

# Qualitative and Quantitative Determination of Montmorillonite Using Infrared Spectrometry

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**Abstract:** The present study investigates the various possibilities of qualitative and quantitative analysis of montmorillonite ( $(1/2\text{Ca}, \text{Na})_{0.7}(\text{Al}, \text{Mg}, \text{Fe})_4(\text{Si}, \text{Al})_{8020}(\text{OH})_4 \cdot n \text{H}_2\text{O}$  (MT)), major constituent of Bendonite coming from the island Milos-Greece, using infrared (IR) spectroscopy and preparing the samples with KBr. X-Ray diffraction diagrams were obtained for the determination of their mineralogical composition. Observation of IR spectra of sample with different MT content revealed that the Si-O-Si vibration band at  $1038\text{cm}^{-1}$  sharpens with increasing MT content. The combination of the above techniques led to a convenient determination of the minerals, contained in the sample and to a discrimination of identical oscillations, observed in different minerals at the same wave number ( $1038\text{cm}^{-1}$ )<sup>[1]</sup>. As far as the quantitative analysis concerns, in the case of MT, thirteen comparative samples of known composition were analysed. The obtained spectra were digitized and smoothed, within the area from 800 to  $1200\text{cm}^{-1}$ , using the Savitzky – Golay method, followed by Lorentz function transformation. Due to overlap from other substances, the plot of a calibration curve for MT, and consequently the development of a model, describing the absorption / concentration correlation for a specific sample, were not satisfactory. So the calibration curve according to Lambert-Beer law<sup>[2,3]</sup>, required use of samples with high concentration of MT. To overcome this problem the calibration curve for MT was constructed using dilutions of standard samples containing more than 85% of the mineral, with  $\text{SiO}_2$ , at the wave number of  $1038\text{cm}^{-1}$ . This curve was used for the determination of MT in unknown samples giving very good results compared with the mineralogical composition obtained by XRD.

**Keywords:** IR, MT, XRD, Savitzky Golay, Lambert-Beer, Lorentz, KBr.

## I. INTRODUCTION

Infrared spectrometry is one of the most popular instrumental methods of analysis, allowing the analysis of physical parameters of different materials and it is based on the vibrations of the bonds of ionic lattice compounds. The qualitative and quantitative analysis of various minerals, using IR-analysis has been the subject of great scientific interest. However, the great majority of

relative references came from the decade of 1950, mainly due to the rapid development of sophisticated analytical methods. Thus, Sholze H. (1960) shown that the water peak area is presented in  $3\mu$  vibration (caused by OH vibration), the deforming  $\text{H}_2\text{O}$  vibration in  $6\mu$  and the combination of the two mentioned vibrations at  $1.93\mu$ . If water exists in its molecular form the peak area of  $6\mu$  is interfered by other peak areas. For quantitative analysis the choice of the lowest wavelength is preferable, especially at low concentrations of water. R. Fisher and C. Ring (1957) determined quantitatively fluoroapatite and hydroxyapatite in the range of  $16\mu$ , with 1.5% mean of error as for fluoroapatite. J. Hynt and D. Tyrner (1953) shown that two different kinds of element replacements can exist in trioctahedral minerals. The first involves the replacement of a simple ion from other, such as  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  in talc mineral. The second involves a double replacement of equal electric charge, such as  $\text{Si}^{4+}$  from  $\text{Al}^{3+}$  and  $\text{Na}^+$ . Stubcan and Roy (1959) shown the peak area of dioctahedral and trioctahedral complex minerals in the range of  $400\text{-}5000\text{cm}^{-1}$  and characteristic changes in their IR-spectrum were observed. In the present work the possibility of the qualitative and quantitative analysis of montmorillonite was investigated and evaluated.

## II. EXPERIMENTAL

### Instrumentation

For the IR analysis of the samples the IR-spectrometer Perkin-Elmer 883 was used. The study of the samples structure was achieved using the Siemens 5000D- XRD spectrometer and for the sample preparation a specific press instrument SPECAC (Perkin Elmer) was used.

### Reagents

All samples came from Milos Island, Greece, as it is presented in Table 1, while KBr was supplied by CARLO ERBA.

## III. ANALYTICAL PROCEDURE

All samples that are presented in Table 1 underwent a decrease of their size, so as to have

the suitable one for IR-analysis. The samples were diluted with KBr in a proportion KBr: sample 1.5: 200 mg and by applying 7 Atm pressure using the SPECAC press were converted into a pellet. After analyzing the samples using IR spectroscopy, the obtained spectrums were first qualitatively evaluated. For the correct quantitatively determination is the absence of various interferences of the same wavelengths from other minerals and, consequently, the total mineral qualitative analysis before the IR-analysis, as it is presented in Table 2, is necessary. However, the kind of element replacements in various syntactic areas of mineral crystallite should be investigated, for the correct evaluation of possible interferences in the peak areas or the removal of the zone. The characteristic zones of montmorillonites are: 3225, 115-1009, 1038-1026, 915, 878, 845-835, 797-790, 623, 522 and 467 cm<sup>-1</sup>. Calcite gives a peak at 1400 cm<sup>-1</sup>, while the corresponding one of quartz is 798-400 cm<sup>-1</sup> and kaolinite at 3698 and 915 cm<sup>-1</sup> (sample No 18). For low concentrations doublet quartz gives a single zone at 796-800 cm<sup>-1</sup> and because of the low Fe content (Fe<sub>2</sub>O<sub>3</sub><10%) the characteristic zone of Fe-O-H at 3576 cm<sup>-1</sup> is absence. The zone presented at 3200-3250 cm<sup>-1</sup> is caused of the present of water molecules, which are highly bonded with montmorillonite surface. XRD-analysis, which was carried out, determined, apart from montmorillonite, alternative concentrations of quartz, crystoballite, albite, orthoclase, illite and kaolinite.

Sample's name	Sample species	Place of sample
M-1207	Bendonite	Milos-Greece
M-1211	Bendonite	Milos-Greece
M-1201	Bendonite	Milos-Greece
M-1202	Bendonite	Milos-Greece
M-14	Bendonite	Milos-Greece
M-1004	Bendonite	Milos-Greece
M-18	Bendonite	Milos-Greece
M-21	Bendonite	Milos-Greece
M-22	Bendonite	Milos-Greece
M-10	Bendonite	Milos-Greece
M-8	Bendonite	Milos-Greece
M-75	Bendonite	Milos-Greece

Table 1: Source of samples

Dried Sample	M-1207	M-1211	M-1201	M-1202	M-14	M-1004	M-18	M-75	M-21	M-10	M-8	M-1204
SiO <sub>2</sub>	74,36	67,56	62,16	63,40	69,22	47,36	55,01	52,01	51,58	59,44	53,69	68,72
SO <sub>3</sub>	0,06	0,74	3,15	0,07	0,90	2,54	0,15	0,07	0,22	-	-	0,05
Fe <sub>2</sub> O <sub>3</sub> <sup>tot</sup>	0,76	1,21	4,96	1,94	2,39	5,08	4,60	4,69	2,25	4,71	5,77	1,08
Al <sub>2</sub> O <sub>3</sub>	9,52	11,97	9,45	13,06	16,33	15,52	22,30	16,84	18,76	19,97	19,90	11,63
CaO	0,92	0,69	0,76	1,05	1,15	0,89	1,46	2,40	8,44	2,42	4,11	1,15
MgO	0,82	1,15	1,72	2,26	1,92	2,67	3,12	4,11		3,63	3,10	0,85
K <sub>2</sub> O	0,71	3,58	1,08	0,18	0,96	0,96	4,13	1,28	0,51	0,36	0,55	1,67
Na <sub>2</sub> O	0,40	0,35	0,43	0,29	0,66	0,37	0,70	1,47	0,71	1,47	0,86	1,06
TiO <sub>2</sub>	-	-	-	-	0,16	-	0,66	-	0,66	0,56	0,56	-
Loss of firing	12,70	10,65	15,89	16,54	6,75	21,65	8,10	16,52	13,20	7,53	11,11	13,16
Total	100,26	97,89	99,60	98,79	99,47	97,04	100,90	99,40	99,11	100,90	99,65	99,38

Illite	3,5	37,7	-	-	17,00	-	-	11,00	4,5	3,00	5,00	-
Montmorillonite	41,00	28,00	56,00	65,00	32,00	76,00	70,00	54,00	86,00	81,00	88,00	41,00
Kaolinite	3,00	IXNH	-	-	7,00	-	-	-	-	-	-	-
Quartz + Cristobalite	56,00	39,00	40,00	35,00	38,00	20,00	2,00	24,00	-	5,00	-	41,00
Alvitis	-	-	4,00	-	6,00	-	6,00	11,00	-	13,00	-	9,00
Calcite	IXNH	IXNH	1,00	IXNH	IXNH	IXNH	IXNH	IXNH	15,00	IXNH	7,00	IXNH
Gypsum	-	-	-	-	-	5,00	-	-	-	-	-	-
K-feldstyt	-	-	-	-	-	-	22,00	-	-	-	-	9,00
Hematite	-	-	-	-	-	-	-	-	-	-	-	-

Table 2: Chemical and Mineral composition of analyzed Bentonite samples (Wt %)

#### IV. RESULTS AND DISCUSSION

The vibrations in clay minerals can be categorized in the vibrations of OH, Si, octahedral cations and internal cations. This categorization is complete for the high frequency stretching vibrations of OH, found in the area of 3400-3750 cm<sup>-1</sup>, but not for the stretching vibrations Si-O (700-1200 cm<sup>-1</sup>) that are over-right from other vibrations but the bending vibrations Si-O (200-600 cm<sup>-1</sup>) that are over-right strongly from vibrations of octahedral cations and from vibrations of displacement of the OH group. The vibrations of the internal cations by the V.C. Farmer, found between 70 and 150 cm<sup>-1</sup> can be proven to be topical, despite the fact of the possible interaction with the less strong deformations of Si anion. Montmorillonite is a mineral with a structure of 2:1 and its chemical form is:(Al, Fe, Mg)<sub>2</sub>(OH)<sub>2</sub>I(Si, Al)<sub>4</sub>(O, OH)<sub>10</sub>K(K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, the characteristic zones of montmorillonite are 3624, 3420, 3225, 1115-1090, 1038-1026, 915, 878, 845-835, 797-790, 623, 522, 467cm<sup>-1</sup>.

The calcite can be seen at 1400 cm<sup>-1</sup>, the quartz in the area of 798-400 cm<sup>-1</sup> and the kaolinite at 3698 and 915 cm<sup>-1</sup> (sample M-18). For very small concentrations the couple of peaks in the film of quartz is limited in a simple zone at 798 to 800 cm<sup>-1</sup>. Because of the small concentration of the samples in Fe

(Fe<sub>2</sub>O<sub>3</sub><10%), there is not any zone at 3576 cm<sup>-1</sup> due to Fe—O-H. The zone that is present at 3200-3250 cm<sup>-1</sup> is a result of the water molecules that are strongly connected with the surface of montmorillonite. The analysis that was carried out with X-Ray Diffraction (fig) determined except the montmorillonite some alternative concentrations of quartz, cristoballite, alvite, orthoclase, illite and kaolinite. The characteristic zones of montmorillonite are: 3624, 3420, 3225, 1630, 1038-1026, 915, 845-835, and 522 cm<sup>-1</sup>. The characteristic zones of illite are: 3643, 3622, 1080, 1022, 912, 875, 830, 752, 692, 523, 475 cm<sup>-1</sup>. The characteristic zones of gypsum are: 3543, 3485, 3240, 1685, 1620, 1162, 1142, 1112, 668, 606 cm<sup>-1</sup>. The characteristic zones of alvite are: 1150, 1096, 1035, 995, 786, 760, 744, 650, 594, 536, 467, 428 cm<sup>-1</sup>. The characteristic zones of aimatite are: 600, 463, 425 m<sup>-1</sup>. The characteristic zones of quartz are: 1172, 1082, 798, 778, 693, 512, 478, 460 cm<sup>-1</sup>. The characteristic zones of cristoballite are: 1200, 1166, 1098, 792, 622, 520, 488, 476, 445 cm<sup>-1</sup>.

Infrared spectrums of the analyzed samples of bentonite. The five diagrams given above between others have small concentrations of montmorillonite and the rest have high concentrations. The concentration optically can be seen from the opening of the shoulder of the wave numbers 1026, 1038, 1090 and 1115 cm<sup>-1</sup>. In the wave numbers 474, 522, 915, 1026, 1038, 3420 and 362 cm<sup>-1</sup>, the Vibrations of Si-O, Si-O-Al, Al—O-H, Si-O-Si, Si-O-Si, H-O-H, (Mg, Al)-O-H are given respectively.

Wavelength (cm <sup>-1</sup> )	Vibration
3642	(Mg, Al)...O-H
3624	Al...O-H
3420	H-O-H
3225	H-O-H
1630	H-O-H
1168	Si-O
1115-1090	Si-O
915	Al...O-H
878	(Al, Fe)...O-H
845-835	(Al, Mg)...O-H
796	(Al, Mg)...O-H
695	Si-O-Al
623	Al...O-H
578	Al...O-H
522	Si-O-Al
474	Si-O
467	Si-O-Mg
450	Si-O-Fe
426	Si-O

Table 3: Vibration wavelength in IR spectrum of montmorillonite

## V. CONCLUSION

The qualitative as well as the quantitative analysis of montmorillonites is possible only if the mineralogical composition of the samples has been identified, which can be achieved using XRD spectrometry or electronic microscopy. Elementary analysis is substantial for the identification of the elements, which take part in the vibration giving information for elements' replacements in the mineral's crystal structure. Elements' replacements cause changes in the transmittance values and, as a result, errors in the quantitative evaluation. In case of montmorillonite:

- A low concentration of MgO makes 915 cm<sup>-1</sup> zone become less separable from the main zone of 1028 cm<sup>-1</sup>, contrary to when the concentration of MgO is higher. In the latter case this separation is good.
- The zone of 1028 and 1038 cm<sup>-1</sup> tend to form "shoulder" between them, whose size is reversely proportional to the montmorillonite concentration. Therefore, it is possible 2 comparative calibration curves of 0-50% and 50-100% montmorillonite concentration, respectively, to be obtained for the grouping of montmorillonite samples.

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