Laserinduced Fluorescence as Sensor for Mining
- A guide for geologists and mining engineers -

Von der Fakultät für Georessourcen und Materialtechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen

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Working on a relatively new field of research with a prototype implicates problems. Research on such a field needs freedom – to think, to discuss and to run into the wrong direction for a while. I want to thank Prof. Nienhaus for giving me this freedom as well as great trust in independence and competence. I enjoyed the straight way of discussing and the practical approach to engineering science at BGMR.

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Appendix
1 Introduction

1.1 Motivation

The utilisation of real-time sensors in mining processes plays an important role for improvement of productivity. This can be either achieved during the mining or the transport operation. During mining, real-time analysis of mined material could reduce waste rock and thereby lead to lower material transportation. During transportation, real-time analysis could be used for dividing host- from waste rock and thereby decrease material processing. In seam-like mineral deposits analysis during the mining process is favourable, whereas for other operations analysis during transportation (i.e. over conveyor belts) is often better suited as selective mining is restricted by mine layout.

This thesis demonstrates the usage of a sensor based on laserinduced fluorescence (LIF) focusing on the application during the transport process. Due to the high information content of LIF signals, distinction of host- and waste rocks as well as quality control can be realised. Studies of different raw materials and problems are described as well as influence of disturbance factors typical for mining operations. Additionally, utilisation of classification algorithms is discussed. The results presented here are based on a three year scientific work at Aachen university and address mining engineers as well as geologists. Aim of this work is to give an overview about LIF as a sensor for mining and to serve as a guideline for practitioner who consider utilisation of sensor technology to increase productivity in their operation. To give an overview of alternative sensor systems, a choice of online sensors for mining applications are presented in a summarized form.
1 Introduction

1.2 Structure of thesis
The thesis is divided into eight chapters, which contents are described in the following

1 Introduction
The introduction explains motivation and background of this thesis.

2 Online sensors in the mining Industry
This chapter gives an overview about sensors utilised in the mining industry. Sensors installed on mining machines as well over conveyor belts are discussed.

3 Principles of LIF
Physical principles of LIF as well as technical setup of the utilised LIF-Analyzer are presented in this chapter. Also principles of LIF measurements on rock samples are explained.

4 Pattern recognition and classification
Principles of pattern recognition and classification are described here. Additionally advice for practical application of support vector machines is given.

5 LIF-Measurement setup and influence of disturbing factors
This chapter gives an overview about general measurement setup and discusses the influence of disturbing factors such as air moisture, dust and water content of samples.

6 Results
Suitability of LIF for different raw materials is given in table form. Studies on three materials are presented in detail in this chapter: Measurements on lignite and associated waste rocks as an example for the distinction of many different materials and the utilisation of pattern recognition. Studies on diamond bearing rocks illustrate the distinction of only two material groups with few fluorescence parame-
1 Introduction

ter. Finally, kaolinite samples show the possibility of direct correlation between fluorescence and quality parameters. Results on further materials are given in brief form.

7 How to apply LIF in the mine

A guide to setup test measurements for different applications as well as economical considerations and technical problems are presented. Considerable parameters for correct layout of a LIF-Analyser are discussed

8 Conclusions

Main outcomes of the studies performed for this thesis are given and an outlook of further chances of LIF as a sensor for mining operations are discussed.
2 Online sensors in the mining Industry

2.1 Mining sensors: Review of CID (Coal Interface Detection) approaches

The utilisation of sensors on mining machines to date is limited to seam-like deposits such as coal or salt. Most work in this field has been done on sensors for coal mining, where continuous miners, shearer loaders and ploughs are utilised. The basic idea is to develop a sensor which is capable to distinguish coal and waste rocks, which are usually made up of sandstone, siltstone or shale. Knowledge of the coal seam height and position could then be used as a signal for steering the mining machine, hence make possible unmanned operation. First approaches for CID reach back to the 1970s, detailed studies were carried out by Mowrey in 1991 [MOW-91]. The following sensor principles were found to be most promising and will be presented shortly in this work.

*Gamma Ray sensors*

Gamma Ray sensors utilise natural gamma emission from shale, which is usually emitted from K40. As coal emits only low amounts of gamma ray compared to shale, this sensor can be used to distinguish the two. Furthermore, as coal absorbs gamma rays, the signals could be used to estimate the height of remaining coal before cutting the roof or floor. The technology is limited to mines with shale as host rock and needs frequent calibration especially for variation of gamma ray emission throughout the mine. [MAK-94]

*Infrared*

Infrared sensors in the mid infrared (IR) spectra (7-14 µm) can be used to detect heat of the face. As mid IR penetrates dust as well as
moisture, it is basically suited for mining operations. Distinction of coal and waste rock is based on different friction during the cutting process, leading to stronger heating of hard rock compared to coal. If certain spots at the face are measured at different times after the cutting process, differences in thermal conductivity could be also used for distinction. This sensor principle only works if the hardness contrast between coal and waste rock is high enough [BAS-97].

**Optical Camera**

An optical camera for visible light (400-750 nm) combined with a laser or lamp can measure differences in reflectance of the materials [HOL-99]. As optical light is strongly affected by heavy dust and moisture, installation of the camera needs to be very close to the face.

**Impact sound**

Cutting of different hard materials leads to different vibrations in the machines body. Measurement of those vibrations at significant frequencies can be used for distinction. The main problem of impact sound is the spatial information, i.e. it can be easily recorded that the machine cut harder/softer material, but for steering algorithms knowledge of the waste rocks position is crucial. Cutting a harder rock layer in the lower, middle or upper part of the seam can hardly be distinguished.

**Radar**

Radar waves emitted to the roof/floor can be used to distinguish the CID. Although radar is very robust and not effected by dust or moisture, the main problem is the reflectance of the signal at the air/rock boundary if the sensor is not in contact with the material. Therefore approaches to integrate the sensor in cutting drums have been carried out, for example by Stolar Horizon [STO-96].
2 Online sensors in the mining Industry

**Geoelectrical sensor**

Geoelectrical sensors such as BEAM (Bore-Tunnelling Electrical Ahead Monitoring) are utilised in tunnel construction for detection of voids and water inclusions [BRU-04]. In principle, electrical currents are focussed in the face by using a combination of measurement electrodes and a surrounding shield electrode, which have the same potential. The resistivity of the material is measured at different frequencies. However, no investigations in mining have been made so far.

**Seismic sensors**

Seismic sensors are based on interpretation of sonic waves induced by the cutting process [MOW-98]. Accelerometers are affixed to the roof and floor behind the mining machines. Hence this system is only usable for continuous miners. Via receiving data during training cuts in coal, roof and floor the system is calibrated to distinguish the seismic patterns. Adapting the accelerometers on shields could allow usage for shearer operation.

In general, CID can be distinguished in surface recognition approach and depth thickness approach. The first approach recognise the material by surface characteristics and therefore requires periodical cutting of roof or floor. The latter one measures the thickness of coal to the coal/waste rock boundary. The following table gives an overview of the presented systems as well as an assignment to the CID approach.
2 Online sensors in the mining Industry

*Table 1: Overview of coal-interface detection systems including surface as well as depth thickness sensors*

<table>
<thead>
<tr>
<th>SENSOR</th>
<th>CID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared</td>
<td><img src="image" alt="Surface approach" /></td>
</tr>
<tr>
<td>Pick force</td>
<td><img src="image" alt="Surface approach" /></td>
</tr>
<tr>
<td>Impact sound</td>
<td><img src="image" alt="Surface approach" /></td>
</tr>
<tr>
<td>Gamma-ray</td>
<td><img src="image" alt="Surface approach" />, <img src="image" alt="Depth thickness approach" /></td>
</tr>
<tr>
<td>Geoelectric</td>
<td><img src="image" alt="Depth thickness approach" /></td>
</tr>
<tr>
<td>Georadar</td>
<td><img src="image" alt="Depth thickness approach" /></td>
</tr>
<tr>
<td>Seismic</td>
<td><img src="image" alt="Depth thickness approach" /></td>
</tr>
</tbody>
</table>
2 Online sensors in the mining Industry

2.2 Conveyor belt sensors: Review of on-line analysis systems

Conveyor belt sensors are utilised in cases where selective mining is limited by mine layout or geology. Parameters for sorting are various, i.e. humidity, ore concentration or abundance of unwanted minerals. The results of the sensing process can be used to separate material and/or for mixing purposes to get a standardized product. Among others the following systems are utilised most frequently in the mining industry.

X-Ray Fluorescence (XRF)

XRF sensors are the most common type of sensor in the mining industry. Based upon excitation of samples by energy rich x-rays and element specific emissions of photons, XRF allows for analysis of elements with atomic numbers > 11 (Sodium). Whereas most XRF measurements are carried out on pills, which have to be produced from the sampled material, recently sensors for online analysis have been developed. Those offer analysis of grain sizes from 5-150 mm and throughput up to 40 t/h. For example, the “MikroSort X-Tract” developed by CommoDaS GmbH is utilised for extracting diamonds and can also be used for different metals as well as coal [MIN-06]. An overview about XRF systems is given by Bond [BON-00].

Optical Sensors

Wherever minerals can be distinguished by colour or reflectance, optical sensors can be used for sorting. Common examples are sorting of industrial minerals such as limestone or kaolinite. Grain sizes from 1 mm to 250 mm can be sorted using optical properties. As camera resolution and speed increases throughput goes up to 300 t/h [COM].
2 Online sensors in the mining Industry

*Microwave Sensors*

Unlike the other presented sensors, microwave based sensors are not used for material recognition but for measurement of moisture content. Especially in dry mining environments, water must be added to the mined material to prevent intense dust formation. At the same time the amount of water added must be minimized as material handling gets more difficult with increased water content. In coal mining customers require limits on moisture content not to be exceeded, making real-time measurements of moisture content necessary for automated moisture control [INT-05].

*Prompt Gamma Neutron Activation Analysis (PGNAA)*

PGNAA applications in mining use a neutron source like Californium-252 to generate gamma ray emissions. These emissions penetrate the sample and are measured by an gamma ray detector, i.e. NaI scintillation crystals with PMT. A common setup is to have the emission beneath a conveyor belt and the detector above. As a variety of elements can be detected, PGNAA systems can be used for mineral as well as coal ash content analysis. As time required for the measurements takes about a minute, throughput of at least 100 t/h are necessary for high accuracy [REG-97]. A related system is the Dual Energy Gamma Transmission (DUET) which utilises a second neutron source.
3 Principles of LIF

3.1 Physical principles

Laserinduced fluorescence, as the name depicts, describes the generation of fluorescence by laser energy. Fluorescence itself is a long known phenomenon, which was first observed in the eponymous mineral fluorite. Fluorescence is a special kind of luminescence, the following Figure 1 gives an overview about different luminescence processes:

![Figure 1: Overview of luminescence processes](image)

LIF measurements on rocks are carried out in three consecutive steps. First, monochromatic light in the ultraviolet (UV) range is used to excite the material. Second, fluorescence at higher wavelength is emitted and received by highly sensitive photomultiplier. Third, the gathered data is processed to distinguish between different kinds of rocks, for example coal, sandstone and shale.

In a simplified physical model, fluorescence is caused by shifting of electrons on unstable energy levels and following emission of photons while returning to the original level. As shown in Figure 2 [AME-00] an electron is excited by light and lifted from the stable level $S_0$ to the excited level $S_1'$. This instable level usually lasts for only a few
nanoseconds. By emitting thermal energy the electron then “relaxes” itself and reaches the intermediate energy level $S_1$. Finally, by falling back to the original level $S_0$ a photon with a longer wavelength than the excitation wavelength is emitted. As the energy difference between excited and stable level differs, photons of different wavelengths can be emitted. These emitted photons cause the fluorescence which can then be captured by photomultipliers.

$$\frac{\lambda_{EM}}{c} = \frac{h \cdot c}{\Delta_{EM}}$$

with $h$ and $c$ equal to Planck constant and speed of light and $\Delta_{EM}$ representing the energy difference between the excited and stable condition [BAY-04].

### 3.2 Applications of LIF

Laserinduced fluorescence has been long used in analytic processes for measuring concentrations in liquids and especially gases. Most important is the three-dimensional analysis of combustion processes in engines or power plant processes [DAI-00, KOH-90]. Furthermore,
3 Principles of LIF

LIF is applied in medicine for measurements on cancerous skin [ALF-84].

3.3 LIF on rocks and minerals

The characteristic fluorescence of rocks and minerals is caused by trace elements and defects in the crystal structure. Two kind of information can be derived from the fluorescence, these are wavelength of the fluorescence and decay behaviour. The first one gives fluorescence spectra like the one shown on the left side of Figure 3. As one can see the fluorescence intensity differs for different excitation and emission wavelength – giving one criteria to distinguish different materials. It has to be noted that in LIF applications usually only certain excitation wavelengths are used. Second, as shown on the right side of Figure 3, the decay behaviour, i.e. fluorescence over time, can be measured for every wavelength [BRO-99]. If two or more materials show similar spectra, one may use different decay behaviour to distinguish those. Wavelength filter and ultra fast triggering of photomultiplier allow for simultaneously reception of different wavelengths as well as different decay times. Especially for LIF measurements on rocks and minerals, PMT are the only receiving devices which can capture the very short living fluorescence signals. To date, charge-coupled device cameras do not possess comparable response time.

Depending on the task, two different ways of further processing of the LIF signals are possible. If different rock classes are to be distinguished, LIF based material detection works similar to identification of fingerprints. LIF sensors need to be calibrated to the fluorescence attributes of the rocks occurring in the particular mine. Algorithms for pattern recognition based on Support Vector Machines (SVM) have been utilised for material detection and will be presented in more detail in chapters 4 and 6.
If only few rock types are to be distinguished or quality control is required, e.g. to measure concentration of certain minerals in one kind of rock, correlation between the mineral concentration and fluorescence measurements has to been established. In that case a less complex approach can be used. Favourable are correlations with quotients of either wavelength or decay behaviour. The following Figure 4 shows fluorescence measurements from Kiruna Ore mine (Sweden) [BRO-98].

Figure 3: Emission spectra and decay characteristics of fluorescence signals

Figure 4: Usage of fluorescence ratios
3 Principles of LIF

In this setting the fluorescence ratio of 355 and 440 nm is used to separate apatite rich ore and quarzporphyry. The fluorescence intensity ration 355 nm/440 nm can be calculated as follows:

\[
\text{Ore (high apatite)}: \frac{\text{fluorescence intensity (355 nm)}}{\text{fluorescence intensity (440 nm)}} \approx \frac{420}{110} \approx 3.8
\]

\[
\text{Quarzporphyr}: \frac{\text{fluorescence intensity (355 nm)}}{\text{fluorescence intensity (440 nm)}} \approx \frac{110}{330} \approx 0.3
\]

As a result, the ratio of the apatite rich ore and the quarzporphyr differ in more than one magnitude and allow reliable distinction of the materials. Furthermore, fluorescence decrease caused by lower laser energy or aging of the photomultipliers would affect fluorescence readings at all wavelengths. Therefore the ratios would still be stable and could be used for material distinction.

3.4 Technical data of the LIF-Analyser

The LIF-Analyser used for the measurements consists of a transmitting and a receiving unit as well as auxiliary components. The laser emits pulsed high-energy UV-light beams at set wavelengths in the UV (355 nm) or deep UV (266 nm). The lasers can excite the material at frequencies of up to 20 pulses per second. On the receiving side of the LIF-Analyser, two photomultiplier tubes (PMT) detect the fluorescence signals from the material surface at wavelengths between 320 nm and 720 nm. Band pass filters select the distinct area of interest in the emission spectra of the measurements. Furthermore, fluorescence for each wavelength is measured at three different time integrals (50·10^{-9} s before to 230·10^{-9} s after excitation), which allows utilisation of different decay behaviour. An industrial computer within the unit gathers the data from the PMT and acts as a PLC for the unit. An internal cooling unit prevents overheating of the lasers. A portable computer, which can be connected to the LIF-Analyser, enables a software-driven control and analysis of the data using text
3 Principles of LIF

and Excel files. A picture of the used LIF-Analyser is shown in Figure 5.

![LIF-Analyser in BGMR's lab](image)

*Figure 5: LIF-Analyser in BGMR's lab*

Emitting and receiving units are illustrated in the following figures. Note that both figures are from the bird eye’s view and the two units are placed in two different levels beneath each other. At the emitting unit (compare Figure 6), one can see the path of the two laser beams. (1) and (2) are the two lasers with 266 and 355 nm, respectively. In the optical chamber (3) the laser beams are widened, parallelised and reflected by several mirrors. This allows utilisation of only one beam exit (4), where both laser beams leave the LIF-Analyser.
The receiving unit as illustrated in Figure 7 shows the infrared distance meter (5) and the telescopes (6) in front of the photomultiplier (9). In between are three filter wheels, of which the first two (7) are equipped with filters for different emission wavelengths. Filter wheel (8) is equipped with attenuators. One adjusting screw for both receiving units (10) are used for pivoting. This allows focussing of the telescopes for different measurement distances from 1.5 to 12 m.
Part of the measurements, i.e. analysis of limestone and gypsum, were carried out on a desktop fluorescence spectrometer (Jasco FP 780). This LIF system uses a mercury lamp for excitation of the fluorescence instead of a laser. The samples are placed on a small object holder inside the desktop. As only small sample volumes ($\approx 10 \text{ ml}$) can be measured, the material has to be in a homogeneous and fine grained form.
4 Pattern recognition and classification

In an ideal situation the raw materials which are to be separated show great differences in their fluorescence behaviour and can easily be distinguished by using only one or two emission wavelength or their ratio. This situation can be found for example in Kiruna iron ore mine, where apatite rich ores show much higher fluorescence than ores with low apatite concentration (cf. chapter 3.1).

More frequently, fluorescence spectra of rocks from the same geological environment are similar to each other and consequently not easy to distinguish. In that case computerized pattern recognition and classification are the only way to get reasonable results.

4.1 The idea of feature extraction

For the measurement setup used in this work, each sample can be characterised by eight emission wavelength (320, 360, 380, 400, 420, 440, 460, and 480 nm) and three time integrals (W1, W2, W3). This results in 24 values or features which describe each sample. Also each of the features has a standard deviation which is caused by variation of the laser energy as well as in homogeneities of the samples.

In that case a software tool such as a support vector machine (SVM) can be used to extract the most useful features to distinguish a given set of samples. The following example shall give a better understanding of the functionality:

Four cars (Car A, B, C and D) have to be distinguished. They are characterised by certain features such as colour, horsepower etc. like illustrated in the following table:
As one can easily see none of the given features can be used alone to clearly identify one of the cars. Furthermore, it becomes clear that there are more and less useful features. For example, the feature “Number of tires” can not be used because it is the same for all classes or cars. Also, the combination “Colour” and “Fuel” can be used to distinguish Car A, B and C but shows no difference between Car B and Car D.

One could use the combinations “Colour” and “Brand” or “Horsepower” and “Brand” to get a clear result – therefore at least two features are necessary to clearly identify the right car. Consequently, with increasing number of classes and features the classification becomes more and more complicated and cannot be carried out by hand with reasonable afford. For use in SVM, the mentioned features have to be translated in numbers and scaled to either (-1,1) or (0,1). As measurements presented here are already available as numbers, transformation will not be addressed here. A good overview on that topic is given by Zelch et Engel [ZEL-05].

In case of the example given above, the feature “Horsepower” could be scaled by setting the maximum value to 1. One would get 0.96, 1, 0.78 and 1 for Car A, B, C and D, respectively. Transferred to LIF measurements, all intensity values have to be divided by the maximum value, leading to a range of results between 0 and 1.
4 Pattern recognition and classification

4.2 Theoretical background of SVM

In this chapter the mathematical foundations for SVM in two dimensions will be presented. In a simplified approach, SVM can be described as a classifier, which separates objects by using a line, or, in more dimensional problems, a hyperplane. For convenience only the term “hyperplanes” will be used in the following. The core of SVM are kernels, which can use different algorithms for calculation of the best hyperplane. Common kernels are:

- **linear**: $K(x, y) = x \cdot y$
- **polynomial**: $K(x, y) = (\gamma \cdot x \cdot y + r)^d$
- **radial basis function**: $K(x, y) = \exp\left(-\gamma \cdot \|x - y\|^2\right)$
- **sigmoid**: $K(x, y) = \tanh(\gamma \cdot x \cdot y + r)$

where $\gamma$, $r$ and $d$ are kernel parameters [HSU, MAR-03]:

- $\gamma$: width of Gaussian bell
- $r$: additive constant
- $d$: degree of polynomial

As there are infinite numbers of possible hyperplanes, the most suited one is chosen by maximising the distance to both objects. This is achieved by utilisation of so called support vectors, which are perpendicular to the separating hyperplane and support parallel planes which define the upper and lower limit of the hyperplane. Imagine two classes of data plotted into a regular x-y diagram such as follows (Figure 8):
The task performed by the SVM is to find a separating hyperplane between material 1 and material 2. X and Y are two features, e. g. fluorescence intensity at 380 and 420 nm at a given time interval. All separating hyperplanes L1, L2 and L3 are suited to separate material 1 and 2. Nonetheless, L1 is suited best as the support vectors are large enough for robust classification. A common problem is overfitting of the classifier. It may be better to accept errors while classifying training data to get larger support vectors and hence a more robust classification on blind data. This problem is illustrated in the following figures. Training data are shown on the left part of Figure 9 as solid triangles and circles. Again, two materials are to be separated with two features X and Y. If correct classification of all training data should be achieved, the width of the separating hyperplane is
4 Pattern recognition and classification

rather small. If the hyperplane is used to classify blind data as shown on the right side of the diagram, three samples (two triangles and one circle) are classified wrong.

![Figure 9: Overfitting caused by a precise but non robust separating hyperplane (training data on left side, blind data on right side), after Hsu et al.](image)

In contrast Figure 10 shows generation of a hyperplane where one wrong classification during training is accepted leading to larger support vectors. Consequently a better classification of the blind data can be achieved.

![Figure 10: More robust classifier accepting wrong classification during training (training data on left side, blind data on right side), after Hsu et al.](image)
4.3 Practical application of Support Vector Machines

For a traditionally trained geologist or mining engineer complex classification and pattern recognition algorithms such as SVM are not typical skills. Furthermore, programming of suited algorithms is time-consuming and costly. Consequently, the approach used in this thesis was to find a standard program which was not especially developed for mining purposes but is still suited for material detection of LIF. As a result, the program LIB-SVM was chosen, as it has high acceptance in the scientific world and can be downloaded from the world wide web without charge (http://www.csie.ntu.edu.tw/~cjlin/libsvm/). At the web page, also a two dimensional graphical tool is available to illustrate functionality of SVM on two dimensional data. For application purposes, the core LIB-SVM program has to be combined with other programs, which are also available on the web site. The critical kernel parameters are calculated by the program itself or experienced based default, therefore first results can be achieved quickly. Furthermore, interfaces to other programs such as MATLAB or LABVIEW are available. Figure 11 illustrates the main steps of LIB-SVM from loading of the data to classification success. A great advantage of LIB-SVM is the computing speed. Complete classification of data sets such as used in this thesis can be calculated in seconds up to a few minutes. Therefore testing with different parameters and combinations of training and blind data can be carried out quickly.
At BGMR, a graphical interface was developed to get a comfortable working environment for the whole process which consists of loading, scaling, training and classification (Figure 12). Also directories of the
4 Pattern recognition and classification
different data as well as sub programs such as python or gnuplot can be adjusted here. The most important feature is the choice of the kernel, as this has the highest effect on classification success (cf. appendix 2).

Figure 12: Graphical User Interface for LIB-SVM
5 LIF-Measurement setup and influence of disturbing factors

During the research work different raw materials were examined by LIF measurements. The general measurement setup will be described in this chapter. As mining environment can be critical for optical measurement devices, the influence of dust and water will also be discussed.

5.1 Measurement setup

All measurements presented in this work were carried out in the lab. Field measurements were carried out twice in open cast lignite mines in the Hambach mine and were discussed in detail by Bayer [BAY-04]. The following table gives an overview about the measurement parameters used – variations are specified in chapter 6:

*Table 3: Measurement parameters of the LIF-Analyser*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>266</td>
<td>nm</td>
</tr>
<tr>
<td>Laser current</td>
<td>102</td>
<td>Ampère</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20</td>
<td>Hz</td>
</tr>
<tr>
<td>Pre-shots</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Measurement shots</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>PMT Voltage</td>
<td>1050</td>
<td>Volt</td>
</tr>
<tr>
<td>Detected wavelengths</td>
<td>320 – 480</td>
<td>nm</td>
</tr>
<tr>
<td>Measurement times: W1</td>
<td>variable</td>
<td>ns</td>
</tr>
<tr>
<td>Measurement times: W2</td>
<td>variable</td>
<td>ns</td>
</tr>
<tr>
<td>Measurement times: W3</td>
<td>variable</td>
<td>ns</td>
</tr>
<tr>
<td>Sample distance</td>
<td>2.33</td>
<td>m</td>
</tr>
</tbody>
</table>
5 LIF-Measurement setup and influence of disturbing factors

The shorter emission wavelength at 266 nm turned out to be more effective to generate distinguishable fluorescence signals. Summing up pre-shots and measurement shots, in total 2000 shots were fired at the samples for each detected wavelength. At a repetition rate of 20 Hz, the measurement for each wavelength takes 100 s. Pre-shots were necessary for stabilizing the laser’s energy level. As investigation of disturbance factors revealed the strong influence of airborne moisture, longer detection wavelengths than 480 nm were not used for the measurements.

Different measurement times were used to detect peak (W1), decay (W2) and total fluorescence (W3), respectively. Due to small delay in triggering of the PMT, the peak fluorescence measurement starts 5 ns prior to the laser shot. Total fluorescence includes 50 ns before the laser pulse to measure background signal of the PMT.

5.2 Influence of disturbing factors

The influence of dust and moisture was tested in BGMR’s lab. Results are shown in Figure 13 and Figure 14 [VIN-05B].

5.2.1 Dust

Dust shows similar effect on different emission wavelength, so Figure 13 illustrates the impact of dust for one emission wavelength only (440 nm). During the test 3,000 laser shots were fired at a standard ceramic sample. The first 1,000 shots represent the undisturbed fluorescence which shows intensities about 8,000 (arbitrary units). Compared to the spectra of Figure 14, this value fits well the measured fluorescence of the ceramic sample at 440 nm. Following that, lignite dust was scattered between the laser and the sample. Change in the fluorescence measurements was observed while dust was scattered close to either the sample or the laser. Dust concentration was about
one kg/m³. The lignite dust consisted of coarse dust with grain size around one mm. In total, only 2.5 % of the measured fluorescence values were identified as outliers and could be related to reflections of the laser beam to the wall of the test chamber. Therefore it can be concluded that coarse lignite dust shows no significant alteration of fluorescence. It has to be noted that deposition of dust on the laser and sample would cause greater disturbance and has to be avoided in practice. Also the influence of fine dust (< 10 µm) as well as dust from other raw materials can not be directly concluded from these measurements. Nonetheless the observed results indicate that dust from other materials at similar grain sizes should show a similar effect.

Figure 13: Influence of dust on fluorescence measurements

5.2.2 Air moisture

Investigations on the impact of water vapour by laserinduced fluorescence have been carried out by Neij and Aldén [NEI-94]. Their research focussed on the visualisation of water vapour in combustion environments and was carried out with a 248 nm excimer laser at
pulse energies between 1 mJ and 80 mJ and fluorescence readings between 400 and 500 nm. At ambient air conditions with air moisture of approx. 30 % maximum emission was observed at 440 nm. Although little influence of air moisture could be detected at this wavelength during the measurements presented here, main influence was observed at longer wavelengths. This could be related to the different excitation wavelength used, i.e. 248 nm vs. 266 nm as used for this work. However, discussion with members from Fraunhofer Institute for Laser Technology [JAN-07] indicate that no research has been carried out on this topic with comparable laser setup as used in this thesis.

As shown in Figure 14 complete fluorescence spectra of a standard ceramic sample was recorded for different humidity level. Whereas fluorescence for lower wavelength are only slightly affected, peaks at 500, 540 and 600 nm show high influence of moisture at higher wavelength. Tests with water directly sprayed between laser and sample confirmed these results. As a consequence, wavelengths higher than 480 nm are not used for distinction of different rocks.

![Figure 14: Influence of humidity on fluorescence measurements](image-url)
5.2.3 Water content of samples

If variations in water content of the samples are expected, influence of the water content on the fluorescence characteristics has to be investigated. Mixtures of samples with defined water contents can be easily generated and measured. Investigations by Weber [WEB-01] indicate that increase in moisture content leads to decreasing fluorescence intensity. However, compared to a strong drop in fluorescence when comparing dry material with 1% of weight water added, further increase in water content showed relatively little decrease of fluorescence. For this thesis lime sand bricks were studied in dry (drying over 24 h at 105°C) and water saturated (over 24 h) condition. Figure 15 shows fluorescence spectra of a lime sand brick sample (10 cm · 10 cm · 10 cm) in dried and water saturated condition. As one can see absolute fluorescence intensity of the wet sample is lower. As the decrease in fluorescence intensity can be observed over the complete spectra, utilisation of intensity ratios instead of single wavelength readings should be used.

![Fluorescence spectra of lime sand brick samples](image)

*Figure 15: Influence of sample’s water content on fluorescence intensity*
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6.1 Suitability of LIF for different raw materials
The suitability of LIF was tested for different raw materials. For three research projects, including distinction of lignite and waste rocks, distinction of diamond bearing rock and waste and finally determination of Potassium- and Iron content in Kaolinite, results will be presented in more detail. Results of further measurements will be presented briefly. The following table summarizes the studied materials. Note that two measurements were performed with a desktop fluorescence spectrometer and one on secondary raw material.
6 Results

Table 4: Overview of studied materials and recognition success

<table>
<thead>
<tr>
<th>Material</th>
<th>Success of LIF analysis</th>
<th>LIF-system used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite and waste rock</td>
<td>good</td>
<td>LIF-Analyser</td>
</tr>
<tr>
<td>Lamphroite (diamond bearing magmatite)</td>
<td>good</td>
<td>LIF-Analyser</td>
</tr>
<tr>
<td>Kaolinite (Iron- and Potassium content)</td>
<td>intermediate</td>
<td>LIF-Analyser</td>
</tr>
<tr>
<td>Rock salt (Halite, Sylvinite etc.)</td>
<td>bad</td>
<td>LIF-Analyser</td>
</tr>
<tr>
<td>Limestone (Iron- and Magnesia content)</td>
<td>intermediate</td>
<td>Jasco FP 780</td>
</tr>
<tr>
<td>Gypsum (Anhydrite- und Calcite content)</td>
<td>intermediate</td>
<td>Jasco FP 780</td>
</tr>
<tr>
<td>Coal and waste rock</td>
<td>good</td>
<td>LIF-Analyser</td>
</tr>
<tr>
<td>Plastics (Separation of dark plastics)</td>
<td>good</td>
<td>LIF-Analyser</td>
</tr>
</tbody>
</table>
6 Results

6.2 Lignite and waste rock

LIF measurements on lignite and related unconsolidated rocks were performed in cooperation with RWE Power AG, who operates three open cast mines (Garzweiler, Hambach, Inden) in the Rhenish area between the cities of Aachen, Cologne and Monchengladbach. Figure 16 shows a satellite image of the three mines. Results presented here are based on the study of samples from the Inden open cast mine.

![Figure 16: Open cast lignite mines in the Rhenish area](image)

6.2.1 Task

For automation purposes of the bucket wheel excavators used in lignite mining, LIF was evaluated as one possible sensor system for material recognition. In the Inden open cast mine, distinction be-
6 Results

tween lignite and waste rock as well as between different waste rocks themselves are important for further processing. Besides the annual production of 25 million tons of lignite, about 100 million tons of overburden are produced.

6.2.2 Geology

The lignite deposits in the Rhenish area were formed about 20 million years ago in the Tertiary. In an environment similar to nowadays wetlands dead plants were preserved from oxidation processes and accumulated thick peat layers. During a following cooler period transgression of the North Sea brought sandy sediments which covered the peat layers. In the following, regression and transgression changed, leading to marine as well as fluvial sedimentation processes. Consequently, encountered waste rocks during mining operation are unconsolidated sediments such as clay, sand and gravel. Loess builds up the uppermost layer.

6.2.3 Measurement setup

Fourteen different lignite and soil samples were taken from Inden open cast mine. Additionally, one sample of lignite dust was taken and used for studying of disturbing factors as presented in chapter 5.2. Each sample was split in two sub-samples and used as reference and blind sample for pattern recognition algorithms, respectively. The following table displays the studied samples. Material classification and moisture content were provided by RWE Power’s laboratory. Detailed analysis of selected samples are given in appendix 2.
### Table 5: Lignite and waste rock samples of Inden mine

<table>
<thead>
<tr>
<th>Material</th>
<th>Moisture content [%]</th>
<th>ID for pattern recognition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loess (dry)</td>
<td>15.9</td>
<td>1a/1b</td>
</tr>
<tr>
<td>Loess (wet)</td>
<td>19.3</td>
<td>2a/2b</td>
</tr>
<tr>
<td>Sand (dry)</td>
<td>5.0</td>
<td>3a/3b</td>
</tr>
<tr>
<td>Sand (wet)</td>
<td>16.4</td>
<td>4a/4b</td>
</tr>
<tr>
<td>Sand (dry)</td>
<td>2.7</td>
<td>5a/5b</td>
</tr>
<tr>
<td>Sand (wet)</td>
<td>6.7</td>
<td>6a/6b</td>
</tr>
<tr>
<td>Lignite with wood layers</td>
<td>n. a.</td>
<td>7a/7b</td>
</tr>
<tr>
<td>Lignite</td>
<td>n. a.</td>
<td>8a/8b</td>
</tr>
<tr>
<td>Lignite with soil layers</td>
<td>n. a.</td>
<td>9a/9b</td>
</tr>
<tr>
<td>Clay</td>
<td>n. a.</td>
<td>10a/10b</td>
</tr>
<tr>
<td>Clay (used for sealing)</td>
<td>n. a.</td>
<td>11a/11b</td>
</tr>
<tr>
<td>Tailings (Sulphur content &gt; 0.2%)</td>
<td>19.2</td>
<td>13a/13b</td>
</tr>
<tr>
<td>Gravel (bright)</td>
<td>n. a.</td>
<td>14a/14b</td>
</tr>
<tr>
<td>Gravel (dark, iron rich)</td>
<td>n. a.</td>
<td>15a/15b</td>
</tr>
</tbody>
</table>

About 2 kg of each sample were placed in a ceramic bowl and measured three times. Soil samples were stirred in between whereas solid samples were turned and measured at three different areas. The samples are shown in Figure 17.
As one can see especially the sand samples (No. 3 – 6) show only little visible differences. Also clay and the clay used for sealing are difficult to distinguish. The measurement parameters used are specified in the following table:
6 Results

Table 6: Measurement parameters for lignite and waste rock samples from Inden mine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>266</td>
<td>nm</td>
</tr>
<tr>
<td>Laser current</td>
<td>102</td>
<td>Ampère</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20</td>
<td>Hz</td>
</tr>
<tr>
<td>Pre-shots</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Measurement shots</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>PMT Voltage</td>
<td>1050</td>
<td>Volt</td>
</tr>
<tr>
<td>Detected wavelengths</td>
<td>320 – 480</td>
<td>nm</td>
</tr>
</tbody>
</table>

Measurement times:
- W1: -5 to 30 ns
- W2: 30 to 75 ns
- W3: -50 to 230 ns
- Sample distance: 2.33 m

6.2.4 Fluorescence measurements

Fluorescence of all samples was measured for three different time integrals, i.e. W1, W2 and W3. The spectra for peak fluorescence (W1) is shown in the following figure:
Especially lignite with wood layers and soil with lignite show high fluorescence values. In contrast, gravel shows very low signals. It also becomes clear that the greatest differences between the samples can be found at higher wavelength between 400 and 480 nm. Highest fluorescence is measured at 440 and 460 nm, whereas a minimum can be found at 380 nm. Also evident is the need for pattern recognition algorithms as many samples cannot be distinguished by only few wavelengths. It has to be mentioned that the fluorescence spectra is constructed from measurements at eight distinct wavelengths. Adding up the results from W1, W2 and W3, in total 24 values or features are available for pattern recognition algorithms. Figure 19 shows the standard deviation of the samples – each sample was measured three times for 1,000 shots and stirred in between (solid samples were measured at three different locations). For most samples and wavelengths the standard deviation is below 10 %. For measurements at 380 nm and also for the low fluorescent gravel samples, standard deviation exceeds 10 % and reaches up to 70 %. At very low fluorescence values, the signal-to-noise ratio decreases dramatically – which leads to high standard deviations. Nonetheless this can also be used

![Fluorescence spectra of lignite and associated waste rocks during W1](image-url)
6 Results

for pattern recognition as high standard deviation at most wavelengths can be treated as a characteristic feature of the gravel samples.

![Figure 19: Standard deviation of fluorescence measurements for lignite and associated waste rocks during W1](image)

The decay behaviour is measured during W2 as illustrated in Figure 20. Fluorescence intensities are about one order of magnitude lower compared to W1. The sand samples, which showed little intensity during W1, reach the highest values. Also one of the tailing samples shows high intensity at 365 nm. This suggests differences between the blind and the reference sample, which have no influence on peak intensity. Standard deviations (cf. Figure 21) are very high and reach up to 120% reflecting low fluorescence signals compared to noise.
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Figure 20: Fluorescence spectra of lignite and associated waste rocks during W2

Figure 21: Standard deviation of fluorescence measurements for lignite and associated waste rocks during W2

Fluorescence measurements during W3 (Figure 22) cover the complete possible measurement time and show only little higher signals than W1. Therefore, it can be concluded that most of the fluorescence
6 Results

is generated up to 30 ns after the laser shot. As expected, standard deviation of W3 as shown in Figure 23 shows great similarities with W1.

Figure 22: Fluorescence spectra of lignite and associated waste rocks during W3

Figure 23: Standard deviation of fluorescence measurements for lignite and associated waste rocks during W3
6.2.5 Usage of pattern recognition and classification algorithms

As one can see from the former figures the separation of all samples by using only few wavelengths is not possible. Therefore, pattern recognition offers the best chance to identify suitable features for separation. The LIB-SVM system formerly described was trained with A-samples and then used for automatic identification of the B-Samples and vice versa. Compared to the spectra shown, four additional emission wavelengths (520, 532, 560 and 640 nm) were used leading to twelve more features.

Practically, a data set consisting of 14 materials and 36 features was built up. 100 values of the A-sample set with the corresponding standard deviation were given per material and feature building up a 1400·36 matrix. An 1400·1 identification matrix was given in addition.

A second 1400·36 matrix was built up with values from the B-samples. Then the procedure was repeated with usage of the B-samples as training data and the A-samples as blind data. Due to higher heterogeneity, the B-samples turned out to be better suited as training data. Using the A-samples as training data, overfitting as described in chapter 4.2 occurs. Four different kernels, i.e. linear, polynomial, radial basis function and sigmoid were used. Classification success for the different kernels and samples used as blind data is shown in the following table:

<table>
<thead>
<tr>
<th>Kernel</th>
<th>Training Data: A-samples Success [%]</th>
<th>Training Data: B-samples Success [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>67.4</td>
<td>86.9</td>
</tr>
<tr>
<td>polynomial</td>
<td>46.4</td>
<td>84.1</td>
</tr>
<tr>
<td>RBF</td>
<td>64.3</td>
<td>88.3</td>
</tr>
<tr>
<td>sigmoid</td>
<td>71.1</td>
<td>88.2</td>
</tr>
</tbody>
</table>

Table 7: Classification Success of different training data sets and kernels
Detailed figures of the classification are given in appendix 2.

Figure 24 displays the best result based on the radial basis function kernel.

The graph shows a virtual profile based on 100 data points per material. Training data are plotted as massive grey, leading to a stair-like distribution of the data. The gap for material “12” is caused by the lignite dust sample, of which no blind sample was available. The smaller black dots represent the material classification of the blind data. Consequently, an overlap of both data sets indicates correct identification of the blind data. Identification problems are caused by three materials, clarified by the encircled areas. Part of sample “3” (dry sand) is classified as sample “5” (also dry sand). Also part of sample “11” (clay used for sealing) is classified as sample “2” (wet loess). Finally part of sample “15” (dark gravel) is classified as sample “13” (tailings). If recognition of the both different wet sand samples is accepted, recognition success raises to 92 %.
Using the “wrapper 2” algorithm developed by Bayer [BAY-04], recognition successes between 74 and 98.5 % could be achieved (cf. Figure 25), yet at a much higher computational effort with computing times of several hours up to days [VIN-05A].

![Graph showing results of material recognition with the "wrapper 2" algorithm](image)

**Figure 25: Results of material recognition with "wrapper 2" algorithm**

### 6.2.6 Suitability

Measurements on different coal and waste rock samples of Inden open cast mine as well as field measurements formerly carried out by Bayer in the Hambach open cast mine approve the potential of LIF for utilisation in lignite mining [BAY-04]. However, further studies on technical applicability show that installation over the conveyor belts are easier to implement than at the bucket wheel [VIN-05B]. Additional improvements of sensor technology is necessary for successful realisation of LIF in lignite mining operations.
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6.3 Diamond bearing rocks
LIF measurements on volcanic rocks from Argyle Diamond mine (Australia) were carried out in association with Rio Tinto. Rocks from the Argyle mine include possibly diamond bearing rocks (NSL, Non Sandy Lamproits and SL, Sandy Lamproits) and waste rocks.

6.3.1 Task
Sorting in diamond mining operations is crucial due to the huge amount of waste rock per ore. In a worldwide average, diamond concentrations are in the range of ppm or even less – often more than one ton of rock has to be processed to extract one gram of diamond. Consequently, pre-sorting and separation of possible host rocks have an enormous impact on profitability of the mine. The suitability of LIF for application over conveyor belts during the transport process was studied.

6.3.2 Geology
The Argyle mine is located in the north-western part of Australia, close to the city of Kununurra (compare Figure 26). Unlike most diamond mines, which are based in kimberlite pipes, the diamonds of Argyle mine are found in a volcanic lamproite pipe. This pipe is located at the strongly deformed margin of the proterozoic Kimberley craton and dips north at an angle of about 30° [SHI-01]. Radiometric dating suggests a forming age of the pipe around 1.18 billion years with formation of the diamonds 0.4 billion years earlier. Although diamonds from the mine are of minor quality and size, Argyle contributed up to 40 % of the worldwide diamond production during 1990s. The ore/waste ratio at 3 – 6 carats/ton is very high compared to other mines (0.5 – 1.0 ct/t), also very rare pink diamonds are produced here. The gross production is brown and yellow diamonds and only 5 % of the total production is gem quality.
6.3.3 Measurement setup

Fifteen samples (2 ore, 13 waste rock) were measured during the investigation. The samples consisted of crushed material with grain sizes of 10 cm. Each sample was divided in five sub-samples of one kg. For six out of fifteen samples, sub-samples were measured to study variance and standard deviation. The following table gives an overview about the samples:

Figure 26: Location of Argyle mine, adapted from Atkinson et al. (1984b, figure 3B)
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Table 8: Ore and waste rock samples of Argyle mine

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sample identification</th>
<th>Ore/Waste</th>
<th>Variance measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NSL</td>
<td>Ore</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>Pch</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pcl 1</td>
<td>Waste</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>Pcl 2</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Pcl 3</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pcl 4</td>
<td>Waste</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>Pv 1</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Pv 2</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Pv 3</td>
<td>Waste</td>
<td>Yes</td>
</tr>
<tr>
<td>10</td>
<td>Pv 4</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Pv 5</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Pv 6</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Pv 7</td>
<td>Waste</td>
<td>Yes</td>
</tr>
<tr>
<td>14</td>
<td>Pv 8</td>
<td>Waste</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>SL</td>
<td>Ore</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The samples were placed on a metal rotary table and measured during rotation to cover a representative amount of pieces. Figure 27 shows the assembly of the samples with identification.
As preliminary studies performed by [BRO-02] indicated suitability of certain excitation wavelengths, the measurements described here were performed only for these wavelengths. Measurement parameters are given in the table below:
6 Results

Table 9: Measurement parameters for ore and waste rock samples from Argyle mine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>266 nm</td>
</tr>
<tr>
<td>Laser current</td>
<td>102 Ampère</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Pre-shots</td>
<td>1000 -</td>
</tr>
<tr>
<td>Measurement shots</td>
<td>1000 -</td>
</tr>
<tr>
<td>PMT Voltage</td>
<td>1050 Volt</td>
</tr>
<tr>
<td>Detected wavelengths</td>
<td>320, 365, 440 nm</td>
</tr>
</tbody>
</table>

Measurement times:

- W1: -25 to 200 ns
- W2: 0 to 15 ns
- W3: 20 to 150 ns

Sample distance: 2.33 m

6.3.4 Fluorescence measurements

To determine statistical properties such as average, standard deviation and scatter of the measurements, a special measurement routine was applied for certain samples, namely NSL, Pcl 1, Pcl 4, Pv 3, Pv 7 and SL. For these samples each of the five sub samples was measured individually with 1,000 laser pulses. The emission was measured at 365 nm. After that, the material was stirred and the procedure repeated in reverse order. In addition, 1,000 laser pulses were fired after the rotating plate was stopped, that means only one piece of rock was measured. This allows distinguishing the laser inherent scatter from the scatter caused by the inhomogeneity of the sample material.

An evident illustration of the measuring procedure is given in Figure 28, in this case for sample NSL. The first 1,000 data points result from the pulses during rotation of the plate. Data points 1,000 –
2,000 were collected with the same measurement parameters after stirring the sample. The periodic peaks result from the rotation of the plate, meaning the same piece of rock was measured six times in 1,000 data points. Data points 2,000 – 3,000 show only little scatter, these measurements were carried out after the plate was stopped. For sub-sample 1, the three measurements are separated by dotted red lines. The total number of 15,000 data points results from the measurement of all five sub-samples. Some of the very high intensity outlier could be related to laser pulses fired on the steel plate instead of the sample material. One can see that samples 1, 2 and 5 show higher homogeneity than samples 3 and 4.

![Graph showing intensity vs. data point for sub-samples 1-5.](image)

**Figure 28: Variance measurements on NSL sub-samples**

Because fluorescence intensity was only measured at three wavelength, a complete fluorescence spectra is not given. Instead, certain ratios between wavelengths and time integrals are useful for separation of the samples. The following Figure 29 shows all 15 samples plotted at W1 320 nm/365 nm versus W1 365 nm/440 nm. The waste samples on the right side of the diagram show a higher 320 nm/365 nm ratio and a lower 365 nm/440 nm ratio than the ore.
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samples. An exception is the waste sample Pv 5, which shows similar values as the ore samples SL and NSL. Keeping in mind the sample photos (Figure 27), Pv 5 and SL show similarities in the visual spectra as well.

Figure 29: Fluorescence ratios of ore and waste samples from Argyle Diamond mine

Another way of separating the samples is the utilisation of the different decay behaviour, i.e. how fast fluorescence decreases after the excitation. As shown in Figure 30 not only peak fluorescence, but also excited-state deactivation differs for the samples. Multiple information regarding the temporal fluorescence behaviour can be derived from this figure, which shows a selection of the samples. First, for all of the displayed samples, fluorescence intensity peaks about 10 ns after the laser’s excitation. Second, fluorescence fades out of after 75 ns. Third, ranking of the samples can change over time. The Pch sample shows the highest peak fluorescence, but declines quickly and shows only fourth highest fluorescence after 25 ns. On the other hand, SL, one of the ore samples, starts with third highest peak fluorescence but shows highest fluorescence after about 20 ns and fur-
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ther on. According to this allowance of the temporal fluorescence behaviour significantly increases the chance to separate the samples.

Accordingly to the previous remarks, different time integrals can be used as well for separation of the samples. This is illustrated in Figure 31. Whereas the ore samples show high values for peak as well as decay fluorescence, the waste samples show much lower decay fluorescence. Again, sample waste sample Pv 5 shows similar behaviour like the ore samples and can not be separated. Comparing the temporal fluorescence curves of the ore samples in Figure 30, it becomes clear that Pv 5 indeed shows very similar characteristics over the whole time. Further fluorescence data is given in appendix 3.

Figure 30: Temporal fluorescence behaviour of selected samples
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![Graph: Decay and peak fluorescence of ore and waste samples from Argyle Diamond mine]

**Figure 31: Decay and peak fluorescence of ore and waste samples from Argyle Diamond mine**

### 6.3.5 Suitability

As the presented results show, separation of the ore from the waste samples is possible with exception of waste sample Pv 5, meaning that under lab conditions over 90% of the waste could be separated by LIF. Transferring this result to the mine could result in a great decrease in processing costs. However, only installation of a LIF Scanner over conveyor belts and extensive testing could approve the suitability of LIF under field conditions.

### 6.4 Kaolinite

LIF measurements on rocks from a kaolinite mine were performed in cooperation with Amberger Kaolin Werke (AKW), who are run by Quarzwerke Frechen GmbH. The kaolinite is mined in open cast mines with hydraulic excavators. Also one small bucket wheel excavator is utilised.
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6.4.1 Task
Kaolinite is an important mineral for ceramic as well as paper industry. The most important quality parameter are the so called “whiteness”, which indicates the purity and brightness of the material and the potassium content.
Consequently, instead of material recognition, a correlation between K$_2$O (potassium content) and Fe$_2$O$_3$ (whiteness) to the fluorescence characteristics was in focus of the study.

6.4.2 Geology
Kaolinite is a typical weathering mineral which is mainly formed from Feldspar, i.e. Orthoclase. As usually Kaolinite is build up directly from weathered granite or similar magmatic rocks, in case of the kaolinite deposit in Hirschau the generation is more complex. The basement in this area consists mainly of granites and gneiss. One model indicates that weathered material of the basement was transported and deposited as arkoses by rivers. Arkoses are sandstones with an feldspar content of at least 25 %. After that process, chemical transformation of the feldspars led to kaolinite. This took place during the main Bundsandstein (Triassic). The extent of the kaolinite deposit between the villages of Hirschau and Schnaittenbach is about 2.5·0.6 km with an average thickness of 60 m. Figure 32 shows the location of three open cast mines between Hirschau and Schnaittenbach. Two of the three mines in this area are operated by AKW. The kaolinite bearing arkoses are confined by Keuper sediments in the north and Permian sediments as well as the basement complex in the south.
The average kaolinite content of the soil varies between 10 and 25 % from west to east. Quartz is the most abundant mineral with about 80 % of the soil. Mica and heavy minerals are also represented.
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6.4.3 Measurement setup

Seven samples with varying iron and potassium content were measured. The Fe$_2$O$_3$ content showed little variation from 0.048 % to 0.145 %, whereas the K$_2$O content showed greater variations from 0.10 % up to 4.41 %. The LIF measurements were performed on milled material with a grain size of about 2 mm. Therefore, homogeneity of the samples was much higher.

Figure 32: Geology of Kaolinite Mine Hirschau-Schnaittenbach, after KROLL & BORCHERT, 1969
6 Results

Table 10: Kaolinite samples from Hirschau mine

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sample identification</th>
<th>Fe₂O₃ [%]</th>
<th>K₂O [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S.W. P1</td>
<td>0.048</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>S.H. 1540</td>
<td>0.145</td>
<td>0.60</td>
</tr>
<tr>
<td>3</td>
<td>H.W. SO</td>
<td>0.080</td>
<td>4.09</td>
</tr>
<tr>
<td>4</td>
<td>S.H. 1530</td>
<td>0.134</td>
<td>2.68</td>
</tr>
<tr>
<td>5</td>
<td>S.O1. U</td>
<td>0.114</td>
<td>3.51</td>
</tr>
<tr>
<td>6</td>
<td>S.O1. O</td>
<td>0.099</td>
<td>4.41</td>
</tr>
<tr>
<td>7</td>
<td>S.H. 1550</td>
<td>0.129</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 33 shows six of the seven samples, no photo was taken of sample S.H. 1530. One can easily see the high homogeneity of the samples as well as the similarity between each other. A distinction of the samples by eye is difficult.

![Sample Images](image1.png)

**Figure 33: Kaolinite samples from Amberger Kaolin Werke**

Test measurements showed best suitability of the following measurement parameters:
6 Results

Table 11: Measurement parameters for kaolinite samples from Hirschau mine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>266 nm</td>
</tr>
<tr>
<td>Laser current</td>
<td>102 Ampère</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Pre-shots</td>
<td>1000</td>
</tr>
<tr>
<td>Measurement shots</td>
<td>1000</td>
</tr>
<tr>
<td>PMT Voltage</td>
<td>1050 Volt</td>
</tr>
<tr>
<td>Detected wavelengths</td>
<td>320 - 480 nm</td>
</tr>
<tr>
<td>Measurement times:</td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>-5 to 30 ns</td>
</tr>
<tr>
<td>W2</td>
<td>30 to 75 ns</td>
</tr>
<tr>
<td>W3</td>
<td>-50 to 230 ns</td>
</tr>
<tr>
<td>Sample distance</td>
<td>2.33 m</td>
</tr>
</tbody>
</table>

1,000 pre-shots and 1,000 measurement shots were fired at the material at 20 Hz repetition rate. Emission wavelengths as well as measurement times correspond to those used for the lignite measurement setup. Measurements on the homogeneity of the samples were carried out for two wavelengths, i.e. 320 and 480 nm. For these measurements the samples were measured for three times and stirred in between.

6.4.4 Fluorescence measurements

Fluorescence of all samples was measured for three different time integrals, i.e. W1, W2 and W3. The spectra for peak fluorescence (W1) is shown in Figure 34. Compared to the spectra of the lignite samples, average fluorescence over the complete spectra is higher. Especially at 320 nm fluorescence readings reach very high values from 20,000 to 35,000. On the other hand, minimum fluorescence at 380 nm resemble the measurements on lignite and associated waste rocks. Nonetheless, with values around 10,000 fluorescence at
6 Results

380 nm is still very high compared to the background. This interrelationship is supported by the low standard deviation over the complete spectra as illustrated in Figure 35. Except for samples S.H. 1530 and S.W. P1 standard deviation is below 5 % over the complete spectra.

![Fluorescence spectra of kaolinite samples during W1](image)

**Figure 34: Fluorescence spectra of kaolinite samples during W1**

![Standard deviation of fluorescence measurements for kaolinite samples during W1](image)

**Figure 35: Standard deviation of fluorescence measurements for kaolinite samples during W1**
6 Results

The decay behaviour, i.e. fluorescence from 30 to 75 ns (W2) is illustrated in Figure 36. Again, readings at 320 nm show very high values, but also at 400 nm fluorescence shows a peak. On average, decay fluorescence reaches about 25 % of the peak fluorescence measured during W1, which is significantly high compared to the decay fluorescence of the lignite samples. High decay fluorescence is especially shown by those samples, which possess high potassium content.

As average fluorescence during W2 is lower than during W1, standard deviation is slightly higher (compare Figure 37). Nonetheless standard deviation rarely exceeds 10 %.

![Figure 36: Fluorescence spectra of kaolinite samples during W2](image)

Figure 36: Fluorescence spectra of kaolinite samples during W2
6 Results

Figure 37: Standard deviation of fluorescence measurements for kaolinite samples during W2

Finally, total fluorescence during W3 as illustrated in Figure 38 shows an overlay of peak and decay fluorescence. Readings are high over the complete spectra and show peaks at 320 and 400 nm. Minima are reached at 380 and 480 nm. Standard deviation is below 5 % for most of the samples.

Figure 38: Fluorescence spectra of kaolinite samples during W3
For correlation between the fluorescence measurements and the critical quality parameter, ratios between either wavelengths or time integrals can be used. The temporal behaviour of the fluorescence is shown in the following graph (Figure 40). Herein, fluorescence of the two samples with lowest and highest potassium content is plotted over time, respectively. The three measured time integrals (W1, W2 and W3) are also labelled. While fluorescence during W1 shows high similarity for both samples, the intensity shows great differences in the decay behaviour. The sample with high K₂O still shows remarkable fluorescence at the end of time integral W3. This illustrates once more the importance of wavelength and time based measurements.
6 Results

Figure 40: Temporal fluorescence behaviour of kaolinite samples with different potassium content

Figure 41 shows the ratio of total fluorescence (W3) over peak fluorescence (W1) for the complete spectra. As one can see increase in fluorescence correlates well with increase in potassium content. Especially around 400 nm emission wavelength, the samples with high potassium content exhibit very high ratios between 2.5 and 3.0. As potassium contents get lower, fluorescence also decreases and falls below 1.5. This behaviour can be related to the influence of potassium on the decay fluorescence. Samples with high potassium contents show high fluorescence in the decay time - leading to a total fluorescence almost three times as high as peak fluorescence. Low potassium samples, on the other hand, only fluoresce shortly after the excitation and decay quickly.
The correlation between selected fluorescence parameters and the critical quality parameters, i.e. iron and potassium content, is described in the following. The corresponding ratios were picked with the aid of a correlation matrix, which calculates the correlation coefficients between wavelength and time ratios and the quality parameters.

Regarding the potassium content, the wavelength ratio 400 nm/420 nm at W3 turned out to be most useful. It varies from 1 for 0.10 % K₂O to 1.5 for 4.41 % K₂O. The correlation coefficient \( R^2 \) with 0.99 shows, that the wavelength ratio can be perfectly used for quality control.

Looking at the iron content, correlation is not as good (compare Figure 43). Here, the ratio 320 nm/420 nm at W3 turned out to be most useful. Although \( R^2 \) only reaches 0.62, a significant increase in fluorescence with increasing Fe₂O₃ can still be found. Also one has to keep in mind, that the variation of the iron content is very low compared to the potassium content. Measurement of additional samples with higher Fe₂O₃ content could increase correlation.
6 Results

**Figure 42**: Correlation between fluorescence ratio and potassium content for kaolinite samples

**Figure 43**: Correlation between fluorescence ratio and iron content for kaolinite samples

Measurements on the homogeneity of the samples are shown in the next graph (Figure 44) for 320 nm. As described earlier, for these
6 Results

measurements the samples were measured three times with 1,000 shots each and stirred in between. One can see the high homogeneity of the samples. Only sample S.01. O shows slightly higher variations.

Measurements on homogeneity at 320 nm
W1 [-5 to 30 ns]

Figure 44: Homogeneity of kaolinite samples

6.4.5 Suitability

Especially for the measuring of the potassium content, LIF shows very good correlation between selected emission wavelengths and the K\textsubscript{2}O content. A correlation between the fluorescence and the iron content, on the other hand, turned out to be more difficult. Here, the correlation coefficient R\textsuperscript{2} only reached 0.62 – not least due to the small variations of the investigated samples. Further data on the kaolinite samples is given in appendix 4.

6.5 Other raw materials

Beside the measurement on lignite, lamphroitic rocks and kaolinite, further measurements have been performed and will be presented in a consolidated form.
6 Results

Rock salt

Samples of mine Werra (operated by Kali+Salz AG) close to the village of Hattingen were measured focusing on the distinction between halite (NaCl) and sylvite (KCl) and recognition of clay layers. Whereas the latter could be achieved by LIF, the different salts showed no characteristic fluorescence and could not be separated. It was concluded that LIF is not suited for application in the mine investigated. Further data is given in appendix 5.

Limestone

Samples from limestone mines Rohdenhaus and Donnerkuhle (operated by Rheinkalk GmbH & Co. KG) were measured with focus on aluminium, iron and magnesium contents. For the Rohdenhaus mine, samples with contents smaller than 1.4 % Al₂O₃ and 0.4 % Fe₂O₃ were measured but showed low correlation to fluorescence characteristics. At the Donnerkuhle mine, correlation between MgO and Fe₂O₃ with fluorescence showed better results. The following table shows the results for different parameters:

Table 12: Results of correlation of fluorescence signals to selected quality parameter of limestone mines Rohdenhaus and Donnerkuhle

<table>
<thead>
<tr>
<th>Mine</th>
<th>Parameter</th>
<th>Content [weight %]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rohdenhaus</td>
<td>Fe₂O₃</td>
<td>0.05 – 0.36</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>0.03 – 1.34</td>
<td>0.54</td>
</tr>
<tr>
<td>Donnerkuhle</td>
<td>MgO</td>
<td>2.09 – 20.40</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>0.22 – 1.50</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Further data on the limestone samples is given in appendix 6.

Gypsum

In cooperation with Knauf Gips KG milled samples from mine Hüttenheim were measured. Beside gypsum and anhydrite content, also
calcite, magnesite, sodium, potassium and clay content was investigated regarding the influence on the fluorescence signals. The following table gives an overview of the investigated parameter and reached correlation coefficients:

Table 13: Results of correlation of fluorescence signals to selected quality parameter of gypsum mine Hüttenheim

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Content [weight %]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum [CaSO₄·2H₂O]</td>
<td>9.60 – 74.10</td>
<td>0.69</td>
</tr>
<tr>
<td>Anhydrite [CaSO₄]</td>
<td>0.10 – 81.20</td>
<td>0.93</td>
</tr>
<tr>
<td>Calcite [CaCO₃]</td>
<td>1.60 – 19.10</td>
<td>0.92</td>
</tr>
<tr>
<td>Magnesite [MgCO₃]</td>
<td>1.30 – 16.30</td>
<td>0.75</td>
</tr>
<tr>
<td>Sodium oxide [Na₂O]</td>
<td>0.03 – 0.11</td>
<td>0.85</td>
</tr>
<tr>
<td>Potassium Oxide [K₂O]</td>
<td>0.04 – 0.16</td>
<td>0.77</td>
</tr>
<tr>
<td>Clay</td>
<td>0.80 – 15.80</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Note the comparable high correlation coefficients for sodium and potassium oxide, although the contents are very low. This reflects the lower variations of the excitation device of the desktop fluorescence spectrometer compared to the LIF-Analyser. Further data on the gypsum samples is given in appendix 7.

Coal

Five samples of Deutsche Steinkohle AG were measured to investigate distinction of coal and waste rocks [VIN-06A]. Especially the decay behaviour of coal shows great differences from those of the waste rocks, as the coal emits fluorescence over much longer time. Figure 45 shows fluorescence spectra during W2 for coal and waste rock samples. Note that fluorescence readings are scaled, i.e. relative to highest fluorescence reading during W3 (total fluorescence). While
host rocks emit less than 5 % of the fluorescence during W2, the coal sample emits between 10 and 23 % of the fluorescence.

Figure 45: Fluorescence spectra of coal and associated waste rocks

Dark plastics

Due to increase of the recycling quotes and problems with sorting of dark plastics, suitability of LIF for different types of plastic was studied [SAN-05, VIN-06B]. While coloured plastics can be separated easily by standard NIR (near infrared), high absorption of black plastics inhibit successful recognition. Samples consisting of polyamide, polypropylene/ethylene, styrene and polyvinyl chloride were measured. Figure 46 depicts fluorescence spectra of different plastic types. Especially longer emission wavelengths between 400 and 480 nm are suited for recognition of the material as large differences in intensity in combination with small standard deviation can be measured. Note that a slightly different time integral was used for this measurements. Using suited classification parameters, correct separation of the samples could be achieved.
Figure 46: Fluorescence spectra of black plastic samples
7 How to apply LIF in the mine

Guidance given in this chapter should allow the reader to evaluate the suitability of LIF for the special situation in the particular mine. Furthermore, hints for successful setup of test measurements are given. However, all remarks given here assume the application of LIF for sorting of already mined material. From the experience of the author, application of LIF on mining machines such as shearer loader, bucket wheel excavators or continuous miners is much more complex and consequently installation over conveyor belts should be preferred. Nonetheless, most of the problems discussed here could be transferred to application on mining machines.

7.1 Economical considerations

Economical considerations are crucial for application of LIF. It is important to notice that LIF for mining applications is not available as an “out of the shelf” technology. Consequently, to date LIF Sensors are individual items for each mine. If the sorting task important for the mine in question can be solved with an established technology such as X-ray ore optical sensors, those should be used. LIF is an option where conventional technologies fail. Calculation of the individual benefit by better sorting is always necessary – one should just keep in mind that even a simple LIF device costs at least 0.1 Mio. €. If a more complex system is needed, costs can rise up to 0.25 Mio. €. A detailed financial evaluation is given by [RIE-02]. Based on an intermediate complex LIF system (175,000 €), annual operating and maintenance costs of 15,000 € and a lifetime of the whole system of five years, total cost sum up to approx. 250,000 € (assuming an annual interest rate of 15 %). Consequently an annual sorting benefit of at least 50,000 € has to be generated to justify investing in a LIF system. Especially the estimated benefit of sorting necessary reflects
7 How to apply LIF in the mine

current costs of a LIF system. If component costs decrease in the future, this number could get much lower.

As a first and very simplified estimate, the following flowchart could be used to judge general applicability of a LIF system in a mine.

![Flowchart](image)

Figure 47: Simplified flow chart for evaluation of LIF as a suited sorting device
Also desired accuracy of the LIF measurements plays an important role. From results presented in this thesis, determination of differences in mineral contents lower than 0.1% are hard to realise. Besides installation costs, running costs will be generated for the flash lamps of the lasers. These normally last about 20 Mio. shots and have to be replaced more or less frequently depending on measurement frequency used.

### 7.2 Setup of test measurements

Several steps are necessary for successful testing. First, representative samples have to be picked and either classified (for material distinction) or chemically analysed in the lab (for quality control). Then the following parameter have to be investigated:

- Laser type (flash lamp or diode pumped)
- Laser energy
- PMT type and emission wavelengths
- PMT Voltage
- Dimension of time integrals
- Beam diameter
- Heterogeneity of the samples
- Influence of water content on samples

The type of laser chosen mainly depends on desired measurement frequency and environmental conditions, especially vibrations. Diode pumped lasers show longer lifetime of the pumping device, whereas flash-lamp pumped lasers are less sensitive against vibrations. As many laser producer supply military vibration tests are quite common. For example, BIGSKYLASER perform vibration tests with acceleration up to 7g for frequencies ranging from 20 to 2000 Hz for one hour per axis.
7 How to apply LIF in the mine

The laser energy needed mainly depends on the beam diameter as well as needed measurement frequency. The beam diameter in turn depends on size and heterogeneity of the samples. If sand grain sized samples have to be studied, a beam diameter of 1 cm will cover a representative area. On the other hand, measurements on several cm sized material need a larger beam diameter and therefore laser energy. The measurement frequency is a function of belt velocity and desired resolution over time. If single particles have to be measured at high belt velocities, highest measurement frequencies are needed. If composition of the measured material changes more slowly, lower measurement frequencies can be used. As Figure 48 illustrates, measurement frequency and laser energy show a negative correlation.

![Frequency and energy of pulsed lasers](image)

**Figure 48: Energy and frequency of common lasers**

The laser used in this thesis, a diode pumped DIVA II by Thales, has very low energy and uses a beam diameter of roughly 2 cm. This is high enough to generate fluorescence in the most materials under lab and field conditions for distances up to 5 m. As really high distances should seldom be necessary, need for higher energy mainly comes...
from greater beam diameters. For example, if the measurement spot on the material should be 10 cm in diameter with the same energy per area as the laser used here, 50 mJ of laser energy are needed.

Also maintenance intervals for the flash lamps should not be underestimated. If a continuous operation and higher measurement frequencies are desired, replacement of the flash lamps have to occur every month or even more often. In that case diode pumped lasers should be used, which have much longer lifetime but higher initial cost and higher sensitivity against vibrations. The following Figure 49 gives an overview about maintenance intervals at different measurement frequencies for the lasers shown in Figure 48. The flash lamp pumped lasers form BIGSKYLASER, for example, need replacement of the flash lamp every 12 days at 20 Hz frequency, which is not acceptable for practical use. As a rule of thump one should keep in mind that flash lamp lasers should be used for low frequencies and rough environment, whereas diode lasers are advantageous when high frequencies are necessary.

![Maintenance intervals for different lasers and 24/7 operation](image)

Figure 49: Lifetime of pump devices for common lasers
To determine the most suited emission wavelengths a photomultiplier with different filters should be used. Emission wavelength between 320 and 480 nm turned out to be most suited as lower wavelengths are influenced by reflectance and longer wavelengths by air humidity. As shown in chapter 3.3, at least two emission wavelengths should be used to use ratios and thereby compensate for fluctuations of laser energy or influence of disturbing factors. If sample distinction can be carried out by using only two or three different wavelength, one PMT in combination with the particular optical filters should be used. If more wavelengths are necessary, a multi-wavelengths PMT, which has several optical filters installed on a matrix, could be preferable.

Voltage of the photomultipliers should be calibrated in such way, that the highest fluorescence measured shows no overamplification and low fluorescing samples still show sufficient intensity. If lowest possible PMT voltage still leads to overamplification of the signals, attenuator filter could be installed in front of the PMT.

Time integrals have to be chosen depending on the fluorescence behaviour of the measured material. Interpretation of the temporal behaviour like shown in Figure 40 allows selection of the suited time integrals. One time integral each should represent peak fluorescence and decay fluorescence, respectively. A third time integral could either represent further decay behaviour or total fluorescence. In cases where fluorescence spectra (i.e. fluorescence at different wavelengths) are too similar for distinction of the materials, further time integrals could become necessary. However, in most cases a combination of three time integrals and two or more emission wavelengths will be sufficient to distinguish the materials.

Choice of the suited beam diameter depends on various parameters. Higher grain sizes as well as higher heterogeneity of the material lead to higher beam diameters. On the other hand, if single particle measurements are not aspired, movement of the belt allows representative measurement even with comparable low beam diameters. As all la-
How to apply LIF in the mine

Lasers show divergence of the beam, in general higher distances lead to greater beam diameters. Common lasers show divergence between 0.75 and 7 mrad. At a distance between laser and measured material of 3 m this leads to beam diameters between 0.2 and 2.1 cm. Consequently, for many applications an optical setup for widening of the beam to a defined and distance independent diameter will be necessary. If a straight laser to sample beam can be realised, a simple setup with one widening and one parallelizing lens can be arranged.

Heterogeneity of the material can be investigated with a sample setup on a rotary table compared to those described in chapter 6.3.3. Higher heterogeneity of the material indicate that moving averages should be used in practical application – material recognition based on only few measurements is not possible in that case. Measurements of the fluorescence characteristics of the conveyor belt material should also be carried out to avoid misinterpretation of fluorescence signals.

7.3 Aspects of machine requirements

If detailed testing as discussed previously showed that LIF is suited for the sorting task, correct technical layout is the next step for successful implementation. Several aspects have to be considered:

- Capsulation of the system
- Cooling
- Threshold limit value (TLV) and explosion prevention
- Measures against dust
- Accessibility for maintenance and calibration
- Integration into mine processes

As the laser as well as the optical components for beamguide and receiving units are sensitive against dust and humidity, airtight capsulation of the complete system is a must. In an ideal setup, only an
How to apply LIF in the mine

optical interface like a hardened window should have direct contact to the working environment of the mine.

Although lasers can be operated at temperatures between 10 and 40°C (with special cooling liquids -10 to 50°C), the other components such as lenses and mirrors as well as PMT are more vulnerable to variations in temperature. Additionally, as operation of the electrical devices causes heating, cooling of the complete system is not only needed to avoid variations in temperature, but also for evacuation of the heat generated.

UV-lasers like the ones used for LIF are rated class 4, which means that they could cause serious harm for eye and skin. If capsulation of the LIF-system is not possible or explosion prevention has to be considered, layout of laser energy and beam diameter is crucial. Two limits have to be considered – the threshold limit value (TLV) and explosion prevention. The TLV is limited to 30 J/m² whereas the limit for explosion prevention is set to 100 J/m². Typical laser energies for LIF-laser are in the range of 2 to 170 mJ. Even low energy is capable of inducing detectable fluorescence measurements. The following example shows correct layout of laser beam:

A laser with 20 mJ energy is chosen for a LIF sensor. The lowest possible beam diameter is then calculated as:

\[ d_{min} = 2 \cdot \sqrt{\frac{20mJ}{TLV \cdot \pi}} = 2 \cdot \sqrt{\frac{20mJm^2}{30000mJ \cdot \pi}} = 2.9cm \]

To comply with TLV the laser diameter should not fall below 3 cm – which usually gives sufficient resolution. If smaller diameters are aspired, one could either choose lasers with lower energy or equip the operating staff with safety goggles. The limiting value then would be the one for explosion prevention (100 J/m²).

If capsulation of the system is implemented as described before, only windows for transmission of the emitted laser beam and the received fluorescence have direct contact to the working environment of the
7 How to apply LIF in the mine

mine. The most important measure then is to avoid accumulation of dust on the windows. If possible, one should use gravity, meaning installation of the LIF system over the conveyor belt should be aspired. Active defence against dust can be achieved with a fan or compressed air parallel to the laser beam. If compressed air is used, it is very important to use oil free air, otherwise fluorescence of the oil spray will influence the measurements.

As LIF systems need replacement of the pumping device (flash lamp or diode) and for calibration purposes, accessibility of the system has to be assured. The most critical parameter which will change over time as the pumping device ages is the laser energy. Some laser manufacturer offer onboard energy measurement which allows continuous recording of the pulse to pulse energy variations. To control correct calibration of the whole system, fluorescence measurements on calibration samples should be carried out at regular intervals. In lack of special fluorescence calibration standards, which are up to date only available in liquid form, a typical ore or waste rock from the mine could be used. As an alternative, successfully tested during this work, a standard ceramic sample (better known as coffee cup) can also be used. This has the advantage of a very homogenous and resistant surface which shows no alteration over time. To check functionality of all receiving filters and PMT respectively, the total fluorescence spectra should be recorded during setup and checked whilst calibration. Important parameter such as sample distance, brightness of the surrounding and humidity have to be the same for each calibration. Also standard cleaning of the samples as well as the transmitting window with an organic solvent (i.e. iso-propanol) followed by a defined time interval for evaporation of the cleaning liquid should be carried out each time.

After conditions for successful installation are met, integration of the LIF system is necessary. To increase lifetime of the pumping device, operation of the laser should be connected to the conveyor belt. In
that way the laser can shut down if the conveyor belt halts and vice versa. An important topic to consider is warming of the laser, i.e. laser energy only rises to the operation level after a certain amount of shots fired. Consequently, after restart of the system, measurements can be used only after the desired energy level has been reached. The number of shots needed for warm-up of the laser from stand-by mode is laser specific but should be in the range of a hundred shots. If loading of the belt varies and leads to different distances between the LIF-system and the material measured, the optical system should be calibrated in that way, that at minimum and maximum distance fluorescence signals show similar values. In extreme cases, a correction factor based on the sample distance has to be used. Measurement of the sample distance is also useful for safety aspects – excess of a limit value can be used to shut down the laser.
The suitability of laserinduced fluorescence as a mining sensor has been studied in this thesis. Laserinduced fluorescence is a long known phenomenon, which finds main applications in combustion analysis and medicine. Utilisation of LIF on minerals is based on a fingerprinting approach, meaning that calibration of the system to the minerals which have to be sorted is always necessary.

Over a three year period, measurements on different raw materials have been performed as well as investigations on disturbance factors. Additionally, concepts for testing and application have been developed. Principally, two different type of tasks can be carried out with LIF. One is the separation of material groups, the other is a quantitative correlation between fluorescence characteristics and mineral contents. For the first type, usage of classification systems such as support vector machines is advised, if a large number of different materials has to be separated. In other cases, where only two or three groups are to be distinguished, choice of suited fluorescence wavelength can normally be carried out by hand.

For the quantitative correlation of fluorescence to mineral contents, several samples with known mineralogical composition have to be measured and a correlation between certain wavelength ratios and the desired mineral has to be established.

For both applications, though, detailed testing and technical layout is a must for successful implementation.

The great advantages of LIF are on the one hand the high information content, based on the combination of wavelength and time resolved measurements. On the other hand, LIF shows only little sensitivity to disturbance factors such as dust and moisture compared to other optical sensors in the visible spectra. As disadvantages, LIF is not
Conclusions

well established in the mining industry and has to be setup for each application. Although central components needed for a LIF system are available from different manufacturers, only few companies offer complete LIF systems. Also integration of a LIF system in the mining environment is technically complex and costly. Consequently, LIF should only be considered, if more established sensor systems can not solve the sorting task in question. Notwithstanding the discussed limitations and challenges, the results presented in this thesis clearly document the suitability of LIF for different sorting tasks in the mining industry. Especially for the case of lignite and associated waste rocks, sorting of a large number of materials with LIF resulted in high recognition results which have to be challenged by other sensor systems.

Future developments and applicability of LIF systems in the mining industry strongly depend on advancement of the laser as well as optical systems.
9 Zusammenfassung


Messungen an verschiedenen Rohstoffen sowie Untersuchungen von im Bergbau typischen Störgrößen wurden durchgeführt. Im Rahmen der Arbeit werden Messungen an Braunkohle und Nebengesteinsproben, diamantführenden vulkanischen Gesteinen sowie an Kaoliniten detailliert dargestellt. Die Untersuchungsergebnisse weiterer Rohstoffe werden in komprimierter Form wiedergegeben.


Zur quantitativen Korrelation der LIF-Messungen zu Mineralgehalten ist eine Kalibrierung an Referenzproben mit bekannten Mineralgehalten notwendig – hier liegt der Fokus auf der Auswahl weniger Para-
meter, die dann durch Quotientenbildung eine stabile Korrelation zum gesuchten Mineralgehalt ermöglichen.

Vor dem Einsatz der LIF sind in beiden Fällen detaillierte Voruntersuchungen sowie eine genaue Auseinandersetzung mit der technischen Realisierung notwendig, da LIF-Systeme bis heute nur als Prototypen verfügbar sind und dementsprechend für die jeweilige Anwendung ausgelegt werden müssen.


Nichtsdestotrotz zeigen die in dieser Arbeit präsentierten Untersuchungen, dass für viele Rohstoffe eine Unterscheidung in Materialgruppen bzw. Korrelation mittels LIF möglich ist – gerade die hohe Erfolgsquote bei der Unterscheidung der Braunkohlen- und Nebengesteinsproben dokumentiert das große Potential der laserinduzierten Fluoreszenz. Die weitere Entwicklung der LIF im Bereich der Bergbauanwendungen wird im Wesentlichen von der weiteren Ertüchtigung
9 Zusammenfassung

der Laser und optischen Komponenten für den Einsatz in rauen Arbeitsumgebungen abhängen.
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Appendix

A1  Technical Data of LIF-Analyser
A2  Further Data on Lignite and Waste Rock Samples
A3  Further Data on Diamond bearing Rock Samples
A4  Further Data on Kaolinite Samples
A5  Further Data on Evaporate Samples
A6  Further Data on Limestone Samples
A7  Further Data on Gypsum Samples
A1 Technical Data of LIF-Analyser

LIF-Analyser

**ohne Beine**
Abmessungen BxHxT (mm) 1200 x 1100 x 1000
Raumbedarf BxHxT (mm) 1200 x 1100 x 1000
Gewicht (kg) ca. 240 kg

**mit Beinen**
Abmessungen BxHxT (mm) 1330 x 2185 x 1000
Raumbedarf BxHxT (mm) 1330 x 2185 x 1000
Gewicht (kg) ca. 320 kg

Werkstoff, Gehäuse und Beine Stahl, rostfrei, blank
Werkstoff, Scanner-Meßkopf Stahl und Aluminium, elox.
Energieversorgung über den Steuerschrank
Schutzart IP 54
Umgebungstemperatur +5 °C bis +40 °C
Luftfeuchtigkeit 10 % bis 75%

Power Unit

Hersteller Rittal
Typ Kompakt-Schaltschrank
Modell 1648.600
Abmessungen BxHxT (mm) 800 x 1200 x 400
Raumbedarf BxHxT (mm) 1200 x 1200
Werkstoff Stahl lackiert
Gewicht ca. 200 kg
Energieversorgung 1x230 V / N / PE / 50 Hz
Sicherung der Zuleitung max. 16 A
Schutzart IP 54
Umgebungstemperatur +5 °C bis +40 °C
Luftfeuchtigkeit 10 % bis 75%
### A1 Technical Data of LIF-Analyser

#### Cooling Unit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
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</thead>
<tbody>
<tr>
<td><strong>Hersteller</strong></td>
<td>Rittal</td>
</tr>
<tr>
<td><strong>Typ</strong></td>
<td>Dachaufbau-Kühlgerät</td>
</tr>
<tr>
<td><strong>Modell</strong></td>
<td>SK-3290.100</td>
</tr>
<tr>
<td><strong>Abmessungen BxHxT (mm)</strong></td>
<td>600 x 400 x 430</td>
</tr>
<tr>
<td><strong>Raumbedarf BxHxT (mm)</strong></td>
<td>800 x 600 x 600</td>
</tr>
<tr>
<td><strong>Werkstoff</strong></td>
<td>Stahl lackiert</td>
</tr>
<tr>
<td><strong>Gewicht</strong></td>
<td>ca. 45 kg</td>
</tr>
<tr>
<td><strong>Energieversorgung</strong></td>
<td>1x230 V / N / PE / 50/60 Hz</td>
</tr>
<tr>
<td><strong>Sicherung der Zuleitung</strong></td>
<td>max. 6 A T</td>
</tr>
<tr>
<td><strong>Kühlleistung</strong></td>
<td>1060 W</td>
</tr>
<tr>
<td><strong>Temperaturbereich</strong></td>
<td>+20° bis +55° C</td>
</tr>
<tr>
<td><strong>Schutzart</strong></td>
<td>IP 54</td>
</tr>
<tr>
<td><strong>Umgebungstemperatur</strong></td>
<td>+5 °C bis +35 °C</td>
</tr>
<tr>
<td><strong>Luftfeuchtigkeit</strong></td>
<td>10 % bis 75%</td>
</tr>
</tbody>
</table>
A1  Technical Data of LIF-Analyser

Mechanical Drawing

(1) and (2) Laser

(3) and (4) optical Components
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 1a, 1b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Intensität [rel. Einheiten]

Wellenlänge [nm]

Löß, trocken
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 2a, 2b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Löß, nass
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 3a, 3b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Sand, trocken

Wellenlänge [nm]

Intensität [rel. Einheiten]

- W1-3A
- W2-3A
- W3-3A
- W1-3B
- W2-3B
- W3-3B

3a 3b
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 4a, 4b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Sand, nass

Wellenlänge [nm] | Intensität [rel. Einheiten]
---|---
300 | 0
350 | 2000
400 | 4000
450 | 6000
500 | 8000
550 | 10000
600 | 12000
650 | 14000

-W1-4A | -W2-4A | -W3-4A
-W1-4B | -W2-4B | -W3-4B
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 5a, 5b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Intensität [rel. Einheiten]
Wellenlänge [nm]

Sand, trocken
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 6a, 6b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Intensität [rel. Einheiten]

Wellenlänge [nm]

Sand, nass
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 7a, 7b

266 nm Anregungswellenlänge

Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kohle mit Holzfasern
Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 8a, 8b

266 nm Anregungswellenlänge

Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kohle
Fluoreszenzspektrum Proben 9a, 9b

266 nm Anregungswellenlänge

Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kohle, Zwischenmittel
Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 10a, 10b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 11a, 11b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Ton, für Abdichtungen geeignet
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Probe 12
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kohlenstaub

12
Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 13a, 13b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Versauerungsempfindlicher Abraum mit einem Schwefelgehalt > 0.2 %
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 14a, 14b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kies hell

Wellenlänge [nm]

Intensität [rel. Einheiten]
A2 Further Data on Lignite and Waste Rock Samples

Fluoreszenzspektrum Proben 15a, 15b
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Kies dunkel (durch erhöhten Eisengehalt)
A2 Further Data on Lignite and Waste Rock Samples

Results of Support Vector Machine Material Recognition

**Training Data: B Samples, Blind Data: A Samples**

SVM Kernel: **linear**, C=32, G=0.03125, Success: 86.9%

**Training Data: B Samples, Blind Data: A Samples**

SVM Kernel: **polynomial**, C=32, G=0.03125, Success: 84.1%
A2 Further Data on Lignite and Waste Rock Samples

Training Data: B Samples, Blind Data: A Samples
SVM Kernel: RBF, C=32, G=0.03125, Success: 88.3%

Training Data: B Samples, Blind Data: A Samples
SVM Kernel: sigmoid, C=32, G=0.03125, Success: 88.2%

Measurement No. [-] Sample ID [-]
A2 Further Data on Lignite and Waste Rock Samples

Training Data: A Samples, Blind Data: B Samples
SVM Kernel: linear, $C=32$, $G=32$, Success: 67.4%

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Loess (dry)</td>
</tr>
<tr>
<td>2</td>
<td>Loess (wet)</td>
</tr>
<tr>
<td>3</td>
<td>Sand (dry)</td>
</tr>
<tr>
<td>4</td>
<td>Sand (wet)</td>
</tr>
<tr>
<td>5</td>
<td>Sand (dry)</td>
</tr>
<tr>
<td>6</td>
<td>Sand (wet)</td>
</tr>
<tr>
<td>7</td>
<td>Lignite with wood layers</td>
</tr>
<tr>
<td>8</td>
<td>Lignite</td>
</tr>
<tr>
<td>9</td>
<td>Lignite with soil layers</td>
</tr>
<tr>
<td>10</td>
<td>Clay</td>
</tr>
<tr>
<td>11</td>
<td>Clay (used for sealing)</td>
</tr>
<tr>
<td>12</td>
<td>Tailings (sulphur content &gt; 0.2%)</td>
</tr>
<tr>
<td>13</td>
<td>Gravel (bright)</td>
</tr>
<tr>
<td>14</td>
<td>Gravel (dark, iron rich)</td>
</tr>
</tbody>
</table>

Training Data: A Samples, Blind Data: B Samples
SVM Kernel: polynomial, $C=32$, $G=32$, Success: 46.4%
A2 Further Data on Lignite and Waste Rock Samples

Training Data: A Samples, Blind Data: B Samples
SVM Kernel: RBF, C=32, G=32, Success: 64.3 %

Sample ID: [1 Loess (dry), 2 Loess (wet), 3 Sand (dry), 4 Sand (wet), 5 Sand (dry), 6 Sand (wet), 7 Lignite with wood layers, 8 Lignite, 9 Lignite with soil layers, 10 Clay, 11 Clay (used for sealing), 13 Tailings (sulphur content > 0.2%), 14 Gravel (bright), 15 Gravel (dark, iron rich)]

Training Data: A Samples, Blind Data: B Samples
SVM Kernel: sigmoid, C=32, G=32, Success: 71.1 %

Sample ID: [1 Loess (dry), 2 Loess (wet), 3 Sand (dry), 4 Sand (wet), 5 Sand (dry), 6 Sand (wet), 7 Lignite with wood layers, 8 Lignite, 9 Lignite with soil layers, 10 Clay, 11 Clay (used for sealing), 13 Tailings (sulphur content > 0.2%), 14 Gravel (bright), 15 Gravel (dark, iron rich)]
A3  Further Data on Diamond bearing Rock Samples

Ratio L1 - 266 nm
a365 nm/a440 nm vs. a365 nm/a500 nm

Ratio L1 - 266 nm
a365 nm/a440 nm vs. a365 nm/a532 nm
A3 Further Data on Diamond bearing Rock Samples

Ratio L1 - 266 nm
a365 nm/a500 nm vs. a365 nm/a532 nm

- NSL
- PV S
- SL

a365/a532 vs. a365/a500

waste

a365/a500 vs. a365/a532
Fluoreszenzspektrum Probe H.W. SO
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,08 %
K₂O: 4,09 %

Fluoreszenzspektrum Probe S.W. P1
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,048 %
K₂O: 0,1 %
**Fluoreszenzspektrum Probe S.O1. O**

266 nm Anregungswellenlänge

Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,099 %
K₂O: 4,41 %

**Fluoreszenzspektrum Probe S.H. 1540**

266 nm Anregungswellenlänge

Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,145 %
K₂O: 0,6 %
Further Data on Kaolinite Samples

Fluoreszenzspektrum Probe S.H. 1550
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,129 %
K₂O: 1,04 %

Fluoreszenzspektrum Probe S.O1. U
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

Fe₂O₃: 0,129 %
K₂O: 1,04 %
A4 Further Data on Kaolinite Samples

Fluoreszenzspektrum Probe S.H. 1530
266 nm Anregungswellenlänge
Integrationszeitraum W1: -5 bis 30 ns; W2: 30 bis 75 ns; W3: -50 bis 230 ns

FeO: 0,134 %
K2O: 2,68 %
Homogeneity of the samples

A4  Further Data on Kaolinite Samples
Wiederholungsmessungen an den untersuchten Proben bei 640 nm Emissionswellenlänge
Zeitintegral W1 (-5 bis 30 ns)
Anregung bei 266 nm

Intensity (rel. Einheiten)

640 nm Messung 1
640 nm Messung 2
640 nm Messung 3


A5  Further Data on Evaporate Samples

Samples of Seam Hessen
A5  Further Data on Evaporate Samples

Probe H III
Oberes Werrasteinsalz (Na 1 γ)
Tonlöser
Steinsalzbänke

Probe H IV
Wurmpartie
A5 Further Data on Evaporate Samples

Probe H V
Oberes Wernekeinsalz Na 1 γ
Tonlöser
Steinsalzbänke

Probe H VI
Flockensalz
A5  Further Data on Evaporate Samples

Probe II VII Wurmstufe

Probe II VIII Wurmstufe
A5  Further Data on Evaporate Samples

Samples of Seam Thüringen

Probe Th I
unteres Werrasteinsalz (Na 1 α)

Probe Th II
Obere kieseritreiche Gruppe
Further Data on Evaporate Samples

Probe Th III
Trümmerkarnallitit
Steinsalzleitbank 3

Probe Th IV
Mittderes Werrasteinsalz (Na 1 β)
Trümmerkarnallitit
Oder Sylvin/Halit-Zone??
A5 Further Data on Evaporate Samples

Probe Th V
Trümmerkarnallit mit Haliteinschlüssen

Probe Th VI
Trümmerkarnallit mit Haliteinschlüssen
Steinsalzleitbank 3
A5 Further Data on Evaporate Samples

Probe Th VII
Sylvenit/Halit-Zone

Probe Th VIII
Trümmercarnallit
Sylvenit/Halit-Zone
A5  Further Data on Evaporate Samples

Scan Angles of selected Samples

Probe H II

6.0°
7.5°
10.0°
12.5°
15.0°
17.5°
18.5°
A5 Further Data on Evaporate Samples
A5  Further Data on Evaporate Samples

Probe H III – Scan parallel zur Schichtung

14.0°
15.0°
16.0°
17.0°
18.0°
19.0°
A5  Further Data on Evaporate Samples
A5  Further Data on Evaporate Samples

Probe Th I

- 21.5°
- 23.0°
- 24.0°
- 25.5°

Probe Th II

- 21.0°
- 23.0°
- 25.0°
A5 Further Data on Evaporate Samples

Probe Th III

21.5°

23.0°

25.0°
A5  Further Data on Evaporate Samples
A5 Further Data on Evaporate Samples

Probe Th V

18.5°
20.0°
22.5°
25.0°
A5  Further Data on Evaporate Samples

Fluorescence of scanned samples

Probe H II
Anregung L1 (266 nm) / Emission PMT A Wheel 1 320 365 380 nm

Probe H III
Anregung Laser 1 (266 nm) / PMT A Wheel 1 320 365 380 nm
A5  Further Data on Evaporate Samples

Probe H III - Scan parallel zur Schichtung
Anregung Laser 1 (266 nm) / PMT A Wheel 1 320 365 380 nm

Probe H IV
Anregung Laser 1 (266 nm) / PMT A Wheel 1 320 365 380 nm
A5  Further Data on Evaporate Samples

Probe Th IV
Anregung Laser 1 (266 nm) / PMT A Wheel 1 320 365 380 nm

Probe Th V
Anregung Laser 1 (266 nm) / PMT A Wheel 1 400 420 440 nm
Further Data on Evaporate Samples

**Probe Th III**
Anregung Laser 2 (355 nm) / PMT B Wheel 1 400 420 440 nm

**Probe Th II**
Anregung Laser 2 (355 nm) / PMT A Wheel 1 460 480 500 nm
A5 Further Data on Evaporate Samples
Further Data on Limestone Samples

Fluorescence Intensity [rel. Units] vs. Emission Wavelength [nm]

Donnerkuhle, 266 nm (low), Fe const
Further Data on Limestone Samples

Rohdenhaus, 266 nm

Fe2O3 [%]

Intensität [rel.Einheiten]

R² = 0.6475
R² = 0.4946
R² = 0.5854

SB 375-385
SB 460-470
SB 295-315
Linear (SB 460-470)
Linear (SB 375-385)
Linear (SB 295-315)

Fe2O3 [%]

Quotient [

R² = 0.6118
R² = 0.6108

SB 415-425 SB 635-645
SB 430-440 SB 460-470
Linear (SB 430-440 SB 460-470)
Linear (SB 415-425 SB 635-645)
A6  Further Data on Limestone Samples

Rohdenhaus, 266 nm

- \( R^2 = 0.4389 \)
- \( R^2 = 0.4627 \)
- \( R^2 = 0.4086 \)

\[ \text{Intensität [rel. Einheiten]} \]

\[ \text{Al}_2\text{O}_3 \% \]

- Linear (SB 460-470)
- Linear (SB 375-385)
- Linear (SB 295-315)

Rohdenhaus, 266 nm

- \( R^2 = 0.5413 \)
- \( R^2 = 0.4944 \)

\[ \text{Quotient [ ]} \]

\[ \text{Al}_2\text{O}_3 \% \]

- Linear (SB 430-440 SB 460-470)
- Linear (SB 415-425 SB 635-645)
Further Data on Limestone Samples

Donnerkuhle, Fe const, 266 nm

Donnerkuhle, Mg const, 266 nm (low)

R² = 0.8346

R² = 0.8735

R² = 0.867

R² = 0.7642
A6 Further Data on Limestone Samples

Donnerkuhle, Mg const, 266 nm

Donnerkuhle, Mg const, 266 nm

Donnerkuhle, Mg const, 266 nm
### A6 Further Data on Limestone Samples

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### A6  Further Data on Limestone Samples

#### Chemical Analysis of Donnerkuhle Samples

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A7 Further Data on Gypsum Samples

Knauf, 266 nm Anregungswellenlänge, niedrige Auflösung

Knauf, 355 nm Anregungswellenlänge
A7  Further Data on Gypsum Samples

266 nm, niedrige Auflösung, Gips [CaSO$_4$$\cdot$2H$_2$O]

$R^2 = 0.6374$

266 nm, mittlere Auflösung, Gips [CaSO$_4$$\cdot$2H$_2$O]

$R^2 = 0.6953$

266 nm, hohe Auflösung, Gips [CaSO$_4$$\cdot$2H$_2$O]

$R^2 = 0.6555$
A7 Further Data on Gypsum Samples

\[ \text{Quotient } 476-486/609-617 \]

\[ \text{Quotient } 298-304/487-508 \]

\[ \text{CaSO}_4\cdot2\text{H}_2\text{O} < 30\% \]

\[ \text{CaSO}_4\cdot2\text{H}_2\text{O} > 50\% \]

\[ R^2 = 0.9309 \]

\[ R^2 = 0.8885 \]
A7 Further Data on Gypsum Samples

266 nm, niedrige Auflösung, Anhydrit [CaSO$_4$]

$R^2 = 0.8527$

$R^2 = 0.8793$

CaSO$_4$ [%]

Quotient $\left[ \frac{487-508}{600-608} \right]$

Quotient $\left[ \frac{487-508}{609-617} \right]$

CaSO$_4$ < 30%

30% < CaSO$_4$ < 60%

CaSO$_4$ > 60%

266 nm, mittlere Auflösung, Anhydrit [CaSO$_4$]
Further Data on Gypsum Samples

266 nm, mittlere Auflösung, Calcit [CaCO$_3$]

- $R^2 = 0.7154$
- $R^2 = 0.8156$
- $R^2 = 0.7908$

Quotient $\frac{284-297}{487-508}$

Quotient $\frac{298-304}{476-486}$

Quotient $\frac{309-314}{600-608}$

266 nm, mittlere Auflösung, Calcit [CaCO$_3$]

- $R^2 = 0.7908$
- $R^2 = 0.9188$

Quotient $\frac{309-314}{600-608}$

Quotient $\frac{309-314}{476-486}$
A7 Further Data on Gypsum Samples

266 nm, mittlere Auflösung, Calcit [CaCO₃]

![Graph showing data for Calcite](image)

266 nm, niedrige Auflösung, Magnesit [MgCO₃]

![Graph showing data for Magnesite](image)
A7 Further Data on Gypsum Samples

266 nm, mittlere Auflösung, Magnesit [MgCO₃]

\[ R^2 = 0.5041 \]

266 nm, niedrige Auflösung, Natriumoxid [Na₂O]

\[ R^2 = 0.7906 \]

\[ R^2 = 0.8539 \]

\[ R^2 = 0.8271 \]
Further Data on Gypsum Samples

266 nm, niedrige Auflösung, Kaliumoxid [K$_2$O]

\[ R^2 = 0.7532 \]

\[ R^2 = 0.7719 \]

266 nm, niedrige Auflösung, in HCl unlösliche Bestandteile

\[ R^2 = 0.9525 \]

\[ R^2 = 0.9605 \]

\[ R^2 = 0.9566 \]
### Chemical Analysis of Samples

#### Further Data on Gypsum Samples

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<th>CaSO₄ [%]</th>
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<th>HCl (unlöslich) [%]</th>
<th>Na₂O [%]</th>
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