

***Development and improvement of quantitative
composition analysis methods for species relevant
to gas industry with benchtop NMR spectroscopy***

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Sergio Alejandro Ortiz Restrepo, M. Sc.

aus

Medellín, Kolumbien

Berichter: PD Dr. rer. nat. Alina Adams, Vertretungsprofessorin
Universitätsprofessor Dr. rer. nat. Jürgen Klankermayer

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I, Sergio Alejandro Ortiz Restrepo, declare that this thesis titled, “Development and improvement of quantitative composition analysis methods for relevant species to gas industry with benchtop NMR spectroscopy” and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.
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“Work as hard as you possibly can on at least one thing and see what happens.”

Jordan Peterson

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List of Abbreviations

C1	Methane
C2	Ethane
C3	Propane
C4i	Isobutane
C4n	Butane
C5i	Isopentane
C5n	Pentane
C5o	Neo-pentane
C6n	n-hexane
FID	Free Induction Decay
FT	Fourier-Transformation
FWHM	Full Width at Half Maximum
GC	Gas Chromatography
HP	High-Pressure
HENG	Hydrogen Enriched Natural Gas
IHM	Indirect Hard Modeling
IR	Infrared
ISO	International Organization for Standardization
LOD	Limit of Detection
LOQ	Limit of Quantification
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance
PEEK	Polyether Ether Ketone

PLS	Partial Least Squares
rf	Radio Frequency
SNR	Signal-to-Noise Ratio

List of Symbols

$\mathbf{B}_0$	Static Magnetic Field Vector
B_0	Static Magnetic Field Magnitude
$\mathbf{B}_1$	Radio Frequency Magnetic Field Vector
ΔE	Energy Difference
δ	Chemical Shift
γ	Gyromagnetic Ratio
I	Spin Quantum Number
$\mathbf{M}_0$	Macroscopic Magnetization at Thermal Equilibrium
$\mathbf{M}_z$	Magnetization in z-Direction
$\mathbf{M}_y$	Magnetization in y-Direction
ω_L	Larmor Frequency
T_1	Longitudinal Relaxation Time
T_2	Transverse Relaxation Time
Θ	Flip Angle

Chapter 1

Introduction

The early developments of Nuclear Magnetic Resonance (NMR) trace their roots back to the early 20th century when the phenomenon of a non-zero magnetic moment was first observed by Gerlach and Stern in 1922 [1]. Subsequent breakthroughs by Rabi and others in 1938 with the description of an experiment that allowed the measurement of Nuclear Magnetic Moments, which could be extended to various nuclei [2], paved the way for further exploration in this field. However, it was not until 1945 when Purcell and Bloch conducted experiments describing nuclear induction and spin resonance [3,4], that NMR truly began to flourish as one of the most versatile analytical methods known today. Its potential to extract thorough information about species under diverse and complex chemical environments has led to outstanding advances in materials science, medicine, chemical engineering, and process control [5,6]. Its crucial role within the scientific community and its importance in contributing to the well-being of humankind has been recognized by numerous Nobel prizes. For his development and applications of the molecular beam method, Otto Stern was awarded the Nobel Prize in Physics in 1935 [7]. In addition, over time, further Nobel prizes were awarded to remarkable contributions, including Isidor I. Rabi, who was awarded in 1946 [8], Bloch and Purcell in 1946 [9], Richard R. Ernst in 1991 [10], and Kurt Wüthrich in 2002 [11], which contributed to consolidating nuclear magnetic resonance as an analytical method. In 2003, the Nobel Prize in Physiology or Medicine was awarded to Paul C. Lauterbur and Peter Mansfield for their discoveries concerning the use of

magnetic resonance to visualize different structures, which led to the development of modern magnetic resonance imaging (MRI) [12].

For many applications, NMR spectroscopy is the method of choice because it provides detailed molecular information at atomic level. However, it typically requires highly homogeneous magnetic fields to ensure accurate results [13,14]. Furthermore, the net equilibrium magnetization exhibits a linear dependence on the strength of the external magnetic field, resulting in enhanced sensitivity [15]. The race for higher magnetic fields began in the 1950s, initially utilizing iron magnets with strengths reaching up to 100 MHz ^1H frequency [14,16]. Currently, Nb_3Sn -based low-temperature superconducting (LTS) wire technology at 1.9 K allows proton frequencies up to 1 GHz [14], while hybrid designs of rare-earth barium-copper oxides combined with LTS extend magnetic field technology above 1 GHz [17]. The current high-field NMR technology relies on superconducting magnets, which, while providing exceptional resolution and sensitivity, are expensive and limited to laboratory environments. In parallel, significant efforts have been made to develop low-cost, portable NMR devices using permanent magnets. These efforts have aimed to make NMR technology accessible for broader applications outside traditional laboratories [18]. By employing echo techniques discovered in 1949 to mitigate magnetic field inhomogeneities as a result of using permanent magnets, it became possible to conduct relaxation time studies but not to obtain spectroscopic information [18]. The development of miniaturized NMR devices, such as the NMR Mobile Universal Surface Explorer (MOUSE) [19], allowed their widespread adoption in both academic and industrial communities, where they found diverse applications such as in oil exploration, materials science, chemistry, and the food industry [18,19].

The first benchtop NMR spectrometer appropriate for spectroscopy measurements and compact enough to fit in spaces equivalent to a conventional fume

hood, was introduced in 2011 [20]. ^1H NMR spectra of sufficient quality, suitable for many applications, could be acquired at a significantly lower cost without the need for high-field NMR [21]. This favorable cost-performance ratio facilitates the analysis of samples without the need for deuterated solvents or cryogens, such as helium and nitrogen, which are typically required for high-field spectrometers. This broadens the applicability of NMR spectroscopy, making it a powerful chemical analytical tool, even in laboratories where NMR was previously considered unaffordable [21]. Currently, several companies are strongly contributing to the development of benchtop NMR, leading to the development of spectrometers with static magnetic fields up to 2.3 T [21]. Furthermore, despite their smaller size, benchtop NMR manufacturers strive to integrate into these modern devices features similar to those found in their high-field counterparts, such as two-dimensional spectroscopy, autosamplers, sample- and magnet- temperature control, as well as pulsed field-gradients. As a result, benchtop NMR spectroscopy has consolidated its applications in various fields of activities such as reaction and process monitoring, quality control, characterization and analysis of complex samples or systems [21].

The analysis of complex samples under extreme conditions such as high-pressure has been of high interest for understanding molecular behavior since the early days of NMR [22,23]. High-pressure analysis in high-field NMR has been successfully used to extract quantitative composition information of natural gas (NG) [24], but its high costs have restricted its use to a few research groups. Recent advancements in high-pressure hardware, combined with low-cost, compact benchtop NMR devices have enabled the determination of quantitative composition analysis of complex NG mixtures [25,26]. The purpose of this thesis is to introduce novel and refined tools and methodologies to increase the robustness, accuracy, and precision of benchtop NMR spectroscopy for the analysis of complex NG mixtures. By doing so, this work presents an affordable and practical alternative to high-field NMR devices within this specific application domain. The proposed methodologies,

along with their achievements, are demonstrated in three separate chapters presented in this work as follows.

Chapter 3 reports a novel methodology to boost the robustness of the composition analysis of complex gaseous mixtures of various hydrocarbon (HC) species typically found in real reservoirs of NG. It is based on the combination high-pressure (HP) benchtop ^1H NMR spectroscopy with indirect hard modelling (IHM) as initially reported in ref. [22]. The proposed method within this thesis includes among others the use of a state-of-the-art high-pressure tube design and the introduction and application of quality control (QC) parameters to select highly reproducible ^1H NMR spectra from a large set of single-scan spectra acquired over time. The developed IHM at 200 bar was tested on complex spectra of mixtures pressurized at 200 bar and 160 bar. In a further application, the same methodology was applied for the composition analysis of an exemplary three-components NG gaseous mixture containing triethylene glycol (TEG) solution as a liquid contaminant. TEG is a common dehydration agent used for the water removal of NG [27]. Its presence in the NMR sensitive volume significantly increased the peak shape deformation of the spectra acquired over time. This made necessary the development of more robust QC parameters to ensure the quality and homogeneity of the selected spectra for the final composition analysis. The performance of the new QC parameters was demonstrated by assessing the quality of the NG sample pressurized at 200 bar and recorded in presence of stationary TEG solution and in presence of dynamic TEG droplets. Additionally, valuable quantitative information about TEG in the sensitive volume, such as quantification limit (LOQ) and detection limit (LOD), could be extracted. The final species composition analysis of the HC species in the NG mixtures with the introduced methodologies were in excellent agreement with the vendor certificates. This demonstrates the potential of the novel experimental strategies towards the implementation of HP NMR spectroscopy in real in-field applications.

The last part of chapter 3 describes the rapid water content quantification in binary water-glycol mixtures using benchtop ^1H NMR spectroscopy. The use of the lineshape analysis (LSA) method has proven to be highly effective in determining even traces amounts of water with detection limits down to 0.05 wt% for water in ethylene glycol (EG) and 0.15 wt% in TEG. Finally, it could be demonstrated the excellent agreement between the NMR results and the Karl-Fischer method, considered the gold standard method for detecting water in glycols [28,29]. This quantitative information is crucial for applications requiring the quantification and control of water content in glycolic solutions, such as in NG dehydration units, to ensure process efficiency.

In chapter 4 a flow-cell suitable for flow HP benchtop NMR spectroscopy up to 245 bar was for the first time designed and implemented. It is based on commercial polyether ether ketone (PEEK) material parts which are commonly found in high-pressure liquid chromatography (HPLC) applications. This inexpensive and innovative design has the potential for implementation in in-field applications. It is also amenable to automation. Its high spectroscopic performance was demonstrated through the quantitative analysis of hydrogen-enriched NG. The tested compositions are particularly relevant to the ongoing decarbonization efforts within the energy sector [30]. Moreover, ^1H NMR spectroscopy measurements conducted with the same flow-cell HP setup were used for the quantification of non-hydrogen bearing gas components (CO_2 and N_2) in complex gaseous NG mixtures as a proof of concept. Specifically, in the case presented here, new IHM composition analysis results from a new set of recorded spectra for different NG mixtures with this novel setup were included in a data-driven calibration concept to estimate the amounts of CO_2 and N_2 present in the mixtures.

The experimental methods presented in this thesis have enabled benchtop proton NMR spectroscopy to conduct simple and low-cost quantitative analysis of

complex gaseous mixtures containing species even at trace levels with high accuracy. As enhanced robustness, reliability, and affordability are key criteria for selecting an analytical method, we believe that the presented results pave the way for a more widespread implementation of modern benchtop NMR spectrometers in industrial and academic research applications.

Chapter 2

Basics of Nuclear Magnetic Resonance Spectroscopy

2.1 Principles of NMR

NMR exploits the nuclei's spin to extract information at the molecular level. The nuclear spin is characterized by the quantum number I and this can only take discrete values, multiples of $\pm 1/2$. The combined spins of protons and neutrons in the atom's nucleus define its overall spin. When both the number of protons and neutrons are even, the nucleus has a zero nuclear spin and thus is invisible to the NMR experiment. Contrarily, when either the sum of neutrons or protons results in an odd number, the nucleus exhibits a non-zero nuclear spin and is considered to be NMR active. During the NMR experiment, the nuclei which are exposed to a static magnetic field $\mathbf{B}_0$ are exhibiting a determined number of orientations $m_I = 2I + 1$ which leads to discrete energy levels as a consequence of the Zeeman interaction [31]. Considering a single spin with $I = \frac{1}{2}$, its interaction with a static magnetic field leads to two possible energy levels with $m_I = \frac{1}{2}$ (parallel to $\mathbf{B}_0$) and $m_I = -\frac{1}{2}$ (anti-parallel to $\mathbf{B}_0$), with the orientation anti-parallel to $\mathbf{B}_0$ having the highest energy level. The energy difference between these two energy levels is described by the following equation:

$$\Delta E = \hbar \omega_0 = \gamma \hbar \mathbf{B}_0 \quad (2.1)$$

The precession of the spin magnetic moment around B_0 occurs with an angular frequency ω_0 , called the *Larmor frequency*. The gyromagnetic ratio γ is the constant of proportionality between ω_0 and B_0 . With γ being a constant that depends on each isotope, as B_0 increases, the energy difference between the two energy states also increases. From Boltzmann's law, this energy difference leads to a difference in the population number between the two spin states, which increases with increasing ΔE . Only this small population difference leads to a measurable net nuclear magnetic moment, called macroscopic magnetization denoted M_0 . To initiate signal generation, a low energy electromagnetic field B_1 is generated by a radio-frequency coil with a frequency matching ω_0 . This causes M_0 to deflect at an angle θ with respect to the direction of B_0 . Once the B_1 pulse is turned off, the deflected magnetization vector M_0 will start to precess around the B_0 -axis while recovering its equilibrium position along the direction of the magnetic field B_0 . As M_0 recovers to align with B_0 , its transverse component (transverse magnetization M_{xy}), which precesses in the plane perpendicular to B_0 , induces a voltage in the detection coil orthogonal to B_0 which also corresponds to the coil responsible for the pulse generation. This signal, known as the free induction decay (FID), is only detectable as long as there is a transverse magnetization component.

Normally, to record 1D spectra for quantitative analysis, a 90° pulse is used. However, its effectiveness may vary from sample to sample, and the signals of interest can experience interference from background signals, which hampers the analysis [32].

2.2 Nuclear Magnetic Relaxation

After excitation by a pulse, the spins return to thermal equilibrium through two relaxation mechanisms: longitudinal relaxation and transverse relaxation. These

processes are characterized by the longitudinal relaxation time T_1 and the transverse relaxation time T_2 , respectively. Understanding these relaxation processes is of key importance when choosing or optimizing the experimental parameters in NMR [33]. To describe these relaxation processes, the behavior of M_0 in relation to B_0 is considered in a coordinate system rotating with the Larmor frequency. This way, only the deviation from the Larmor frequency is observed. Initially M_0 is aligned with B_0 along the z-axis at thermal equilibrium. During the B_1 pulse, M_0 flips by typically 90 degrees onto the x-y plane. Right after the pulse, the spins start to lose their phase coherence due to magnetic field inhomogeneities, and local magnetic field fluctuations caused by molecular rotational and translational motions. This loss of coherence leads to a decrease of M_{xy} . This relaxation process describes the decay of transverse magnetization with the time t , and it is characterized by the spin-spin relaxation time (T_2) as described in equation 2.2:

$$M_{xy} = M_0 e^{-t/T_2} \quad (2.2)$$

The spin-lattice relaxation involves transferring energy from spins to the environment (the “lattice”). It is described by the T_1 spin-lattice relaxation time, which can be determined using equation 2.3. In this equation, M_z represents the recovered longitudinal magnetization as a function of time (t) after the B_1 pulse. The time $t = T_1$ corresponds to the point at which 63% of the magnetization M_0 equilibrium has built up following pulse excitation.

$$M_z = M_0 (1 - e^{-t/T_1}) \quad (2.3)$$

Accurate determination of relaxation times in NMR is a critical step for designing reliable experiments. For instance, if T_1 is not properly accounted for, spins may not have sufficient time to relax between pulses, leading to incomplete signal recovery. Normally, a repetition time of five times T_1 is used between consecutive scans in multi-scan experiments to allow full recovery of the spins. The

lack of reliable T_1 and T_2 relaxation parameters can lead to poor data quality, misinterpretation of molecular dynamics, and incorrect sample characterization in both qualitative and quantitative analysis [34].

2.3 NMR Spectrum

The FID recorded during the spins' precession after the 90° radiofrequency pulse encompasses various spin precession frequencies corresponding to their unique chemical environments. In NMR spectroscopy, magnetic field homogeneity is crucial. In this manner, the FID will contain only the precession frequencies strictly associated with their local magnetic environments and not with the external magnetic field inhomogeneities. In an extremely homogeneous magnetic field, the local magnetic field environment for each nucleus depends on the molecular structure, stereochemistry, functional groups and type of neighboring atoms, nearby non-covalently bound molecules like solvent molecules, and molecular dynamics affecting electron distribution [35]. These aspects affect the electrons orbiting the nucleus, which create a magnetic shielding effect that often weakens the strength of the external magnetic field. The resulting FID stores all this information in the form of a sinusoidal function decaying exponentially. Interpreting the time-domain signal can be challenging, hence, the Fourier Transformation (FT) is applied, converting the time-domain FID into a frequency-domain signal. The equation which defines the FT is given by the equation 2.4, where $F(\omega)$ and $f(t)$ are the frequency and time domain signals respectively [36].

$$F(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt \quad (2.4)$$

The FT extracts valuable information from the FID, presenting distinct signals from nuclei in unique chemical environments within a molecule and

revealing their quantity through signal integration. In order to maximize the outcome of the FT, NMR spectroscopists can implement different strategies, e.g., to optimize the signal-to-noise-ratio (SNR) of the peaks of the NMR spectrum. After recording the FID, common practices before FT include filling zeroes in the time domain to increase the number of data points, enhancing the resolution of the spectrum after the FT [36]. Apodization is a technique in NMR spectroscopy that involves multiplying the free induction decay (FID) signal by a window function before Fourier transformation. It reduces truncation artifacts (Gibbs ringing) and improves the SNR by smoothing the FID signal. However, while it reduces noise, apodization can also cause peak broadening, which worsens spectral resolution and makes it harder to distinguish closely spaced signals. Balancing this trade-off is crucial for optimizing NMR experiments [36]. After FT, a phase correction is applied to the spectra to provide them in pure absorption mode, which means a signal totally above the baseline [36]. Finally, the baseline of the spectrum must be corrected to eliminate variations resulting from instrumental instabilities or unwanted signal artifacts [36].

A fundamental variable that contributes to the molecular characterization is the position of each functional group in the spectrum known as chemical shift. The chemical shift δ is defined according to the equation 2.5 and it is expressed in ppm.

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\nu_{reference}} \times 10^6 \quad (2.5)$$

This compensates for magnetic field differences between spectrometers, enabling standardized interpretation. For example, for ^1H (proton) NMR experiments, tetramethylsilane (TMS) is widely used as reference and is recommended by the International Union of Pure and Applied Chemistry (IUPAC) [37]. Stronger magnets increase sensitivity of NMR measurements and provide greater frequency separation between peaks, making it easier to distinguish signals from nuclei in different chemical environments.

Another fundamental spectral feature is produced by the indirect coupling of spins through chemical bonds. This spin-spin interaction reveals multiplets instead of single peaks, with each splitting characterized by a coupling constant J , which reflects the strength of the interaction. In cases where multiple couplings occur, different J -values may be observed. J -coupling requires the participation of electrons in covalent bonds and a limited number of chemical bonds connecting two spins for measurable coupling. This criterion allows us to elucidate functional group arrangements within a molecule. Multiplet structures arise because the observed spins experience small frequency differences depending on the nuclear spin states (spin down or spin up) of their neighboring protons in different environments. The J -coupling of a single $\frac{1}{2}$ spin with a neighboring group containing n spins of spin $\frac{1}{2}$ yield a signal with $n + 1$ multiplets separated by a characteristic J coupling constant denoting their distance in Hertz. The complexity increases with the number of chemically distinct neighbors, making spectra intricate, especially for large molecules. NMR experiments provide chemical shifts, coupling constants, relaxation times and peak areas, all of which are essential for characterizing complex matrix samples. While chemical shifts, coupling constants, and relaxation times help identify and differentiate components, integrating peak areas enables a straightforward quantitative analysis to determine the amount of the different species in the sample.

Chapter 3

Refined Methodologies for Robust Composition Analysis of Complex Mixtures of Species Found in Natural Gas Processing Plant Conditions by Benchtop ^1H NMR Spectroscopy

The work presented in a large part of this chapter describes a collaborative effort between Equinor ASA, Gassco AS, Baker Hughes INTEQ GmbH, and RWTH Aachen University aiming to boost the robustness of the composition analysis of NG by benchtop high-pressure ^1H NMR spectroscopy. As a result of this academia-industry cooperation, it has been previously demonstrated that high-pressure (HP) benchtop ^1H NMR spectroscopy combined with IHM is a cost-effective method for the quantitative composition analysis of NG [38]. In the first part of this chapter, novel strategies are introduced to increase the reliability and accuracy of the original method. They include a recently published high-pressure tube design introduced in reference [39] and single-scan acquisition combined with new quality control (QC) parameters, which resulted in highly reproducible ^1H NMR spectra over extended periods. The improved methodology has been tested on complex mixtures at pressures of 200 bar and 160 bar, yielding compositions in excellent agreement with vendor certificates. These results are published in reference [40]. All NMR-related

data were obtained at RWTH Aachen University, while the IHM investigations were performed in cooperation between Baker Hughes and the RWTH Aachen University.

The new methodology was further tested in sub-chapter 3.4 on the composition analysis of NG samples at 200 bar in the presence of liquid contaminants, such as glycols commonly found in NG processing lines after dehydration units. The obtained results make the body of a publication submitted for publication. For this case, the acquisition of the NMR data, the IHM, and data analysis were conducted at RWTH Aachen University.

Sub-chapter 3.5 introduces a straightforward approach for the fast and low-cost quantification of water content in glycols [41] , which is a measurement of high relevance in various industrial applications, including dehydration units in NG processing. This work is done solely by RWTH Aachen University. Finally, the entire topics covered throughout chapter 3 demonstrate the robustness of low-field proton NMR spectroscopy and highlight its potential for broader application across scientific and technical landscapes within the energy industry.

3.1 Introduction and motivation

Modern high-field NMR spectrometers are constantly undergoing continuous upgrades to achieve stronger magnetic fields, addressing the inherent low sensitivity of NMR spectroscopy [14]. These state-of-the-art and sophisticated analytical devices have led also to significant developments of the hardware suitable for high-pressure NMR spectroscopy [24,38,39]. Being a critical component, the HP NMR probe vessels play an integral role in the HP hardware design as they serve as the interface between the sample and the magnetic fields associated with the NMR experiment. For this purpose, materials with low magnetic field susceptibility and chemical inertness are essential. As a result, these HP-dedicated components are

constructed using materials such as beryllium-copper [22], glass [42,43], silica [44], or titanium [45], covering pressure ranges from a few bar above atmospheric pressure up to 5 kbar. To ensure their use with the borehole of commercial high-field NMR spectrometers, high-pressure vessels, shaped similarly to standard NMR tubes have been proposed in the literature, typically made of zirconia [24,46–48], polyether ether ketone (PEEK) [49,50], and sapphire [51–53]. With all these vessels developed in the context of high-field NMR spectroscopy, the inherent drawbacks associated with the high demands of specialized personnel, costs, and facilities make these sophisticated concepts constrained to dedicated facilities and research groups with enough resources to afford such applications.

Low-field NMR, particularly systems without spectral resolution, offers significant versatility due to their customizable high-pressure hardware [54,55] allowing the assessment of samples across a broad range of pressures and temperatures using experimental relaxation techniques [56–58]. This approach offers an avenue to delve into the intricate connection between molecular motion and molecule nuclear relaxation [23]. For instance, low-field NMR relaxometry has been demonstrated to be effective in detecting different populations of absorbed molecules at different partial pressures based on their T_1 and T_2 relaxation times. Moreover, a correlation of the relaxation times with the pore structure and loading in porous material was done [59,60].

In the case of mid-field spectrometers, commercial tabletop NMR spectrometers designed with permanent magnets featuring magnetic strengths ranging from 1 T to 2.3 T have shown significant advancements in the race towards enhanced hardware performance and optimized spectral resolution [21]. Very recently, the development and implementation of HP hardware compatible with these spectrometers to enable spectroscopy measurements has started [26,39]. In this context, the first HP setup with a maximum working pressure of 200 bar was

designed and built at the Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University [26]. This was accompanied by the implementation of HP NMR tubes made of sapphire material, usually chosen for its high tensile strength, resistance to temperature, pressure, and chemical inertness [26,38,39,61–64]. Such HP tubes proved to be highly effective for the quantitative composition analysis of NG samples by analyzing the recorded spectra with IHM, a mechanistical multivariable regression method [38]. The same HP hardware allowed SABRE hyperpolarization experiments up to 200 bar, demonstrating further signal enhancement beyond the current maximum of 10 bar of the state-of-the-art *p*-H₂ SABRE experiments [25]. However, further improvements in tube quality were necessary, which ended in the design of a new sapphire tube with a PEEK cap, which forms the part of the experimental methodology presented in the sub-chapters 3.3 and 3.4.

More specifically, based on the demonstrated proof-of-concept for the quantitative analysis of NG using benchtop NMR spectroscopy, in sub-chapter 3.3 further strategies to address the main challenges associated with these mid-field spectrometers and enhance their robustness will be thoroughly presented and discussed. The effectiveness of all these strategies to boost the HP benchtop NMR capabilities will be demonstrated with the composition analysis of NG samples covering a broad range of concentrations with up to 8 different hydrocarbons (HCs).

In another scenario, considering the analysis of NG samples under in-field-like conditions, sub-chapter 3.4 further develops the methodology presented in sub-chapter 3.3 for the analysis of NG samples in the presence of liquid contaminants. This is necessary because NG extracted from wells contains significant amounts of water, which must be removed to meet the quality grade required for commercial pipelines [27]. To achieve this, NG undergoes a dehydration process, typically using glycols as the most efficient option [65], with Tri-Ethylene Glycol (TEG) being the

most used [66]. Although Gas Chromatography (GC) is presently acknowledged as the primary analytical method for NG [67], the necessity of conducting experiments at atmospheric pressures, using specific carrier gases, ensuring constant calibrations, and requiring qualified personnel restricts the application of this analytical method to laboratories with well-controlled experimental conditions [68,69]. As alternatives to GC, optical analytical methods such as Infrared (IR) and Raman spectroscopy have been proposed for NG composition analysis [70–73]. However, the implementation of these analytical methods is challenging because of temperature and pressure-dependent changes in signal spectra [74,75]. Additionally, in gas-liquid experiments, these optical methods have been reported to be highly sensitive to sample homogeneity, requiring a complementary stirring apparatus [76,77]. Even more, in Near Infrared (NIR) water has an absorption band that strongly overlaps with the NG spectral signal, requiring advanced analytical approaches to extract quantitative information [75]. All these implications make implementing these analytical methods for NG composition analysis a challenging task since traces of liquid aqueous TEG could accumulate in the sample matrix over time. However, the method proposed in sub-chapter 3.4 addresses these challenges, demonstrating the robustness of HP-benchtop NMR in performing reliable composition analysis of NG, even under in-field like conditions.

Finally, considering the significant role of aqueous TEG in the demonstrated capabilities of high-pressure NMR for the quantitative analysis of natural gas, sub-chapter 3.5 introduces a novel low-field NMR method for the rapid, cost-effective determination of water content in glycols, without the need for reagents or calibration data. This measurement is relevant also in other industrial applications beyond the energy market [78,79]. Given their hygroscopic nature, even trace amounts of water in glycols can significantly alter their chemical and physical properties. Most studies on water content in glycols have relied on Karl-Fischer titration, which is considered the gold standard method for water determination in

these substances [28,80]. However, this chapter effectively demonstrates the excellent agreement between Karl-Fischer titration and NMR for water determination. This final sub-chapter also highlights the versatility of NMR spectroscopy, expanding its applicability beyond natural gas analysis to address analytical challenges in other domains.

3.2 Benchtop NMR High-Pressure Setup and the New Sapphire Tube Design

Figure 3.1 depicts the HP setup placed within a fume hood, emphasizing its small size adequate for use in a conventional laboratory. The detailed description of the HP apparatus can be found in the reference [26]. However, here a general description is given for better context comprehension. The main body of the HP setup is defined by the metal panel on which the various accessories that allow the gas sample to be prepared at different pressures up to 200 bar are installed. The port inlets of the gas sample and the inert gas are installed on the front side of the metal panel, which are connected directly to the associated gas bottles through steel capillary lines (Figure 3.1a). A piston cylinder containing two internal compartments is placed on top of the metal panel. One chamber of the piston cylinder is used as the gas sample reservoir, while the second serves as reservoir for the inert gas used to pressurize the adjacent chamber containing the sample. Turning a three-way valve allows the sample in the gas chamber reservoir to be redirected via capillaries to the HP sapphire tube resting inside the NMR spectrometer, here a 60 MHz ^1H NMR spectrometer. The final sample pressure is adjusted by filling pressurized nitrogen into the inert chamber and controlling its pressure using a manometer.

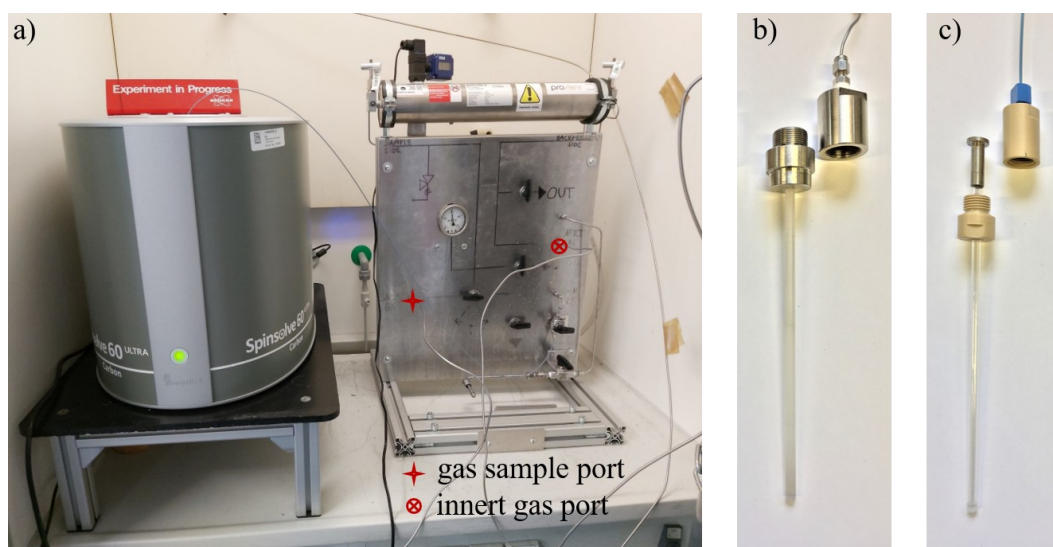


Figure 3.1: a) High-pressure setup and a benchtop NMR spectrometer placed in a laboratory fume hood. b) First-generation HP tube design utilizing a titanium bulk cap and a sapphire tube abraded using tools containing paramagnetic particles. c) Second-generation HP tube design with a PEEK cap and a sapphire tube machined using no-paramagnetic tools. Adapted from refs. [39,40].

Figure 3.1b and 3.1c depict the first- and second-generation sapphire tube designs recently used in benchtop NMR spectroscopy [26,39]. The first-generation design is characterized by a bulky cap made of titanium and an opaque surface resulting from the manufacturing process. During its fabrication, this sapphire tube was ground using paramagnetic abrasive tools, which cause surface contamination and lead to spectra distortions and lower NMR sensitivity [39]. However, this tube was successfully used to acquire ^1H NMR spectra with a benchtop NMR spectrometer of pressurized gas samples up to 200 bar for the first time. By analyzing the recorded spectra with IHM, the achieved quantitative composition of complex HC mixtures was in excellent agreement with the GC method [38]. In addition, the first-generation sapphire tube capabilities were successfully demonstrated in the analysis of other complex systems [25,26]. However, a second HP tube design was recently proposed as depicted in Figure 3.1c [39]. It includes the following improved features: 1) A less opaque sapphire tube wall achieved as a consequence of the

replacement of the abrasive magnetic tools; 2) a PEEK capillary line connecting the main metal panel to the sapphire tube instead of a steel capillary; and 3) a less bulky cap made of PEEK rather than titanium.

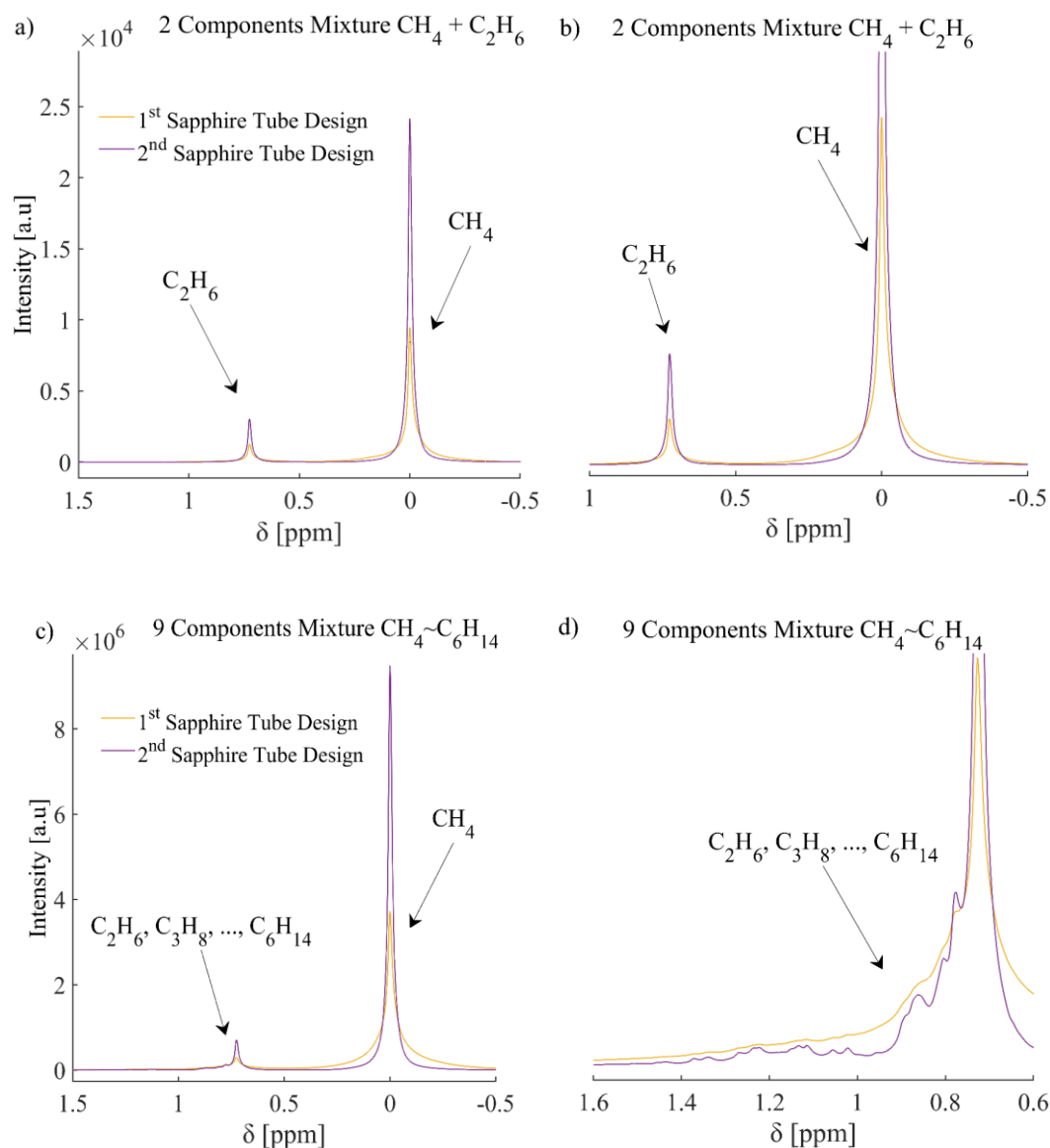


Figure 3.2: Low-field ^1H NMR spectra recorded at 200 bar with the first-generation and second-generation tube designs: a) binary mixture of methane (CH_4) - ethane (C_2H_6), b) zoom view of the spectrum depicted in a), c) complex mixture containing 9 different HCs, d) zoomed view of the spectrum in c) in the spectral region between 0.6 ppm and approximately 1.6 ppm where the higher-order HCs have their signals. Adapted from ref [40].

All the hardware improvements mentioned above led to significant spectra quality enhancements. For instance, Figure 3.2 shows the ^1H NMR spectra of two NG mixtures that represent the typical species found in real NG. As detailed in reference [39] and here in Figure 3.2a, a significant SNR enhancement of about 80% as a result of the dramatic linewidth reduction by 58.37% and 8.11% at 0.55% and at 50% peak height respectively, can be observed. Figure 3.2b illustrates how these improvements contribute to a better peak separation and a better spectral resolution making the fine structure of the higher order HCs clearer, while with the first sapphire tube generation it was hardly distinguishable.

3.3 Experimental Methodology for the Reliable Quantitative Analysis of Pressurized HCs Mixtures

The main requirement to ensure the reliability of the results obtained with quantitative NMR (qNMR) is the proper definition of the experimental parameters to collect the highest possible data quality [13]. When assessing the NMR spectrum, the SNR is one of the key parameters used to describe its quality. This parameter is significantly influenced by the analyte concentration and the instrument performance. For instance, in NMR, magnetic field inhomogeneities cause signal distortions, leading to distorted peak shapes, poor resolution, and a low SNR of the recorded spectra [13,38,81–83].

To overcome these issues, various approaches have been implemented by NMR spectroscopists. For example, for liquid-state experiments conducted in high-field NMR devices, the signals of deuterated solvents are used to lock the field frequency and to correct linear drifts over time [81,84]. As an alternative to hardware

correction approaches, software-based methods have been successfully implemented in post-processing steps to correct identified magnetic field drifts after spectra acquisition [84]. Magnetic field stability is compromised over time in gas-phase NMR experiments with samples lacking a deuterated signal for setting a reference and locking the field frequency [24]. As a solution to this issue, a set of multi-scan spectra was aligned and averaged to compensate for signal shifts to correct magnetic field inhomogeneities during the post-processing phase [24]. This approach has been proven to be effective in increasing SNR when the standard practice of using deuterated solvents to lock the field frequency is not feasible [85].

In contrast, due to the technological design of table-top NMR devices which are based on rare earth permanent magnets with a high temperature coefficient, the magnetic field stability is highly sensitive to thermal variations [81,83,86,87]. To compensate for these magnetic field disturbances, benchtop NMR instruments have an integrated external lock, i.e., an independent and adjacent compartment next to the active region where a substance reference is located [85]. In spite of this integrated external lock frequency technology, the control of magnetic field disturbances still remains challenging in facilities with variation in temperature. The absence of prolonged control over field homogeneity significantly impacts the quality of recorded spectra over extended periods. This leads to peak shape distortion, poor SNR, and, consequently, a lack of reproducibility in the recorded spectra at different points in time [38].

Recently, in reference [38], HP benchtop NMR spectroscopy was used for the quantitative composition analysis of five pressurized mixtures at 200 bar. These samples included four ternary mixtures containing methane, ethane, and propane at various concentrations and a complex mixture of 9 HCs. Despite the challenges inherent to benchtop NMR instruments, the implementation of IHM allowed the extraction of quantitative information from these samples. Following this successful

proof-of-concept, also approaches were identified to improve the robustness and reliability of the approach considering its implementation towards automatized and unsupervised applications. Therefore, this sub-chapter presents the following improvements developed to address: 1) a better spectra resolution, thanks to a refined sapphire tube design allowing a better peak differentiation among the various higher-order HCs whose signals strongly overlap in the same region; 2) a more straightforward quantitation of methane thanks to the improved peak separation between methane and the other HCs; 3) better reproducibility of the results by acquiring NMR spectra with similar quality over time and; 4) SNR enhancement by adding and averaging selected high-quality spectra. Figure 3.3 provides an overview of the proposed methodology that enabled the acquisition of reproducible, high-quality ^1H NMR spectra of pressurized NG samples at 160 bar and 200 bar, and their subsequent composition analysis using IHM. The description of the methodology here presented can be found in reference [40] and will be discussed in the following sections.

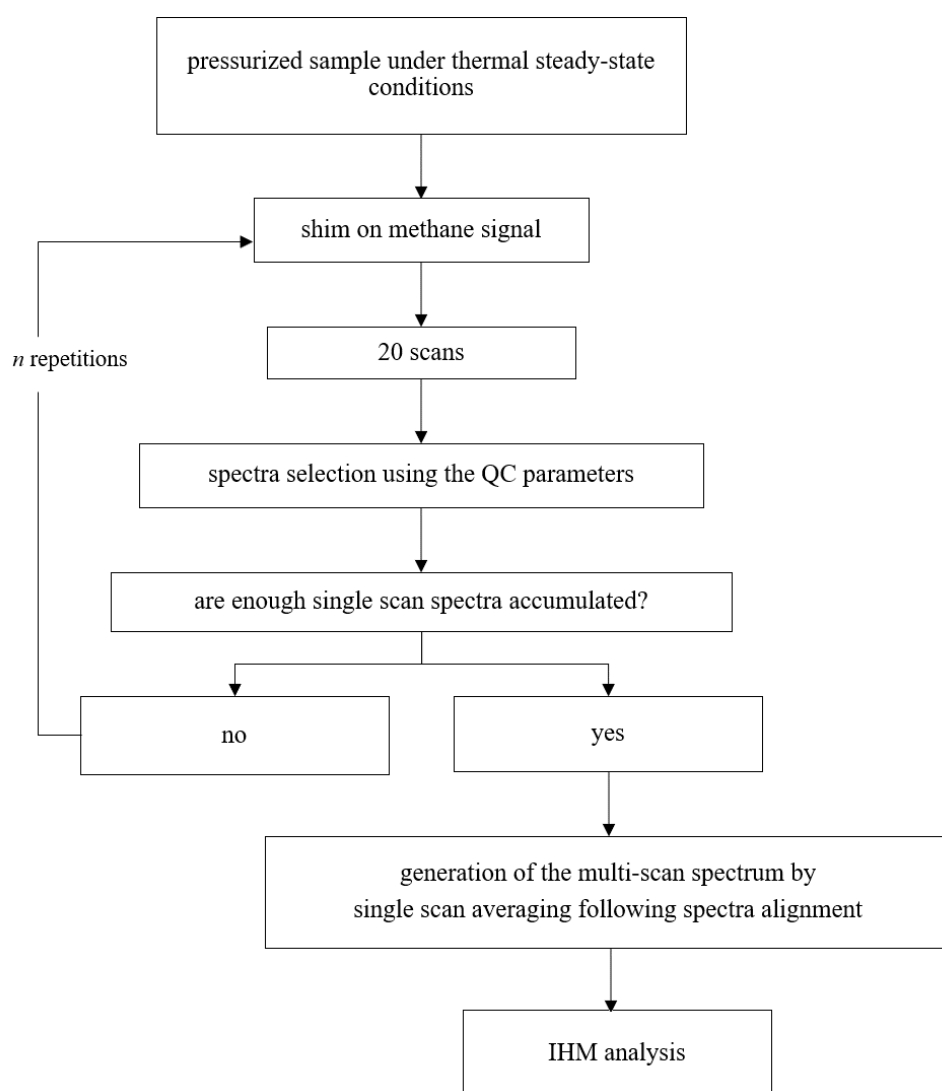


Figure 3.3: Proposed methodology for the composition analysis of NG using benchtop HP proton NMR spectroscopy. The variable n is defined by the user based on the required number of reproducible high-quality single-scan ^1H NMR spectra needed to generate a final high-quality multi-scan spectrum with the desired signal-to-noise ratio (SNR). Adapted from ref. [40].

3.3.1 Quality Control Parameters to Select High-Quality ^1H NMR Spectra

To define the quality control parameters which will be discussed in this sub-chapter, ^1H NMR spectra were recorded by using the second-generation HP sapphire tube design depicted in Figure 3.1c. During this work, a large data set of single-scan ^1H NMR spectra were recorded for various certificate HCs mixtures pressurized at 200 bar and 160 bar. To assess large numbers of accumulated single-scan spectra for each data set, a MATLAB script was developed to perform the characterization automatically. The methane Full-Width-at-Half-Maximum (FWHM) was determined from each spectrum for each series of single-scan spectra. In addition, the room temperature at which each spectrum was acquired was also extracted from the spectrometer acquisition file. This information revealed that changes in the room temperature influence the magnetic field homogeneity as depicted in Figure 3.4. A shim on the methane signal was included after every 20 scans to maintain the magnetic field homogeneity, proving to be an effective way to compensate for unpredictable room temperature fluctuations. Subsequently, two QC criteria were developed after thoroughly observing all single-scan spectra recorded at 200 bar and 160 bar (in the order of hundreds). Displaying them allows for immediate identification of whether the experimental conditions are appropriate.

The first QC criterion is the integral of the frequency domain, with integration limits between -0.5 and 1.8 ppm. This parameter is sample dependent, and its value was defined as the normalized integral of the averaged steady and reproducible value derived from all recorded spectra for each sample as depicted in Figure 3.4a. This QC criterion should allow to detect pressure loss over the measuring time. Even undetectable leaks, which do not show up on the manometer due to pressure compensation by the inert gas chamber, were expected to be identified in samples with residence times shorter than five times the T_1 relaxation

time of any HCs present in the matrix sample. However, during this work, such leakages were not encountered.

The second QC parameter was the FWHM of the methane signal, as methane is the main component in NG and the magnetic field is shimmed based on this peak. In addition, during this work, it was observed that the quality of the methane peak could serve as a primary indicator of the signal quality also of other HCs present in the same sample. A narrower methane peak, as reflected in a smaller FWHM, and a visually more symmetric shape, coincided also with better spectral resolution and improved signal quality of the other HCs. Thus, to determine the upper and lower thresholds of this parameter, the FWHM values of methane signal for the recorded spectra at 160 bar and 200 bar with the most homogeneous and repeated peak shape were averaged. As a result, the thresholds values were found to be 1.66 ± 0.06 Hz and 1.51 ± 0.06 Hz respectively. Here it is important to indicate that no appreciable variations were identified on the methane FWHM among the different species concentrations of the samples investigated.

Finally, the boundaries of these QC parameters were integrated into the MATLAB script with a tolerance of 10% for both criteria, which proved to be sufficient to identify reproducible spectra over time. In this work, the selected spectra according to these QCs criteria were classified as reproducible and of high quality. Figure 3.4 illustrates an example of these two QC parameters determined on single-scan proton spectra of the sample containing $84.86 \pm 0.11\%$ methane, $10.1 \pm 0.10\%$ ethane, and $5.04 \pm 0.05\%$ propane, according to the vendor certificate, measured at 200 bar. As mentioned above, the total integral remained constant, close to the mean value, as an indication of the properly sealed HP setup. On the other hand, the FWHM exhibits a strong variation at the beginning of the experiments associated with the room temperature stabilized. Afterwards, the FWHM stayed within the defined thresholds.

The MATLAB script presented in this chapter can be integrated into an automated measuring process, where various amounts of single-scan spectra are selected. This allows for the generation of multi-scan spectra with sufficient SNR, even for species present at trace levels in the matrix sample. The lower the concentration of the species of interest, the larger the number of single-scan spectra needed to obtain a spectrum with sufficient SNR.

In this work, the spectra selected using the MATLAB script were logged in a separate folder. Each file containing the raw FID was zero-filled to 256k data points, Fourier transformed, and the spectra were aligned and averaged using the software package PEAXACT version 5.0 (S.PACT GmbH, Aachen, Germany). The spectra recorded by the Spinsolve software had the correct phase and baseline, so no further corrections were necessary. This approach allowed the creation of a high-quality library of individual hard models, which were used to generate a final IHM for the composition analysis of pressurized samples at 200 bar and 160 bar, recorded using the same methodology as explained in the following sections.

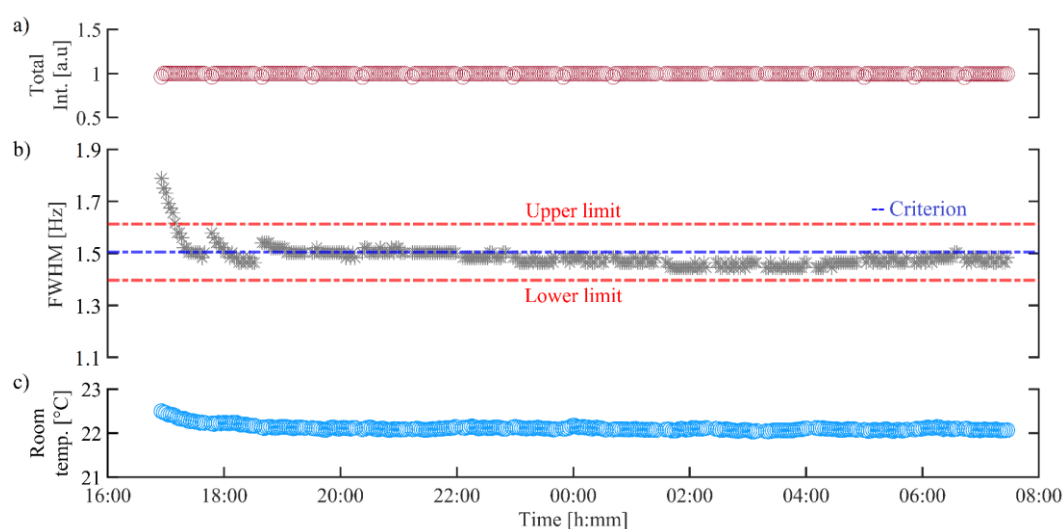


Figure 3.4: QC criteria to select reproducible and high-quality low field ^1H NMR spectra of a NG samples containing $84.86 \pm 0.11\%$ methane, $10.1 \pm 0.10\%$ ethane, and $5.04 \pm 0.05\%$ propane recorded at 200 bar with the second-generation tube design: a) integral over the whole frequency domain with integration limits between

-0.5 and 1.8 ppm, b) FWHM of the methane peak along with the upper and lower threshold values, and c) room temperature over time. To maintain the spectra quality along the measuring time a shim on the methane peak was conducted every 20 scans. The blue line, defined as the criterion in (b), corresponds to the FWHM value of methane at 200 bar. The blanks between each set of 20 scans correspond to the shim periods. The lower values of the integrals reflect the spectra recorded immediately after shimming, without sufficient time for full recovery of the magnetization. Adapted from ref. [40].

3.3.2 Improved Natural Gas Quantitative Composition

Analysis with a Refined Indirect Hard Model

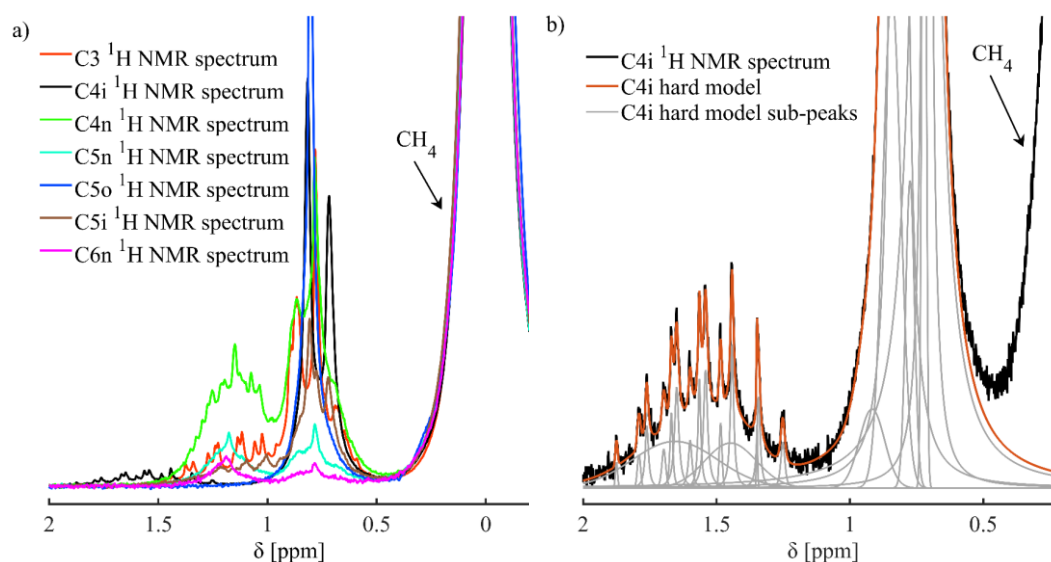
As depicted in Figure 3.2 and already demonstrated in recent studies [26,38–40,88], the proton spectra of NG samples are highly complex. Methane (C1), the predominant component in any NG sample, produces a single signal that is relatively isolated from the signals of other species in the gas mixture. However, the signals from higher-order HCs such as ethane, propane, butane, iso-butane, pentane, iso-pentane, neo-pentane, and n-hexane overlap significantly in the same spectral region (Figure 3.2b). The reduced magnetic field strength of benchtop NMR devices compared to high-field spectrometers leads to lower SNR and spectral resolution. Additionally, proton low-field NMR spectra tend to be broader due to lower magnetic field homogeneity and second-order effects where J -coupling values are close to chemical shift differences [24,81,89]. These factors complicate the quantification of the individual components using simple integration or lineshape analysis. But recently, it has been demonstrated that this issue can be effectively addressed using IHM [38].

IHM was initially developed to model vibrational spectra from Raman or mid-IR spectroscopy [90], but its application has been extended to NMR spectroscopy [38,91]. IHM uses parameterized peak-shaped signals derived from the

pure component spectra of individual substances. These peak-shaped signals are linear combinations of Pseudo-Voigt functions, which themselves are combinations of Gaussian and Lorentzian functions. Each Pseudo-Voigt function is defined by parameters such as position, maximum intensity, FWHM, and the Gaussian fraction. When fitting an IHM to a spectrum, these parameters are adjusted to minimize the root-mean-square (RMS) difference between the model and the observed spectrum. This approach allows for the accurate quantification of components even in the presence of spectral distortions and variations. In this chapter, an IHM was implemented after combining the various hard models of the individual components expected in the mixture as depicted in Figure 3.5. The flexible fitting algorithm of IHM, which sets tolerance ranges for parameter variations, significantly reduces the calibration efforts compared to other methods like Partial least squares regression (PLS).

To obtain a more robust and reliable IHM in comparison to the one proposed in reference [92], a refined model was developed based on higher quality hard models (HMs). To develop these HMs, first, sets of single-scan ^1H NMR spectra for each pure component were recorded at 200 bar and high quality single-scan spectra were automatically selected with the QC parameters integrated into the MATLAB script as mentioned in sub-chapter 3.3.1. While ethane was recorded using a reference binary mixture containing 7.57% ethane and 92.43% methane according to the mixture producer's certificate, the higher-order HCs were measured based on self-made ternary mixtures of each HC diluted in argon and mixed with pure methane. A list of approximate mixing pressure ratios is provided in Table A1 in the Appendix. These ratios were experimentally optimized to supply sufficient methane for magnetic field shimming while keeping the methane signal low enough to allow the detection of the small signals from other species in the mixture. In contrast to the measuring method followed in reference [92], where the magnetic field was shimmed on pure methane and then the sapphire tube evacuated prior to recording

the spectra of each pure HC diluted in argon, in this work, the methane signal is always included in the matrix of each HC sample. This is also the same condition found on real NG samples. With the accumulated spectra, multi-scan spectra with a significantly higher SNR could be obtained. This is particularly beneficial for the higher-order HCs at low concentration, which require a large number of scans to reach an appropriate SNR. Figure 3.5a depicts the obtained ^1H NMR spectra for the higher-order components recorded at 200 bar. It can be observed how the signals for all measured HCs can be well differentiated thanks to the improved SNR and resolution using the new HP tube and the measuring concept. Figure 3.5b illustrates the developed hard model for iso-butane (C4i). There, it can be noticed the sub-peaks of the hard model used to produce a hard model that matches the experimental ^1H NMR spectrum of this component. For each hard model, the individual peaks of each pure component were grouped to maintain the area ratio among them during the fitting process. This was done to align with the proton contribution ratio observed in the component's corresponding ^1H NMR experimental spectrum.



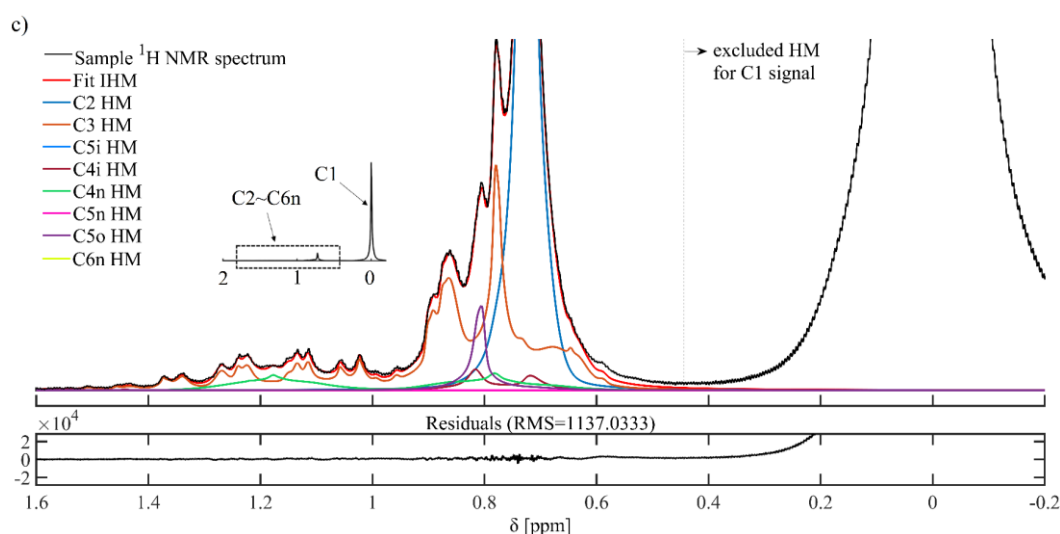


Figure 3.5: Experimental ^1H NMR spectra recorded at 200 bar of: a) individual HCs mixed with methane used to produce high-quality hard models, and b) hard model developed for iso-butane (C4i). c) IHM fit on the experimental ^1H NMR spectrum of the complex 9-components HC mixture recorded at 200 bar. The frame in the insert corresponds to the chemical shift range between 0.5 ppm and 1.6 ppm where the higher-order HCs strongly overlap. Here, it can be observed how the individual components contribute to the total IHM fit despite the strongly overlapped signals. For the methane peak no hard model was included. The figures are adapted from ref. [40].

All the individual hard models were compiled and merged into an individual complex 9-components refined IHM (Figure 3.5c). Similar to the reference [92], the IHM was performed using the commercially available software package PEAXACT and the same “maximal interaction” fitting mode was chosen to allow a simultaneous adjustment of global and local peak parameters. Additionally, a tolerance of 0.02 ppm horizontal peak displacement was included to allow the global model and local peaks to cope with chemical shifts differences between the experimental spectra and the original IHM. Unlike the IHM approach proposed in reference [92], in this refined IHM, the fitted hard model for methane was skipped, since the good separation between methane and the higher-order HCs allowed a more

straightforward molar composition determination of methane. Here, the methane area was determined by subtracting the total IHM fit area from the total integral of the frequency domain between -2 ppm and 4 ppm. In this way, the errors attributed to the misfits of the higher HCs are accumulated into methane, which due to their low concentrations, are expected to make an insignificant contribution. This procedure helps enhance the reproducibility and reliability of the predicted results.

The capabilities of the refined IHM developed in this work were tested on two large sets of ^1H NMR spectra of complex gaseous mixtures. The first set of spectra was obtained using 15 certificated mixtures at 200 bar and a second set of spectra was recorded for 11 out of 15 mixtures at 160 bar. For each set of recorded ^1H NMR spectra, the effect of the number of scans on quantification accuracy was investigated by producing three multi-scan spectra containing 16, 32, and 64 high-quality single-scans, respectively. To benchmark the results determined by IHM against the vendor's certificates, the degrees of equivalence, which show the agreement or discrepancy between the IHM analysis results and the vendor certificates, are depicted in Figure 3.6, as proposed in the references [24,93]. The results obtained at 200 bar (Figure 3.6a) show that the NMR compositions derived using the spectra acquired with different number of scans are reproducible with a deviation lower than 0.5 mol% compared to the vendor values. This consistent IHM performance of the predicted results at 200 bar is attributed to the similar quality between the HMs and the spectra of the test samples in terms of peak shape and position, owing that the IHM was developed on pure components recorded at 200 bar. Thus, during the fitting process, the model solely has to account for changes in peak intensities. When the same IHM was tested on ^1H NMR spectra of samples pressurized at 160 bar, a slightly reduced deviation between the predicted results and the certificate values can be observed, and a slight increase in the dispersion of the predicted value for each species in the matrix sample using the spectra recorded with different numbers of scans (Figure 3.6b). The slight accuracy enhancement at 160

bar was attributed to better peak separation between methane and higher-order HC peaks at lower pressures. The more scattered results are attributed to algorithm iteration errors, as the IHM developed at 200 bar had to account for changes in multiple parameters such as the width of the signal, position, and intensity of the peaks when fitted to spectra at 160 bar (Figure 3.6b).

These results demonstrate the transferability of the IHM for performing quantitative composition analysis based on spectra of pressurized samples at different pressures than the developed IHM. The IHM model developed at 200 bar could be applied to data recorded at 160 bar without needing to create a new IHM model. This transferability is advantageous, as it reduces the number of samples needed for IHM development. The accuracy and precision of the composition analysis were excellent for both pressures, with disparities between the NMR results and the vendor certificates not exceeding 0.5 mol%. It should be noted, however, that larger differences in the peaks' chemical shift, width, and intensity between the IHM and the analyzed sample spectrum can reduce the precision of the predicted results. Comparing the results obtained at 160 bars with those at 200 bar, slightly more scattered results were observed at 160 bar, especially for spectra containing a different number of scans. In addition, even with as few as 16 scans, very good results were achieved, demonstrating that shorter acquisition times can still yield accurate composition data.

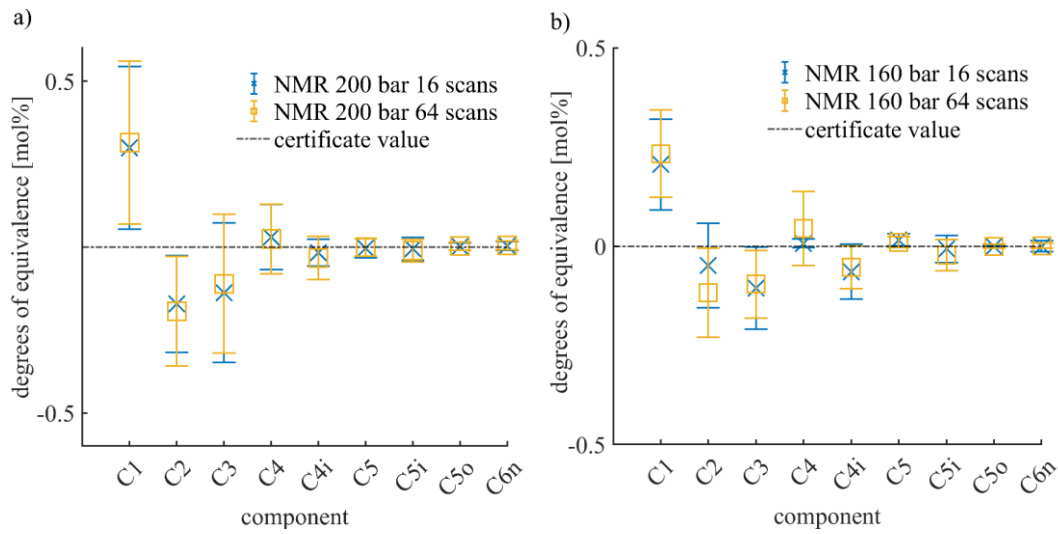


Figure 3.6: Degrees of equivalence between the IHM results and the vendor certificates: a) results of the 15 mixtures (Table A2 and Table A3) measured at 200 bar and b) results of 11 mixtures (selected from Table A2) measured at 160 bar. Both sets were measured using 16, 32, and 64 scans. Adapted from ref [40].

From the determined molar concentrations, physical properties of NG can be calculated using the open-source Non-Equilibrium_Simulator (NeqSim) for MATLAB [94]. According to the guidelines of the Norwegian Petroleum Directorate, the relative error of the molecular weight and the heating value should not exceed 1% and 0.3% of the certificate values, respectively. Figure 3.7 depicts the results of the heating capacity values determined for both data sets. For most of the samples, these critical values to define the NG commercial value were determined with a relative error below 0.3%. However, deviations can be observed for samples 1, 4, and 6 which are attributed to the magnetic field instabilities during the measurements caused by large room temperature variations in the laboratory. For the molecular weight, the relative errors for both data sets are below the maximum error. In all the predicted results, the 9-component mixture exhibited the largest deviation and relative error, since it wasn't possible to acquire a spectrum of good quality for this sample. However, the relative error remained below the 1% threshold required by the Norwegian Petroleum Directorate.

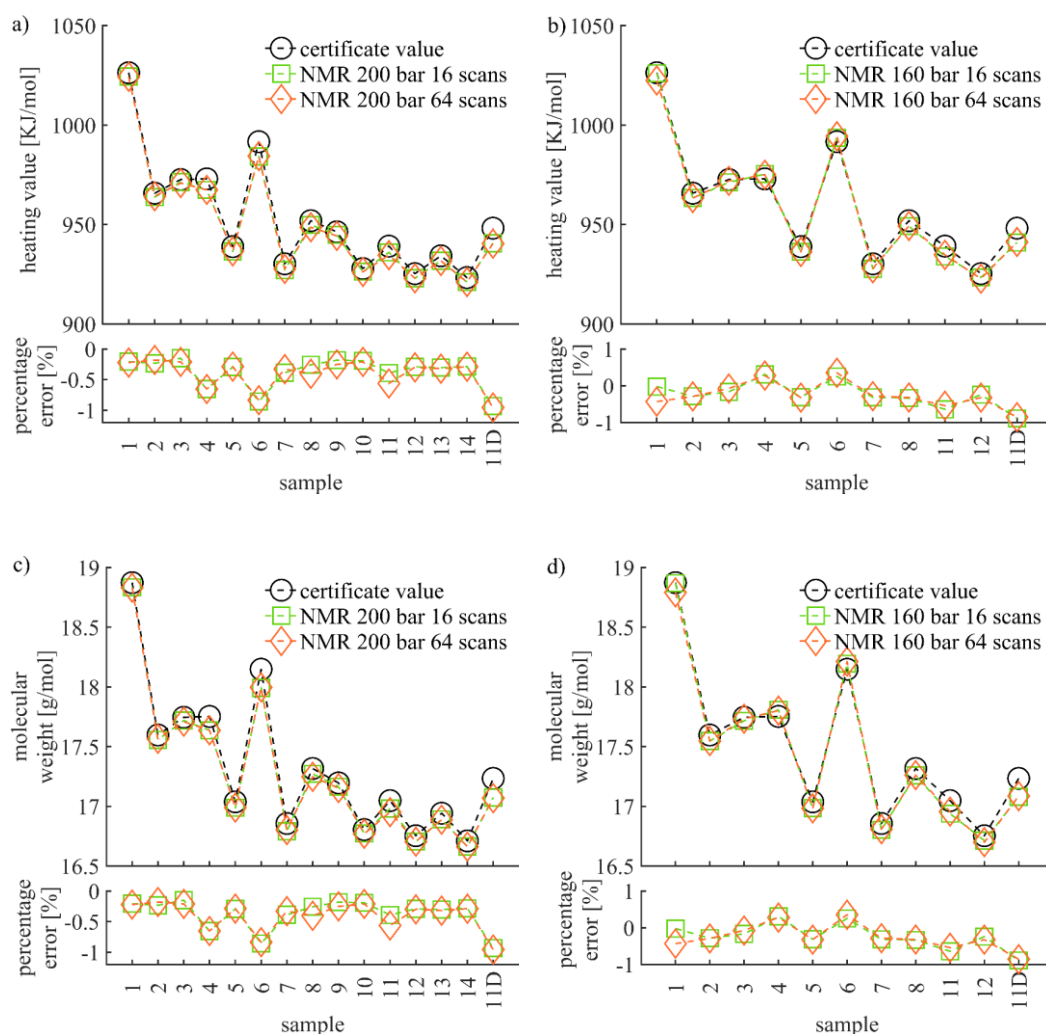


Figure 3.7: The derived physical properties determined from the IHM composition quantification: Heating values of the samples analyzed at 200 bar (a) and 160 bar (b), respectively. The molecular weight of the samples at 200 bar (c) and 160 bar (d), respectively. The 200 bar samples correspond to the entire sets in Table A2 and Table A3, while the 160 bar samples correspond to 11 selected samples from Table A2. Adapted from ref. [40].

In summary, this sub-chapter presented a methodology to enhance the accuracy and reproducibility of quantitative composition analysis of NG samples using high-pressure low-field proton NMR spectroscopy and IHM. This was made possible through various hardware and software developments, particularly the

implementation of a novel high-pressure sapphire tube, which significantly improved the FWHM and symmetry of all signals. This led to a larger separation of the methane signal from other HCs, enabling the implementation of strategies such as single-scan acquisition, periodic shimming (each 20 scans), automatic selection of high-quality spectra based on QC parameters, spectra alignment and averaging to obtain multi-scan ^1H NMR spectra of superior quality. The robustness of this methodology was validated on gaseous mixtures containing up to nine different HC species at 200 bar and 160 bar. The results demonstrated high accuracy, as disparities between NMR results and vendor certificates did not exceed 0.5 mol%. This study confirms that low-field HP ^1H NMR spectroscopy is an efficient method for the rapid analysis of complex gaseous mixtures with significant potential for routine online composition analysis under real conditions. Moreover, some of the proposed concepts could be valuable for other fields requiring the acquisition of a large number of spectra over extended periods.

3.4 Composition Analysis of Pressurized NG

Samples in Presence of Liquid Contaminants

This sub-chapter demonstrates the proficiency of HP ^1H NMR spectroscopy in quantitatively analyzing NG in the presence of liquid contaminants, building on the excellent performance of the methodology discussed in the previous sub-chapter 3.3 by exploring an in-field-like scenario. Water vapor, in particular, is a common contaminant in NG streams, with significant detrimental consequences. Its presence decreases the heating value [27], causes corrosion of commercial pipelines, and when mixed with methane, the main constituent of NG, can lead to the formation of solids called hydrates [95]. This can increase the corrosion rate, resulting in valves and pipeline infrastructure plugging [65,96].

The removal of water vapor from NG is carried out in dehydration units, which usually employ common methods such as: 1) refrigeration dehydration, which lowers the gas temperature to condense water vapor; 2) adsorption dehydration, which uses solid desiccants like zeolites and alumina to adsorb water molecules; and 3) absorption dehydration, where liquid desiccants, such as glycols, absorb water vapor from the gas stream [95,96]. Among these methods, those using liquid glycols are the most efficient and widely implemented. This is due to the high affinity of glycols for water, making them the preferred choice in NG dehydration units. The use of glycols ensures effective water removal, preventing issues like gas hydrate formation and corrosion, thus maintaining the integrity of the NG processing system [66,97–99]. These simple chemical compounds, characterized by their hydrophilic nature attributed to two hydroxyl groups (-OH), are chemically defined by the formula $\text{HO}-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{H}$. Among them, TEG with $n = 3$ is the most used glycol in dehydration units, thanks to its efficiency that outperforms other glycols [100].

Hence, to continuously monitor the NG composition along the processing pipeline, it is necessary to develop an analytical method with sufficient robustness to tolerate a certain degree of sample contamination, a common condition outside controlled laboratory environments. The methodology presented in this sub-chapter will be tested and its capabilities will be demonstrated through the composition analysis of a mixture composed of the three most predominant HCs found in NG samples (methane, ethane, and propane) in the presence of aqueous EG at 200 bar. Moreover, the quantification of the EG amount present in the sensitive volume was carried out.

3.4.1 ^1H NMR Spectra of Natural Gas Sample at 200 bar in the Presence of Aqueous TEG

Figure 3.8 depicts the 60 MHz ^1H NMR spectra of the three-component NG sample and of pure TEG recorded with the second-generation HP tube design introduced in sub-chapter 3.2. The ^1H NMR spectrum of the aqueous TEG sample with 22.5 wt.% water content (Figure 3.8a) was acquired with 16 scans and a repetition time of 4 s, which is higher than five times its 0.53 seconds value for the T_1 value measured by the inversion recovery method. The signals of the methylene (CH_2) and hydroxyl (OH) groups are at 3.67 ppm and 4.70 ppm, respectively. These chemical shifts are in agreement with previously reported values [41,101]. To prepare the aqueous TEG sample, TEG was stored with activated molecular sieves under an argon atmosphere for over four months to reduce water content. The residual water in TEG was determined using the Karl-Fisher method, and a final H_2O -TEG mixture with 22.5 wt% water was prepared gravimetrically under argon. The mixture was then stored in an argon-filled container to prevent additional water uptake from the atmosphere.

The 64 scans ^1H NMR spectrum of the pressurized NG sample at 200 bar containing methane (85 mol%), ethane (10 mol%), and propane (5 mol%) (Figure 3.8b) was acquired following the acquisition methodology proposed in sub-chapter 3.3.

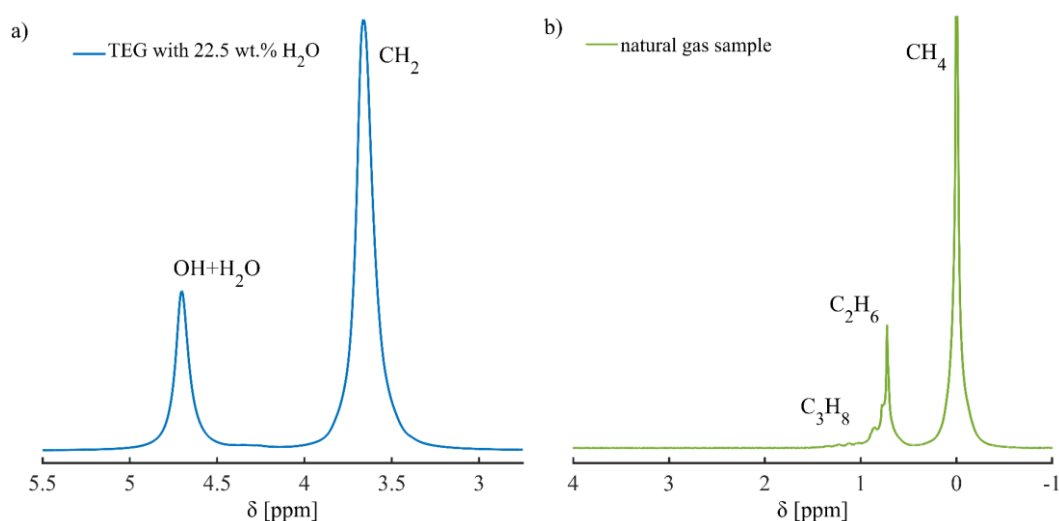


Figure 3.8: 60 MHz ^1H NMR spectra of: a) aqueous TEG with 22.5 wt.% H_2O and b) 3-component HCs gas mixture containing 85% methane, 10% ethane, and 5% propane pressurized at 200 bar. Adapted from ref. [102].

As one of the main goals of this work is to assess the IHM performance to determine the quantitative composition of a NG sample in the presence of liquid aqueous TEG, for the first time, both samples were brought together in the NMR tube and analyzed as depicted in Figure 3.9. To change the NG-TEG ratio in the sensitive volume, spacers that allow controlling the vertical displacement of the sapphire tube were added below the PEEK cap (Figure 3.9a). With this simple approach, it was possible to record ^1H NMR spectra of pressurized NG at 200 bar with various aqueous TEG contents ranging from 0 to 100%, corresponding to 0 mg to 57 mg aqueous TEG. To have a detailed quantitative characterization of this two-phase matrix sample, the limit of detection (LOD) and limit of quantification (LOQ) of TEG in the HP-tube in presence of the NG sample at 200 bar were determined. This was done using the response slope of the intercept method according to reference [103]. This method determines the detection and quantification limits by dividing the standard deviation of the residuals from a calibration curve by the slope of the curve and multiplying by specific factors (3.3 for LOD and 10 for LOQ) to account for statistical confidence and precision. In this work, values of 0.85 mg and

2.83 mg, respectively, were achieved based on the calibration curve depicted in Figure A1b in the Appendix. This valuable information can serve as an early alert system for TEG accumulation in NG dehydration units, triggering a response when TEG levels exceed acceptable thresholds. By providing timely data, this method enhances decision-making regarding maintenance and operational adjustments, ultimately improving both the measurement process and the overall efficiency of the NG processing line.

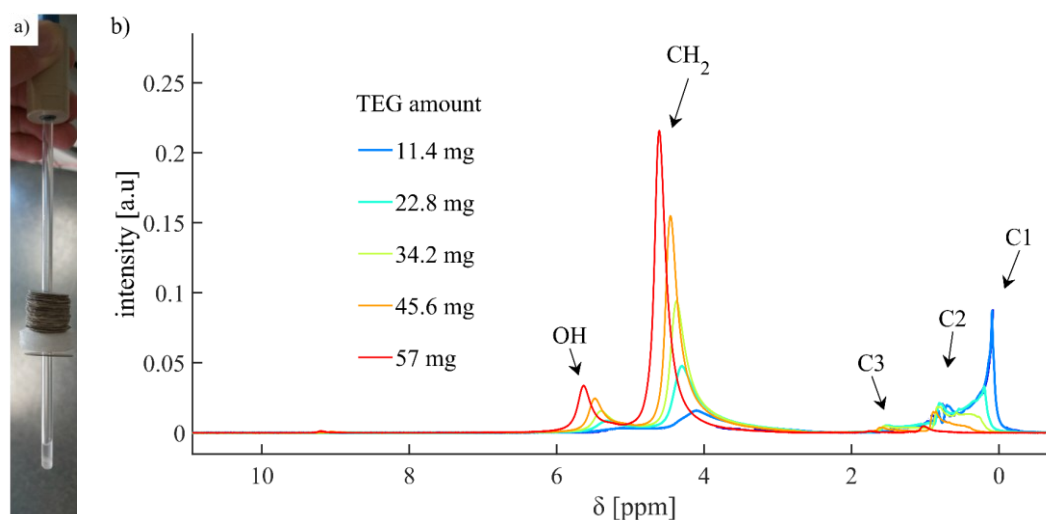


Figure 3.9: Biphasic mixture pressurized at 200 bar: a) sample prepared in second-generation HP sapphire tube with aqueous TEG sitting at the bottom of the HP tube and pressurized NG sample occupying the upper remaining volume. b) ^1H NMR spectra of the two-phase mixture with various aqueous TEG contents in the sensitive volume up to a completely filled (57 mg) sensitive volume. Adapted from ref. [102].

In the ^1H NMR spectra depicted in Figure 3.9, the amount of the pressurized NG sample and its SNR is decreased by increasing the aqueous TEG content in the sensitive volume. Additionally, with the increase in the linewidth of the gas signals owed to the signal overlapping between the three HCs in the sample, the spectra resolution is deteriorated. Nevertheless, the methane (CH_4) peak, being the most abundant in the NG sample, could be observed even when the sensitive volume was

filled to half capacity with the aqueous TEG solution. Beyond the half-filled volume, the CH₂ peak of TEG became predominant in the acquired spectra which makes the automatic shim program to use this signal to optimize the magnetic field homogeneity which led to the improvement of the TEG signals but not those from NG. In this sub-chapter the implementation of a manual shim wasn't considered, since it won't be a feasible option in in-field-like conditions. In addition, a linear correlation between the FWHM of CH₄ and the amount of aqueous TEG in the sensitive volume was observed as depicted in Figure 3.10. With a correlation coefficient of $R^2=0.98668$, this mathematical approach provides a simple alternative for identifying the amount of TEG contamination in the NMR tube while at the same time can serve to monitor the quality of the recorded spectra as demonstrated in sub-chapter 3.3. This method, based solely on methane FWHM, is effective until the tube is half full. These FWHMs were measured on spectra recorded under steady thermal conditions after shimming the magnetic field based on the methane signal at fixed aqueous TEG contents in the sensitive volume. For contents greater than 28.5 mg, extracting FWHM was not possible due to severe peak deformation. The linewidth at 10% signal height could be quantified up to 11.4 TEG mg in the sensitive volume, beyond this amount owed to the peak overlapping at the peak base this measurement wasn't possible anymore. The measured values are given in Table 3.1.

Table 3.1: Aqueous TEG content in the sensitive volume and the corresponding FWHM of the methane (CH₄) peak in the ¹H NMR spectra of the NG sample pressurized at 200 bar in the same matrix.

TEG [mg]	FWHM CH ₄ [Hz]	Linewidth at 10% CH ₄ Peak Height [Hz]
34.2	---	---
28.5	7.47	---
22.8	5.95	---
17.1	4.34	---
11.4	3.35	31.89
5.7	2.21	21.21
0	1.35	14.19

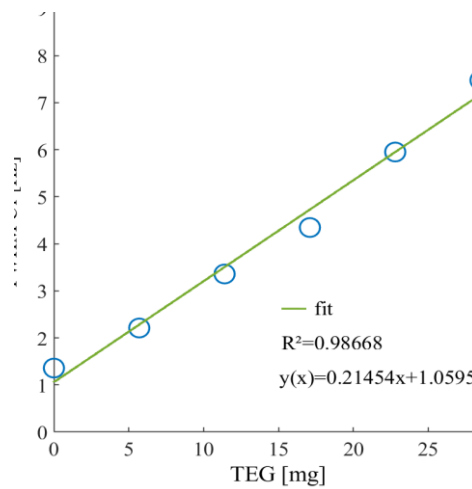


Figure 3.10: Linear fit between the methane FWHM values and the aqueous TEG content. Adapted from ref. [102].

During real-time online NG analyses, after the dried gas exits the dehydration units, where it comes into direct contact with a pure TEG column to remove water vapor from the wet gas, traces of TEG are expected [66][27]. Hence, NMR spectra were acquired with the droplet running through the active region as depicted in Figure 3.11a. Such moving droplets are expected to cause a strong spectra quality distortion due to the magnetic susceptibility effects [104].

For this droplet experiment, a small droplet of the TEG solution with 22.5 wt.% water, previously kept under an argon atmosphere, was placed on the upper side of the sapphire tube while in a horizontal position, which was also previously filled with argon. After sealing the HP tube with the PEEK cap, the argon atmosphere was exchanged with the NG sample and pressurized to 200 bar. The ^1H NMR spectra depicted in Figure 3.11b were recorded immediately after the HP tube was placed vertically in the spectrometer. To acquire the spectra, a series of single scans were conducted with a repetition time of 2 minutes over approximately 30 minutes. According to Figure A1 in the Appendix, the sensitive volume length was estimated to be 5 mm. Given that the droplet signal could be observed for 10 minutes, the estimated speed of the droplet was 0.5 mm/min. In Figure 3.11b, the TEG droplet can be seen passing through the active region at an average speed, being detected at different times. The results for integrals, SNR, and masses are reported in Table A4 in the Appendix. For clarity, Figure 3.11 shows the spectra at 4-minute intervals. In this experiment most of the droplet could be observed in the sensitive volume between the minute 4 and 8. At minute 0, the starting point, no TEG amount can be detected in the spectrum. With integrals values above the LOQ by minute 4 and minute 8 the droplet mass of 3.94 mg and 2.66 mg respectively could be quantified in the sensitive volume. Between minutes 8 and 12, no more TEG signal was detected, indicating that the droplet had settled at the bottom of the sapphire tube, outside the sensitive volume.

The effect of the TEG droplet on the ^1H NMR spectra of the NG is depicted in Figure 3.11b. According to Table A4, while the CH_4 exhibited an SNR of 6.58×10^3 at minute 0, this SNR dropped to 1.56×10^3 at minute 4, representing just 23.7% of the SNR at minute 0. By minute 12, the SNR returns to a similar level as at minute 0. The presence of TEG, causing significant peak distortions in the spectra of the NG sample, hampers further analysis with IHM to extract quantitative information, particularly for ethane and propane. These distortions are depicted in Figure 3.11b.

Nevertheless, by continuing with the long-term ^1H NMR spectra acquisition as discussed in sub-chapter 3.3, shimming the magnetic field was sufficient to fully recover the signal quality.

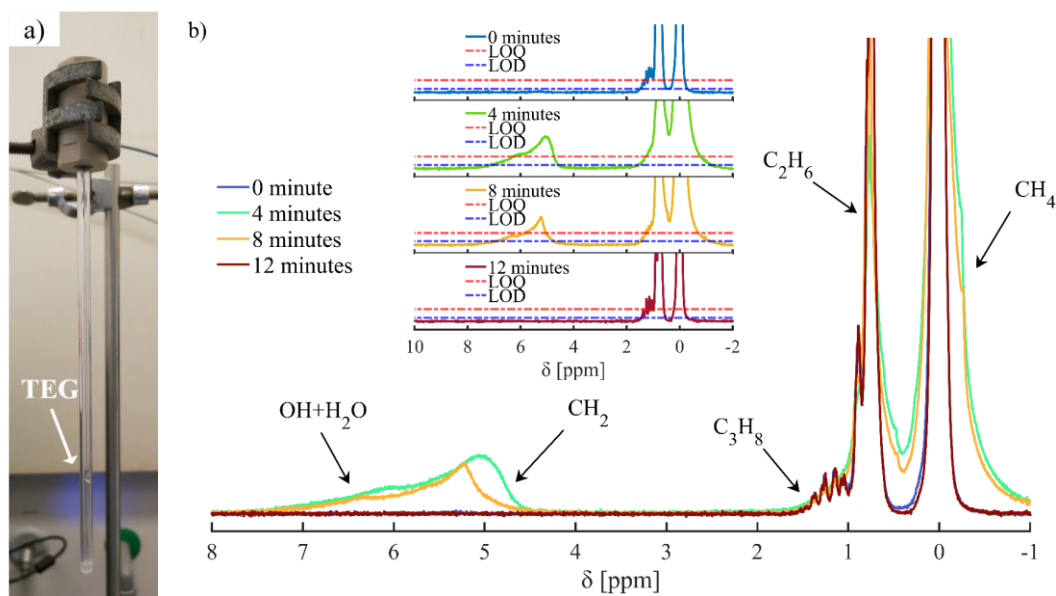


Figure 3.11: Aqueous TEG droplet experiment: a) visual illustration of the aqueous TEG droplet running down in the second-generation HP sapphire tube containing the 3-components NG sample pressurized to 200 bar. b) ^1H NMR spectra of the pressurized two-phase sample mixture recorded over time while the aqueous TEG droplet was moving downwards inside the tube. The LOD and LOQ correspond to the values 0.85 mg and 2.83 mg determined in Figure A1 in the Appendix. Adapted from ref. [102].

3.4.2 Robust Quality Control Parameters for the ^1H NMR Spectra Acquisition of Pressurized Natural Gas Samples in the Presence of Aqueous TEG

During the ^1H NMR spectra acquisition of the NG sample in the presence of TEG as a contaminant, either stationary at the bottom of the sapphire tube or flowing through the sensitive volume, it was observed that the QC parameters developed in sub-chapter 3.3.1 were insufficient to identify more complex peak deformations. This is also depicted in Figure 3.9, where deformations at the base of the CH_4 peak and peak asymmetry can be clearly observed and thus they need to be considered. Hence, additional control parameters were introduced. The first new QC is the linewidth at 10% height of the CH_4 peak, allowing for a characterization of the signal width at the peak base. Together with the FWHM, three symmetry parameters were developed to describe the right and left flank and global peak symmetry based on sub-variables (a_1 , a_2 , b_1 and b_2) which are visually described in Figure 3.12a. They can identify the position of the CH_4 signal's maximum, which is defined by the value of the chemical shift which can vary whilst FWHM and the peak width at 10% signal height may remain constant. The new peak symmetry parameters at 10% peak height and at FWHM can respond to shoulders formation and displacement of the maximum signal, even when the peak width at 10% signal height and the FWHM remain unaltered during these peak deformations.

$$\text{if } \Delta_{10\%} = \frac{b_1}{b_2} > 1 \text{ then } \Delta_{10\%} = \frac{b_2}{b_1} \quad (1)$$

$$\text{if } \Delta_{50\%} = \frac{a_1}{a_2} > 1 \text{ then } \Delta_{50\%} = \frac{a_2}{a_1} \quad (2)$$

$$\text{if } \Delta_{\text{signal}} = \frac{b_2 - a_2}{b_1 - a_1} > 1 \text{ then } \Delta_{\text{signal}} = \frac{b_1 - a_1}{b_2 - a_2} \quad (3)$$

These new QC parameters were integrated into the MATLAB script developed to select the spectra as described in sub-chapter 3.3.1 automatically. These QC parameters, determined from the methane signal measured on 140 single-scan ^1H NMR spectra of the three-component mixture over approximately 15 hours, are depicted in Figure 3.12b. As in sub-chapter 3.3, a shim every 20 scans were included to correct any external magnetic field disturbance. As observed for the first 40 scans, the new parameters are way more sensitive than just considering solely the FWHM of the methane signal. For instance, while the FWHM and the linewidth at 10% peak height show negligible variations visually, the new symmetry indicators clearly reveal changes in the peak shape. In this case, a shoulder forming in the upper half of the peak is reflected by a strong deviation in the symmetry at FWHM and in the signal. However, at 10% signal height, the symmetry remains steady because the position of the signal's maximum point on the x-axis does not change. This deformed peak is depicted in Figure A2 in the Appendix, corresponding to spectrum No. 40 from the set of spectra shown in Figure 3.12b.

The thresholds for these new QC parameters were averaged based on the values obtained in the steady region, which, as shown in Figure 3.12b, corresponds to the spectra recorded from approximately 19h. The values determined in this region correspond to spectra obtained with reproducible quality. The obtained threshold values corresponding to the peak widths at FWHM and at 10% peak height were 0.99 ± 0.06 Hz and 2.30 ± 0.06 respectively. For the symmetry parameters, the values at FWHM and at 10% peak height were 0.51 ± 0.06 and 0.72 ± 0.06 respectively and for the signal symmetry was 0.91 ± 0.06 . For instance, the CH_4 signal in the spectrum depicted in Figure 3.8 corresponds to the quality achieved after averaging 64-scan spectra selected within the determined thresholds. Similar as in sub-chapter 3.3.1, a tolerance of 10% for each parameter was included in the MATLAB script. Thus, it is important to highlight that the proposed parameters need to be calibrated by defining the reference values and thresholds recording long-term

experiments with the high-pressure tube chosen for the application. Moreover, such changes in hardware will also affect the linewidths at different liquid contents in the sensitive volume shown in Figure 3.10.

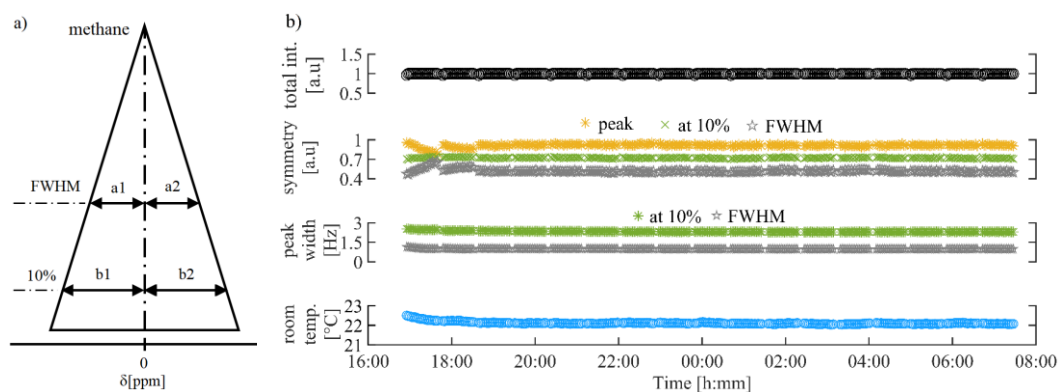


Figure 3.12: QC criteria: a) Schematic illustration of the methane signal with the variables to define the signal quality parameters. b) Determined QC parameters of 140 single-scan ^1H NMR spectra recorded over time of the 3-components gaseous mixture containing 85% methane, 10% ethane, and 5% propane pressurized at 200 bar. A shim was used every 20 scans. The blanks between the data correspond to the shim periods. Adapted from ref. [102].

To perform the composition analysis of the NG sample pressurized at 200 bar in the presence of aqueous TEG, just the ethane and propane hard models developed in sub-chapter 3.3.2 were used for IHM. The CH_4 area is determined like in sub-chapter 3.3.2, by subtracting the total IHM fit area from the total integral of the frequency domain between -1 ppm and 1.8 ppm. Figure 3.13 depicts the IHM fit on a 64 scan ^1H NMR spectrum of the NG sample with 28.5 mg TEG in the sensitive volume. It can be observed that the predominant signal contribution comes from the aqueous TEG. Still, because of the good peak separation between methane, the higher HCs and TEG, the HC signals could properly be fitted.

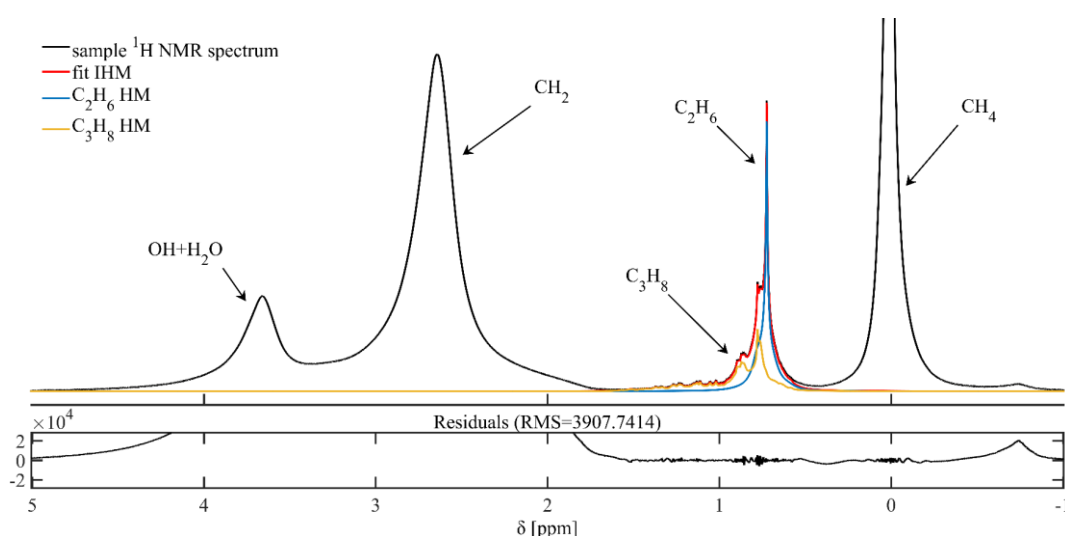


Figure 3.13: IHM fits NG ^1H NMR spectrum of the two-phase matrix sample containing 28.5 mg of aqueous TEG under an atmosphere of pressurized 3-components NG at 200 bar. Adapted from ref. [102].

The results of the IHM on recorded ^1H NMR spectra of the NG sample pressurized at 200 bar and in the presence of different aqueous TEG contents in the sensitive volume are depicted in Figure 3.14 as degree of equivalences for a better comparison. For the TEG contents in the sensitive volume of 0 mg, 5.7 mg and 11.4 mg, three different multi-scan spectra containing 64-scan each were generated using the proposed QC parameters in this sub-chapter. For a TEG content of 28.5 mg, three different multi-scan spectra were generated by selecting spectra based on the QC parameters proposed in sub-chapter 3.3.1, as the peak width at 10% could not be measured (see Table 3.1). Additionally, only one multi-scan spectrum containing 64 scans could be acquired at 34.2 mg of TEG in the sensitive volume, selected by visual inspection from a large set of recorded single-scan spectra, as they did not meet the QC parameters proposed in this thesis.

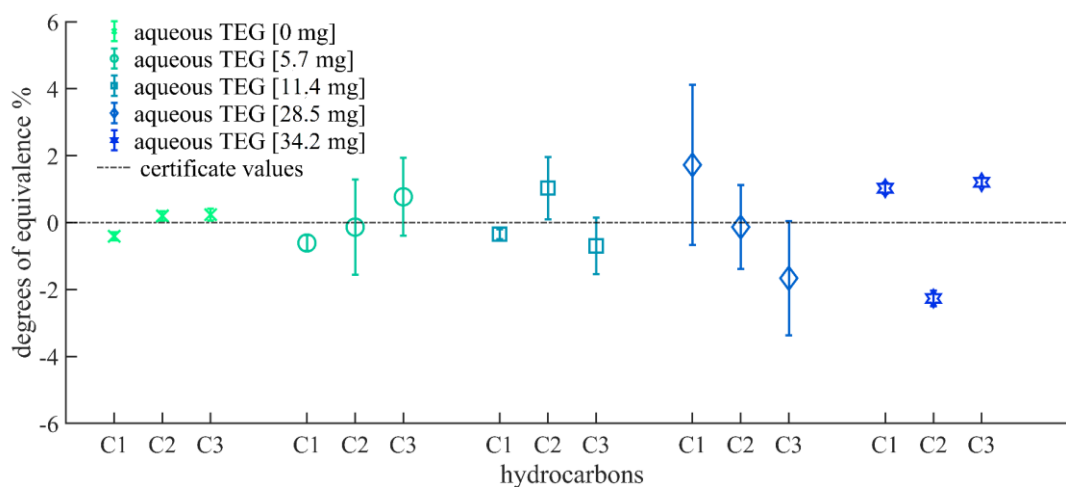


Figure 3.14: Degrees of equivalence between the determined IHM results of the 3-components NG sample containing 85% methane, 10% ethane, and 5% propane pressurized at 200 bar at various steady aqueous TEG content resting on the bottom of the sensitive region. The error bars are determined from the IHM analysis using three sets of 64 scans spectra. Adapted from ref. [102].

Figure 3.14 shows that the IHM-predicted concentrations are in excellent agreement with the certified values of the NG sample pressurized at 200 bar with 0 mg, 5.7 mg, and 11.4 mg TEG content. As expected, the lowest dispersion and highest accuracy are achieved at 0 mg TEG. However, even at 5.7 mg and 11.4 mg TEG, the mismatch is maintained below 1%, with comparable dispersion, which is attributed to the successful implementation of the full set of QC parameters discussed in this chapter. Due to the less constrained QC parameters for the recorded spectra at 28.5 mg TEG, the results exhibit greater dispersion, with errors approximately twice those obtained at lower concentrations. At 34.2 mg TEG, the agreement with the certified values is less accurate. Nevertheless, these results underscore the robustness of IHM in extracting quantitative information from pressurized HCs in the presence of liquid contaminants. These promising findings could significantly expand the application of benchtop NMR spectroscopy for

quality control in NG processing facilities. Additionally, other fields facing similar analytical challenges could benefit from this proposed methodology.

3.5 Water Content Determination in Glycols with Benchtop NMR Spectroscopy

As discussed in the previous sub-chapter, glycols are chemical compounds of significant importance in the NG industry, primarily employed for moisture control in dehydration units [105,106]. Although TEG is commonly used in such applications, ethylene glycol (EG) enjoys equivalent popularity as an effective hydrate inhibitor. These versatile compounds, whose molecular structures are depicted in Figure 3.15, can be used continuously, contributing to low operation costs. For instance, after leaving the NG dehydration unit, aqueous glycols are treated in regeneration units for reuse [107,108]. These two water absorbers cover an even broader range of applications outside the energy sector such as pharmaceuticals, self-care, and the food industry [78,79,109,110]. Their extraordinary water affinity and the influence it has on their physical-chemical properties define their role in the application and are of interest to scientists within and outside academia. For instance, aqueous EG solutions are commonly used as an antifreeze and heat transfer agent thanks to their low freezing point and elevated boiling point [111]. Furthermore, in glycol-based cosmetic applications, the product's moisture control of the product contributes to its long-term preservation [112].

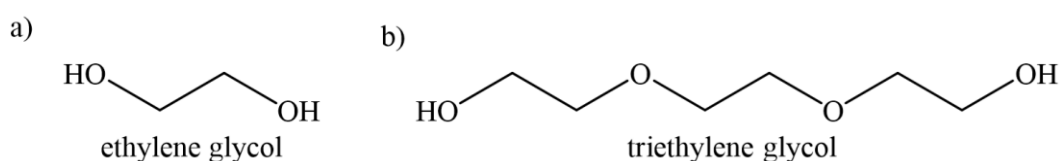


Figure 3.15: Molecular structure of the investigated glycols: (a) EG and (b) TEG.

The determination of the water content is crucial to ensure a cost-efficient and environmentally friendly operation of glycols-based applications. Currently, the Karl-Fischer titration is the gold standard method to quantify water in glycols, as it offers high accuracy, enabling reliable quantification even at trace levels [28,29,80,113–121]. However, the reaction is conducted in an alcoholic solution that necessitates constant renewal under intensive use. Additionally, it predominantly involves expensive and toxic compounds, making this highly sensitive method unsuitable for routine experiments [118,122].

Up to the time of writing this work, only very few studies have reported novel methods or more environmentally friendly alternatives to Karl-Fischer method for determining water content in glycols. They include optical analytical methods such as Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy, as well as NMR spectroscopy [123–125].

For instance, FTIR spectroscopy was applied to identify and quantify various components, including water in four-component samples (methyl diethanolamine (MDEA)-H₂O-CO₂-EG/TEG). Here, the quantitative information from the recorded spectra was extracted with a PLS regression algorithm, reaching very good accuracy in predicting water content in samples prepared gravimetrically [123]. While PLS is a well-established chemometric method for analyzing complex samples, its demanding calibration requires large datasets with characteristics similar to those of the test samples to ensure analytical accuracy. This can lead to poor results when the sample experiences the influence of unpredictable external factors, such as temperature, which are not accounted for in the PLS model. Compared to FTIR spectroscopy, quantitative analysis using proton NMR spectroscopy is often more straightforward, thanks to the direct linear relationship between the signal integral and the number of contributing protons. Moreover, in many cases, composition

analysis can be determined by simple spectral integration [13,126,127]. Nevertheless, indirect analysis approaches such as linear calibration curves, taking into account the chemical shift difference between the water-associated signal and signals of reference, have already been proposed for quantifying water up to 10% in various solvents [128]. Water content has also been effectively quantified with high-field NMR devices at concentrations higher than 10% in heat exchange fluids containing EG and propylene glycol (PEG) [124]. However, despite the excellent sensitivity of the high-field devices, they are usually impractical due to the high operation costs [129]. Hence, this sophisticated analytical tool is limited to a few labs with the economic capacity to afford these high-performance devices. For this reason, the development of versatile, easy-to-use, fast, and affordable analytical methods is of great interest in fields where high-field NMR devices are not feasible.

The affordability and technical capabilities of low-field benchtop NMR devices recently allowed the determination of glycol content in aqueous EG solutions with water content higher than 20 wt.% including relevant additives in NG dehydration units [106]. The feasibility of time-domain low-field NMR for the water content determination was demonstrated on lyophilized proteins [130], allowing a non-invasive, fast, and non-destructive analysis at the expense of the structural identification of the investigated sample.

In this work, an analytical methodology is proposed for the fast water content determination in glycols up to about 11 wt.% with benchtop proton NMR spectroscopy. The NMR results obtained are compared with those from the Karl-Fischer titration, reaching an excellent agreement. These results open the possibility of integrating tabletop NMR spectroscopy into the routine analysis of water content in glycols used in dehydration units, thereby helping to ensure the efficacy of these water inhibitors. The ability to detect low amounts of water in glycols provides valuable data for decision-making prior to their use in dehydration units, as the water

content directly impacts the efficiency of the process. Additionally, since NMR does not require solvents, it offers a more environmentally friendly alternative to the traditional Karl-Fischer titration. Moreover, the proposed methodology has the potential to be extended to the analysis of water content in more complex samples, including those with higher water concentrations, making it suitable for routine online analysis in various applications.

3.5.1 ^1H NMR Spectra of Aqueous TEG and EG

The samples investigated in this work were binary mixtures of water-EG and water-TEG. EG and TEG were purchased from Sigma-Aldrich with a reported purity of 99.5% and 99% respectively. To identify the initial water content of the samples as received from the manufacturer, Karl-Fischer titration was performed on both glycols, revealing a water content of 2 wt%. Considering this water content, the samples with water content above 2 wt.% up to about 11 wt.% were prepared gravimetrically. To obtain samples with water content below 2 wt.%, the glycols were stored in samples container with molecular sieves of type 4 Å, which were purchased from Sigma Aldrich and activated at 600 °C for 8 h and then stored under an argon atmosphere. The samples were stored for four months and periodically monitored until minimal water contents of 0.06 wt.% for EG and 0.09 wt.% for TEG were achieved. The NMR experiments were performed with a Magritek Spinsolve 40 Carbon tabletop NMR spectrometer with a proton frequency of 43 MHz operating at 28 °C. For all the binary mixtures, the proton spin-lattice relaxation time T_1 were determined with the inversion recovery method. The highest determined T_1 value among the samples investigated was 0.65 s. The ^1H NMR spectra were recorded with 16 scans and a repetition time of 4 s, being longer than $5 \times T_1$, leading to a maximum measuring time of 1 min per sample.

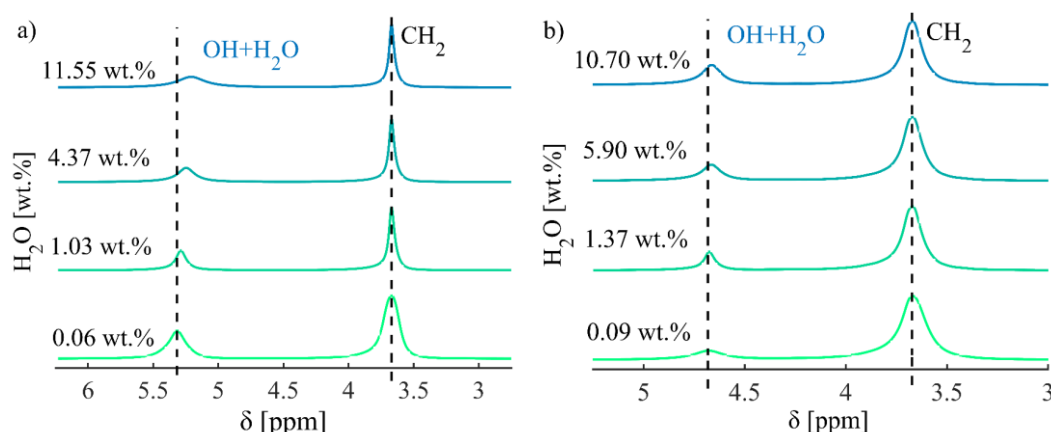


Figure 3.16: ^1H NMR spectra of binary aqueous glycol samples at different water contents: a) water-EG and b) water-TEG. Adapted from ref. [41].

The recorded ^1H NMR spectra for both sets of binary mixtures are depicted in Figure 3.16. For both glycols, the methylene (CH_2) signal is displayed in the upfield direction, while the hydroxyl (OH) signal, with the water signal on top of it, appears in the downfield region. The position of the CH_2 group around 3.67 ppm matches the values reported in the reference [101]. For both glycols, the CH_2 FWHM decreases progressively with increasing the water content, which is attributed to lower viscosity and higher molecular mobility [131]. The OH signal, associated with hydrogen bonding interactions among glycol molecules themselves and with water, reveals a more intricate pattern. These changes in the signal, driven by varying water content, result from distinct molecular conformations that arise due to the shifting balance between intermolecular and intramolecular interactions [100,132–136]. While the $\text{OH}+\text{H}_2\text{O}$ signal for TEG shows a monotonic reduction of its FWHM with an increase of its peak intensity, for EG an upfield shift and a peak broadening can be observed. In the case of EG, similar observations have been reported while increasing the temperature for the pure EG associated with a decrease in the hydrogen-bonded associations between the molecules in the mixture [136]. Compared with TEG, EG has a higher probability of H-bonding with water and a

greater lifetime of water-water H-bonds [137]. Additionally, it has been indicated that at high TEG concentrations, the TEG-TEG interactions are predominant, and the TEG-water interactions are mostly influenced by the ether oxygen [100]. Although correlation curves based on chemical shift differences between signals like those observed for EG in Figure 3.16 have been proven to be an effective way to determine water contents [122,128], the demonstrated temperature dependence of these chemical shifts would make the development of a calibration curve at each temperature necessary. Additionally, it was found in this work that the chemical shift differences between the OH+H₂O and CH₂ peaks in the EG samples changes with increasing water content, as the OH + H₂O signals shift closer to the CH₂ signal. Although these differences are relatively small, they could potentially be used for a calibration approach similar to that described in references [122,128]. In the case of TEG, no chemical shift changes were detected, regardless of the water content.

3.5.2 Water Content Determination in Glycols

The mass concentration of water ([wt.%]) was determined with the equation number 4. The detailed development of this expression can be found in reference [41]. This mathematical expression takes advantage of the quantitative nature of NMR by considering the number of protons contributing to the signals observed in the spectrum. More specifically, A_{CH_2} and A_{OH+H_2O} correspond to the area of the methylene and hydroxyl-water peaks; P_{CH_2} correspond to the number of protons in the methylene group which varies depending of the glycol being analyzed; M_{H_2O} and M_{Gl} are the molar mass of water and glycols respectively.

$$H_2O[wt. \%] = \frac{M_{H_2O}P_{CH_2}A_{OH+H_2O} - 2A_{CH_2}M_{H_2O}}{M_{H_2O}P_{CH_2}A_{OH+H_2O} - 2A_{CH_2}M_{H_2O} + 2A_{CH_2}M_{Gl}} * 100 \quad (4)$$

This equation's only inputs are the areas of the recorded NMR spectra. Thus, an appropriate determination of these experimental variables is critical to ensure the reliability of the predicted results. The simpler approach is by simple integration; however, it was found that the spectra dispersion was insufficient with the used magnetic strength to ensure a perfect peak separation between the OH+H₂O and CH₂ signals. The remaining overlap can be observed via visual inspection by zooming in on the common region between both signals (see Figure A3 in the Appendix). This signal overlap, although seemingly negligible, can become problematic for the quantification of low water contents [38,138]. In addition, as the chemical shift changes for EG, the overlap at the peak base increases, necessitating manual determination of the integration limits, which makes this approach less robust. Therefore, the whole spectrum was deconvoluted to tackle the mentioned issue using a line shape analysis (LSA). Thus, each functional group was modeled with a subset of pseudo-Voigt peaks for both aqueous glycols. The OH+H₂O signal was modeled with two peaks, while the CH₂ group required a maximum of four sub-peaks. These number of pseudo-Voigt functions were necessary to create an optimized model considering the asymmetry of the low-field NMR signals. For the sake of illustration, a typical deconvolution model is depicted in Figure 3.17 on 40 MHz proton NMR spectra of the aqueous EG sample containing 0.30 wt.% water content.

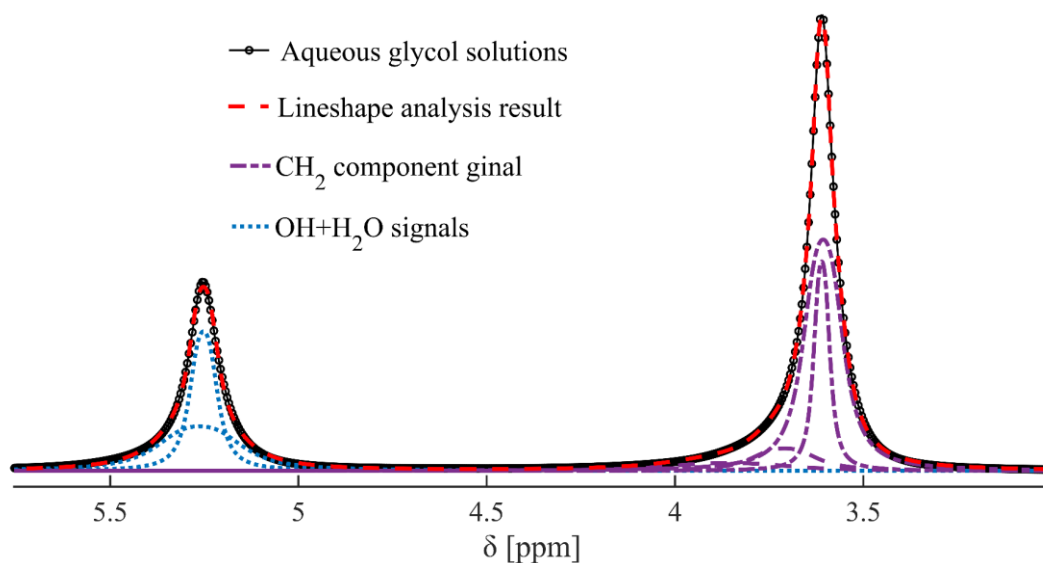


Figure 3.17: Exemplarily line shape analysis for the water content determination of the binary aqueous EG mixture with a water content of 0.30 wt.%. Adapted from ref. [41]

The area values extracted using the LSA method and, for comparison purposes, by simple integration were used as the experimental inputs in equation 4 for each investigated aqueous glycol sample and were compared with the Karl-Fischer results. As shown in Figure 3.18, the NMR integration results demonstrate good accuracy for water content values only above approximately 5 wt.%. However, below this threshold, accuracy decreases, with larger discrepancies observed when compared to the Karl-Fischer results as the water content decreases. These observations confirm that small inaccuracies in the determined areas have a more critical impact on lower water content regimes. The best correlation was achieved with the LSA results, achieving an excellent agreement even for values below 2 wt.% water. The limit of quantification (LOQ) and limit of detection (LOD) were determined following the approach proposed in reference [103]. The results prove that even concentration values as low as 0.45 wt.% and 0.17% can be quantified for TEG and EG respectively within a 1-minute measuring time.

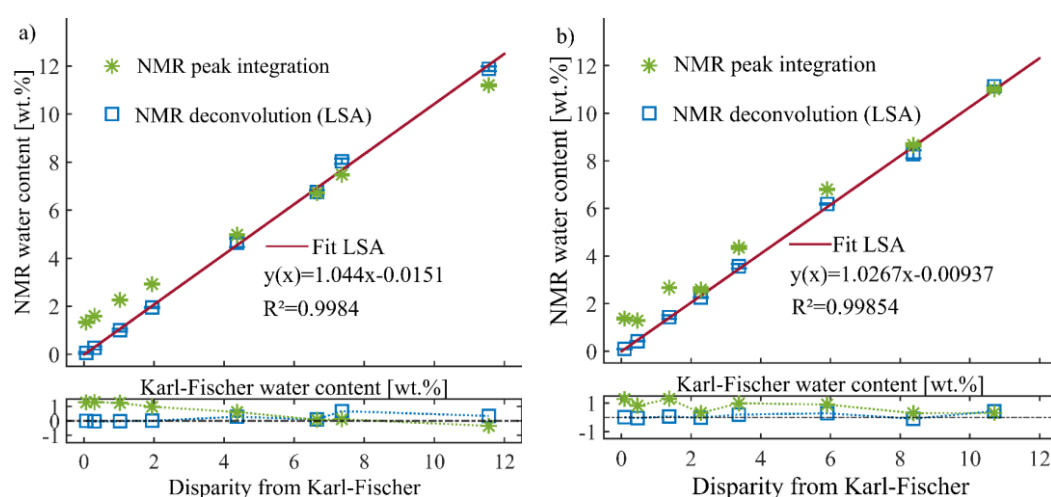


Figure 3.18: Water content determination of binary aqueous samples by Karl-Fischer, simple integration, and LSA: a) EG and b) TEG. The best linear fit was reached between the LSA NMR results and the Karl-Fischer results. Adapted from ref. [41].

This simple but effective method to estimate the water content in glycols has the potential to be integrated into a routine water content control procedure. For instance, it can help to rapidly determine the water content of the glycol used in an NG dehydration unit.

Chapter 4

Flow-Through Cell for Composition Analysis of ^1H NMR-Active and Non-Active Constituents in Natural Gas-Based Samples Using Benchtop HP NMR Spectroscopy

The work presented in this chapter continues the efforts to advance benchtop NMR spectroscopy for the composition analysis of real NG and hydrogen-enriched NG samples under in field conditions. The first section introduces high-pressure benchtop ^1H NMR spectroscopy as a novel and cost-effective method for quantifying hydrogen-enriched natural gas (HENG) blends. The NMR method addresses the critical need for accurate composition analysis, given the impact of HENG blends composition on their thermo-physical properties and on the mechanical stability of NG infrastructure. Developed entirely by RWTH scientists, this approach includes the design and testing of an inexpensive HP flow-through cell capable of operating at up to 245 bar, with successful demonstration on selected blends and in-situ monitoring of compositional changes over time.

This part of the work presents a proof of concept developed in a joint effort between Equinor ASA, Gassco AS, Baker Hughes INTEQ GmbH and RWTH Aachen University to determine the composition of the whole species present in the investigated samples with HP benchtop NMR. Here, an approach is proposed and

tested to determine the absolute concentrations of non-hydrogen-bearing species in the gas mixture using an inverse algorithm by optimizing the difference between the areas corresponding to the proton signal spectra of HCs obtained with IHM and modeled areas of the same HCs determined by solving equations of state (EOS) which considers the presence of the non-hydrogen-bearing species present in the samples. This proof-of-concept algorithm is fully integrated in MATLAB. The measurements of the samples required for this data-driven approach and their composition analysis with IHM were performed at the RWTH facilities. The inversion model algorithm and its integration in MATLAB were developed between Equinor ASA and Baker Hughes INTEQ GmbH. The performance of the proposed algorithm was tested at the RWTH facilities. The results of the HC species obtained with IHM in Chapter 3 using the 2nd design sapphire tube, and those from the flow-through cell in the first part of this chapter, demonstrated improved prediction accuracy, proving the advantages of the new design proposed in this chapter. In contrast, the proposed inverse algorithm produced slightly less accurate results compared to IHM. However, given that the calibration was conducted with a limited number of samples, we believe that significantly larger dataset could potentially enhance the algorithm's performance. This collaborative effort highlights the enhanced robustness and broader applicability of the improved NMR methodology within the energy industry.

4.1 Introduction and Motivation

As mentioned in sub-chapter 3.2, a key hardware component for HP NMR spectroscopy is the HP tube [24–26,38,39,139]. Although recent publications and the work presented in chapter 3 expanded the capabilities of this customized HP hardware allowing the analysis of complex HC mixtures up to 200 bar with benchtop NMR spectroscopy, the practical implementation of these tubes with a single opening still limits online NMR applications. When using this hardware in industrial

facilities for monitoring real samples during routine analysis, such as NG that may contain traces of glycols as discussed in sub-chapter 3.4, the accumulation of these substances over time in the tube negatively impacts the quality of the analysis. This contamination leads to inconvenient waiting times due to the need for regular tube cleaning before reusing. Additionally, with the existing manufacturing technology, it is not possible to produce sapphire HP tubes with two openings and long enough for going through standard NMR boreholes.

Furthermore, flow NMR is widely used for applications such as reaction monitoring, process control, and industrial screening [5,6,87,140,141], but its application at higher pressures, from 30 to 210 bar as required for NG in-field-like conditions [142], is limited due to the absence of commercially available HP flow-cells. Nonetheless, some attempts to overcome such challenges are reported in the literature; for instance, although most existing designs are restricted to atmospheric or low-pressure conditions, there are a few examples capable of operating above 30 bar [143–145]. In reference [145], a flow cell manufactured via additive processes has demonstrated functionality up to 100 bar. Additionally, a flow cell design based on grown sapphire capable of withstanding up to 200 bar was proposed in reference [144]. Still, due to the cap size of the two open sides, it had to be adapted with a custom-made radiofrequency, which must be replaced each time the tube had to be removed for cleaning. The major drawbacks of these concepts are their complex designs and the degree of customization that hampers their implementation outside of specialized facilities.

However, in this work, we present for the first time a novel flow-through cell specifically designed for low-field HP NMR spectroscopy, enabling measurements at pressures as high as 245 bar, capable of addressing the demands of higher-pressure applications, such as those encountered in NG-based samples. The new HP flow-cell design is based on commercial and inexpensive PEEK tubing components

commonly found in (HPLC) applications and is easily assembled in a plug-and-play manner and can be installed in standard commercial benchtop NMR spectrometers. PEEK components offer significant benefits in NMR applications due to their polymeric nature, which results in minimal magnetic susceptibility [146]. Additionally, PEEK has high thermal stability and is an excellent fire resistance material even under various oxygen concentrations as reported in Ref. [147]. For example, PEEK components are widely used in NG infrastructure, including bearings, couplings, seals, and flow control devices such as valves [148,149].

The performance of the new PEEK flow-cell in context of low-field NMR spectroscopy was assessed using the HP hardware described in sub-chapter 3.2 and a set of certified samples containing components commonly found in NG and by benchmarking the recorded ^1H NMR spectra against those from the first- and second-generation high-pressure sapphire tube designs. Subsequently, the reproducibility and long-term stability of the spectra are presented, emphasizing the fast and cost-effective quantitative composition analysis of NG blended with hydrogen at various industrially relevant concentrations. Finally, in sub-chapter 4.5, the composition analysis of non-active ^1H NMR species in NG mixtures such as CO_2 , N_2 and Ar will be introduced as proof-of-concept for the first time. It is based on the combination of IHM and equations of state (EOS).

4.2 Flow-Through Cell Design Suitable for HP NMR Spectroscopy

This flow-cell is suitable to work at pressures up to 245 bar and also opens the road towards on-line continuous HP NMR measurements for samples in both stopped- and continuous-flow. The individual components are depicted in Figure 4.1a. The

design can be described by three main sub-assemblies from bottom to top as follows:

- 1) a HP reduction (Figure 4.1a, 2) with a blind 1/16" ferrule (Figure 4.1a, 1) with a 10-32 thread at the bottom to serve as a plug of the entire flow-vessel and a second ferrule (Figure 4.1a, 3) to fix the tube to a 1/8" outer diameter HP PEEK capillary.
- 2) The main flow-cell (Figure 4.1a, 4) with key physical features such as a customizable length (here 500 mm), 1/8" (3.175 mm) outer diameter (o.d.) and 0.060" (1.52 mm) inner diameter (i.d.), small enough for the 5 mm i.d. of the RF coil (Figure 4.1a, 8) and a customizable length according to the full spectrometer height.
- 3) A second HP reduction (Figure 4.1a, 2) with two ferrules, one at the bottom (Figure 4.1a, 3) connecting the 1/8" tube and other on the top (Figure 4.1a, 11) connecting to the 1/16" tube which connects directly to HP setup. All these PEEK components are easy to attach and replace, and were purchased from VICI Jour (Schenkon, Switzerland).

Since the only commercially available PEEK capillary with an o.d. below 5 mm suitable for installation through the spectrometer coil was the 1/8" (~3.175 mm o.d.) HP PEEK capillary, a gap remained between the outer diameter of this flexible flow-cell and the i.d. of the RF coil. To address this, a commercial medium-wall NMR sample tube with a 3.43 mm i.d. (Figure 4.1a, component 7) was cut at the bottom and placed in the standard spectrometer tube holder (Figure 4.1a, components 9 and 10) to fill the gap and keep the flexible flow-cell straight within the cylindrical magnet arrangement (Figure 4.1a, component 6). This simple solution ensured consistent sample positioning within the region of highest magnetic field homogeneity [150], even after a full component replacement was required.

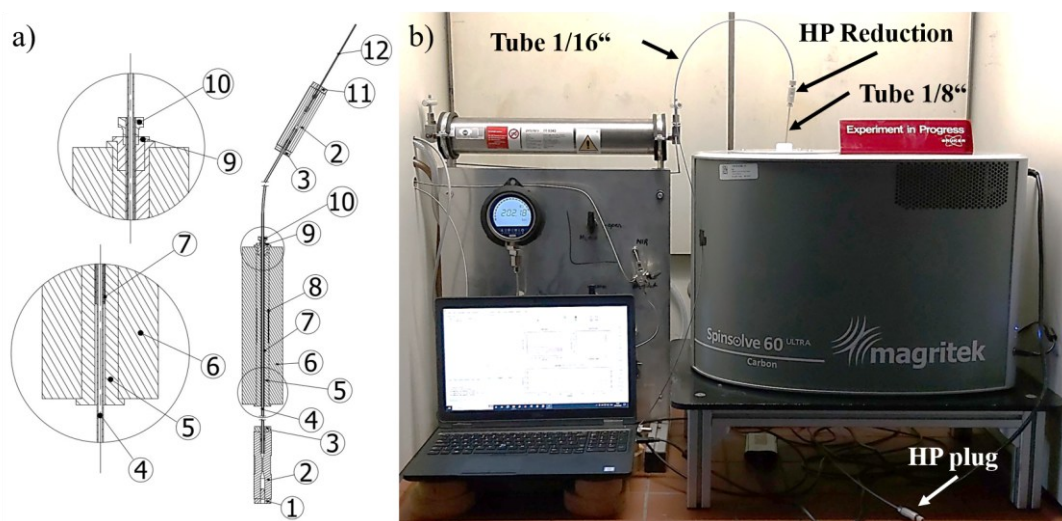


Figure 4.1: Technical drawing of the a) HP flow-cell consisting of the following PEEK components: (1) HP plug; (2) HP reduction; (3) ferrule with 1/8" inner diameter; (4) flow-cell 1/8" outer diameter; (5) bore of spectrometer; (6) arrangement of cylindrical magnets; (7) medium wall NMR sample tube; (8) NMR coil; (9) spectrometer tube holder; (10) open port cap for NMR tube; (11) ferrule with 1/16" inner diameter and (12) tube 1/6" outer diameter. The length of the PEEK flow-cell was adapted to the length of the Spinsolve device depicted in b). Adapted from ref. [151].

As demonstrated in chapter 3, the implementation of second-generation HP tube design with a tube cap and capillary lines made of PEEK instead of metallic components largely contributes to the thermal and magnetic stability of the NMR instrument. Yet, with the implementation of the new full PEEK flow-cell, further improvements in long-term experimental stability and, thus, spectra reproducibility is expected since its low thermal conductivity inhibits heat transfer between the sample, environment, and the NMR magnets.

4.3 Flow-Cell Performance Assessment

To assess the performance of the new flow-cell design, the spectral quality and long-term stability were investigated. To quantitatively and qualitatively characterize these aspects, ^1H NMR spectra of two HC mixtures pressurized at 200 bar were recorded with the flow-cell and compared to spectra obtained with the first- and the second- generation sapphire tube designs. A 60 MHz NMR spectrometer was used to record each ^1H NMR spectrum with 16 scans and a repetition time of 2 minutes to ensure signals with quantitative information. Additionally, the signals were zero filled in the time domain up to 256k points before applying the Fourier Transformation.

Figure 4.2 visualizes the improvements achieved with the new flow-cell when compared with the previous designs. For instance, in the spectra of the HC mixture containing 92.43% methane and 7.57% ethane depicted in Figure 4.2a, a reduction in the FWHM of 20% and 14% was achieved for methane compared to the first- and second- generation designs, respectively. An even more remarkable improvement can be observed at 0.55% signal height, with a methane linewidth reduction of 87% and 83% when compared with the first- and second- generation designs respectively. For the second mixture methane/propane, the FWHM of methane signal was 47% smaller with the first- than for the second-generation sapphire tube design, and at 0.55% methane peak height the reduction in peak width was 81%. At the time that the second sample presented in Figure 4.2b was prepared, it couldn't be measured with the first-generation HP tube design as that the tube was broken. However, an already recorded ^1H NMR spectra of a binary mixture methane/propane with unknown concentration was included in Figure 4.2b to visually highlight the improvements in spectra resolution achieved for the cluster of propane multiplets.

This extraordinary improvement in linewidth at 50% and at 0.55% peak height of the spectra recorded with the flow-cell, led to an overall enhancement in

spectral resolution. Thus, the spectra exhibit a better peak separation among the signal of the different components present in the same matrix sample. In the case of NG, methane shows a significant signal separation from larger HCs. Well defined integration limits allow thus accurate methane quantification, minimizing small errors that largely affect the quantification accuracy of the higher order HCs.

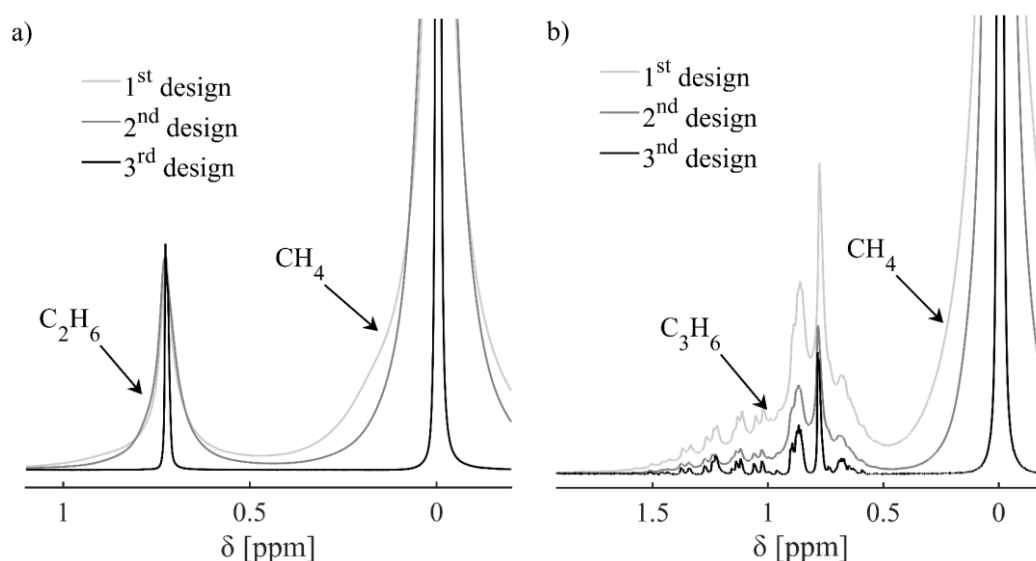


Figure 4.2: ^1H NMR recorded with the three HP tubes designs at 200 bar for two binary HCs mixtures: a) 92.43% methane and 7.57% ethane and b) self-made mixtures of unknown concentration containing methane and propane. All the recorded spectra have methane set to 0 ppm and are normalized to the maximum amplitude of methane signal for a better visual comparison between the spectra measured with the different designs. Adapted from ref. [151].

Among the three designs, the lower i.d. of the new flow-cell led to the lowest sample volume available in the sensitive region when compared to the 3.2 mm i.d. of the sapphire tube. This leads to a reduction in SNR, which should be more problematic for higher-order HCs present at low amounts in the mixtures. However, as depicted in Figure 4.2, the narrow linewidths increase spectral resolution, improving the spectral signature. Even for crowded peak clusters, as depicted for

propane in Figure 4.2b, the good resolution allows a clear visualization of the individual peaks.

Two different long-term experiments were conducted to demonstrate the experimental stability in NMR spectroscopy for the analysis of HC mixtures up to 200 bar using the flow-cell. 1) Figure 4.3a shows two ^1H NMR spectra of the 3-components mixture containing methane (85 mol%), ethane (10 mol%), and propane (5 mol%) pressurized at 200 bar and measured 8 weeks apart. Each spectrum was recorded with 16 scans and 2 minutes of repetition time. This experiment demonstrates that identical spectra can be reproduced, even though the flow-cell experienced significant vertical displacements during the time gap due to various necessary hardware manipulations, such as disassembling and reassembling the entire setup to allow different experiments with the spectrometer required by other users. 2) A second experiment consists of single ^1H NMR spectra of pure hydrogen pressurized at 200 bar recorded every 2 minutes over 36 hours (Figure 4.3b). In the literature, very few studies are reported regarding the long-term PEEK stability in the presence of H_2 at high pressures. For instance, it has been reported that during accelerated H_2 aging experiments at 85 bar and 80 °C, PEEK exhibited no significant changes in its thermal properties, phase transitions, or morphology changes when compared with other high-performance polymers [152]. In this work, the PEEK tubing components were used at room temperature. For the experimental results depicted in Figure 4.3b, each recorded H_2 signal was characterized by its total integral in the frequency domain, FWHM, linewidth at 25% peak height, and magnetic frequency stability. Due to the short spin-spin relaxation time T_2 of hydrogen, its signal is broad, and measuring the linewidth at 10% peak height is significantly impacted by noise, making such measurements less reliable. The obtained results show a constant integral during the entire experimental time, demonstrating that the PEEK components of the flow-cell design are completely gas-tight even for the small hydrogen molecule. Assuming that peak shape

reproducibility over time can be described by tracking the signal peak width at two different heights, the FWHM and the linewidth at 25% peak height, the peak shapes remained constant, despite a broad dispersion owed to the noise inherent in the single-scan spectrum. This high reproducibility was also possible thanks to the excellent stability of the magnetic field, which could be maintained despite the natural fluctuations of the room temperature over a continuous time frame of 36-hours. These results demonstrate that the proposed flow-cell is suitable for long-term measurements of HCs and gaseous H₂ pressurized at 200 bar.

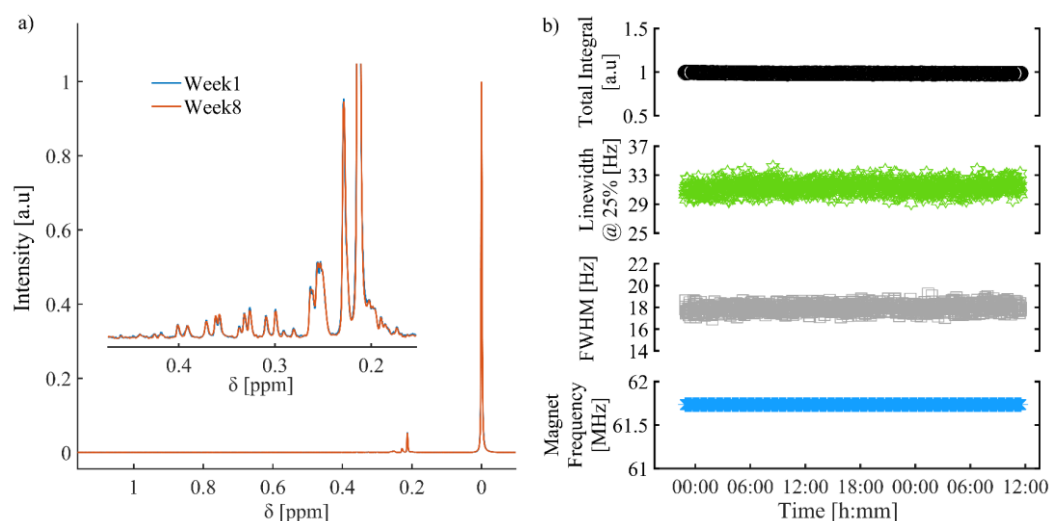


Figure 4.3: a) 16 scans ¹H NMR spectra reproducibility test using a 3-components gaseous mixture with methane (85 mol%), ethane (10 mol%), and propane (5 mol%) pressurized at 200 bar measured with a difference of 8 weeks. b) Long-term measurements of pure H₂ pressurized at 200 bar over 36 hours. Adapted from ref. [151].

4.4 Quantitative Composition Analysis of NG-H₂ Mixtures

The use of NG within the ongoing energy context is recognized as a transition towards greener and more sustainable energy sources due to its lower CO₂ emissions when compared to traditional sources such as wood, crude oil, and coal [153]. However, despite its lower CO₂ emissions, methane which is the main component of NG, has a stronger greenhouse effect than CO₂ [154]. In this regard, H₂ has emerged as another key energy source, which can significantly contribute to the decarbonization of the energy sector by replacing NG in its applications either partially or completely [30]. Additionally, its high energy density of about 120 MJ/Kg at 300 K and 1 atm, which is much higher than other fuels with 44 MJ/kg and 50 MJ/Kg for gasoline and methane respectively and its potential to be produced from removable energy sources, makes H₂ a promising and efficient green energy carrier [30,155].

According to the EU's climate-neutral strategic vision, hydrogen is planned to increase its share in Europe's energy sector from less than 2% to 24% by 2050 [155]. Unfortunately, being the smallest and lightest element in the universe, makes handling H₂ particularly challenging in key logistic aspects such as storage, distribution, and utilization [155]. Still, the existing well-interconnected NG infrastructure, which is currently undergoing sustained expansion [30], is considered the best short-term solution to transport-controlled amounts of H₂ mixed with NG [30,156]. Along with the implementation of this strategical solution, further technical aspects have to be considered. This is because heating value, density, viscosity, and flow properties strongly depend on the amount of added hydrogen [157–159]. Furthermore, for safe NG infrastructure operation, its compatibility with various H₂ contents is the subject of numerous investigations [160,161]. For

instance, in gas engines, the range of investigated hydrogen concentrations in NG spans from 1% up to 100%. This is particularly relevant in light of the intensive development of state-of-the-art turbines designed to operate solely on hydrogen. Such turbines aim to ensure grid stability during periods of insufficient wind or solar energy supply [162]. Additionally, H₂ concentrations up to 50% are currently being investigated to assess the implications for the entire NG distribution system [161,163,164].

Consequently, for decision-making and ongoing research along the entire NG value chain, the development of an affordable, reliable, and quick analytical method for the composition analysis of NG-H₂ blends would be highly beneficial [165,166]. Currently, GC is the gold standard method for performing accurate composition analysis of complex NG mixtures with low detection limits [68,69,167,168]. For the analysis of hydrogen-enriched natural gas (HENG) samples, GC is equipped with a thermal conductivity detector, and helium is commonly used as the carrier gas in the separation column instead of hydrogen, which is unsuitable for H₂ analysis [169,170]. Among spectroscopy methods suitable for detecting H₂, Raman spectroscopy has demonstrated strong capabilities for analyzing HENG composition [69]. Raman detects both *para*-H₂ and *ortho*-H₂ nuclear spin states of the H₂ molecule present in the mixture [171]. However, drawbacks from spectral artifacts and background induced by its fiber optic equipment, in addition to the need of more sensitive detectors to improve the detection limits, complicate the implementation of Raman spectroscopy for in-field applications.

To perform a reliable quantitative analysis of molecular H₂ using benchtop NMR, a brief overview of the quantum mechanical principles governing its behavior is provided. Hydrogen exists in two nuclear spin isomeric forms, *ortho*- and *para*-H₂ which differ in both in their rotational states and their nuclear spin states [172].

The wave function of a diatomic molecule can be written as a product of translational, rotational, vibrational, electronic, and nuclear spin wave functions [172]:

$$|\psi\rangle = |\psi\rangle_t |\psi\rangle_r |\psi\rangle_v |\psi\rangle_e |\psi\rangle_s \quad (5)$$

Because protons are fermions, the overall wave function $|\psi\rangle$ given in equation (5) must be antisymmetric with respect to exchanging them [172,173]. The translational $|\psi\rangle_t$, vibrational $|\psi\rangle_v$ and electronic $|\psi\rangle_e$ wave functions are unaffected by proton exchange, whilst the product $|\psi\rangle_r |\psi\rangle_s$ is antisymmetric [172]. The rotational wave function $|\psi\rangle_r$ is symmetric when the rotational quantum number (J) is even ($J = 0, 2, 4, \dots$), and antisymmetric when J is odd ($J = 1, 3, 5, \dots$) [172,173]. Consequently, rotational states with even J numbers must pair with an antisymmetric nuclear spin wave function $|\psi\rangle_s$, meaning that the two protons occupy the singlet spin state [172,173]. In contrast, rotational levels with odd J requires a symmetric spin wave function, corresponding to the three triplet spin states [172,173]. This symmetry constraint determines the spin states of the *ortho*- and *para*- H_2 to be expressed as follows:

$$|T_+\rangle = |\alpha\alpha\rangle, \quad (6)$$

$$|T_0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle), \quad (7)$$

$$|T_-\rangle = |\beta\beta\rangle, \quad (8)$$

$$|S\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle), \quad (9)$$

These four wave functions are grouped according to their angular momentum number [174]. The three symmetric nuclear spin functions constitute the triplet (nuclear spin $S = 1$) associated with *ortho*- H_2 while the antisymmetric spin function corresponds to the singlet state (nuclear spin $S = 0$) associated with *para*- H_2

[173,174]. Given that *para*-H₂ has a spin $S = 0$, it is non-detectable by NMR spectroscopy.

For the quantification of H₂, considering its spin isomeric composition, it is also necessary to understand the thermodynamical equilibrium between the triplet and singlet state which is governed by Boltzmann's distribution law [175]. According to this law, at temperature T , the fraction of the molecules (N_J) in the rotational level characterized by the rotational quantum number J with respect to the total number of molecules (N_o) is expressed as follows [172,175]:

$$N_J = N_o p_J \cdot e^{-E_J/kT} \quad (10)$$

where:

k is the Boltzmann's constant

$E_J = \frac{J(J+1)\hbar^2}{2I}$ corresponds to the energy of the rotational states

I is the moment of inertia of the H₂ molecule

and

$p_J = 2J + 1$ represents the degeneracy of the J -th state

Thus, the ratio of molecules number between the singlet und triplet states can be written as follows [175]:

$$\frac{[p-H_2]}{[o-H_2]} = \frac{\sum_{J=even} (2J+1) e^{-E_J/kT}}{\sum_{J=odd} 3(2J+1) e^{-E_J/kT}} \quad (11)$$

From the equation (11), it can be deduced that at high temperatures, $[p - H_2]/[o - H_2] = 1/3$. This *ortho/para* ratio is already reached at around room temperature and it indicates that molecular hydrogen is composed of 1/4 *para*-H₂

and 3/4 *ortho*-H₂ [175]. At lower temperature the ratio $[p - \text{H}_2]/[o - \text{H}_2]$ changes [175,176]. For instance, at liquid nitrogen temperature proportions of 50% for both isomers are reached [176]. At lower temperatures, below 20 K, and in thermal equilibrium, pure *para*-H₂ can be obtained, as depicted in Figure 4.4 [175,177].

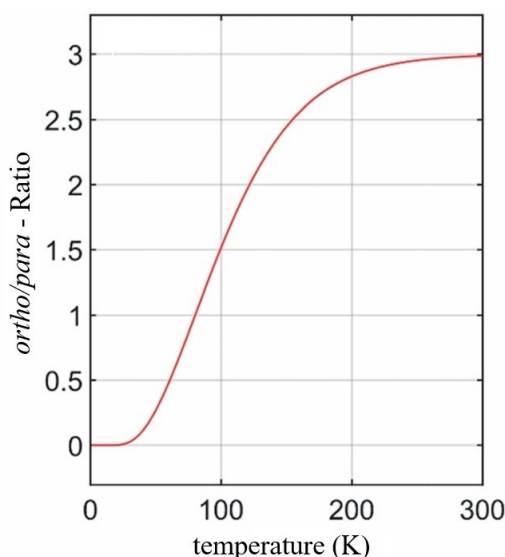


Figure 4.4: Ratio of orthohydrogen and parahydrogen as a function of the temperature. Adapted from ref. [177].

Pressure studies of molecular H₂ in gas phase up to 13 GPa, show no evidence of changes in the equilibrium *ortho/para* ratio [178]. This observation confirms the distribution given by Boltzmann law where mainly the temperature determines the equilibrium of the *ortho/para* ratio. Owing to the pressure range up to 120 bar used in this work, no changes are expected in the *ortho/para* ratio of the analyzed samples due to this external parameter.

As the *para*-H₂ has a nuclear spin $S = 0$, then just the *ortho*-H₂ which has a nuclear spin $S = 1$ is detectable with NMR [171,179]. Therefore, to calculate the molecular hydrogen content using the area of the spectra recorded with NMR, the value needs to be corrected by multiplying it by 4/3 [178]. This correction factor was also used in this work.

To assess the feasibility of the HP NMR set-up modified with the new flow-cell for the investigation of mixtures of natural gas with hydrogen, a further long-term test was performed on a NG-H₂ blend. This mixture was prepared manually using the HP setup by mixing methane, ethane and hydrogen. Once prepared, the mixture was pressurized at 200 bar and the proton NMR spectra was recorded at 60 MHz. Here, 860 single-scan ¹H NMR spectra were recorded over 36 hours. During these experiments, the static magnetic field remains stable during the whole measuring time. At the same time, the FWHM and the peak width at 10% peak height of methane remain largely constant. Although some minimal distortions can be seen, the overall performance could be maintained with periodic shims. The sample composition was tracked for each scan by simple signal integration (integral [a.u.]) of the detected proton signals of the three gaseous components given their good spectral separation. This was in turn used to compute the molar concentration (mol [%]) of each species (Figure 4.5). In the case of this experiment, a progressive change in the molar concentrations in the sensitive volume could be detected over the measuring time, most notably a decrease of the H₂ concentration accompanied by a change in the methane-ethane ratio. A change in the molar ratio of hydrocarbons over time inside a mixture was observed only for this sample but not for any other samples investigated during this PhD work. Given that the entire setup, including the PEEK assembly, was continuously monitored for leaks using a high-sensitive H₂ detector (Agilent Technologies G3388A) before and during all the experiments presented in this chapter, this change couldn't be attributed to gas losses. In addition, after releasing the inert gas in the chamber of the piston cylinder and pressurizing it again, the initial species composition was recovered as indicated in the Figure 4.5. Thus, the observed changes in the composition can most likely be attributed to technical issues.

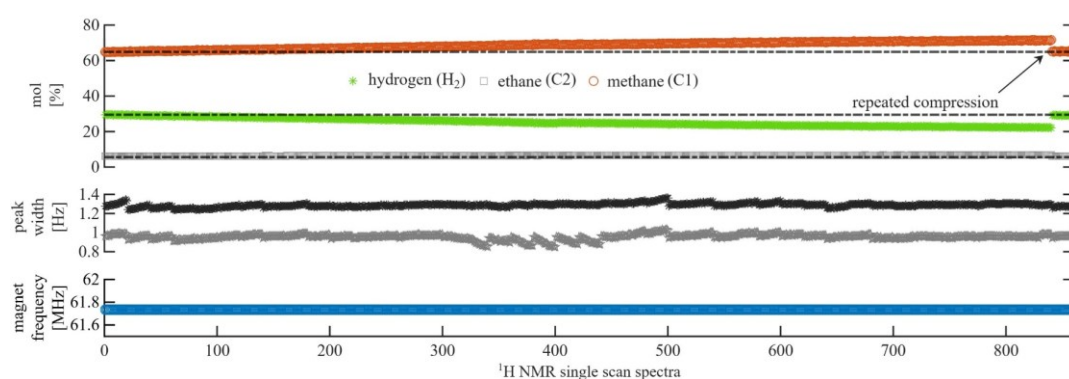


Figure 4.5: Long-term behavior of a 3-components gaseous mixture containing methane, ethane, and hydrogen pressurized at 200 bar and recorded with the 60 MHz spectrometer and the new HP flow-cell. The determined composition took into account the correction factor due to the presence of *para*-H₂. The stability of the instrument could be confirmed by the static magnetic field presented in terms of frequency versus the measuring time. In average, the linewidths at 50% and at 10% could be successfully maintained by the shim on the methane signal done every 20 scans. Adapted from ref. [151].

To further demonstrate the applicability of the new flow-cell, its performance on the quantitative composition analysis of NG-H₂ blends with commercially relevant compositions (Figure 4.6) was tested. The blends whose proton spectra depicted in Figure 4.5 were prepared by adding H₂ to a certificated 3-components sample containing 95 mol%, 3 mol%, and 2 mol% of methane, ethane, and propane, respectively. As depicted in Figure 4.6, H₂ possesses a well separated peak at a chemical shift of around 4.3 ppm. Moreover, it was observed that the ethane peak is at a chemical shift where propane has a negligible signal contribution (Figure A4 in the Appendix). This good peak separation, enabled for the first time the quantitative composition analysis of ternary NG mixtures containing CH₄, C₂H₆ and C₃H₈ by simple integration of the corresponding ¹H low-field NMR spectrum, which until now was just possible by advanced chemometric methods as demonstrated in chapter 3. Thus, the quantitative analysis of the recorded spectra could be done by a

straightforward signal integration. Changes in concentration were reflected in the various peak integrals as expected, however neither changes in peak position nor peak width could be detected for any of the main peaks of the different components in the mixture. Thus, the same integration limits could be used for the whole concentrations range.

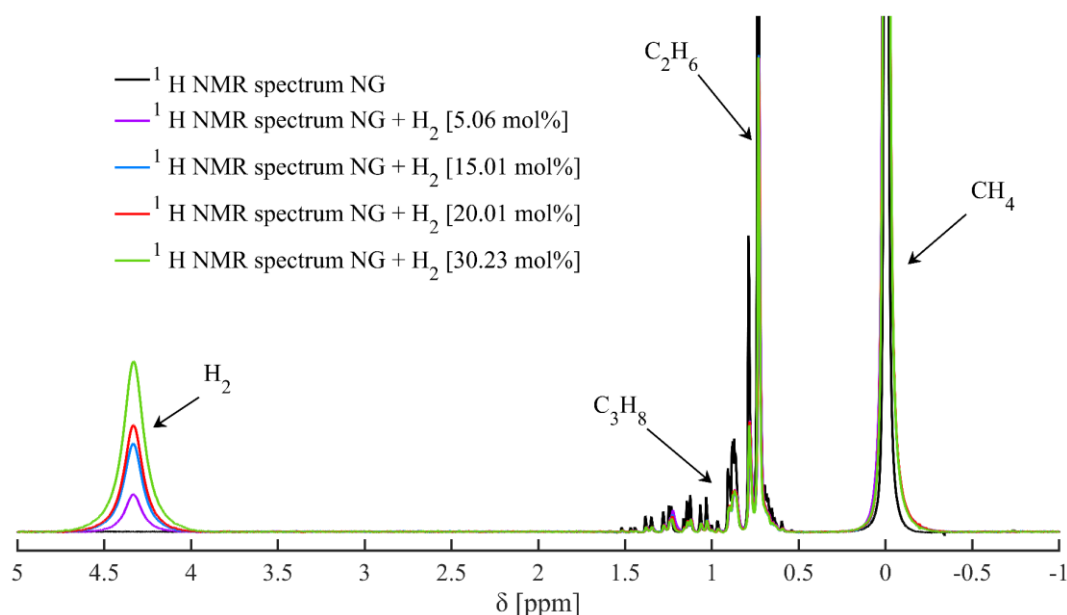


Figure 4.6: ^1H low-field NMR spectra of NG- H_2 mixtures were recorded at industrial relevant concentrations. Each spectrum was recorded with 16 scans and using 2 minutes repetition time. The magnetic field was then shimmed on the sample before recording the spectra. Adapted from ref. [151].

During the sample preparation, low partial pressures were used to mix H_2 with the certificate NG mixture at room temperature [88], reaching a maximum total pressure of 43 bar for these mixtures. As depicted in Figure 4.7a, simulations with the software NeqSim confirmed that this low-pressure regime at room temperature keeps the compressibility factor of the involved gaseous samples very close to the unity, which allows the assumption of an ideal gas behavior under these mixing conditions. These observations are confirmed by the experimental compressibility factors (Z) reported in reference [180]. Due to the high methane content in the NG sample, its compressibility factor was compared with the reported values for

methane in the literature. Figure 4.7 shows the linear correlation between the molar concentration determined with NMR and the composition derived from the partial pressure approach, confirming the agreement between both methods.

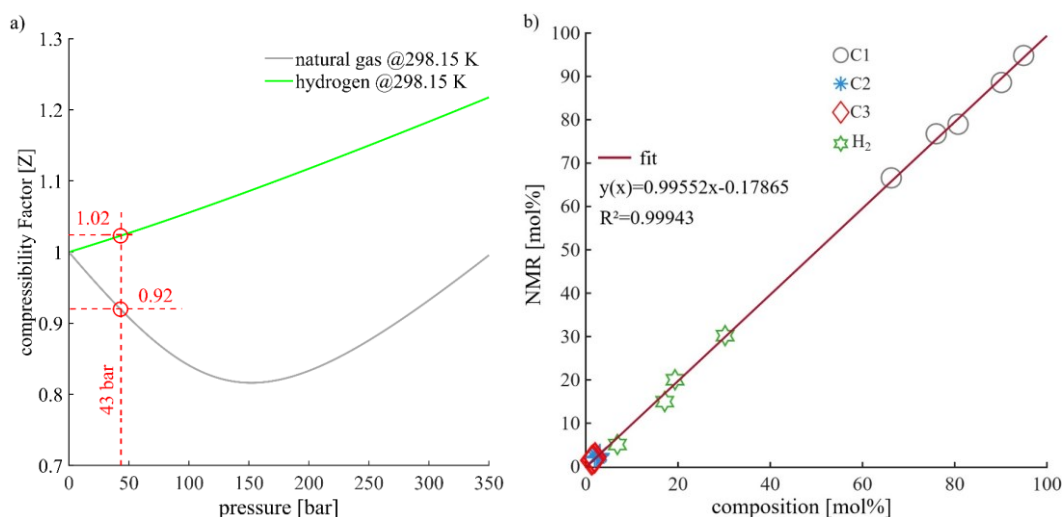


Figure 4.7: Quantitative composition analysis of NG-H₂ blends: a) Compressibility of the 3-components NG sample containing methane (95 mol%), ethane (3 mol%), and propane (2 mol%) and of pure hydrogen determined with the software Non-Equilibrium-Simulator (NeqSim version 2.5.5) for MATLAB at room temperature (298.15 K). The maximum mixing pressure of 43 bar during the sample preparation for both samples is marked with a red dashed line. b) Linear fit of the quantitative composition analysis of the NG-H₂ blends using the NMR spectra depicted in Figure 4.6 for comparison with the calculated composition. The depicted composition in b) took into account the correction factor due to the presence of *para*-H₂.

The results presented in this sub-chapter demonstrate the feasibility achieved with the new flow-cell to perform the quantitative composition analysis of the NG mixed with H₂. Although these results were obtained in a stop-flow manner, the new flow-cell enables further developments toward measurements in an automated manner. Moreover, in applications where analytes are present at very low concentrations in the matrix sample, long-term data acquisition could be beneficial for enhancing the SNR by following the approach proposed in chapter 3.

4.5 Quantification of ^1H NMR-Active and Non-Active NMR Species in NG via ^1H NMR Spectroscopy

Before being processed, typical components found in natural gas include methane, other light hydrocarbons such as ethane, propane, and butane, heavy hydrocarbons, water (H_2O), carbon dioxide (CO_2), hydrogen sulfide, helium, argon (Ar) and nitrogen (N_2) [96,181]. The mixture of these different species determines the energy content, safety, and usability of natural gas. Methane, being the primary component, provides most of the combustible energy. Light hydrocarbons like ethane and propane are valuable as feedstock for petrochemical industries. On the other hand, impurities like CO_2 and H_2S must be removed due to their corrosive properties and potential to form harmful byproducts during combustion. Helium, argon and nitrogen, being inert gases, are generally non-combustible but can affect the calorific value of natural gas [96,181]. Moreover, in alternative fuel gases such as biogas, which primarily consists of 60–70% methane, CO_2 is typically present in amounts ranging from 30–40%, along with smaller quantities of other gases such as nitrogen [182]. Thus, to meet market quality requirements, fuel gases such as NG and biogas are processed to maximize energy content, ensure safety, and maintain infrastructure reliability, making the determination of their composition necessary throughout various treatment processes [181,182]. In the previous chapter of this thesis, an improved method was proposed for quantifying the relative concentrations of HC components in pressurized natural gas mixtures using low-field ^1H NMR spectroscopy. The quantified species were hydrogen-bearing hydrocarbons, which can be detected during the ^1H NMR experiment. In this sub-chapter, an approach is proposed to quantify the amount of non- ^1H NMR-active species such as CO_2 , N_2 and Ar . First, the relative concentrations of the ^1H NMR-active components are determined using a newly IHM model. This IHM was generated by applying the

method proposed in chapter 3 to quantify the species of NG samples considering the ^1H NMR spectra recorded at 160 bar and 200 bar and further refined with the spectral improvements achieved using the new flow-cell design. The obtained results are then used in a calibration process to match the molar densities, as determined by equations of state (EOS) during the optimization process integrated in MATLAB and to finally predict the concentrations of the non-active species present in the mixture.

4.5.1. ^1H NMR Spectra of Pure NG Components at 120 bar

In this sub-chapter the proposed method introduced in chapter 3 was implemented to record high quality ^1H NMR spectra of pure HC components pressurized at 120 bar using the new flow-cell design as this pressure level is expected in various applications. As previously proposed, methane was measured as a pure component, while all higher-order HCs which were diluted in argon were measured in the presence of methane as ternary mixtures. To produce these ternary mixtures, the approximate pressure ratios as shown in Table A1 were used. Although the lower pressure used to record the spectra resulted in reduced molecular density within the sensitive volume, the improved spectral resolution achieved with the new flow-cell design allowed the IHM model to perform well in spectral recognition even with a low number of scans. Additionally, when analyzing spectra with a higher number of scans, the accuracy further improved due to the enhanced SNR for higher-order hydrocarbons.

The QC parameters discussed in subchapter 3.4.2 were implemented also here as the main criteria for selecting high-quality spectra to generate the multi-scan spectra used for building hard models. Like chapter 3, for the spectrum selection

with the algorithm integrated into MATLAB, a 10% tolerance was included for the linewidth at 50% and 10% signal height. Since no leaks were detected, the integral magnitudes remained stable without significant deviations from their mean values. Although a 10% tolerance was applied, this parameter did not trigger any spectrum selection, as it demonstrated greater stability compared to the other quality control parameters, as shown in Figure 4.8. For the symmetry condition the selection criteria was set such that $\Delta_{signal} > \Delta_{10\%} > \Delta_{50\%}$. Similar to sub-chapter 3.31: a) the limits for the integral QC parameter were set between -0.5 ppm and 1.8 ppm. b) For the peak width QC parameters, the selection criteria were established based on minimum and maximum thresholds, considering the mean average values of the linewidths at 10% height and at 50% height. After averaging the various sets of recorded spectra, it was determined that the mean linewidths of the recorded spectra under thermal steady conditions and with reproducible quality were $0.94 \text{ Hz} \pm 0.12$ at 10% height and $0.61 \text{ Hz} \pm 0.08$ at 50% height. An example of the QC selection process, considering the criteria defined above, is shown in Figure 4.8 for sample no. 2 (Table A2 in the Appendix).

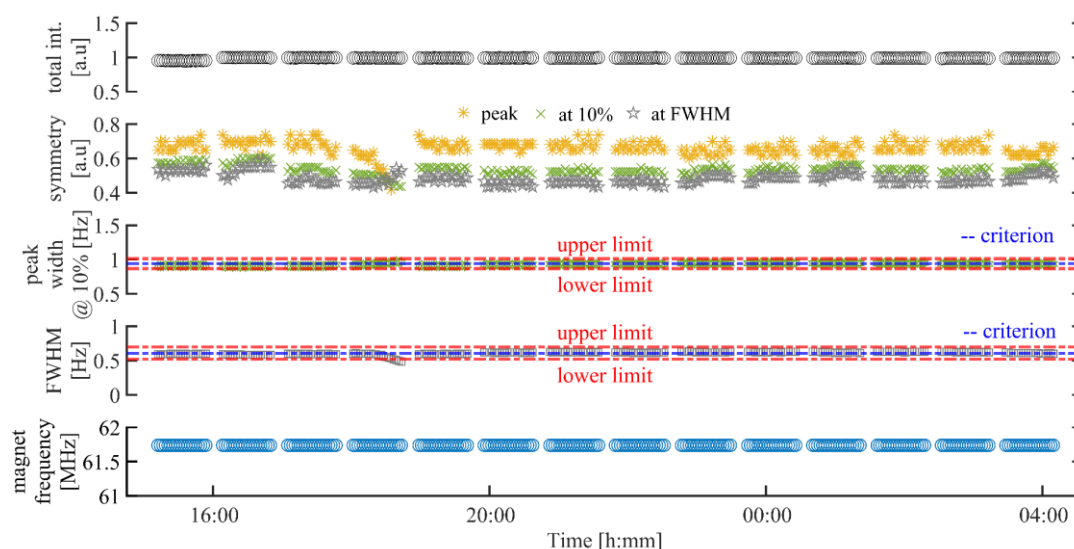
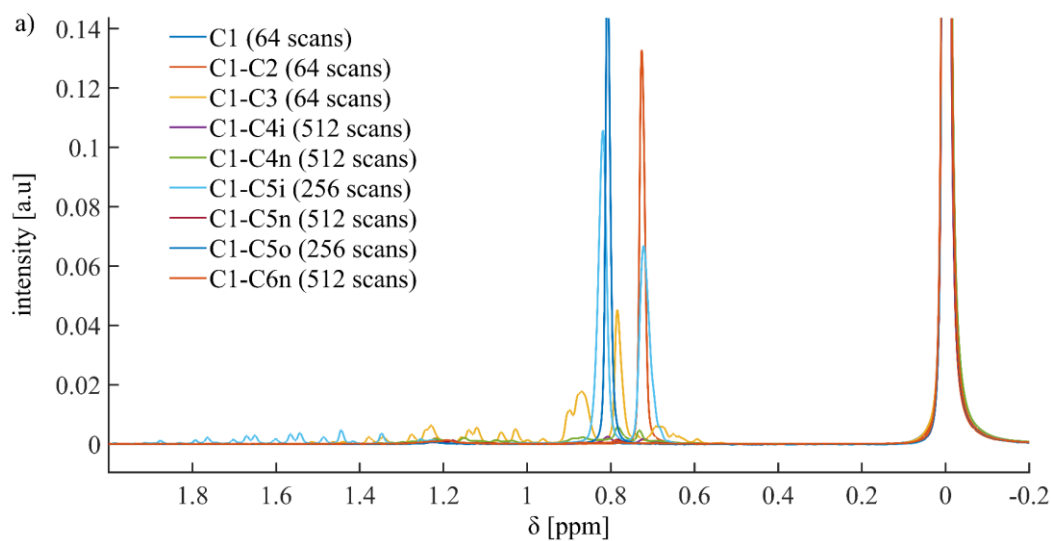


Figure 4.8: Values of the QC parameters determined from single-scan spectra acquired over several hours of measuring time with exemplification on sample 2

from Table A2. Appendix. The empty spaces in between the data represent the shim periods.

This approach has facilitated the generation of a final multi-scan spectra with improved SNR, compensating for the higher noise levels due to the reduced sample volume in the sensitive region of the 3rd design compared to previous designs. Figure 4.9 presents the final spectra of various individual HC components recorded at 120 bar along with the total number of single scans considered for each final spectrum. Well-defined peaks can be observed among the various species and even small peaks of species typically found at very low concentrations are visible to the naked eye. A significant consequence of the linewidth reduction was an increase in the number of detectable signals for higher-order HCs.



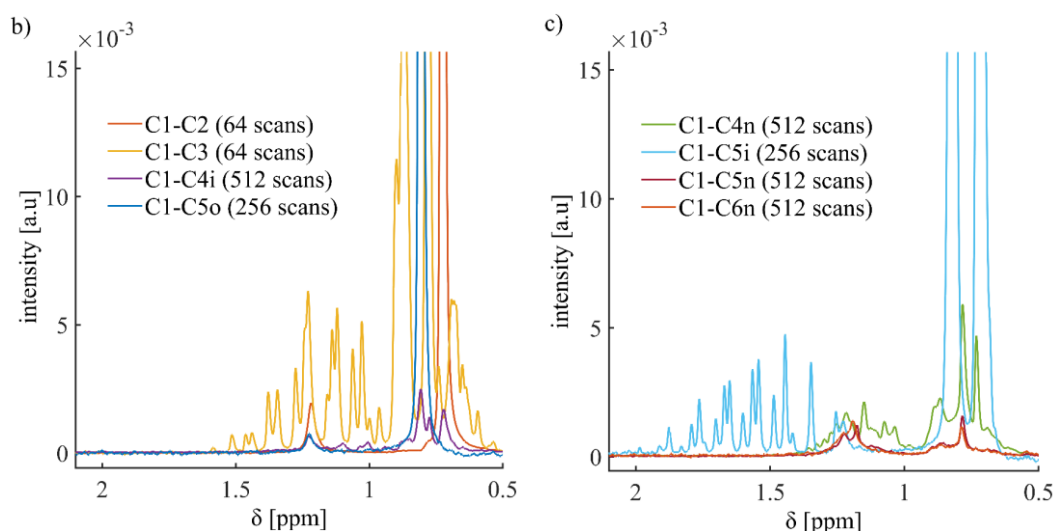


Figure 4.9: High-quality multi-scan ^1H NMR spectra of: a) individual HC components recorded at 120 bar with the PEEK low-cell. b), c) zoomed view between -0.5 ppm and 2.1 ppm of the 8 different higher order HCs. For better readability, the spectra are presented in two groups.

4.5.2. IHM at 120 bar

The proton spectra depicted in Figure 4.9 allowed for the creation of the corresponding hard models for each individual HC component. Several Pseudo-Voigt functions, were fitted to the spectrum of each HC. Figure 4.10 illustrates the application of the IHM fit on sample no. 6, as listed in Table A2 in Appendix. Unlike the IHM procedure proposed in chapter 3, where the area of the methane signal was calculated by subtracting the IHM areas from the total integral of the entire frequency domain of the obtained NMR spectra, the methane signal in this analysis was determined using its own dedicated hard model. This approach avoids the accumulation of mismatches that occurred when subtracting the summed areas of all IHM-fitted C2-C6n components from the total frequency domain. The result from Figure 4.10 shows how the four species present in this sample are fitted by the corresponding models for each component. One can clearly observe that despite the

strong signal superposition of the higher HCs, the IHM fit is able to accurately model the experimental data. With the dramatic improvement in spectral resolution, the species recognition through the IHM on the recorded spectra is expected to reduce the mismatches between the model and the recorded spectra, thereby enhancing the method's reliability.

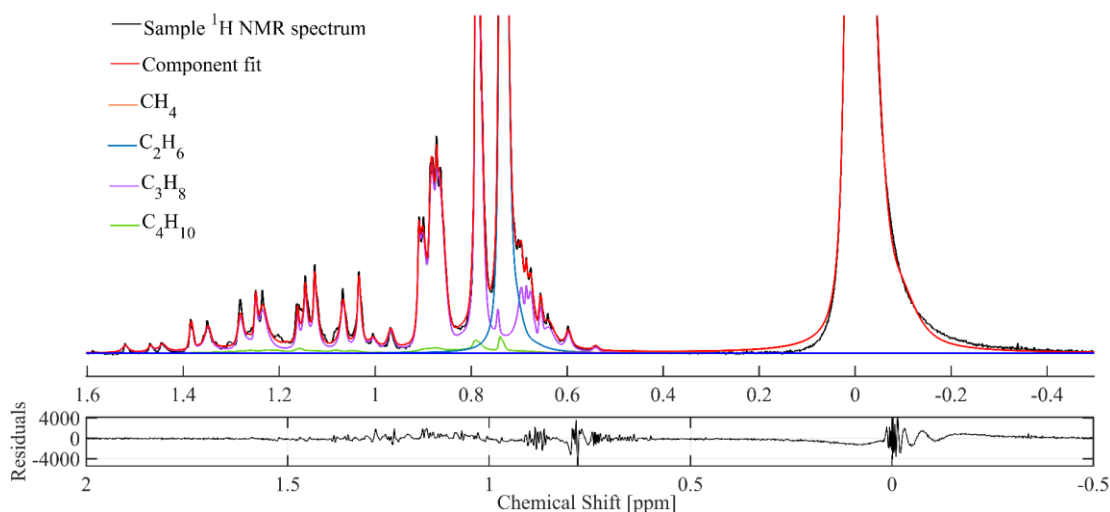
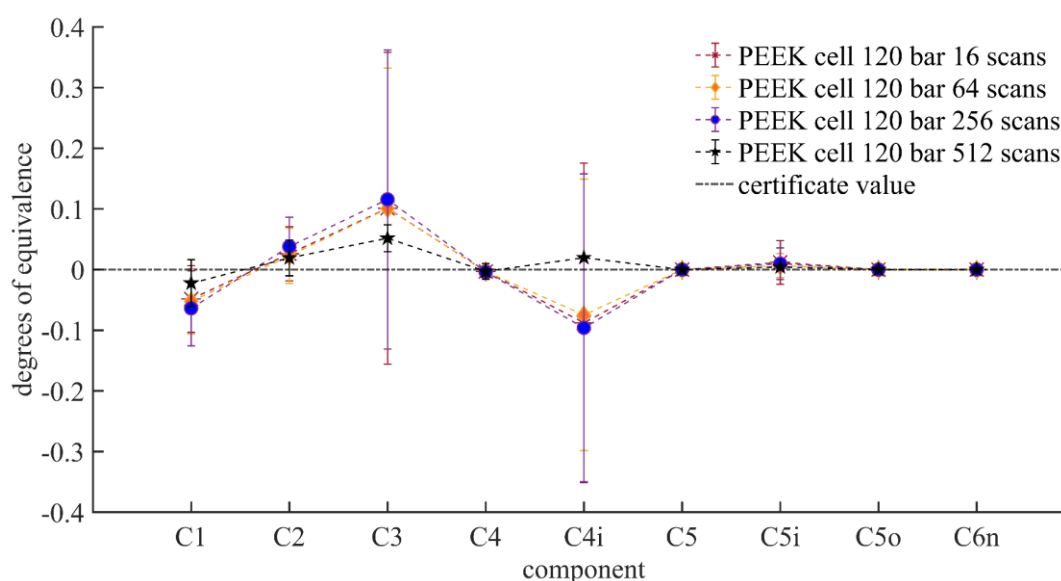


Figure 4.10: IHM fit on the experimental ^1H NMR spectra of a 4-components HC mixture (sample no. 6 in Table A2Appendix) recorded at 120 bar.

To assess the performance of this new IHM, the first seven samples from Table A2 were analyzed by acquiring high-quality single-scan spectra sets which then led to multi-scan spectra containing 16, 64, 256, and 512 scans for each sample recorded at 120 bar. The results of this analysis are illustrated in Figure 4.11, using the same degrees of equivalence method as in chapter 3 to compare the agreement between the vendor certificates and the IHM results. Here it can be observed that, for all components, the predicted results of the samples analyzed exhibit a disparity of less than 0.1 mol%, regardless of the number of scans.

These findings confirm the observations made in chapter 3. The consistent selection of high-quality spectra with reproducible peak shapes at 120 bar enabled the generation of multi-scan spectra with high SNR and well-defined resolution.

These spectra were used to build HMs for individual components, which, when combined into an IHM, allowed for accurate fitting of multi-scan spectra from pressurized samples recorded under identical conditions. The homogeneously selected peak shape quality of the spectra (both for the pure component spectra used to build the IHM and for the recorded spectra of the analyzed samples) enabled the optimization of the IHM fitting process. This was achieved by reducing the number of parameters the algorithm needed to account for during the fitting, thereby improving the accuracy of the compositional analysis. Thus, it can be observed that with just 16 scans was sufficient to achieve highly accurate results, despite the much smaller inner diameter of the flow-cell as compared with the sapphire-based HP tubes and the lower measuring pressure. Interestingly, increasing the number of scans did not significantly improve the agreement with the GC data or the vendor certificates, which is contrary to initial expectations, as also indicated in the referenced study [139]. To better illustrate the improvements in accuracy achieved with the flow-through cell (3rd design), Figure 4.11 also presents the results obtained in chapter 3 using the IHM developed with the 2nd design. It is important to note that the results shown for the sapphire tube at 200 bar, which include 512 scans, correspond to the 15 measured samples listed in Table A2 and Table A3.



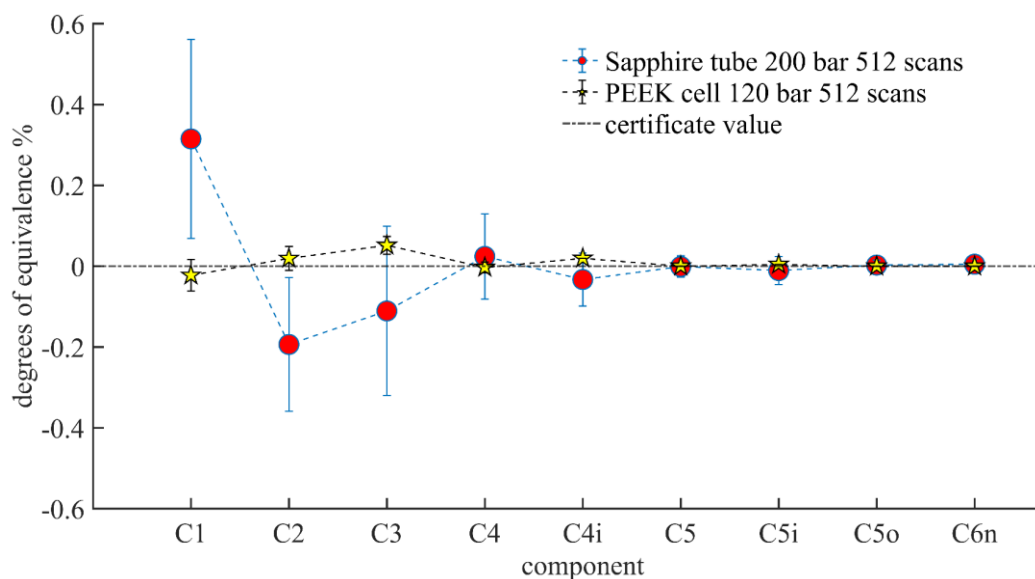


Figure 4.11: Degrees of equivalence between the quantification of ^1H NMR-active HCs via IHM results and the vendor certificates for: a) the first 7 samples listed in Table A2, based on high-quality spectra recorded at 120 bar using the flow-through cell with 16, 64, 256, and 512 scans. b) The sapphire tube results correspond to the 15 measured mixtures (Tables A2 and A3Appendix) recorded at 200 bar with 512 scans.

4.5.3. Quantification of non-active ^1H NMR Species Present in the NG Samples

Building on the IHM developed at 120 bar in sub-chapter 4.5.2, we now extend our analysis to components that are not directly detectable by ^1H NMR spectroscopy. In this sub-chapter, a novel method is proposed that combines the absolute areas of NMR signals for each species, the relative concentrations derived from IHM, and equations of state (EOS). This approach offers a comprehensive solution for analyzing complex gas mixtures under in-situ conditions, while accounting for the behavior of real gas mixtures. This method is based on the following key assumptions and considerations:

We consider first the case of molecules which are proton NMR active. During the NMR measurements, the NMR cell ensures a constant volume of sample to be measured in the sensitive region. The recorded NMR integral of a single, particular HC_i species inside a mixture, obtained in arbitrary units (a.u.), is proportional to its concentration (C_i) within this mixture at a given total pressure (P) and temperature (T). Moreover, within the sensitive volume, the molar density of each component is proportional with the corresponding number of molecules in the sample. Thus, the molar density of a HC_i component is proportional to its absolute NMR signal integral divided by the number of protons contributing to the signal. In the case of the mixtures studied here, the absolute integrals are extracted from the IHM model. Thus, assuming the use of the same tube for all measured NMR data, the molar density of a particular HC_i species can be expressed as being proportional to the extracted IHM integral as follows:

$$\rho_i \propto \frac{HC_{IHM,i}}{N_{p,i}} \quad (12)$$

Where:

ρ_i molar density of a particular HC_i species in the sample

$N_{p,i}$ number of protons of the particular HC_i species contributing to the corresponding NMR signal in the sample

$HC_{IHM,i}$ IHM absolute integral (area) of a particular HC_i species in the sample

The molar density in equation (12) considers exclusively the NMR signal of a ^1H NMR active component (HC) in the sample. But many NG samples contain both HC and non-hydrocarbon (non-HC) components, with the last ones giving no signal in ^1H NMR. Thus, for the purpose of the proposed method, the relative HC

concentrations of the species in the NG sample are represented by the vector **HC** as follows:

$$\mathbf{HC} = \begin{bmatrix} HC_1 \\ HC_2 \\ HC_3 \\ \vdots \\ \vdots \\ HC_n \end{bmatrix}, \quad \text{with } \sum_i HC_i = 1 \quad (13)$$

where HC_i represents the relative concentration of i -th hydrocarbon species in the **HC** vector, such that the sum over all HC_i equals 1.

To represent the full composition of the NG sample, including the non-HCs such as Ar, N₂ and CO₂, a new composite vector **NG** is formed as follows:

$$\mathbf{NG} = \begin{bmatrix} \mathbf{HC} \cdot X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix}, \quad \text{with } \mathbf{HC} \cdot X_1 + \sum_k X_k = 1 \quad (14)$$

The **HC** vector is scaled by X_1 , which represents the relative concentration of HCs in the gas NG mixture. The relative concentration of the individual non-HC components in the NG mixture are represented separately by X_k , where k denotes the species in the **NG** vector, for example, X_2 for N₂, X_3 for Ar and X_4 for CO₂. The sum of all relative concentrations in the overall **NG** composition vector equals 1.

Considering real gas behavior, the molar density expressed in equation 15 is determined using the Redlich-Kwong EOS [183] as implemented in the NeqSim simulation library [184]. This approach allows accurate estimation of the compressibility factor accounting for the composition of the vector **NG** described equation 14, at a given pressure and temperature.

$$\rho_n = \frac{n}{V} = \frac{P}{R \cdot T \cdot Z} \quad (15)$$

where:

n number of moles

V volume [m^3]

P total pressure of the mixture [bar]

R universal gas constant [$J \cdot K^{-1} \cdot mol^{-1}$]

T temperature [K]

Z is compressibility of the mixture with the known composition

Using NeqSim calculations, molar densities of each HC_j species in vector **NG** are determined and are translated to derived IHM component areas ($HC_{IHM,i}$) for each HC_i species in vector **HC**, through a calibration factor, F , as depicted in the following expression:

$$\rho_i = F \cdot \frac{HC_{IHM,i}}{N_{p,i}} = \frac{HC_j \cdot P}{R \cdot T \cdot Z} \quad (16)$$

where:

F calibration factor

HC_j relative composition of each HC_j of j -th constituent within the vector **NG**.

To determine the calibration factor F , a set of samples with known composition is required to correlate the NMR signals with the NeqSim results

according to equation 16. Figure 4.12 shows a linear calibration curve to obtain the factor $F=9.422 \times 10^5$ with a correlation coefficient $R^2 = 0.9999$ between the derived IHM component areas and the molar densities used in NeqSim calculations. It is important to note that the calibration process to obtain F is currently based on a limited data set that just includes the samples 1-7 in Table A2 and the three samples containing CO_2 in the Table A5 in the appendix. It is important to mention that the reliability of the calibration factor F is expected to improve with a larger number of measurements covering the full range of pressure, temperature and composition for samples with unknown composition to be measured. The calibration of the 7 samples depicted in Figure 4.12 were conducted at 120 bar and at room temperature. A small calibration set of samples could lead to false composition predictions, when a tested sample of unknown concentration is measured at different pressure, temperature or compositions from those used for the considered set of calibration samples.

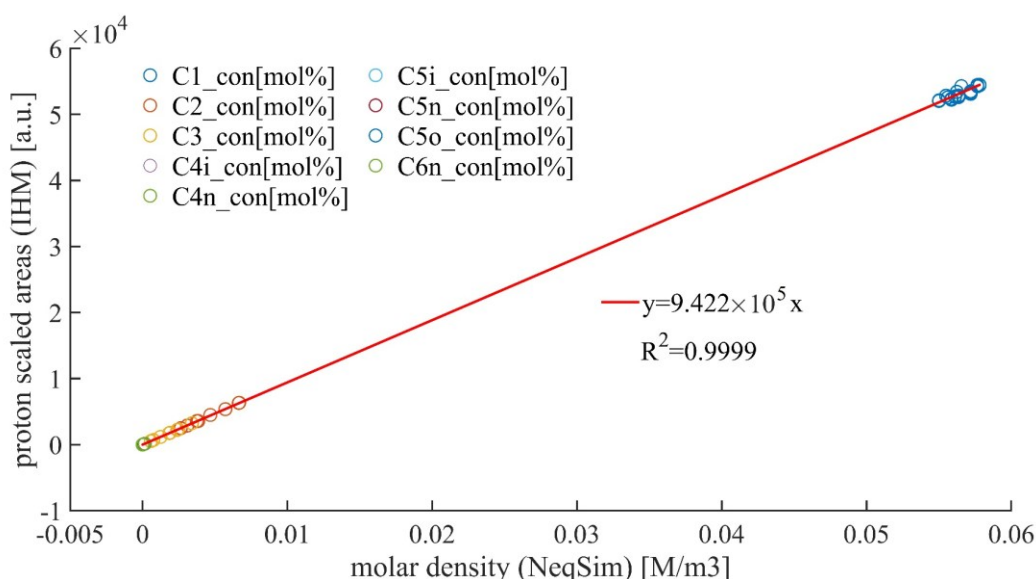


Figure 4.12: Initial calibration of absolute NMR area (IHM results of the HCs in the first 7 samples listed in Table A2 and the three samples listed in Table A5 in the appendix) and molar densities at 120 bar pressure. Here the calculated F factor corresponds to $F=9.422 \times 10^5$.

When measuring the samples of unknown concentration, to obtain the constituent concentrations X_k of the NG mixture, the differences between the determined proton scaled absolute NMR areas of the different HC_i components via IHM in the mixture (=areas) $= HC_{scl,i} = \frac{HC_{IHM,i}}{N_{p,i}}$ already introduced in equation 12 and modeled areas of the same $HC_{mod,j} = \rho_{n,j}/F$ components in the vector $\mathbf{NG}$ calculated according to equation 16 are minimized in an iterative manner by adjusting all constituent concentrations X_k of the mixture (inverse modeling). Herein, $HC_{mod,j}$ are functions of the components' respective molar density derived by solving the EOS for Z . This iterative process is integrated into MATLAB using NeqSim to update the EOS during the optimization process.

For a clearer understanding of the proposed method, Figure 4.13 presents the flow diagram of the methodology implemented in MATLAB for predicting the concentration of the non-HC NMR species. At the beginning, a set of samples with known concentrations (calibration samples) are measured under well-defined pressure and temperature conditions (here, 120 bar and 26.5 °C). The absolute proton-scaled areas $HC_{scl,i}$ corresponding to the various HC_i components inside a mixture are determined by IHM. Then, the calibration factor F is determined by a linear regression. This is done by correlating the proton-scaled NMR areas, obtained from the IHM results, with their corresponding molar densities using NeqSim, taking into account real gas behavior and including non-HC components in the concentration calculations. In the next step for checking the quality of the approach, test samples are considered. Here, the same set of samples as for calibration purposes is considered. For these samples, in addition to the absolute proton-scaled NMR areas, also the relative HCs concentrations are determined using the IHM results. Additionally, the sample's pressure and its room temperature are taken into account for the EOS solutions using NeqSim. In the final phase, the inverse modeling method is applied iteratively to minimize the discrepancy between the proton-scaled areas

derived from the IHM integrals and the modeled areas, which are obtained from the calculated molar density scaled by the calibration factor F for hydrocarbons. Once the optimal difference is achieved or the maximum number of iterations is reached, the concentrations of all constituents in the modeled area are reported as calculated from EOS.

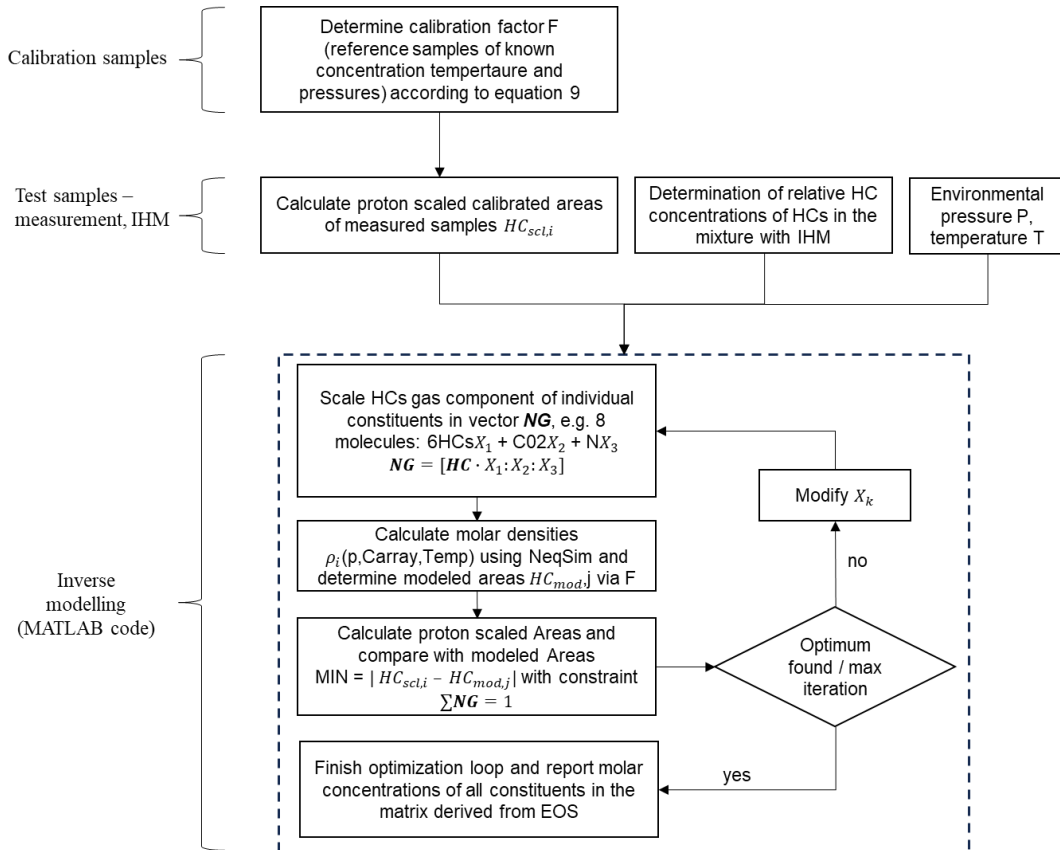


Figure 4.13: Inverse modelling optimization algorithm using NeqSim to update EOS implemented in MATLAB to predict the composition of non-active NMR species.

Initial results from this inverse modeling concept, using data from various single scan averages of the mentioned samples, are plotted in Figure 4.14. Although the matches still exhibit significant uncertainties, non-HC components (such as CO_2) were successfully identified and quantified within the investigated mixtures. Due to the calibration-based nature of this proposed method, additional analyses using

additional gases with varying concentrations of non-HC gases should be conducted to further evaluate this concept. This new proof-of-concept is expected to pave the way for broader applications of NMR within the energy sector and other fields.

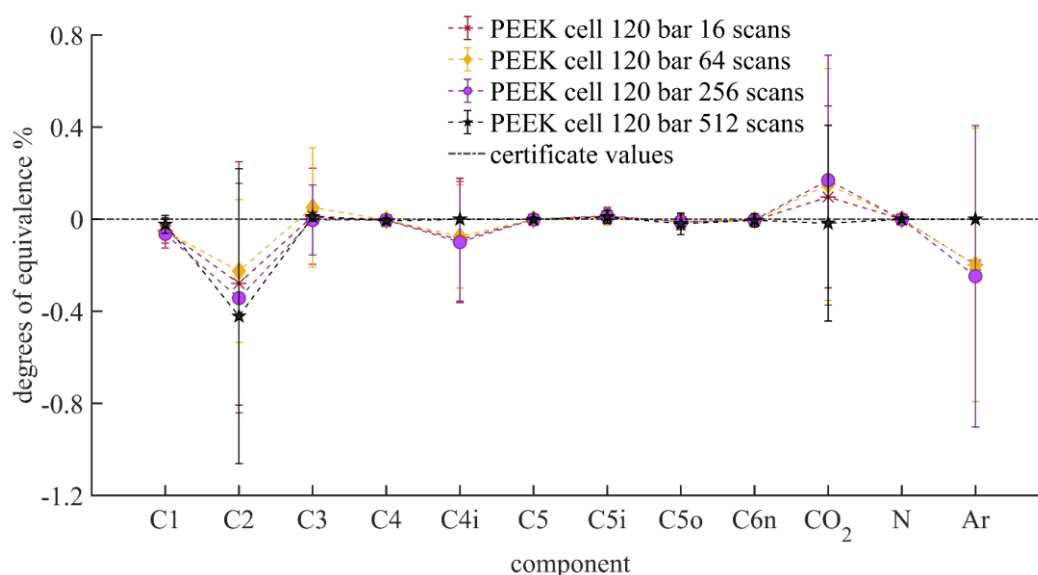


Figure 4.14: Degrees of equivalence between the proposed inverse modeling concept results and the vendor certificates for the quantitative analysis of the HCs in the first 7 samples listed in Table A2 and the three samples listed in Table A5 in the appendix, based on high-quality spectra recorded at 120 bar using the flow-through vessel design with 16, 64, 256, and 512 scans.

Chapter 5

Summary and Perspectives

This thesis started presenting the development of an improved methodology to enhance the accuracy and reproducibility of quantitative composition analysis of NG samples using high-pressure low-field proton NMR spectroscopy combined with IHM. This was made possible through various hardware and software advancements. Notably, the implementation of a new high-pressure sapphire tube design significantly improved the FWHM and the symmetry of all signals, allowing for better separation of the methane signal from other HCs. This facilitated the development of a higher quality 9-component IHM [40] as compared to the proposed IHM presented in reference [38]. Additionally, a comprehensive strategy including single-scan acquisition, periodic shimming, automatic selection of spectra based on QC parameters, and spectra alignment was implemented, resulting in the generation of ^1H NMR spectra of higher quality. The robustness of this methodology was thoroughly tested on up to 15 complex gaseous mixtures containing various HCs at typical industrial concentrations, recorded at pressures of 200 bar and 160 bar. The results showed excellent agreement with vendor certificates, with deviations not exceeding 0.5 mol%. Remarkably, the IHM developed at 200 bar was applicable to data recorded at 160 bar without the need for a new IHM model, offering a significant advantage over other chemometric methods like PLS. Furthermore, it was demonstrated that as few as 16 scans were sufficient to achieve highly accurate results, confirming the efficiency and potential of this approach for routine online composition analysis of complex gaseous mixtures under real conditions.

The capabilities of high-pressure low-field NMR spectroscopy were further expanded to include the composition analysis of NG in the presence of liquid contaminants, demonstrated for the first time in this work. Building upon the previously developed methodology, four new QC parameters were introduced to improve signal characterization based on the methane signal: linewidth at 10%, peak symmetry at 50% and 10% peak height, and signal symmetry derived from the slopes of the methane peak's flanks. These parameters were tested on ^1H NMR spectra of a three-component certified gaseous sample pressurized at 200 bar with TEG in the sensitive volume. The results demonstrated the feasibility of HP ^1H NMR spectroscopy to determine NG composition in the presence of aqueous TEG, leading to results in excellent agreement with the vendor certificate. Even under dynamic conditions, where a flowing aqueous TEG droplet caused spectral distortions, the QC parameters effectively were used to determine the quality of the recorded spectra. This work underscores the robustness of HP-NMR spectroscopy for analyzing gas mixtures in field applications where liquid contaminants might compromise the performance of traditional analytical methods.

In addition to gas mixtures, a low-cost and rapid methodology was proposed for quantifying low water content in glycols using benchtop ^1H low-field NMR spectroscopy. This approach, based on lineshape analysis, eliminates the critical dependence on integration limits and was validated on EG and TEG samples including low water concentrations. The results, which were in excellent agreement with Karl-Fisher titration, demonstrated the potential of this NMR-based method as a fast and environmentally friendly alternative. The methodology also offers the possibility for automation or online continuous flow analysis, enabling high-throughput monitoring of water content in glycols, with applications extending to other aqueous-based systems.

Additionally, this thesis presents the first composition analysis of HENG blends using high-pressure ^1H NMR spectroscopy. A novel flow-through cell design, capable of operating at pressures up to 245 bar, was introduced, utilizing commercially available PEEK HPLC components. This design is not only simple and inexpensive but also easily replicable, making it accessible to a wider range of scientists, including those outside the traditional NMR community. The flow-through cell demonstrated significant improvements in spectral quality and long-term stability when analyzing both NG and pure hydrogen. The experimentally determined compositions of HENG blends showed the agreement with theoretical predictions.

In the final part of this thesis, a proof-of-concept approach was introduced to quantify non- ^1H NMR-active species also present in real NG samples. This method begins with the calibration of the absolute NMR areas and molecular densities based on available samples. The relative composition of the HCs in the mixture is obtained from IHM and then scaled with a factor corresponding to the HCs constituents in an array that includes the other constituents of the sample which are non-NMR active. Subsequently, the calibrated NMR areas are matched against solutions of molar densities calculated via automatic equations of state (EOS) integrated into MATLAB, allowing for the prediction of non- ^1H NMR-active component concentrations. While this approach shows great promise, further investigations with a much larger set of samples are recommended to fully validate and establish the method's robustness and reliability.

These advancements represent a significant step toward fully automated, online composition analysis of complex natural gas (NG) samples typically found in in-field conditions and processing lines. This includes the analysis of NG in the presence of contaminants such as glycols from dehydration units, as well as hydrogen-enriched natural gas (HENG) blends, and the quantification of non- ^1H

NMR-active species. Understanding the composition and temporary changes in these complex mixtures is critical for ensuring the safety of infrastructure and optimizing decision-making processes across the natural gas network. The initial stages of automated data acquisition and analysis have already been implemented. These findings not only advance the field of NG composition analysis but also hold potential for other industrial applications, such as catalyst research for pressurized chemical reactions, where real-time monitoring can significantly enhance efficiency and safety. The methodologies developed in this thesis have the potential to drive innovations across various fields. In particular, they can significantly enhance analytical chemistry applications, where precise and accurate compositional analyses of complex mixtures are essential. The use of low-cost, compact benchtop NMR devices makes these methods accessible for routine monitoring and material characterization in diverse laboratory settings. In process monitoring, especially within the energy sector, high-pressure NMR spectroscopy offers real-time insights into natural gas processing, improving both operational control and safety. Additionally, in the pharmaceutical industry, these methodologies could contribute to the reliability during characterization of drug compounds and impurities, accelerating drug development and ensuring stringent quality control. Overall, the advancements presented in this thesis open new avenues in NMR spectroscopy and broader analytical sciences, with the potential to impact multiple disciplines.

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Appendix A

Table A1: Mixing pressure ratios used to prepare the ternary samples for measuring the ^1H NMR spectrum of each individual HC component.

ternary sample (C3-C6 diluted in argon)	mixing pressure ratios (C1: HC sample) [bar]
methane (C1) + propane (C3)	1:1
methane (C1) + n-butane (C4n)	7:10
methane (C1) + iso-butane (C4i)	5:10
methane (C1) + n-pentane (C5n)	6:10
methane (C1) + iso-pentane (C5i)	5:10
methane (C1) + neo-pentane (C5o)	3:10
methane (C1) + n-hexane (C6n)	3:10

Table A2: Molar concentrations according to the delivery certificate of the 14 complex gaseous mixtures purchased from Linde.

Sample	Component [mol%]								
	C1	C2	C3	C4	C4i	C5n	C5i	CO ₂	Ar
No. 1	84.86 ^{a)}	10.1	5.04	--	--	--	--	--	--
	0.11 ^{b)}	0.101	0.05	--	--	--	--	--	--
No. 2	89.92	9.08	1.00	--	--	--	--	--	--
	0.09	0.09	0.02	--	--	--	--	--	--
No. 3	89.09	5.96	2.97	--	--	--	--	1.98	--
	0.08	0.06	0.06	--	--	--	--	0.04	--
No. 4	89.03	5.99	2.98	--	--	--	--	--	2.00
	0.08	0.06	0.06	--	--	--	--	--	0.04

No. 5	94.93	3.05	2.02	--	--	--	--	--	--
	0.07	0.06	0.04	--	--	--	--	--	--
No. 6	89.99	6.01	3.00	1.00	--	--	--	--	--
	0.09	0.06	0.06	0.02	--	--	--	--	--
No. 7	95.65	3.03	1.20	--	0.12	--	--	--	--
	0.07	0.06	0.02	--	0.00	--	--	--	--
No. 8	94.54	3.05	1.20	--	1.21	--	--	--	--
	0.07	0.06	0.02	--	0.02	--	--	--	--
No. 9	94.79	3.20	1.01	1.00	--	--	--	--	--
	0.07	0.06	0.02	0.02	--	--	--	--	--
No. 10	95.79	3.10	1.01	0.10	--	--	--	--	--
	0.07	0.06	0.02	0.00	--	--	--	--	--
No. 11	95.63	3.03	--	--	1.22	--	0.12	--	--
	0.07	0.06	--	--	0.02	--	0.00	--	--
No. 12	96.40	3.01	--	--	0.30	--	0.29	--	--
	0.06	0.06	--	--	0.01	--	0.01	--	--
No. 13	95.88	3.02	--	1.00	--	0.10	--	--	--
	0.06	0.06	--	0.02	--	0.00	--	--	--
No. 14	96.49	3.01	--	0.25	--	0.25	--	--	--
	0.06	0.06	--	0.01	--	0.00	--	--	--

^{a)}Nominal concentration on the certificate of analysis, ^{b)}Analytical uncertainty
(concentration error)

Table A3: Molar concentrations and analytical uncertainty of the 11D sample used in this work, supplied by Gassco AS (Haugesund, Norway), with concentration values certified according to DIN EN ISO 6141.

component inside 11D	HC content [mol%]
methane (C1)	88.62 ±0.08

ethane (C2)	4.04 ± 0.6
propane (C3)	0.99 ± 0.6
iso-butane (C4i)	0.20 ± 0.8
n-butane (C4)	0.20 ± 0.8
iso-pentane (C5i)	0.05 ± 0.8
n-pentane (C5n)	0.05 ± 0.8
neo-pentane (C5o)	0.05 ± 0.8
n-hexane (C6n)	0.04 ± 0.8
nitrogen	3.98 ± 0.5
carbon dioxide	1.50 ± 0.9

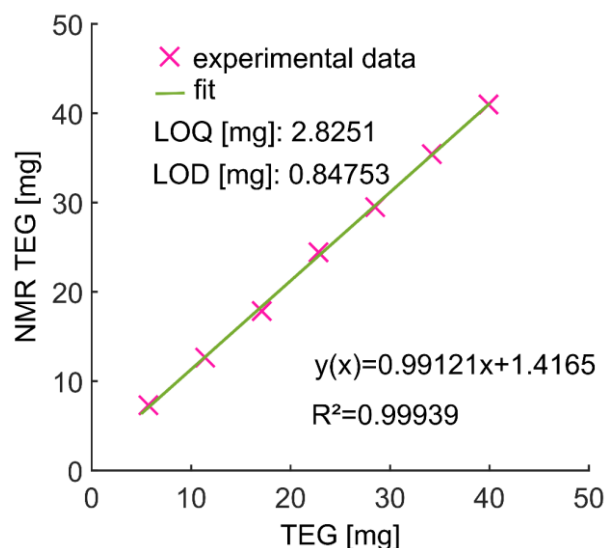


Figure A1: Experiment to determine the length of the sensitive volume of the 60 MHz spectrometer. In the figure is depicted the linear fit of the experimental data points obtained by controlling the TEG amount by displacing the sapphire tube vertically, as depicted in Figure 3.9a. By adding spacers, starting with TEG below the sensitive volume, a linear increase in integral intensity was observed over a total of 11 spacers, indicating a sensitive volume length of 5 mm. After spacer number 11, the integral intensity remained steady, signifying that the sensitive volume was completely filled with TEG.

Table A4: Experimental results of a TEG droplet with 22.5 wt.% water content running down in the second-generation HP sapphire tube containing a 3-component natural gas sample pressurized to 200 bar.

time (minute)	integral TEG (a.u.)	SNR TEG (a.u.)	droplet mass (mg)	SNR CH ₄ (a.u.)
0	4.65×10^{-5}	2.84×10^{-4}	0.03	6.58×10^3
2	3.30×10^{-3}	5.10×10^{-3}	2.62	2.30×10^3
4	5.00×10^{-3}	3.90×10^{-3}	3.94	1.56×10^3
6	3.70×10^{-3}	3.80×10^{-3}	2.90	3.30×10^3
8	3.40×10^{-3}	3.40×10^{-3}	2.67	3.83×10^3
10	2.90×10^{-3}	3.10×10^{-3}	2.28	4.03×10^3
12	0.00	0.00	0.00	6.91×10^3

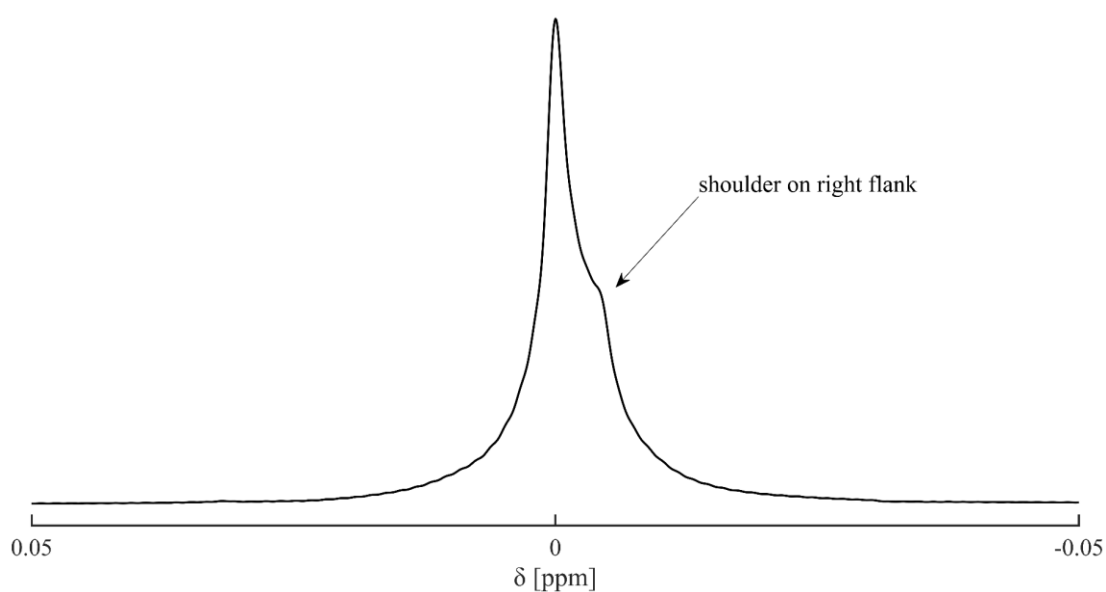


Figure A2: Deformed CH₄ peak of spectrum no. 40 depicted in Figure 3.13b, for the three-component gaseous mixture containing 85% methane, 10% ethane, and 5% propane, pressurized at 200 bar.

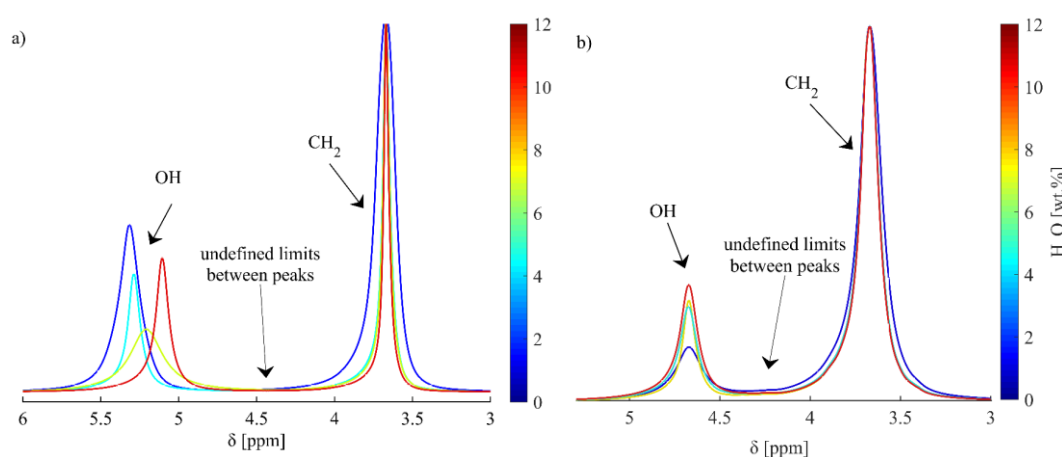


Figure A3: Illustration of the region between the OH+H₂O and CH₂ signals for (a) aqueous EG and (b) aqueous TEG at different water concentrations. One can observe that the two signals are not well separated such that a quantification of their integrals by simple signal integration will strongly depend on the chosen limits for the integration.

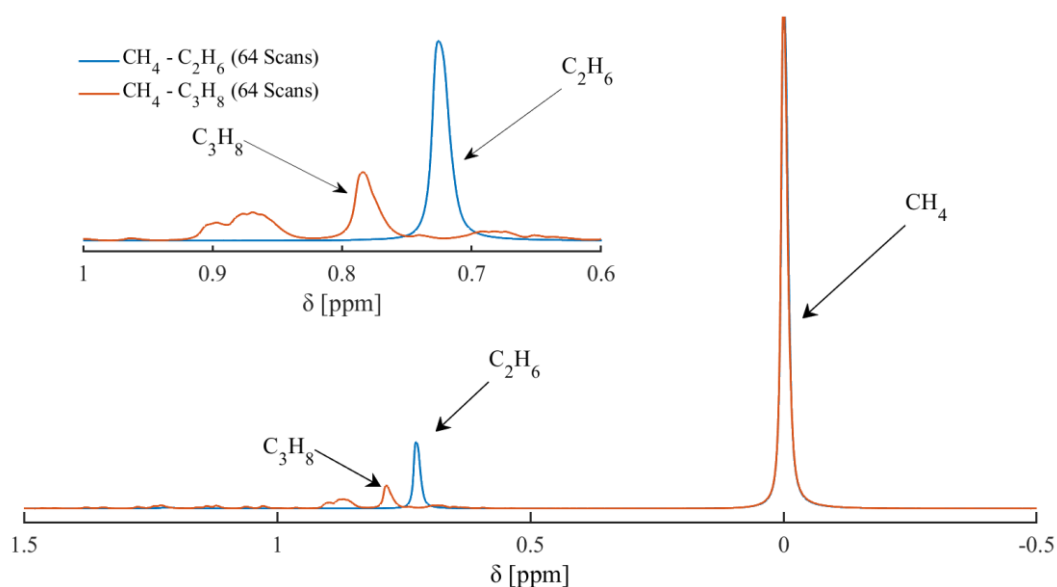


Figure A4: Overlaid ¹H NMR spectra of methane-ethane and methane-propane gas mixtures acquired with 64 scans at 200 bar. The insert shows a zoom of the region with the signals of ethane and propane.

Table A5: List of samples containing active- and non-active ^1H NMR active components purchased from Linde which were measured at 120 bar.

Sample	Component [mol%]								
	C1	C2	C3	C4	C5n	C5i	C5o	C6n	CO ₂
No. 1	94.36 ^{a)}	4.50	--	--	--	--	0.10	0.04	1
	0.08 ^{b)}	0.06	--	--	--	--	0.01	0.00	0.01
No. 2	92.91	5.00	--	--	--	--	0.07	0.02	2
	0.09	0.09	--	--	--	--	0.00	0.00	0.02
No. 3	92.88	4.00	--	--	0.10	0.02	--	--	3
	0.08	0.06	--	--	0.00	0.00	--	--	0.04

^{a)}Nominal concentration on the certificate of analysis, ^{b)}Analytical uncertainty (concentration error)