APPLICATION OF INFRARED SPECTROSCOPY AND CHEMOMETRIC METHODS TO IDENTIFICATION OF SELECTED MINERALS

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ABSTRACT
A new way of identification of minerals was suggested. The identification was based on chemometric analysis of measured IR spectra of selected minerals. IR spectra were collected using diffuse reflectance technique. The discriminant analysis and principal component analysis were used as chemometric methods. Five statistical models were created for separation and identification of clay minerals. Up to 60 samples of various mineral standards (clay minerals, feldspars, carbonates, sulphates and quartz) from different localities were selected for the creation of statistical models. The results of this study confirm that the discriminant analysis of IR spectra of minerals could provide a powerful tool for mineral identification. Even differentiation of muscovite from illite and identification of mixed structures of illite-smectite were achieved.

KEYWORDS: minerals, identification, IR spectroscopy, discriminant analysis, principal component analysis

1. INTRODUCTION

Knowledge of mineral composition is essential to characterize the geochemical and physico-mechanical properties of rocks. Nature and content of minerals (especially clay minerals) present in rocks have a significant influence on the behaviour and properties of rocks as well as on the whole rock massif.

In general, several conventional analytical methods exist that can be used to examine the mineral composition of rocks: optical microscopy, electron microscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR spectroscopy), Raman spectroscopy, thermal analysis (TG/DTA) and bulk chemistry analysis (Kodama et a., 1989; Chipera and Bish, 2001; Srodon, 2002; Vogt et al., 2002; Vaculíková, 2006). Unfortunately, the exact identification of clay minerals by means of these methods is rather complicated and often inaccurate. The main analytical difficulties are related to variable chemical composition and common structural disorders of clay minerals. Another reason consists in the fact that the individual clay minerals occur in the form of mixtures (illite – montmorillonite, chlorite – montmorillonite, etc.) with various ratios of particular clay minerals.

The current FTIR spectroscopy makes it possible to analyze individual minerals, noncrystalline admixtures and, simultaneously, to detect the presence of organic matter.

Very useful for processing of IR spectra are multivariate statistical methods. The big advantage of multivariate statistical methods is their capability to extract required spectral information from IR spectra and explore this spectral information for qualitative or quantitative applications. The most frequently used multivariate statistical methods (often called chemometric methods) are factor analysis (FA), principal component analysis (PCA), discriminant analysis (DA), principal component regression (PCR), multiple linear regression (MLR) and partial least-squares regression (PLS). DA, FA and PCA are very useful tools for qualitative analysis.

The discriminant analysis allows quantification of the probability with which an object can be assigned to an individual class. DA generates a discriminant function as a linear combination of measured variables, which gives maximum separability for objects from different classes. The ratio of between-class to pooled within-class sample variance is commonly used as a criterion J for measuring the separability of different classes:

$$J = \frac{a^T B a}{a^T W a} \qquad (1)$$

where a is a vector maximizing the discriminant criterion and B and W are the between-class and the within-class covariance matrixes, respectively (Jiang et al., 2002).

The discriminant analysis uses results of another chemometric method – principal component analysis (PCA). PCA is one of the most common multivariate methods wide-spread also in infrared spectroscopy (e.g. Tesch and Otto, 1995; Dahlberg et al., 1997; Rusnak et al., 2003). IR spectrum is composed of many points connected by the line; each point in the IR spectrum is defined by wavenumber and intensity (for example absorbance). In PCA, each spectrum is represented by a point in multidimensional space, whereas the number of dimensions corresponds to the number of points in the spectrum (in other words the number of variables). Because this multispace is very difficult to comprehend, PCA introduces a new coordinate system as a linear combination of the old coordinates. Most of the variances (it means the most of information from the IR spectrum) are concentrated in only a few of the new coordinates – called *principal components*. This can be expressed as the decomposition of the data matrix (D) into two other matrixes - the score matrix (P) and the loading matrix (T). For better understanding of the decomposition of the data matrix we can use the following graphical representation (Geladi and Kowalski, 1986):

D matrix has the dimensions of number of samples (n) by intensity (at particular wavenumbers) of IR spectra (m). The score matrix (P) has the dimensions of number of samples (n) by principal components (a) and this matrix represents the location of the samples in the new principal component space. The loading matrix (T) has dimensions of intensity (m) by principal components (a); loading matrix represents the recipes by which each of the principal components was constructed from the old variable - intensity at each wavenumber. The most important information is included in the first two or three principal components. The rest of the principal components contain only minor characteristics of samples and noise, so that can be ignored. The main advantage of PCA consists in reducing the influence of noise and exploiting the subtle differences in the IR spectra of samples to obtain relevant and significant spectral information.

In PCA of spectral data, the loading matrix is very important. This matrix shows us which spectral information (regions or bands) are important in the principal component space. The most significant way of projection of loading matrix in spectral analysis is so-called loading spectra. They often look like "typical spectra" and positive and/or negative band can be present at the loading spectra. The positive bands represent spectral information positively correlated through particular principal component; the negative ones represent spectral information negatively correlated through particular principal component.

Both of the above-mentioned chemometric methods (DA and PCA) are described in a lot of statistical textbooks (Meloun and Militký, 2004; Hendl, 2006) in full details. Likewise, DA and/or PCA of IR spectra are used in many studies (Tesch and Otto, 1995; Dahlberg et al., 1997; Kher et al., 2001; Tsuchikawa et al., 2003; Ritz, 2007).

This paper describes a new approach to clay minerals and some accessories minerals identification based on chemometric analysis of IR spectra of clay minerals. All IR spectra were collected using diffuse reflectance technique (DRIFT). The aim of the study was the creation of statistical models for minerals identification by discriminant analysis of measured IR spectra.

2. MATERIALS AND METHODS

2.1. SAMPLES OF MINERALS

The research has been focused on the basic clay mineral specimens (kaolinite, montmorillonite, nontronite, illite, chlorite and vermiculite) including micas (muscovite, biotite) and the associated minerals (quartz, feldspar, carbonates and sulphates). The standards of above-mentioned minerals were selected according to their authenticity and a degree of purity. These mineral standards were obtained from the collection of minerals available at the Institute of Geonics, Nanotechnology Centre of VŠB-Technical University Ostrava and from Source Clays Repository of the Clay Minerals Society, USA.

60 samples of mineral standards were collected for the preparation of statistical models. 51 samples of clay minerals (including micas) and 9 samples of associated minerals (quartz, feldspars, carbonates and sulphates) were used. Some of mineral standards were treated by jet mill; other ones were prepared by sedimentation to obtain fraction grain size less than 5 μm. Some standards were used as unmodified ("raw" standards). A list of all used samples of mineral standards is shown in Table 1.

2.2. FTIR MEASUREMENTS

Approximately 5-10 mg of sample of mineral standards was ground with approx. 400 mg dried KBr. This mixture was used to collect IR spectra.

The IR spectra were collected using FTIR spectrometer Nexus 470 (ThermoScientific, USA). Diffuse reflectance measurement technique (DRIFT) was used. This technique was selected for its fastness and simplicity. The measurement parameters were as follows: spectral region 4000-400 cm^{-1}, spectral resolution 8 cm^{-1}; 128 scans; Happ-Genzel apodization.

Table 1 List of samples.

Sample	Mineral	Locality	Description
Bio1	Biotite	Ktíš, Czech Republic	fraction ≤ 5 μm
Bio2	Biotite	Ktíš, Czech Republic	"raw" standard
Bio3	Biotite	Dolní Bory, Czech Republic	fraction ≤ 5 μm
Mus1	Muscovite	India	"raw" standard
Mus2	Muscovite	Měděnec, Czech Republic	fraction ≤ 5 μm
Mus3	Muscovite	Otov, Czech Republic	fraction ≤ 5 μm
Mus4	Muscovite	Měděnec, Czech Republic	"raw" standard
Mus5	Muscovite	Rožná, Czech Republic	fraction ≤ 5 μm
Mus6	Muscovite-Chlorite	Měděnec, Czech Republic	"raw" standard
Ill1	Illite	Hungary	fraction ≤ 5 μm
Ill2	Illite (IMt-1)	Montana, USA	fraction ≤ 5 μm
Ill3	Illite	Karlov, Czech Republic	"raw" standard
Ill4	Illite (IMt-2)	Montana, USA	"raw" standard
Ill5	Illite (IMt-1)	Montana, USA	jet mill
Ill6	Illite (IMt-2)	Montana, USA	"raw" standard
Ill7	Illite-Smectite (ISCz-1)	Czechoslovakia	"raw" standard
Ch1	Chlorite (CCa-2)	California, USA	fraction ≤ 5 μm
Ch2	Chlorite	Letovice, Czech Republic	fraction ≤ 5 μm
Ch3	Chlorite	Orlické hory, Czech Rep.	fraction ≤ 5 μm
Ch4	Chlorite (CCa-2)	California, USA	"raw" standard
Ch5	Chlorite (CCa-2)	California, USA	jet mill
Kao1	Kaolinite	Božíčany, Czech Republic	"raw" standard
Kao2	Kaolinite	Horní Bříza, Czech Republic	"raw" standard
Kao3	Kaolinite (KGa-1b)	Georgia, USA	fraction ≤ 5 μm
Kao4	Kaolinite	Kadaň, Czech Republic	"raw" standard
Kao5	Kaolinite	Kaznějov, Czech Republic	"raw" standard
Kao6	Kaolinite	Sedlec, Czech Republic	"raw" standard
Kao7	Kaolinite	Únavov, Czech Republic	"raw" standard
Kao8	Kaolinite (KGa-1b)	Georgia, USA	"raw" standard
Kao9	Kaolinite (KGa-2)	Georgia, USA	"raw" standard
Kao10	Kaolinite	Sedlec, Czech Republic	"raw" standard
Kao11	Kaolinite	Sedlec, Czech Republic	fraction ≤ 5 μm
Dic1	Dickite	Krásno, Czech Republic	fraction ≤ 5 μm
Hal1	Halloysite	Bílá Hora, Slovakia	"raw" standard
Mon1	Montmorillonite	Ivančice, Czech Republic	fraction ≤ 5 μm
Mon2	Montmorillonite	Jelšový potok, Slovakia	fraction ≤ 5 μm
Mon3	Montmorillonite (SWy-1)	Wyoming, USA	"raw" standard
Mon4	Montmorillonite (SWy-1)	Wyoming, USA	fraction ≤ 5 μm
Mon5	Montmorillonite (SWy-2)	Wyoming, USA	"raw" standard
Mon6	Montmorillonite (SAz-2)	Arizona, USA	fraction ≤ 5 μm
Mon7	Montmorillonite (SAz-2)	Arizona, USA	"raw" standard
Mon8	Montmorillonite (STx-1b)	Texas, USA	"raw" standard
Non1	Nontronite (Nau-1)	Uley Mine, South Australia	"raw" standard
Non2	Nontronite (Nau-2)	Uley Mine, South Australia	"raw" standard
Hec1	Hectorite (SHCa-1)	California, USA	"raw" standard
Ver1	Vermiculite	China	expanded
Ver2	Vermiculite	Aldrich standard	expanded
Ver3	Vermiculite	Aldrich standard	expanded, jet mill
Ver4	Vermiculite	Letovice, Czech Republic	not expanded
Ver5	Vermiculite	Brasil	not expanded
Ver6	Vermiculite	Brasil	not expanded, jet mill
Acc1	Quartz	Otov, Czech Republic	"raw" standard
Acc2	Siderite	Dúbrava, Slovakia	"raw" standard
Acc3	Magnesite	Nižná Slaná, Slovakia	"raw" standard
Acc4	Calcite	Štramberk, Czech Republic	"raw" standard
Acc5	Gypsum	Nothern Bohemia, Czech Rep.	"raw" standard
Fel1	Albite	West. Bohemia, Czech Rep.	"raw" standard
Fel2	Feldspar (Na, K)	West. Bohemia, Czech Rep.	"raw" standard
Fel3	Feldspar (Na, K)	West. Bohemia, Czech Rep.	"raw" standard
Fel4	Feldspar (Na, Ca)	West. Bohemia, Czech Rep.	"raw" standard

Every sample was prepared and consequently measured several times (3 – 5 times). The mean IR spectrum of every sample was calculated for subsequent statistical processing.

2.3. DISCRIMINANT ANALYSIS

The discriminant analysis (DA) was performed using TQ Analyst software (ThermoScientific, USA). Two spectral regions 4000-3000 cm^{-1} and 1300-400 cm^{-1} of each IR spectrum were used for DA. A one-point baseline was used in every spectral region. A multiplicative signal correction of pathlength was used for calculation. The Mahalanobis distance was used to formulate a distance between clusters.

Before DA, principal component analysis (PCA) carried out. The task of PCA was reduction of redundant spectral information and finding of important spectral features which had a significant influence on spectral variance. The number of principal components used for the preparation of model was 10.

Validation of statistical models has been carried out by means of a validation spectra set (TQ Analyst software does not allow cross-validation for discriminant analysis). The IR spectra of minerals were split into two groups in each class used in DA – calibration group of spectra and validation group of spectra. The group of calibration spectra was used to create a discrimination model; the group of validation spectra was used to verify this model. Most of the IR spectra in each class were used as calibration spectra; up to three IR spectra in each class were used as validation spectra. There were no validation spectra used in one-member classes only. The selection of calibration and validation spectra has been performed by TQ Analyst software. The following samples were used for collection of validation spectra: Bio2, Mus1, Mus4, Ill1, Ill4, Ch3, Kao2, Kao7, Kao8, Mon3, Mon6, Non2, Ver4, Fel3 and Acc3. The models in this study were considered correct when all validation spectra occurred inside their class clusters. All discrimination models mentioned in this paper fulfill this condition.

3. RESULTS AND DISCUSSION
3.1. STRATEGY OF MODEL CREATION

The creation of a unique statistical model for all used samples was a primary idea of the authors. During the process of creation of the unique model serious problems occurred. A lot of minerals were classified into incorrect classes because of considerable variability of spectral bands. The solution to this problem was a creation of partial models; five partial models were created in this study. These partial models have allowed separation and subsequent identification of clay minerals in a few steps. A brief summary of the created models is in Table 2.

Model 1 was created for the separation of clay minerals from accessory minerals like feldspars, quartz, carbonates (calcite, siderite and magnesite) and sulphates (gypsum). General discrimination of clay minerals was performed in Model 2. The clay minerals were classified into particular groups of clay minerals in this model: biotite, muscovite-illite, chlorites, kaolin-serpentines, smectites and vermiculites. The remaining models were created for identification of individual members of selected clay mineral groups. Model 3 has allowed identification of minerals of the kaolin-serpentine group (kaolinite, dickite and halloysite), Model 4 has allowed identification of minerals of the smectite group (Na-montmorillonite, Ca-montmorillonite, nontronite and hectorite) and Model 5 has allowed identification of micas (biotite, muscovite) and illite.

3.2. MODEL 1 – SEPARATION OF CLAY MINERALS FROM ACCESSORY MINERALS

This model was created for the selection of clay minerals from accessory minerals. There were three classes used in Model 1 (Clay minerals, Feldspars and Accessory minerals). The first class included all used samples of clay minerals (biotite, muscovite, illite, chlorite, kaolinite, dickite, halloysite, montmorillonite, notronite, hectorite and vermiculite). The first class (Clay minerals) involved 51 samples as members of this class. The second class (Feldspars) had 4 members; three samples of mixed feldspars and one sample of albite. The third class (Accessory minerals) included 5 members (quartz, siderite, calcite, magnesite and gypsum). The Mahalanobis distance plot is shown in Figure 1. All minerals were clearly distributed into three clusters whereas the cluster of Feldspars is relatively close to the cluster of Clay minerals. The cluster of Accessory minerals is evidently isolated from the other two clusters.

The principal component analysis was used as integral part of the discriminant analysis. Ten principal components (PCs) were calculated in Model 1. These ten PCs described 99.3 % of variance of spectral information, whereas almost 95 % of variance was involved in the first four PCs. Loadings spectrum of the first principal component (PC1) includes spectral bands of kaolinite only: stretching bands of inner-surface hydroxyl groups (3695 cm^{-1}, 3668 cm^{-1}, 3652 cm^{-1} and 3620 cm^{-1}), Si-O stretching band (1100 cm^{-1}), in-plane Si-O stretching bands (1030 cm^{-1} and 1010 cm^{-1}), deformation band of inner-surface hydroxyl groups (915 cm^{-1}), Si-O stretching bands (795 cm^{-1}, 755 cm^{-1} and 695 cm^{-1}) and deformation bands Al-O-Si, Si-O-Si and Si-O, respectively (540 cm^{-1}, 470 cm^{-1} and 430 cm^{-1}). Assignment of IR spectral bands of minerals according to literature (Russel et al., 1994; Madejová and Komandel, 2001; Vaculíková and Plevová, 2005) was used in this paper. PC1 described 76.3 % of variance. The second principal component (PC2)

Table 2 Brief summary of statistical models.

Name of model	Used minerals	Classes
Model 1	All mineral samples	Clay minerals
		Feldspars
		Accessory minerals
Model 2	Clay minerals	Biotite
		Muscovite-illite
		Chlorite
		Kaoline-serpentine
		Smectite
		Vermiculite
Model 3	Minerals of kaoline-serpetine group	Kaolinite
		Dickite
		Halloysite
Model 4	Minerals of smectite group	Na-Montmorillonite
		Ca-Montmorillonite
		Nontronite
		Hectorite
		Mixed illite-smectite structure
Model 5	Micas	Biotite
		Muscovite
		Illite
		Mixed illite-smectite structure
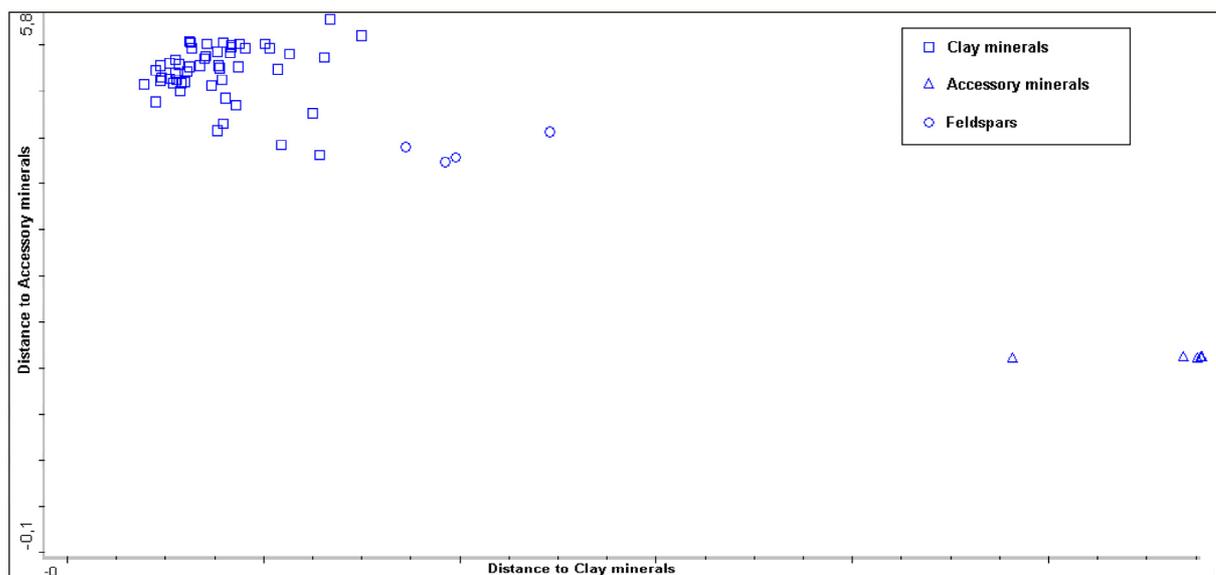
Fig. 1 Mahalanobis distance plot of three clusters of minerals (Model 1).

described 9.3 % of variance and its loadings spectrum included again the kaolinite bands only. Contrary to the PC1, the entire spectral band in PC2 loadings spectrum had negative intensities of bands. The third principal component (PC3) described 5.9 % of variance. The PC3 loadings spectrum included also negative bands of kaolinite and moreover a doublet of Si-O stretching bands of quartz (800 cm^{-1} and 780 cm^{-1}) and a doublet of stretching bands of the hydroxyl group of gypsum (3550 cm^{-1} and 3400 cm^{-1}). The bands of quartz and gypsum had normal orientation (e.g. they did not have negative intensities of bands). The fourth principal component (PC4) described 2.8 % of variance and PC4 loadings spectrum included the same bands as PC 3 loadings spectrum but entire bands had negative intensities. The loadings spectra of the above-mentioned PCs are shown in Figure 2.
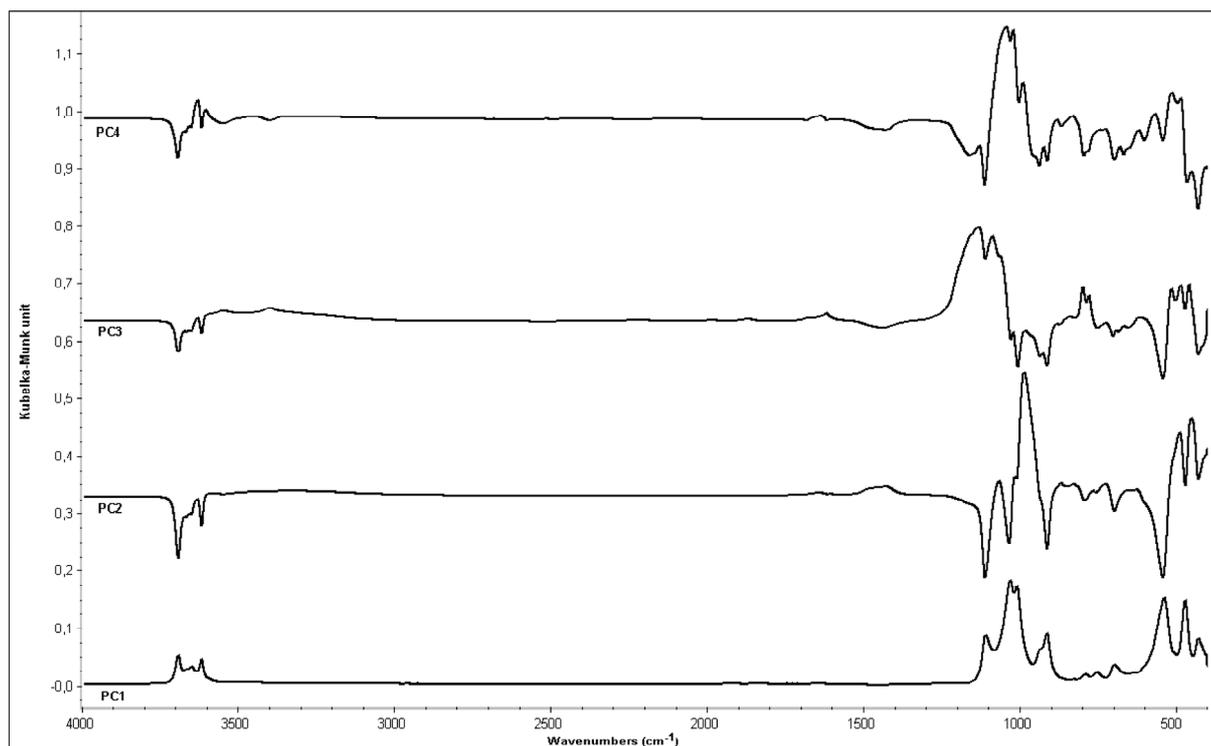
Fig. 2   Loadings spectra of the first four principal components (Model 1).

3.3. MODEL 2 – IDENTIFICATION OF CLAY MINERALS GROUPS

This model was created for classification of clay minerals into particular groups of clay minerals. Classification of clay minerals according to Weiss and Kužvart (Weiss and Kužvart, 2005) was used in this study. Model 2 involved six classes (Biotite, Muscovite-illite, Chlorite, Kaoline-serpentine, Smectite and Vermiculite). In this model the first two classes represented the micas group of clay minerals; the other classes represented the remaining groups of clay minerals. The micas group had to be split into two classes (Biotite and Muscovite-illite) by reason of bad creation of clusters. In the Biotite class were samples of biotite only; in the Muscovite-illite class were samples of muscovite and illite. In the Chlorite class were chlorite samples only. In the Kaoline-serpentine class were samples of kaolinite, dickite and halloysite. In the Smectite class were samples of montmorillonite, nontronite and hectorite. In the Vermiculite class were samples of vermiculite only. With exception of sample Ill7 all minerals were clearly classified into appropriate classes after performance of discriminant analysis. The above-mentioned sample (mixed illite-smectite structure) was classified between the class Muscovite-illite and class Smectite (Fig. 3).

Ten principal components (PCs) were calculated in Model 2. These ten PCs described 99.9 % of variance of spectral information, whereas almost 97 % of variance was involved in the first four PCs. PC1 loadings spectrum included spectral bands of kaolinite only as well as PC1 in Model 1. PC1 described 79.4 % of variance. PC2 described 10.8 % of variance and its loadings spectrum included negative bands of kaolinite and "positive" broad and very weak band at 3400 cm^{-1} (stretching vibration of water). PC3 described 4.0 % of variance and its loadings spectrum contained negative bands of kaolinite and "positive" bands of stretching vibration of water (higher intensity than in PC2). PC4 described 2.3 % of variance and PC4 loadings spectrum included also negative bands of kaolinite and "positive" band of water, whereas the intensity of the last-mentioned band was higher than in PC3 loadings spectrum.

The band at 1645 cm^{-1} (in PC2, PC3 and PC4 loadings spectrum) belongs to deformation vibration of water. This band very probably presents moisture of samples. The band at 1645 cm^{-1} has not been used for the creation of Model 2.

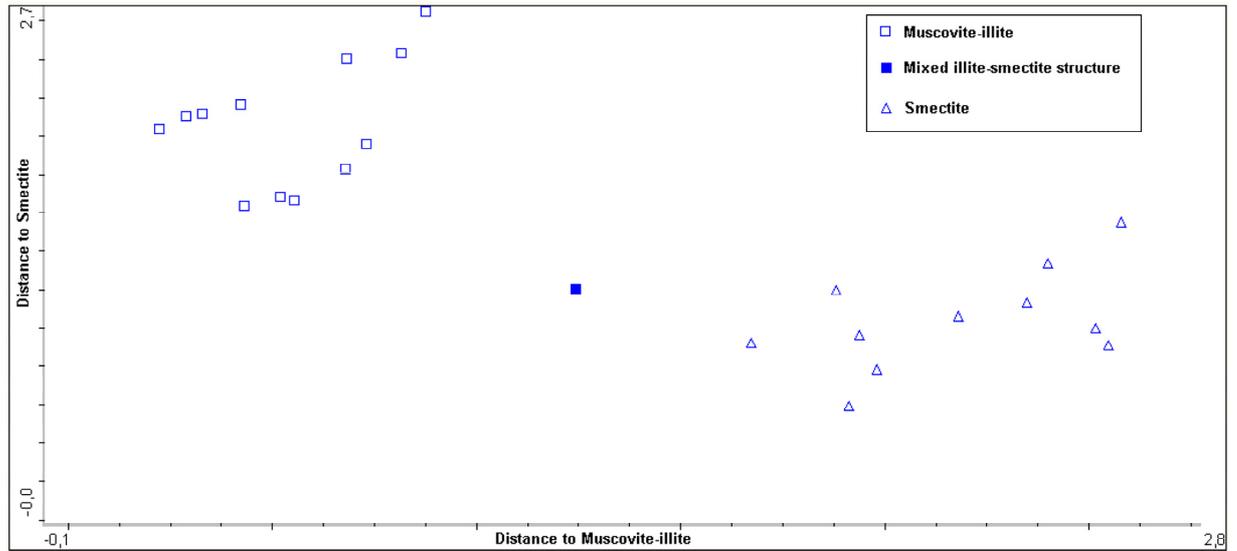The loadings spectra of the above-mentioned PCs are shown in Figure 4.

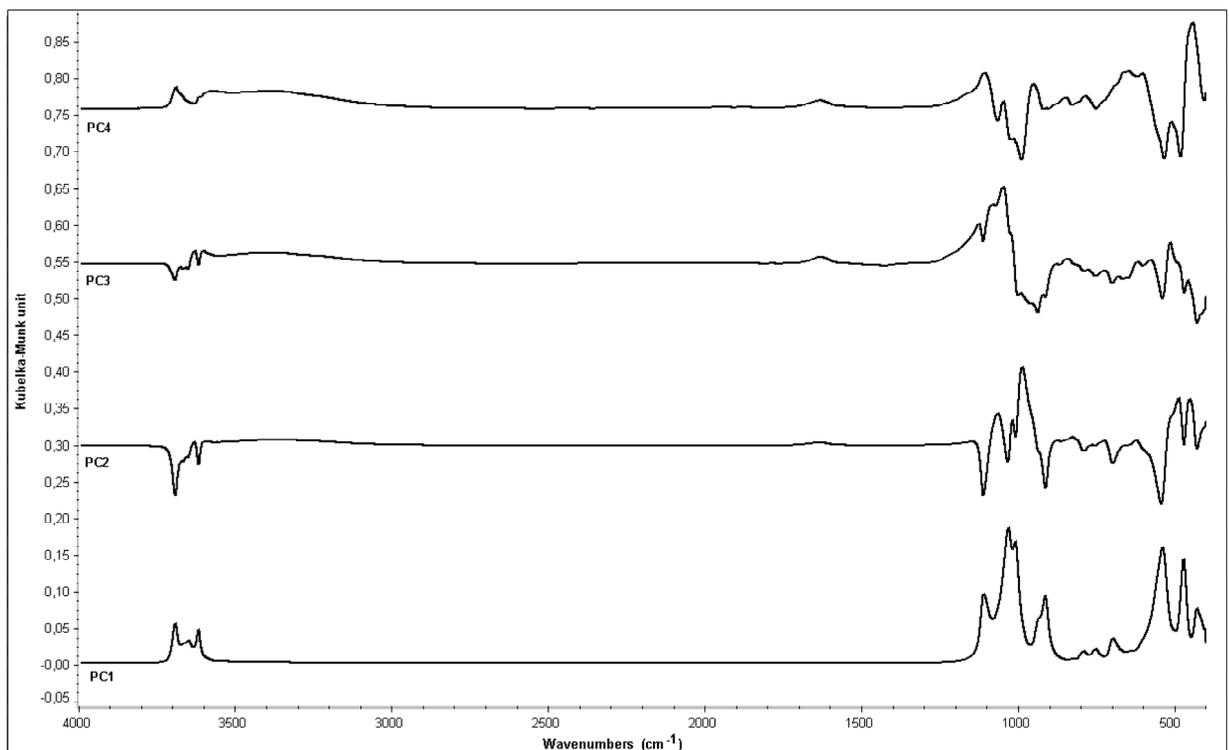**Fig. 3** Mahalanobis distance plot of classes Muscovite-illite and Smectite (Model 2).

Fig. 4 Loadings spectra of the first four principal components (Model 2).

3.4. MODEL 3 – IDENTIFICATION OF MINERALS OF KAOLINE-SERPENTINE GROUP

This model was created for identification of individual members of the Kaoline-serpentine group of clay minerals. Kaolinite, dickite and halloysite were used in this study as representatives of the Kaoline-serpentine group of clay minerals. Thus the Model 3 included three classes (Kaolinite, Dickite and Halloysite). All minerals were clearly distributed into used classes by discriminant analysis.

Ten principal components (PCs) were calculated in Model 3. These ten PCs described 99.9 % of variance of spectral information, whereas almost 97.5 % of variance was involved in the first three PCs. PC1 described 82.5 % of variance, PC2 described 11.3 % of variance and PC3 described 3.6 % of
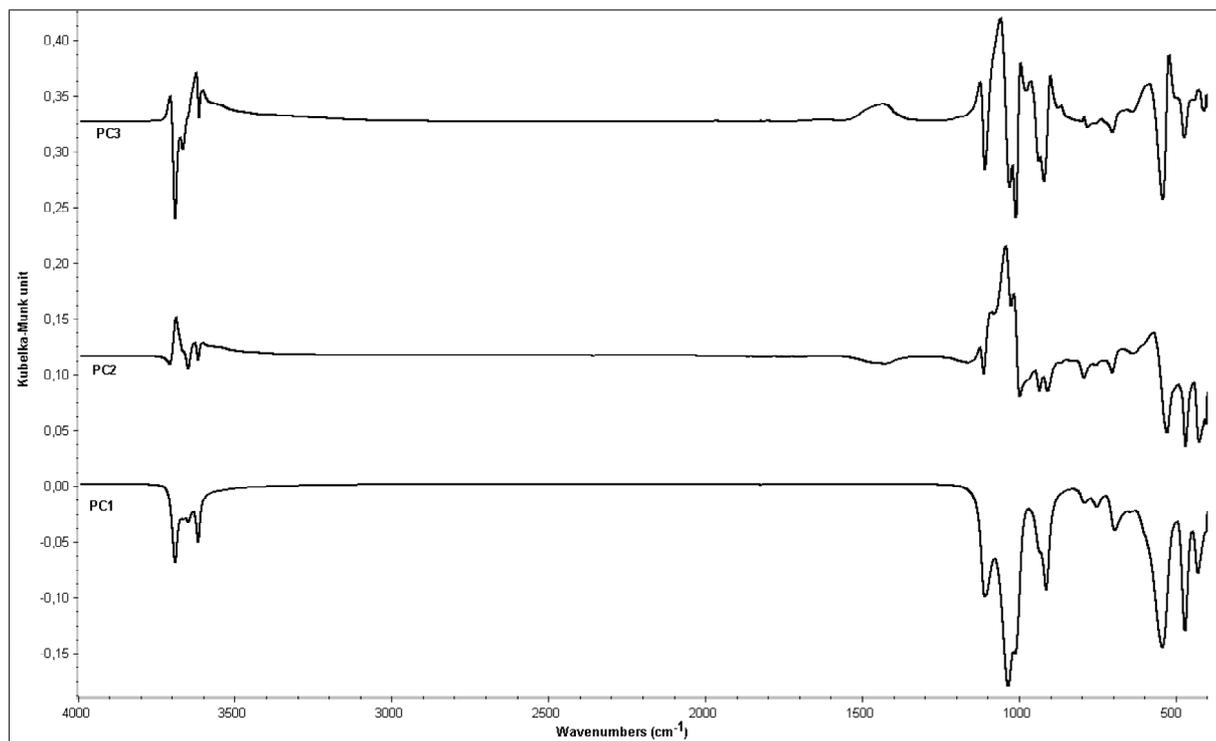
Fig. 5 Loadings spectra of the first three principal components (Model 3).
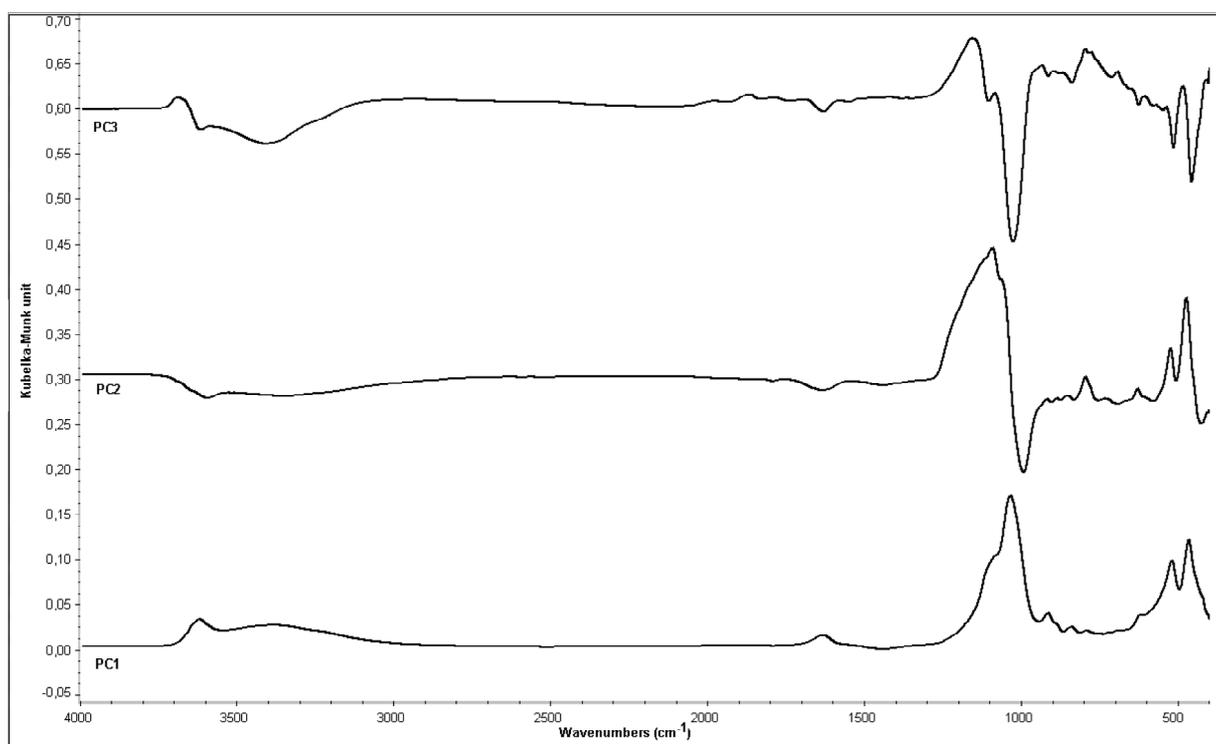

Fig. 6 Loadings spectra of the first three principal components (Model 4).
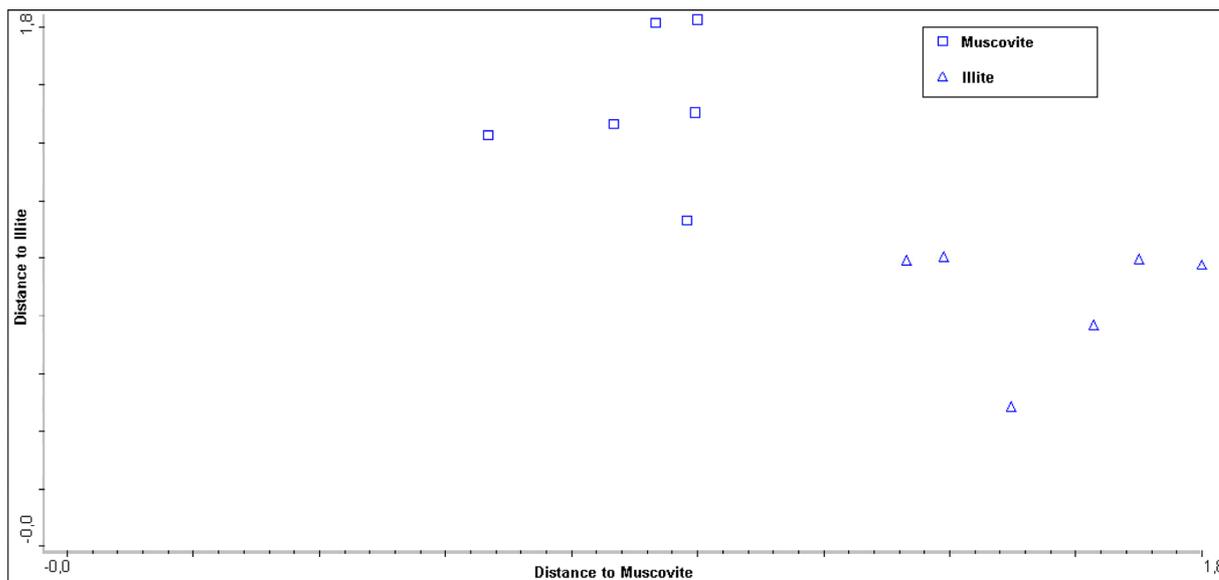
Fig. 7   Mahalanobis distance plot of Muscovite and Illite classes (Model 5).

variance. All three PC loadings spectra included negative bands of kaolinite. The particular loadings spectra differed only in intensities of bands. Bands of the highest intensities were in PC1 loadings spectrum. The band at 1440 cm^{-1} (negative intensity in PC2 loadings spectrum and positive intensity in ureC3 loadings spectrum) belongs to stretching vibration of carbonates present as impurity in the sample of dickite. This band has not been used for the creation of Model 3. The loadings spectra of the above-mentioned PCs are shown in Figure 5.

3.5. MODEL 4 – IDENTIFICATION OF MINERALS OF SMECTITE GROUP

This model was created for identification of individual members of the smectite group of clay minerals. Na-montmorillonite, Ca-montmorillonite, nontronite and hectorite were used in this study as representatives of this group of clay minerals. Model 4 included five classes: Na-montmorillonite (Mon1 - Mon5), Ca-montmorillonite (Mon6 - Mon8), Nontronite, Hectorite and Mixed illite-smectite structure. All minerals were clearly distributed into used classes by discriminant analysis.

Ten principal components (PCs) were calculated in Model 4. These ten PCs described 99.9 % of variance of spectral information, whereas almost 97.5 % of variance was involved in the first three PCs. The loadings spectrum of the first principal component (PC1) included spectral bands of montmorillonite only: stretching bands of structural hydroxyl groups (3640 cm^{-1}), broad stretching band of water (3440 cm^{-1}), deformation band of water (1650 cm^{-1}), band of Si-O stretching (1040 cm^{-1}), deformation bands of Al-Al-OH vibration (915 cm^{-1}), deformation bands of Al-Mg-OH

vibration (840 cm^{-1}), Si-O stretching band of silica (800 cm^{-1}), coupled out-of-plane vibration band of Al-O and Si-O (625 cm^{-1}) and deformation bands Al-O-Si, Si-O-Si, respectively (525 cm^{-1} and 470 cm^{-1}). PC1 described 86.0 % of variance. PC2 described 7.2 % of variance and its loadings spectrum included negative bands at 3640 cm^{-1}, 3440 cm^{-1} and 1650 cm^{-1} and positive bands at 800 cm^{-1}, 625 cm^{-1}, 525 cm^{-1} and 470 cm^{-1}. PC3 described 4.3 % of variance and the loadings spectrum contained negative bands at 3640 cm^{-1}, 3440 cm^{-1}, 1650 cm^{-1}, 525 cm^{-1} and 470 cm^{-1}. All bands in the loadings spectra of PC2 and PC3 belonged to montmorillonite too. The band at 1650 cm^{-1} has not been used for the creation of Model 4 by reason of potential interference intensity of this band by samples moisture.

The loadings spectra of the above-mentioned PCs are shown in Figure 6.

3.6. MODEL 5 – IDENTIFICATION OF MINERALS IN GROUP OF MICAS

This model was created for identification of individual members of micas. Biotite, muscovite and illite were used in this study as representatives of this group of clay minerals. Model 5 included four classes (Biotite, Muscovite, Illite and Mixed illite-smectite structure). All minerals were clearly distributed into used classes by discriminant analysis. The Mahalanobis distance plot of Muscovite and Illite classes is shown in Figure 7.

The clusters of muscovite and illite were relatively close to each other but they were clearly separated. IR spectra of muscovites and illites can be very similar (on account of similar chemical composition and structure) and common identification
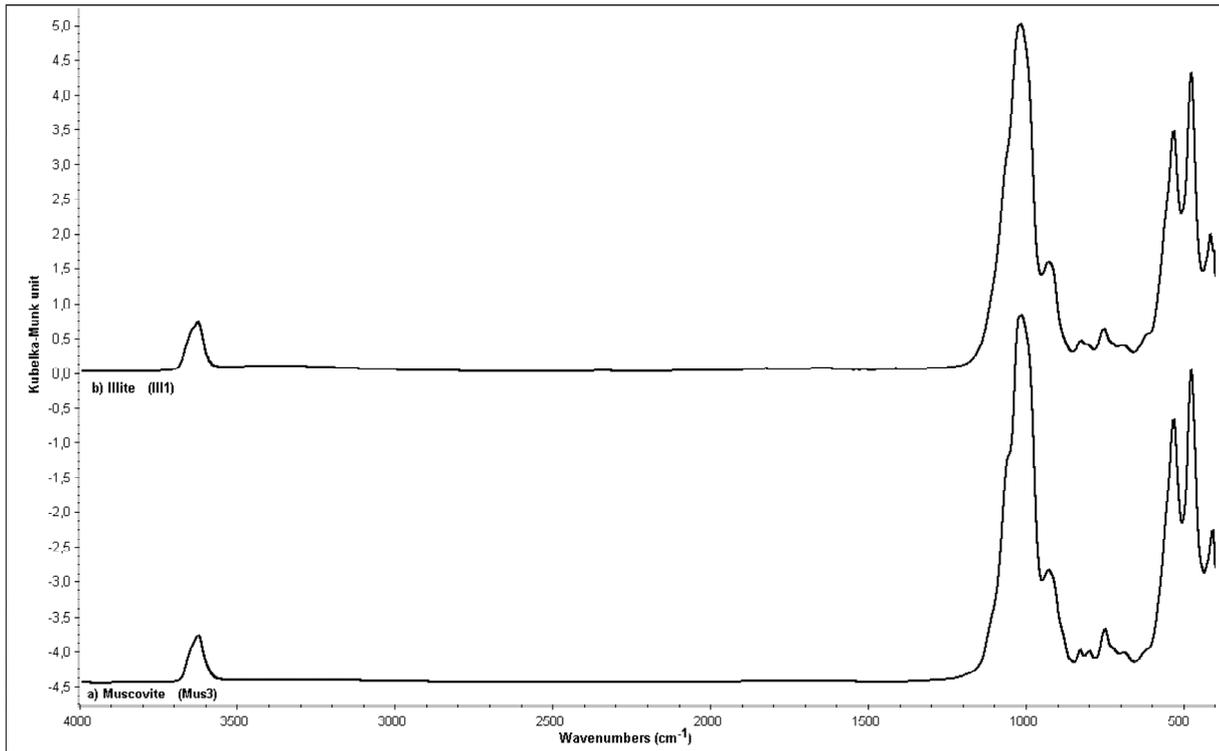
Fig. 8   IR spectra of muscovite (a) and illite (b).

of both minerals by their IR spectra is practically impossible (Vaculíková, 2006). IR spectra of both mentioned minerals are shown in Figure 8.

Ten principal components (PCs) were calculated in Model 5. These ten PCs described 99.9 % of variance of spectral information, whereas almost 97.5 % of variance was involved in the first two PCs. The loadings spectrum of PC1 included the following spectral bands applied to the creation of Model 5: stretching bands of structural hydroxyl groups (3600 cm^{-1}), band of Si-O stretching (1010 cm^{-1}), deformation bands of Al-Al-OH vibration (935 cm^{-1}), deformation bands of Al-O-Si in-plane vibration (755 cm^{-1}), Si-O deformation band (700 cm^{-1}), deformation bands Al-O-Si, Si-O-Si, respectively (535 cm^{-1} and 480 cm^{-1}). Bands at 3600 cm^{-1}, 1010 cm^{-1}, 700 cm^{-1} and 480 cm^{-1} belonged to biotite; bands at 3600 cm^{-1}, 1010 cm^{-1}, 935 cm^{-1}, 755 cm^{-1}, 700 cm^{-1}, 535 cm^{-1} and 480 cm^{-1} belonged to muscovite and illite. PC1 described 90.6 % of variance. PC2 described 6.8 % of variance and its loadings spectrum included negative bands at 3600 cm^{-1}, 935 cm^{-1}, 755 cm^{-1}, 700 cm^{-1}, 535 cm^{-1} and 480 cm^{-1}. The band at 1440 cm^{-1} in both PC loadings spectra belonged to carbonates present as impurity in the sample of biotite (Bio3). The presence of carbonates in this standard of biotite was very small, thus the intensity of 1440 cm^{-1} band in IR spectra was very weak. In PC loadings spectra the intensity of this band has risen by reason of significant influence of this band on the variability of spectra. The band of

1440 cm^{-1} has not been used for the creation of Model 5. The loadings spectra of the above-mentioned PCs are shown in Figure 9.

4.   CONCLUSION

The discriminant analysis of IR spectra of 60 samples of mineral standards (clay minerals, feldspars, carbonates, sulfides and quartz) is presented in this paper. Identification of individual clay minerals is possible using the created five statistical models. Model 1 served for the separation of clay minerals from feldspars and accessories minerals. Model 2 was created for the splitting of clay minerals into individual groups of clay minerals. Model 3, Model 4 and Model 5 were drawn for the identification of clay minerals from the groups of kaoline-serpentine, smectite and mica minerals, respectively.

Principal component analysis (PCA) was used to find useful spectral information. Very important spectral bands for PCA of clay minerals included vibration bands of hydroxyl groups and vibration bands of Si-O and Al-O bonds in clay minerals. Relatively significant were bands of kaolinite in Model 1, Model 2 and Model 3.

Identification of clay minerals by discriminant analysis of IR spectra was very successful in this study. Differentiation of muscovite from illite was even achieved by this method. Muscovite and illite had too similar IR spectra and these two clay minerals are almost undistinguishable when common methods of identification by IR spectroscopy are used. The
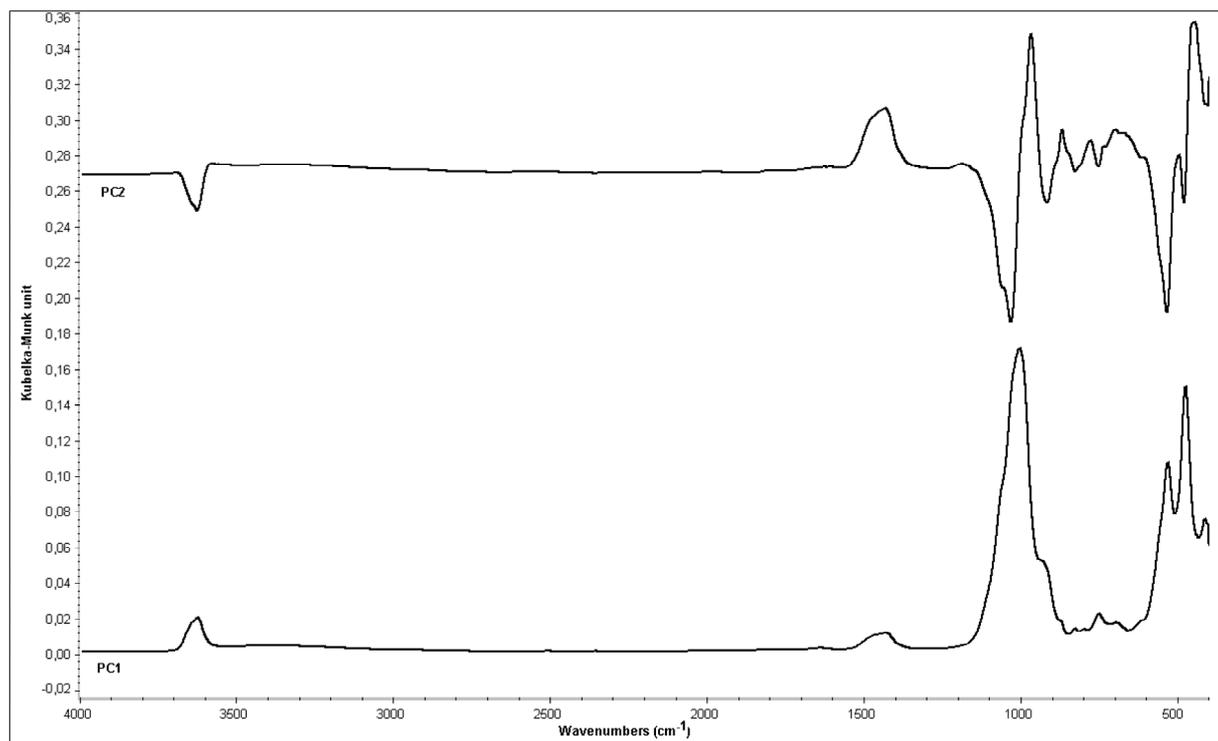
Fig. 9 Loadings spectra of the first two principal components (Model 5).

probable reason for a successful differentiation of muscovite from illite was the use of PCA as a component of discriminant analysis. The principle component analysis is able to find the very slight differences at IR spectra of muscovite and illite standards. Another advantage of the discriminant analysis as an identification tool is the ability to identify mixed structures of clay minerals (e.g. illite-smectite mixed structure).

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