamber of the microscope was found to be beneficial to allow some of the organic molecules to evaporate and obtain a good, stable vacuum condition. An equivalent alternative is to plasma clean the samples in the exchange chamber. Apart from time saving, plasma cleaning in the current system did not present any additional benefit than the overnight pumping in terms of contamination reduction.

**Low X-ray intensity** There are not too many ways around the low intensity of the C K–L\textsubscript{2,3} X-rays, as this is a physical limitation. One can either increase the measurement time, increase the beam current or improve the detection efficiency. In the light of the aforementioned contamination problem, the first solution is counterproductive. Improvements of the precision are compensated by a worse accuracy due to the higher contamination. In the context of measurements at a high spatial resolution, the increase of the beam diameter as a function of the beam current for a given accelerating voltage (Fig. 3.4) puts a limit on the benefits of the second option. The detection efficiency was greatly improved with the introduction of layered dispersive elements, albeit not without consequences such as their irregular reflectivity (§3.1.3.3). These
3.2. Acquisition and quantification strategies

<table>
<thead>
<tr>
<th>X-ray transition</th>
<th>Resolution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lateral</td>
</tr>
<tr>
<td>C K–L₂,3</td>
<td>476.2</td>
</tr>
<tr>
<td>Si K–L₂,3</td>
<td>560.1</td>
</tr>
<tr>
<td>Cr K–L₂,3</td>
<td>449.6</td>
</tr>
<tr>
<td>Mn K–L₂,3</td>
<td>429.5</td>
</tr>
<tr>
<td>Fe K–L₂,3</td>
<td>407.0</td>
</tr>
</tbody>
</table>

Table 3.2: Simulated lateral and depth resolution of different X-ray transitions. Sample contains 1 mass % of C, Si, Cr and Mn, balance Fe (mass density of 7622 kg m⁻³). An accelerating voltage of 15 kV, a beam current of 100 nA (beam diameter of 78 nm), 50 000 electrons were used in the simulations with NISTMONTE [300].

Factors were weighted and a standard set of analytical conditions were selected as a starting point for the steel quantification: a measurement time of 5 s per point, a beam current of 100 nA at an accelerating voltage of 15 kV and, if possible, the use of two spectrometers to acquire the C K–L₂,3 X-ray intensity. The optimization of these parameters depending on the goals and requirements of a measurement is discussed in §3.4.

Spatial resolution  The choice of 15 kV as the accelerating voltage may appear counterintuitive for measurements at a high spatial resolution. Lowering the accelerating voltage would decrease the electron interaction volume and emission volume of each type of X-rays. As shown in §3.1.2.2, the enlargement of the beam diameter at low accelerating voltages is one limitation to this strategy. The other is the large inaccuracies in the quantification when the L₃–M₄,5 X-ray transitions of Fe, Cr and Mn are used instead of the higher energy K–L₂,3 X-ray transitions (§2.4 and Chap. 5). From a quantification perspective, there is little gain in resolving smaller microstructural features if the uncertainty on their composition is as large as 30 % [214]. Although the K–L₂,3 X-ray transitions of Fe, Cr and Mn could be ionized with an accelerating voltage between 8 and 9 kV, their low X-ray intensities would affect the precision of the measurements. An accelerating voltage of 15 kV was therefore selected as a compromise between the accuracy, precision and spatial resolution. Based on Monte Carlo simulations, the lateral and depth resolutions for the main alloying elements are given in Tab. 3.2. They correspond to an X-ray emission volume containing 95 % of each emitted X-ray transition.

Interferences of high order X-ray reflections  The low mass fraction of Cr, Mn and Ni in low alloy steels limits the impact of high order X-ray reflections. With energy filtration using a PHA window of 4 V (§3.1.3.1), their peaks are indistinguishable.

Determination of the background  From the ISO 16592 on the “Guidelines for determining the carbon content of steels using a calibration curve method”, the background intensity underneath the C K–L₂,3 peak is said to consist in four contributions: (1) carbon contamination due to specimen preparation, (2) carbon contamination due to electron irradiation, (3) the intensity of any overlapped peak and (4) the “true”
background from the Bremsstrahlung X-rays. As demonstrated in §3.1.3.2 and 3.1.3.3, the reflectivity of the dispersive element and total internal reflection are two other contributions to the background intensity.

The first contribution, originating from leftover debris from diamond solution polishing or other polishing agents, can easily be avoided by careful sample preparation and cleaning [32, 73, 260, 303]. The increase of the background intensity due to the interferences of high order X-ray reflections is negligible for small concentrations of Cr, Mn and Ni, and appropriate energy filtration by the PHA. The same conclusion applies to the total internal reflection of Si L\(_{3}\)-M\(_{1}\). Only the 3rd order reflection of the Fe L\(_{1}\)-M\(_{4}\) and L\(_{1}\)-M\(_{5}\) X-ray transitions have an inescapable influence on the background intensity.

As such, the measurement of the background intensity on pure iron at the C K–L\(_{2,3}\) offers a solution to the remaining contributions. From the predominance of the Fe concentration in low alloy steels, many similitudes with pure iron can be assumed: the emission of Bremsstrahlung X-rays, the reflectivity of the dispersive element (similar energy distribution of the Bremsstrahlung X-rays), the intensity of the high order reflections, and the level of carbon contamination. From all these assumptions, the latter is the most critical aspect for line scan acquisition, due to the overlapping effect of the carbonaceous rings.

The experience drawn by running line scans on pure iron and different steel samples on various occasions revealed inconsistencies in the carbon contamination behaviour, even with the use of an oxygen jet. Three examples of line scans acquired on pure iron over one year and a half are shown in Fig. 3.17. The differences between the line scans highlight the peculiarity of the carbon contamination and its dependence on the amount of organic molecules present on the sample surface and the vacuum condition during the acquisition. In the case of a 16-\(\mu\)m line scan, large variations are observed in the first 4 micrometers, while after this distance the intensity becomes relatively stable. In sum, although it is not possible to determine a background intensity at every point of the line scan, the average C K–L\(_{2,3}\) intensity measured on pure iron after 4\(\mu\)m can be taken as the background X-ray intensity for the line scans acquired on samples with an unknown composition. This implies (1) the acquisition of line scans under identical conditions (length, step size, dwell time, accelerating voltage, beam current, etc.) on pure iron, on the reference material(s) and on the unknown samples, (2) a similar contamination level on all these samples, and (3) large uncertainties in the carbon quantification in the first micrometers. The first two implications are to ensure a similar contribution of the contamination to the background X-ray intensity after 4\(\mu\)m. The aforementioned sample preparation strategy, where all samples are polished, cleaned and left overnight inside the microscope, sets the amount of organic molecules, whereas the conditions used for the line scans control the overlapping of the carbonaceous rings. These conditions, especially the step size, also influence the magnitude of the uncertainties and the length of the uncertain region at the beginning of each line scan.

Selection of reference materials As for the quantification of any other element by EPMA, one or several reference materials are needed to quantify carbon. The large majority of publications on the quantification of carbon used a calibration curve to convert the C K–L\(_{2,3}\) X-ray intensities into concentrations [164, 211, 250, 303,
3.2. Acquisition and quantification strategies

Figure 3.17: Experimental C K–L\textsubscript{2,3} intensity along 16-\textmu m line scans (40 nm step size, 5 s dwell time) measured on pure iron at 15 kV and 100 nA with an oxygen jet and the LDE2H dispersive element.

413, 423]. For reasons that will be detailed below, the use of a single reference material, Fe\textsubscript{3}C, was found more appropriate for the carbon quantification at high spatial resolution.

From a practical point of view, the calibration curve is time consuming. In order to construct a calibration curve, the C K–L\textsubscript{2,3} X-ray intensity is acquired on pure iron and steel alloys containing different amounts of carbon. For single spot acquisitions, this procedure is straightforward and does not significantly increase the total calibration time. For high resolution acquisitions, the larger influence of contamination on the measurements requires the acquisition of a line scan on each reference material to determine the (background) X-ray intensity. Assuming that each line scan approximately takes 30 min, the construction of a calibration curve would necessitate at least 2 h of instrument time, every time new samples are inserted inside the electron microprobe.

The calibration curve assumes a linear relationship between the carbon mass fraction and the C K–L\textsubscript{2,3} X-ray intensity (Eq. 2.44). The intercept (at 0 mass%) of this linear function is equal to the background X-ray intensity measured on pure iron. The slope is normally determined by measuring the C K–L\textsubscript{2,3} X-ray intensity from carbon containing steel alloys. Intuitively, increasing the number of data points, i.e. the number of reference materials, helps improve the accuracy of the slope. However, this reasoning is only valid if the alloys have an homogeneous composition and their carbon mass fraction is accurately known. Unfortunately, not all steels, normally used to construct the calibration curve, comply with these two criteria. Fig. 3.18 shows line scans acquired on four reference steel alloys with a carbon mass fraction of 0.16, 0.36, 0.64 and 1.01%. The composition of these reference samples is shown in Tab. 3.3. In
comparison to the line scans on pure iron (Fig. 3.16 and 3.17), more fluctuations are observed in these line scans, notably after the first micrometers. To produce these reference materials, steels containing different amounts of carbon are quenched to form a fully martensitic microstructure where the carbon atoms are uniformly distributed. Being metastable (§2.2.1), the microstructure of martensite evolves over time, even at room temperature, causing the segregation of the carbon atoms, as testified by the sharp peaks in Fig. 3.18. In all, this inhomogeneity combined with an unpredictable extent of the tempering reaction increases the uncertainty on the carbon content of these alloys. It is worth pointing out that this phenomenon would go unnoticed under more traditional acquisition conditions: single spot measurements using a thermionic emitter and/or a defocused electron beam. The large beam essentially averages out the observed fluctuations. This is obviously not the case in high resolution acquisitions, rendering these reference materials unusable unless their homogeneity at the sub-micrometer scale can be improved.

On the contrary, cementite, Fe₃C, is a line compound, meaning that all cementite grains have a fixed and stable carbon mass fraction of 6.689% (Fig. 2.12). Normally in steels, cementite appears near ferrite forming a fine microstructure such as pearlite. As part of the MICROLITE project [4], Saunders et al. [319] enlarged cementite grains to several micrometers through a long carburization treatment and successfully produced a certified reference material of Fe₃C for EPMA. In terms of the calibration curve, replacing several steels alloys with a carbon mass fraction less than 1% by only two reference materials, pure Fe and Fe₃C, has a negligible influence on its slope and intercept. The assumption of a linear relationship between the carbon mass fraction
Table 3.3: Composition of four carbon containing reference steel alloys manufactured by TNO, Netherlands. All values are expressed as mass % C. The balance is assumed to be iron. The carbon mass fractions are the nominal provided by the manufacturer. The mass fractions of the other alloying elements were experimentally measured (15 kV, 100 nA, point measurements, counting time of 10 s for peak intensity and 5 s for each background, Cr and Cu measured using LIF dispersive element, Si with PETH).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Cu</th>
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<tr>
<td>1B</td>
<td>0.16</td>
<td>0.22</td>
<td>0.10</td>
<td>0.27</td>
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<tr>
<td>2B</td>
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<td>4B</td>
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<td>0.24</td>
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</tbody>
</table>

Figure 3.19: Simulated calibration curves using several reference materials with a carbon mass fraction less than 1%, and using only pure Fe and Fe₃C. An accelerating voltage of 15 kV and 50 000 electrons were used in the simulations with NISTMONTE [300].

and C K–L₂,₃ X-ray intensity extends above 1%, up to 6.689%. This is demonstrated using Monte Carlo simulations in Fig. 3.19, where the difference between the two slopes is equivalent to a 3-% relative error on the carbon mass fraction.

As pointed out by Almagro et al. [4], one caveat of the calibration curve is that the influence of other alloying elements on the C K–L₂,₃ X-ray intensity is disregarded. Even in low alloy steels, small concentrations of Mn and Cr change the absorption of the C K–L₂,₃ X-rays. From Monte Carlo simulations, the C K–L₂,₃ X-ray intensity decreases by 2.5 % with the addition of 1 mass% of Si, Mn and Cr. To take this effect
into consideration, an experimental k-ratio for carbon can be obtained by combining the peak intensity measured on the unknown sample \( I_{\text{peak, unk}}^{C\ K-L_{2,3}} \), the peak intensity measured on pure iron \( I_{\text{peak, Fe}}^{C\ K-L_{2,3}} \), i.e. background intensity, and the peak intensity measured on Fe\textsubscript{3}C \( I_{\text{peak, Fe}_3\text{C}}^{C\ K-L_{2,3}} \):

\[
k_{\text{exp}}^{C\ K-L_{2,3}} = \frac{I_{\text{peak, unk}}^{C\ K-L_{2,3}} - I_{\text{peak, Fe}}^{C\ K-L_{2,3}}}{I_{\text{peak, Fe}_3\text{C}}^{C\ K-L_{2,3}} - I_{\text{peak, Fe}}^{C\ K-L_{2,3}}},
\]

assuming all intensities are acquired using the same beam current and acquisition time. As for the calibration curve, the assumption is made that the background intensities on the unknown and on the reference material, i.e. Fe\textsubscript{3}C, are equal to the peak intensity measured on pure iron. The experimental k-ratio from Eq. 3.4 can then be used in the quantification equation (Eq. 2.41) with the other experimentally measured k-ratios for iron and the alloying elements to solve for the composition. The influence of all elements on the C K–L\textsubscript{2,3} X-ray intensity is then automatically handled by the analytical intensity models and the optimization procedure. The measurement time is also reduced as only two reference materials (Fe and Fe\textsubscript{3}C) must be measured.

One argument in favour of the calibration curve was its independence on the MACs. As a last check, the same set of k-ratios are quantified using four different MACs in order to evaluate their influence on the final carbon concentration. The k-ratios were obtained from Monte Carlo simulations using the NISTM Monte [300] program, the MAC database from Chantler et al. [72] and an accelerating voltage of 15 kV. The unknown samples was a steel alloy containing 1 mass% of C, Si, Cr and Mn, whereas the reference materials were pure metals, except Fe\textsubscript{3}C for carbon. The quantification was performed using the XPP [273] \( \Phi(\rho z) \) model implemented in DTSA-II [302]. Tab. 3.4 gives the calculated carbon mass fraction using each MAC, as well as the MAC value of the C K–L\textsubscript{3} X-ray transition in pure iron and the value of the matrix correction term, \( ZAF \). Despite deviations between the different MAC databases, the carbon mass fraction is fairly unaffected. This can be explained by the resemblance between the composition of the unknown and Fe\textsubscript{3}C, minimizing the absorption correction and the influence of the MACs.

### 3.2.1.2 Experimental procedure

Based on the assumptions and solutions from the previous section, the next paragraphs list the typical steps of the experimental procedure to quantify carbon in low alloy steels.

#### Sample preparation

The objective of any sample preparation for EPMA is to produce a flat surface with minimal rugosity. This requirement comes from the analytical models which make this assumption in order to calculate the theoretical X-ray intensity (Eq. 2.33). The absence of roughness is also critical to have a stable contamination behaviour. To illustrate this point, line scans were acquired on the same location before and after nital etching. Results are shown in Fig. 3.20, with the corresponding SE images of the two surface conditions. The influence of the rugosity on the X-ray intensity is visible on the right-hand side of the martensite island (around 10 \( \mu \text{m} \)).
3.2. Acquisition and quantification strategies

<table>
<thead>
<tr>
<th>MAC database</th>
<th>((\mu/\rho)) (m(^2)kg(^{-1}))</th>
<th>(ZAF)</th>
<th>Carbon mass fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pouchou and Pichoir [273]</td>
<td>1350</td>
<td>1.0589</td>
<td>1.0057</td>
</tr>
<tr>
<td>Henke et al. [145]</td>
<td>1582</td>
<td>1.0575</td>
<td>1.0032</td>
</tr>
<tr>
<td>Heinrich [144]</td>
<td>1366</td>
<td>1.0578</td>
<td>1.0046</td>
</tr>
<tr>
<td>Chantler et al. [72]</td>
<td>1165</td>
<td>1.0591</td>
<td>1.0041</td>
</tr>
</tbody>
</table>

Table 3.4: Influence of the mass attenuation coefficient on the carbon mass fraction. Sample contains 1 mass % of C, Si, Cr and Mn, balance Fe. Quantification was performed using the XPP [273] \(\phi(\rho z)\) model implemented in DTSA-II [302] based on k-ratios simulated by NISTMONTE [300] at an accelerating voltage of 15 kV. The second column are the MAC value of the C K–L\(_3\) X-ray transition in pure iron. The third column corresponds to the matrix correction term using each MAC.

![Figure 3.20: Experimental C K–L\(_{2,3}\) intensity along 16-\(\mu\)m line scans (40 nm step size, 5 s dwell time) measured on a flat polished and a nital etched sample at 15 kV and 100 nA with an oxygen jet and two LDE2 dispersive elements. The insets show SE images acquired after each line scan. The direction of the line scans was from left to right.](image)
Ideally, the sample preparation should also remove all residual deformation from the sample surface. While this is a necessity for EBSD acquisitions (see §3.5.3), a defect-free surface allows the channelling of the incident electrons through the atom lattice, resulting in an enhanced grain contrast and easier identification of the different constituents. The SE image in the top left corner of Fig. 3.20 exhibits this effect. The sample preparation for the carbon quantification at high spatial resolution was therefore developed to minimize roughness and residual deformation.

After sectioning using a diamond blade, the samples of interest are hot-mounted in the conductive resin *ProbeMet* (Buehler, Lake Bluff, Illinois, USA), consisting of copper flakes in a thermoset epoxy. The choice of this resin was predicated on its lower carbon content in comparison to other conductive resins. The two relevant reference materials for carbon quantification, pure Fe and Fe$_3$C, are also mounted together in the same resin.

After mounting, the samples are prepared by a series of grinding and polishing steps. Tab. 3.5 summarizes the routine sample preparation recipe used to polish all steels in this work prior to EPMA measurements. The method was taken from the guide by Vander Voort and Geertruyden [367] on “Specimen preparation for electron backscattered diffraction”. A last step was added to clean leftover SiO$_2$ particles on the surface. The polishing cloths mentioned in Tab. 3.5 are trademarks by Struers (Ballerup, Denmark), but could easily be replaced by equivalent products from other manufacturers. For the mount with the reference materials, only the last two steps are performed to refresh their already polished surface. After polishing, the samples and reference materials are cleaning in an ultrasonic bath using high-purity ethanol for 5 to 10 min. They are then dried under hot air for $\approx$ 5 min and inserted inside the electron microprobe, where they are either plasma cleaned or left overnight under vacuum.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Abrasive / Size</th>
<th>Lubricant</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC paper</td>
<td>P320 grit</td>
<td>water</td>
<td>1.0</td>
</tr>
<tr>
<td>MD-Allegro</td>
<td>9μm diamond suspension</td>
<td>water-based</td>
<td>5.0</td>
</tr>
<tr>
<td>MD-Dur</td>
<td>3μm diamond suspension</td>
<td>water-based</td>
<td>4.0</td>
</tr>
<tr>
<td>MD-Dur</td>
<td>1μm diamond suspension</td>
<td>water-based</td>
<td>3.0</td>
</tr>
<tr>
<td>MD-Chem</td>
<td>OP-S – 0.05μm SiO$_2$ suspension</td>
<td>water</td>
<td>1.5</td>
</tr>
<tr>
<td>MD-Chem</td>
<td>(cleaning)</td>
<td>water</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 3.5: Recipe for preparation of steel samples [367].
3.2. Acquisition and quantification strategies

![Graph showing line scans of Fe, Fe₃C, and DP steel](image)

Figure 3.21: Example of line scans acquired on pure iron, on Fe₃C and on a DP steel sample (15 kV, 100 nA, 40 nm step size, 5 s dwell time, LDE2H dispersive element for carbon and LiFH dispersive element for manganese). The shaded areas correspond to the regions used to calculate the average intensities.

**Line scan acquisitions** Typically only four or five elements are of interest in low alloy steels, and a spectrometer is assigned to each element. The measurement of Fe K–L₂,₃ X-rays can be avoided by assuming that the unmeasured balance is iron. To adjust the position of each spectrometer, a quick spectrum is acquired on the relevant reference material to find the position with the maximum intensity. During the line scans, the spectrometers are immobile, i.e. only the peak X-ray intensities are recorded. The length and step size of the line scans are selected based on the size of the features of interest on the unknown samples. For line scans with a length less than 30 μm, the beam is scanned across the feature(s), whereas for longer line scans, stage scanning is used to minimize Bragg defocusing of the spectrometers. Although line scans of different lengths or step sizes could be acquired, it is more advisable to keep these conditions fixed for the line scans on pure iron and Fe₃C. The strict minimum number of line scans is three: one on the unknown sample, one on pure iron and one on Fe₃C. Fig. 3.21 shows an example of each line scan for the C K–L₂,₃ and Mn K–L₂,₃ X-ray transitions.

During all line scan acquisitions, the oxygen jet is used. Using the needle valve, the oxygen pressure inside the specimen chamber is adjusted to reach a vacuum pressure of 1 × 10⁻³ Pa, one order of magnitude worse than without the oxygen jet. The pressure usually becomes stable after 5–10 min.

Apart from the line scans, net X-ray intensities are acquired on the reference materials other than Fe and Fe₃C using the traditional strategy of acquiring peak and background X-ray intensities. The k-ratio equation for other alloying elements follows
the one for the C K–L₂₋₃ X-rays (Eq. 3.4), with the exception that the denominator becomes the net intensity measured on the reference material. For the Mn K–L₂₋₃ X-rays, the k-ratio equation looks like:

\[
k_{\text{Mn K–L}_2}^{\text{exp}} = \frac{I_{\text{peak, unk, Mn K–L}_2} - I_{\text{peak, Fe, Mn K–L}_2}}{I_{\text{peak, Mn, Mn K–L}_2} - I_{\text{bckg, Mn, Mn K–L}_2}},
\]

where \(I_{\text{peak, unk, Mn K–L}_2}\) is the peak intensity measured on the unknown sample, \(I_{\text{peak, Fe, Mn K–L}_2}\), the peak intensity measured on pure iron, \(I_{\text{peak, Mn, Mn K–L}_2}\), the peak intensity measured on pure manganese, and \(I_{\text{bckg, Mn, Mn K–L}_2}\), the background intensity measured on pure manganese. For the numerator of Eq. 3.5, the same assumption as in Eq. 3.4 that the background intensity below the Mn K–L₂₋₃ peak on the unknown sample is equal to the one on pure iron.

Quantification After all the line scans and net X-ray intensities have been acquired, the quantification is performed using DTSA-II [302] and its implementation of the XPP [273] \(\phi(\rho z)\) model. For the carbon quantification, the peak intensities measured on pure iron and on Fe₃C, \(I_{\text{peak, Fe, C K–L}_2}^{\text{Fe}}\) and \(I_{\text{peak, Fe, C K–L}_2}^{\text{Fe}_3}\), in Eq. 3.4, are taken as the average intensity of the region with stable contamination in each respective line scan. Examples of this manual selection are shown in Fig. 3.21 by the shaded areas. For the other alloying elements, the peak intensity measured on pure iron, e.g. \(I_{\text{Mn, Mn K–L}_2}^{\text{Fe}}\), is the average intensity of the whole line scan. With these information, the set of k-ratios obtained at each point of the line scan is quantified and the composition is saved.

This concludes the presentation of the acquisition and quantification strategy for low alloy steels. In summary, it overcomes many challenges of carbon quantification at a high spatial resolution, without increasing the time and complexity of the measurements.

3.2.2 High alloy steels

Although the low-alloy-steel approximation applies to many steels, worthy exceptions are TWIP steels with a high manganese concentration and bearing steels like SAE52100 (also known as 100Cr6) with high chromium containing carbides. As discussed §2.2.2 and 3.1.3.1, the influence of high order X-ray reflections from Cr and Mn on the C K–L₂₋₃ X-ray intensity can no longer be ignored. The assumption that the background intensity of an unknown steel can be measured on pure iron does not hold anymore due to the large difference in the mean atomic number. The similar carbon contamination behaviour between the reference materials and the unknown samples is also questionable.

Instead of trying to individually quantify and neutralize for all these factors, a strategy was developed to empirically correct the carbon mass fraction after the quantification based on the quantified steel composition. Due to the multiple and conflicting contributions to the X-ray intensity, the empirical correction is a straightforward solution to a complex problem, which would require extensive amount of experimental measurements and modelling. The current strategy follows up the proposal of Almagro et al. [4] to use an empirical equation to correct the background
3.2. Acquisition and quantification strategies

X-ray intensity of high alloy steels. The correction of the carbon mass fraction was chosen to avert modifications of the quantification procedure (the iterative loop would need to count for the change in the C K–L\textsubscript{2,3} k-ratio as a function of the previous calculated composition).

**Experimental procedure** In a first approximation, the empirical equation calculates a correction on the carbon mass fraction as a function of the steel composition, or mathematically formulated:

\[
w_C = w'_C - \sum_{i=0}^{N} a_i w_i ,
\]

(3.6)

where \(w_C\) is the true carbon mass fraction, \(w'_C\), the apparent carbon mass fraction obtained from the normal quantification, \(w_i\), the mass fraction of element \(i\) in a sample containing \(N\) elements (carbon is excluded), and \(a_i\), the linear correction coefficient expressing the contribution of element \(i\) to the carbon mass fraction. For several steel samples, Eq. 3.6 can be rewritten as a linear matrix equation:

\[
\mathbf{w} \hat{\mathbf{a}} = \mathbf{b} ,
\]

(3.7)

where \(\mathbf{w}\) is a \(M \times N\) matrix of \(M\) steel samples and \(N\) elements, \(\hat{\mathbf{a}}\) is a column vector of \(N\) rows, and \(\mathbf{b}\), a column vector of \(M\) rows corresponding to the difference between the apparent and true carbon mass fractions \((w'_C - w_C)\). Expanding the equation gives:

\[
\begin{pmatrix}
w_0^0 & \cdots & w_i^0 & \cdots & w_N^0 \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
w_0^j & \cdots & w_i^j & \cdots & w_N^j \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
w_0^M & \cdots & w_i^M & \cdots & w_N^M
\end{pmatrix}
\begin{pmatrix}
a_0 \\
\vdots \\
a_i \\
\vdots \\
a_N
\end{pmatrix}
=
\begin{pmatrix}
(w'_C - w_C)^0 \\
\vdots \\
(w'_C - w_C)^j \\
\vdots \\
(w'_C - w_C)^M
\end{pmatrix} .
\]

(3.8)

If the number of samples measured is greater than the number of elements \((M > N)\), the problem is overdetermined and can be solved using least-squares regression. The solution is found by finding the vector \(\hat{\mathbf{a}}\) minimizing the Euclidean 2-norm \(\|\mathbf{b} - \mathbf{w} \hat{\mathbf{a}}\|^2\). This solving methodology differs from Almagro et al. [4] as the values of the correction coefficients \(\hat{a}\) are simultaneously optimized with respect to all the alloying elements, not only to a particular element such as Cr or Mn.

In order to fill in the matrix \(\mathbf{w}\) and vector \(\mathbf{b}\), the apparent carbon mass fraction of 13 high alloy steel samples was determined. The nominal composition of these reference steel alloys is given in Tab. 3.6, where all have a carbon mass fraction \((w_C)\) less than 0.1%.

On each sample, the peak intensity of the C K–L\textsubscript{2,3} X-ray transition was measured at 25 locations at an accelerating voltage of 15 kV and a beam current of 75 nA using an oxygen jet and the LDE2H dispersive element. The peak intensity was converted into an apparent carbon mass fraction using a calibration curve constructed from the peak intensity measured on pure iron and Fe\textsubscript{3}C (as in Fig. 3.19). To minimize the influence of the other alloying element on the carbon mass fraction, the intensi-
ties were corrected for absorption based on Philibert-Heinrich absorption correction model (Beer-Lambert law) implemented in DTSA-II [302]. Eq. 3.9 summarizes the conversion from peak intensities to mass fractions.

\[
(w'_C)^j = \left( \frac{I_{\text{peak},j}^{\text{C K-L}_2,3}/A_{\text{C K-L}_2,3}}{m} \right) - b
\]

(3.9)

where \(I_{\text{peak},j}^{\text{C K-L}_2,3}\) is the peak X-ray intensity measured on reference steel alloy \(j\), \(A_{\text{C K-L}_2,3}\) the absorption correction term for the reference steel alloy \(j\), and \(m\) and \(b\) are calculated as follows:

\[
\begin{align*}
    m &= \frac{I_{\text{peak},\text{Fe}_3\text{C}}^{\text{C K-L}_2,3}/A_{\text{Fe}_3\text{C}}^{\text{C K-L}_2,3}}{-w_{\text{Fe}3\text{C}}^C - w_{\text{Fe}}^C} \\
    b &= I_{\text{peak},\text{Fe}}^{\text{C K-L}_2,3}/A_{\text{C K-L}_2,3}
\end{align*}
\]

(3.10)

where \(I_{\text{peak},\text{Fe}}^{\text{C K-L}_2,3}\) and \(I_{\text{peak},\text{Fe}_3\text{C}}^{\text{C K-L}_2,3}\) are the peak X-ray intensities measured on Fe and Fe\(_3\)C respectively, \(A_{\text{Fe}}^{\text{C K-L}_2,3}\) and \(A_{\text{Fe}_3\text{C}}^{\text{C K-L}_2,3}\) are the absorption correction term for Fe and Fe\(_3\)C respectively, and \(w_{\text{Fe}3\text{C}}^C\) is the carbon mass fraction of Fe\(_3\)C, i.e. 6.689%.

The vector \(\vec{b}\) from Eq. 3.7 is then constructed from the experimental apparent carbon mass fractions ((\(w'_C\)^j)), as well as the matrix \(w\) from the nominal composition in Tab. 3.6. Only the elements potentially contributing to the apparent carbon mass fraction are included in matrix \(w\), namely the major alloying elements, Si, Cr, Mn, Fe and Ni. The least-squares regression of linear matrix equation implemented in NUMPY [174] was used to solve Eq. 3.7.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.02</td>
<td>0.04</td>
<td>0.37</td>
<td>16.77</td>
<td>1.61</td>
<td>67.19</td>
<td>0.13</td>
<td>10.58</td>
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</tr>
<tr>
<td>350</td>
<td>0.04</td>
<td>0.02</td>
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<td>0.08</td>
<td>19.40</td>
<td>0.15</td>
<td>0.21</td>
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<td>535</td>
<td>0.04</td>
<td>0.04</td>
<td>0.35</td>
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<td>0.02</td>
<td>0.17</td>
<td>0.06</td>
<td>1.00</td>
</tr>
<tr>
<td>800</td>
<td>0.01</td>
<td>0.01</td>
<td>0.35</td>
<td>11.67</td>
<td>0.34</td>
<td>86.99</td>
<td>0.01</td>
<td>0.15</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>A4</td>
<td>0.10</td>
<td>0.17</td>
<td>0.36</td>
<td>16.09</td>
<td>13.73</td>
<td>65.91</td>
<td>0.00</td>
<td>1.53</td>
<td>2.00</td>
<td>0.02</td>
</tr>
<tr>
<td>A5</td>
<td>0.08</td>
<td>0.17</td>
<td>0.18</td>
<td>16.96</td>
<td>10.52</td>
<td>67.33</td>
<td>0.02</td>
<td>2.60</td>
<td>1.95</td>
<td>0.02</td>
</tr>
<tr>
<td>A6</td>
<td>0.07</td>
<td>0.20</td>
<td>0.20</td>
<td>17.32</td>
<td>6.40</td>
<td>69.73</td>
<td>0.00</td>
<td>4.51</td>
<td>1.17</td>
<td>0.30</td>
</tr>
<tr>
<td>P02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.29</td>
<td>5.01</td>
<td>0.21</td>
<td>93.56</td>
<td>0.00</td>
<td>0.12</td>
<td>0.02</td>
<td>0.65</td>
</tr>
<tr>
<td>P07</td>
<td>0.05</td>
<td>0.06</td>
<td>0.32</td>
<td>18.29</td>
<td>1.41</td>
<td>70.79</td>
<td>0.12</td>
<td>8.10</td>
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</tr>
<tr>
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<td>0.05</td>
<td>0.48</td>
<td>17.18</td>
<td>1.48</td>
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<td>11.24</td>
<td>0.31</td>
<td>2.16</td>
</tr>
<tr>
<td>P13</td>
<td>0.00</td>
<td>0.03</td>
<td>1.34</td>
<td>24.98</td>
<td>1.61</td>
<td>50.57</td>
<td>0.05</td>
<td>20.02</td>
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<td>0.40</td>
</tr>
<tr>
<td>P15</td>
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<td>0.02</td>
<td>0.61</td>
<td>28.65</td>
<td>0.78</td>
<td>25.19</td>
<td>0.03</td>
<td>39.82</td>
<td>1.58</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Table 3.6: Composition of the steel samples used to construct the empirical equation. All values are in mass fraction percent.
3.2. Acquisition and quantification strategies

Table 3.7: Experimentally measured apparent carbon mass fractions ($w'_C$) and their uncertainty ($\Delta w'_C$) for the different reference steel alloys. The nominal carbon mass fraction ($w_C$) is given for comparison. All values are in mass fraction percent.

<table>
<thead>
<tr>
<th></th>
<th>$w_C$</th>
<th>$w'_C$</th>
<th>$\Delta w'_C$</th>
<th>$w'_C - w_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.018</td>
<td>0.065</td>
<td>0.013</td>
<td>0.048</td>
</tr>
<tr>
<td>350</td>
<td>0.043</td>
<td>0.095</td>
<td>0.021</td>
<td>0.052</td>
</tr>
<tr>
<td>535</td>
<td>0.043</td>
<td>0.066</td>
<td>0.010</td>
<td>0.023</td>
</tr>
<tr>
<td>800</td>
<td>0.014</td>
<td>0.021</td>
<td>0.017</td>
<td>0.007</td>
</tr>
<tr>
<td>A4</td>
<td>0.095</td>
<td>0.185</td>
<td>0.018</td>
<td>0.090</td>
</tr>
<tr>
<td>A5</td>
<td>0.078</td>
<td>0.157</td>
<td>0.018</td>
<td>0.079</td>
</tr>
<tr>
<td>A6</td>
<td>0.067</td>
<td>0.142</td>
<td>0.020</td>
<td>0.075</td>
</tr>
<tr>
<td>P02</td>
<td>0.026</td>
<td>0.048</td>
<td>0.015</td>
<td>0.022</td>
</tr>
<tr>
<td>P07</td>
<td>0.052</td>
<td>0.100</td>
<td>0.015</td>
<td>0.048</td>
</tr>
<tr>
<td>P11</td>
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<td>0.071</td>
<td>0.012</td>
<td>0.071</td>
</tr>
<tr>
<td>P13</td>
<td>0.000</td>
<td>0.084</td>
<td>0.015</td>
<td>0.084</td>
</tr>
<tr>
<td>P15</td>
<td>0.038</td>
<td>0.068</td>
<td>0.021</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Results  
The average apparent carbon mass fraction ($w'_C$) measured for each reference steel alloy is given in Tab. 3.7. The comparison with the nominal carbon mass fraction reveals different overestimations of the carbon mass fraction from 0.007 to 0.09%. The large difference corresponds to the sample with the highest manganese content, sample A4 with 13.73 mass%. The effect of chromium can also be observed by looking at the sample P07 where the carbon mass fraction was overestimated by 0.048% in absolute terms.

Using these results, the correction coefficients ($a_i$) were calculated from the least-squares regression of Eq. 3.7 and the correction equation (Eq. 3.6) becomes:

$$w_C = w'_C - (-8.62 \times 10^{-6} w_{Ni} - 3.50 \times 10^{-8} w_{Fe} + 4.60 \times 10^{-5} w_{Mn}$$

$$+ 1.56 \times 10^{-5} w_{Cr} + 3.90 \times 10^{-4} w_{Si})$$ (3.11)

The magnitude of each correction must be weighted against the range of compositions found in the reference steel alloys. For instance, although silicon has the largest correction coefficient, its contribution to the overall correction is small due to its low mass fraction in the studied steels (< 1.34%). Higher silicon containing steels would be required to properly evaluate the effect of total internal reflection on the apparent carbon mass fraction. Following the inspection of apparent carbon mass fractions in Tab. 3.7, manganese and chromium unsurprisingly have the next largest correction coefficient. This observation falls in line with the explanations about the interferences of high order X-ray reflections in §2.2.2 and 3.1.3.1.

To verify Eq. 3.11, the absolute error on the apparent and corrected carbon mass fractions are plotted in Fig. 3.22 as a function of the C, Si, Cr, Mn, Fe and Ni mass fractions for the different reference steel alloys. The absolute error corresponds to the difference with the nominal carbon mass fraction reported in Tab. 3.6. In all
plots, the reduction of the absolute errors can be observed regardless of the sample composition. On average, the empirical correction decreases the absolute error on the carbon mass fraction from 0.0524 to 0.0007%.

Discussion From Fig. 3.22, it is difficult to conclude on the relationship between the alloying element mass fraction and the measured apparent carbon mass fraction. No specific trend can be established for any given alloying element. Even for carbon, the apparent carbon mass fraction does not linearly increase with the nominal mass fraction. This clearly illustrates that all these alloying elements influence the measured C K–L$_{2,3}$ X-ray intensity in different manners. The correction must therefore consider all these contributions simultaneously as in Eq. 3.11.

Equivalently, the higher apparent carbon mass fractions measured in high alloy steels can be interpreted as an increase of the background intensity in comparison to pure iron. It is well-known that the sample composition influences the background intensity, which tends to increase with the mean atomic number of the sample [92, 197]. The calculation of the background X-ray intensity from the mean atomic number is often used in EPMA performed with WD spectrometers to reduce the measurement time by eliminating the acquisition of the background X-ray intensities [66, 92, 171]. Unfortunately, the relationship between the background intensity and the mean atomic number does not seem to hold for the C K–L$_{2,3}$ X-rays, even with the absorption correction [92]. This conclusion is illustrated in Fig. 3.23 where the absolute errors from Fig. 3.22 are plotted as a function of the mean atomic number. The
absolute errors essentially corresponds to the background X-ray intensities expressed as carbon mass fractions. The trend from Fig. 3.23 suggests that the absolute errors decrease with increasing mean atomic number, contrary to the expected behaviour. Furthermore, relatively large increases of the background intensity are observed in spite of the fact that the mean atomic numbers of the reference steel alloys are almost equal to the one of pure iron. In sum, the change in the Bremsstrahlung X-ray emission with the sample composition cannot alone explain the measured apparent carbon mass fractions. As it excludes the contribution of high order X-ray reflections and total internal reflection, the mean atomic number technique cannot be used to calculate the background intensity underneath the C K–L$_{2,3}$ X-ray peak of steel alloys.

In conclusion, the developed empirical correction equation improves the accuracy of the carbon quantification in high alloy steels, without any additional measurement or modification to the acquisition procedure explained in §3.2.1.2. By correcting the carbon mass fraction and not the C K–L$_{2,3}$ X-ray intensity, the procedure is less sensitive to long-term beam current fluctuations, PHA variations, instrumental instabilities, etc. Its validity for steels with higher alloying contents could not be tested due to the lack of reference materials. The remaining errors, as seen in Fig. 3.22, may be related to the carbon contamination, inhomogeneity of the reference steel samples, and imprecision due to the counting statistics. Additional reference steel samples would also help improve the accuracy of the correction coefficients of Eq. 3.11.
Chapter 3. High resolution characterization of steel microstructure

3.3 Validation

This section assesses the validity of the strategy developed to measure low alloy steels at a high spatial resolution in terms of the accuracy (§3.3.1) and precision (§3.3.2) of the carbon quantification. The achievable spatial resolution calculated by Monte Carlo simulations (Tab. 3.2 in §3.2.1.1) is also experimentally validated (§3.3.3).

3.3.1 Accuracy

The accuracy of the carbon quantification primarily depends on the measurement of the background X-ray intensity underneath the C K–L$_{2,3}$ X-ray peak. As aforementioned, the background determination is a challenge for the quantification of any low concentration element [171], but additional factors complicate this determination for the carbon content in steels (§2.2.2 and §3.2.1.1). The carbon contamination with the formation of a carbonaceous deposit and the interference of high order X-ray reflections have the consequence to artificially increase the background intensity. Even with the measurement of the background intensity on pure iron, different contamination behaviours between the samples and incomplete filtering of the high order X-ray reflections can lead to large inaccuracies in the measured carbon content. Evaluating the experimental and quantification methods using well-characterized reference samples both with and without carbon is critical to assess the accuracy.

Unfortunately, it appears that very few steel samples completely fulfill the requirements to be accepted as reference materials to evaluate the carbon quantification. As previously reported in §3.2.1.1 and shown in Fig. 3.18, this fact is a significant shortcoming of the calibration curve strategy, which relies on the accurate knowledge of the carbon content in 4 to 5 steel alloys. Evidently, the accuracy of a quantification strategy cannot be evaluated if the reference materials have inaccurate and/or inhomogeneous compositions. It is also ill-advised to use a very low carbon containing reference sample as imprecisions may outweigh the inaccuracies, the two becoming indistinguishable from each other.

Faced with this dilemma, it was decided to assess the accuracy using the best available reference steel alloy, the most homogeneous sample with a carbon mass fraction greater than 0.25%. Hence, a line scan was performed on the reference material from Fig. 3.18 containing 0.64 mass % C using the acquisition and quantification methodology presented in §3.2.1.2. The quantified results are shown in Fig. 3.24.

At the beginning, the measured carbon concentration starts below the nominal composition of the reference material (dashed line), increases up to 0.86 mass % C after 2μm and then decreases to reach a plateau. This follows the typical trend observed on all samples, including pure iron and Fe$_3$C, as shown in Fig. 3.16 and 3.21. As previously described, the competing carbon contamination mechanisms of cracking, surface diffusion and etching explain the observed profile. The lower carbon concentration at the beginning of the line scan is an artifact of the quantification procedure which uses constant values for the background intensity on pure iron and peak intensity on Fe$_3$C. Both are extracted from the plateau of their respective line scan. The measurements within the first micrometer are therefore overcorrected for contamination.
3.3. Validation

For all these reasons, the first 4 to 5 μm must be excluded from the quantitative analysis as, under the selected operating conditions, a stable contamination offset is only obtained after this distance. Nonetheless, this line scan provides some assessment of the accuracy. After reaching a steady-state contamination, the measured carbon concentration matches the nominal composition of the reference material with an absolute error of 0.02 mass % C (calculated as the average mass fraction from 5 to 16 μm). This does not exclude the possibility of higher errors due to variations of the contamination level from sample to sample. Since it cannot be completely eliminated, careful sample preparation, clean electron microscope and efficient anti-contamination device(s) are the best remedies against the contamination problem.

3.3.2 Precision

In the last 10 μm of the line scan shown in Fig. 3.24, the fluctuations around the average value are related to the precision. In EPMA, there are two main sources of uncertainties, classified as random and systematic uncertainties [220]. The random uncertainties are unavoidable and entirely dependent on the number of detected X-rays. They follow Poisson statistics which stipulates that the uncertainty is equal to the square root of the number of counts. The low fluorescence yield of C K–L\textsubscript{2,3} X-rays combined with its high absorption coefficient in iron leads to high random uncertainties. The beam current and/or the counting time must be increased to improve the statistics. For typical EPMA measurements, systematic uncertainties can be minimized by rigorous calibration, good sample preparation and use of accurate reference materials. However, unstable contamination, surface topography and beam
drift can have a large influence on the precision of carbon measurements. Proper specimen cleaning and anti-contamination device(s) reduce the magnitude of the contamination, but cannot eliminate variable factors such as inhomogeneous coverage of organic molecules on the sample surface, changes in the electron scattering behaviour affecting the cracking rate, etc.

To quantify the precision of the developed strategy, measurements were performed over the carbon containing reference materials shown in Fig. 3.18. The objective is to compare the achievable precision between the classical acquisition approach of well-separated individual point measurements and the one presented in this work of high spatial resolution line scans. As for the accuracy, the selected reference samples are not ideal due to their inhomogeneity, inevitably increasing the magnitude of the systematic uncertainties. However, they can still provide a valuable comparison between the two different acquisition strategies.

The total uncertainty ($\sigma_{\text{measured}}$) can be assessed by measuring the C K–L$_{2,3}$ X-ray intensity several times on the same sample and calculating the standard deviation.

$$\sigma_{\text{measured}} = \sqrt{\frac{1}{N} \sum (I_i - \bar{I})^2}.$$  

(3.12)

where $I_i$ is the C K–L$_{2,3}$ X-ray intensity (in count) measured at point $i$, and $\bar{I}$ is the average intensity of all $N$ points. The random and systematic uncertainties can be extracted to understand better their contribution to the precision. Since the random uncertainty ($\sigma_{\text{random}}$) is known from Poisson statistics for a given intensity, the systematic uncertainty ($\sigma_{\text{systematic}}$) is then:

$$\sigma_{\text{systematic}}^2 = \sigma_{\text{measured}}^2 - \sigma_{\text{random}}^2$$  

(3.13)

$$= \sigma_{\text{measured}}^2 - \left(\sqrt{\bar{I}}\right)^2$$

$$= \sigma_{\text{measured}}^2 - \bar{I}.$$  

Experimentally, the intensity was acquired on each sample at 25 different locations separated by at least 20 $\mu$m for 5 s. The 30- $\mu$m line scans were also performed on each sample using a 40-nm step size and a dwell time of 5 s. In order to avoid any unfair comparison, only the last 25 points of the line scans were considered in the calculation of the uncertainties. The accelerating voltage and beam current were kept constant at 15 kV and 100 nA, respectively. The oxygen jet was used throughout all measurements. To convert these intensities into mass fractions, Eq. 3.9 was used, which implies that point measurements and line scans were also acquired on pure iron and Fe$_3$C under the same analytical conditions.

Fig. 3.25 compares the random and systematic uncertainties obtained from the two types of acquisition strategy. Note that the height of each bar is not equal to the total uncertainty ($\sigma_{\text{measured}}$), as uncertainties are added in quadrature (Eq. 3.13). A circle marker is added to visually assess the total uncertainty.

Both acquisition strategies have similar random uncertainties on all samples, since the same electron dose (i.e. acquisition time and beam current) was used. The random uncertainties increase in absolute value with the carbon mass fraction, but relatively decrease due to the increase of the C K–L$_{2,3}$ X-ray intensity. In order to reduce the random uncertainties, the electron dose should be increased at the expense of
3.3. Validation

Figure 3.25: Precision of carbon measurements for well-separated point and line scan acquisition. The random, systematic and total uncertainties are reported as carbon mass fraction in percent. The acquisition parameters are for the well-separated points: distance between point of \( \leq 20 \mu \text{m} \), 5 s measuring time; for the line scan: 40 nm step size, 5 s dwell time; and common to both: 15 kV, 100 nA, LDE2H dispersive element.

Despite these uncertainties, the precision, the total uncertainty on the carbon mass fraction, measured using the line scan acquisition mode is at least better than 0.05 mass % C. In comparison to the classical well-separated point approach, the main difference of the developed strategy for carbon quantification at high spatial resolution is that the precision is more variable and sample dependent.

3.3.3 Spatial resolution

Tab. 3.2 gave the lateral and depth resolutions obtained by Monte Carlo simulations of an hypothetical steel alloy (1% C, Si, Cr, Mn, balance as Fe) measured at an accelerating voltage of 15 kV. The depth resolution can difficultly be experimentally
Figure 3.26: Comparison between simulated and experimental line scan across a ferrite-martensite boundary. The experimental C K−L$_{2,3}$ intensities were acquired under the following conditions: 15 kV, 100 nA, 40 nm step size, 5 s dwell time, and LDE2H dispersive element. The simulated intensities were obtained by Monte Carlo simulations (CASINO 2 [95, 155]) under the same conditions assuming a Gaussian beam with a diameter of 78 nm. The composition of martensite in the simulations was derived from the quantification of the experimental results, giving a carbon concentration of 0.8 mass% C. Ferrite was assumed to be pure iron.

measured unless special multilayer samples are produced with a tracer layer [289], but the lateral resolution can be verified by a line scan across a sharp boundary. Using the latter methodology, a line scan was performed across a ferrite-martensite boundary in a DP steel. The boundary was manually selected to have a sharp and perpendicular interface with the direction of the electron beam. Subsequently, the same experiment was simulated in the CASINO 2 [95, 155] Monte Carlo program under the same analytical conditions. Based on the quantification of the experimental line scan, the composition of martensite was taken as 0.8 mass% C (balance Fe), and the one of ferrite as 100 mass% Fe.

The results from the experimental and simulated line scans are shown in Fig. 3.26. The two profiles are in good agreement, except that the experimental one has a longer tail on the left-hand side. One possible explanation would be the imperfect perpendicularity of the experimental ferrite-martensite interface.

By interpolating the experimental results, a lateral resolution of 562 nm was estimated using the 5-95% change rule measured from the two intensity plateaus in the ferrite and martensite. The limits are shown in Fig. 3.26. The experimental lateral resolution is comparable to the simulated one of 505.2 nm reported in Tab. 3.2.
This supports the possibility to evaluate the spatial resolution using Monte Carlo simulations if the beam diameter at the analytical conditions used was previously experimentally determined.

### 3.4 Optimization of analytical conditions

Ideally, a measurement should be as accurate and precise as possible with the best spatial resolution. In other words, the objective is to optimize the experimental parameters in order to obtain the best accuracy, precision and spatial resolution. Mathematically, this translates into an optimization problem, where the objective is to find a set of experimental parameters \( \vec{x} = \{x_0, \ldots, x_M\} \) minimizing an objective function \( f(\vec{x}) \). The latter is defined by the accuracy \( A = f(\vec{x}) \), precision \( P = f(\vec{x}) \), depth resolution \( D = f(\vec{x}) \) and lateral resolution \( L = f(\vec{x}) \) of each measured element \( i \). Another less physical component of the objective function is the monetary cost of an analysis \( C = f(\vec{x}) \).

\[
\text{minimize} \sum_{i=1}^{N^i} \left\| f_i \left( A_i(\vec{x}), P_i(\vec{x}), D_i(\vec{x}), L_i(\vec{x}), C_i(\vec{x}) \right) \right\|^2, \tag{3.14}
\]

where \( N^i \) is the total number of elements measured.

Before minimizing Eq. 3.14, the relevant experimental parameters must be selected. In the context of the quantification by EPMA, they can be roughly classified in three categories. First, the fixed parameters are defined by the instrumental setup, such as the type of electron emitter, the type of detector, the take-off angle and the solid angle of the detectors, etc. Changes in these parameters can lead to important improvements of the quantification capabilities. For example, the introduction of Schottky guns led to smaller probe size at low accelerating voltages or larger detectors, to improved sensitivity. As these parameters cannot be routinely modified for a given instrument, their optimization is beyond the reach of a regular microscopist. The second category contains the parameters which are part of the calibration. The PHA for WD spectrometers or the energy calibration for ED spectrometers are two examples. The assumption that these parameters are properly adjusted will be implied in the following paragraphs. Finally, the third category includes the accelerating voltage \( E_0 \), the beam current \( I_p \), the measuring time \( \tau \) and the X-ray transitions chosen for the analysis \( \vec{t} = \{t_0, \ldots, t_i, \ldots, t_{N^i}\} \). There are the four main adjustable experimental parameters that have the largest influence on the accuracy, precision and spatial resolution of the quantification [255].

These parameters are also part of the “expert system for EPMA” developed by Fournier et al. [115] for electron microprobes. Although the optimization strategy described here approaches the one of an “expert system”, it exclusively aims at finding best experimental parameters, assuming that the electron microscope and spectrometers are already well adjusted. Additionally, this work optimizes for the X-ray spatial resolution and includes the effect of carbon contamination. It automatizes the optimization procedure presented in [256].

Although it is non-adjustable, the sample composition \( \vec{w} = \{w_0, \ldots, w_i, \ldots, w_{N^i}\} \) is another critical parameter influencing the accuracy, precision and spatial resolution. It is obviously not known before performing the measurement and quantification, but
an approximate composition can usually be estimated in most cases. In the context of EPMA performed in an electron microprobe, the experimental parameters are confined by physical and practical limits. For the accelerating voltage and beam current, the boundaries are selected based on the beam diameter measurements presented in Fig. 3.4, numerically from 3 to 25 kV and 1 to 100 nA. The measuring time is bound from 1 to 500 s. As for the X-ray transitions, different combinations will be tested, but this study focuses on the influence of the K–L$_{2,3}$, L$_3$–M$_{4,5}$ and L$_3$–M$_1$ X-ray transitions on the measurements.

In order to solve for Eq. 3.15, a solver iterates over the dimensional space defined by the experimental parameters. From an initial guess, it calculates the objective function at each iteration and determines the gradient towards the next vector minimizing $f(\vec{x})$. The iterations continue until a minimum, either local or global minimum, is reached. The solver used in this work is the Levenberg-Marquardt algorithm, a damped non-linear Newtonian least square solver. The least square is denoted in Eq. 3.14 by the Euclidean norm $\|\ldots\|^2$.

This type of solve requires that the objective function is differentiable and $\partial f/\partial \vec{x}$ exists for any value of $\vec{x}$. It adds the constraint that the functions for the accuracy, precision, spatial resolution and cost return a value for any combination of accelerating voltage, beam current, measuring time and X-ray transitions for a given steel composition. To fulfill this requirement, interpolation between measured or calculated values was used to create continuous functions. All interpolations is based on bivariate spline approximation over a rectangular mesh, as implemented in the PYTHON library SciPY [174]. The differentiable condition also implies that the X-ray transitions $(\vec{t})$ cannot be optimized by a non-linear solver [394]. For instance, the X-ray transition for Fe is either K–L$_{2,3}$, L$_3$–M$_{4,5}$ or L$_3$–M$_1$; there is no intermediate X-ray transitions. To circumvent this mathematical problem, the optimization is performed for different sets of X-ray transitions, finding the best experimental parameters for each set.

Summarizing the last paragraphs, the vector $\vec{x}$ in Eq. 3.14 becomes $\{\vec{w}, E_0, I_p, \tau, \vec{t}\}$, where the vectors $\vec{w}$ and $\vec{t}$ are selected prior to the optimization, and $E_0$, $I_p$ and $\tau$ are the independent variables. For completeness, Eq. 3.14 can be written as:

$$\text{for given } \{\vec{w}, \vec{t}\}, \quad \text{minimize} \quad \sum_{i=1}^{N_t} \left\| \begin{array}{c} A_i(E_0, I_p, \tau, t_i, \vec{w}), \\ P_i(E_0, I_p, \tau, t_i, \vec{w}), \\ D_i(E_0, I_p, \tau, t_i, \vec{w}), \\ L_i(E_0, I_p, \tau, t_i, \vec{w}), \\ C_i(E_0, I_p, \tau, t_i, \vec{w}) \end{array} \right\|^2.$$ (3.15)

To evaluate the objective function, functions for the quality metrics, i.e. the accuracy, precision, lateral resolution, depth resolution and cost, as a function of the experimental parameters must be defined. A combination of experimental and simulated results were used to define these functions. The methodology, reasoning and assumptions are described in §3.4.1. It is then followed in §3.4.2 by a description regarding the implementation of the optimization equation (Eq. 3.15). The results for typical steel compositions are presented in §3.4.3. Finally, the limits of the optimization strategy and its possible applicability to other materials are discussed in §3.4.4.
3.4. Optimization of analytical conditions

3.4.1 Definition of quality metrics

The definition of the precision, depth and lateral resolution functions rely on X-ray intensities and spatial distributions calculated by 950 Monte Carlo simulations ran using NISTMONTE [300]. Eleven compositions, thirteen accelerating voltages and six beam currents were simulated. Each simulation used 50 000 electrons. The definition, execution and analysis of the simulations were performed with PYMONTECARLO [265].

The functions for accuracy and precision were designed to return relative values to facilitate their comparison for different elemental concentrations. As their is no reference point for the resolutions, the functions for the depth and lateral resolution return exact resolution values. The same goes for the monetary cost function which returns euros. The fact that the accuracy, precision, spatial resolutions and cost are expressed in different scales will be addressed in §3.4.2 by the selection of appropriate weights in the objective function.

3.4.1.1 Accuracy

The accuracy of quantification results depends on many factors: intensity models [263, 273], MACs [125, 214, 301], backscattering coefficients [301], oxidation/contamination effects [379], peak shape alterations [35], interference problems [235, 295], etc. For the purpose of this optimization strategy, the description of the accuracy is considerably simplified, concentrating on the scope of this work, i.e. to optimize the experimental parameters to quantify steel alloying elements. A more general description should undeniably implement a complete uncertainty budget as described by Ritchie and Newbury [301].

The choice of which X-ray transition is measured for a given element has a large influence on the accuracy. For overvoltages greater than 1.5, the quantification accuracy using the K–L$_2$,L$_3$ is generally accepted to be better than 2 % [124, 273]. At lower overvoltages, uncertainties in the ionization cross sections may lead to larger inaccuracies, although Armstrong [15] and Richter and Pinard [296] reported good results under these conditions. As explained in §2.4, the quantification using soft X-rays faces many challenges, especially for the L$_3$–M$_4$,M$_5$ X-ray transitions of first transition series metals. Tab. 2.6 relates relative deviations as high as 40 %. The accuracy using the L$_3$–M$_1$ X-ray transitions approaches the one using the K–L$_{2,3}$, but remains slightly worst as shown by deviations above 5 % for some samples in Tab. 2.8. Since the X-ray transitions are not directly optimized in the objective function, the accuracy function does not need to reflect these differences, but leaves the selection of the accurate set of X-ray transitions to the user.

Another factor influencing the accuracy is the carbon contamination. It primarily affects the accuracy of the carbon quantification, but also the quantification of other alloying elements when soft X-rays (L$_3$–M$_{4,5}$ and L$_3$–M$_1$) are used. As it will be studied in Chap. 4, the magnitude and influence of carbon contamination on a measurement depend on several factors, including the three experimental parameters subjected to the current optimization. Again for the sake of simplicity, the accuracy function only considers the influence of contamination on the carbon quantification as a function of the measuring time. Modelling of the other factors could certainly be envisaged for future improvements of the optimization strategy.
From §3.3.1 and Fig. 3.24, the absolute error on the carbon mass fraction was determined to be 0.02 mass % C for a 16-μm line scan acquisition on a 0.64 mass % C reference material. This yields a relative accuracy of 2.33 % for a dwell time, measuring time per measurement point, of 5 s. As proposed by Mitchell [226] and shown in §2.3.3.3, the height of the carbonaceous deposit seems to follow a square root relationship with the measuring time (Eq. 2.50). The rate constant depends on the experimental conditions, including whether an anti-contamination device is used. Assuming that the contamination observed after the first 5 μm of a line scan follows the square root relationship without any incubation period and that the accuracy is directly proportional to the the height of the carbonaceous deposit, the relative accuracy for carbon can be defined from the results of Fig. 3.24 as:

\[
A_C(E_0, I_p, \tau, t_C = K - L_{2.3}, \overline{w}) = 0.01\sqrt{\tau} + 0.02 ,
\]

where the last term, 0.02, reflects the generic inaccuracies associated with the quantification of any element. As only the accuracy on the carbon quantification is considered in the optimization, the overall accuracy function becomes:

\[
A_i(E_0, I_p, \tau, t_i, \overline{w}) = \begin{cases} 
0.01\sqrt{\tau} + 0.02, & \text{if } i = C \\
\text{ignore}, & \text{otherwise}
\end{cases} .
\]

### 3.4.1.2 Precision

As described in §3.3.2, the precision combines random and systematic uncertainties. Considering first the random uncertainties, they follow Poisson statistics, varying with the square root of the number of detected X-rays, i.e. the X-ray intensity. In total, four intensities are measured to formulate a k-ratio and quantify any given element, the peak and background X-ray intensities on the unknown sample and reference material. Propagating the random uncertainty associated with each intensity measurement through Eq. 2.39, the relative uncertainty \( \sigma(k)/k \) on the k-ratio of element \( i \) is:

\[
\left( \frac{\sigma(k_i)}{k_i} \right)^2 = \left( \frac{\sigma(I_i^{\text{unk}})}{I_i^{\text{unk}}} \right)^2 + \left( \frac{\sigma(I_i^{\text{ref}})}{I_i^{\text{ref}}} \right)^2 + \frac{\sigma^2(I_i^{\text{peak,unk}}) + \sigma^2(I_i^{\text{bckg,unk}})}{(I_i^{\text{peak,unk}} - I_i^{\text{bckg,unk}})^2} + \frac{\sigma^2(I_i^{\text{peak,ref}}) + \sigma^2(I_i^{\text{bckg,ref}})}{(I_i^{\text{peak,ref}} - I_i^{\text{bckg,ref}})^2} \\
= \frac{\sqrt{I_i^{\text{peak,unk}}}}{I_i^{\text{peak,unk}} - I_i^{\text{bckg,unk}}} + \frac{\sqrt{I_i^{\text{bckg,unk}}}}{I_i^{\text{peak,unk}} - I_i^{\text{bckg,unk}}} + \frac{\sqrt{I_i^{\text{peak,ref}}}}{I_i^{\text{peak,ref}} - I_i^{\text{bckg,ref}}} + \frac{\sqrt{I_i^{\text{bckg,ref}}}}{I_i^{\text{peak,ref}} - I_i^{\text{bckg,ref}}} \\
= \frac{I_i^{\text{peak,unk}} + I_i^{\text{bckg,unk}}}{(I_i^{\text{peak,unk}} - I_i^{\text{bckg,unk}})^2} + \frac{I_i^{\text{peak,ref}} + I_i^{\text{bckg,ref}}}{(I_i^{\text{peak,ref}} - I_i^{\text{bckg,ref}})^2} .
\]

(3.18)
where \( I \) is the X-ray intensity (in count). If different measuring times or beam currents are used to measure the intensities, the relative uncertainty on the unknown or reference intensity can be written using normalized intensities (\( I' \)) expressed in count s\(^{-1}\) A\(^{-1}\):

\[
\frac{\sigma(I_i)}{I_i} = \sqrt{\frac{I_{i,\text{peak}}' I_{p,\text{peak}} - I_{i,bckg}'}{I_{p,\text{peak}}'}},
\]

where \( I_p \) is the beam current (in A), and \( \tau \), the measuring time (in s). From Eq. 3.18, the contribution of the reference material to the k-ratio uncertainty of element \( i \) is usually negligible in comparison to the unknown, as the reference material has a larger concentration of element \( i \), a higher X-ray intensity, and thus a lower relative uncertainty. In the optimization, only the uncertainties from the unknown are considered and \( \sigma(I_{i,\text{ref}}')/I_{i,\text{ref}}' \) is ignored.

To evaluate \( \sigma(I_{i,\text{ref}}')/I_{i,\text{ref}}' \), a simple model was developed based on X-ray intensities calculated by Monte Carlo simulations [256]. It allows to quickly estimate the random uncertainties from simulated intensities or different sample compositions, accelerating voltages and beam currents without the need of experimental intensity measurements. As the uncertainties can only be calculated with experimental intensities, the model makes the assumption that the simulated intensities are directly proportional to the experimental ones. The proportionality is only valid for a specific X-ray transition as the detector efficiency changes based on the selected dispersive element and type of counting detector as well as the solid angle, based on the dispersive element position. The premise also disregards possible inaccuracy in fundamental parameters such as the ionization cross-section and fluorescence yield [120].

To calculate the proportionality constant for each X-ray transition and dispersive element, the peak and background intensities were measured on different reference materials at various accelerating voltages. The resulting net X-ray intensities were compared to the characteristic X-ray intensity obtained from the simulations. The simulated background intensities were obtained by summing the X-ray counts over a 10-eV energy range below each X-ray peak in the simulated ED spectra of an ideal detector without characteristic X-ray peaks. The theoretical concept of an ideal detector practically means a windowsless detector with 100% efficiency. An example is shown in Fig. 3.27 for the Fe K–L\(_{2,3}\) peak.

The proportionality between simulated and experimental intensities can be assessed from Fig. 3.28, where the intensities from different X-ray transitions of Fe are plotted. The proportionality constant \( m \) is calculated by linear regression, enforcing that the intercept \( b \) equals 0 (no simulated X-ray should give no experimental X-ray):

\[
I_{i,\text{exp}}' = m I_{i,\text{sim}}' + b'.
\]

The calculated constants are listed in Tab. 3.8. For a given X-ray transition, two constants are given, one for the net intensity and one for the background intensity, since the simulated intensities are obtained from two different results of the Monte Carlo simulations. Fig. 3.28 shows the influence of the dispersive element on the intensity of the L\(_3\)–M\(_{4,5}\) X-rays. The higher efficiency of the LDE1 crystal translates into a higher proportionality constant for this dispersive element in comparison to the TAP crystal.
Figure 3.27: Simulated ED spectrum around the Fe K–L\(_{2,3}\) peak for a pure iron sample at 10 kV. The shaded area shows the area selected for the simulated background intensity.

<table>
<thead>
<tr>
<th>X-ray transition</th>
<th>Dispersive element</th>
<th>Proportionality constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K–L(_{2,3})</td>
<td>LDE2H</td>
<td>1.06 \times 10^{-6} 5.77 \times 10^{-7}</td>
</tr>
<tr>
<td>Si K–L(_{2,3})</td>
<td>TAP</td>
<td>8.02 \times 10^{-7} 1.04 \times 10^{-6}</td>
</tr>
<tr>
<td>Cr K–L(_{2,3})</td>
<td>LIF</td>
<td>2.84 \times 10^{-7} 5.74 \times 10^{-7}</td>
</tr>
<tr>
<td>Cr L(<em>{3-M</em>{4.5}})</td>
<td>LDE1</td>
<td>7.15 \times 10^{-7} 7.62 \times 10^{-7}</td>
</tr>
<tr>
<td>Cr L(<em>{3-M</em>{1}})</td>
<td>LDE1</td>
<td>7.15 \times 10^{-7} 7.62 \times 10^{-7}</td>
</tr>
<tr>
<td>Mn K–L(_{2,3})</td>
<td>LIFH</td>
<td>1.18 \times 10^{-6} 3.60 \times 10^{-6}</td>
</tr>
<tr>
<td>Mn L(<em>{3-M</em>{4.5}})</td>
<td>LDE1</td>
<td>8.49 \times 10^{-7} 1.09 \times 10^{-6}</td>
</tr>
<tr>
<td>Mn L(<em>{3-M</em>{1}})</td>
<td>LDE1</td>
<td>8.49 \times 10^{-7} 1.09 \times 10^{-6}</td>
</tr>
<tr>
<td>Fe K–L(_{2,3})</td>
<td>LIF</td>
<td>6.21 \times 10^{-7} 1.20 \times 10^{-6}</td>
</tr>
<tr>
<td>Fe L(<em>{3-M</em>{4.5}})</td>
<td>LDE1</td>
<td>1.10 \times 10^{-6} 1.75 \times 10^{-6}</td>
</tr>
<tr>
<td>Fe L(<em>{3-M</em>{1}})</td>
<td>TAP</td>
<td>8.13 \times 10^{-8} 6.63 \times 10^{-8}</td>
</tr>
<tr>
<td>Fe L(<em>{3-M</em>{1}})</td>
<td>LDE1</td>
<td>1.10 \times 10^{-6} 1.75 \times 10^{-6}</td>
</tr>
</tbody>
</table>

Table 3.8: Proportionality constants calculated from the linear regression of the simulated and experimental net and background intensities: \( I^{\text{exp}} = m I^{\text{sim}} \).
3.4. Optimization of analytical conditions

Figure 3.28: Comparison between experimental and simulated (a) net and (b) background intensities for Fe. Measurements and simulations at 3, 5, 810, 15 and 20 kV are shown. The dash lines are the linear regression fit.
Based on the relationships between the simulated and experimental intensities, the relative random uncertainties on the k-ratio, i.e. the relative precision on the quantification, can be calculated for different combinations of accelerating voltages, beam currents, measuring times and X-ray transitions by merging Eq. 3.18, 3.19 and 3.20 and assuming that the measuring time for the peak and background are equal ($\tau = \tau_{\text{peak}} = \tau_{\text{bckg}}$), and that $\sigma(I',\text{net}) \approx \sigma(I',\text{peak})$:

$$P_i(E_0, I_p, \tau, t_{i,k}, \vec{w}) = n\frac{\sigma(I_{\text{unk}})}{I_{\text{unk}}}$$

$$= n \sqrt{m_{\text{net}} I_i^{\text{sim,net}}(E_0, t_{i,k}, \vec{w}) I_p \tau + m_{\text{bckg}} I_i^{\text{sim,bckg}}(E_0, t_{i,k}, \vec{w}) I_p \tau}$$

$$m_{\text{net}} I_i^{\text{sim,net}}(E_0, t_{i,k}, \vec{w}) I_p \tau$$

(3.21)

where $t_{i,k}$ is the $k$ X-ray transition of element $i$, and $n$, the confidence index. The assumption of identical measuring time for the peak and background intensities is conformed with the acquisition strategy described in §3.2.1, where the background intensities are measured on pure iron using the same experimental parameters as the peak intensities on the unknown sample.

Fig. 3.29 shows the relative precision using the C K–L$_{2,3}$, Mn K–L$_{2,3}$ and Mn L$_{3}$–M$_{4,5}$ X-ray transitions for a sample containing C, Si, Cr and Mn, each with a mass fraction of 1%, as a function of the accelerating voltage and electron dose. The electron dose (in Coulomb) is the product of the beam current and the measuring time. For all three X-ray transitions, increasing the electron dose improves the relative precision. At 15 kV, an electron dose of 100 nC is necessary to have a relative precision below 5% using the C K–L$_{2,3}$ and Mn K–L$_{2,3}$ X-ray transitions, whereas the Mn L$_{3}$–M$_{4,5}$ requires an electron dose of 5000 nC. The decrease of the X-ray intensity at low overvoltage, i.e. at accelerating voltage just above the ionization energy, is demonstrated by the steep increase of the relative precision for all three X-ray transitions, but especially for the Mn K–L$_{2,3}$. The worsening of the C K–L$_{2,3}$ relative precision at high accelerating voltages can be explained by the increase of the photoelectric absorption, decreasing the X-ray intensity. At higher electron doses, this effect is relatively less pronounced due to the higher X-ray intensities.

In the case of first transition series metals, the X-ray intensity can be measured from three transitions. The influence of this choice can be visually assess from Fig. 3.30, where the relative precision of iron in the aforementioned hypothetical sample is plotted for its three X-ray transitions at an electron dose of 500 nC. Below an accelerating voltage of 12 kV, it becomes more advantageous, from a precision point of view, to use the L$_{3}$–M$_{4,5}$ X-ray transition instead of the K–L$_{2,3}$. Due to its higher X-ray reflectivity, the layered dispersive element, LDE1, is a better choice to improve the precision using the L$_{3}$–M$_{4,5}$ X-ray transition, although the accuracy might be affected due to the poorer spectral resolution. Besides the spectral resolution, the accuracy of the L$_{3}$–M$_{4,5}$ X-ray transition suffers from other factors described in §2.4, which led authors to suggest the use of the L$_{3}$–M$_{1}$ instead for quantification. The main disadvantage of this solution is clearly illustrated in Fig. 3.30, where significantly higher uncertainties were calculated for this X-ray transition, even if the sample contains 96 mass% Fe. From the relative precision calculations based on Monte Carlo
3.4. Optimization of analytical conditions

(a) C K–L$_{2,3}$

(b) Mn K–L$_{2,3}$
Chapter 3. High resolution characterization of steel microstructure

Figure 3.29: Relative precision of the (a) C K–L\textsubscript{2,3}, (b) Mn K–L\textsubscript{2,3} and (c) Mn L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions as a function of the accelerating voltage and electron dose. Sample contains 1 mass % of C, Si, Cr and Mn, balance Fe.

simulations, it seems unlikely that the L\textsubscript{3}–M\textsubscript{1} can be used to precisely measure low concentration elements, such as Mn and Cr from the hypothetical sample, unless an electron dose of more than 5 mC is used.

To complete the definition of the precision function, the remaining part is the systematic uncertainties. From §3.3.2, the systematic uncertainties associated with the carbon quantification were shown to vary between 0.003 to 0.04 mass % C for the line scan acquisition strategy. The fluctuations were attributed to the instability and inhomogeneity of the contamination level. To reflect this source of uncertainty, an offset of 2\%, the average of the systematic uncertainties from Fig. 3.25, is added to the relative precision of the C K–L\textsubscript{2,3} X-ray transition. This influence of the carbon contamination on the other soft X-rays (L\textsubscript{3}–M\textsubscript{4,5} and L\textsubscript{3}–M\textsubscript{1}) is ignored as for the accuracy. This gives the follow precision function for the optimization:

\[
P_i(E_0, I_p, \tau, t, \bar{w}) = \begin{cases} 
   \text{Eq. } 3.21 + 0.02, & \text{if } i = \text{C} \\
   \text{Eq. } 3.21, & \text{otherwise}
\end{cases} \tag{3.22}
\]

Note that the confidence index \( n \) should be selected \textit{a priori} (Eq. 3.21). Unless specified \( n = 1 \) is used in this work.

### 3.4.1.3 Spatial resolution

In EPMA, the spatial resolution is defined by the X-ray emission volume where the detected X-rays are emitted. For the optimization, the size of the X-ray emission volume is evaluated based on its depth and radial extent. These are the two critical
Figure 3.30: Relative precision of the Fe K–L\textsubscript{2,3}, L\textsubscript{3}–M\textsubscript{4,5} and L\textsubscript{3}–M\textsubscript{1} X-ray transitions as a function of the accelerating voltage at an electron dose of 500 nC. Sample contains 1 mass\% of C, Si, Cr and Mn, balance Fe.

dimensions, since the X-ray emission volume of an homogeneous sample is radially symmetrical. The lateral resolution is therefore defined as twice the radial resolution. While the measuring time has no influence on the spatial resolution, the X-ray transition measured, the sample composition and primarily the accelerating voltage change the size of the X-ray emission volume. As for the beam current, it has an indirect influence on the lateral resolution in concert with accelerating voltage, since the beam diameter varies with these two experimental parameters. The effects of all these factors were simulated in order to calculate the spatial resolution.

From the Monte Carlo simulations, the depth resolution is extracted from the $\phi(z)$ distribution, X-ray emission probability as a function of the depth $z$, available in NISTMONTE [300], whereas a new radial distribution, X-ray emission probability as a function of the radius $r$, was created for the radial resolution. Often disregarded by Monte Carlo programs, one important consideration for this distribution is to either normalize the X-ray probability by the area covered by each radius interval, or to setup the radius intervals to have an equal area on the sample surface. Otherwise, it is clear that a smaller area, like the one close to the electron beam, would return a smaller X-ray probability. From these distributions, the resolution was defined as the distance, the depth or radius, where 95\% of the X-rays are emitted. Mathematically the following equation is solved for $d$:

$$0.95 = \frac{\int_{x=0}^{d} f(x) \, dx}{\int_{x=0}^{\infty} f(x) \, dx} , \quad (3.23)$$
Chapter 3. High resolution characterization of steel microstructure

Figure 3.31: Depth resolution of the C K–L$^{2,3}$, Fe K–L$^{2,3}$, L$_{3}$–M$_{4,5}$ and L$_{3}$–M$_{1}$ X-ray transitions as a function of the accelerating voltage. Sample contains 1 mass% of C, Si, Cr and Mn, balance Fe.

where $f(x)$ represents the X-ray emission probability distribution as a function of either the depth or radius. Examples of each distribution are shown in the following paragraphs.

The calculated values for the depth and lateral resolution are then used to construct an empirical equation relating the resolution to the accelerating voltage and beam current for each sample composition and X-ray transition. The value returned by these spline functions is directly used in Eq. 3.15 to calculate $D_i$ and $L_i$.

**Depth** Similarly to Fig. 2.28, Fig. 3.31 shows the depth resolution as a function of the accelerating voltage for the C K–L$_{2,3}$ and the three Fe X-ray transitions. The same sample as Fig. 3.29 and 3.30 is used in these simulations. Without any surprise, the resolution of all X-ray transitions improves as the accelerating voltage decreases. Interestingly below 9 kV, there is no significant difference between the resolution of the C K–L$_{2,3}$, Fe L$_{3}$–M$_{4,5}$ and Fe L$_{3}$–M$_{1}$, simplifying the interpretation of the results as all X-rays are emitted from approximately the same volume. For the soft X-ray transitions, the photoelectric absorption limits the increase of the resolution at high accelerating voltages, particularly for the C K–L$_{2,3}$ X-ray transition. As shown in Fig. 3.32a, most of the emitted X-rays come from a shallow depth in comparison to the total X-ray generation volume. At 10 kV, only 27.5% of the generated X-rays escape the sample. In other words, although the photoelectric absorption worsens the precision by decreasing the X-ray intensity (the area under the curves of Fig. 3.32a), it improves the depth resolution of the C K–L$_{2,3}$ X-ray transition in steels.
3.4. Optimization of analytical conditions

Figure 3.32: Simulated (a) depth and (b) radial X-ray emission distribution of the C K–L$_{2,3}$ X-ray transition at four accelerating voltages. The distributions with and without absorption are shown. The simulated results were filtered using the Savitzky-Golay algorithm to remove noise. Sample contains 1 mass % of C, Si, Cr and Mn, balance Fe.
Lateral The effect of the photoelectric absorption of C K–L$_{2,3}$ X-ray transition is also observed in the lateral resolution. In Fig. 3.32b, the lateral X-ray distribution with absorption, i.e. the true distribution, remains near the impact point of the electron beam (at 0 nm) even as the accelerating voltage increases. At high accelerating voltages, X-rays generated at a large radial distance from the electron beam are also likely to be generated at a large depth, as the incident electrons travel deeper inside the sample. The exceptions are C K–L$_{2,3}$ X-rays generated by BSEs closer to the surface. These X-rays explain the decaying tail of the X-ray distributions.

As for the depth resolution, decreasing the accelerating voltage improves the lateral resolution as shown in Fig. 3.32b. This is more explicitly shown in Fig. 3.33, where the lateral resolution is plotted as a function of the accelerating voltage for different beam currents for the C K–L$_{2,3}$, Fe K–L$_{2,3}$ and Fe L$_{3–M4,5}$ X-ray transitions. For beam currents greater than 10 nA, the improvement of the C K–L$_{2,3}$ and Fe L$_{3–M4,5}$ lateral resolution at lower accelerating voltages reaches a minimum between 4 and 7 kV. The interpretation of these results requires the reexamination of Fig. 3.4, where the diameter of the electron beam was experimentally determined for different combinations of accelerating voltages and beam currents. These beam diameters, taken as the FWHM of a Gaussian distributed beam, were also used in the Monte Carlo simulations to reflect the experimental limitations of the electron focusing optics. The presence of minimums in the lateral resolution distributions of Fig. 3.33 correlates with the steeper increase of the beam diameter at high beam currents and low accelerating voltages, shown in Fig. 3.4. At some accelerating voltage, the enlargement of the beam diameter becomes the dominating factor on the resolution, instead of the X-ray emission volume. In sum, this puts a limit on the resolution improvements of low accelerating voltage measurements. Finding this limit while maintaining a good precision with a sufficient electron dose and a good accuracy with a small measuring time to prevent extensive carbon contamination is at the core of the optimization problem described in this section.

Moreover, the improvement of the resolution at small overvoltage ratios is demonstrated for the Fe K–L$_{2,3}$ X-ray transition in Fig. 3.31 and 3.33. At 10 kV, a better lateral resolution is achieved using the Fe K–L$_{2,3}$ than the L$_{3–M4,5}$ X-ray transition, even at much lower accelerating voltages. Again here, the gain in spatial resolution at low overvoltages must be weighted against the accuracy, precision and spatial resolution of all measured X-ray transitions.

3.4.1.4 Monetary cost

The cost of an analysis is added to the objective function to constrain the measuring time. A long measuring time would undeniably give a very precise measurement, but would also block the electron microscope for several hours. The monetary cost function is constructed based on the hourly rate for the instrument ($\dot{r}$) and the number of points to measure ($M$):

$$C_i(E_0, I_p, \tau, t_i, \bar{w}) = \dot{r}M\tau. \quad (3.24)$$
3.4. Optimization of analytical conditions

(a) C K–L$_{2,3}$

(b) Fe K–L$_{2,3}$
Chapter 3. High resolution characterization of steel microstructure

Figure 3.33: Lateral resolution of the (a) C K–L$_{2,3}$, (b) Fe K–L$_{2,3}$ and (c) Fe L$_{3}$–M$_{4,5}$ X-ray transitions as a function of the accelerating voltage for different beam currents. Sample contains 1 mass% of C, Si, Cr and Mn, balance Fe.

It is independent of all experimental parameters except the measuring time. The choice of the hourly rate and number of points will influence the objective of the optimization. For instance, if only a dozen of points need to be measured, the measuring time can be extended. On the other side, a shorter measuring time is more optimal for line scan acquisitions.

In this work, the hourly rate is set to 150 €/h and the number of points to 400 points. The latter corresponds to the number of points normally used in a line scan acquisition.

3.4.2 Implementation

The optimization algorithm is implemented in PYTHON using the lmfit [239] and SciPy [174] libraries. After selecting the sample composition ($\vec{w}$) and the set of X-ray transitions to optimize, the optimizer function calculates the optimal accelerating voltage, beam current and measuring time. Internally, each function described above is called with the experimental parameters, vector $\vec{x}$. The return values are tabulated in a matrix consisting of 5 rows, one row for each function, and $N^i$ columns, one column for each X-ray transition. As the quality of a measurement rests on the X-ray transition with the worst accuracy, precision and spatial resolution, the maximum value in each row of the matrix is calculated, resulting in a vector containing five values to be minimized by the least square solver.
3.4. Optimization of analytical conditions

In optimization problems, one challenge of the solver is to find the global minimum and not to get stuck in a local minimum. To circumvent this problem, the initial values of the accelerating voltage, beam current and measuring time are randomly selected within their respective allowed range. This process is repeated 30 times, each time yielding a new solution. After removing outliers using the “winsorisation” algorithm [137], the average of these solutions is taken as the optimal solution, and the standard deviation is an indication of its robustness.

As aforementioned, a critical aspect of the optimization is the selection of the weights in order to optimize values with different units. For example, how does a relative accuracy of 4% compare with a depth resolution of 400 nm or a cost of 40 €. No ideal solution was found to automatically select the weights, except trial and errors in order to obtain reasonable accuracy, precision, spatial resolutions and cost. The following weights were selected for the accuracy, precision, depth resolution, lateral resolution and monetary cost functions respectively: 1, 5, \(10^6\), \(10^6\) and 0.0025.

From these details, Eq. 3.15 can be updated to reflect the current implementation:

\[
\begin{align*}
\text{for given } \{\vec{w}, \vec{t}\}, \quad \text{minimize} \quad & \max_{\vec{w}} \begin{bmatrix}
w_A A_i(E_0, I_p, \tau, t_i, \vec{w}) \\
w_P P_i(E_0, I_p, \tau, t_i, \vec{w}) \\
w_D D_i(E_0, I_p, \tau, t_i, \vec{w}) \\
w_L L_i(E_0, I_p, \tau, t_i, \vec{w}) \\
w_C C_i(E_0, I_p, \tau, t_i, \vec{w})
\end{bmatrix}^2
\end{align*}
\]

where \(w_g\) represents the weight of function \(g\), and \(\max\) indicates that the maximum value from the values calculated for each element \(i\) is taken.

3.4.3 Results

The developed optimization will be tested against different experimental scenarios and goals. For each solution, the optimal accelerating voltage, beam current and measuring time are reported, including their standard deviation calculated from the repeated solutions. The calculated accuracy, precision, depth resolution, lateral resolution and monetary cost of each X-ray transition using these experimental parameters is also listed in a complementary table.

3.4.3.1 Only carbon

The first scenario is the simplest one; the goal is to find the optimal experimental parameters to measure the carbon concentration in steels, regardless of the other alloying elements. From a quantification point of view, it would require to either know their concentrations, or to neglect them, assuming the balance as iron.

For a hypothetical sample containing C, Si, Cr and Mn, each with a mass fraction of 1%, the best solution from the optimization is an accelerating voltage of 5.3 kV, a beam current of 67.1 nA and a measuring time of 3.0 s. The accuracy, precision, depth resolution, lateral resolution and cost are given in Tab. 3.9. In comparison to the experimental conditions used to develop the carbon quantification in §3.2.1, the depth and lateral resolutions of the C K–L\(_{2,3}\) X-ray transition are improved, 220 to
Chapter 3. High resolution characterization of steel microstructure

<table>
<thead>
<tr>
<th>Accelerating voltage (kV)</th>
<th>Beam current (nA)</th>
<th>Measuring time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3130 ± 0.0030</td>
<td>67.0993 ± 0.0853</td>
<td>2.9711 ± 0.0034</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X-ray transition</th>
<th>Dispersive element</th>
<th>Accuracy (%)</th>
<th>Precision (%)</th>
<th>Depth (nm)</th>
<th>Lateral (nm)</th>
<th>Cost (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K–L_{2,3}</td>
<td>LDE2H</td>
<td>3.7</td>
<td>4.7</td>
<td>83.4</td>
<td>211.1</td>
<td>49.5</td>
</tr>
</tbody>
</table>

Table 3.9: Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze only carbon.

107 nm and 505 to 280 nm respectively, without sacrificing the precision or increasing the measuring time. This improvement is achieved by decreasing the accelerating voltage from 15 to 5.3 kV and reducing the beam current from 100 to 67 nA.

All things considered, the hypothetical sample used in the optimization contains a fairly high amount of carbon for a low alloy steel (1 mass % C). To evaluate the influence of the carbon concentration on the optimal experimental parameters, the optimization was repeated for carbon mass fractions from 0.1 to 1.0 %. The results are shown in Fig. 3.34. As the carbon concentration decreases, the optimal measuring time increases to compensate for the lower X-ray intensity and minimize the loss in precision. Nonetheless, the precision worsens at low carbon concentrations up to 10 % for a carbon mass fraction of 0.1 %, a precision of 0.01 mass % C in absolute terms. The accuracy and monetary cost follow the measuring time since the carbon contamination and the total measuring time increases. Below 0.3 mass % C, the beam current reaches the maximum allowable value in this optimization (100 nA). It is conceivable that higher beam currents might be more beneficial to measure low carbon concentrations. As seen in Fig. 3.33a, increasing the beam current shifts to higher values the optimal accelerating voltage to obtain the best lateral resolution. This is also observed in Fig. 3.34. The slightly higher accelerating voltage minimizes the worsening of the lateral resolution, which remains relatively constant at all carbon concentrations. In sum, the carbon concentration mostly impacts the optimal measuring time.

### 3.4.3.2 Using the K–L_{2,3} X-ray transitions

With an optimal accelerating voltage of 5.3 kV, the previous optimization would imply the use of the L_{3–M_{4,5}} or L_{3–M_{1}} X-ray transitions for the quantification of Cr, Mn and Fe. With all the challenges associated with the quantification using soft X-rays (§2.4), increasing the accelerating voltage might still pass as a valid alternative, albeit the loss of spatial resolution. In a sense, this scenario trades off the spatial resolution for a better accuracy.

For the same hypothetical sample, the best solution from the optimization with all alloying elements is an accelerating voltage of 11.0 kV, a beam current of 100.0 nA and a measuring time of 5.3 s. The change in the quality metrics for these experimental parameters can be observed in Tab. 3.10.

The increase of the accelerating voltage from 5.3 to 11.0 kV results in the worsening of the depth and lateral resolutions of the C K–L_{2,3} X-ray transition by 83 and 184 nm respectively. The spatial resolution is however governed by the Si K–L_{2,3} X-ray transition with a depth resolution of 271 nm and a lateral resolution of 355 nm. The
3.4. Optimization of analytical conditions

Figure 3.34: Variation of (a) the optimal experimental parameters and (b) resulting quality metrics as a function of the carbon mass fraction in a hypothetical steel also containing 1 mass% of Si, Cr and Mn.
Chapter 3. High resolution characterization of steel microstructure

<table>
<thead>
<tr>
<th>Accelerating voltage (kV)</th>
<th>Beam current (nA)</th>
<th>Measuring time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9785 ± 0.0004</td>
<td>99.9999 ± 0.0002</td>
<td>5.3323 ± 0.0007</td>
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</table>

<table>
<thead>
<tr>
<th>X-ray transition</th>
<th>Dispersive element</th>
<th>Accuracy (%)</th>
<th>Precision (%)</th>
<th>Depth (nm)</th>
<th>Lateral (nm)</th>
<th>Cost (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>K–L₂,₃</td>
<td>LDE2H</td>
<td>4.3</td>
<td>3.7</td>
<td>183.8</td>
<td>360.7</td>
</tr>
<tr>
<td>Si</td>
<td>K–L₂,₃</td>
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<td>1.3</td>
<td>270.5</td>
<td>354.5</td>
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<tr>
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<td>K–L₂,₃</td>
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<tr>
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<td>220.2</td>
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<tr>
<td>Fe</td>
<td>K–L₂,₃</td>
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<td>...</td>
<td>0.5</td>
<td>187.3</td>
<td>198.9</td>
</tr>
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</table>

Table 3.10: Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze the alloying elements using their K–L₂,₃ X-ray transition.

The large overvoltage and low absorption of the Si K–L₂,₃ X-ray transition explain its worst spatial resolution. Oppositely, the low overvoltage restrains the X-ray emission volume of the Cr K–L₂,₃, Mn K–L₂,₃ and Fe K–L₂,₃ X-ray transitions. With its high concentration, the precision on Fe is not affected by the low overvoltage. It is another story for the precision on Mn and especially Cr. Both elements have a worst precision than C, even though they have the same concentration. Their higher precision follows the trends observed in Fig. 3.29b.

With respect to the default experimental parameters to quantify steel (15 kV, 100 nA, 5 s), the optimization suggests improvements of the measurement quality by lowering the accelerating voltage. To assess these improvements, Tab. 3.11 gives the quality metrics for the default experimental parameters used in §3.2.1. Overall, the optimal experimental parameters deliver a better spatial resolution for all elements and precision for carbon. The downsides are the higher precision for Cr and Mn, and the higher cost of analysis. It comes down to the selection of the weights in the objective function (Eq. 3.25). Lowering the weight of the depth and lateral resolutions from $1 \times 10^6$ to $0.3 \times 10^6$ would change the optimal experimental parameters to an accelerating voltage of 15.1 kV, a beam current of 97.6 nA and a measuring time of 3.6 s, approaching the default values. Regardless of the weights, the quantification of all alloying elements with their K–L₂,₃ X-ray transition inevitably requires a higher accelerating voltage than the quantification of only carbon. The extent of this increase depends on the desired precision and spatial resolution.

3.4.3.3 Using the L₃–M₄,₅ X-ray transitions

The study of this scenario is purely theoretical as the large inaccuracies associated with the L₃–M₄,₅ X-ray transitions of Cr, Mn and Fe prevent their use for quantification. The optimal experimental parameters found by the solver are an accelerating voltage of 8.1 kV, a beam current of 100 nA and a measuring time of 8.5 s, giving the quality metrics presented in Tab. 3.12. The first observation is that the optimal accelerating voltage is higher than the 5 kV expected for low accelerating voltage measurements. The precision on Cr and Mn puts a limit on the decrease of the accelerating voltage. Both elements have a worst precision at 8.1 kV than at 11.0 kV.
3.4. Optimization of analytical conditions

<table>
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<th>Accelerating voltage (kV)</th>
<th>Beam current (nA)</th>
<th>Measuring time (s)</th>
</tr>
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<tbody>
<tr>
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<td>100</td>
<td>5</td>
</tr>
<tr>
<td>X-ray Dispersive Accuracy</td>
<td>Precision</td>
<td>Depth</td>
</tr>
<tr>
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<td>LDE2H</td>
<td>4.2</td>
</tr>
<tr>
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<td>...</td>
</tr>
<tr>
<td>Cr K–L$_{2,3}$</td>
<td>LIF</td>
<td>...</td>
</tr>
<tr>
<td>Mn K–L$_{2,3}$</td>
<td>LIFH</td>
<td>...</td>
</tr>
<tr>
<td>Fe K–L$_{2,3}$</td>
<td>LIF</td>
<td>...</td>
</tr>
</tbody>
</table>

Table 3.11: Accuracy, precision, depth resolution, lateral resolution and cost for the default experimental parameters presented in §3.2.1.

<table>
<thead>
<tr>
<th>Accelerating voltage (kV)</th>
<th>Beam current (nA)</th>
<th>Measuring time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1229 ± 0.0006</td>
<td>100.0000 ± 2.7563 × 10$^{-5}$</td>
<td>8.4990 ± 0.0008</td>
</tr>
<tr>
<td>X-ray Dispersive Accuracy</td>
<td>Precision</td>
<td>Depth</td>
</tr>
<tr>
<td>C K–L$_{2,3}$</td>
<td>LDE2H</td>
<td>4.9</td>
</tr>
<tr>
<td>Si K–L$_{2,3}$</td>
<td>TAP</td>
<td>...</td>
</tr>
<tr>
<td>Cr L$<em>{3}$–M$</em>{4,5}$</td>
<td>LDE1</td>
<td>...</td>
</tr>
<tr>
<td>Mn L$<em>{3}$–M$</em>{4,5}$</td>
<td>LDE1</td>
<td>...</td>
</tr>
<tr>
<td>Fe L$<em>{3}$–M$</em>{4,5}$</td>
<td>LDE1</td>
<td>...</td>
</tr>
</tbody>
</table>

Table 3.12: Accuracy, precision, depth resolution, lateral resolution and cost for the optimal solution found to analyze the alloying elements using their L$_{3}$–M$_{4,5}$ X-ray transition.

Despite a longer measuring time (8.5 s vs. 5.3 s). This tendency of the precision is shown in Fig. 3.29c, where the precision on Mn worsens as the accelerating voltages decreases. The combination of low concentrations with the low X-ray fluorescence of L$_{3}$–M$_{4,5}$ X-ray transitions hinders the improvements of the spatial resolution at low accelerating voltages.

Overlooking the cost of analysis, the optimization finds a lower optimal accelerating voltage, 5.4 kV, but with a 26 times longer measuring time, 223.7 s per point. The optimal beam current would be 60.4 nA. With these experimental parameters, the precision on all elements falls below 4 % with similar depth and lateral resolutions as those in Tab. 3.9. These good quality metrics however come at an impossible price of a 400-point line scan acquisition lasting more than one day. Besides the cost of such measurement, the instability of the instrument would certainly also affect its accuracy. A more feasible solution would be to increase the solid angle by using more than one spectrometer for Cr and Mn.
3.4.3.4 Using the $L_3$–$M_1$ X-ray transitions

Based on the results of the previous scenario, the one where the $L_3$–$M_1$ X-ray transitions are used for the quantification of steels containing low concentrations of Cr and Mn may even be more hypothetical. At 10 kV, the X-ray intensity of the $L_3$–$M_1$ X-ray transitions for Cr, Mn and Fe is respectively 13, 44 and 64% lower than the one of the $L_3$–$M_{15}$ X-ray transitions, based on the X-ray intensities obtained by Monte Carlo simulations. This undoubtedly adds pressure on the solver to minimize the precision. As such, the optimal accelerating voltage is pushed to even a higher value than in §3.4.3.3, 16.8 kV. It however has little effect on the precision on Cr and Mn which escalates above 130%. Even relaxing the optimization from the cost constraint does not improve the results; the optimal accelerating voltage remains above 15 kV while the measuring time hits the upper limit of 500 s. In a caricatural manner, the good accuracy of the $L_3$–$M_1$ X-ray transitions hits the “precision wall”. Unless the detection efficiency is significantly increased, their use for quantification of low concentration elements appears hopeless.

3.4.4 Discussion

The conclusions drawn from the results presented in the last section hang on the accuracy of the Monte Carlo simulations and the fundamental parameters used in these simulations. For instance, a higher transition probability or a lower MAC for the Mn $L_3$–$M_1$ X-ray transition would lead to a different precision and ultimately to different optimal experimental parameters. The influence of the uncertainty on the fundamental parameters should technically be included in the optimization problem as Ritchie and Newbury [301] did in their uncertainty budget. Other potential sources of errors are the experimentally determined values, the beam diameter and X-ray intensities used to calculate the proportionality constants (Eq. 3.20). The enlargement of the beam diameter at low accelerating voltages and high beam currents is a critical factor limiting the improvement of the lateral resolution. As the extent of this enlargement is instrument specific and may change with the re-alignment of the electron column, the optimization may produce different conclusions. The same applies to the X-ray intensities, where the configuration and adjustment of the spectrometers have a large influence on the measured intensities (e.g. slit position). One should be careful in extrapolating the interpretation of the presented results to other electron microscopes.

That being said, this study emphasizes the fundamental fact that the experimental parameters (accelerating voltage, beam current and measuring time) cannot be independently determined as they differently influence the quality of a measurement. In other words, each experimental parameter will either have a positive effect on the accuracy, precision or spatial resolution, but never for all three [255, 256]. Designing an optimization strategy based on Monte Carlo simulations is certainly an improvement over rule of thumb and trial and error methods.

Although the presented optimization was designed for low alloy steels, it can easily be extended to other materials. Since the focusing capability of the electron column is already determined, the only missing piece is the proportionality constants between experimental and simulated X-ray intensities for other X-ray transitions. Ideally, these constants can be predetermined for all measurable elements of the periodic
3.5 Applications

Over the last four years, the developed acquisition and quantification strategies described in §3.2 have been applied to characterize various AHS steel grades. Although the type of measurements performed from these samples may look alike, distinctive results were obtained in each case with various significances and areas of applicability, such as the understanding of manufacturing processes, elaboration of hypotheses to explain microstructural phenomena, input parameters for modelling, validation of models, etc. §§3.5.1 and 3.5.2 present a selected set of these measurements for low and high alloy steels. After a brief description of the characterization goals and the experimental method, the results for each example are presented followed by a discussion about their significance. Finally, to expose the complementarity of EPMA with other analytical techniques, §3.5.3 gives an example of combined analysis by EPMA and EBSD for the study of steel microstructure.

Before starting with the presentation of the applications, several colleagues deserve acknowledgement for their contribution to this work. More than providing the samples analyzed, their need for quality EPMA measurements at a high spatial resolution shaped and justified the efforts invested in the development of an acquisition and quantification strategy. In no particular order, Napat Vajragupta, Ali Ramazani, Xiaoxiao Li and Ulrich Prahl from the Institut für Eisenhüttenkunde [IEHK] for providing the DP steel samples (§3.5.1.1 and 3.5.3), Piyada Suwanpinij (IEHK) for the DP and TRIP steel samples (§3.5.1.1 and 3.5.1.2), Mehmet Özel (Institut für Werkstoffanwendungen im Maschinenbau) and Francisco Guzman (Institut für Maschinenentelemente und Maschinenegestaltung) for the bearing steel samples (§3.5.2.2) and Mengji Yao (Max-Planck-Institut für Eisenforschung) for the high manganese TWIP steel samples (§3.5.2.1). The collaboration with these colleagues led in several instances to publications and conference presentations, which are cited in the following paragraphs.

3.5.1 Low alloy steels

3.5.1.1 Dual phase steels

Problem statement The microstructure of DP steels consists of ferrite grains with disperse martensitic islands in a volume fraction of approximately 20 % [16, 280]. The combination of the ductility of ferrite and the hardness of martensite gives this type of AHS a high strength (＞550 MPa) while maintaining a good toughness, attractive properties for the automotive and aerospace industry [16, 280, 322, 366].

The heat treatment responsible for producing the DP microstructure consist of at least three steps. First a hypo-eutectoid steel is heated to the austenite zone of the iron-carbon phase diagram (Fig. 2.12) to dissolve all carbides and homogenize the steel to a fully austenitic microstructure. Secondly, the steel is cooled in the intercritical austenite-ferrite zone either continuously (continuous annealing) or held at a fixed temperature (isothermal annealing) [16]. During this stage, the ferrite
grains form, pushing austenite stabilizer atoms out (C, Mn, etc.) and encouraging ferrite stabilizer atoms in (Si, Cr, Mo, etc.) \cite{41, 277}. The diffusion of the alloying elements depends on many factors including the temperature, the cooling rate or holding time, and the diffusion coefficient of each alloying element. These factors also influence the final volume fraction of ferrite, the size and strength of the martensite islands, and ultimately the mechanical properties of the steel \cite{3, 63, 84, 278-280, 322, 366}. For instance, the carbon and manganese content primarily control the strength of the martensite \cite{279}. The second step of the heat treatment is often divided into smaller steps involving different cooling rates or holding times to avoid the formation of pearlite and bainite (Fig. 2.13). Finally, the steel is quenched to transform the remaining austenite into martensite. A small fraction can remain as retained austenite.

In order to relate the mechanical properties with the microstructure, several models have been developed to simulate the heat treatment process and the deformation behaviour (flow behaviour) of DP steels. The former type, referred to later as “process modelling”, simulates the diffusion of the alloying elements and the austenite to ferrite phase transformation based on thermodynamic calculations \cite{346}, whereas the latter, “deformation modelling”, predicts the macroscopic stress-strain curve by calculating the partitioning of stress and strain between ferrite and martensite using a representative volume element approach \cite{279, 366}. For both types of modelling, EPMA provides valuable information, validating the simulation results of the former and supplying the chemical concentration of martensite needed as input parameters for the latter.

Materials and methods The process modelling results are part of the Ph.D. thesis of Suwanpinij \cite{346}, more particularly the results from the “Mn–Mo DP” steel. The reader are referred to the thesis for the details about its chemical composition and heat treatment as well as the modelling strategy. Two types of EPMA measurements were performed: (1) qualitative mappings to observe the carbon distribution, and (2) quantitative line scans to measure the carbon content.

The deformation modelling results are taken from the work of Vajragupta et al. \cite{366} on a commercial DP steel, grade 600. Quantitative line scans were performed over 5 martensite islands to deduce their average chemical composition. The line scans also illustrate the final state of the elemental partitioning during the heat treatment.

All line scans and mappings were acquired at 15 kV and 100 nA. The dwell time was 5 s for the line scans and 100 ms for the mappings. The quantification of the line scans was done with the method described in §3.2.1.

Results Starting with the microstructure evolution during the heat treatment, Fig. 3.35 shows a qualitative comparison between modelling and EPMA results where the final carbon distribution inside the microstructure is presented. For the large martensite islands, both theoretical and experimental mappings show a higher carbon concentration on their boundary. Carbon concentrations around 0.55 mass% were experimentally measured at the boundaries, slightly higher than the simulated values, approximately 0.4 mass% C. The inside of the large martensite islands has a lower concentration, but still higher than the surrounding ferrite grains. In contrast
to the simulations, more fluctuations in the carbon concentration were experimentally observed inside the large martensite islands, pointing to a bainitic structure. This concentration gradient is not observed inside the smaller martensite islands.

The research of Suwanpinij [346] demonstrated that molybdenum enhances the nucleation of ferrite grains at triple junctions and grain boundaries instead of from inside the grains. The existence of small and large austenite grains is the consequence of this inhomogeneous nucleation. As ferrite grains grow, the carbon atoms peripherally diffuse out of ferrite into the remaining austenite. Small austenite grains are trapped in between the expanding ferrite grains, and their carbon content rapidly saturates. In larger austenite grains, carbon atoms does not have enough time to diffuse further inside the grains and remains near the former ferrite-austenite boundary after quenching.

The results from the commercial DP steel paint a different picture. Fig. 3.36 shows the carbon and manganese concentration profile across two martensite islands, which can be identified from the BSE image by their brighter appearance. The high dislocation density in the martensite reduces electron channelling, or conversely increases electron scattering.

Several observations can be extracted from the C and Mn concentration profiles. First, the higher C and Mn concentration confirms their higher affinity for austenite. The partitioning of these elements is clearly observed from Fig. 3.36, although more Mn atoms remained in the ferrite.

Secondly, in contrast to the Mn–Mo DP steel, the carbon diffused further inside the austenite grain during the intercritical annealing. The martensite islands in the DP600 steel have a more uniform carbon distribution. The peak on the left side of the largest martensite island subsists as a vestige of the carbon diffusion. Oppositely, a higher Mn concentration is observed near the former ferrite-austenite boundaries, similarly to carbon in Fig. 3.35. Mn atoms do not have enough time to diffuse in austenite and reach an homogeneous distribution. The larger width of the Mn profile also corroborates the slower diffusion of Mn atoms in comparison to C atoms. It is worth pointing out that this difference in width cannot be interpreted as a resolution artifact as the lateral resolutions of the C K–L$_{2,3}$ and Mn K–L$_{2,3}$ are similar for the acquisition parameters (Tab. 3.2).

Thirdly, Mn atoms appear to diffuse differently in ferrite and austenite. Looking at the right side of the largest martensite island or on both sides of the smallest martensite island, depression in the Mn concentration profile are observed in ferrite. The existence of these peak-depressions at these former ferrite-austenite boundaries suggests a stronger driving force for manganese to diffuse out of the ferrite than to diffuse through the austenite.

Fourthly, although the carbon concentration in ferrite is below the detection limit, the fact that concentrations close to zero were measured serves as a verification of the quantification procedure. An incorrect background determination or an unstable contamination behaviour on the unknown or pure iron would be reflected by inconsistent carbon concentrations in the ferrite grains.

Finally, the line scan also gives some indications of the achievable spatial resolution. The smallest martensite with a width of approximately 0.65 μm (measured from the BSE image) approaches the simulated lateral resolution of 0.51 μm (Tab. 3.2). Despite its smaller size, the carbon concentration at its centre matches the average
Figure 3.35: Comparison between (a) experimental and (b) simulated carbon distribution of a Mn−Mo DP steel sample [346]. Note that the colour scheme used in the two figures are not equivalent.
carbon concentration of the larger martensite island. Assuming that each martensite has more or less the same carbon concentration, the result suggests the possibility to quantify microstructural features as small as 0.65 μm.

**Discussion** There is no better proof for a model than an experimental validation. The qualitative carbon distributions and quantitative carbon concentrations obtained for the Mn–Mo DP steel sample provide a direct comparison with the modelling results obtained by Suwanpinij [346]. This example further demonstrates the improved spatial resolution of the Schottky emitter electron microprobe, as the carbon segregation at the ferrite-martensite boundaries could not be identified using a tungsten emitter instrument.

Apart from helping understand the elemental partitioning during the heat treatment process, quantitative line scans procure valuable input values to the deformation modelling. A critical information is the von Mises stress of martensite, the maximum shear stress criterion. It combines the Peierl’s stress, the threshold to initiate dislocation motion, and other material properties such as the shear modulus and length of the Burger’s vector [278–280, 366]. Empirical modelling has shown that the Peierl’s stress can be calculated from the chemical composition using the following equation [305]:

\[
\sigma_0 = 77 + (3065w_C - 161) + 5000w_N + 750w_P + 60w_Si + 60w_Cr + 80w_Mo + 80w_Cu + 45w_{Ni} + 11w_Mo
\]  

(3.26)

where \(\sigma_0\) is expressed in MPa and \(w_i\) represents the mass fraction in % of element \(i\). The large factor in front of the carbon mass fraction demonstrates its considerable influence on the Peierl’s stress and consequently on the results of the deformation
modelling. In sum, the accuracy, precision and spatial resolution achievable by the developed quantification strategy fulfill the modelling need for an accurate and statistically relevant composition of martensite islands in DP steels. Moreover, §3.5.3 will also highlight how EPMA in combination with EBSD can improve the identification of constituents in DP and TRIP steels.

3.5.1.2 Transformation induced plasticity steels

Problem statement TRIP steels are characterized by a high toughness delivering high energy absorption capabilities. This arises from a complex microstructure consisting of ferrite, bainite, martensite and especially retained austenite, which progressively transforms to martensite at high strains, i.e. the “TRIP effect” [41, 347]. This transformation provides additional work hardening at high strain levels [409]. The stability of the retained austenite under deformation depends, among others, on its carbon content, which basically determines at which strain level the TRIP effect begins. By adjusting the carbon content, TRIP steels can be manufactured for a given application, e.g. low carbon for stamping and forging, and high carbon for crash absorbers [409].

The volume fraction of retained austenite and its carbon content are therefore important parameters controlling the mechanical properties of TRIP steels. Suwanpinij et al. [347] measured these two parameters for TRIP steels produced by different heat treatments using high energy X-ray diffraction from a synchrotron radiation source. These samples were then analyzed by EPMA to assess the carbon content and distribution on the microstructural scale, complementing the bulk measurements from X-ray diffraction.

Materials and methods The heat treatment to produce the analyzed steel samples is presented in details in [347]. It consists of three main stages: (1) deformation after annealing in the austenite zone (austenization), (2) isothermal holding in the austenite-ferrite zone to form ferrite, and (3) isothermal holding at a lower temperature to form bainite. The results for samples deformed at a strain rate of 0.6, at a bainite forming temperature of 450 °C and for a holding period of 20 and 300 s are presented below to study the influence of the holding period on the microstructure and elemental partitioning.

As for the DP steels, qualitative mappings and quantitative line scans were performed on the samples, using the same accelerating voltage, beam current and dwell times. Other alloying elements, Al, Si, Cr and Mn, were also measured.

Results Fig. 3.37 shows the carbon distribution over an 150µm × 150µm area in the two studied samples with different holding time in the bainite transformation stage. The mappings are purposely displayed using the same colour scale to highlight the composition difference between the two heat treatments. While martensite and retained austenite islands cannot be differentiated from Fig. 3.37, bainite appears as a broken structure with a lower carbon content. Fig. 3.37b shows a higher fraction of bainite in comparison to Fig. 3.37a, confirming the influence of the longer holding time at the bainite transformation temperature. Overall, Fig. 3.37b has a more heterogeneous carbon distribution than Fig. 3.37a, where the carbon containing
features roughly have the same carbon concentration. During the second isothermal holding, carbon atoms rearrange themselves inside the austenite grains, forming a bainitic structure and enriching the remaining austenite grains. As a secondary effect of enhancing the formation of bainite, the longer holding time strengthens the austenite grains. With their higher carbon concentration, these austenite grains will not transform into martensite during quenching increasing the fraction of retained austenite in the final microstructure and the TRIP effect. These explanations deduced from Fig. 3.37 match the X-ray diffraction results, where a higher fraction of retained austenite ($\approx 18\%$) was measured after a holding time of 300 s than one of 20 s ($\approx 11\%$) (Figure 6(b) in [347]).

To confirm the carbon enrichment of austenite, quantitative line scans were performed on the two samples. They are shown in Fig. 3.38 along the variation of the other major alloying elements. As expected, increasing the holding time from 20 to 300 s causes the carbon mass fraction to increase on average from 0.78 to 1.29 % in the carbon-rich islands. These concentration values stack up with those obtained by X-ray diffraction (Fig. 5f in [347]). The decrease in the width of the measure island (6.0 vs. 2.9 $\mu$m) is conformed with the refinement of the microstructure observed in Fig. 3.37. In comparison to the commercial DP600 steel (Fig. 3.36), no significant segregation of the alloying elements, especially Mn, is observed in these TRIP steel samples. As it would require a long holding time and a high temperature, the short holding time (20 s) at the ferrite formation temperature (660 $^\circ$C) probably prevented the diffusion of these atoms.

**Discussion** Although the fraction of retained austenite cannot be directly measured by EPMA, the presented results complement in two ways those obtained by X-ray diffraction from a synchrotron radiation source. First, the microstructural changes in the carbon distribution observed in Fig. 3.37 explain the macroscopic differences in the retained austenite fraction measured by X-ray diffraction. Secondly, the results from Fig. 3.38 provides a verification for the carbon concentrations calculated based on the austenite lattice parameter (FCC crystal structure) measured by X-ray diffraction. Based on the work of Cheng et al. [74] the following equation was derived to relate the chemical composition of austenite to its lattice parameter ($a_{\text{austenite}}$):

$$a_{\text{austenite}} = 3.556 + 0.0453w_C + 0.00095w_{\text{Mn}} + 0.0056w_{\text{Al}},$$  

(3.27)

where $a_{\text{austenite}}$ is expressed in Å and $w_i$ represents the mass fraction in % of element $i$. For the two samples measured, the carbon concentrations obtained by both techniques differ by less than 0.02 mass % C, a difference below the precision of the EPMA measurements.

### 3.5.2 High alloy steels

#### 3.5.2.1 Twinning induced plasticity steels

**Problem statement** TWIP steels are austenitic steels recognized for their high strain hardenability, delivering high energy absorption capabilities, significantly higher than TRIP steels. Other properties such as oxidation and corrosion resistance make TWIP steels attractive in industrial applications [42]. The “TWIP effect”
Figure 3.37: Carbon distribution of TRIP steels produced with a holding period of (a) 20 s and (b) 300 s in the bainite transformation stage [347]. 15 kV, 100 nA, 100 ms dwell time, 500 nm step size.
Figure 3.38: Carbon, manganese, aluminum and silicon mass fraction along a 30-μm line scan across TRIP steels produced with a holding period of (a) 20 s and (b) 300 s in the bainite transformation stage [347]. The corresponding BSE image is shown below. 15 kV, 100 nA, 5 s dwell time, 6.25 nm step size.
arises from the formation of deformation twins impeding the movement of dislocations. The formation of deformation twins is related to the stacking fault energy [SFE], a material property expressing the surface energy of stacking faults [64, 251]. At low SFE values, twins are unlikely to form and the main deformation mechanism is the transformation of austenite to martensite, the “TRIP effect”. “Generally, as the SFE increases, the dominant deformation changes from TRIP to TWIP” [414] to accommodate the deformation. This transition strongly depend on the chemical composition. As shown by Saeed-Akbari et al. [313], TWIP deformation only occurs at high carbon and manganese concentrations. Furthermore, the addition of Al as an alloying element improves the yield strength by the formation of nanometer-sized $\kappa$-carbides, although the influence of these precipitates is still under investigation [42, 414].

Because of “serious problems in conventional casting processes” [83], TWIP steels are typically produced by continuous strip casting, where the molten metal is simultaneously solidified and rolled. Regardless of the production process, the as-cast microstructure is characterized by a strong chemical segregation [42, 83]. As the composition influences the SFE, and therefore the deformation mechanism, the determination of the local concentration is essential to understand the mechanical properties.

As introduced in §2.2.2 and further shown in §3.1.3.1, the high Mn concentration (> 17 mass % Mn) in TWIP steels complicate the accurate quantification of carbon due to the strong interference of the 2nd order Mn L$_3$–M$_1$ X-ray transition. This section presents results where the heterogeneous elemental distribution across a Fe–Mn–Al–C TWIP steel sample was measured by EPMA. Although this acquisition does not qualify as a high spatial resolution measurement (a step size of 10 $\mu$m was used), it nonetheless allows to evaluate the developed correction procedure for high alloy steels (§3.2.2).

Materials and methods The steel sample was analyzed under its as-quenched state to assess the initial heterogeneity, before the homogenization and ageing heat treatments to form the $\kappa$-carbides. The same sample was also used in other studies where details about the production process are given [131, 414]. The alloy was determined by wet chemistry to be composed of 1.28 mass % C, 7.74 mass % Al, 29.8 mass % Mn and 61.2 mass % Fe.

A 2-mm quantitative line scan was performed across the sample diameter using the routine analytical conditions of an accelerating voltage of 15 kV, a beam current of 100 nA and a dwell time of 5 s. A step size of 10 $\mu$m was used. The correction equation, Eq. 3.11, was then applied to correct the composition measured at each measurement location. Carbon was measured by a LDE2H dispersive element, Al on TAP, and Mn on LIFH. In this example, instead of quantifying Fe by elemental difference, Fe K–L$_{2,3}$ X-rays were measured using a LIF dispersive element. As the alloy should only contain trace amounts of other alloying elements, the sum of the Fe, Mn, Al and C concentrations can be used to evaluate the correction procedure.

Results Fig. 3.39 shows the quantification results before and after applying the correction equation. The wavelike profile of the C and Mn concentrations confirms the elemental heterogeneity of this as-quenched sample. The C and Mn variations
Table 3.13: Average composition from the wet chemistry and EPMA measurements. All values are expressed as mass fraction.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet chemistry</td>
<td>1.28</td>
<td>7.74</td>
<td>29.80</td>
<td>61.20</td>
<td>100.02</td>
</tr>
<tr>
<td>Without correction</td>
<td>1.47</td>
<td>7.95</td>
<td>31.09</td>
<td>60.18</td>
<td>100.69</td>
</tr>
<tr>
<td>With correction</td>
<td>1.29</td>
<td>7.95</td>
<td>31.09</td>
<td>60.18</td>
<td>100.51</td>
</tr>
</tbody>
</table>

are synchronized, both exhibiting a relative amplitude of approximately 3% and a period of 110μm. In contrast, Al concentration varies by less than 1% over a 2-mm distance and does not appear to follow the C or Mn variations.

In order to compare the results from Fig. 3.39 with those from wet chemistry, the average composition was calculated after removing outliers by a winsoring statistical transformation [137]. The average composition with and without correction is given in Tab. 3.13, along with the total composition. After applying the correction, the average carbon mass fraction decreases from 1.47 to 1.29 %, a 14 % error correction. The total mass fraction equivalently improves to 100.51 %.

**Discussion** This example gives encouraging results supporting the developed correction procedure for high alloy steels. The corrected carbon mass fraction is almost identical to the one obtained by wet chemistry. This is particularly interesting for two reasons. First, the correction equation was not specifically developed for TWIP steels, but is a generic equation that corrects for interferences of Si, Cr, Mn, Fe and Ni. Secondly, no reference material used to establish the correction equation contained Mn concentration above 14 mass %. The good agreement between wet chemistry and EPMA measurements suggests that the carbon concentration correction is also applicable to high manganese steels, although measurements on reference materials with higher Mn concentrations would certainly help refine the coefficients in Eq. 3.11.

Apart from carbon, the deviations observed between the wet chemistry and EPMA results fall within the normal error associated with both techniques, relatively ≈ 2 %. Moreover, as the volume measured by wet chemistry is significantly larger than the one EPMA, even for a 2-mm line scan, this fact could also potentially explain the observed differences.

A secondary objective of this work was to assist the APT measurements by identifying interesting areas where to mill out needle-like APT specimens. As the elemental segregation spreads over a larger distance than the size of an APT needle, EPMA measurements provide a time and cost effective screening method. Furthermore, EPMA helped in this work to solve the problem of isotope overlaps between $^{54}$Fe$^{2+}$ and Al$^{1+}$ [414].

### 3.5.2.2 White etching areas in bearing steels

**Problem statement** Different hypotheses have been proposed to explain the premature failure of bearings due white etching cracks [WECs] and white etching areas [WEAs] in 100Cr6 (SAE52100) [38, 104, 105, 154, 262, 337]. The simple fact, that only the initial and final state of the bearing microstructure can be studied, illus-
Figure 3.39: Carbon, aluminum, manganese and iron mass fraction along a 2-mm line scan across an as-quenched TWIP steel (a) before and (b) after applying the correction equation (Eq. 3.11). 15 kV, 100 nA, 5 s dwell time, 10 μm step size. Dashed horizontal line indicates the average composition after removing outliers.
3.5. Applications

\(\frac{\text{trates the challenging task of understanding the mechanisms leading to the failure.}}{\text{The large number of parameters influencing the failure mechanism also adds to the}}\)
\(\frac{\text{complexity of this problem [133]. As such, hypotheses have been formulated to relate}}{\text{the experimental observations to the internal mechanisms and understand the evolution}}\)
\(\frac{\text{of the microstructure during the bearing operation. Although the protagonists}}{\text{are unambiguous (white etching areas and cracks), two main schools of thought exist}}\)
\(\frac{\text{to explain how they are involved in the bearing failure. Their opinions differ on the}}{\text{chronological sequence of events. One hypothesis argues that the microscopic cracks}}\)
\(\frac{\text{are first initiated at weak areas in the microstructure (inclusions, pores, martensitic}}{\text{plates, and prior austenite grain boundaries) and then rubbing of the crack surfaces}}\)
\(\frac{\text{would lead to high stresses, heating, break-up of the microstructure, dissolution of}}{\text{carbides and formation of WEAs [38, 104, 337]. The other hypothesis suggests that}}\)
\(\frac{\text{plastic deformation along shear bands causes dissolution of the carbides, local accumulation}}{\text{of dislocations, formation of dislocation networks, formation of WEAs and ultimately initiation of cracks [88, 154].}}\)

Regardless of the theories with respect to the premature bearing failure, the WEAs unequivocally play an important role. As for any microstructural constituent in steels, the chemical composition, and especially the carbon concentration, is a determining factor of its atomic structure and mechanical properties. At the same time, discordant results are reported in the literature regarding the carbon concentration inside the WEAs. Evans et al. [105] describes them to be supersaturated with carbon in solid solution (\(\approx 1\) mass %), citing the Master’s thesis of Grabulov. Bhadeshia and Solano-Alvarez [38] and Grabulov et al. [126] infer the need for a high carbon concentration to stabilize its nanocrystalline grain structure. The most convincing experimental measurements were published by Kang et al. [183], who used APT to study the internal chemical structure of two WEAs. Their results show the segregation of C and Si atoms at the grain boundaries. The highest carbon concentration measured inside atom clusters was 9 atom % (\(\approx 2.1\) mass %). Although it was not reported by Kang et al. [183], their results certainly imply an average carbon concentration inside WEAs below the nominal concentration of \(100\)Cr6 (\(\approx 0.97\) mass % C) [154]. While EPMA cannot compete with the spatial resolution of APT, it rivals with its possibility to perform more measurements on the same sample. As such, this work reports the first EPMA measurements of WEAs.

Although the nominal chromium mass fraction of this steel alloy is below 2 %, its microstructure is characterized by the presence of spherical carbides with a Cr mass fraction of approximately 10 % [256]. WEAs are also known to have a high Cr concentration around 2 mass % Cr [88, 154]. As per the definition of §3.2, \(100\)Cr6 qualifies as a high alloy steel from the point of view of carbon quantification and the correction developed in §3.2.2 should be applied.

Materials and methods  The analyzed sample was preloaded with hydrogen (concentration measured to be approximately 7 ppm) and run for 57 h in a four-wheel test rig. The description of the test rig and other running parameters is given in [133] where the sample is labelled as VSP2. Quantitative line scans were performed over seven WEAs using the same experimental parameters as the line scans previously reported in this section.
Figure 3.40: Carbon, silicon and chromium mass fraction along a 16-µm line scan across three WEAs [133]. The corresponding BSE image is shown below. 15 kV, 100 nA, 5 s dwell time, 3.2 nm step size.

**Results**  
Fig. 3.40 shows the variation of the carbon, silicon and chromium concentration across three WEAs. For each example, the WEA was identified and highlighted based on the associated BSE image. As the quantification only works for flat, polished surfaces, the composition measured in the crack adjacent to each WEA is shadowed and excluded from the analysis.

In short, not all WEAs are the same, even in the same sample. Using the average matrix composition as a comparison point (≈ 0.7 mass% C excluding the carbides), the carbon mass fraction is lower in some (≈ 0.3%) and higher in others (> 1.4%). Fig. 3.40c further highlights this duality showing two adjacent WEAs with different
carbon concentrations. In a sense, the results support all previous assumptions and measurements aforementioned as WEAs with both low and high carbon concentrations were measured. Furthermore they demonstrate that the formation or at least the existence of WEAs does not depend on a particular carbon content. No relationship between the carbon concentration and the size of shape of the WEAs could be established.

To further understand the observed chemical differences, a lamellae was milled by a focused ion beam [FIB] at the exact location of the line scan in Fig. 3.40c. Bright field STEM images of the left (low carbon content) and right WEA (high carbon content) are shown in Fig. 3.41 at a magnification of 320 kX. Comparing their respective grain size, the right WEA has a finer grain structure than the left one. This is also confirmed by selective area diffraction patterns. These preliminary results suggest a relationship between the carbon concentration and grain size: WEAs with a smaller grain size contains more carbon. Relating this observation with the APT results of Kang et al. [183], a finer grain structure has more grain boundaries than a coarse structure, relatively. Approximating the average grain diameter for the left and right WEA to be respectively 7.5 and 19 nm and assuming spherical grains, the surface area ($4\pi r^2$) of the smaller grain is 5.4 times larger than the one of the bigger grain. Hypothetically, this additional “space” around the grains could accommodate more carbon atoms, thus giving a possible explanation for the overall higher carbon concentration measured in the left WEA.

As for the chromium content, it is steadily higher than the one of the matrix in all measured WEAs, including those measured in other bearing samples produced with different hydrogen contents and Hertzian contact pressures. The chromium mass fraction averages around 1.7 %, whereas the one of the matrix is approximately equal to 1.2 %, excluding the carbides. The results match the observations of other authors [88, 154]. In contrast to Kang et al. [183], no silicon segregation was measured, as the Si content is more or less uniform across all line scans.

Discussion Although it would be premature to consecrate either hypotheses on the premature failure of bearings, the presented results certainly emphasize the complexity of the internal microstructural changes occurring during the life cycle of a bearing. The higher chromium content measured in all WEAs implies that the carbides, the only microstructural features with a higher chromium content, are dissolved in the formation process of WEAs. As chromium atoms cannot easily diffuse at the temperatures used for the bearing operations ($< 200^\circ$C [133]), the driving force for the carbide dissolution must be large shearing forces created from the accumulation of dislocations in the surrounding of the carbides. Sheared carbides are sometimes also observed in the vicinity of WEAs [88].

In contrast to the chromium content, different carbon concentrations were measured inside adjacent WEAs, between WEAs from the same sample and between different samples. These differences may indicate different stages of their formation process. The relationship between the carbon concentration and grain size also suggests the importance of this element in stabilizing the nanocrystalline microstructure of WEAs [38, 126]. In sum, more investigations are required to understand which mechanisms are responsible for the internal microstructural changes observed in this work.
Figure 3.41: Bright field STEM images of the (a) left (low carbon content) and (b) right WEA (high carbon content) at a magnification of 320 kX. Images were acquired on a FEI Tecnai F20 (Hillsboro, Oregon, USA).
3.5.3 Combination of EPMA and EBSD

Problem statement  As described in §3.5.1.1, the production of DP steels involves either a continuous or isothermal annealing at a temperature in the austenite-ferrite zone of the iron-carbon phase diagram (Fig. 2.12). As shown in Fig. 2.13 for the case of isothermal annealing, an excessive holding time may result in the formation of pearlite and/or bainite, depending on the temperature [43, 304]. Concretely, this situation may occur during the continuous cooling of thick DP steel sheet, where the centre of the sheet undergo a slower cooling than the outside, resulting in the formation of bainite islands [281]. Due to silicon inhibiting the formation of cementite, the bainite is composed of bainitic ferrite and fine retained austenite laths. A small amount of this constituent in DP steels generally improves the toughness and yield strength, but reduces the tensile strength [281, 314, 344].

From a characterization perspective, the presence of bainite in the microstructure complicates the identification of the different constituents of DP steels [1, 260]. Three main challenges exist. First, the small size of the bainitic regions, as well as some of martensite islands, prevents their unambiguous identification using a LOM based on the classical approach of chemical etching [13, 230]. Modern alloys require the use of electron microscopes and techniques such as EBSD. The latter has been used by many authors for measuring multiphase steels, although the identification of their constituents is not as straightforward as with other alloys and materials.

The second challenge arises from the limited angular resolution of EBSD. As the deviations between the ferrite, bainite and martensite crystal lattice are too small to be indexed as different phases, only ferrite (BCC) and retained austenite (FCC) can unambiguously be distinguished based on their crystal structure. As summarized by Tab. 2.4, methods have nevertheless been developed to discriminate bainite and martensite from ferrite. The quality of the diffraction patterns is most often used to differentiate between ferrite and martensite [253, 310, 351, 412]. Higher lattice distortion in martensite leads to a more diffuse diffraction and a lower quality of its diffraction patterns. These crystallographic defects have a predominant effect on the diffraction quality over other factors such as the the crystal orientation [411]. Ryde [310] noted that averaging the diffraction quality inside each grain gives a better discriminator than a pixel-based comparison. As for bainite, its heterogeneous structure reduces the diffraction quality, but this reduction is less pronounced and more variable than for martensite. Zaefferer et al. [418] utilized the higher concentration of dislocations in bainite, measured using the KAM, to segment out bainitic regions from ferrite grains in a TRIP steel. The diffraction quality and the KAM were also the criteria selected in the European report on Microstructural quantification of multiphase steels (Micro-Quant) to partition steel constituents [1].

The same report however states that “no effective method for partitioning of these constituents in DP has yet been developed” and that “the image quality [IQ]/KAM combination approach [...] was not extensively investigated for DP grades” [1]. The additional challenge for DP steels originates from the transformation of the remaining austenite grains to martensite upon quenching. Because of its inherent volume expansion (∼ 3 % [41]), the martensitic transformation induces strain on the ferrite grains creating zones of high dislocation density around martensite islands. From an EBSD
Chapter 3. High resolution characterization of steel microstructure

standpoint, these zones are indistinguishable from the bainitic regions; both are characterized by high KAM values (Tab. 2.2.2). Bainite could therefore be erroneously identified.

To solve this ambiguity, the carbon concentration measured by EPMA can be used as an additional discriminating criterion. Bainite regions are identified as regions with high misorientations containing carbon, whereas dislocation zones have a carbon content similar to the one of ferrite. The methodology to combine EPMA and EBSD results is presented in the following paragraphs for a commercial DP800 steel. Another example of this combined method is given in [260].

Materials and methods The commercial DP800 steel sample was embedded in a copper containing resin and was mechanically polished up to 0.05\textmu m colloidal silica to minimize surface relief and topography caused by the hardness difference of the DP steel constituents. This preparation was found to be adequate for combined EPMA and EBSD measurements. No repolishing was performed in between the measurements [260].

Qualitative carbon mapping was first performed inside the electron microprobe (JEOL JXA-8530F, JEOL Ltd., Japan) as this measurement is evidently more sensitive to carbon contamination. The mapping covered an area of 50\textmu m × 50\textmu m, with a step size of 100 nm. An accelerating voltage of 15 kV, a beam current of 100 nA and a dwell time of 100 ms was used.

EBSD mapping was then acquired on a Schottky SEM (JEOL JSM-7000F, JEOL Ltd., Japan), equipped with a Hikaki camera and TSL OIM software version 6. (AMETEK Inc., USA). Although the carbonaceous layer left by the EPMA measurement reduces the quality of the diffraction patterns, no significant difference in the indexing accuracy and confidence index was noted. An accelerating voltage of 20 kV, a step size of 100 nm on an hexagonal grid and a dwell time of 7 ms (4x4 binning) were used. After dynamic background subtraction, the intensity of diffraction patterns was normalized based on their histogram. Grains were delimited using a 5° misorientation criterion. The KAM was calculated from the perimeter of the third nearest neighbour kernel (equivalent to a misorientation over a 300 nm distance). The maximum misorientation angle allowed was set to 3° to prevent the influence of grain boundaries.

The combination of the EPMA and EBSD datasets was performed with an in-house software making extensive use of the PYTHON libraries NumPy [174], SciPy [174] and Scikit-image [375]. The steps and assumptions involved in the combination are described below.

Results The first step towards the identification of the constituents is to align and merge the EPMA and EBSD datasets to construct a single hyper-dimensional dataset where each pixel contains the chemical and crystallographic information. One problem comes from the fact that the datasets are acquired on two instruments with different sample holders. Furthermore, the sample is tilted to 70° for the EBSD acquisition whereas it lies flat in the electron microprobe. The outcome is a complex misalignment between the two datasets, which cannot be simply corrected by rotations and translations.

Instead a piecewise affine transformation was defined using control points manually selected to bring in correspondence the BSE image acquired during the qualitative mapping by the electron microprobe (Fig. 3.42a) and the IQ map from EBSD
3.5. Applications

Martensite islands and grain boundary triple junctions are easily identifiable in both images. Since EBSD has a better spatial resolution than EPMA, the transformation direction was selected to transpose the EPMA dataset into the EBSD dataset. The piecewise affine transformation works as follows [375]. A Delaunay triangulation is applied over the control points found in each image. A local affine transformation matrix is calculated for each pair of triangles between the two images. The three largest Delaunay triangles are shown in Fig. 3.42. The affine transformation is then applied over the pixels inside the triangle. For each pixel in the EBSD dataset, the transformation gives the coordinate of the corresponding pixel in the EPMA dataset. Bilinear interpolation is finally used to determine the value at this coordinate for a given signal, e.g. the C K–L$_{2,3}$ X-ray intensity. Applying the affine transformation of each Delaunay triangle gives the global transformation, as shown in Fig. 3.42c.

After the alignment procedure, each constituent is identified based on different criteria. First, the retained austenite is directly obtained from the phase information of the EBSD dataset. Secondly, the martensite islands are extracted from the average grain IQ map, which consists in the average IQ value inside every grain (Fig. 3.43a). From the frequency distribution (Fig. 3.43b), a threshold value is selected to isolate the martensitic grains.

Thirdly, out of the remaining pixels, two subsets are created: (1) pixels with a KAM greater than 0.5° (Fig. 3.44a) and (2) pixels with a C K–L$_{2,3}$ X-ray intensity greater than a threshold value automatically determined from the Otsu image clustering method [243] (Fig. 3.44b). The first subset separates ferrite grains (low KAM values) from bainite and dislocation-rich regions (high KAM values), whereas the second separates ferrite grains and dislocation-rich regions (low carbon intensities) from bainite regions (high carbon intensities). Pixels common to the two subsets are assigned to bainite, whereas the others to dislocation zones.

Fig. 3.45 shows the result of the segmentation of the different constituents. Martensite, bainite and retained austenite respectively cover 15.9, 8.6 and 1.6% of the measured area. The rest is ferrite, where 14.2% contains a high density of dislocations.

**Discussion** This example demonstrates the need of both EPMA and EBSD measurements to accurately identify constituents in DP steels. If the identification would rely on only EBSD measurements, the fraction of bainite would be overestimated by more than 65%. In several instances, EBSD measured large regions with a high dislocation density (high KAM values) that did not contain carbon. On the other side, the steel constituents cannot be identified by EPMA only. As their carbon content vary, retained austenite and martensite are difficult to differentiate. This owes to the generally worst precision of mapping in comparison to point and line scan acquisitions. Besides the larger random uncertainties due to the shorter dwell time, the small step size increases the systematic uncertainties related to carbon contamination. Using the exact same strategy as in §3.3.2 to evaluate the precision, the uncertainty on the carbon mass fraction for mapping acquisitions on five steel reference materials is shown in Fig. 3.46 [260]. The acquisition conditions were the same as the EPMA mapping used in the combination (Fig. 3.44b). In comparison to Fig. 3.25, the random uncertainty dominates the total uncertainty which is two to three times greater than for well-separated point or line scan acquisition. Nonetheless, this level of uncertainty is
Figure 3.42: Example of the alignment and merging of EPMA and EBSD datasets. 
(a) BSE image acquired during the qualitative mapping by the electron microprobe, 
(b) IQ map from EBSD, (c) aligned BSE image on the EBSD dataset. Control points 
are displayed in each figure with matching marker symbol and colour. The three 
largest Delaunay triangles are overlaid to illustrate the transformation between the 
two datasets.
Figure 3.43: (a) Grain average IQ map and (b) its histogram showing the separation between martensite and the other constituents.
Figure 3.44: (a) KAM and (b) C K–L\textsubscript{2,3} X-ray intensity map of the remaining non-martensitic pixels.

Figure 3.45: Identified steel constituents from the combination of EPMA and EBSD mappings. The colour identification is: ferrite with a low dislocation density (blue), ferrite with a high dislocation density (pink), retained austenite (yellow), martensite (red) and bainite (green).
3.5. Applications

Figure 3.46: Precision of carbon measurements for mapping acquisition. The random, systematic and total uncertainties are reported as carbon mass fraction in percent. The acquisition parameters are an accelerating voltage of 15 kV, beam current of 100 nA, dwell time of 100 ms, step size of 100 nm, LDE2H dispersive element.

usable for the combination as it only requires a qualitative assessment of the carbon concentration, i.e. checking whether a region has a C K–L\textsubscript{2,3} X-ray intensity greater than the background intensity measured in ferrite.

Another caveat is the difference between the spatial resolution of EPMA and EBSD. For the latter technique, diffracted BSEs are generated within a small volume located close to the electron beam and the surface, due to the high tilt angle and low energy loss of diffracted electrons \[85\]. Zaeffferer \[417\] estimated the depth resolution to be 5.5 nm at 15 kV whereas Humphreys \[161\] reported a lateral resolution of 10 nm for iron at 20 kV. As shown in Tab. 3.2, the spatial resolution for the C K–L\textsubscript{2,3} X-ray transition is approximately 40 times worse. In the EPMA measurement, the carbon-rich regions therefore appears larger due to the worse spatial resolution. This can be observed in Fig. 3.47 where carbon is detected outside the ferrite-martensite boundary delimited using the image quality. Since martensite islands are segmented from the EBSD measurements, there is no bias on their area fraction. However, an ambiguity arises whether the carbon detected beyond the boundary of a martensite island is an effect of the spatial resolution or originates from the presence of a narrow bainite region near the interface (assuming the existence of high misorientation in the vicinity). This scenario unfortunately occurs around some martensite islands in Fig. 3.45.

The simultaneous acquisition of the EPMA and EBSD dataset would obviously be an improvement of the developed method, removing the tedious re-alignment step. Besides the technical difficulty to position a WD spectrometer and an EBSD detector around the electron microscope chamber, both techniques have different analytical re-
Figure 3.47: Overlay of the ferrite-martensite boundary determined from the grain average IQ map (blue line) on the C K–L$_{2,3}$ X-ray intensity map of a martensite island [260].

requirements, especially regarding the dwell time, 7 ms for EBSD vs. 100 ms for EPMA. A longer EBSD dwell time could lead to larger sample drift due to the 70° tilt. The question is how much could the EPMA dwell time be reduced without affecting the identification?

Summary

Beyond the validation of §3.3, the examples presented in the last section concretely confirm that the acquisition and quantification strategies developed in this work allow the characterization of various low and high alloy steel samples, and comply with the original objective of this work. The variety of the samples analyzed also testifies to the applicability and relevancy of EPMA measurements for steel research. The development of these strategies was made possible by the detailed characterization of an electron microprobe (§3.1), in-depth understanding of the physical phenomena (§2.2.2) and systematic consideration of the challenges (§3.2). All this knowledge was put to use in the elaboration of an optimization procedure (§3.4), a template to find the optimal experimental parameters to characterize any sample using Monte Carlo simulations.

Among the remaining and persistent challenges for the high resolution characterization of steel constituents, the carbon contamination and the quantification of first transition series metals using soft X-rays reside on the top of the list. Both severely affect the accuracy of an analysis and limit the improvement of the spatial resolution at low accelerating voltages (§3.4). Their impairment of EPMA measurements definitely surpasses the characterization of steels. The following chapters present further investigations undertaken on these two topics.
Carbon contamination

Carbon contamination is detrimental to any analysis in an electron microscope, but certainly more to the quantification of the carbon content. Not far from the observer effect [398], the act of bombarding a sample with an electron beam to measure its carbon content by EPMA changes the effective measured carbon content, the combination of the “true” content inside the sample and the artificial one from the carbonaceous deposit. Assuming, *arguendo*, that the carbon contamination is sample independent, its erroneous contribution to the measured carbon content increases as the carbon concentration inside a sample decreases. This situation exactly corresponds to the one described in this work, the quantification of carbon in steels. It emphasizes the need to understand the carbon contamination phenomenon and to minimize it within the practical limits of an electron microprobe.

The extensive literature review in §2.3 helped identify the dominating mechanisms involved in the carbon contamination phenomenon, namely adsorption, desorption, surface diffusion, cracking, polymerization and etching, and clarify the factors influencing them. Already, it allowed the reevaluation of published results, unscrambling ambiguous explanations, and providing more physical and convincing arguments. The mechanisms behind anti-contamination devices such as the cold trap and gas jet (§2.3.3.2), as well as the relationship between the contamination and the beam current (§2.3.3.4) are two examples. Inconsistencies however remain and fewer publications, eleven out of one hundred, reported results regarding the carbon contamination phenomenon inside a SEM or electron microprobe at the typical analytical conditions for microanalysis, < 40 kV and > 1 nA [9, 32, 62, 69, 96, 158, 193, 242, 284, 303, 350].

Another contentious subject is the method used to create and measure the carbonaceous deposit left by an electron beam on the surface of a sample. Authors formed carbonaceous deposits by either scanning the electron beam over an area [156, 207, 284, 306] or along a line [9], or by holding the electron beam to a single focused [80, 160, 181, 189, 323, 416] or defocused spot [69, 156, 158, 284]. Some also changed the irradiation frequency by adjusting the scanning speed [9, 60] or adding a delay in between exposures [9, 147]. The literature review tallied over a dozen different methods to characterize the carbonaceous deposit or, in many instances, the “contamination rate”, i.e. the growth rate of the deposit. These include measuring the C K–L$_{2,3}$ X-ray intensity using a ED or WD spectrometer [32, 192, 193, 201, 217, 242, 284, 350], determining the thickness of the deposit by energy filtering in a TEM [98, 127, 162, 226, 274], acquiring BSE images in a SEM [54, 60, 62, 150] and profiling the deposit using an AFM [9, 158, 205, 306, 365, 376]. These different strategies to analyze carbon contamination obviously lead to different interpretations and conclusions.

Carbon contamination is a dynamic process, where the rate limiting step, the dominating mechanism, may vary depending on the experimental parameters and over time. Whether the electron beam is scanned to acquire a line scan or map,
in its simplest expression, it consists of a well-focused beam irradiating a specific location of the sample for a certain dwell time. The final carbonaceous deposit produced by scanning the beam is the sum of the carbonaceous deposits produced at every irradiated location, albeit not a simple summation due to the dynamic nature of carbon contamination. Although many measurements in an electron microscope involved scanning the electron beam, it logically seems more straightforward to first study the carbon contamination phenomenon by analyzing the carbonaceous deposit produced by a well-focused beam at a single location, i.e. a spot measurement. To offer a comparison, both acquisition strategies are used in this work. The contamination produced by single spots and line scans (scanning the electron beam along one direction) is compared.

Weighting the pros and cons, the characterization method based on AFM measurements turns out as the ideal strategy to obtain a quantitative, unambiguous measure of the amount of contamination. It can determine the exact, complete, three-dimensional profile of carbonaceous deposits with a high sensitivity. With an accurate calibration, profiling can also be performed using BSE images, but this method lacks the sensitivity of the AFM and the image acquisition may disturb the carbonaceous deposit analyzed (e.g. increase of the contamination or decrease due to etching). It is however a worthy method if an AFM is not available. On the contrary, measuring the contamination using the C K-L\textsubscript{23} X-ray intensity should be avoided, as it only assesses the contamination created underneath the beam, not the one forming the walls of the ring (Fig. 3.14). This method is certainly valid to evaluate the contamination inside rings produced by well-separated spot measurements, but, for closely spaced, high spatial resolution measurements, both the contamination inside and forming the ring has an influence on the carbon quantification. All in all, in order to study the contamination mechanisms, the complete profile of carbonaceous deposits should be analyzed.

Understanding carbon contamination is challenging because it is influenced by several factors which are difficult to control. In the literature review, they were first identified based on the formulation of the mechanism equations (§2.3.2) and then grouped into five principal categories (§2.3.3): (1) chemical substances, (2) initial condition, (3) irradiation time, (4) beam current and (5) accelerating voltage. An experiment to study the carbon contamination should be meticulously designed to separate the contribution of the different factors. Ideally, each factor should be independently studied while the other are kept constant. While this is not always possible, each experiment in this work was designed with a clear scope in mind, aiming at minimizing the influence of irrelevant factors, eliminating ambiguities and allowing a comprehensible interpretation of the results. The thought process behind the experimental design is described in §4.1.

This work reports eight set of experiments covering four of the five principal categories of factors. The initial condition was varied using different cleaning methods, vacuum conditions and anti-contamination devices. The influence of the irradiation time, beam current and accelerating voltage on carbon contamination was separately evaluated over a range of values typically used for EPMA. For each experiment, a particular attention was paid in §4.1 to the description of the methodology used. More often than not, missing information in some reviewed publications prevented a deeper reinterpretation of their findings. The absence of experiments for the first category is due to experimental limitations. Although the substrate plays a determining role
4.1. Materials and methods

in the adsorption and diffusion of organic molecules, only one sample, GaAs wafer, was found to be easily accessible and meet the criteria required for the experiments (low roughness, constant crystal orientation and homogeneous composition, etc.). No experiment was performed to study the type of organic molecules involved in carbon contamination, as no surface characterization instrument, such as XPS, was readily available. To further understand the trends observed in the experimental results, simulations based on numerical solutions of the PDEs formulated in the literature review (§2.3.2) were performed. The results of the experiments and simulations are presented and discussed in §4.2.

A final remark from the literature review is the difficulty to compare measurements performed on different instruments, under different experimental parameters and over a period of more than fifty years. These differences instigated this work, aiming at evaluating the carbon contamination in a modern electron microprobe equipped with high-end vacuum system and anti-contamination devices.

4.1 Materials and methods

4.1.1 Instrument

All experiments were performed in the electron microprobe described in §3.1.1. Of particular importance to this study of contamination, it is equipped with two turbo molecular pumps (Turbovac Mag W 400 P, Leybold Oerlikon, Pfäffikon, Switzerland) and two scroll pumps (DIS-251, ULVAC, Methuen, MA, USA), making the complete vacuum system oil free. Samples are inserted inside the microscope chamber through a sample exchange airlock. The stable vacuum pressure inside the chamber, as measured by a Penning gauge, is approximately $10^{-4}$ Pa.

4.1.2 Material

The substrate used for all measurements was gallium-arsenide (GaAs). Pieces were cleaved from larger Si-doped GaAs wafers (American Xtal Technology, Inc., Fremont, CA, USA), provided by Oliver Schön (Aixtron, Herzogenrath, Germany). The selection of GaAs as the substrate emerged from the following thought process. From §2.3.3.1, the role of the substrate on the carbon contamination remains unclear, whether the critical material property is the composition (atomic number or BSE yield) or the thermal and electrical conductivity. By selecting a single, perfectly homogeneous substrate for all experiments, the influence of the substrate is effectively eliminated, allowing the study of the other relevant factors without any interference. Another argument in favour of GaAs is its constant crystal orientation, $\{100\}$ ($\pm 0.5^\circ$ [8]). As shown in Fig. 2.16 and discussed in §2.3.2.4 of the literature review, cracking of adsorbed organic molecules by electrons depends on the energy distribution of the PEs, SEs and BSEs. Due to channeling effects, the crystal orientation changes the SE and BSE emission, and thus theoretically may influence the contamination process. Using a single crystal as the substrate removes this potential source of error. As a sample for electron microscopy, GaAs is also a good electrical conductivity ($> 10^3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [8]). No charging effect was observed even at high beam currents (100 nA). Its high mean atomic number ($\bar{Z} \approx 32$) gives a good atomic contrast (BSE signal) with the carbonaceous deposits ($\bar{Z} \approx 6$). For the AFM, the detection and
measurement of carbonaceous deposits demand a low surface roughness. Attempts on mechanically and electrolytically polished samples of Cu, Fe and W gave unsatisfactory results, where the carbonaceous deposits were barely discernible from the sample roughness. As used by other authors to study contamination [37, 44, 150, 228, 306, 356], Si wafers could be an alternative to GaAs, but it was found that carbonaceous deposits on GaAs were more easily detectable in the AFM from the phase contrast signal. Amman et al. [9] also used GaAs wafer in their experiments.

4.1.3 Sample preparation

As advocated by several authors (§2.3.3.2), a critical factor influencing the contamination behaviour is the initial amount of organic molecules adsorbed on the sample surface before electron irradiation, which depends on an innumerable quantity of other factors (sample storage, cleaning, temperature, humidity, vacuum conditions, etc.). Since experiments were performed over a period of two years, it is unlikely that these factors stayed constant. A specific methodology was therefore followed to control, as well as possible, the concentration of adsorbed organic molecules. First, each series of experiments (e.g. contamination as a function of the beam current) is performed either on the same piece of GaAs, or on pieces prepared and inserted inside the instrument at the same time. This ensures that the state of the samples is roughly the same within a given series, allowing a more rigorous analysis of the observed trends. Comparisons between results of different series are avoided. Secondly, unless otherwise specified, the same sample preparation was used for all the GaAs wafer pieces. After cleaving, they were cleaned in ethanol in a ultrasonic bath, dried under hot air, mounted and inserted inside the electron microprobe. Regarding the mounting, the pieces were held by a copper retaining clip on an aluminum holder (PELCO SEMClip, Ted Pella, Redding, CA, USA) without any adhesive or paint (Fig. 4.1). A dot with a marker pen was made on each piece to help locate the carbonaceous deposit in the AFM.

Figure 4.1: Sample holder used to hold the GaAs wafer pieces.
4.1.4 Experiments

Eight factors influencing carbon contamination were separately evaluated: (1) sample cleaning solution, (2) plasma cleaning, (3) vacuum pumping time, (4) cold trap, (5) oxygen jet, (6) irradiation time, (7) beam current and (8) accelerating voltages. Five cleaning solutions typically used in electron microscopy labs were investigated: distilled water, ethanol (99.9\%), methanol (99.5\%), isopropanol and petroleum benzine (boiling range of 40 to 60 °C). In each case, a GaAs wafer piece was immersed in the solution and ultrasonic cleaned for 10 min before being dried under hot air. Using the Evactron 25 plasma cleaner (XEI Scientific, Redwood City, CA, USA) mounted in the exchange chamber airlock, plasma cleaning was performed under two sets of settings: (1) a plasma pressure of 53.3 Pa and power of 14 W (recommended/default values), and (2) a plasma pressure of 13.3 Pa and power of 20 W. The other parameters of the plasma cleaner were kept constant: no purge, ambient air as the gas mixture, an ignite pressure of 53.3 Pa and a cleaning time of 5 min. For the influence of the pumping time, carbonaceous deposits were produced after 5 min, 1, 2 and 19.5 h. The cold trap and oxygen jet were individually evaluated against a control sample, where neither anti-contamination device was used. Three irradiation times were tested: 10, 30 and 60 s. For the last two factors, different combinations of these experimental parameters were examined, including accelerating voltages of 3, 5, 10, 15, 20 and 30 kV and beam currents of 1, 10, 25, 50, 75, 100 and 200 nA.

4.1.5 Production of carbonaceous deposits

The principal strategy used to produce carbonaceous deposits was by a stationary, well-focused electron beam perpendicularly impinging the sample surface, resulting in a ring-shaped deposit. The following procedure was executed for each experiment after the insertion of the GaAs piece(s) inside the instrument and the stabilization of the vacuum (15 to 30 min). Except for the experiments on these factors, the experimental parameters were an accelerating voltage of 15 kV, a beam current of 100 nA and an irradiation time of 30 s. For each experiment, a measurement location was determined using the LOM from the microprobe, thus avoiding any pre-irradiation of the surface by electrons. For the same reason, the electron beam was focused far away from the measurement location. At every location, nine carbonaceous deposits (3 x 3 grid) were produced by moving the stage and bombarding the surface with the electron beam for 30 s. The Faraday cup was inserted and retracted in between each irradiation to prevent additional contamination. The acquisition procedure was fully automated by an in-house developed script to ensure reproducibility. After the deposition, a SE image was acquired at a low magnification with a fast scanning rate to locate the deposits with respect to the marker dot. The sample was then measured in the AFM to obtain the three-dimensional profile of each carbonaceous deposit.

A second deposition strategy was used for the beam current factor, the one extensively discussed in Chap. 3, the line scan acquisition. The electron beam is stepwise moved in one direction, remaining stationary for a certain dwell time at each step. As for the carbon quantification (Fig. 3.16, 3.17 or 3.21), the C K-L\(_2,3\) X-ray intensity was recorded using the LDE2H dispersive element. Each line scan presented in this chapter was acquired over a distance of 16 μm with a step size of 50 nm and a dwell
time of 5 s. Although the carbonaceous deposit produced by the line scans was not measured in the AFM, the variation of the C K–L$_{2,3}$ X-ray intensity along the length of the line scan provide additional information to the AFM measurements.

4.1.6 Atom force microscope measurements

All measurements were performed using a Bruker Neos AFM (Bruker GmbH, Berlin, Germany) operated in non-contact mode. A single scan was used to profile the nine carbonaceous rings (1024 px $\times$ 1024 px). The area covered varied between 30 $\mu$m $\times$ 30 $\mu$m to 50 $\mu$m $\times$ 50 $\mu$m with a step size varying from 29.3 to 48.8 nm. The topographical data was exported in an ASCII file format for further evaluation without any post-acquisition processing (e.g. background removal, filtering, etc.). Dr. Anke Aretz performed the AFM measurements.

4.1.7 Evaluation

Fig. 4.2a shows a typical result from an AFM measurement of a carbonaceous ring. The three critical dimensions from this profile are the diameter, height and width of the ring, as defined in Fig. 4.2b. The objective of the evaluation is to extract these dimensions from the AFM measurements. As such, a evaluation procedure was developed using custom programs and scripts written in Python. It consists in five steps, which are described in the following paragraphs for one carbonaceous ring. The steps are repeated for each of the nine deposited carbonaceous rings for a given experiment to obtain statistically relevant results.

The first step is to find the centre of the carbonaceous ring using the theorem that the “perpendicular bisector of any chord passes through the centre of a circle” [387]. It is schematically shown in Fig. 4.3a. Specifically, three points are manually selected along the circumference of the ring, defining three chords, “straight line segment whose endpoints lie on a circle” [386] (solid line in Fig. 4.3a). The perpendicular line to each chord is then calculated at their midpoint, the perpendicular bisector (dashed lines in Fig. 4.3a). The intersection of all three perpendicular bisectors gives the centre of the circle.

Secondly, the centre of circle serves as the rotation centre to extract the two-dimensional profiles (Fig. 4.2b) at every 5° increment. In total, 36 profiles are extracted from each carbonaceous ring, as shown in Fig. 4.3b and saved in a separate file.

Thirdly, an analytical function is fitted over each profile using a least squares function from the LMFIT [239] library. The fittings allows to determine the critical dimensions while minimizing the influence of noise and spurious peaks due to small debris on the surface. The formulated analytical function consists in the summation of three functions: two Gaussian functions to approximate the carbonaceous ring and a linear function with changing intercept for the background. The carbonaceous rings do not strictly speaking follow a Gaussian distribution due to their asymmetry; their outer edge has a long tail than the inner one, as shown in Fig. 4.2b. The Gaussian distribution nevertheless properly estimates the height and width dimensions. The linear function attempts to model the background, which is typically lower inside the carbonaceous ring than outside. To reflect this characteristic, the profile is divided in two regions, outer and inner regions, and a different intercept ($b$ in $y = mx + b$) is
Figure 4.2: (a) Three-dimensional and (b) two dimensional profile of a typical AFM measurement of a carbonaceous ring. The critical dimensions are identified in (b).
Figure 4.3: (a) Method to find the centre of the carbonaceous ring based on three points (square marker) defining three chords (solid lines) and the intersection of their perpendicular bisectors (dashed lines). (b) Method to extract two-dimensional profiles across the carbonaceous ring every $5^\circ$. (c) Fit of the experimental profile in Fig. 4.2b.
assigned to each region. Free parameters define the delimitation of each region. The complete formulation of the analytical function expressing the elevation $y$ along the profile is given by

$$y = p_0G(x, p_4, p_5) + p_6x + \begin{cases} p_9 & x \leq p_7, \\ p_{10} & p_7 < x \leq p_8 \\ p_9 & x > p_8 \end{cases}$$

where (4.1)

$$G(x, \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-0.5 \left( \frac{x - \mu}{\sigma} \right)^2 \right],$$

and $\vec{p} = \{p_0, \ldots, p_{10}\}$ are the free parameters. The fit of one experimental profile from Fig. 4.2b is shown in Fig. 4.3c.

Fourthly, the critical dimensions are calculated from the fitted parameters, $\vec{p}$, as follows:

$$d = p_4 - p_1$$

$$h_1 = \max_{\forall x} \{p_0G(x, p_4, p_5)\}$$

$$h_2 = \max_{\forall x} \{p_3G(x, p_4, p_5)\}$$

$$w_1 = 2p_2$$

$$w_2 = 2p_5.$$ (4.2)

The diameter ($d$) is taken as the distance between the central location of the two Gaussian distributions. At this point, the height ($h$) and width ($w$) of each Gaussian distribution are retained to help with the filtering of unsatisfactory results, the ensuing step.

The presence of small debris on the surface is unavoidable. Apart from changing the overall shape of the profile, debris may be considered by the fitting procedure (3rd step) as one of the peaks of the carbonaceous ring. The fifth step therefore aims at removing profiles affected by debris, as well as unsatisfactory fits where large differences remain with the experimental profiles. A satisfactory profile meet two criteria: (1) a coefficient of determination, $r^2$ [388], greater than 0.5 and (2) critical dimensions falling within the 5 to 95 percentile of all analyzed profiles. The first criterion ensures satisfactory fits, whereas the second effectively removes outliers, principally profiles distorted by debris. The criteria are sequentially applied to filter out inadequate fits before the calculation of the percentile distribution. In total, up to 324 profiles are considered, 36 profiles times 9 carbonaceous rings.

Finally, the average diameter ($\bar{d}$), height ($\bar{h}$) and width ($\bar{w}$) are calculated from the remaining profiles and compiled to compare the different experiments. The total volume of the carbonaceous deposit ($V$) is also calculated from the critical dimensions assuming a Gaussian profile rotated around a circle of diameter $d$:

$$V = \pi \bar{d} \bar{h} \int_{x=-3\bar{w}/2}^{3\bar{w}/2} G(x, 0, \bar{w}/2) \, dx.$$ (4.3)
The integration of the Gaussian distribution is performed over a distance of \( 6\sigma \) using its CDF.

The evaluation of the line scans requires fewer steps than the AFM measurements, but two corrections are applied to the measured C K–L\(_{2,3}\) X-ray intensities. First, the net X-ray intensities are calculated by removing the contribution of Bremsstrahlung X-rays from the measured peak X-ray intensities \( (I_{\text{peak}}) \). The background X-ray intensity \( (I_{\text{bckg}}) \) is approximately equal to the peak X-ray intensity measured in the first micrometer of the line scans, before the electron beam excites the carbon atoms of the first deposited carbonaceous rings. The second correction is the normalization by the electron dose to remove the dependence on the beam current \( (I_p) \) and measuring time \( (\tau) \). In sum, the corrected C K–L\(_{2,3}\) X-ray intensity \( (I') \) of any given point along a line scan is equal to

\[
I' = \frac{I_{\text{peak}} - I_{\text{bckg}}}{I_p \tau}.
\]

### 4.1.8 Simulations

In the literature review, partial differential equations were formulated in §2.3.2 describing each contamination mechanism. As for those representing electron-matter interactions (§2.1.2), these equations can either be solved using numerical solvers [9, 19, 55, 76, 100, 110, 149, 150, 153, 181, 194, 210, 216, 232, 282, 311, 358, 365] or Monte Carlo simulations (often referred to as “kinetic Monte Carlo”) [55, 330, 331, 336]. Both schemes have been used in the field of EBID to study the factors influencing the deposition process, akin to the contamination process. Results obtained from the former method are presented in this work, based on numerical solutions calculated using the FiPy [132] framework. The assumptions made in the calculations are detailed below along with the references and models used for the different parameters.

The first assumption is to ignore the adsorption, desorption and etching mechanisms, focusing on the dynamics between surface diffusion and cracking processes. As the AFM results will show, adsorption of organic molecules inside the specimen chamber is negligible and adsorbed organic molecules have a very long residence time on the sample surface. For the time span of a single measurement \(< 30 \text{s}\), absorption and desorption have no substantial influence on the contamination behaviour. Another reason to exclude these mechanisms is the scarcity, or simply the nonexistence, of references for the parameters in their equations, for instance the electron stimulated desorption cross sections, the sticking coefficients or the probability of an etching molecules to react with the carbonaceous deposit. In no way, this statement implies a higher level of certainty for the parameters of the surface diffusion and cracking equations, namely the diffusion coefficient and cracking cross sections. The elimination of some processes allows to study a smaller parametric field and better understand the influence of these parameters on carbon contamination.

From the calculations of Alman et al. [5] (Eq. 2.57 and 2.58), the cracking cross section increases with the length of the hydrocarbon chain, i.e. the number of carbon atoms (Fig. 2.16a). Brand et al. [53] and Cohen and Zeiri [79] reported from their experiments on the surface diffusion of alkanes on ruthenium and tungsten, respectively, that the maximum diffusion coefficient \( (D_0) \) in Eq. 2.52 is independent of the hydrocarbon chain length, but the activation energy \( (E_{\text{dif}}) \) linearly increases with
4.1. Materials and methods

the number of carbon atoms. As there is no clear consensus on the nature of the adsorbed organic molecules involved in carbon contamination (§2.3.3.1), the impact of the hydrocarbon chain length is studied in §4.2.2 for different alkynes (C\(_n\)H\(_{2n-2}\)), assuming that only one type of organic molecules is adsorbed on the sample surface. The cracking cross sections are calculated based on Eq. 2.57 and 2.58, whereas the following relationship was defined for the diffusion coefficient (\(D\)) based on the results of Brand et al. [53]

\[
D = (1.5 \times 10^{-5}) \exp \left( \frac{2677.76(C) + 4476.88}{RT} \right) \text{m}^2 \text{s}^{-1},
\]  

(4.5)

where \((C)\) is the number of carbon atoms, \(R\), the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \(T\), the temperature in K (always taken as 298 K in this work).

With the additional assumption of radial symmetry, the simulation of the carbon contamination process involves solving a set of PDEs consisting of the surface diffusion (Eq. 2.51), cracking (Eq. 2.55) and polymerization equations (Eq. 2.59):

\[
\left( \frac{\partial n(r,t)}{\partial t} \right) = DN^2n(r,t) - n(r,t) \int_0^{E_0} \sigma_c(E) \frac{j(E,r)}{e} \, dE \text{ and}
\]

\[
\left( \frac{\partial N(r,t)}{\partial t} \right) = n(r,t) \int_0^{E_0} \sigma_c(E) \frac{j(E,r)}{e} \, dE,
\]

(4.6)

where \(n(r,t)\) is the number of absorbed molecules at radius \(r\) and time \(t\), \(N(r,t)\), the number of cracked molecules at radius \(r\) and time \(t\), \(D\), the diffusion coefficient (m\(^2\) s\(^{-1}\)), \(E_0\), the energy of the PEs (eV), \(\sigma_c\), the cracking cross section (m\(^2\)), and \(j(E,r)/e\), the flux of electrons with an energy \(E\) at radius \(r\) (electron m\(^{-2}\) s\(^{-1}\)).

The remaining undefined parameter is the electron flux, the rate of electrons traversing an infinitesimal area of the sample surface. As stipulated by Eq. 2.56, all sources of electrons should be included in the electron flux, not only the flux of PEs. The SEs are of particular importance due to the higher cracking cross sections for electrons with an energy below 1 keV (Fig. 2.16). Eq. 2.56 can be rewritten as follows:

\[
\frac{j(E,r)}{e} = \left( \frac{I_p}{e} \right) \left( n_{PE}(E = E_0,r)(1 + \delta_{SE}(E',E)) + n_{BSE}(E,r)(1 + \delta_{SE}(E',E)) \right) \left( \Delta A \right) N_{PE},
\]

(4.7)

where \(I_p\) is the beam current (A) and \(e\), the elementary charge. \(n_{PE}\) and \(n_{BSE}\) respectively express the number of PEs and BSEs with energy \(E\) traversing an area \(\Delta A\) of the sample surface at radius \(r\). In the case of \(n_{PE}\), the energy distribution at any position is a Dirac delta function of the beam energy, i.e. the accelerating voltage \((E_0)\). \(N_{PE}\) corresponds to the total number of PEs. \(\delta_{SE}(E',E)\) is the emission rate of SEs, the probability that an electron with energy \(E'\) causes the emission of a SE with energy \(E\). The multiplication by \(n_{PE}\) gives the SE1 yield, and by \(n_{BSE}\), the SE2 yield. The numerator of Eq. 4.7 therefore regroups all four contributions to the electron energy-spatial distribution: PE, BSE, SE1 and SE2.
Similarly to Lobo et al. [216], \( n_{\text{PE}} \) and \( n_{\text{BSE}} \) were determined using Monte Carlo simulations at different accelerating voltages. As in §3.4, the beam diameter used in the simulations was set according to the experimentally determined values at different beam currents. The beam was assumed to be Gaussian with a FWHM equal to the values of Fig. 3.4. The Monte Carlo program NISTMONTE [300] was modified to record the position and energy of each PE and BSE in separate three-dimensional distributions (energy, radius and number of electrons). Along the energy axis, the intervals were fixed to 10 eV, whereas the radii were selected in order to have an equal area of each interval, i.e. \( \Delta A = \pi (r_2^2 - r_1^2) = \pi (r_2^2 - r_1^2) \). For each combination of accelerating voltage and beam diameter, \( 5 \times 10^6 \) electrons were simulated, implying that \( N_{\text{PE}} = 5 \times 10^6 \).

The calculation of \( \delta_{\text{SE}}(E', E) \) is split into two parts: (1) the calculation of \( \delta_{\text{SE}}(E') \), the probability of an electron with energy \( E' \) to cause the emission of a SE, and (2) the calculation of \( E \), the energy of the emitted SE. The method of Lin and Joy [209] was used to calculate \( \delta_{\text{SE}}(E') \). It assumes that the energy loss (\( dE' \)) by an electron of energy \( E' \) over a distance \( ds \) generates \( (1/\epsilon) \) SEs, where \( \epsilon \) is the effective energy required to produce an SE. Out of these generated SEs, only 50% escape from a depth no greater than \( \lambda \), the effective SE escape depth. The combination of these assumptions gives

\[
\delta_{\text{SE}}(E') = 0.5 \left( \frac{\lambda}{\epsilon} \right) \left( -\frac{dE'}{ds} \right) , \tag{4.8}
\]

where \( E' \) is either equal to the energy of the PEs (\( E_0 \)) for the SE1s or to the energy distribution of the BSEs for the SE2s. The energy loss (\( dE'/ds \)) was calculated using the modified Bethe equation from Joy and Luo [177] as transcribed in [124]. \( \epsilon \) and \( \lambda \) were extracted from the tabulations of Lin and Joy [209]. As only values for Ga were available, those for As were interpolated between Ge and Se. Values of \( \epsilon \) and \( \lambda \) for GaAs used in this work are respectively equal to 64 eV and 1.1 nm.

Based on Koshikawa and Shimizu [195], the energy of a SE can be computed from a uniform distributed random number (\( \xi \)), the Fermi energy (\( E_F \)) and work function (\( \phi \)) as follows [196, 335]:

\[
E = \frac{\xi E_F - \alpha (E_F + \phi)}{\xi - \alpha} , \text{ where } \alpha = \frac{E' - E_F}{E' - E_F - \phi} . \tag{4.9}
\]

This equation is repetitively applied over the number of emitted SEs calculated by Eq. 4.8, taking \( E_F = 0.712 \text{ eV} \), half of the band gap of GaAs [393], and \( \phi = 5.2 \text{ eV} \) [219].

Finally, here are a few additional details regarding the implementation and strategy used for the simulations. It was found that the statistical noise in the \( n_{\text{PE}} \) and \( n_{\text{BSE}} \) distributions calculated by Monte Carlo simulations has a detrimental impact on the simulations. To smooth the integral term in Eq. 4.6, the cracking rate at radius \( r \), two parabola were fitted over the calculated values:

\[
\ln \left( \frac{E_0}{\int_0^{E_0} \sigma_c(E) \frac{j(E, r)}{e} \, dE} \right) = \max_{\forall r} \left\{ ar^2 + b, cr^2 + d \right\} , \tag{4.10}
\]
4.1. Materials and methods

Figure 4.4: Cracking rate (integral term in Eq. 4.6) as a function of the radius. The figure compares the original calculated values with the two-parabola fit used to smooth the data (Eq. 4.10).

where $a$, $b$, $c$ and $d$ are the fitting parameters, restricting $a$ and $c$ to be less than zero. An example of the fit is shown in Fig. 4.4 for the cracking rate at 30 kV, 1 nA.

Using the tools offered by the FiPy [132] framework, the PDEs in Eq. 4.6 were solved over a one-dimensional cylindrical mesh (radial symmetry) spanning a radius of $10\mu$m with a step size of 50 nm. The initial number of adsorbed organic molecules was set to a constant value for all radii ($n(r, t = 0) = n_0$), but this value was varied between simulations to emulate different surface coverages. A boundary condition which stipulates that the concentration at infinite radius is equal to $n_0$ was also added, $n(r = \infty, t) = n_0$. For each set of parameters (e.g. accelerating voltage, beam current, type of organic molecules), the number of cracked molecules after an irradiation time $t_f$ ($N(r, t = t_f)$) was iteratively computed over smaller time steps using the default numerical solver of FiPy [132]. Besides providing more accurate results, the evolution of carbon contamination processes can be evaluated. The time steps were progressively increased for each iteration, starting at 10 ns up to 100 ms.

In order to compare the simulated and experimental results, the number of cracked molecules, $N(r, t)$, was converted into an equivalent height of a carbonaceous deposit. The results at 15 kV and 100 nA ($C_{19}H_{36}$, $n_0 = 0.5$) were taken as the calibration point, yielding that $h_{\text{sim}} \approx 23N(r, t)$. The width and diameter were directly extracted from the simulated profiles using the method described in §4.1.7, with the exception that only one Gaussian distribution was used due to the radial symmetry.
4.2 Results and discussion

4.2.1 Experiments

The AFM and C K–L₂,₃ X-ray intensity line scan results are sequentially presented for the eight studied factors. For the AFM results, each figure displays the averaged diameter, height and width obtained from the fitted profiles as well as the calculated total volume of a carbonaceous deposit. Error bars correspond to the standard deviation, expressing the variability between the critical dimensions of the profiles.

4.2.1.1 Cleaning solution

Fig. 4.5 shows the AFM results for the influence of the cleaning solution on the carbon contamination. The diameter and width are independent of the cleaning solution, but higher contamination spots were measured for isopropanol (5.53 nm) and water (5.30 nm). The height for the other solutions was approximately 3 nm. The volume follows the same trend as the height; the carbonaceous deposits produced on the wafers cleaned with isopropanol and water are approximately 65% more voluminous than those after cleaning with ethanol, methanol or petroleum benzine.

In a sample preparation procedure, the cleaning step has the objective to remove adsorbed organic molecules from preceding preparation steps or simply from the environment. Liquid solutions decrease the physisorption forces of the adsorbed organic molecules and dissolve them (§2.3.3.2). Apart from water, all tested solutions consist of organic molecules (ethanol: C₂H₅O, methanol: CH₃OH, isopropanol: C₃H₇O and petroleum benzine: C₅ and C₆ hydrocarbons), which may also remain adsorbed on the sample surface after drying. The adsorbed amount depends on several factors such as the purity of the solvent and the temperature at which the cleaning step is performed.
as the sticking coefficient, sample temperature, boiling point and vapour pressure of the organic molecules. Comparing the last two properties for the studied solutions provides some explanations of the AFM results.

Among the organic solutions, isopropanol has the highest boiling point (82.6°C) and lowest vapour pressure (5.3 kPa at 23.8°C) [396]. Oppositely, petroleum benzine has a very low boiling point (< 60°C) and high vapour pressure (31 kPa at 20°C) [399]. The values for ethanol and methanol fall in between those of isopropanol and petroleum benzine. The higher contamination measured on the wafer cleaned with isopropanol may be explained by a larger amount of C₃H₈O molecules remaining adsorbed on the surface after cleaning.

This explanation is obviously not applicable to the results with distilled water. As not all organic molecules are soluble in water, it is likely that water cannot force their desorption and they remain adsorbed on the surface. The same argument could also apply to isopropanol, which may have a low solubility for the adsorbed organic molecules. Unfortunately, since their nature is unknown, it is not possible to draw more precise conclusions, except that cleaning with either ethanol, methanol or petroleum benzine yields the lowest contamination.

Finally, although the current results support those of Roediger et al. [306], they contradict their general conclusion that the cleaning solution has no influence on contamination. Roediger et al. [306] observed no contamination difference between silicon wafers cleaned with acetone, isopropanol and distilled water. Excluding the results from ethanol, methanol and petroleum benzine cleaning, the same finding would emerge from this work. Based on the results of Roediger et al. [306], the similar contamination behaviour after acetone cleaning bolsters the role of the organic molecules solubility in the cleaning solution as a determining factor, since acetone has a low boiling point (56°C) and high vapour pressure (30.6 kPa at 25°C) [383].

4.2.1.2 Plasma cleaning

As demonstrated by various authors, the AFM results equally confirm the effectiveness of plasma cleaning to reduce contamination (Fig. 4.6). Plasma cleaning more than halves the height and volume of the carbonaceous deposits. A slight, but reproducible increase of the diameter is observed for carbonaceous rings after plasma cleaning. A lower gas pressure and higher power achieve no significant gain over the default plasma cleaner settings in terms of contamination reduction.

The measured contamination reduction is nonetheless less significant than the one reported in the literature [127, 162, 368, 420]. Even after plasma cleaning, a exposure of 30 s produces an observable carbonaceous deposit under the default experimental parameters (15 kV and 100 nA). The sample dependence of plasma cleaning as investigated by Mitchell [226], the plasma cleaner configuration or the type of reactive gas used could certainly explain the lower plasma cleaning efficiency observed in this work.

4.2.1.3 Pumping time inside specimen chamber

A common question regarding contamination is the source of the organic molecules; are they introduced in the vacuum by the samples, the seals, the pumps, etc.? To attempt to answer this question, tests were performed after different pumping times.
Chapter 4. Carbon contamination

Figure 4.6: Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces with and without plasma cleaning. Results obtained from plasma cleaning under different pressures and powers are shown.

Fig. 4.7 shows the variation of the critical dimensions as well as the pressure readings from the Pirani gauge of the specimen chamber as a function of pumping time. The decrease of the height and volume of the carbonaceous deposits after 19.5 h supports the theory where the organic molecules are introduced by the sample, and do not originate from the seals or pumps.

Pumping for a long period of time can actually remove some organic molecules adsorbed on the sample surface, albeit less effectively than the plasma cleaner. In terms of the carbonaceous deposit volume, pumping for 19.5 h reduces the contamination by 24%, whereas a 5-min plasma cleaning yields a 50% reduction. From Fig. 4.7, while the specimen chamber reaches a stable vacuum condition after 2 h, a lower contamination is not directly observed, but only after a longer pumping time. Without reacting radicals and/or UV radiations, desorption in the vacuum range of electron microscopes is evidently a slow process with a very long residence time (Eq. 2.48).

Comparing the results of Fig. 4.7 with those of Roediger et al. [306] in Fig. 2.18, the vacuum system has certainly an influence on the contamination behaviour. They observed a significant decrease of the carbonaceous volume after two hours of pumping and a stabilization after seven hours. While fewer carbonaceous deposits were evaluated in Fig. 4.7 and different substrates were used (GaAs vs. Si), the desorption appears to be a slower process in the present electron microprobe.

4.2.1.4 Liquid nitrogen cold trap

The AFM results with and without a cold trap are shown in Fig. 4.8. From all the anti-contamination devices tested, the cold trap gives the largest contamination reduction, > 70%, evaluated both from the height and volume of the carbonaceous deposit. The
4.2. Results and discussion

Figure 4.7: Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces after different pumping times inside the specimen chamber. Vacuum pressure values read from the Pirani gauge are also presented.

Figure 4.8: Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces with and without a liquid nitrogen cold trap.

cold trap in the electron microprobe used for the tests is located approximately 3 mm above the sample. This localized vacuum improvement forces the desorption of organic molecules from the sample surface in a similar fashion as the vacuum pumping system (Fig. 4.7), but more efficiently due to the lower vacuum pressure. In a sense, the cold trap serves as an additional pump just above the sample.
As in the plasma cleaning and pumping time results, the diameter of the carbonaceous rings increases with the use of a cold trap, from 2.66 to 3.56 µm. This increase was anticipated from the variation of the C K–L\textsubscript{2,3} intensity along a 16-µm line scan, shown in Fig. 3.16. In comparison to the line scan without any anti-contamination device, the one with a cold trap exhibits a longer initial plateau, extending up to approximately 4 µm. While the extent of the plateau and the diameter measured by AFM do not corroborate, both are indications that anti-contamination devices influence not only the height, but also the diameter of the carbonaceous deposits. More generally, the results suggest that the diameter increases as the surface concentration of adsorbed organic molecules decreases. At this moment, there is no clear explanation for these observations based on the contamination mechanisms reviewed in §2.3.2.

### 4.2.1.5 Oxygen jet

Similarly, the carbonaceous deposits produced while O\textsubscript{2} is blown above the sample by an injection nozzle have a larger diameter (Fig. 4.9), although the increase is less significant than for the cold trap (2.65 to 3.01 µm). The reduction of their height and volume is also slightly lower than the one measured with a cold trap, approximately 65%.

The AFM results contrast with the C K–L\textsubscript{2,3} X-ray intensity variation along a line scan shown in Fig. 3.16, where a lower intensity was measured using the oxygen jet than the liquid nitrogen cold trap. The discrepancy may confirm the dual effect of O\textsubscript{2} molecules on the contamination reduction. On the one hand, O\textsubscript{2} molecules inhibit the cracking and polymerization processes, as exhibited by the lower height and volume of the carbonaceous deposits in Fig. 4.9. On the other hand, the contamination reduction is not sufficient to explain the line scan results, which indirectly demonstrates the
etching of previous carbonaceous deposits by the O$_2$ molecules and the electron beam. Without etching, higher C K–L$_{2,3}$ intensities would have been measured for the line scan using an oxygen jet than the one with a cold trap.

As stated by several authors [4, 32, 96, 303], the removal of already deposited contamination by etching is certainly an additional benefit of using oxygen as the injected gas. The recommended use of a decontamination time (30 to 100 s) before contamination-sensitive measurements follows this logic. For acquisitions with a large number of measurements, the decontamination time quickly becomes impractical. Interestingly, line scan acquisitions at a high spatial resolution have the advantage to naturally include a decontamination time, as shown by the lower C K–L$_{2,3}$ X-ray intensity in Fig. 3.16. While the small step size amplifies the overlap of the carbonaceous deposits, it also compounds the etching action of each measurement position along the line scan. In other words, as the electron beam moves from one measurement position to another, etching not only partially removes the previously deposited contamination surrounding this position, but also the one of the next positions. In sum, the use of an oxygen jet is particularly advantageous for measurements at a high spatial resolution necessitating small step sizes.

For well-separated carbonaceous deposits, the contamination reduction by an oxygen jet was either explained in the literature review (§2.3.3.2) by the reaction of O$_2$ molecules with the organic radicals produced by the cracking process before their polymerization, or by an increase of the overall surface concentration resulting in a slower diffusion of adsorbed organic molecules. Unfortunately, the results in this work cannot clarify which one is the dominating mechanism.

4.2.1.6 Irradiation time

The influence of the irradiation time on the carbon contamination is shown in Fig. 4.10. The height and volume of the carbonaceous deposits increase with the irradiation time, while the diameter and width remain relatively stable over the irradiation period studied. No conclusion can be drawn regarding the kinetics, the relationship between the critical dimensions and the irradiation time due to the lack of measurements and relatively short irradiation times in comparison to other studies [80, 150, 189, 323, 356]. Although the results suggest linearity, the kinetics relationship proposed by Mitchell [226] (Eq. 2.50) could match the results, as represented by the dashed line in Fig. 4.10.

The fit yields a rate constant, $K_p$, of $0.68 \text{ nm s}^{-0.5}$ and $6.5 \times 10^{-3} \text{ m}^3 \text{s}^{-0.5}$ for the equivalent height and volume, respectively. Taking the rate constant based on the height, it is in general two to three orders of magnitude smaller than those calculated from the results of Conru and Laberge [80] (92.8 nm s$^{-0.5}$), Knox [189] (129.5 nm s$^{-0.5}$), Tomita et al. [356] (63.8 nm s$^{-0.5}$) and Schiffmann [323] (88.9 nm s$^{-0.5}$). All authors measured the contamination kinetics using the height of cone-shaped carbonaceous deposits. Despite using lower beam currents than in this work (<1 nA), faster contamination kinetics was observed for cone- than ring-shaped carbonaceous deposits. From the simulations of Rykaczewski et al. [311] (Fig. 2.21), the slow kinetics of ring-shaped carbonaceous deposits points to a diffusion limited regime, whereas cone-shaped deposits would prevail under a mixed regime.
Figure 4.10: Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces after different irradiation time.

4.2.1.7 Beam current

The beam current is a critical factor directly influencing the cracking process, appearing as part of the electron current density, $j_s(E, \vec{r})$, in Eq. 2.55. Generally speaking, higher is the electron current density, high will be the probability for an electron to crack an adsorbed organic molecule and form a carbonaceous deposit. As shown in Fig. 2.24, a large range of beam currents, 8 pA to 1 nA, were used in the literature to study carbon contamination. The current study concentrates on beam currents typically used for EPMA: 1 to 100 nA. The AFM results are shown in Fig. 4.11 for carbonaceous deposits produced at an accelerating voltage of 15 kV. With increasing beam current, the critical dimensions vary as follows: the diameter increases, the height decreases, and the width and volume stay constant.

The reduction of the diameter as the beam current decreases matches the simulations of Lobo et al. [216] (Fig. 2.23), and the relationship between the shape of the carbonaceous deposit and the beam current determined in Fig. 2.24. As the beam current decreases, the carbonaceous deposit produced by a well-focused electron beam transforms from a ring to a cone. This can be partially explained by the diffusion kinetics of the organic molecules adsorbed on the sample surface. A low beam current implies longer intervals between each electron irradiating the surface, giving organic molecules the possibility to move/diffuse over larger distances. There are therefore more organic molecules available to be cracked closer to the centre of the electron beam at low beam currents.
Figure 4.11: Critical dimensions of the carbonaceous deposits produced on GaAs wafer pieces using different beam currents.

Another observation from the results is that the beam current does not seem to influence the total amount of cracked organic molecules. The volume of the carbonaceous deposits stays fairly constant despite the fact that fewer electrons hit the sample at low beam currents. This is another evidence that carbon contamination in an electron microscope is a diffusion limited process, where organic molecules are cracked as soon as they enter the electron irradiated area. Under low beam currents, they can travel further inside this area, explaining the change in shape of the carbonaceous deposits. Even at 1 nA there is an excess of electrons over the number of adsorbed organic molecules. The change to a reaction limited regime occurs at smaller beam currents, 60 pA based on the results of Roediger et al. [306] and 155 pA for Mitchell [226]. The increase of the height at low beam currents is a consequence of the smaller diameter, and not an increase of the cracking probability.

For a line scan acquisition performed at a high spatial resolution, only a portion of the total deposited contamination affects the measurements. As the electron beam moves along the line scan and the carbonaceous rings overlap, the carbonaceous volume underneath the electron beam becomes a continuous, uniform, thin carbonaceous film [62], with a thickness approximately equal to the height of a single carbonaceous ring for small step sizes. In this case, the apparent carbonaceous volume is independent of the diameter of the carbonaceous rings, but strongly depends on their height. This is illustrated in Fig. 4.12, where the C K–L$_{2,3}$ X-ray intensities (normalized as per Eq. 4.4) were recorded along 16-µm line scans. In the last 10 µm, lower intensities are measured as the beam current increases. The increase of the diameter with the beam current, noted in the AFM results, is also observable in the first 2 µm of the
Chapter 4. Carbon contamination

Figure 4.12: Experimental C K–L\textsubscript{2,3} intensity along 16 µm line scans (40 nm step size, 5 s dwell time) measured on GaAs at 15 kV and different beam currents. The C K–L\textsubscript{2,3} X-ray intensity was acquired using a WD spectrometer equipped with a LDE2 dispersive element.

line scans. Large diameters are detrimental to measurements based on the strategy described in §3.2.1, because they extend the region of unstable contamination, region deliberately excluded from the quantitative analysis. Notwithstanding the influence of the beam current on other analytical aspects (e.g. precision and spatial resolution), a compromise should be found between the smaller diameter of low beam currents and the thinner contamination film at high beam currents.

4.2.1.8 Accelerating voltage

The last studied factor is the accelerating voltage, which indirectly influences the total electron current density (Eq. 2.56) by changing the emission probability and spatial distribution of SEs and BSEs, \( j_{SE}(E, \vec{r}) \) and \( j_{BSE}(E, \vec{r}) \) respectively. A significant determining factor of the spatial distribution, especially of SE1s, is the beam diameter, which was shown to vary as a function of the accelerating voltage and beam current (Fig. 3.4). As such, carbonaceous deposits were produced on GaAs wafer pieces using five accelerating voltages (3, 5, 10, 15 and 30 kV) and three beam currents (1, 10 and 100 nA). The AFM results are shown in Fig. 4.13. Note that the measurement at 30 kV and 100 nA is missing because the critical dimensions could not reliably determined from the profiles. Visually, the carbonaceous deposits have a large diameter and width and a low height, following the trends observed in the other results at 1 and 10 nA.

All critical dimensions have one inflection point in the range of accelerating voltages studied. As the accelerating voltage increases, the diameter and the width decreases to a minimum value before increasing again, whereas the inverse behaviour occurs for the height. The statistical fluctuations make it difficult to deduce any trend
4.2. Results and discussion

for the volume, although it more closely follows the one of the height. The accelerating voltage at the inflection point is almost identical for every critical dimension and increases to higher accelerating voltages as the beam current increases (i.e. from 3–5 kV at 1 nA to 10–15 kV at 100 nA).

The variations of the diameter can be interpreted from the enlargement of the beam diameter and interaction volume at low and high accelerating voltages, respectively. As discussed in §2.1.1 and §3.1.2.2, chromatic aberrations become significant at low accelerating voltages and enlarge the beam diameter, which evidently also causes the size of the contaminated area to increase. Similarly, increasing the beam current broadens the electron beam due to the fixed reduced brightness of the electron emitter (Eq. 2.6). In Fig. 4.13, there is a monotonous shift towards carbonaceous deposits with larger diameters at any accelerating voltage as the beam current increases. All in all, the focusing limitation of the electron optics is one possible explanation for the larger diameters at low accelerating voltages.

For bulk sample, as the size of the interaction volume increases with the accelerating voltage, BSEs and SE2s are emitted further away from the electron beam. In a diffusion limited regime, adsorbed organic molecules diffusing towards the electron beam will most likely be cracked by these electrons, primarily SE2s in accordance to the cracking cross sections (Fig. 2.16). This matches the AFM results in this study as well as those from Rykaczewski et al. [312] and Hristu et al. [159], who measured ring-shaped carbonaceous deposits with larger diameters as they increase the accel-
Chapter 4. Carbon contamination

These authors reported larger diameter values than Fig. 4.13. This fits within this explanation as they used substrates with a lower mean atomic number (Si for [312], and hydroxyapatite for [159]).

The interpretation of the height and width variations as a function of the accelerating voltage would require precise knowledge about the contribution of SEs and BSEs to the total current density, not only in terms of the magnitude of this contribution, but also the spatial distribution of these electrons. This is the objective of the comparison between simulated and experimental carbonaceous deposits, presented in the following section.

4.2.2 Simulations

Assuming accurate cracking cross sections and surface diffusion coefficients, the remaining two unknown parameters required to solve the PDEs (Eq. 4.6) are the type and initial amount of organic molecules adsorbed on the sample surface. The influence of these parameters on the critical dimensions of the carbonaceous deposit is first evaluated in §4.2.2.1, leading to the selection of a default set of parameters for the following simulations. Simulations were then performed to study each of the four main contamination factors analyzed in this work, namely the initial conditions (§4.2.2.2), irradiation time (§4.2.2.3), beam current (§4.2.2.4) and accelerating voltage (§4.2.2.5).

4.2.2.1 Default parameters

Fig. 4.14 shows simulated contamination profiles for different alkynes as well as the corresponding cracking rate. The other parameters were kept constant, i.e. an accelerating voltage of 15 kV, a beam current of 100 nA (beam diameter of 78.13 nm), an irradiation time of 30 s and an initial surface coverage of 25%. As the number of carbon atoms in an organic molecule increases, the shape of the deposit gradually changes from a cone to a ring with an intermediate interval where both geometries coexist. This behaviour can be explained from Eq. 2.58 and 4.5. While the cracking probability increases with the number of carbon atoms, the surface diffusion coefficient decreases. The carbon chain length significantly affects more the latter, varying from approximately $5 \times 10^{-11}$ m$^2$s$^{-1}$ for C$_{10}$H$_{18}$ to $2.0 \times 10^{-20}$ m$^2$s$^{-1}$ for C$_{30}$H$_{58}$. In comparison, the maximum ionization or dissociation cross sections ($\sigma_{\text{ion,max}}$ or $\sigma_{\text{diss,max}}$), stay within the same order of magnitude, $10^{-19}$ m$^2$. Physically, this allows short hydrocarbons to diffuse across a longer distance before being cracked, whereas longer hydrocarbons are cracked soon after they enter the electron irradiated area. The superposition of the contamination profile and cracking rate reveals that SE1s are mainly responsible for cracking short hydrocarbons, or more generally organic molecules with a high surface diffusion coefficient. Based on these calculations, cracking by SE2s dominates for hydrocarbons with more than 14 carbon atoms.

The other unknown parameter, the initial surface coverage of adsorbed organic molecules, is studied in Fig. 4.15, where the critical dimensions of the simulated deposit are plotted as a function of both unknown parameters. Deposits that do not exhibit a ring shape are excluded from the analysis. In short, the diameter, height and volume increases, and the width decreases with the surface coverage. The largest change is observed for the height (and consequently the volume) which varies by
4.2. Results and discussion

Figure 4.14: Simulated contamination profiles for different organic molecules as well as the corresponding cracking rate ($E_0 = 15$ keV, $I_p = 100$ nA, $t_f = 30$ s and $n_0 = 25\%$).

almost three orders of magnitude for surface coverages from 1 to 100 %. For a given surface coverage, the diameter increases with the number of carbon atoms. The width reaches a maximum for hydrocarbons containing between 20 and 22 carbon atoms, while the height plateaus around the same number of atoms.

Without any exception, all experiments reported in the previous section produce a ring-shaped carbonaceous deposit under an accelerating voltage of 15 kV and a beam current of 100 nA. The results of Fig. 4.14 suggest that carbon contamination inside an electron microscope is caused by fairly large organic molecules, slowly diffusing on the sample surface. From the simulations, the production of a ring-shaped carbonaceous deposit requires a hydrocarbon chain containing at least 16 carbon atoms ($\text{C}_{16}\text{H}_{30}$). This certainly exceeds the size of organic molecules used in other simulation works on electron beam induced carbon deposition: $\text{C}_2\text{H}_5$ [330], $\text{C}_4\text{H}_6$ [312], $\text{C}_4\text{H}_{11}$ [358] or $\text{C}_9\text{H}_{20}$ [216]. Whereas the cracking cross sections from Alman et al. [5] were unanimously used by almost all authors, the surface diffusion coefficient was determined from different sources. Rykaczewski et al. [312] used an empirically determined diffusion coefficient of $7.5 \times 10^{-22} \text{m}^2\text{s}^{-1}$, which would be equivalent to the one calculated for a $\text{C}_{33}\text{H}_{64}$ alkyne molecule by Equation 4.5. Lobo et al. [216] appear to rely on the same reference as this work, Brand et al. [53], but neither the actual diffusion coefficient nor the extrapolation equation is disclosed. All in all, knowing the type of adsorbed organic molecules only helps the determination of the cracking cross sections and surface diffusion coefficient if reliable values are available. Evidently, although the mechanisms can be modelled, fundamental work would be required to determine accurate quantities for the conditions involved in carbon contamination.
Figure 4.15: Critical dimensions of simulated contamination profiles as a function of the number of carbon atoms in the adsorbed organic molecules for different surface coverages ($E_0 = 15$ keV, $I_p = 100$ nA, $t_f = 30$ s).

Regardless of the surface coverage or number of carbon atoms, the simulated diameter is always smaller than the experimental ones presented in the previous section at 15 kV and 100 nA, on average $(2.97 \pm 0.30) \mu$m. The comparison between the experimental and simulated height is impossible due to the calibration factor, which depends on the simulation parameters used. As for the width, different combinations of organic molecule and surface coverage can match the average experimental width of $(0.45 \pm 0.05) \mu$m at 15 kV and 100 nA.

Another comparison point is the contamination kinetics, as discussed in §4.2.1.6. Fig. 4.16 shows the rate constant, $K_p$, as a function of the number of carbon atoms for different surface coverages, obtaining by fitting the volume of the simulated contamination profiles for irradiation times from 1 to 200 s using Eq. 2.50. The rate constant decreases as the number of carbon atoms increases or the surface coverage decreases. Slower diffusion and/or lower amount of organic molecules lead to a lower contamination rate.

Putting together Fig. 4.15 and 4.16, the kinetics restricts the possible choices for the type of organic molecules. While increasing the number of carbon atoms yields carbonaceous deposits with large diameters, approaching the average experimental diameter, it also slows down the contamination rate. Based on the simulations, it is not possible to satisfy both requirements of a diameter approximately equal to $3 \mu$m and a rate constant near $6.5 \times 10^{-5} \text{m}^3\text{s}^{-0.5}$. The latter requirement is subjectively
4.2. Results and discussion

Figure 4.16: Rate constant, extracted from simulated contamination profiles, as a function of the number of carbon atoms in the adsorbed organic molecules for different surface coverages ($E_0 = 15$ keV, $I_p = 100$ nA, $t_f = 30$ s).

privileged, leading to the fact that the type of organic molecules used in the simulations can be selected from Fig. 4.16 in order to match the experimentally determined rate constant assuming a certain surface coverage.

While the largest diameter was simulated with a 100-% surface coverage, it intuitively seems unlikely that the surface is entirely covered by organic molecules. As it will further be discussed in the following section, the influence of the surface coverage on the diameter diminishes above 10 %. Comparing the experimental and simulated widths in Fig. 4.15, a reasonable agreement is obtained at a surface coverage of 50 % for C$_{19}$H$_{36}$ molecules (experimental: 0.45 vs. simulation: 0.46 $\mu$m). The same is true for the rate constant in Fig. 4.16 (experimental: $6.5 \times 10^{-3}$ vs. simulation: $7.4 \times 10^{-3} \mu$m$^3$ s$^{-0.5}$). Without a more objective way to select the type and initial amount of adsorbed organic molecules, the following simulations will assume a sample surface half-covered by C$_{19}$H$_{36}$ molecules.

4.2.2.2 Initial conditions

Looking back at the AFM results using anti-contamination devices (plasma cleaning, cold trap or oxygen jet), the following general trend can be extracted: the expected decrease of the height is accompanied by an increase of the diameter of the carbonaceous deposit. The same behaviour is also observed after a long pumping time inside the specimen chamber, but not for different cleaning solutions. For instance, the measured diameter remains roughly equal to 2.75 $\mu$m between ethanol and isopropanol even though the height of the former is 46 % smaller. Except for the oxygen jet due to the additional etching phenomenon, the contamination reduction in all other experiments is theoretically explained by the desorption/removal of organic molecules
from the sample surface, i.e. a decrease of the surface coverage. To simulate this effect, critical dimensions were extracted from simulated profiles with different initial surface coverages, 1, 10, 25, 50, 75 and 100 % (Fig. 4.17).

While the decrease of the height with decreasing surface coverage is unsurprisingly confirmed by the simulations, the diameter does not follow the experimental observations. It monotonously decreases with exponentially larger drop as the surface coverage decreases. The inverse occurs for the width, a behaviour which the experimental measurements do not statistically confirm other than for the oxygen jet (Fig. 4.9). As the surface coverage could not be experimentally determined, the apparent linear relationship between the height/volume and the surface coverage cannot be verified.

The disagreement between the simulated and experimental diameters suggests a reexamination of the assumption that all adsorbed organic molecules have the same chemistry. Taking the opposite argument, anti-contamination devices likely have a stronger influence on the surface concentration of small organic molecules due to their weaker van der Waals forces. For instance, improved vacuum from longer pumping times or the liquid nitrogen cold trap certainly favours the desorption of small organic molecules. From Fig. 4.15, this preferential depletion would result in the production of carbonaceous rings with a larger diameter as large organic molecules remain adsorbed on the sample surface. In this hypothetical situation, the decrease of the height would equally be explained by the lower overall surface coverage. Here again, the direct measurement of the surface chemistry and coverage would be an essential information in order to understand the carbon contamination behaviour.
4.2. Results and discussion

Fig. 4.18: Critical dimensions of simulated contamination profiles as a function of the irradiation time ($C_{19}H_{36}$, $E_0 = 15$ keV, $I_p = 100$ nA, $n_0 = 50\%$).

4.2.2.3 Irradiation time

Fig. 4.18 shows the variation of the critical dimensions as a function of the irradiation time. Longer irradiation times (up to 240 s) were simulated to assess the square root relationship between the irradiation time and height or volume of the carbonaceous deposits. The relationship proposed by Mitchell [226] (Eq. 2.50) gives a good agreement with the simulated results (dashed line in Fig. 4.18). The saturation of the growth rate for long irradiation times (Fig. 4.18) and the lower rate constant of large hydrocarbon molecules (Fig. 4.16) are two strong arguments in favour of surface diffusion being the rate limiting process in carbon contamination inside a modern electron microscope.

Regarding the other critical dimensions, experimental measurements with longer irradiation times would be necessary to assess the trends observed in the simulation results. Whereas the diameter of the experimental carbonaceous deposits is roughly constant between 10 to 60 s, the simulations show a monotonous increase of the diameter over the same range, saturating at longer irradiation times. As the irradiation time progresses, the depletion of organic molecules near the electron irradiated area accentuates the concentration gradient forcing further molecules to diffuse towards the electron beam. These molecules must travel over a longer distance to reach the electron irradiated area. This has the consequence of enhancing the diffusion limited regime. The height and volume saturates due to the decreasing number of organic
Figure 4.19: Critical dimensions of simulated contamination profiles as a function of the irradiation time for different beam currents (C\textsubscript{19}H\textsubscript{36}, E\textsubscript{0} = 15 keV, n\textsubscript{0} = 50\%).

molecules available for cracking. The oversupply of electrons in comparison to the number of organic molecules means that cracking occurs as soon as a molecule enters the electron irradiated area, hence the larger diameters and smaller widths.

When the beam current is reduced, the electron to organic molecule ratio decreases. The organic molecules wander more into the electron irradiated area before being cracked, resulting in either a cone-shaped carbonaceous deposit or a dual structure. Based on experiments such as those of Conru and Laberge [80], the diffusion limited regime nevertheless persists. This situation is depicted in Fig. 4.19 where the contamination kinetics was simulated for beam currents of 0.5, 1, 5 and 10 pA (assuming the same beam diameter as for 1 nA, 39 nm).

The simulated rate constant at 5 pA approaches the one extracted from the cone height measurements of Conru and Laberge [80] at the same beam current (33.8 vs. 92.8 nm s\textsuperscript{-0.5}), and is forty times greater than the one at 100 nA. The reduction of the contaminated area cannot alone explain the higher contamination rate at low beam currents since the total volume also increases. Revisiting Fig. 4.15, another explanation is the exponentially higher cracking rate underneath the electron beam. Although the type and initial amount of adsorbed organic molecules are constant between Fig. 4.18 and 4.19, the higher cracking probability of SE1s in comparison to SE2s increases the contamination rate. The simulations however demonstrate that below \( \approx 1 \) pA the contamination reaction becomes a reaction limited process. This transition is observed in Fig. 4.19 where the relationship between the height/volume with the irradiation time tends towards linearity as the beam current decreases, no longer following a square root relationship (Eq. 2.50). For a given irradiation time, the
switch to a reaction limited region leads to a decrease of the contamination, which now only depends on the cracking probability (i.e. beam current). The influence of the beam current on the amount of contamination produced and shape of the carbonaceous deposits is discussed in the next section.

A last point regarding the irradiation time is the high contamination rate in the first few seconds. From Fig. 4.18, the volume of contamination after 1 s constitutes more than half of the one after 10 s. Decreasing the irradiation time from 120 to 5 s will certainly have a larger impact on contamination sensitive measurements than a decrease from 5 to 1 s. This limits the effect of shorter irradiation times on the contamination reduction.

4.2.2.4 Beam current

Similarly as Fig. 4.15, Fig. 4.20 shows the evolution of the simulated contamination profiles and cracking rate distributions, but this time, as a function of the beam current. Each subplot was adjusted to have the same scaling, facilitating the comparison. All three carbonaceous deposit geometries reported in the literature review are depicted (Fig. 2.14). As the beam current increases, the ring geometry progressively takes over the cone geometry, with an intermediate interval where both coexist. The simulated contamination profiles match the correlation between the shape and beam current established from experimental measurements in Fig. 2.24b. Both sets of results suggest critical beam currents for each shape of carbonaceous deposits: cone below $\approx 100 \, \text{pA}$, a dual structure between $\approx 0.1$ to 1 nA and a ring above $\approx 1 \, \text{nA}$. This agreement between the experiments and simulations is an encouraging sign that simulations based on solutions of PDEs correctly model the contamination behaviour and that the selected default parameters were acceptable estimates.

Since it was not included in the simulation model, no conclusion can be drawn regarding the influence of etching on the shape of carbonaceous deposits, as advocated by Lobo et al. [216]. Nonetheless, the results demonstrate that etching is not a requirement for the production of ring-shaped deposits. The radial distribution of SEs (especially of SE2s), the prevalence of a diffusion limited regime and a high beam current are the key ingredients, in line with the theory and explanations of Utke et al. [364].

As pointed out in the literature review, one remaining interrogation is the influence of the beam diameter/area on the relationship between the beam current and shape of carbonaceous deposits. Fig. 2.25 shows a dependence between the beam current and beam area, following the fundamental brightness equation (Eq. 2.6). The two areas of Fig. 2.25 lacking experimental results were studied using simulations. They correspond to conditions of low beam currents and large beam diameters (i.e. high defocus of the electron beam), and high beam currents and small beam diameters (practically unachievable conditions due to brightness equation, Eq. 2.6). The variation of the simulated profile shapes over the same range of beam currents and beam areas as Fig. 2.25 is shown in Fig. 4.21. The simulations suggest that the relationship between the deposit shape and beam current stands for any beam diameter. In other words, even with a brighter electron emitter allowing smaller beam diameters at high beam currents (upper left area of Fig. 4.21), carbonaceous rings would equally be produced. Increasing the beam area eliminates the formation of a dual cone/ring structure and shifts to higher values the critical beam current separating the cone
Figure 4.20: Simulated contamination profiles for different beam currents as well as the corresponding cracking rate ($C_{19}H_{36}$, $E_0 = 15 \text{ keV}$, $t_f = 30 \text{ s}$ and $n_0 = 50 \%$).

and ring geometries. At large defocus, the electron beam dictates the shape of the total current density distribution, as the contribution of BSEs (and SE2s) relatively decreases. Overall, Fig. 4.21 concords with Fig. 2.25 and all the explanations given so far.

Moving back to the evaluation of the AFM results, the corresponding simulation results are shown in Fig. 4.22. Only the increasing trend of the diameter with the beam current matches the experimental measurements (Fig. 4.11). Although Fig. 4.22 shows an increase of the height and volume, relatively to Fig. 4.17 and 4.18, these critical dimensions marginally vary over the simulated range of beam currents. The largest variation is observed for the width, which decreases with the beam current. This is also noticeable in the simulated profiles of Fig. 4.20 between 1 to 100 nA. While adsorbed organic molecules are still primarily cracked by SE2s at low beam currents, they travel slightly further inside the electron irradiated area, enlarging the ring width. This broadening was experimentally observed by Reimer and Wächter [291], but not in the experiments of §4.2.1.7. As it will become more apparent in the following section, the discrepancies between the experimental and simulated results may originate from an incorrect assumption of a Gaussian distributed electron beam.

4.2.2.5 Accelerating voltage

For the same conditions as Fig. 4.13, Fig. 4.23 shows the variation of the critical dimensions as a function of the accelerating voltage for three beam currents. Starting the comparison with the general trends, the simulation results match the experimental
4.2. Results and discussion

Figure 4.21: Shape of the simulated contamination deposit as a function of the beam current and beam area ($C_{19}H_{36}$, $E_0 = 15$ keV, $t_f = 30$ s and $n_0 = 50\%$).

Figure 4.22: Critical dimensions of simulated contamination profiles as a function of the beam current ($C_{19}H_{36}$, $E_0 = 15$ keV, $t_f = 30$ s, $n_0 = 50\%$).
ones above 10 kV. At any beam current, the diameter and width increases, and the height decreases with the accelerating voltage. The only exception is in the simulated results with a beam current of 1 nA, where the diameter starts to decrease around 20 kV.

These trends can be better understood by looking at the simulated profiles and corresponding cracking rate distributions, as shown in Fig. 4.24. The cracking rate, the integral term of Eq. 4.6, varies as a function of the accelerating voltage due to three factors: the beam diameter, the size of the interaction volume and the SE yield. First, as the accelerating voltage increases, chromatic aberrations have a lesser effect on the electron beam, and the beam diameter narrows (Fig. 3.4). This has little to no effect on the results of Fig. 4.23 above 10 kV. Secondly, high accelerating voltages obviously imply larger interaction volumes. As the PEs travel deeper inside the sample, BSEs and SE2s are emitted at larger distances. In Fig. 4.24, the cracking rate distribution at 30 kV is approximately three times wider than at 10 kV, matching the increase of the ring diameter, both in the experimental and simulated results. Finally, more energetic electrons have a longer mean free path and lose less energy per unit length (dE/Δs), translating into a lower SE yield per Eq. 4.8. This is valid for both SE1s and SE2s as a higher accelerating voltage also entails higher energy BSEs. Above 10 kV, the decrease of the deposit height with the accelerating voltage in Fig. 4.23 correlates with the decrease of the cracking rate in Fig. 4.24. In the same manner as decreasing the beam current (Fig. 4.20), the lower cracking rate and broader distribution at high accelerating voltages allow further diffusion of adsorbed organic molecules, increasing the width of the carbonaceous ring.
4.2. Results and discussion

The experimental results below 10 kV require more explanations, as they are counterintuitive to the simulations and aforementioned reasoning based on the variation of the cracking rate with the accelerating voltage. Predominantly at high beam currents, the carbonaceous rings measured by AFM exhibit a larger diameter, larger width and smaller height with decreasing accelerating voltage below 10 kV (Fig. 4.13). This essentially corresponds to a reversal of the trends observed above 10 kV. Only the simulation at 3 kV and 100 nA starts following this behaviour.

Two fundamental principles of the contamination reaction (Rxn. 2.1) are the direct interaction between an electron and an adsorbed organic molecule, and the almost instantaneous polymerization of the organic molecules. Taking as an example the carbonaceous deposit at 3 kV and 100 nA, its ring diameter of 5 µm implies the presence of electrons at this distance. For these conditions, a beam diameter of 364 nm was experimentally determined in §3.1.2.2 and the corresponding Monte Carlo simulation gives a maximum radial distance for BSEs emission of ≈ 800 nm. The discrepancy between these values obviously raises the question where are the electrons involved in the formation of large carbonaceous rings coming from?

A hypothetical answer involve the departure from the assumption of a Gaussian distributed electron beam, assumption inferred throughout this work in all Monte Carlo simulations. In his work on contamination, Wendt [379] attributed the formation of a ring-shaped carbonaceous deposit to the stray electrons, electrons scattered in the microscope column. Although there are significant evidences that stray electrons are not mandatory to produce ring deposits, they could surely enlarge the
electron beam and hypothetically explain the experimental results. Besides stray electrons, another explanation would be the influence of lens aberrations and aperture diffraction on the beam profile, especially at high beam currents as mentioned by Barth and Kruit [26], and others. The “broadening of the electron beam at low energies” was also hypothesized by Schiffmann [323] to explain her results.

To evaluate this possibility, the beam profile was changed in the simulations, adding an exponential tail to the existing Gaussian distribution. The following equation was used to randomly select the radial position \( r \) of each incident electron:

\[
    r = \begin{cases} 
        \sigma \xi_G & \text{if } \exp \left( -\xi_G^2 \right) \geq 0.1 \\
        3\sigma \text{sign}(\xi_G) \ln (\xi_U) & \text{otherwise}
    \end{cases}
\]

where \( \sigma \) is the standard deviation of the Gaussian distribution \( \sigma = \frac{d_{\text{FWHM}}}{2\sqrt{2\ln 2}} \), \( \xi_G \), a Gaussian distributed random number, and \( \xi_U \), a uniform distributed random number. From Eq. 4.11, the exponential tail starts below 10% of the Gaussian distribution height, and is equal to \( \frac{1}{(3\sigma)} \exp \left( -r/(3\sigma) \right) \). The corresponding profile is shown in Fig. 4.25 on a logarithmic scale for \( 5 \times 10^6 \) electrons. Although the FWHM of both distributions is almost equal, the new beam profile extends up to a radial distance of \( \approx 4 \mu \text{m} \), four times further than the Gaussian beam profile.

The critical dimensions extracted from the new simulated profiles are shown in Fig. 4.26. The experimental trends below 10 kV are now reproduced by the simulations, including the larger variations of the diameter and width as the beam current increases. Similarly to the AFM results, the height peaks around an accelerating voltage of 5–10 kV depending on the beam current. The only difference is the lower maximal height at 1 nA. As many results presented in this section, the absolute com-
Figure 4.26: Critical dimensions of simulated contamination profiles as a function of the accelerating voltage for three beam currents using a Gaussian beam profile with an exponential tail \((C_{19}H_{36}, t_f = 30 \text{ s}, n_0 = 50\%\).

Comparison between the experimental and simulated height, and corresponding volume, reveals large differences, suggesting a reevaluation of the calibration that each cracked molecule has a height of 23 nm.

Nonetheless, the results demonstrate the large influence of the beam profile on the contamination behaviour, especially in a diffusion limited regime where organic molecules are cracked soon after they diffuse in the electron irradiated area. While the beam profile described by Eq. 4.11 is purely speculative, the agreement between the experimental and simulated carbonaceous deposits supports the hypothesis of a long-tailed electron beam. The larger increase of the diameter and width at high beam currents also indicates broadening of the beam profile with the beam current, correspondingly to the experimental measured beam diameter (Fig. 3.4). It is however impossible to conclude how the beam profile varies with the accelerating voltage, since BSEs and SE2s emitted at the extremity of the interaction volume determine the extent of the electron irradiated area at high accelerating voltages. PEs in the extended tail of the electron beam, and the SE1s they produced, only influence the contamination behaviour at low accelerating voltages (below 10 kV in this work). Needless to say, measurements of beam profiles under different conditions would certainly provide more insight into the contamination phenomenon.

**Summary**

Five main conclusions can be drawn from this experimental and analytical work on carbon contamination inside a modern electron microprobe. First, a methodology was established to produce, analyze, compare and simulate carbonaceous deposits under different experimental conditions. The systematic approach reduced the influence of
external and uncontrollable factors such as sample preparation, electron channelling, surface roughness, vacuum pressure, etc. Despite of subjective assumptions, simulations reproduced and helped the understanding of experimentally observed trends.

Secondly, the results clearly demonstrate that no sample cleaning, plasma cleaning, pumping time, liquid nitrogen cold trap or oxygen jet can completely prevent carbon contamination. The liquid nitrogen cold trap is the most efficient at decreasing the total volume of contamination produced (decrease of 70%), followed by the oxygen jet (65%), plasma cleaner (50%) and pumping time (23% after 19.5 h). The oxygen jet, due to its additional/enhancing etching effect, is advantageous for closely-spaced measurements where the carbonaceous deposits overlap. The decrease of the contamination at longer pumping times proves that organic molecules taking part in carbon contamination mainly originate from the sample itself, and not from the pumps, seals or internal surfaces of the specimen chamber. Moreover, these experimental results, and those of all anti-contamination devices studied in this work, support a low desorption rate of adsorbed organic molecules. The comparison with simulations arguably suggests that the sample surface is covered with different types of organic molecules, where larger ones would have a longer residence time.

Thirdly, the variation of the critical dimensions as a function of the irradiation time and beam current exemplifies the predominance of the diffusion limited regime under the experimental conditions used for EPMA. Above all other factors, the beam current is the determining factor for the shape of the carbonaceous deposit produced by a single, well-focused electron beam. By specifying the cracking rate, it dictates the average distance an adsorbed organic molecule travel inside the electron irradiated area before being cracked: a longer distance at low beam currents, yielding cone-like deposits, and a shorter distance at high beam currents, forming rings. Although this could not be verified with simulations, the AFM results show that the carbonaceous volume is independent of the beam current, sustaining a saturation of the cracking rate above 1 nA and a high electron to organic molecule ratio. Based on simulations, the diffusion limited regime persists down to 1 pA regardless of the deposit shape.

Fourthly, no clear relationship could be established between the accelerating voltage and the contamination behaviour. While deposits with a lower height were measured at low (3 kV) and high accelerating voltages (30 kV), the results with regard to the total carbonaceous volume produced remain ambiguous. This is partially explained by the large and opposite influence of the beam profile on the critical dimensions. In the end, some agreement was reached between experimental and simulated results, but it necessitated the modification of the beam profile, from a Gaussian distributed to a hypothetical long-tailed electron beam. The extent of this tail, its magnitude in terms of electron density, its impact on the spatial resolution, its relation to the accelerating voltage and beam current, etc. are all, at this point, unknown.

This reality leads to the final conclusion that a deeper understanding of carbon contamination would unavoidably require further knowledge about (1) the initial state of the sample surface (chemistry of adsorbed organic molecules and their concentration), (2) fundamental quantities such as cracking cross sections and surface diffusion coefficients, and (3) the electron beam profile. The study of other factors influencing carbon contamination, e.g. type of substrate, substrate temperature, flooding, etc., would certainly complement the results presented in this work and provide some of this additional knowledge. The use of other analytical and spectroscopy techniques should also be considered.
Quantification using soft X-rays

In the field of EPMA, the goal of achieving a high spatial resolution is a continuing subject of research. Improvements of the electron optics have significantly improved the analytical possibilities by providing smaller beam sizes, but the physical limitation of the X-ray generation volume still remains. In other words, the analytical resolution is no longer limited by the beam diameter, but by the size of the interaction volume where X-rays are produced. Three main solutions have been proposed over the years to address this issue: (1) lowering the overvoltage ratio, (2) improving intensity models for heterogeneous samples, and (3) lowering the accelerating voltage.

Generally, the spatial resolution can be improved by lowering the ratio between the accelerating voltage and the energy of the X-ray transition of interest, i.e. the overvoltage ratio [237, 261, 296]. This directly improves the spatial resolution by decreasing the size of the interaction volume. For multi-element samples, this solution is however not practical. To have the same spatial resolution for all elements, the beam energy should be adjusted for each X-ray transition. As the position of the beam on the sample can slightly vary when changing the beam energy, it is experimentally complicated to ensure that the exact location on the sample is always measured [296]. In addition, the ionization cross sections used to calculate theoretical intensities in the quantification procedures are less characterized and have more uncertainties at low overvoltage.

The second solution is to relieve the constraint that the sample must be homogeneous within the interaction volume. In the late 80’s, microscopists were faced with the challenge of characterizing multilayer samples for the semi-conductor and micro-electronic industry. Since the layers are very thin (< 200 nm), the electrons penetrate both the layer(s) and the substrate. The quantification of a single layer is therefore not possible using the classical bulk quantification procedures available at that time. This led to the development of new models to calculate the X-ray distribution as a function of depth ($\phi(\rho z)$, Eq. 2.37) and iterative procedures to solve for both the composition and mass thickness of the layers [33, 273]. This method expanded the range of possible analyzes with an electron microscope and is now considered as a routine measurement. Nevertheless, this solution is only applicable to a particular type of sample geometry (multilayers) and requires the composition to only vary as a function of depth. More recently, Mevenkamp [225] showed the possibility to use Monte Carlo simulations to reconstruct different geometries such as a buried vertical layer inside a matrix or a hemisphere inside a matrix [256, 299]. Although it is promising, this method requires long Monte Carlo simulations, reducing its practicality as a quantification method. Its susceptibility to ambiguous solutions is also another drawback.

The third solution, which has become more attractive due to the instrumental improvements, is to lower the accelerating voltage, implying the use other X-ray transitions for the quantification. This has the similar effect as a small overvoltage
ratio; the size of the interaction volume is also reduced [25, 223]. As presented in §2.4, this solution however comes with many complications. On top of the list are the large inaccuracies in the quantification of the first transition series metals [125, 175, 214, 264, 341]. One can wonder what is the worth of a measurement with an extraordinary spatial resolution if the measured concentrations have an uncertainty of 30%? From the explanations and experimental results reported in the literature review, it appears clear that this problem is a solid-state physics problem. The underlying factor is the electronic configuration of the atoms in solids as they form chemical bonding with other atoms, and share, give or receive electrons from their valence band.

The samples used to study the problems associated with the quantification using soft X-rays can be divided in two categories based on the type of chemical bonding: covalent or metallic. Nickel aluminides [272], iron silicides [125], nickel silicides [142] and nickel glass [175] fall in the former category, whereas the latter contains the stainless steels. Being directional and localized (direct interaction between two atoms), covalent bonds should intuitively have a stronger influence on the electronic configuration than metallic bonds where electrons are shared across the whole lattice (delocalized). The quantification results presented in Tab. 2.6 suggest otherwise, as similar or greater relative errors were obtained from the stainless steel samples as the other covalent-bonded compounds. Since stainless steels contain several alloying elements, which may differently influence the electronic configuration, it is hard to discern the root causes for the large inaccuracies.

To simplify the problem, this section presents results acquired on three Fe–Ni binary alloys (25, 50 and 75 atom % Fe). The aim of these measurements is to understand the quantification problem and identify its source(s) with simpler, homogeneous, single phase reference materials. The same strategy as Pouchou and Pichoir [272] is used to study these alloys, the measurement of X-ray intensities and k-ratios as a function of the accelerating voltage. Although the quantification using $L_3-M_{4,5}$ X-rays at 20 kV would be pointless, the variation of the accelerating voltage gives an additional degree of freedom and may help understand energy-dependant physical interactions such as ionization and photoelectric absorption. In order to measure X-ray intensities on the reference materials, the acquisition strategy was designed to address the experimental challenges listed in §2.4.2. The description of the experimental procedure is given in §5.1 along the tools and programs used for the evaluation. The results are presented and discussed in §5.2 following a systematic approach attempting to answer all “what-if” questions and explore all evaluation possibilities.

5.1 Materials and methods

5.1.1 Sample preparation

The three Fe–Ni binary alloys were prepared by A. Kodentsov (TU Eindhoven, Eindhoven, The Netherlands) and donated for the current experiments by Erkki Heikinheimo (Aalto University, Espoo, Finland). They were produced in an arc melting furnace in an argon atmosphere ($\approx 250$ mmHg) from high purity iron and nickel powders. To improve homogeneity, the ingots were re-melted at least three times. From the phase diagram (Fig. 5.1), Fe and Ni are completely miscible within the composition range of the three binary alloys (in mass fractions 24.08, 48.75 and 74.05 % Fe).
5.1. Materials and methods

Figure 5.1: Fe–Ni phase diagram obtained from [65] based on the calculations using [12]

The three Fe–Ni alloys as well as the Fe and Ni pure reference materials were mounted in a single copper-containing conductive mount, polished using the recipe given in Tab. 3.5 up to colloidal silica, ultrasonically cleaned in ethanol, inserted in the microprobe and left inside for one night before starting the measurements. These preparation steps tackle the first two challenges described in §2.4.2, the carbon contamination and oxidation. The fact that all samples are mounted, polished and cleaned together ensures a similar coverage of organic molecules and therefore a similar carbon contamination behaviour. Moreover, this minimizes oxidation differences between the samples as all samples are polished together and exposed to air for the same amount of time.

5.1.2 Acquisition

Two types of acquisition are used to collect the X-ray intensities on an electron microprobe (JXA8530F, JEOL Ltd., Tokyo, Japan), the classical peak/background method and the more time consuming peak area approach based on WD spectra. The classical method, where the net intensity is obtained from the measurements of the peak intensity and two background intensities, was slightly modified to minimize the influence of carbon contamination and achieve a reasonable precision. Unconventionally, the peak and background intensities were acquired in two passes. The peak intensities were first measured at all accelerating voltages, and then the process was repeated for the background intensities. The counting time was automatically adjusted to collect at least 50 000 counts for the peak intensity. Based on Poisson statistics, this yields a relative precision of approximately 0.45 %. This adaptive counting time, implemented in an in-house program, circumvents the low intensity problem of soft X-rays. For the background intensities, the counting time was set to 30 s at each position. As described in §2.4.2.4 and 2.4.2.5, satellite peaks, self-absorption and carbon contamination may shift the position of $L_3$–$M_{4.5}$ peaks [125]. To avoid any inaccuracy, the peak position was determined at each accelerating voltage before the measurement of the peak intensity.
To measure Fe L$_{3-4}$ and Ni L$_{3-4}$ X-ray intensities, LDE1 and TAP dispersive elements part of WD spectrometers equipped with a P10-filled gas proportional counter were respectively used. The worst spectral resolution of the LDE1 dispersive element does not disturb the measurements of Fe–Ni alloys as there is no interference between the X-ray peaks of Fe and Ni, although the Fe L$_{2-3}$ interferes to a certain extent with the Fe L$_{3-4}$. This interference is discussed later. From the two background intensities measured on either side of the peak, an exponential and linear interpolation was respectively used to calculate the background intensity for the Fe L$_{3-4}$ and Ni L$_{3-4}$ X-ray transitions.

X-ray intensities were measured at accelerating voltages from 2 to 30 kV using a beam current of 75 nA. To minimize the carbon contamination, a liquid nitrogen cold trap was used throughout all the measurements and the beam was defocused to a diameter of 10 pm. The measurements on each sample and at each accelerating voltage were repeated at least 6 times.

For the acquisition of WD spectra, a TAP dispersive element was used to measure the X-ray transitions of both elements in order to achieve the best spectral resolution. The spectrometers were continuously moved from a wavelength of 0.653 to 1.021 nm for Fe and 1.33 to 1.70 nm for Ni. The speed of the spectrometer was 0.008 mm s$^{-1}$ in spectrometer units or 73.59 fm s$^{-1}$ in wavelength units, giving a total acquisition time of 1.39 h for each measurement. As for the peak/background acquisition, a liquid nitrogen cold trap and a 10-μm beam was used. WD spectra were acquired at 3, 5, 8, 10, 15, 20, 25 and 30 kV using beam currents between 400 to 1500 nA. The evaluation procedure to extract the X-ray intensities from the spectra is explained below. Both acquisition methods were automatized using in-house program written in PYTHON with the libraries PYZMQ and pyHMSA [258]. More information about the electron microprobe is given in §3.1.1.

5.1.3 Fitting of wavelength dispersive spectra

A least-square fitting procedure was used to remove the background and decompose all the peaks from the WD spectra, each peak corresponding to a different X-ray transition. As Fournier et al. [114] and Rémond et al. [295], the peaks were assumed to follow a pseudo-Voigt function, a linear combination of the Gaussian and Lorentzian functions [239]:

$$f(\lambda, a, b, c, f) = (1 - f)G(\lambda, a, b, c) + fL(\lambda, a, b, c)$$

$$G(\lambda, a, b, c) = \left(\frac{a}{\sqrt{2\pi}}\right)\exp\left\{-\frac{(\lambda - b)^2}{2(c/\sqrt{2\ln 2})^2}\right\}$$

$$L(\lambda, a, b, c) = \frac{a}{\pi c\left[1 + \left(\frac{\lambda - b}{c}\right)^2\right]}, \quad (5.1)$$

where $a$, $b$ and $c$ are respectively the amplitude, the centre position and width of the peak, $f$ is the fraction of the Lorentzian contribution to the pseudo-Voigt function, and $\lambda$ is the spectrometer position expressed as a wavelength. All four variables are free parameters in the least-square fitting procedure. Experience has however demonstrated the need to constrain the parameters to obtain an acceptable fit in
a reasonable amount of time. One important information is the spectral resolution of each dispersive element as a function of the spectrometer position (Eq. 2.30). For the TAP dispersive element, this calibration curve was \textit{a priori} determined by measuring the width of different X-ray peaks. The following equation was derived from these measurements, \( \hat{c} = (2.88 \times 10^6)b^2 - (4.49 \times 10^{-3})b + 3.11 \times 10^{-12} \), where \( \hat{c} \) is the expected peak width (in m) for an X-ray transition with a wavelength \( b \) measured using a TAP dispersive element. The initial wavelength of the different X-ray transitions \( (b_0) \) was taken from the tabulations inside PENELLOPE [213, 315]. From the expected peak width, the peak position was constrained to vary between \( b_0 - (1.25)\hat{c} \) and \( b_0 + (1.25)\hat{c} \), whereas the peak width was bounded between \( (0.75)\hat{c} \) and \( (1.25)\hat{c} \). The amplitude was free to take any positive value \((a > 0)\). The Lorentzian fraction was bounded between 0.0 and 1.0.

The following X-ray transitions were fitted for Fe and Ni: L\(_3\)–M\(_{4,5}\), L\(_2\)–M\(_4\), L\(_3\)–M\(_1\) and L\(_2\)–M\(_1\). Other X-ray transitions, such as L\(_3\)–M\(_2\) (L\(_t\)) and L\(_3\)–M\(_3\) (L\(_s\)), were neglected as they were not visible in the WD spectra. One additional peak for Fe and two for Ni were added to the fitting equation to match the longer tail on the high energy side of Fe L\(_3\)–M\(_{4,5}\), Ni L\(_3\)–M\(_{4,5}\) and Ni L\(_2\)–M\(_4\). It is not clear whether this tail corresponds to satellite peaks originating from the multiple ionization of an atom (§2.1.2.0.2 and §2.4.2.4) or X-ray transitions from the N\(_1\) (4s\(_1/2\)) subshell (Fe L\(_2\)–N\(_1\), Ni L\(_2\)–N\(_1\) and Ni L\(_3\)–N\(_1\)). These additional peaks will be here referred to as satellite peaks, although their initial wavelength \((b_0)\) was approximated from the X-ray transitions.

For each spectrum, at least 5 peaks were fitted along the exponential background \((g(\lambda, d, e) = d \exp (-\lambda/e))\), resulting in a total of 22 free parameters. The Levenberg-Marquardt non-linear solver implemented in the PYTHON library \textsc{lmfit} [239] was used to calculate the best fit. Most fits gave a coefficient of determination \((R^2)\) above 0.98. From the \( a, b, c \) parameters of each peak, the intensity was calculated using a trapezoidal integration function. Fig. 5.2 shows an example of the fitting procedure for pure iron measured at 10 kV. The \( R^2 \) value for this fit was 0.9856.

\subsection*{5.1.4 Evaluation}

The evaluation of the experimental X-ray intensities consists in two main parts: (1) the quantification, i.e. the comparison of experimental and calculated k-ratios, and (2) the determination of empirical MACs based on the experimental X-ray intensities. The method used to calculate empirical MACs is described in the following section.

For the quantification, the experimental k-ratios were calculated based on Eq. 2.39 and experimental X-ray intensities acquired from both acquisition methods. The quantification was then performed using different analytical models (PAP [273], XPP [273] and PROZA [28]) and databases of MACs (Chantler et al. [72], Heinrich [144], Henke et al. [145] and Pouchou and Pichoir [273]), all implemented in DTSA-II [302]. To more directly evaluate the quantification inaccuracies, the experimental and calculated k-ratios were also directly compared, including the comparison with k-ratios obtained by Monte Carlo simulations (NISTMONTE [300]).
Chapter 5. Quantification using soft X-rays

5.1.5 Calculations of empirical mass attenuation coefficients

As mentioned in the literature review (§2.4.2.5) and highlighted in the results of Pouchou [271], photoelectric absorption has a strong influence on the intensity of soft X-rays, and especially \( L_{3} - M_{4,5} \) X-rays of first transition series metals due to the phenomenon of anomalous absorption. The idea behind the calculations of empirical MACs is to evaluate whether the Fe–Ni alloys have a different absorption behaviour than the pure iron and nickel metals, or it follows the expected mixing rule of Eq. 2.36. The methodology to determine MACs from experimental X-ray intensities was first proposed by Pouchou and Pichoir [269] and is available commercially in the XMAC [271] software. It consists in adjusting the MAC value for a given X-ray transition in a compound of known composition until the calculated intensities match the experimental intensities measured at several accelerating voltages:

$$
\text{minimize} \sum_{j=1}^{N_j} \left( I_{i,k}^s(E_j) - \alpha_{i,k}^s \hat{I}_{i,k}(E_j, \chi_{i,k}^s, \bar{w}^s) \right)^2, \quad (5.2)
$$

where \( I_{i,k}^s(E_j) \) is the experimental X-ray intensity of transition \( k \) of element \( i \) measured at an accelerating voltage \( E_j \) on sample \( s \), \( \hat{I}_{i,k}(E_j, \chi_{i,k}^s, \bar{w}^s) \), the calculated X-ray intensity for the absorption function \( \chi_{i,k}^s \) (Eq. 2.36) and sample composition \( \bar{w}^s \), \( \alpha_{i,k}^s(E_j, \chi_{i,k}^s) \), a proportionality constant between the experimental and calculated X-ray intensities.
5.1. Materials and methods

(exactly like the constant $m$ in Eq. 3.20), and $N_j$, the number of measurements at different accelerating voltages. Pouchou and Pichoir [269] derived the following equation to calculate $\alpha$:

$$\alpha_{i,k}^s = \frac{\sum_{j=1}^{N_j} I_{i,k}^s(E_j) \hat{I}_{i,k}(E_j, \chi_{i,k}^s, \vec{w})}{\sum_{j=1}^{N_j} \hat{I}_{i,k}^s(E_j, \chi_{i,k}^s, \vec{w})}. \tag{5.3}$$

From the fundamental intensity equation (Eq. 2.33), $\alpha$ merges all the terms into a single constant value, except for $w_i$ and $\gamma_{i,k}(E_0, \vec{w})$. The calculated X-ray intensity is therefore equal to $w_i \gamma_{i,k}(E_0, \vec{w})$, where $\gamma_{i,k}$ is specified in Eq. 2.38 for $\phi(\rho z)$ models.

Eq. 5.2 however poses a problem for the current set of binary alloys, both the MAC values for the Fe and Ni L$_3$–M$_4$$_5$ X-ray transitions are considered unreliable, i.e. they should be empirically determined. This differs from the Ni aluminides of Pouchou [271], where the MAC value of Al K–L$_2$$_3$,X-ray transition in Ni can safely be taken from a database, or equivalently for the Fe silicides of Gopon et al. [125]. Eq. 5.2 was therefore modified to consider both Fe and Ni L$_3$–M$_4$$_5$ X-ray transitions and simultaneously solve for their MAC value. Specifically for the Fe–Ni alloys, the minimization equation becomes

$$\min \sum_{j=1}^{N_j} \left[ \left( I_{Fe,k}^s(E_j) - \alpha_{Fe,k}^s \hat{I}_{Fe,k}(E_j, \chi_{Fe,k}^s, \vec{w}) \right)^2 + \left( I_{Ni,k}^s(E_j) - \alpha_{Ni,k}^s \hat{I}_{Ni,k}(E_j, \chi_{Ni,k}^s, \vec{w}) \right)^2 \right], \tag{5.4}$$

where $k$ corresponds to the L$_3$–M$_4$$_5$ X-ray transition. $\chi_{Fe,k}^s$ or $\chi_{Ni,k}^s$ is defined as

$$\chi_{i,k}^s = \frac{\mu}{\rho}_{i,k} \cosec \psi, \tag{5.5}$$

where $(\mu/\rho)_{i,k}^s$ is the compound MAC of sample $s$, the MAC for the binary alloy $s$, of the X-ray transition $k$ of element $i$. Knowing the composition of the binary alloy, the elemental MACs, the MAC in pure element, can be calculated from the mixture rule:

$$(\mu/\rho)_{i,k}^s = w_{Fe}^s (\mu/\rho)_{Fe}^{Fe}_{i,k} + (1 - w_{Fe}^s) (\mu/\rho)_{Ni}^{Ni}_{i,k}, \tag{5.6}$$

where $w_{Fe}^s$ is the iron mass fraction in the binary alloy $s$.

In the same fashion as the fitting procedure of WD spectra or the optimization procedure of experimental parameters, Eq. 5.4 can be solved using a non-linear solver such as the Levenberg-Marquardt algorithm. Here the implementation in DTSA-II [302] was used along the $\phi(\rho z)$ analytical model XPP [273] to calculate the X-ray intensities. The determination of empirical MACs also required other modifications in the DTSA-II [302] source code to handle compound MACs.

5.1.6 Oxidation measurements

To evaluate the level of native oxidation on the studied samples, the thickness of the oxide layer was determined by EPMA using the program STRATAGem [270], as Heikinheimo and Llovet [141] for pure metals. On each unknown and reference
Chapter 5. Quantification using soft X-rays

materials, the O K–L\textsubscript{2,3} X-ray transition was measured five times at an accelerating voltage of 10 kV and a beam current of 75 nA. A multilayer dispersive element, LDE1, mounted on a spectrometer with a P10-filled gas proportional counter, was used. As for the acquisition of the L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions, the beam was defocused to a diameter of 10\(\mu\)m to minimize the influence of carbon contamination. An uncoated Fe\textsubscript{2}O\textsubscript{3} sample was used as the reference material to minimize the absorption correction. To avoid interferences of high order X-ray reflections, different background positions were selected for the alloys and reference material. In STRATAGEM [270], the composition of the native oxide layer was assumed to be mono-oxygen. In other words, the oxide has only one atom of oxygen, for instance FeO for pure Fe, NiO for pure Ni and (Fe\textsubscript{x}Ni\textsubscript{1-x})O, where \(x\) and \(y\) correspond to the atomic composition of the Fe–Ni alloy. To convert the calculated mass thickness into a thickness in nm, the mass densities of FeO (5.745 g cm\textsuperscript{-3} [395]) and NiO (6.67 g cm\textsuperscript{-3} [397]) were used for the pure substrates and a combination based on the following equation for the alloys:

\[
\frac{1}{\rho} = \frac{w_{\text{Fe}}}{\rho_{\text{FeO}}} + \frac{w_{\text{Ni}}}{\rho_{\text{NiO}}}. \quad (5.7)
\]

5.2 Results and discussion

5.2.1 Experimental intensities

Fig. 5.3 shows the Fe and Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray intensities measured by both acquisition types as a function of the accelerating voltage on the three Fe–Ni binary alloys and pure metals. Regardless of the sample or the X-ray transition, the intensity follows the same trend, increasing up to a certain accelerating voltage and decreasing afterwards. The latter behaviour is the signature of strong photoelectric absorption. As the accelerating voltage increases, the size of the interaction volume increases and X-rays are generated deeper inside the sample. On average, X-rays travel a longer distance inside the sample before reaching the detector. As the absorption probability exponentially increases with the path length (Eq. 2.34), X-rays are more likely to be absorbed, especially for soft X-rays with their high photoelectric absorption cross section. In comparison, the X-ray intensity of Fe K–L\textsubscript{2,3} increases with the accelerating voltage (Fig. 2.28), due to its lower MAC (in pure Fe, 64 cm\textsuperscript{2} g\textsuperscript{-1} vs. 1964 cm\textsuperscript{2} g\textsuperscript{-1} for the Fe L\textsubscript{3}–M\textsubscript{4,5} [72]).

Looking more closely at the results, the maximum X-ray intensity occurs around 15 kV for the Fe L\textsubscript{3}–M\textsubscript{4,5} X-ray transition, whereas the maximum shifts to lower accelerating voltages for the Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray transition as the Ni concentration decreases. The absorption behaviour of the Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray transition is therefore more sensitive to the composition than the Fe L\textsubscript{3}–M\textsubscript{4,5} X-ray transition.

Comparing the two types of acquisition, the Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray intensities obtained from the peak area (Fig. 5.3d) are unsurprisingly higher than those measured using the peak/background approach (Fig. 5.3b). The height of the Ni L\textsubscript{3}–M\textsubscript{4,5} peak in the WD spectra however matches the values of Fig. 5.3b. Fig. 5.3c displays lower X-ray intensities than Fig. 5.3a, since the peak area measurements were performed with a TAP instead of LDE1 dispersive element.
5.2. Results and discussion

Figure 5.3: Experimental X-ray intensities as a function of the accelerating voltage acquired on Fe, Fe$_{25}$Ni$_{75}$, Fe$_{50}$Ni$_{50}$, Fe$_{75}$Ni$_{25}$ and Ni. X-ray intensities for the Fe L$_{3}$–M$_{4,5}$ X-ray transition are shown in (a) and (c), whereas (b) and (d) show X-ray intensities for the Ni L$_{3}$–M$_{4,5}$ X-ray transition. X-ray intensities in (a) and (b) were measured using the peak/background approach, whereas X-ray intensities from the peak area determined by fitting WD spectra are given in (c) and (d).

In Fig. 5.3a-b, the error bars, representing the standard deviation, are barely visible. As each point corresponds to six X-ray intensity measurements performed on two separate sessions (sample exchanged and cleaned in between), this confirms the reproducibility of the measurements despite the experimental challenges (contamination, oxidation, etc.).

5.2.2 Area to peak factor

The extensive work of Bastin and Heijligers [32] on the quantification of borides, carbides, nitrides and oxides revealed the asymmetrical peak shape for the B, C, N and O K–L$_{2,3}$ X-ray transitions, especially when a dispersive element with high spectral resolution (e.g. lead stearate) is used. The extent or level of asymmetry was also shown to vary as a function of the chemical composition. In terms of X-ray intensity, this implies that the height of a peak, classically measured by WD spectrometers, is
Chapter 5. Quantification using soft X-rays

Figure 5.4: Area to peak factor as a function of the accelerating voltage for the Fe\textsubscript{50}Ni\textsubscript{50} sample, and the Fe and Ni L\textsubscript{3}–M\textsubscript{4.5} X-ray transitions. APFs were calculated from the fit results of the WD spectra.

not proportional to the area underneath the peak, i.e. the true X-ray intensity. To address this issue for soft X-rays, the authors introduced the concept of an area to peak factor [APF], which is calculated with respect to a reference material:

$$\text{APF}_{i,k}(\bar{w}) = \frac{I_{i,k}^{\text{area},s}}{I_{i,k}^{\text{height},s}} \frac{I_{i,k}^{\text{height},\text{ref}}}{I_{i,k}^{\text{area},\text{ref}}}$$

where the subscript $i,k$ denotes the X-ray transition $k$ of element $i$, the superscript $\text{area}$, the X-ray intensity measured from the peak area, the superscript $\text{height}$, the X-ray intensity measured from the peak height, the subscript $s$, the analyzed sample, and the superscript $\text{ref}$, the reference material. Based on the fits of the WD spectra, the APFs between the Fe\textsubscript{50}Ni\textsubscript{50} alloy and the pure reference materials were calculated. In other words, for a given X-ray transition, the $I_{i,k}^{\text{height}}$ and $I_{i,k}^{\text{area}}$ are extracted from its fitted pseudo-Voigt function (Eq. 5.1). The results are shown in Fig. 5.4.

The first observation is that the APF varies with the accelerating voltage. One possible explanation is the influence of the photoelectric absorption, due to the L\textsubscript{3} absorption edge below the Fe and Ni L\textsubscript{3}–M\textsubscript{4.5} X-ray peak. As the accelerating voltage increases, the photoelectric absorption increases, the high energy side of the L\textsubscript{3}–M\textsubscript{4.5} peak is more absorbed, and its shape changes, i.e. the peak area to peak height ratio, $I_{i,k}^{\text{area}}/I_{i,k}^{\text{height}}$. Based on the results in Fig. 5.4, this change is more pronounced for the reference materials, explaining the decrease of the APF at higher accelerating voltages. It is in line with the stronger absorption in pure metals due to resonance absorption.

To illustrate this point, the fitted Ni L\textsubscript{3}–M\textsubscript{4.5}, L\textsubscript{2}–M\textsubscript{4} and satellite peaks from WD spectra acquired at 10 and 25 kV are compared in Fig. 5.5 for the Ni and Fe\textsubscript{50}Ni\textsubscript{50} samples. The ratio between the height of the L\textsubscript{3}–M\textsubscript{4.5} and Ni L\textsubscript{2}–M\textsubscript{4} peaks and between the one of L\textsubscript{3}–M\textsubscript{4.5} and satellite peaks changes with the accelerating voltage and sample composition. The L\textsubscript{2}–M\textsubscript{4} X-ray transition and satellite peak are more absorbed at 25 kV in pure Ni than in Fe\textsubscript{50}Ni\textsubscript{50} alloy, whereas it is the opposite behaviour.
for the L3–M4,5 X-ray transition. The satellite peak almost disappears at 25 kV in Ni. Whether it is measured as the total peak height or the area under the peak, the amplitude of the L2–M4 and satellite peaks influences the Ni L3–M4,5 X-ray intensity. The proximity of the L3 and L2 absorption edges to the L3–M4,5 X-ray transition certainly complicates the determination of the “true” L3–M4,5 X-ray intensity and the absorption correction. It also casts doubt on peak/background acquisition approach, where the influence of the L2–M4 X-ray transition and satellite peak cannot be removed.

5.2.3 Experimental k-ratios

The experimental k-ratios calculated from the X-ray intensities from Fig. 5.3 taking the pure metals as reference materials are shown in Fig. 5.6. For the Fe50Ni50 sample, the k-ratios from both types of acquisition are shown and exhibit strong differences. The Fe L3–M4,5 k-ratios calculated using the fitted peak areas are on average higher than those calculated using the peak heights, whereas the inverse occurs for the Ni L3–M4,5 k-ratios. To a certain extent, these differences can be explained from the APF values of Fig. 5.4, the APF for Fe and Ni L3–M4,5 X-ray transitions being respectively greater and lower than unity. Dividing the peak/background k-ratios by their respective APF does not completely remove the differences between the k-ratios, as shown in Fig. 5.3.

For the Fe L3–M4,5 X-ray transition, another factor explaining the discrepancies is the different dispersive element used to acquire the X-ray intensities. Due to its poor spectral resolution, the LDE1 dispersive element, used for the peak/background acquisition method, cannot separate the Fe L3–M4,5 and L2–M4. The comparison between the k-ratios of the two acquisition methods is therefore problematic. The contribution of the L2–M4 X-ray transition to the peak X-ray intensity is difficult to evaluate, or even correct, since this X-ray transition is certainly more affected by absorption, as shown in Fig. 5.5.

Looking only at the results from the peak/background acquisition, similar trends are observed for the three alloys, suggesting no significant chemical differences. The Fe L3–M4,5 k-ratios are relatively constant as a function of the accelerating voltage. This indicates that the absorption of Fe L3–M4,5 X-rays in Fe–Ni alloys is comparable to the self-absorption in pure Fe. In contrast, the Ni L3–M4,5 k-ratios decrease with increasing accelerating voltage. The decrease of the k-ratios means higher absorption of Ni L3–M4,5 in the presence of Fe atoms. Since the k-ratio is the ratio of two X-ray intensities, its decrease indicates that the Ni L3–M4,5 X-rays are more absorbed in the binary alloys than in pure Ni.

One explanation is the strong absorption probability of Ni L3–M4,5 X-rays by Fe atoms. Databases of Heinrich [144], Henke et al. [145] and Chantler et al. [72] respectively report MAC values of 13 723, 13 040 and 12 874 cm² g⁻¹ for this condition. These values are approximately one order of magnitude greater than those for the absorption of Ni L3–M4,5 X-rays by Ni atoms. The stronger absorption may be explained by a change of the electronic configuration of Fe and Ni atoms with alloying. Based on characteristic isochromat spectroscopy, Chun and Klein [78] concluded that some of the 3d electrons of Ni atoms are transferred to Fe atoms in Fe–Ni alloys. This conclusion corroborates with the results of Fig. 5.6. The lower electron density in the valence band of Ni atoms enhances the self-absorption of Ni L3–M4,5 X-rays, as well
Figure 5.5: Fitted Ni L₃–M₄,₅, L₂–M₄ and satellite peaks from WD spectra acquired at 10 and 25 kV on the (a) Ni and (b) Fe₅₀Ni₅₀ samples.
5.2. Results and discussion

Figure 5.6: Experimental k-ratios for the (a) Fe and (b) Ni L$_{3}$–M$_{4,5}$ X-ray transitions as a function of the accelerating voltage. K-ratios were calculated using pure metals as reference materials. The peak/background acquisition method (labelled “p/b”) was used to acquire X-ray intensities on all three Fe–Ni alloys, whereas the fitted peak area acquisition method (labelled “area”) was used for only the Fe$_{50}$Ni$_{50}$ alloy. “Area” k-ratios divided by the APF of Fig. 5.4 are also shown (labelled “APF”).

as resonance absorption, in Fe–Ni alloys, thus the decrease of the Ni L$_{3}$–M$_{4,5}$ k-ratios with the accelerating voltage. There are more empty subshells for inner electrons to jump to during an photoelectric absorption interaction. For the Fe atoms, the higher electron density has the opposite effect, reducing the self-absorption of Fe L$_{3}$–M$_{4,5}$ X-rays, nullifying the influence of alloying.

The change in electron density should also influence the transition probabilities. For instance, fewer electrons in the M$_{4}$ or M$_{5}$ subshells of Ni are available to relax to the L$_{3}$ subshell after an inelastic interaction, effectively reducing the Ni L$_{3}$–M$_{4,5}$ transition probability in Fe–Ni alloys. The opposite situation occurs for Fe L$_{3}$–M$_{4,5}$ X-rays. The potential influence of the chemical composition on the transition probabilities is ignored in the k-ratio equation (Eq. 2.40), as the transition probability ($p_{i,k}$) in the intensity equation (Eq. 2.33) is technically cancelled out by the ratio. Different transition probabilities between the alloys and reference materials would therefore manifest themselves as an additional factor between the experimental and calculated k-ratios. They however cannot explain the observed trends with the accelerating voltage in Fig. 5.6, since the transition probabilities are independent of the accelerating voltage. The different absorption behaviour between the Fe–Ni alloys and the reference materials appears to be the most likely explanation.

5.2.4 Calculated k-ratios

Regardless of the theoretical reasons behind the k-ratios of Fig. 5.6, an accurate quantification requires the intensity models to reflect these experimental results in the calculated k-ratios and obtain a perfect match. The calculated k-ratios for the three binary alloys are overlaid on the experimental k-ratios in Fig. 5.7. The default databases for each intensity model were used: the MACs database from Pouchou and Pichoir [273] for PAP [273], XPP [273] and PROZA [28], and from Chantler
Figure 5.7: Experimental and calculated k-ratios for the (a) Fe and (b) Ni L$_{3}$–M$_{4,5}$ X-ray transitions as a function of the accelerating voltage comparing calculated k-ratios obtained from four intensity models: PAP [273], XPP [273], PROZA [28] and NISTMonte [300].

et al. [72] for NISTMonte [300]; the ionization cross sections from Pouchou and Pichoir [268] for PAP [273] and XPP [273], from Bastin et al. [28] for PROZA [28] and from Bote and Salvat [50] for NISTMonte [300]. Overall, no intensity model gives calculated k-ratios perfectly matching the experimental ones. The closest match is achieved by the k-ratios from NISTMonte [300] for the Fe L$_{3}$–M$_{4,5}$. All models show large discrepancies for the Ni L$_{3}$–M$_{4,5}$ k-ratios, especially those measured using the peak/background approach.

At first sight, all three analytical models, PAP [273], XPP [273] and PROZA [28], yield similar calculated k-ratios for both Fe and Ni L$_{3}$–M$_{4,5}$ X-ray transitions. A closer evaluation reveals that the MACs have the largest influence on the calculated k-ratios, and not the intensity model nor the ionization cross sections. To directly compare the different MAC database, Fig. 5.8 shows the calculated k-ratios obtained from Monte Carlo simulations using NISTMonte [300] and four MAC databases. For both X-ray transitions, similar calculated k-ratios are obtained from the MAC database of Heinrich [144], Henke et al. [145] and Chantler et al. [72]. The values in these databases are calculated based on fundamental solid state physics equations, and will be referred for simplicity as analytical MACs. Contrarily, the database of Pouchou and Pichoir [273] contains empirically determined MAC values, notably for the Fe and Ni L$_{3}$–M$_{4,5}$ X-ray transitions to improve the absorption correction due to self-absorption [271]. Tab. 5.1 summarizes the MAC values for all four databases.

Considering the k-ratios measured from the peak/background approach, the analytical MACs give similar results, good agreement for the Fe L$_{3}$–M$_{4,5}$, but large discrepancies for Ni L$_{3}$–M$_{4,5}$. The empirical MACs from Pouchou and Pichoir [273] result in a closer agreement for the Ni L$_{3}$–M$_{4,5}$ but show divergences for the Fe L$_{3}$–M$_{4,5}$ at high accelerating voltages. For the k-ratios measured from the fitted peak area, all MAC databases yield too small calculated k-ratios for the Fe L$_{3}$–M$_{4,5}$ X-ray transition, although the analytical MACs conform more to the decreasing trend of the experimental k-ratios as a function of the accelerating voltage. The experimental
5.2. Results and discussion

Figure 5.8: Experimental and calculated k-ratios for the (a) Fe and (b) Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions as a function of the accelerating voltage comparing calculated k-ratios obtained from four MAC databases: Heinrich [144], Pouchou and Pichoir [273], Henke et al. [145] and Chantler et al. [72].

Ni L\textsubscript{3}–M\textsubscript{4,5} k-ratios fall in between the calculated k-ratios from the analytical and empirical MAC databases at high accelerating voltages, whereas all MAC databases overestimate the k-ratios at low accelerating voltages.

### Table 5.1: Mass attenuation coefficients for the Fe and Ni L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions in Fe and Ni from four MAC databases: Heinrich [144], Pouchou and Pichoir [273], Henke et al. [145] and Chantler et al. [72]. All values are expressed in cm\textsuperscript{2}g\textsuperscript{-1}.

<table>
<thead>
<tr>
<th></th>
<th>Heinrich</th>
<th>Pouchou</th>
<th>Henke</th>
<th>Chantler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe L\textsubscript{3}–M\textsubscript{4,5} in Fe</td>
<td>2160.6</td>
<td>3350.0</td>
<td>2151.2</td>
<td>1963.8</td>
</tr>
<tr>
<td>Ni L\textsubscript{3}–M\textsubscript{4,5} in Fe</td>
<td>13722.7</td>
<td>13722.7</td>
<td>13039.7</td>
<td>12873.7</td>
</tr>
<tr>
<td>Fe L\textsubscript{3}–M\textsubscript{4,5} in Ni</td>
<td>2718.1</td>
<td>2718.1</td>
<td>2838.6</td>
<td>2520.1</td>
</tr>
<tr>
<td>Ni L\textsubscript{3}–M\textsubscript{4,5} in Ni</td>
<td>1810.9</td>
<td>3560.0</td>
<td>1802.3</td>
<td>1693.4</td>
</tr>
</tbody>
</table>

5.2.5 Quantification

Interestingly, for the peak/background measurements, small deviations are observed at 2kV regardless of the MAC used in the calculated k-ratios. For the Fe L\textsubscript{3}–M\textsubscript{4,5} X-ray transition, a good correlation is even observed up to 5kV. Overall, the better results at low accelerating voltages are encouraging since it is under these conditions that the use of L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions becomes necessary and the most advantageous in terms of spatial resolution. Nonetheless, the deviations between the k-ratios are larger enough for the quantification to return inaccurate mass concentrations with relative errors greater than 5%, as shown in Fig. 5.9 for both analytical (Chantler et al. [72]) and empirical (Pouchou and Pichoir [273]) MAC databases. The quantification results show similar trends as the k-ratios, but with greater fluctuations at
high accelerating voltages as the iterative procedure failed to converge to a solution. In sum, an accurate quantification is only possible at 2 kV, except for the Fe$_{25}$Ni$_{75}$ sample where the Fe concentration is underestimated.

### 5.2.6 Calculation of empirical mass attenuation coefficients

Whether it is the shape of the X-ray intensity vs. accelerating voltage curves (Fig. 5.3) or the variations of the calculated k-ratios depending on the MAC database used (Fig. 5.8), all the results presented so far point to an incorrect absorption correction, especially for the Ni L$_3$–M$_{4,5}$ X-ray transition. To test this hypothesis, the experimental results were used to calculate the best possible MACs for the Fe–Ni alloys using the procedure described in §5.1.5. Although the use of the empirically determined MACs from Pouchou and Pichoir [273] gave little improvement (Fig. 5.8), the authors only determined and modified the self-absorption MACs (Fe L$_3$–M$_{4,5}$ by Fe atoms or Ni L$_3$–M$_{4,5}$ by Ni atoms). The MACs representing the absorption by the other alloying element were taken from the Heinrich [144] database (Tab. 5.1). From the results, it is however clear that the determination of all four MACs involved in the quantification of Fe–Ni alloys is important. For instance, there are several evidences of the stronger absorption of Ni L$_3$–M$_{4,5}$ X-rays by Fe atoms in the three studied Fe–Ni alloys.

Fig. 5.10 show the calculated X-ray intensities resulting from the optimization of the MACs. For all X-ray transitions, samples and acquisition methods, the non-linear solver found a set of MACs that yields a good agreement between the experimental and calculated X-ray intensities at all measured accelerating voltages. This indicates that the intensity model used, in occurrence XPP [273], can reproduce the X-ray intensity trends described in §5.2.1 with the appropriate set of MACs.

For comparison, calculated X-ray intensities using the MAC database of Pouchou and Pichoir [273] and Chantler et al. [72] are shown in Fig. 5.11. The empirical MACs based on Pouchou and Pichoir [273] comes closer to the experimental Fe and Ni L$_3$–M$_{4,5}$ X-ray intensities than the analytical ones from Chantler et al. [72]. They correctly model the shape of the X-ray intensity vs. accelerating voltages curves. Nonetheless, larger differences are observed than in Fig. 5.10a-b, particularly below 10 kV where the absorption is overestimated and above 20 kV where it is underestimated. Simultaneously solving for both compound MACs for Fe and Ni L$_3$–M$_{4,5}$ allows the minimization of Eq. 5.2 to reach a better overall solution.

Fig. 5.12 shows and Tab. 5.2 tabulates the empirically determined compound MACs in this work for the three Fe–Ni alloys and pure reference materials. Based on Eq. 5.6, the compound MACs should linearly vary with the Fe mass fraction, as they are a linear combination of the elemental MACs in Fe and Ni. Although only three compounds were measured, the results suggest that this relationship holds for the Fe–Ni alloys. This contrasts with the results of Heikinheimo et al. [142] for Ni silicides, where the empirically determined MACs (elemental) exhibit a dependence on the Ni concentration. From these observations, the absorption in Fe–Ni alloys is not affected by the chemical composition and follows the expected rule of mixture (Eq. 2.36).

Using Eq. 5.6, the elemental MACs, $(\mu/\rho)^{\text{Fe}}_{i,k}$ and $(\mu/\rho)^{\text{Ni}}_{i,k}$, were calculated from the slope and intercept of the linear fit shown in Fig. 5.12. This only applies to the MACs determined from the peak/background acquisition method since only one
5.2. Results and discussion

Figure 5.9: Relative error on the (a) Fe and (b) Ni concentrations after quantification using the PAP [273] intensity model and either the MAC database from Pouchou and Pichoir [273] (above) or Chantler et al. [72] (below). The horizontal dash lines delineate the ±5% relative error bracket.
Figure 5.10: Experimental and calculated X-ray intensities as a function of the accelerating voltage acquired on Fe, Fe$_{25}$Ni$_{75}$, Fe$_{50}$Ni$_{50}$, Fe$_{75}$Ni$_{25}$ and Ni. Calculated intensities are obtained from the XPP [273] intensity model after the optimization of the MACs. X-ray intensities for the Fe L$_{3}$–M$_{4,5}$ X-ray transition are shown in (a) and (c), whereas (b) and (d) show X-ray intensities for the Ni L$_{3}$–M$_{4,5}$ X-ray transition. X-ray intensities in (a) and (b) were measured using the peak/background approach, whereas X-ray intensities from the peak area determined by fitting WD spectra are given in (c) and (d).

<table>
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<tr>
<th></th>
<th>Ni</th>
<th>Fe$<em>{25}$Ni$</em>{75}$</th>
<th>Fe$<em>{50}$Ni$</em>{50}$</th>
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<tr>
<td>Fe L$<em>{3}$–M$</em>{4,5}$ (p/b)</td>
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<td>Ni L$<em>{3}$–M$</em>{4,5}$ (p/b)</td>
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<td>6400.6</td>
<td>8438.5</td>
<td>10 853.6</td>
<td>–</td>
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<tr>
<td>Fe L$<em>{3}$–M$</em>{4,5}$ (area)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4316.4</td>
<td>–</td>
</tr>
<tr>
<td>Ni L$<em>{3}$–M$</em>{4,5}$ (area)</td>
<td>3997.3</td>
<td>–</td>
<td>9546.4</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

Table 5.2: Empirically determined compound MACs for the Fe and Ni L$_{3}$–M$_{4,5}$ X-ray transitions based on both types of acquisition: peak/background (p/b) and fitted peak area (area). All values are expressed in cm$^2$ g$^{-1}$. 
5.2. Results and discussion

Figure 5.11: Experimental and calculated X-ray intensities as a function of the accelerating voltage for the (a) Fe and (b) Ni L$_{3}$-M$_{4,5}$ X-ray transition, and the MAC database from Pouchou and Pichoir [273] and Chantler et al. [72].

Figure 5.12: Empirically determined compound MACs for the Fe and Ni L$_{3}$-M$_{4,5}$ X-ray transitions as a function of Fe mass fraction. MACs for both types of acquisition are shown: peak/background (p/b) and fitted peak area (area). Those from the peak/background approach were fitted based on Eq. 5.6.
Table 5.3: Elemental MACs for the Fe L$_{3}$–M$_{4,5}$ X-ray transitions in Fe and Ni from the database of Pouchou and Pichoir [273] and Chantler et al. [72], as well as the newly determined MACs in this work from the peak/background acquisition approach. All values are expressed in cm$^2$g$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Pouchou</th>
<th>Chantler</th>
<th>New (p/b)</th>
</tr>
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<td>Fe L$<em>{3}$–M$</em>{4,5}$ in Fe</td>
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<td>13 722.7</td>
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</tr>
<tr>
<td>Fe L$<em>{3}$–M$</em>{4,5}$ in Ni</td>
<td>2718.1</td>
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<td>4067.0</td>
</tr>
<tr>
<td>Ni L$<em>{3}$–M$</em>{4,5}$ in Ni</td>
<td>3560.0</td>
<td>1693.4</td>
<td>4420.2</td>
</tr>
</tbody>
</table>

5.2.7 Calculated k-ratios with the new mass attenuation coefficients

Using the newly determined MACs, k-ratios were calculated using two approaches, either using the elemental or compound MACs. The first approach is the traditional one, which was used so far for all calculated k-ratios. The same elemental MACs are used to calculate the unknown and reference X-ray intensities. The second approach utilizes the experimentally determined compound MACs from Tab. 5.2. In the k-ratio calculation, the specific compound MACs for each sample (unknown or reference) is used to calculate their X-ray intensity. In other words, the $\chi_{ik}$ in the nominator and denominator of Eq. 2.40 differs. The two approaches are respectively denoted as “elemental” and “compound” in the following figures.

Appending Fig. 5.8, Fig. 5.13 shows the calculated k-ratios based on the two approaches. Several remarks can be formulated from Fig. 5.13. Starting with the results from the peak/background acquisition method (Fig. 5.13a-b), the MACs determined in this work give a closer agreement with the experimental k-ratios, regardless whether the elemental or compound MACs are used to calculate the k-ratios. For the Fe L$_{3}$–M$_{4,5}$ X-ray transition, the calculated k-ratios now match the constant trend of the experimental k-ratios as a function of the accelerating voltage for all three alloys. The fit is particularly improved at high accelerating voltages, indicating a better absorption correction. Smaller discrepancies are observed using the compound MAC, especially for the Fe$_{50}$Ni$_{50}$ and Fe$_{75}$Ni$_{25}$ samples, suggesting some influence of the sample composition on the absorption of Fe L$_{3}$–M$_{4,5}$ X-rays. The same observation applies to the Ni L$_{3}$–M$_{4,5}$ X-ray transition, where the calculated k-ratios using the
5.2. Results and discussion

Figure 5.13: Experimental and calculated k-ratios as a function of the accelerating voltage. Calculated intensities are obtained from the XPP [273] intensity model using different MACs, including those experimentally determined in this work. k-ratios for the Fe L$_{3}$–M$_{4,5}$ X-ray transition are shown in (a) and (c), whereas (b) and (d) show k-ratios for the Ni L$_{3}$–M$_{4,5}$ X-ray transition. k-ratios in (a) and (b) were measured using the peak/background approach, whereas k-ratios from the peak area determined by fitting WD spectra are given in (c) and (d).

compound MACs tend more towards the experimental ones. However, this improvement is insignificant in comparison with the remaining differences. Although the new MACs give promising signs between 25 to 30 kV, no improvement is noted in the interesting range of accelerating voltages for the Ni L$_{3}$–M$_{4,5}$ X-ray transition, expressly 4 to 7 kV.

As for the results obtained from peak area measurements, the new MACs has little to no impact on improving the quantification using the Fe L$_{3}$–M$_{4,5}$ X-ray transition. The discrepancies between the experimental and calculated k-ratios remain the largest observed in this work. For the Ni L$_{3}$–M$_{4,5}$ X-ray transition, the results are slightly better than with the analytical MACs of Pouchou and Pichoir [273].
In general, the interpretation of the results from Fig. 5.13 raises the question why large discrepancies between experimental and calculated k-ratios remain even though Fig. 5.10 shows an excellent agreement between experimental and calculated X-ray intensities. All in all, k-ratios are simply the ratio of these X-ray intensities. A possible explanation is related to the factor \( \alpha_{i,k} \) used in the determination of the compound MACs (Eq. 5.2 and 5.3) and is discussed in the next section.

### 5.2.8 Calculated k-ratios with \( \alpha \) factors

As mentioned in §5.1.5, \( \alpha_{s_{i,k}}^{s} \) is a proportionality constant, allowing the comparison of experimental and calculated X-ray intensities. For a perfect match, the following equality exists from Eq. 5.2:

\[
I_{s_{i,k}}^i(E_j) = \alpha_{s_{i,k}}^{s} \hat{I}_{i,k}(E_j, \chi_{s_{i,k}}^{s}, \vec{w}^{s}) \tag{5.9}
\]

In the minimization procedure used to determine the MACs, an \( \alpha_{i,k}^{s} \) is automatically calculated for each X-ray transition (subscript \( i, k \)) and each sample (superscript \( s \)). For example, the minimization may find a different \( \alpha \) for the Ni L\(_{3}\)–M\(_{4,5}\) X-ray transition in pure Ni than in the Fe\(_{50}\)Ni\(_{50}\) alloy. \( \alpha \) is optimized at each iteration of the MACs to yield the best fit between the experimental and calculated X-ray intensities for a given sample, not for all samples analyzed. This optimization is however absent in Fig. 5.13, where the calculated k-ratios are calculated from the ratio of the calculated X-ray intensities for an unknown sample and a reference material, ignoring the \( \alpha \) values for these samples: Mathematically,

\[
k_{i,k}^{\text{calc}} = \frac{\hat{I}_{i,k}^{\text{unk}}}{\hat{I}_{i,k}^{\text{ref}}} \neq \frac{\alpha_{i,k}^{\text{unk}}}{\alpha_{i,k}^{\text{ref}}} \tag{5.10}
\]

As shown in Fig. 5.14, including the different \( \alpha \) factors gives completely different results than Fig. 5.13. Overall, the agreement of the calculated k-ratios with experimental ones is improved for both acquisition methods, both X-ray transitions and all samples. The improvement is particularly significant for the Fe L\(_{3}\)–M\(_{4,5}\) X-ray transition measured by the fitted peak area acquisition method (Fig. 5.13c). The large differences observed in Fig. 5.13 have disappeared. The same goes for the Ni L\(_{3}\)–M\(_{4,5}\) X-ray transition, although discrepancies persist below 5 kV for both acquisition methods. Speculating on the potential causes for these inaccuracies, the influence of carbon contamination and oxidation could certainly be one explanation. The topic of oxidation is discussed in the next section.

To elucidate the role of the \( \alpha \) factors in the calculation of the k-ratios a closer look at Eq. 5.10 is needed. The \textit{raison d’être} of the k-ratio is the cancellation of several terms from the fundamental intensity equation (Eq. 2.33), the same terms that constitute the \( \alpha \) factor. While the first three groups of Eq. 2.33 can obviously be left out, the assumption that the ratio cancels out most terms related to the electron-photon-matter interactions (fourth group) may be questionable for soft X-rays. By modifying the electron configuration of atoms, chemical bonding is likely
5.2. Results and discussion

Figure 5.14: Experimental and calculated k-ratios as a function of the accelerating voltage. Calculated intensities are obtained from the XPP [273] intensity model after the optimization of the MACs and the $\alpha$ factors. k-ratios for the Fe L$_{3}$–M$_{4,5}$ X-ray transition are shown in (a) and (c), whereas (b) and (d) show X-ray intensities for the Ni L$_{3}$–M$_{4,5}$ X-ray transition. k-ratios in (a) and (b) were measured using the peak/background approach, whereas k-ratios from the peak area determined by fitting WD spectra are given in (c) and (d).
to also influence the physical phenomena described by these terms. A more rigorous formulation of the calculated k-ratio equation based on $\phi(\rho z)$ models (Eq. 2.40) would therefore be

$$k_{i,k}^{\text{calc}} = \left( \frac{p_{i,k}^{\text{unk}} \sigma_{i,k}^{\text{unk}} \int_{i,k}^{\infty} \phi_{i,k}^{\text{unk}} \exp \left( -\chi_{i,k}^{\text{unk}}(\rho z) \right) d\rho z}{p_{i,k}^{\text{ref}} \sigma_{i,k}^{\text{ref}} \int_{i,k}^{\infty} \phi_{i,k}^{\text{ref}} \exp \left( -\chi_{i,k}^{\text{ref}}(\rho z) \right) d\rho z} \right) \left( \frac{\epsilon_{i}^{\text{unk}}}{\epsilon_{i}^{\text{ref}}} \right),$$

(5.11)

where the definition of the terms is found in §2.1.4. As the fluorescence probability is low for soft X-rays [271], the fluorescence contribution (Eq. 2.35) for both unknown and reference materials tends towards unity. The presence of two absorption functions in Eq. 5.11 implies more than a different absorption behaviour between the two samples. It denotes the departure from the assumption that the absorption function obeys the rule of mixture of photoelectric absorption cross sections or MACs (Eq. 2.36). It expresses the k-ratio calculation strategy based on empirically determined compound MACs of Fig. 5.13. Evidenced by the results in this work, unequal $\chi_{i,k}^{\text{unk}}$ and $\chi_{i,k}^{\text{ref}}$ only has a small impact on reducing the differences between the experimental and calculated k-ratios.

Two remaining terms are related to the ionization of the inner shell, $k'$: the ionization cross section, $\sigma_{i,k'}$, the probability of an electron knocking an electron of shell $k'$, and $\phi_{i,k'}$, the number of vacancies produced in shell $k'$ in an infinitesimal layer at a depth $\rho z$ (Eq. 2.37). For the L$_3$–M$_4$,5 X-ray transitions, the shell $k'$ corresponds to the L$_3$ subshell, containing the 2p$^{3/2}$ electrons. As core electrons, chemical bonding has no influence on their binding energy, and thus on their ejection probability from an inelastic interaction. $\sigma_{i,k'}$ and $\phi_{i,k'}$ should not suffer from abnormal chemical effects and conform to the rule of mixture. A further proof of this statement comes from Fig. 5.7. As shown in Fig. 5.8, the differences between the calculated k-ratios were attributed to the MACs and not the models used to calculate $\sigma_{i,k'}$ and $\phi_{i,k'}$. For a given set of MACs, the calculated k-ratios obtained from the different models are indistinguishable.

This leaves one unaddressed term in Eq. 5.11, the transition probability, $p_{i,k}$, “the probability that a vacancy [...] is filled through a radiative transition” [22]. As noted in §2.4.2.6, chemical bonding may modify the occupancy of the valence band, the M$_4$ or M$_5$ subshells for the first transition series metals. Among other things, the transition probabilities depend on the density of occupied states, i.e. the number of electrons in the outer subshell of an X-ray transition [47]. For the Fe or Ni L$_3$–M$_4$,5 X-ray transition, more 3d$^{3/2}$ and 3d$^{5/2}$ electrons would translate into a higher transition probability, and ultimately a higher X-ray intensity.

Looking at the different terms of Eq. 5.11, the transition probability, $p_{i,k}$, “the probability that a vacancy [...] is filled through a radiative transition” [22]. As noted in §2.4.2.6, chemical bonding may modify the occupancy of the valence band, the M$_4$ or M$_5$ subshells for the first transition series metals. Among other things, the transition probabilities depend on the density of occupied states, i.e. the number of electrons in the outer subshell of an X-ray transition [47]. For the Fe or Ni L$_3$–M$_4$,5 X-ray transition, more 3d$^{3/2}$ and 3d$^{5/2}$ electrons would translate into a higher transition probability, and ultimately a higher X-ray intensity.

Looking at the different terms of Eq. 5.11, the transition probability comes out as the most likely term capable of explaining the sample dependence of the $\alpha$ factors. The ratio of $\alpha$ factors from Eq. 5.10 is then approximately equal to the ratio of the transition probabilities:

$$\frac{\alpha_{i,k}^{\text{unk}}}{\alpha_{i,k}^{\text{ref}}} \approx \frac{p_{i,k}^{\text{unk}}}{p_{i,k}^{\text{ref}}}. \quad (5.12)$$

Fig. 5.15 shows the variation of $\alpha$ factors and their ratio for the Fe and Ni L$_3$–M$_4$,5 X-ray transitions as a function of the Fe mass fraction. The $\alpha$ factors for the two acquisition methods differ in terms of magnitude and relation with respect to
5.2. Results and discussion

The native oxide layer extends the total path travelled by any X-ray inside the sample. While this additional distance usually has a negligible impact, the measurement of soft X-rays at low accelerating voltages is a special case resulting in a noticeable decrease of the X-ray intensities. This results from a combination of factors. First, the oxide layer typically contains the same element as the underneath metallic substrate. As soft X-rays have a high self-absorption, X-rays produced in the substrate may also get

Figure 5.15: (a) \( \alpha \) factors for the Fe and Ni L\(_3\)-M\(_{4,5}\) X-ray transitions and both acquisition methods as a function of the Fe mass fraction. (b) Ratio of \( \alpha \) factors using the pure metals as reference materials.

the Fe mass fraction. The results from the fitted peak area method agree with the conclusions of Chun and Klein [78] regarding the transfer of electrons from Ni to Fe atoms in Fe-Ni alloys. In Fig. 5.15a, the \( \alpha_{\text{Ni L}_{3}\text{-M}_{4,5}} \) is higher in pure Ni than in Fe\(_{50}\)Ni\(_{50}\) sample due to more electrons in the valence band, whereas the inverse occurs for the \( \alpha_{\text{Fe L}_{3}\text{-M}_{4,5}} \). Based on the previous explanations, the lower occupancy of the Ni M\(_4\) and M\(_5\) subshells in the Fe\(_{50}\)Ni\(_{50}\) sample decreases the Ni L\(_3\)-M\(_{4,5}\) transition probability in comparison to pure Ni, and analogously the associated \( \alpha \) factor. It is the opposite situation for the Fe L\(_3\)-M\(_{4,5}\) transition probability. From Fig. 5.15b, the transfer of valence electrons affects differently the transition probabilities. The \( \alpha \) ratio of the Fe L\(_3\)-M\(_{4,5}\) X-ray transition is not the mathematical inverse from the one of the Ni L\(_3\)-M\(_{4,5}\) X-ray transition. The electrons gained by Fe atoms has a larger impact on the L\(_3\)-M\(_{4,5}\) transition probability.

All in all, the minimization procedure developed by Pouchou and Pichoir [273] to calculate empirical MACs also determines empirical transition probabilities, not their absolute value, but their ratio between two samples as shown in Eq. 5.12. While the determination of their absolute value would be possible if the solid angle and detector efficiency of the spectrometer are known, the empirical ratio of transition probabilities between the unknown and reference material, \( \frac{p_{\text{unk i,k}}}{p_{\text{ref i,k}}} \), is sufficient for k-ratio based quantification.

5.2.9 Oxidation

The native oxide layer extends the total path travelled by any X-ray inside the sample. While this additional distance usually has a negligible impact, the measurement of soft X-rays at low accelerating voltages is a special case resulting in a noticeable decrease of the X-ray intensities. This results from a combination of factors. First, the oxide layer typically contains the same element as the underneath metallic substrate. As soft X-rays have a high self-absorption, X-rays produced in the substrate may also get
For the quantification using soft X-rays, a critical point is the different chemical composition and thickness of the native oxide layer from the unknown and reference material. For instance, a thicker, more absorbent, oxide layer on the unknown sample would lower the value of experimental k-ratios measured at low accelerating voltages. Fig. 5.16 shows the variation of the oxide layer thickness as a function of the Fe mass fraction for the studied Fe–Ni samples. Although smaller thicknesses were calculated in comparison to Heikinheimo and Llovet [141], the same conclusion is reached that pure Fe has a thicker oxide layer than pure Ni. The oxide layer thickness of the alloys falls in between those of the pure metals.

Going back to Fig. 5.14b, the discrepancies observed at low accelerating voltages may be partially explained by the thickness of the oxide layer. Since the alloys have a thicker oxide layer than pure Ni, the Ni L$_{3}$–M$_{4,5}$ X-rays are slightly more absorbed in the oxide layer of the alloys than in the one of pure Ni. Because of this additional absorption, the experimental k-ratios turn out lower than they would without any native oxide, the hypothetical case implied for the calculated k-ratios.

At this moment, it is however difficult to correct the experimental k-ratios at low accelerating voltages for the absorption in the native oxide layer. First, the MAC for Ni L$_{3}$–M$_{4,5}$ X-rays in the oxide layer calculated based on the rule of mixture is quite certainly inaccurate due to chemical bonding effects, as shown in this work. Secondly, the quantification using compound MACs and/or empirical transition probability ratio is not available in STRATAGem [270], and DTSA-II [302] cannot quantify multilayer samples. The correction of the absorption in the native oxide layer is therefore left as future work.
5.2. Results and discussion

Summary

In conclusion, this exercise reveals that the quantification problems using the L$_3$–M$_{4,5}$ X-ray transitions are related to inaccuracies in the MACs and transition probabilities, and the influence of the sample composition on these fundamental parameters. Whereas the MACs are not significantly affected by the composition of the Fe–Ni alloys (Fig. 5.12) in comparison to other compounds (Fe–Si [125] and Ni–Si [142]), the values in the currently available databases could be improved by empirically determined MACs. This especially applies to the absorption of Fe L$_3$–M$_{4,5}$ X-rays in Ni and Ni L$_3$–M$_{4,5}$ X-rays in Fe (Tab. 5.3). Nevertheless, modifying the MACs only procures a limited improvement. The best agreement is achieved by also using empirical ratios of transition probabilities between the unknown and reference materials (Eq. 5.12) for the k-ratio calculations (Fig. 5.14). Although the empirical ratios appear to be chemistry dependent, no relationship with the alloy content could be deduced from the results. Furthermore, more work is needed to understand the remaining discrepancies below 5 kV.

Throughout §5.2, the results of two acquisition methods were presented. They differ in terms of values and variation as a function of the accelerating voltage. Albeit time consuming, the peak area acquisition is the only method measuring the “true” L$_3$–M$_{4,5}$ X-ray intensities, after the deconvolution of the peak overlaps (Fig. 5.2). Undeniably, this acquisition method should be privileged in the determination of empirical fundamental parameters, notably due to the change of the APFs as a function of the accelerating voltage (Fig. 5.4). Nonetheless, comparable results were obtained using the classical peak/background approach, even though a dispersive element with a low spectral resolution was used (LDE1) for the Fe L$_3$–M$_{4,5}$ X-ray transition and no correction regarding the APFs was applied. This leads to the troublesome conclusion that the minimization procedure can adjust the MACs and ratios of transition probabilities to fit any set of X-ray intensities, at least for the Fe–Ni system. Unless systematic trends as a function of the sample composition can be extracted from these measurements, the empirically determined fundamental parameters dangerously resembles fudging factors.

This work demonstrated a potential solution to the soft X-ray quantification problems, the empirical determination of both MACs and ratios of transition probabilities for the studied sample. One can however question its practically and applicability to complex samples. Taking a low alloy steel as example, new fundamental parameters for the Fe, Cr and Mn L$_3$–M$_{4,5}$ X-ray transitions would need to be determine from reference materials containing various concentrations of Fe, Cr and Mn. Besides the questionable availability of these reference materials, these measurements would certainly be a serious, lengthy undertaking, and may require higher spectral resolution spectrometers.
Chapter 6

Conclusion

EPMA is undeniably an important characterization technique for the development of new AHS steels and manufacturing processes. On the flip side, AHS steels are conjointly the perfect materials to further develop EPMA. Their carefully engineered microstructure consists of several phases and constituents with different sizes and chemical compositions, as described in §2.2.1, summarized in Tab. 2.3 (p. 49) and measured in §3.5. From the micrometric ferrite grains of TRIP steels to the nanometric carbides inside bainite of CP steels, from the trace level of carbon in martensite of DP steels (< 1 mass %), the minor level of chromium in (Fe<sub>x</sub>Cr<sub>y</sub>)<sub>3</sub>C carbides of bearing steels (1–10 mass %) to the major level of manganese in TWIP steels (> 10 mass %), AHS steels encompass, in a single sample, the specificity, strengths and abilities of EPMA as a characterization technique, but also many of its challenges. Through the development of new strategies to characterize steel microstructures at a high spatial resolution in Chap. 3, the study of the carbon contamination phenomenon in Chap. 4 and the investigation of the quantification problems using the L<sub>3</sub>–M<sub>4,5</sub> X-ray transitions of first transition series metals in Chap. 5, the underlying topic of the thesis and universal challenge of EPMA characterization is the quantification of low concentration elements using soft X-rays at a high spatial resolution [255].

Proffering the concept of “steel as the EPMA sample”, steel exemplifies the three interdependent components of this conundrum: (1) soft X-rays, (2) low concentration elements and (3) spatial resolution. All steels contain many alloying elements with a concentration below 1 mass %. This certainly includes light elements such as B, C and N, which only emit soft X-rays, as well as many others (e.g. Cr, Mn, Ni, etc.), which could be measured using their soft X-ray transitions (i.e. L<sub>3</sub>–M<sub>4,5</sub> and L<sub>3</sub>–M<sub>1</sub>). These elements are heterogeneous distributed inside the microstructure, especially in the case of AHS steels, which necessarily imply the need for quantitative measurements at a high spatial resolution. A good conductivity, ease of preparation, availability and industrial significance are other advantageous characteristics of steel samples for EPMA. The following paragraphs will give a synthesis of this work’s contributions to original knowledge and an outlook on future research from the perspective of the aforementioned universal challenge and its three interdependent components.

Soft X-rays The difficulties afflicting the quantification using soft X-rays are not unique to special elements or associated to particular X-ray transitions. For instance, the challenges with the quantification using the C K–L<sub>2,3</sub> X-ray transition in Chap. 3 also apply to the quantification using the Fe and Ni L<sub>3</sub>–M<sub>4,5</sub> X-ray transitions in Chap. 5, and would equally do so for the quantification using the N K–L<sub>2,3</sub>, Cr L<sub>3</sub>–M<sub>4,5</sub> or Ce M<sub>5</sub>–N<sub>6,7</sub> X-ray transitions. All these X-ray transitions share two fundamental characteristics: (1) they are emitted from the relaxation of an electron from the valence band, and (2) they have an energy lower than 1.5 keV. Their low X-ray fluorescence (§2.2.2.2, 3.4.3.3 and 3.4.3.4), their susceptibility to self-absorb
Chapter 6. Conclusion

(§2.4.2.5 and 5.2.6), their dependence on chemical bonding (§2.4.2.6 and 5.2.8), and the emission of satellite peaks (§2.4.2.4 and 5.2.2) relate back to the nature of the radiative relaxation. Their low X-ray energy explains their high absorption by other elements such as carbon atoms of carbonaceous deposits (§2.2.2.1 and 3.2.1.1) or oxygen atoms of a native oxide layer (§2.4.2.2 and 5.2.9). Moreover it complicates their detection due to other X-ray transition and high order X-ray reflection interferences (§2.2.2.3, 2.4.2.3, 3.1.3.1 and 5.1.3) and peculiar X-ray reflectivity of dispersive elements (§2.2.2.4, 3.1.3.2 and 3.1.3.3).

Every strategy to measure the carbon content in steels, including the one developed in §3.2.1, is a practical solution to a complex problem. The well-defined scope allows the formulation of several simplifications, as elaborated in §3.2.1.1. At the top of the list, the use of a certified reference material (Fe$_3$C) with a carbon content approaching the one of the steel sample analyzed effectively eliminates the influence on the quantification of many factors mentioned in the previous paragraph and throughout the thesis. The carbon contamination for measurements at a high spatial resolution and the interferences of high order X-ray reflections for high alloy steels are the two remaining obstacles of the carbon quantification. The latter is discussed along the challenges of low concentration elements.

It goes without saying that carbon contamination has the largest adverse consequence on the carbon quantification, notably for low carbon containing samples, but it also interferes with the quantification using any soft X-ray, as shown in Fig. 2.29 (p. 99) for the Cr L$_{3}$–M$_{4.5}$ X-ray transition. Regardless of the accelerating voltage, electron beam diameter, irradiation time and anti-contamination device(s) used, the results reviewed in §2.3 and presented in Chap. 4 demonstrate that a ring-shaped carbonaceous deposit is produced by a stationary electron beam on any sample at the beam currents typically used for EPMA (> 1 nA), and assuredly required to measure low concentrations with soft X-rays. Corroborating other publications, experiments have confirmed the predominance of the sample as the source of organic molecules involved in the carbon contamination reaction (Rxn. 2.1 on p. 57) inside a modern electron microscope equipped with oil-free vacuum pumps. These molecules have a low desorption rate, evidenced by the persisting carbon contamination even following plasma cleaning (Fig. 4.6 on p. 214), after long pumping times (Fig. 4.7 on p. 215) or under a lower vacuum pressure created by a liquid nitrogen cold trap (Fig. 4.8 on p. 215). In sum, the long residence time of adsorbed organic molecules, the limited influx of organic molecules from the vacuum and the excess of incident electrons establish a surface diffusion limited regime. The experimental and simulated variations of the critical dimensions of the carbonaceous deposits as a function of the irradiation time, beam current and accelerating voltage are evidences that organic molecules are immediately cracked as soon as they enter the electron irradiated area. The extent of the latter equally depends on the interaction volume and the emission of SE2s than on the beam profile, particularly at low accelerating voltages and high beam currents (Fig. 4.13 and 4.26 on p. 221 and 235). While it was not the aim of this work, in the light of the presented findings, the development of new anti-contamination devices should consider three avenues, in decreasing order of importance: (1) higher desorption of adsorbed organic molecules, (2) slowing down their surface diffusion, and (3) more efficient etching of carbonaceous deposits. As stated in Chap. 4, it how-
ever starts with a deeper knowledge of the experimental conditions (surface chemistry, electron beam profile, etc.) and fundamental quantities for simulations (cross sections, surface diffusion coefficients, etc.).

Moving beyond the carbon quantification, other elements play decisive roles in the mechanical properties of steel, e.g. Mn for DP (§3.5.1.1) and TWIP steels (§3.5.2.1), or Cr for bearing steels (§3.5.2.2). Whereas the carbon content normally stays below 1 mass%, the concentration of the other alloying elements vary over a larger range, from a few ppm to more than 30 mass% in high alloy steels. The aforementioned strategy used for carbon, relying on one or several reference materials with a similar composition as the unknown sample, is therefore a nonviable solution for the quantification of alloying elements using their soft X-ray transitions. In the case of first transition series metals, the use of their $\text{L}_3-\text{M}_{4,5}$ and/or $\text{L}_2-\text{M}_1$ X-ray transitions eliminates some pitfalls associated with their $\text{L}_3-\text{M}_{4,5}$ X-ray transitions: no nearby absorption edge hence no self-absorption and no chemical bonding effect since the $\text{M}_1$ is not a subshell of the valence band (§2.4.3). On the other side, the significantly lower X-ray intensity of these X-ray transitions amplifies interference problems and restricts the achievable precision (§3.4.3.4). The challenges due to carbon contamination and native oxidation also persist. Unless spectrometers with a higher spectral resolution and larger solid angle are invented, the quantification using $\text{L}_3-\text{M}_{1}/\text{L}_2-\text{M}_1$ X-ray transitions will always be limited to major elements. Studying the quantification issues with other soft X-rays (i.e. $\text{L}_3-\text{M}_{4,5}$ X-ray transitions of first transition series metals) is consequently a worthy endeavour for none more relevant reason than the characterization of AHS steels.

The systematic investigation of three Fe–Ni binary alloys in Chap. 5 aimed at gaining more insight into this problem based on simple, well-characterized, steel-like reference materials. Through the development of a software to automate acquisitions on a electron microprobe, the elaboration of a strategy to fit WD spectra, the enhancement of an algorithm to determine mass attenuation coefficients and the modification of this algorithm to calculate transition probability ratios, empirical quantities were obtained from measurements at different accelerating voltages. In the end, it was not the peak asymmetry (expressed as by the area to peak factor in Fig. 5.4 on p. 246), not the presence of satellite peaks (Fig. 5.5 on p. 248), not the analytical models or the Monte Carlo simulations (Fig. 5.7 on p. 250), not the rule of mixture of mass attenuation coefficients (Fig. 5.12 on p. 255), nor their values in currently available databases (Fig. 5.8 on p. 251) that could explain the large quantification errors on the Fe and Ni concentrations, but the combination of improved MACs for Fe $\text{L}_3-\text{M}_{4,5}$ X-rays in Ni and Ni $\text{L}_3-\text{M}_{4,5}$ X-rays in Fe, and empirical ratios of transition probabilities. As shown in Fig. 5.14 (p. 259), a good agreement was obtained between experimental and calculated k-ratios for all three Fe–Ni binary alloys, at any accelerating voltage and using both peak/background and peak area acquisitions. The remaining discrepancies below 5 kV may in part be attributed to the different thickness of the native oxide layer between the alloys and pure metals (Fig. 5.16 on p. 262).

There is no point in beating around the bush, EPMA needs new models to approximate the fundamental intensity equation (Eq. 2.33 on p. 39) where the influence of chemical bonding, i.e. the electronic configuration of atoms in solids, on X-ray emission and absorption is considered. Workarounds such as special reference materials, calibration curves, adjustment factors or empirical quantities have reached their limit. In its purest expression, EPMA shall accurately determine the concentration
of any element using any of its X-ray transition without any prior knowledge about
the analyzed sample. The only requirement is for the spectrometer to detect a suffi-
cient number of X-rays. Evidently, the accomplishment of this objective entails the
adaptation of more advanced solid-state physics computations to the present EPMA
problem, the quantification using soft X-rays.

**Low concentration** The quantification of low concentration elements necessitates a
high counting statistics and a proper determination of the background. High counting
statistics, or equivalently a good precision, translates into a large overvoltage ratio, a
high beam current and/or a longer measuring time. In other words, a certain number
of detected X-rays must be detected to minimize the random uncertainties. For low
centration elements, counting statistics affects both the peak and background
intensities per Eq. 3.19 (p. 157), since the peak to background ratio will be close to
unity. A practical consideration of the precision on the carbon content in various
steels was illustrated in Fig. 3.25 (p. 151) and Fig. 3.46 (p. 197) for three different
acquisition strategies and measuring times (same accelerating voltage of 15 kV and
beam current of 100 nA): well-separated point (5 s), line scan (5 s) and mapping (100
ms). Including the influence of the acquisition strategy on the carbon contamination
and its contribution to the systematic uncertainties, the carbon content measured by
a mapping acquisition is on average five to ten times less precise than the one by a
point or line acquisition.

This comparison unfortunately shows that increasing the measuring time in order
to reduce statistical uncertainties is not only synonym to more costly measurements,
but phenomena of contamination become predominant. For high spatial resolution
measurements where measurement locations are closely spaced, it is important to
realize that the contamination leftover by previous neighbouring measurements has
a large influence on the measurement of the following locations (Fig. 3.16 on p. 130).
Using a pre-determined background as described in §3.2.1.1 and expressed by Eq. 3.4
(p. 138) is one solution to minimize the measuring time at one location.

Relatively, the level of imprecision increases as the mass content of an element
decreases. From the optimization routine of §3.4, this was illustrated for carbon in
Fig. 3.34 (p. 171) where its relative precision worsens at low concentrations in spite of
longer optimal measuring times. Decreasing the accelerating voltage from 15 to 11 kV
has the comparable effect on the relative precision of Cr and Mn in the hypothetical
steel of §3.4 (Tab. 3.10 vs. 3.11 on p. 172 and p. 173). Switching to the L₃–M₄,₅ X-ray
transition for these elements further aggravates the relative precision (Tab. 3.12 on
p. 173). In general, the lower ionization cross section and higher photoelectric cross
section of soft X-rays inevitably complicate the quantification of low concentration
elements.

Apart from longer measuring times, increasing the beam current is another way
to counteract the low intensity of soft X-rays and any X-ray emitted from a small
overvoltage ratio. As it will be subsequently discussed, the adverse effect of this
alternative on the spatial resolution limits its usefulness, especially since a higher
spatial resolution is precisely the desired objective when lowering the accelerating
voltage and using non-traditional X-ray transitions.

A proper determination of the background implies an accurate modelling of the
background curvature and the correction or minimization of other X-ray transition
interferences. In an effort to counter the inherently low intensity of soft X-rays, syn-
thetic multilayer dispersive elements are typically designed to have a high reflectivity. One caveat is however their varying reflectivity as a function of the incident angle ($\theta$ in Bragg’s law, Eq. 2.28 on p. 34), resulting in an uneven, irregularly shaped background, as experimentally measured in Fig. 3.5 (p. 117) and theoretically calculated in Fig. 3.9 (p. 123) for a LDE2 dispersive element. The latter calculations demonstrated the influence of the dispersive element on the measured X-ray intensities. Although the step in the continuum around the C K–L$_{2,3}$ X-ray transition would have a minimal effect on the quantification of high carbon containing phases (e.g. carbides), its magnitude is surely comparable to the height of the C K–L$_{2,3}$ X-ray peak of a low carbon concentration analysis. The same applies to the L$_3$ absorption edge under the L$_3$–M$_{4,5}$ X-ray peak of the first transition series metals, which may explain to some extent the quantification inaccuracies.

Another drawback of multilayer dispersive elements is their worst spectral resolution in comparison to single crystal dispersive elements (see Fig. 2.30 on p. 101 for the comparison between LDE1 and TAP). Combined with the fact that the energy separation between soft X-ray transitions is significantly reduced, overlapping and interference problems between adjacent X-ray transitions and high order X-ray reflections are therefore common. Fig. 3.6 (p. 119) confirmed that energy filtration by the pulse height analyzer can minimize the intensity of high order X-ray reflections, yet not without reducing the one of the first order X-ray transitions. The proximity of soft X-ray transitions is a major handicap for steels, which normally contains many elements from the first transition series. Beyond the unavoidable interference corrections, background intensities can only be measured far away from the X-ray peak, accentuating the need for an accurate modelling of the background curvature. The situation where the interfered element has a much lower concentration than the interfering one is also particularly problematic for the quantification using the L$_3$–M$_1$/L$_2$–M$_1$ X-ray transition due to its significantly lower intensity.

Furthermore, the importance of the total internal reflection phenomenon was experimentally assessed using three nickel silicides in Fig. 3.10 (p. 124). In the presence of some specific elements, the background intensity no longer depends on the Bremsstrahlung X-ray emission from the sample (approximately related to the mean atomic number), but also on the total internal reflection of characteristic X-rays by the dispersive element. With variable concentrations of Si, Al and B, this effect adds another challenge to the background determination of steel samples.

The quantification strategy developed for high alloy steels in §3.2.2 addresses all these difficulties related to the background determination with a generic, all-inclusive correction equation (Eq. 3.11 on p. 145). Whereas the forthright elimination of each interference and a specific compensation for irregular X-ray reflectivity would yield a more universal solution to this convoluted problem, a more in-depth knowledge about the dispersive element and an X-ray detector with a better energy resolution than proportional counter would be required. The correction equation is therefore a practical compromise to allow the quantification of high alloy steels without any modification to the normal acquisition procedure.

**Spatial resolution** Subtracting the requirement of measurements at a high spatial resolution, most challenges associated with the quantification of low concentration elements using soft X-rays can be eliminated. First, there is no need to decrease the accelerating voltage, ruling out the use the L$_3$–M$_{4,5}$ X-ray transitions to measure first
transition series metals and maintaining a large overvoltage ratio with their K–L\textsubscript{2,3} X-ray transitions. Secondly, while the measurement of carbon remains trouble-prone, the influence of carbon contamination can be largely minimized by defocusing the electron beam and using a large beam current. Finally, the latter also improves the precision on low concentration elements by increasing their X-ray intensity. Disregarding the spatial resolution, the only constraint on the beam current is the conductivity of the analyzed sample and its sensitivity to beam damage. Here again, a large defocused beam can help reduce the beam current density and thus the heat generation inside the sample as per Eq. 2.53 (p. 66).

The quest to quantify smaller and smaller microstructural features is at the heart of technological and theoretical advancements of EPMA. The introduction of SEMs and electron microprobes equipped with a Schottky emitter has improved the analytical potential of these instruments. They deliver smaller beam diameters than thermionic emitter electron microscopes at any accelerating voltage and beam current. This statement does not however imply that the analytical conditions do not have an influence on the final beam diameter.

After the type of electron emitter, the most influential parameter on the spatial resolution is the accelerating voltage. Lowering the accelerating voltage has the combined effects of decreasing the electron interaction volume and additionally, due to the lower overvoltage, the X-ray emission volume. Inevitably at lower accelerating voltages X-ray transitions with a lower excitation energy must be used to quantify the elements inside a sample. This has obviously several implications, as discussed earlier.

Overlooking, for the sake of argument, the quantification anomalies of soft X-rays and the consequences of carbon contamination, the optimal analytical conditions would be the lowest accelerating voltage capable of ionizing every kind of atoms inside a sample and inducing X-ray emission, and the highest beam current to generate as many X-rays as possible. The lens aberrations and the limited reduced brightness of the electron emitter add additional constraints on the optimal accelerating voltage and beam current, respectively. The relationship between the final beam diameter, accelerating voltage and beam current was theoretically calculated in Fig. 2.6 (p. 17) and experimentally determined in Fig. 3.4 (p. 116). As the accelerating voltage decreases, chromatic aberration and aperture diffraction dominate and the beam diameter increases. Moreover, for a given reduced brightness, the beam diameter increases with the beam current. The expansion of the beam diameter can partly be restrained by increasing the divergence angle, up to a certain boundary defined by the chromatic and spherical aberrations (Fig. 2.5 on p. 16).

The influence of the analytical conditions on the spatial resolution was evaluated using Monte Carlo simulations and the experimentally determined beam diameters for different X-ray transitions. The minimum in the lateral resolution of the C K–L\textsubscript{2,3} and Fe L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions at beam currents greater than 10 nA in Fig. 3.33 (p. 168) demonstrates the determining role of the beam diameter at low accelerating voltages. All in all, this puts a limit on the spatial resolution achievable by the current generation of electron microscopes. There is no advantage to lower the accelerating voltage below 5 kV in the context of EPMA measurements with beam currents greater than 1 nA. The improvement of the depth resolution is offset by the worsening of the lateral resolution (Fig. 3.31 and 3.33 on p. 164 and 168).
The selection of the experimental parameters for a given measurement, namely the accelerating voltage, the beam current, the measuring time and the X-ray transitions chosen for the analysis, is not straightforward because they have a different effect on the accuracy, precision and spatial resolution. A longer measuring time and a higher beam current will always improve the precision (Fig. 3.29 on p. 162), but the former may lead to large inaccuracies due to more pronounced carbon contamination, and the latter worsens the spatial resolution. While the accelerating voltage is the determining factor of the spatial resolution, it also influences the precision by changing the electron energy distribution and consequently the X-ray ionization probability. As decreasing the accelerating voltage shrinks the interaction volume, the smaller over-voltage lowers the intensity of any X-ray transition (Fig. 3.30 on p. 163), necessitating the use of a lower energy X-ray transition when the accelerating voltage falls below the critical ionization energy. The change of X-ray transition can have a drastic effect on the accuracy, for instance the K–L\textsubscript{2,3} vs. L\textsubscript{3}–M\textsubscript{4,5} X-ray transition of first transition series metals. The accuracy on the quantification of other elements may equally be affected as different algorithms and databases are used to calculate the fundamental physical quantities (e.g. ionization cross sections, MACs, etc.). Differences in the X-ray absorption and fluorescence change the spatial resolution and precision of different X-ray transitions. For instance, the high absorption of C K–L\textsubscript{2,3} X-rays by Fe atoms restricts the expansion of its X-ray interaction volume at high accelerating voltages (Fig. 3.31 on p. 164), but further reduces its emitted X-ray intensity (Fig. 3.29a on p. 162).

To encompass all the relationships between the experimental parameters and quality metrics, an optimization strategy was designed in §3.4 based on Monte Carlo simulations and the minimization of an objective function using the Levenberg-Marquardt algorithm. The optimal experimental parameters for different analytical scenarios were computed for a hypothetical low alloy steel. It was found that an accelerating voltage between 5 and 7 kV, a beam current between 65 and 100 nA and a measuring time between 3 and 8 s would yield the best accuracy, precision and spatial resolution for the measurement of the carbon concentration in a steel containing less than 1 mass\% C. The quantification of the other alloying elements raises the optimal accelerating voltage to 11 kV in order to measure the K–L\textsubscript{2,3} X-rays of Cr, Mn and Fe. It is an acceptable compromise between a higher spatial resolution than at high accelerating voltages (e.g. 15 kV) and a better precision than at low acceleration voltages (e.g. 8 kV) while maintaining a good accuracy by avoiding the use of the L\textsubscript{3}–M\textsubscript{4,5} X-ray transitions. Regarding the precision, the optimization strategy also denoted the difficulty to quantify low element concentrations using soft X-ray transitions due to the large random uncertainties, at least with the detection efficiency and solid angle of the currently available spectrometers.

Another aspect of the spatial resolution is the beam profile. As indirectly uncovered by the diameter of the carbonaceous deposits in §4.2.1.8 and 4.2.2.5, the beam profile at low accelerating voltages and high beam currents no longer follows a Gaussian distribution. A profile with an exponential tail gave a good agreement between the experimental and simulated carbonaceous deposits (Fig. 4.13 and 4.26 on p. 221 and 235). It is however unclear how this flared beam profile influences the X-ray spatial resolution, i.e. how many X-rays are produced by incident electrons hitting the sample far away from the centre of the beam.
More than a simple scientific curiosity, the dimensional variation of the carbonaceous deposits as a function of the experimental parameters and anti-contamination device(s) has a significant impact on EPMA measurements at a high spatial resolution; the contamination leftover by previous neighbouring measurements disturbs the following measurements. Since carbon contamination cannot be physically eliminated, it must be artificially corrected in order to subtract its influence on sensitive measurements such as the quantification of carbon or any other element measured using their soft X-rays. The correction inevitably requires (1) a stable, reproducible contamination behaviour and (2) a strategy to evaluate the amount of carbon contamination. In the acquisition and quantification strategy developed in §3.2.1, the stability and reproducibility are achieved by a methodical sample preparation, the use of an in situ oxygen jet, shorter acquisition times (only measuring the peak X-ray intensities), and identical line scan acquisitions on the analyzed sample(s) and reference materials (§3.2.1.2 and Fig. 3.21 on p. 141). The level of carbon contamination is estimated from the acquisition on pure iron and its contribution on the C K–L\textsubscript{2,3} X-ray intensity corrected with Eq. 3.4 (p. 138). Although some instabilities subsist in the first 4–5 µm, the strategies developed in §3.2 give for the first time a practical, validated method to measure the elemental concentrations of carbon and other alloying elements of low and high alloy steels at a high spatial resolution, improving upon the state-of-the-art methods of Bastin and Heijligers [32], the MICROLITE European report [4] and the ISO 16592:2012(E) standard [164]. The examples presented in §3.5 testify the applicability of this work to steel research, in particular to the characterization of AHS steels, by providing input parameters to deformation models (§3.5.1.1), validating heat treatment process models (§3.5.1.2), evaluating chemical segregation (§3.5.2.1), shedding light on microstructural changes (§3.5.2.2), and resolving ambiguities in the constituent identification (§3.5.3). Moreover, the latter application highlights the complementarity of EPMA and EBSD and the advantage to combine analytical techniques. The presented method solves the identification problems of the DP steel constituents reported by Aarnts et al. [1].

**Outlook** Summarizing the summary, the eight original and most significant achievements of this work are:

- Strategy to acquire and quantify the carbon concentration in low alloy steels at a high spatial resolution
- Correction equation to quantify the carbon concentration in high alloy steels
- Development of a method to identify the phases and constituents of DP steels using EPMA and EBSD acquisitions
- Optimization of experimental parameters based on Monte Carlo simulations for accurate and precision measurements at a high spatial resolution
- Definition of mechanisms and factors influencing carbon contamination in an electron microscope
- Characterization of carbonaceous rings produced by an electron microprobe and study of the influence of experimental parameters on their morphological dimensions
• Experimental assessment of the quantification problem with the L$_3$–M$_{4,5}$ X-ray transitions of first transition series metals

• Determination of empirical mass attenuation coefficients and transition probability ratios of compounds from X-ray intensity vs. accelerating voltage curves

Even after 299 pages, not all aspects of the quantification of low concentration elements using soft X-rays at a high spatial resolution were considered. Some omitted topics are the influence of fluorescence on the spatial resolution [111, 212, 215, 374], the phenomenon of beam damage [125, 171, 185] on non-conductive samples, the quantification using multiple accelerating voltages to keep a low overvoltage ratio to all X-ray transitions [15, 296], the quantification of a thin lamella to improve the spatial resolution [48, 118, 256] and the quantification of three dimensional structures using reconstruction algorithms [225, 256, 299]. They nonetheless do not modify the following broader outlook for EPMA and potential improvements for the future.

Despite the aforementioned needs to reduce the carbon contamination and account for chemical bonding effects in the intensity models, the Achilles’ heel of EPMA, and many other analytical techniques, is to have a high signal to noise ratio at a high spatial resolution, or more specifically to produce a large amount of X-rays in a small volume. Since the ionization probabilities of atoms cannot be changed, one can either increase the measuring time, the beam current, the detector efficiency and/or its solid angle. Increasing the measuring time is detrimental due to carbon contamination and more costly analyses. Increasing the beam current enlarges the beam diameter, especially at low accelerating voltages. EPMA would benefit from brighter electron emitters or aberration corrected electron microscopes/microprobes. The beam current stability should however not be compromised. Increasing the reflectivity and spectral resolution of dispersive elements while decreasing high order X-ray reflections, total internal reflections and background anomalies would help the measurement of soft X-rays. For Fe, Cr and Mn, a new dispersive element with a higher reflectivity than TAP and a higher spectral resolution than LDE1 would be worthy for the measurement of their L$_3$–M$_{4,5}$ and L$_3$–M$_1$ X-rays. Finally, one last alternative is to increase the solid angle of the spectrometer(s) by either increasing the number of spectrometers attached to an instrument, by increasing the area of the dispersive element for WD and detector area for ED spectrometers, or by decreasing the sample to spectrometer distance, i.e. bringing the dispersive element or detector closer to the sample. In any case this involves a redesign of the spectrometers and/or instrument.
When available, digital object identifier [DOI] is provided and all DOI references have been tested. Journal titles were abbreviated using the Chemical Abstracts Service Source Index website (http://cassi.cas.org).


275
References


References


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