

# Application of Mid-infrared Reflectance Spectroscopy for the Identification of Minerals Present in Oil & Gas/Mining Exploration

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**Abstract.** This work aims to develop a new core logging technique based on reflectance spectroscopy in the mid-infrared domain (2.08 to 25  $\mu\text{m}$ ). This technique is suitable to analyse the mineralogy of rough surfaces and will be adapted on a rock strength testing machine that scratches the core surface. The FT-IR spectrometer used in this work was tested on a list of minerals which are important in oil & gas and mining exploration. The list contains species of carbonates, halides, phosphates, sulphates, sulphides, tectosilicates and phyllosilicates. Then, a semi-automatic method was developed for mineral identification, mapping and quantification on the rough surfaces. It will be demonstrated that this process is powerful for the estimation of the mineral distribution at the exploration stage. Moreover, as it is non-destructive, low cost and quite fast, it will thus be helpful to extract additional data from the cores in a profitable way. This is critical to improve the resource efficiency, to reduce operational risks and to optimise the production in a sustainable way. These knowledges are the basis of the geometallurgical concept.

**Keywords.** Minerals, core logging, FT-IR spectrometer, mid-infrared, reflectance, scratched surfaces.

## 1 Introduction

Several techniques have already been developed for mineral identification by infrared spectroscopy. Different scales and wavelength domains are used.

First, hyperspectral imaging is widely used in the shortwave and visible to near infrared (VNIR and SWIR, from 0.4 to 2.5  $\mu\text{m}$ ) for remote sensing applications (Taranik and Aslett, 2009). Well known projects are AVIRIS and ASTER developed at the NASA Jet Propulsion Laboratory (van der Meer and de Jong, 2001). Such techniques are also used for core logging, the Hyperspectral Core Imager (HCI-2) developed by Corescan is an example (Pasten *et al.*, 2016). However, minerals such as tectosilicates, many oxides, sulphides and phosphates cannot be identified on these wavelength domains, and additional spectral ranges have to be studied. For example, the HyLogging system developed by the CSIRO covers a range between 6 and 14.5  $\mu\text{m}$  (Schodlok *et al.*, 2016), which is part of the mid-infrared domain (MIR, 3-30  $\mu\text{m}$ ).

Finally, the total MIR range is widely used for mineralogical purposes at the laboratory scale (Nakamoto, 1963 and Chukanov, 2014, among others). However, this

technique uses transmittance spectra which usually require the dilution of the sample into a transparent medium and is thus not suitable for fast and non-destructive core logging.

In this work, the FT-IR spectrometer covers the range from 2 to 25  $\mu\text{m}$  usually used at the laboratory scale but will be used in diffuse reflectance mode. This technique will allow studying the mineralogy of fresh rough surfaces generated by the scratch test in a non-destructive way.

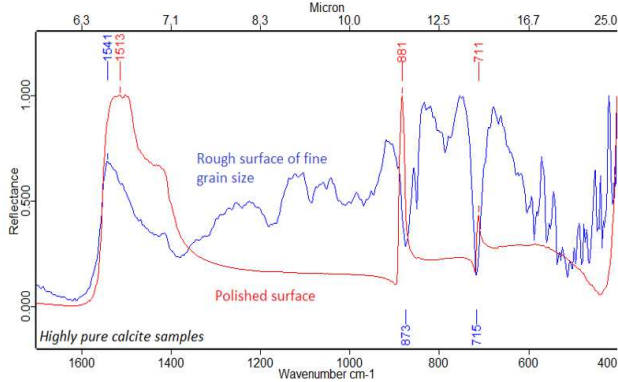
## 2 Theoretical aspects

In the mid-infrared domain, the spectral features of the minerals are due to the vibrational processes of their molecules caused by the energy of absorbed light. The absorptions occur solely at quantised energy levels corresponding to specific radiation frequencies. Therefore, the identification of minerals can be done by correlating the frequencies of absorption to the normal vibrations of isolated groups of atoms such as  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  or neutral molecules such as  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , which are considered independent in the structure. This method is thus adequate for carbonates, phosphates, silicates, etc., but much less for minerals composed of ionic liaisons like halides for which lattice vibrations have to be observed in the far-infrared (30  $\mu\text{m}$  to 1 mm) (Chukanov, 2014).

Infrared spectra of minerals are influenced by several factors. First, it is dependant of the symmetry of the real crystals that can be influenced by solid solutions, alterations and local defects. In addition, the particle size, the surface roughness (Figure 1) and the crystallographic orientation of the samples have non-negligible effects on the spectra in the mid-infrared domain. This is why it is generally preferred to use transmittance or absorbance spectra obtained with an immersion medium (as KBr), which are independent of these effects and considered unique for a given mineral (Vincent and Hunt, 1968; Chukanov, 2014; Salisbury *et al.*, 1987). For these reasons, it may be difficult to find relevant data in the literature for MIR reflectance spectra. Hopefully, three databases contain reflectance spectra of powders and polished surfaces: the United States Geological Survey (USGS), the John Hopkins University (JHU) and the Jet Propulsion Laboratory (JPL) spectral libraries. They are all part of the ASTER spectral library (Baldrige *et al.*, 2009).

The last factor to consider is the effect of mineral mixtures. According to Clark (1999), when two materials of known spectra are mixed, the resulting spectrum is not

necessarily the linear combination of these two spectra. Indeed, there are two principal types of mixtures: linear mixtures and intimate mixtures. In the case of linear mixtures, the materials are optically separated and there is no multiple scattering between them while in intimate mixtures, the materials are in intimate contact (mineral grains of soil for instance) and multiple scattering occurs. In this case, the resulting signal is a highly non-linear combination of the initial spectra. Several authors demonstrated that there was a potential for deriving individual mineral abundance in a particulate surface knowing the reflectance spectra of endmembers (Hapke, 1981; Smith *et al.*, 1985). However, in practice, many of the algorithms of spectral unmixing are based on the linear mixture hypothesis. They generally provide exploitable results, but can lead to approximations for intimate mixtures (Dobigeon *et al.*, 2014).



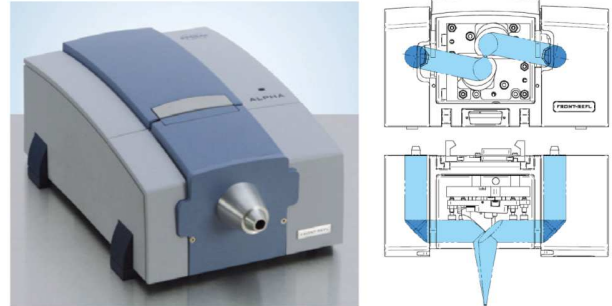
**Figure 1.** Spectra of a highly pure and finely grained calcite sample measured with the ALPHA spectrometer. When comparing the spectra of the rough surface and the polished section, it can be seen that a modification of the particle size and/or of the roughness causes different modifications on reflectance spectra. First, it modifies the intensity of the spectral features, then, it can convert spectral features displayed as minima in maxima or inversely and finally, the frequency of the absorption feature is shifted. This explains why it is particularly difficult to perform analyses on reflectance spectra.

### 3 Materials and method description

The FT-IR spectrometer is the ALPHA model from Bruker Optik with the A241/DL module to perform reflection measurements (Figure 2). It has a sampling spot of 7 mm in diameter and can be used on any type of solid surface without sample preparation. It can also be used on powders. Its optimal resolution is 4 cm<sup>-1</sup> for a time of measurement of about 1 minute per spot.

In addition, minerals which are important in oil & gas and mining exploration were selected (Table 1). Unfortunately, all the minerals of the list were not available as solid samples but every group is represented. The samples were analysed by XRD and appeared highly pure except samples 7 and 10 that appear as mixtures. First, spectra of minerals from the list were studied from the literature and the databases to assess the validity of mid-infrared reflectance spectroscopy for mineral identification.

Then, the reflectance spectra of the high purity samples were measured on rough fresh surfaces with the ALPHA spectrometer and compared to the existing databases to verify their correspondence. Moreover, automatic identification algorithms were tested on these spectra.



**Figure 2.** ALPHA spectrometer with the A241/DL configuration for reflection (Bruker Optik GmbH, available from the OPUS help, 2014).

| Minerals to study |                 | Sample number   |                     |
|-------------------|-----------------|-----------------|---------------------|
| Carbonates        | Aragonite       | /               |                     |
|                   | Calcite         | 1               |                     |
|                   | Dolomite        | 2               |                     |
|                   | Siderite        | 3               |                     |
| Halides           | Halite          | 4               |                     |
| Phosphates        | Chlorapatite    | /               |                     |
|                   | Fluorapatite    | 5               |                     |
|                   | Hydroxylapatite | /               |                     |
| Tectosilicates    | Quartz          | 6               |                     |
|                   | K-feldspars     | Microcline      | /                   |
|                   |                 | Orthoclase      | 7 (mixture)         |
|                   |                 | Sanidine        | 7 (mixture)         |
|                   | Plagioclases    | Albite          | 7 (mixture) and 8   |
|                   |                 | Anorthite       | /                   |
| Phyllosilicates   | Kaolinite       | 9               |                     |
|                   | Smectites       | Montmorillonite | /                   |
|                   |                 | Biotite         | 10 (mixture)        |
|                   | Micas           | Illite          | /                   |
|                   |                 | Muscovite       | 11                  |
|                   | Chlorite        | Clinochlore     | 10 (mixture) and 12 |
| Sulphates         | Anhydrite       | /               |                     |
|                   | Barite          | 13              |                     |
|                   | Gypsum          | 14              |                     |
| Sulphides         | Pyrite          | 15              |                     |

**Table 1.** List of minerals to analyse and their availability as solid samples.

Next, a drill core composed of a red conglomerate cut by two thinner black benches was used. It is part of the rocks underlying the lower orebody of the Kamoto mine, Democratic Republic of the Congo and is 16.8 cm long. It was scratched longitudinally to analyse the rock strength and a fresh rough surface was thus created along it. This groove surface is 1 cm wide. Reflectance spectra were measured along the groove every 7 mm (size of the sampling spot), and 24 spectra were thus obtained. They were then analysed with the semi-automated method calibrated with the highly pure minerals spectra in order to identify the minerals, to map them and to quantify them on the fresh surface. In addition, the powder produced along

the core by the scratch test was recovered and analysed by XRD to validate the results of the semi-automatic method. However, as this powder corresponds to a volume of destroyed rock, a perfect coincidence between the XRD results and the surface analysis is not expected. The powder contained about 35% dolomite, 27% quartz, 23% muscovite, 9% chlorite IIb (probably clinocllore) and 6% hematite. Trace of rutile was detected as well.

In a few words, this semi-automatic method uses four software: OPUS (Bruker Optik) for spectra measurement, and for mineral identification by using the three spectral libraries (USGS, JPL, JHU) ; Matlab (MathWorks) for building an hyperspectral image representing the drill core groove; ENVI (Exelis Visual Information Solutions) to extract the most representative spectra of the image (the so called end-members, to avoid the treatment of each pixel one-by-one) and to perform mineral mapping and quantification by using spectral linear unmixing algorithms and the spectral libraries. The method is said to be semi-automatic because the mineral identification step is not trivial and requires the user's validation and skills. The method nevertheless provided convincing results.

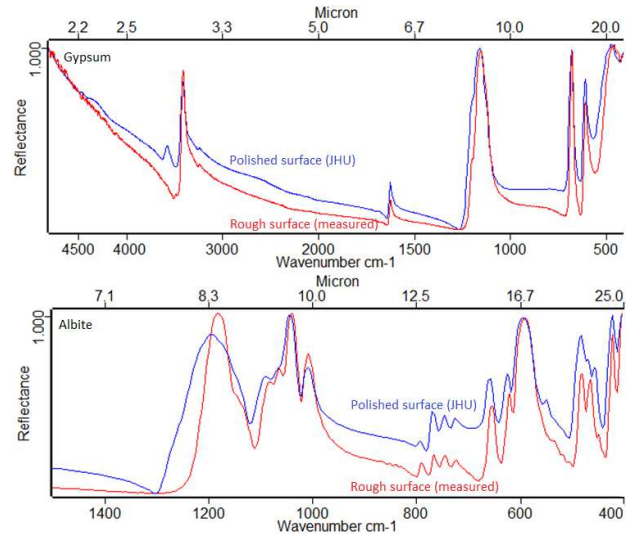
#### 4 Results and discussion

The mid-infrared reflectance spectra of powders and polished surfaces were studied from the literature and the three databases for the minerals of interest (Table 1). It appeared they are reliable identification tools because each mineral has different spectra due to its specific structure and composition. Minerals from the same classes (*ex.* dolomite and calcite) have comparable spectra but their differentiation is possible. The exception concerns minerals which are really similar, such as orthoclase and sanidine, or Mg and Fe-clinocllore, for which the identification can lead to uncertainties, especially when they are mixed together. On the other hand, the MIR spectroscopy is probably not the most adequate method to study the occurrence of sulphides and halides because they have no or few features in the MIR domain; pyrite has only one feature while halite has a flat spectrum.

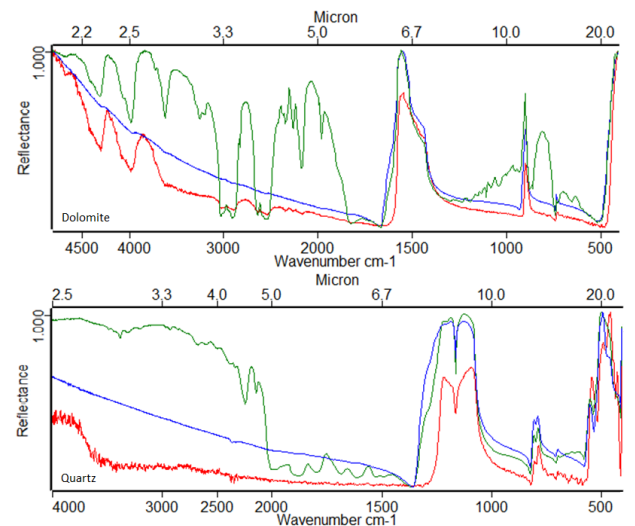
Then, the reflectance spectra of rough surfaces of high purity samples were compared to the existing databases. Despite small discrepancies, it has been shown that the behaviour of measured spectra was highly similar to the reference spectra. An example can be seen in Figure 3 for albite and gypsum. It was also shown that the rough surfaces have intermediate spectra between polished section and powders due to the particle size and roughness effect. This can be seen in Figure 4 for dolomite and quartz. USGS, JHU and JPL libraries can thus be used to analyse the spectra acquired with the ALPHA spectrometer on rough surfaces.

Finally, the Kamoto core was analysed with the semi-automated method in order to identify, map and quantify the minerals before knowing the XRD results, and without advanced geological information. The results are visible in Figure 5. Clinocllore, dolomite, quartz, muscovite and hematite (even if it was not part of Table 1) were correctly identified by using the spectral libraries. However, the trace

of rutile was not detected. In addition, the errors between the mean of the quantification results and the XRD are up to 14%, which is acceptable for the estimation of the minerals distribution. The errors are mainly due to two factors: the use of spectra from database (which are slightly different from the measured spectra due to mineralogical aspects, particle size and roughness effects) and the occurrence of intimate mixtures. Nevertheless, the most important aspect of these results is that two distinct zones of conglomerate and iron oxides can be observed. It proves that the technique can be efficient for mapping the different mineralogical zones of drill cores.



**Figure 3.** Comparison of measured spectra with reference spectra coming from the JHU library for gypsum (top) and albite (bottom). It can be seen that despite some discrepancies (new features, different intensities), the measured spectra (red) are really close to the polished section spectra (blue).



**Figure 4.** Comparison of measured spectra with reference spectra from the JHU library for dolomite (top) and quartz (bottom). It can be seen that measured spectra (red) have behaviour in between the polished section spectra (blue) and the powder spectra (green) due to the particle size and roughness effect. They are nevertheless easily identifiable from the reference spectra.

| Spot n° | RGB image of the groove | Results of mineral mapping and quantification |        |             |          |          |     |
|---------|-------------------------|---|--------|-------------|----------|----------|-----|
|         |                         | Muscovite                                     | Quartz | Clinocllore | Dolomite | Hematite |     |
| 0       |                         | 0%  | 49%    | 22%         | 21%      | 7%       |     |
| 1       |                         | 2%  | 9%     | 15%         | 70%      | 5%       |     |
| 2       |                         | 0%  | 15%    | 24%         | 56%      | 4%       |     |
| 3       |                         | 25%   | 20%    | 1%          | 43%      | 11%      |     |
| 4       |                         | 1%  | 24%    | 17%         | 50%      | 9%       |     |
| 5       |                         | 0%  | 33%    | 36%         | 31%      | 0%       |     |
| 6       |                         | 0%  | 12%    | 21%         | 64%      | 3%       |     |
| 7       |                         | 0%  | 11%    | 22%         | 65%      | 2%       |     |
| 8       |                         | 23%   | 18%    | 0%          | 0%       | 59%      |     |
| 9       |                         | 40%   | 29%    | 0%          | 0%       | 32%      |     |
| 10      |                         | 0%  | 21%    | 32%         | 32%      | 15%      |     |
| 11      |                         | 0%  | 17%    | 26%         | 56%      | 1%       |     |
| 12      |                         | 0%  | 20%    | 28%         | 51%      | 2%       |     |
| 13      |                         | 0%  | 21%    | 25%         | 51%      | 2%       |     |
| 14      |                         | 20%   | 24%    | 1%          | 13%      | 43%      |     |
| 15      |                         | 26%   | 14%    | 0%          | 0%       | 59%      |     |
| 16      |                         | 40%   | 18%    | 0%          | 0%       | 42%      |     |
| 17      |                         | 32%   | 18%    | 0%          | 0%       | 50%      |     |
| 18      |                         | 17%   | 27%    | 28%         | 1%       | 26%      |     |
| 19      |                         | 0%  | 48%    | 51%         | 1%       | 0%       |     |
| 20      |                         | 0%  | 27%    | 73%         | 0%       | 0%       |     |
| 21      |                         | 0%  | 18%    | 13%         | 64%      | 5%       |     |
| 22      |                         | 0%  | 18%    | 9%          | 68%      | 5%       |     |
| 23      |                         | 0%  | 27%    | 33%         | 40%      | 0%       |     |
| 24      |                         | 0%  | 28%    | 39%         | 33%      | 0%       |     |
|         |                         | Mean  | 9%     | 23%         | 21%      | 32%      | 15% |
|         |                         | XRD results                                   | 23%    | 27%         | 9%       | 35%      | 6%  |
|         |                         | Difference                                    | -14%   | -4%         | 12%      | -2%      | 9%  |

**Figure 5.** Results of the semi-automatic method for mineral identification, mapping and quantification on the scratched surface of the Kamoto core. 24 spectra were measured along the surface, each spectrum corresponding to a spot of 7 mm in diameter. The XRD analysis was performed on the powder corresponding to the volume of rock destroyed by the scratch test and results should thus not coincide perfectly with the surface analysis. The five major minerals detected by the XRD were correctly identified and the errors compared to the XRD are acceptable for a first estimation of the mineral distribution. Two zones are clearly visible: the conglomerate is composed of clinocllore and dolomite while the darker layers are composed of hematite and muscovite.

## 5 Conclusion and perspectives

Overall, it can be concluded that mid-infrared reflectance spectroscopy is adequate tool for mineral identification and logging of scratched surfaces. The method developed in this work, despite its non-automatic minerals identification and its limitations for accurate quantitative analysis, is powerful for a first approximation of the minerals distribution at the exploration stage.

One of the innovative aspects of the technique is its suitability to rough surfaces without the need of sample preparation. In addition, the technology allows the detection of much more minerals than VNIR and SWIR instruments (tectosilicates, oxides and some sulphides). Moreover, it is quite fast and can provide quite high resolution maps as 1 minute is needed per spot of 7 mm. The method will thus be helpful to extract additional data from the cores in a profitable way. It represents a step towards automatic core characterisation which is the basis of a coherent geometallurgical approach.

In addition, it can be noticed that the applicability of the MIR reflectance spectroscopy is not limited to core logging. In fact, it would probably bring a non-negligible help in the industry and for other geometallurgical purposes as it

combines grain size and mineralogical information in a single measure. However, further research is needed to develop these particular topics.

## Acknowledgements

This work mainly results from a master thesis conducted as part of the georesources engineering EMerald curriculum. Therefore, special thanks go to the EMerald staff for offering us the chance to participate in such a rewarding experience. Next, thanks go to Xavier Decamps for his involvement in this research, for his guidance, for the amount of data provided and especially for his time and his patience and to Pr. Frédéric Hatert for the XRD analyses. Mineralogical samples came from the Geological and the GeMMe departments of the University of Liège.

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