

Maja Mroczkowska-Szerszeń, Mateusz Orzechowski

Oil and Gas Institute – National Research Institute

Infrared spectroscopy methods in reservoir rocks analysis – semiquantitative approach for carbonate rocks

Experimental results and methodology for mineral composition determination of reservoir rocks by means of Fourier Transformed Infrared Spectroscopy technique (FTIR) was a subject to present in the paper. The FTIR data were calibrated with use of X-ray diffraction and X-ray fluorescence (XRF) methods. This approach allows quantitative and semiquantitative analysis basing on use of statistical methods like PCR (Principal Component Regression) or PLS (Partial Least Squares) to calibrate FTIR ATR in purpose to create efficient and cost saving tool for quick screening analysis of reservoir rocks samples. The presented approach allows for calibration of FTIR ATR using statistical methods like PCR (Principal Component Regression) or PLS (Partial Least Squares) in order to create efficient and cost saving tool for quantitative and semi-quantitative analysis of reservoir rocks samples. In the paper, 18 surface carbonate rocks samples of limestone and dolomite type belonging to the Paleozoic and Mesozoic age from the Kraków–Częstochowa Upland and Main Dolomite from Fore-Sudetic Monocline were analyzed. FTIR results were qualitatively described by analysis together with tentative assignments of their molecular bonds vibrations assignments are presented and a spectra interpretation for typical carbonates associated minerals. The technical constraints of the methodology resulting from proper method calibration and metal oxide analysis limitations were also discussed. Furthermore the behavior of the PCR and PLS algorithms in case of monomineral samples was commented and the necessity of additional qualitative spectra verification was indicated in this case for the final assessment of quantitative data quality. The quantitative results of FTIR analysis were compared with X-ray diffraction (XRD) quantitative data, part of them has been used as validation data. The accordance of the data series was better than 6% for each analyzed mineral phases excluding the outliers indicated by the analytical algorithm. The method was also successfully applied to the quantitative analysis of shale rocks, however, this part of the research will be presented in a separate paper.

Key words: quantitative rock analysis, PCR, PLS, reservoir rocks analysis, FTIR ATR spectroscopy, XRD, carbonate rocks.

Metody spektroskopii w podczerwieni w analizach skał zbiornikowych – podejście półilościowe w badaniach skał węglanowych

Praca przedstawia wyniki eksperymentalne oraz metodologię badania składu mineralnego skał zbiornikowych z zastosowaniem fourierowskiej spektroskopii w podczerwieni (FTIR – Fourier-transformed infrared spectroscopy). Wyniki spektroskopii FTIR kalibrowano z użyciem metod dyfrakcji rentgenowskiej (XRD – X-ray diffraction) oraz fluorescencji rentgenowskiej (XRF – X-ray fluorescence). Takie podejście pozwala na analizę półilościową, a nawet ilościową z zastosowaniem metody FTIR ATR. Metodologia opiera się na użyciu metod statystycznych, takich jak PCR (principal component regression) oraz PLS (partial least squares), do kalibracji metody FTIR ATR za pomocą innych danych w celu stworzenia wydajnego, szybkiego i finalnie niedrogiego narzędzia do zgrubnych (przesiewowych) badań skał zbiornikowych. W opracowaniu przedstawiono przykładowe wyniki analiz skał węglanowych (wapieni i dolomitów) dla 18 próbek skalnych z różnych lokalizacji, w tym próbek powierzchniowych ery paleozoicznej i mezozoicznej z rejonu Jury Krakowsko-Częstochowskiej, z okolic Krakowa, a także próbki reprezentujące dolomit główny z rejonu monokliny przedsudeckiej. Wyniki FTIR opatrzone opisem jakościowym zawierającym szczegółowe przypisania najważniejszych pasm drgań, jak również opisem widm minerałów towarzyszących. Przedstawiono też ograniczenia metody związane z kalibracją, a także z analizami próbek zawierających takie minerały jak piryt i tlenki metali czy też z zachowaniem wybranych algorytmów analizy ilościowej próbek w przybliżeniu monomineralnych. W tym przypadku zaznaczono konieczność przeprowadzenia jakościowej weryfikacji widm dla otrzymanych danych ilościowych, aby zachować ich odpowiednią jakość. Porównano wyniki badań ilościowych FTIR z wynikami ilościowych analiz z użyciem metody dyfrakcji rentgenowskiej (XRD), część wyników traktując jako walidację metody. Otrzymano zgodność na poziomie nie gorszym niż 6% odchyłki dla poszczególnych faz, nie wliczając wyników odstających, które najczęściej odrzuca metoda jako niespełniające kryteriów. Wyniki dodatkowo weryfikowano, stosując technikę fluorescencji rentgenowskiej XRF. Metodologią tą z powodzeniem posłużono się także w przypadku skał łupkowych, jednak ta część wyników zaprezentowana zostanie w oddzielnym opracowaniu.

Słowa kluczowe: metody ilościowe badania składu skał, PCR, PLS, analizy skał zbiornikowych, spektroskopia FTIR ATR, XRD, skały węglanowe.

Introduction

In the last decade, some new analytical methods for mineral composition characterization appeared as techniques useful in routine rocks analysis especially according to shale rocks demanding purposes. They may be described not as new, but upgraded to their faster/easier to use versions. Among the methods which should be mentioned, we may find: SEM/EDS – QemScan[®], XRF- spectroscopy or FTIR and Raman molecular spectroscopies.

These analytical techniques up to now were reserved only for advanced chemical researches in specialized laboratories. Thanks to technological development in the area of measurement as well as data processing this methods became more and more available on the level of routine sample analysis in the mining industry. This way they joined a group of SCAL techniques so called “Special Core Analysis” [1, 3, 27].

The method of molecular spectroscopy in middle infrared range allows identification of main components of rock mixture [15, 21]. Currently, almost exclusively a Fourier transformed type of infrared spectrometer is used in a routine chemical analysis. The method allows qualitative and quantitative or semi-quantitative analysis of rock samples including reservoir rocks. The preliminary analysis of organic matter is also possible after the organic matter extraction (according to laboratory procedure) [14, 18, 25]. This possibility is most important in shale rocks research. According to unextracted kerogen analysis, FTIR technique may be used as a screening qualitative method in case of immature geological formations or ones within oil window phase [18]. In the spectra of these samples, high frequency bands assigned to methyl and methylene groups in aliphatic hydrocarbons are well visible in case when the amount of organic matter approaches about 1.5 wt% (according to TOC method results).

In general FTIR ATR analysis is convenient to solid state (grinded samples), as well as liquid and semi liquid ones, which makes it useful for the mining industry. Well media analysis like drilling muds, different drilling sediments, and others are also possible.

It should be noticed that FTIR method is a self-reliant tool only in terms of qualitative analysis. In the need to use it quantitatively it must be supported (calibrated) by some other techniques [24, 29].

During quantitative analysis of rock mineral composition, for each new series of samples it is recommended to calibrate the method on standards (samples of known or determined by XRD/SEM-XRF (like QemScan) composition) [16, 29, 28], also PCR, PLS or NNLS statistical data analyses processes should be utilized [19, 20, 30].

The calibration may be omitted only if the analyze concerns the samples from formations of very similar characteristics, or if a very general information according to rock composition is needed. The amount of additional calibration analyzes is proportional to the number of phases that we want to determine (usually from a dozen to about 30÷40 calibration samples is needed). Optimally $3N + 1$ standards, should be used, where N is the number of recognized, selected components.

The more components will have analytical bands in similar spectral ranges the more difficult is analysis. However a well-calibrated method is fast – the measurement of one sample itself takes only a few minutes time. This allows very dense testing of interesting intervals up to several hundred measurements in relatively short time. It is also relatively cheap compared to other advanced research techniques.

A counter-example may be the SEM/EDS technique with the option of mineral mapping (eg. by QEMSCAN technology), where we get a result that is basically complete with respect to minerals and their content, but the diameter of the sample in this case in the order of a millimetre, maximum of one centimetre, which requires significant measurement statistics to maintain the representativeness of parameters. The other disadvantage is the measurement time, in an order of hours rather than minutes.

What is more, each sample must be prepared in the form of a special cut – properly cut fragment of the rock should be polished using an ion gun (so-called “ion polisher”). This has an obvious impact on the analysis duration and finally increases the total cost. On the other hand, it may be economically efficient in case when the method is treated as a calibration and validation technique, for FTIR spectroscopy or X-ray diffraction (XRD).

Using FTIR spectroscopy techniques it's necessary to have an appropriate physical base of mineral standards, preferably your own. In case of changes of measuring system configuration, it's possible to reconstruct the analytical method by remeasuring the standards. In terms of mineral composition it's essential to elaborate on precisely defined standards and their spectra should be measured exactly on the same apparatus configuration which is used for analysis of unknown samples. Each change in the apparatus configuration enforces necessity of recalibration of the method by remeasuring the calibration standards. Such a base of standards is developed in the laboratory of the Geology and Geochemistry Department of INiG – PIB, both in the scope of quantitative and qualitative series.

Research scope – the samples

Eighteen rock samples of carbonate origin have been investigated. Among them we may find: surface samples of the Paleozoic and Mesozoic ages collected in the area of the Kraków–Częstochowa Upland, and more precisely, from the vicinity of Zalas, Dębnik, Czerna, and Tenczynek.

They represent respectively: Devonian (1011) sample from Dębnik, Lower Carboniferous (1007÷1010) samples

from Czerna [2], Middle Jurassic samples from Zalas area (1001÷1004) [12]. The samples collection locations are marked on the (Fig. 1) [11].

Samples from 1014 to 1022 represent the Main Dolomite area outside the area of the map below. A separate study will be devoted to the results on a series of shale samples due to the considerable volume of research material.

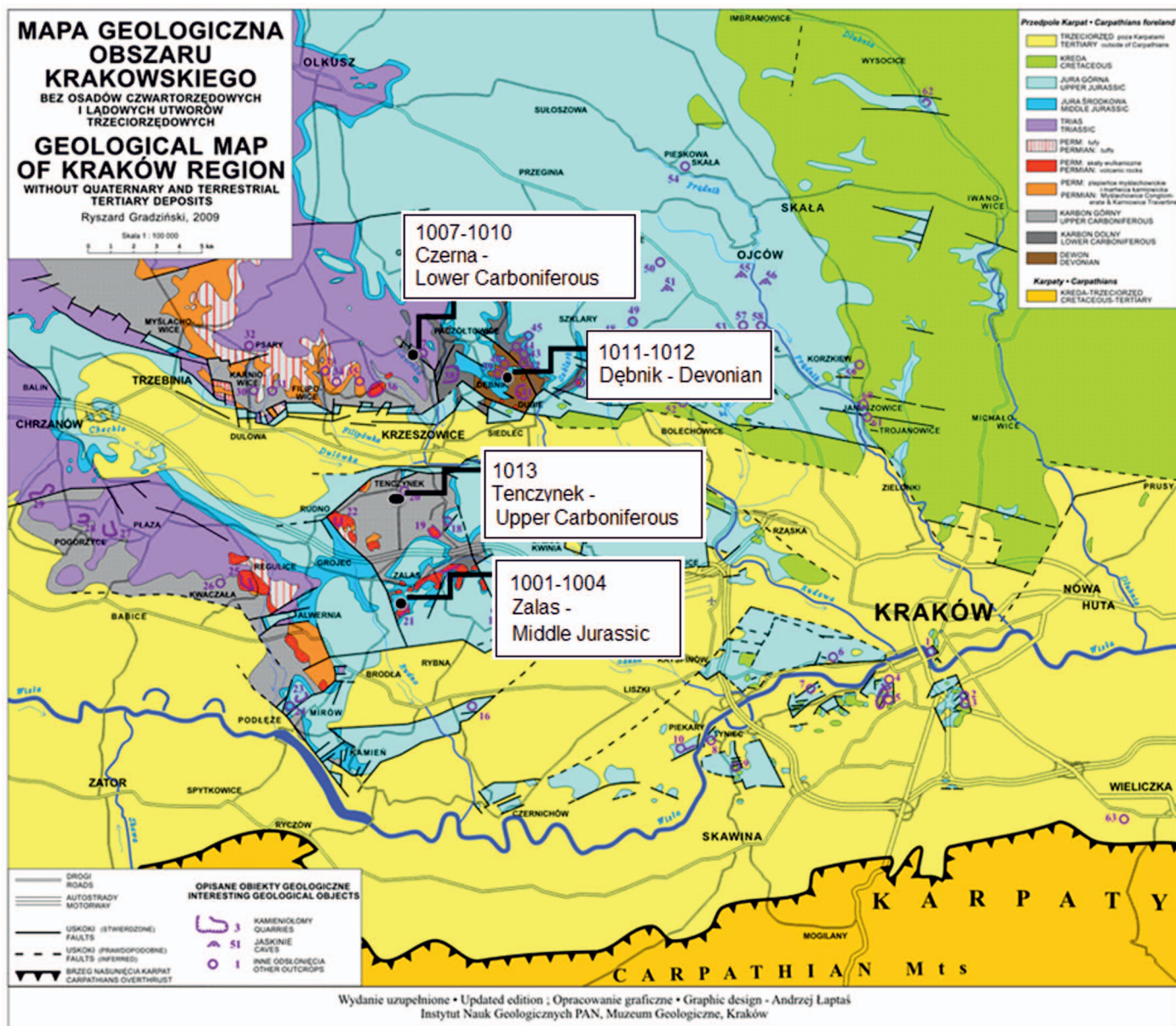


Fig. 1. Outcrops locations for collected samples are marked on the geological map of the Kraków area – Ryszard Gradziński [11]

Experimental

Fourier Transformed Infrared Spectroscopy method – FTIR

The measurements were performed on FTIR Thermo Nicolet 6700 spectrometer with the Raman NXR FT-Raman module.

The Specac Quest diamond ATR (Attenuated Total Reflectance extension) was used for the measurements. The FTIR ATR study was performed in the spectral range 400÷4000 cm⁻¹ using 128 repetitions per measurement. The Specac Quest ATR

module enables an excellent signal-to-noise ratio and wide measurement range (from far infrared up to near IR in case we use additional sources for this ranges).

XRD X-ray diffraction method

The quantitative XRD measurements were conducted with the use of Panalytical X'Pert Pro apparatus with a modern ultra-fast detector (real-time ultra-strip X'Celerator). Voltage 40 kV, current 34 mA, step-width $0,02^\circ 2\Theta$ were applied, samples were scanned from 5° to $65^\circ 2\Theta$.

X-ray fluorescence method (XRF)

Measurements of chemical composition were made by Bruker S1 TITAN spectrometer, using the method of X-ray fluorescence analysis with energy dispersion (EDXRF). S1 TITAN is equipped with an anode Rh (parameters max: 50 kV, 100 uA, 4) and a 10 mm^2 X-Flash[®]Silicon Drift Detector (SDD) with a typical resolution of 147 eV for the line Mn K-alpha [6]. Analysis of the chemical composition was based on the fundamental parameter method, which allows for measurements without using standards.

Sample preparation and methodology

FTIR ATR

The ATR (Attenuated Total Reflectance) technique allows the measurement of powders, gels, and liquids. The method makes possible to measure practically without any special preparation of the analyzed substances, as long as sufficient optical contact between the sample and measuring crystal is assured, and their concentrations are sufficient to obtain the spectrum. Of course, infrared spectroscopy technique excludes measurement of pure metals or their alloys, which behaves like a mirrors for this wave number ranges, making impossible to obtain the spectrum.

However, in the case of quantitative analyzes, the sample, as in other quantitative methods (eg XRD), must be grounded to the appropriate fraction – here – below $20 \mu\text{m}$, and even better would be below $2 \mu\text{m}$ [7]. This is important due to the repeatability of measurements because the variable size of the grain can affect the shape and even the position of the maxima of the bands (especially for samples with significant carbonate contents). In FTIR spectroscopic studies of powder samples, including mineral mixtures, it is also important to avoid various types of optical artifacts, hence the grains of the analyzed material should not be larger than the wavelengths used in the analysis [7].

This effect of homogeneity is best achieved in an automatic ball mill, with the same grinding conditions for each sample – this procedure was also used in the preparation of samples for the present analyzes.

During the measurement, it is important to ensure sufficient optical contact also by appropriate sample pressing against the surface of the measuring crystal – however, this condition is usually fulfilled by the ATR extension construction itself if the sample fraction is appropriate.

XRD and XRF

Mineralogical and chemical composition of the samples were obtained with use of X-ray diffraction (XRD) and X-ray fluorescent (XRF) methods.

After the XRF analysis samples were grinded for 5 minutes in the McCrone micronizing mill in order to reduce the grain size to $<20 \mu\text{m}$. The internal standard (ZnO) was added prior to grinding to obtain full homogenization of the samples. Measurements were conducted on random preparations made by side-loading. Preparations were made according to the method introduced by Środoń et al. [26].

Quantitative XRD analysis was conducted by the Rietveld method with the use of the SIROQUANT software, which is useful for analyzing samples containing clay minerals. The Rietveld method [22] is based on modeling of the crystallographic structures of minerals in the investigated samples. Minerals' actual chemical composition, crystallite dimensions, the presence of structural defects or randomness degree are taken into account during the modeling process. The obtained mineral models are used as standards in the quantitative analysis.

Qualitative phase identification FTIR

Qualitative determination of the mineral composition of rock samples most often depends on comparing the obtained spectra of samples with the laboratory standards spectra or one derived from databases. In the latter case, it should be verified what was the technique for the database spectrum acquisition. The database should contain spectra as close as possible to the method of measurement of analytical data obtained by the analyst in the laboratory analysis. Therefore, if we work on the ATR

adapter equipped with a diamond crystal, we should compare our results with the ATR diamond database of spectra, because each of the measurement techniques comes with a specific type of artifacts. In the case of ATR analyzes, the intensity of the bands is non-linear with respect to the spectra obtained in the transmission technique (the higher the values of the wave numbers, the lower the intensity values are registered). It results from the phenomenon of dispersion of infrared waves in the

measuring crystal which results in signal gain for low wave numbers and its weakening for high values. In addition, the change in the type of measuring crystal will affect not only the degree of occurrence of this phenomenon but also the shape of

the bands themselves in the spectra of the measured samples. For this reason, when comparing the results with, for example, literature data, care should be taken because the positions of maxima depending on the used method, may differ.

Identification of the main components of carbonate rocks along with band assignments

Figure 2 presents a series of spectra of carbonate minerals. Just next to the main minerals of carbonate reservoir rocks such as CaCO_3 calcite, $\text{Ca,Mg}(\text{CaCO}_3)_2$ dolomite, $\text{Ca,Fe}(\text{CO}_3)_2$, we present also siderite, MgCO_3 magnesite, and rare MnCO_3 rhodochrosite spectra.

Obviously, without specifying the positions of the bands' maxima for these minerals, it is difficult to distinguish between presented carbonates. Such a similar arrangement of bands is due to their structural conformity in this case, discriminated only by a cation type which implies differences in bonds lengths, and a crystal symmetry. The analysis of Table 1 and Figure 2 shows that some of these bands are approximately common to these minerals and therefore cannot serve as probes for identification of individual carbonates. This is the case with a very strong asymmetric stretching band of $(\text{CO}_3)^{2-}$ group, which theoretically should have different positions for individual minerals, however, these positions may vary, among others, due to the sample composition and size of the analysed grains [28].

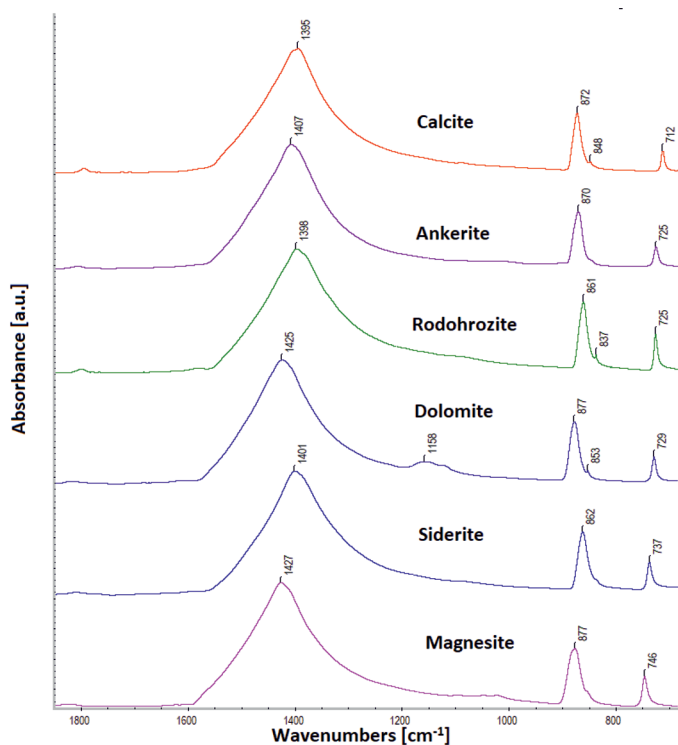


Fig. 2. Diamond FTIR ATR spectra in the measuring range (1850÷680 cm^{-1}). Spectra of mineral standards – carbonate minerals after RRUFF database [8]. Spectra for: calcite, ankerite, rhodochrosite, dolomite, siderite, magnesite

Fortunately, it is possible to indicate analytical bands which are characteristic bands maxima positions for each carbonate rock, which allows its unambiguous identification. Between selected minerals shown on Figure 2 these are in plane bending vibrations of the $(\text{CO}_3)^{2-}$ group (δ in plane vibrations).

The position of the maximum for this band ranges from 712 cm^{-1} for calcite up to 746 cm^{-1} for magnesite. Detailed bands assignments are presented in the table (Table 1).

Table 1. Bands assignments in spectra of standards in FTIR ATR diamond for selected carbonates [9, 15, 28]

Bands maxima positions [cm^{-1}]	Tentative assignments
ν_{as} – Asymmetric stretching vibration of $(\text{CO}_3)^{2-}$ group	
1395 cm^{-1}	calcite (CaCO_3)
1398 cm^{-1}	ankerite $\text{Ca,Fe}(\text{CO}_3)_2$
1425 cm^{-1}	dolomite $\text{Ca,Mg}(\text{CO}_3)_2$
1401 cm^{-1}	siderite $\text{Fe}(\text{CO}_3)$
1427 cm^{-1}	magnesite $\text{Mg}(\text{CO}_3)$
γ – out of plane bending vibration of bonds O–C–O in $(\text{CO}_3)^{2-}$ group	
872 cm^{-1}	calcite CaCO_3
870 cm^{-1}	ankerite $\text{Ca,Fe}(\text{CO}_3)_2$
877 cm^{-1}	dolomite $\text{Ca,Mg}(\text{CO}_3)_2$
862 cm^{-1}	siderite $\text{Fe}(\text{CO}_3)$
877 cm^{-1}	magnesite $\text{Mg}(\text{CO}_3)$
δ – in plane bending vibration of O–C–O in $(\text{CO}_3)^{2-}$ group	
712 cm^{-1}	calcite CaCO_3
725 cm^{-1}	ankerite $\text{Ca,Fe}(\text{CO}_3)_2$
729 cm^{-1}	dolomite $\text{Ca,Mg}(\text{CO}_3)_2$
737 cm^{-1}	siderite $\text{Fe}(\text{CO}_3)$
746 cm^{-1}	magnesite $\text{Mg}(\text{CO}_3)$

In Figure 3 an example of quartz presence is shown. Quartz as one the most common rock forming minerals is almost always present in the clastic rocks samples. We detect it with bands maxima positions 1058 cm^{-1} , 796 cm^{-1} , 776 cm^{-1} .

Another group of minerals, co-existing next to carbonates are sulfates such as anhydrite, gypsum or bassanite. An example of spectra of rocks containing significant amounts of these minerals (about 25%) is shown in Figure 4. In Table 2

the vibrations assignments of specific molecular groups for sulphates are presented. These assays were based on the paper of Bishop and colleagues [5].

Table 2. Bands assignments in spectra of standards in FTIR ATR diamond ATR for selected sulphates [5]

Bands maxima positions [cm ⁻¹]	Tentative assignments
1097 cm ⁻¹	ν_{as} asymmetric vibrations of (SO ₄) ²⁻ group in anhydrite Ca(SO ₄)
1015 cm ⁻¹	ν_{sym} symmetric stretching vibration of (SO ₄) ²⁻ group in anhydrite Ca(SO ₄)
673 cm ⁻¹	δ_{as} asymmetric bending vibrations of (SO ₄) ²⁻ in gypsum
610 cm ⁻¹ , 592 cm ⁻¹	δ_{as} asymmetric bending of (SO ₄) ²⁻ group in anhydrite Ca(SO ₄)

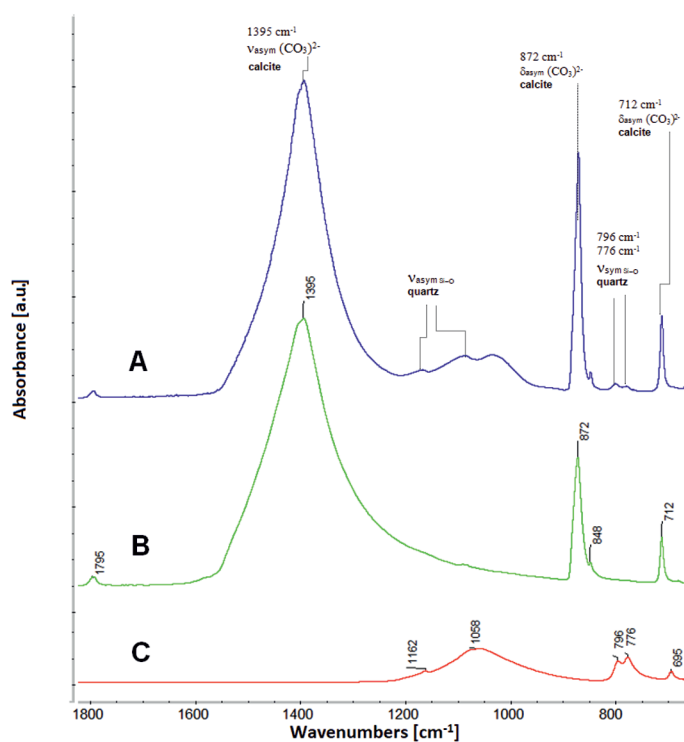


Fig. 3. FTIR ATR diamond spectra for: A – carbonate sample no 1001; B – calcite; C – quartz sample. The analytical bands are marked on the picture spectral range 1830 cm⁻¹ do 680 cm⁻¹

According to detection limits in terms of qualitative identification it should be noticed that they differ for various minerals. E.g. quartz is detectable in quantities of less than 2.5% (when we deal with a mineral mixture with a relatively simple composition). Whereas it is not always a trivial task to distinguish between dolomite and ankerite, even in a case of their quantities higher than 5%. However, identification becomes possible after the use of statistical methods giving us at the same time quantitative data. The details of the methodology which are presented in the further part of the paper.

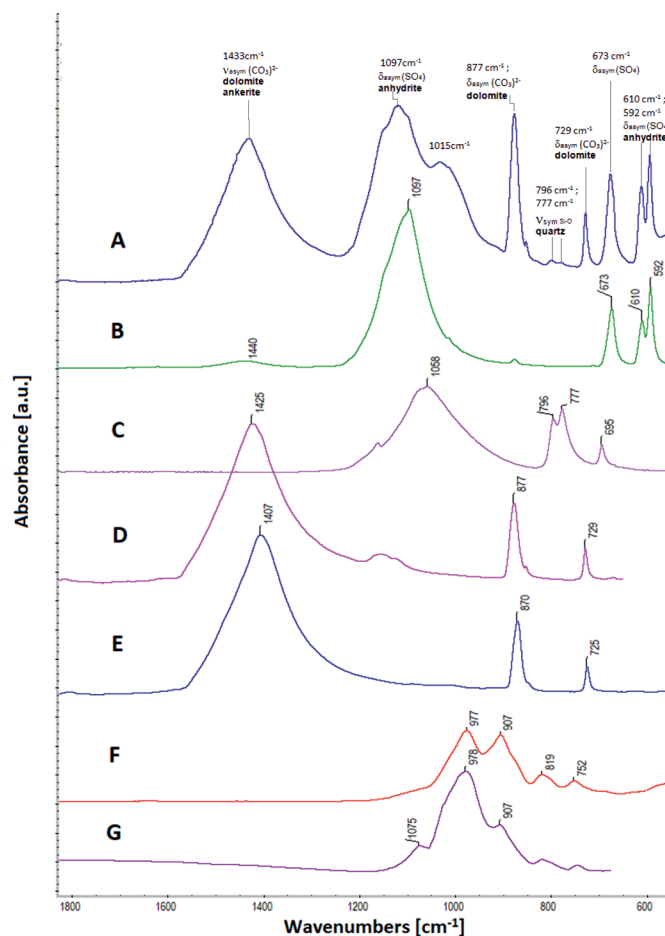


Fig. 4. FTIR ATR diamond for: A – carbonate sample no 1017, and standards of B – anhydrite; C – quartz; D – dolomite; E – ankerite; F – illite; G – muscovite together with positions of analytical bands within the measuring range 1830 cm⁻¹ do 550 cm⁻¹

Results

FTIR analysis

On the following pages, in the figures and tables, an exemplary series of results obtained for carbonate rocks are presented. For clarity, the most important bands were marked to facilitate identification of individual minerals. Some high frequency range spectra are characterized by significant amount of noise. They have been presented since in this range it's possible to confirm presence of kaolinite, as well as it was important to show that

even this quality of spectra may give proper quality of PCR quantitative results. The results of the research have been also tabularized to summarize the results of quantitative FTIR analysis. The Table 3 compares quantitative data from FTIR, XRD methods in order to show the spread of the results from different methods on the same samples. Each series of results was discussed, analyzing spectra quantitatively as well as qualitatively.

Qualitative description based on FTIR spectra – example

The results in the form of spectra were placed for comparison, one above the other, presented on the same scale (normalized to the strongest band in the range, thus mostly to the vibration peak with the maximum in the interval $(1390\div 1430\text{ cm}^{-1})$ corresponding to asymmetric stretching group $(\text{CO}_3)^{2-}$ in various carbonate minerals). This presentation of data facilitates qualitative comparative analysis. Using the example of samples from 1001 to 1013 it is shown how qualitative analysis is taking place in such rocks. Full data set is presented in tabular form together with quantitative results. Figure 5 contains the spectra of samples 1001÷1008 in the low frequency range.

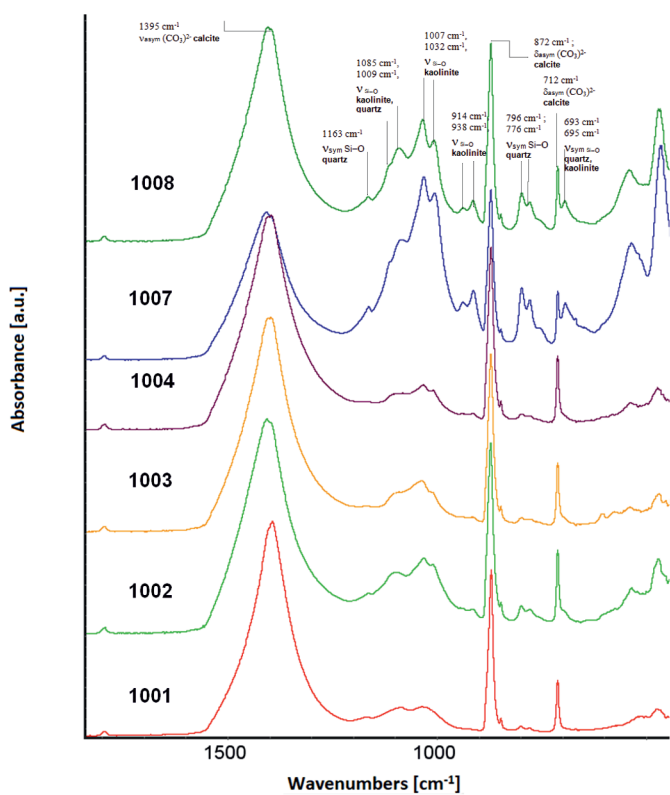


Fig. 5. FTIR ATR diamond spectra for samples 1001÷1008 with the assays of selected analytical bands within the measuring range from 1830 cm^{-1} to 450 cm^{-1}

These samples according to the information on the map (Figure 1) are samples from the location near Zalas and Czerna and represent respectively – from 1001 to 1004 the middle Jura (near Zalas) and 1007 and 1008 lower Carboniferous (Czerna).

As it's visible in Figure 5 in case of analyzed samples the difference in the spectral main features is correlated with download locations.

Samples from Czerna 1007 and 1008 are strongly marked by their higher intensity in a spectral range $960\div 1230\text{ cm}^{-1}$ most often associated with silicate and aluminosilicate phase. The comparison with the RRUFF database [8] and the literature

data [15], allows us to assign maxima in this spectral range to kaolinite and quartz phases. These assumptions are additionally confirmed by the analysis of the results in the high-frequency range (Figure 6), where we may observe the vibration bands characteristic for kaolinite (structural OH groups) in positions $(3620\text{ cm}^{-1}, 3651\text{ cm}^{-1}, 3692\text{ cm}^{-1})$ [4, 23]. In high frequency range, we may also observe some combination bands of carbonates (eg. $2873\text{ cm}^{-1}, 2984\text{ cm}^{-1}$) [10].

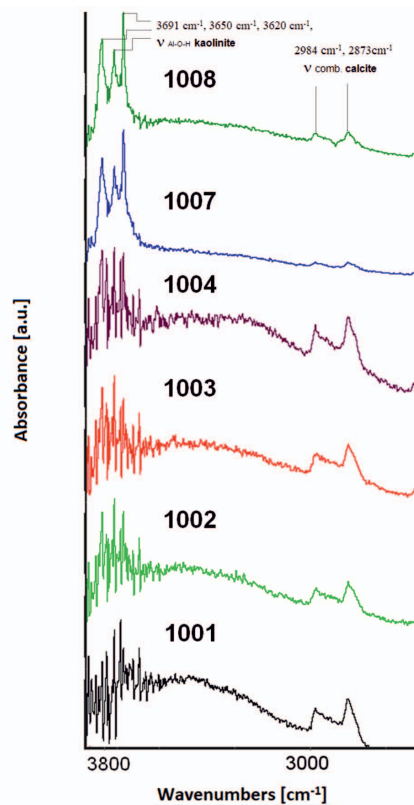


Fig. 6. Diamond FTIR ATR spectra for samples 1001÷1008 with the assays of selected analytical bands in the measuring range from 3750 cm^{-1} to 2640 cm^{-1}

The remaining samples according to spectra shown in Figures 5 and 6 (1001÷1004) have a smaller amount of kaolinite and a larger carbonate component.

However, as we deal with carbonate rocks, the obvious common feature of these spectra is the dominant presence of bands originating from group $(\text{CO}_3)^{2-}$ vibrations. Regarding the distinction of individual carbonates from one another as described before, the analytical band is in plane bending vibration of $(\text{CO}_3)^{2-}$ group which should be used first.

Figures 7 and 8 present spectra of samples numbered from 1009 to 1013 in the low and high frequency ranges. The samples 1009÷1010 are from Czerna (Lower Carboniferous), 1011÷1012 from Dębniak (Devonian), 1013 from Tenczynek (Upper Carboniferous). In these samples, calcite is a predominant

component. The sample from Czerna contains additionally dolomite, and in case of sample 1009 also ankerite, however, in

the scale shown in Figure 7, the ankerite bands are very poorly visible, hence their positions were not determined.

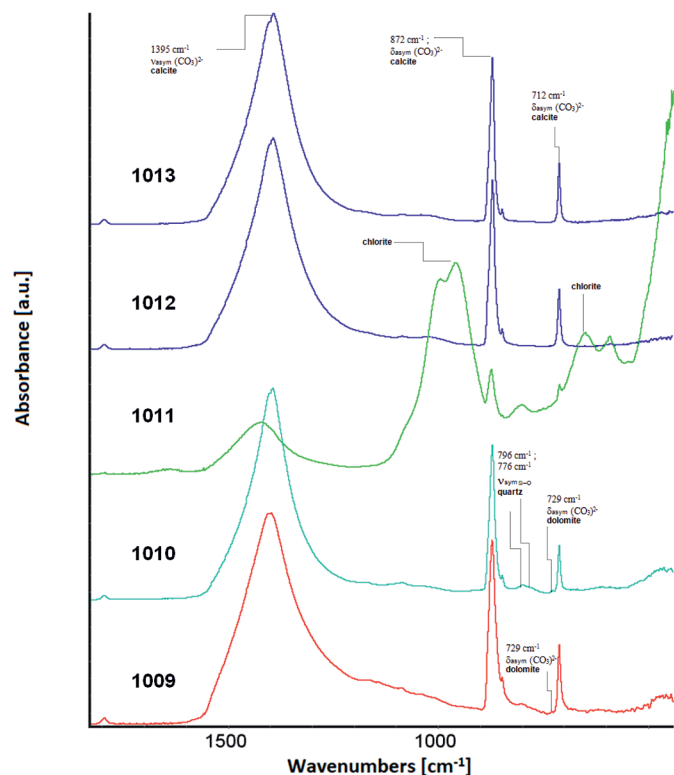


Fig. 7. FTIR ATR diamond spectra for samples 1009÷1013 with determinations of selected analytical bands in the measurement range from 1830 cm^{-1} to 450 cm^{-1}

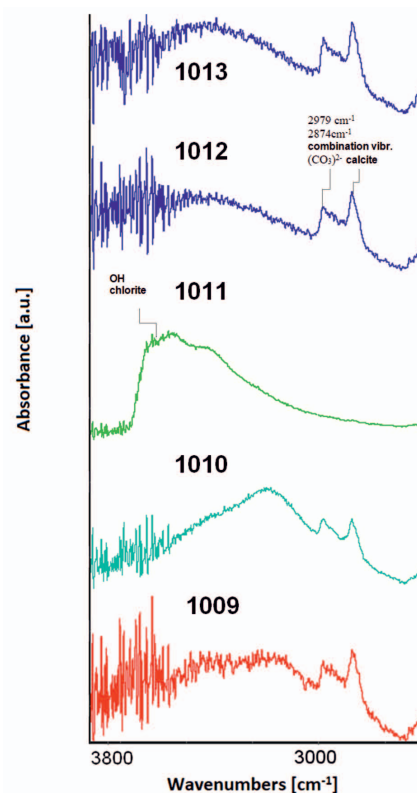


Fig. 8. FTIR ATR diamond spectra for samples 1009÷1013 with determinations of selected analytical bands in the measurement range 3850 cm^{-1} to 2600 cm^{-1}

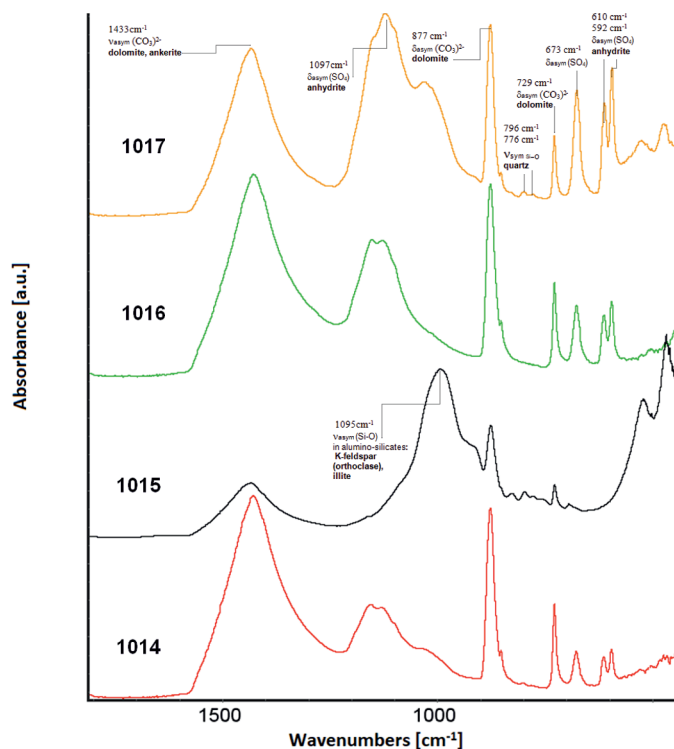


Fig. 9. FTIR ATR diamond spectra for samples 1014÷1017 with determinations of selected analytical bands in the measurement range from 1800 cm^{-1} to 450 cm^{-1}

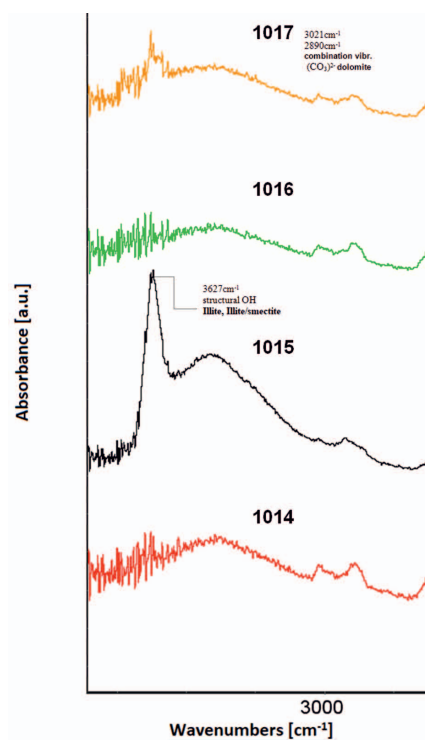


Fig. 10. FTIR ATR diamond spectra for samples 1014÷1017 with determinations of selected analytical bands in the measurement range 3850 cm^{-1} to 2600 cm^{-1}

Sample 1011 from Dębnik is characterized by a different band shape than the rest of the series presented on the figure 7. For wavenumbers from 500 cm⁻¹ up to 1100 cm⁻¹, we may observe some distinctive bands of chlorite phase [13] – the most easily identifiable in high frequencies (shown in Figure 8), where vibrations of its hydroxyl groups are clearly visible. Lack of characteristic high-frequency bands of calcite combination vibrations indicates a much smaller content of this mineral in sample 1011 than in the other ones in Figures 7 and 8.

Samples with numbers from 1014 to 1021 represent the main dolomite, which obviously implies the predominant dolomite

content in these samples. Selected spectra of these samples are shown in Figures 9 and 10. The spectra are characterized by significant intensities of bands originating from the vibrations of the group (CO₃)²⁻ of dolomite (maxima at: 1433 cm⁻¹, 877 cm⁻¹, 729 cm⁻¹) and (SO₄)²⁻ of anhydrite (maxima at: 1097 cm⁻¹, 673 cm⁻¹, 592 cm⁻¹, 610 cm⁻¹). There are also vibrations typical for silicates and aluminum-silicates, e.g. quartz (1058 cm⁻¹, 796 cm⁻¹, 776 cm⁻¹), potassium feldspar (maximum at: 1095 cm⁻¹). Aluminum-silicates may be represented by illite/smectite phase (3627 cm⁻¹, 3400 cm⁻¹, 995 cm⁻¹, 912 cm⁻¹, 828 cm⁻¹) [17].

Quantitative analysis of carbonate samples using the FTIR calibration curves based on statistical methods (PCR)

The carbonate rock samples presented and described qualitatively in accordance with the assumptions of the work were also subjected to quantitative or semi-quantitative analysis. For a series of samples numbered from 1001 to 1021, a com-

putational procedure was carried out to obtain information regarding proportions of the minerals.

The calculations were made on the basis of the “TQ Analyst” software produced by Thermo Electron, using the PCR (Principal

Table 3. A list of semi-quantitative FTIR, XRD analyses and their discrepancies. Explanation of the designations: Q – quartz; C – calcite; D – dolomite; An – ankerite, A – anhydrite

A – FTIR analysis results for rock forming minerals – calibrated by XRD							B – XRD results for rock forming minerals						
Sample No.	Q	C	D	An	A	Sum	Sample No.	Q	C	D	An	A	Sum
	[%]							[%]					
1001 ⁽¹⁾	4.0	91.6	2.3	1.5	0.6	100.0	1001*	2.5	97.5				100.0
1002*	10.4	78.8				89.2	1002*	11.8	73.3	0.6	0.6		86.3
1003	7.2	84.6	2.5	0.4	0.4	95.0	1003	7.9	81.7				89.6
1004	6.1	87.1	1.7	1.1	0.1	96.1	1004	6.9	87.0				93.9
1007 ⁽²⁾	14.0	82.8				73.0	1007	13.6	62.8				76.4
1008 ⁽²⁾	12.0	86.6				92.0	1008	11.4	78.1				89.5
1009	2.5	89.8	4.2	2.5	0.5	99.4	1009	0.6	96.5	1.3	1.6		100.0
1010*	5.5	82.0	4.4	0.0	0.0	91.8	1010*	6.9	76.2	7.3			90.4
1012 ⁽³⁾	1.2	82.7	11.5	2.5	2.0	100.0	1012	0.7	99.3				100.0
1013 ⁽³⁾	1.5	83.5	11.4	0.1	3.5	100.0	1013	0.7	99.3				100.0
1014*	1.8	0.0	79.9	1.7	9.9	93.2	1014*	1.4	0.7	77.6	3.4	10.4	93.5
1015 ⁽⁴⁾	13.3	0.4	38.8	4.3	0.1	56.9	1015*	13.2	1.0	38.5	4.1		56.8
1016	0.0	2.9	72.7		11.1	86.7	1016	1.6		81.1		17.3	100.0
1017*	4.3	0.0	49.7	3.1	4.3	61.3	1017*	3.3		44.4	7.9	25.3	80.9
1018*	0.0	4.7	79.1	16.0	0.0	99.7	1018*	0.5		80.8	17.9	1.0	100.0
1019*	3.0	0.0	85.1	9.8	2.1	100.0	1019*	0.3		81.3	7.2	1.0	90.2
1020*	0.1	4.0	81.2	10.3	3.9	99.5	1020*	0.8		84.1	11.7	3.0	99.2
1021	0.2	2.5	78.1	10.6	2.6	94.0	1021	0.9		81.8	10.0	5.0	97.9

⁽¹⁾ Samples marked with stars * are calibrating samples.
⁽²⁾ Samples 1007 and 1008 contain kaolinite, lack of a proper calibration series for this mineral unables quantitative estimation of kaolinite mineral content, however it’s presence is qualitative undeniable.
⁽³⁾ Samples 1012, 2013 are monophasic carbonates according to XRD results (with accuracy of quartz presence which is below 1%) lack of proper calibration series leads to inaccuracies in quantitative FTIR results for this type of samples.
⁽⁴⁾ Sample 1015 contains illite/smectite and feldspar phases.

Component Regression) calculation module. Calibration was based on the results of XRD quantitative tests performed in INiG – PIB in accordance with the PBN-06/SW-1 test procedure, additionally verified by correlation with XRF analyzes (PBN-15/SW-1 test procedure) (results of correlation to the authors' insight).

The results of quantitative studies obtained by the FTIR method are presented in the table (Table 3) together with the results of X-ray analyzes for calibration and non-calibration samples. Calibration samples in the table are marked with the symbol “*”.

The results were obtained with a significant spread of 20% for samples with a calcite content of 99% and a deviation from XRD data of up to several percent for individual minerals for samples with smaller dominant mineral content (calcite, dolomite), which is satisfactory considering the source of error resulting even from the heterogeneity of the analyzed sample.

Conclusions and summary

The paper presents the results of FTIR, XRD, XRF analysis of carbonate rocks of various origins in the amount of 18 samples.

The methodology for determining the semi-quantitative mineral composition of the above-mentioned rocks has been developed, presented and pre-validated.

1. At the current stage of research, it was found that the method of quantitative and semi-quantitative determination of FTIR ATR mineral composition based on statistical data processing (PCR) methods correctly reflects the proportions of components of the studied rocks, however, it strongly depends on the calibration data.
2. In the case of homogeneous samples (over 99% of the dominant phase), the method may give falsely inflated results for some phases other than the dominant one. Hence qualitative control of the spectra is always recommended to avoid gross errors. This type of mineral spectra should be excluded from the series and analysed independently.
3. If the analysis and in particular the calibration data omit/don't identify any component with significant content, the rest of the analysis will also be subject to a greater error than for full identification of the main components. However, if the components of the mixture with a lower content are not recognized and therefore not taken into account, a semi-quantitative result still may be obtained. In this case, the

The discrepancy between the results obtained from these two methods is similar in the studies of other research teams presenting quantitative results based on FTIR analyzes and statistical methods [19]. Discrepancies refer to specimens mainly doped with kaolinite (1007, 1008) and monophasic samples 1009, 1012, 1013 (where XRD indicates more than 99% presence of calcite or dolomite). Qualitatively for monophasic samples, there is no problem with identifying the dominant phase and determining its almost exclusive presence, but it can be seen that the quantitative method should be improved in this case, since it shows some amount of accessory minerals, which in fact are not present.

It is necessary to independently calibrate kaolinite-containing samples, probably using a different method, such as QemScan, or even by creating own standard blends for calibration curves with known kaolinite contents.

analysis results will not add up to 100%, but it will still describe the other ingredients in the correct way.

4. For satisfying results of each specific mineral mixture component a series of calibrating samples with a proper spread of concentrations should be provided for each analysed mineral. The ranges of concentration should be possibly closest to its concentrations in analysed samples series.
5. It has been found that apart from evidently outlying results (e.g. due to the strongly different shape of bands or incorrect qualitative information on ingredients) – the method reproduces the results of calibration data with an accuracy no worse than a few percent, usually not worse than 5÷6%.
6. The FTIR ATR method is specially sensitive to the components of mineral mixtures, such as kaolinite, which in quantitative determinations would require additional calibration independent of XRD. However, often it does not qualitatively determine the presence of pyrite or metal oxides – it would probably be possible by setting the method on low frequency range spectrometer configuration (in so-called FIR – far infrared range).

An undoubted advantage of the method is the fact that it is relatively fast – after preparing and grinding the sample, only a few minutes are required to obtain the spectra and with proper method calibration in next few minutes quantitative data are also available.

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Maja MROCZKOWSKA-SZERSZEŃ Ph.D., Eng. Assistant Professor at Geology and Geochemistry Department Oil and Gas Institute – National Research Institute ul. Lubicz 25 A 31-503 Kraków E-mail: maja.mroczkowska@inig.pl



Mateusz ORZECHOWSKI M.Sc. Engineering-technical specialist in the Department of Well Logging Oil and Gas Institute – National Research Institute ul. Lubicz 25 A 31-503 Kraków