

# Methods of the montmorillonite content determination in foundry bentonites

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## Abstract

This paper presents results of the measurements montmorillonite content in foundry bentonites and mixtures of bentonite – lustrous carbon carrier by three methods: spectrophotometric method with the use of methylene blue, spectrophotometric method with the use of Cu(II) – triethylenetetramine (Cu-TET) complex, infrared spectroscopic method (FTIR).

**Keywords:** Foundry bentonites, Montmorillonite, FTIR method

## 1. Introduction

An information on the amount of active bentonite in moulding sand after casting knocking-out is necessary in the rebounding process of sands with bentonite. This information decides on the amount of fresh bentonite added to sands and thus influences its technological properties and costs of rebounding processes. The standard method of the active bentonite determination in moulding sands in domestic foundry plants and in the majority of European ones is normalised and based on measuring the adsorbed amount of methylene blue [1]. It is a highly labour-consuming method requiring a long time for performing the determination. The technologists obtain the results after some hours of introducing the rebounded sand into the circulation. This is specially important in the case of various casting productions since due to a different degree of sand overheating they contain different amounts of active bentonite. Therefore several companies dealing with the bentonite or mixtures of bentonite-bright coal carrier production are engaged in intensive investigations of the development of a reliable and fast method of the determination of the active bentonite content in sands. To this end the spectrophotometric determination method using Cu(II)-triethylenetetramine (Cu-TET) complex, applied in geology for an

examination a clay activity, was adapted. This method is faster than the methylene blue adsorption method and simpler from the analytical point of view. The infrared spectrometry method (FTIR) is also more and more often applied. This method allows for a very fast determination of the active bentonite content, which is important under production conditions.

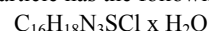
The results obtained by the FTIR method presented in this paper should be treated as the preliminary results indicating the proper direction of montmorillonite changes in the tested bentonite. The team of Authors is currently performing research on the quantitative interpretation of the obtained spectra in correlation with the mentioned above spectrophotometric methods.

## 2. Applied investigation methods

### Spectrophotometric method with the use of methylene blue

This method is based on adsorption of methylene blue on montmorillonite particles contained in bentonite.

Methylene blue particle has the following chemical formula:

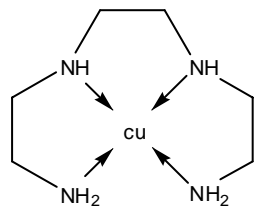


Methylene blue cation is easily adsorbed by clays, including montmorillonite. The adsorption process has three stages [2]. In the first stage, cations of methylene blue form monolayer around clay particles. Then those cations start to substitute other cations present on the clay surface (e.g. sodium or calcium ions in bentonites). Finally methylene blue cations can be physically adsorbed on the clay surface. However, due to large dimensions of those cations a physical adsorption is of a smaller meaning.

Spectrophotometric absorption measurements were made by means of the VIS ODYSSEY DR/2500 spectrophotometer, with an automatic wavelength calibration, of the HACH Company, at a wavelength of 470 nm. The result is recalculated and presented in mg of methylene blue adsorbed by 1 gram of the tested sample.

Spectrophotometric method with the use of Cu(II) – triethylenetetramine (Cu-TET) complex

This method is based on adsorption of Cu-TET copper complex on montmorillonite particles contained in bentonite [3, 4]. The chemical formula of Cu-TET complex is given below:



Spectrophotometric absorption measurements were performed by means of the same equipment as previously, but at a wavelength of 620 nm. The result is given as a consumption of Cu-TET complex in mmol/l, and than recalculated into the cation exchangeability given in percentages.

Infrared spectroscopic method (FTIR)

The characteristic band Si-O occur at a wavelength of 1040  $\text{cm}^{-1}$  [5, 6] for minerals containing montmorillonite. Vibrations of OH groups have maximum at a wavelength of app. 3630  $\text{cm}^{-1}$  [7, 8]. Mutual relations of band intensities (peak heights) as well as surface areas under the band related to Si-O stretching vibrations versus the band related to OH groups stretching vibrations, were analysed.

The infrared spectroscopy belongs to analytical methods allowing for testing samples being in a solid, liquid or gaseous state. The selection of the proper measuring technique for the given sample depends on the purpose in front of the method: qualitative or quantitative analysis, sample size and its state of the matter as well as possibilities of interactions of components present in the analysed sample.

FTIR examinations were performed by means of the Excalibur spectrometer with DTGS detector, produced by BIO-RAD Company. The tests were performed by the transmission technique. Spectra were tested in the wavelength range 4000 – 400  $\text{cm}^{-1}$ , with the resolution of 4  $\text{cm}^{-1}$ .

### 3. Materials applied in examinations

Two series of bentonite (I series: samples 1-3, II series: samples 4-6) and mixtures of bentonite – bright coal carrier (samples 7 and 8) originated from various producers and being currently applied in domestic foundry plants, were used in examinations.

### 4. The obtained results

FTIR spectra obtained for the examined materials are presented in Figures 1 – 3.

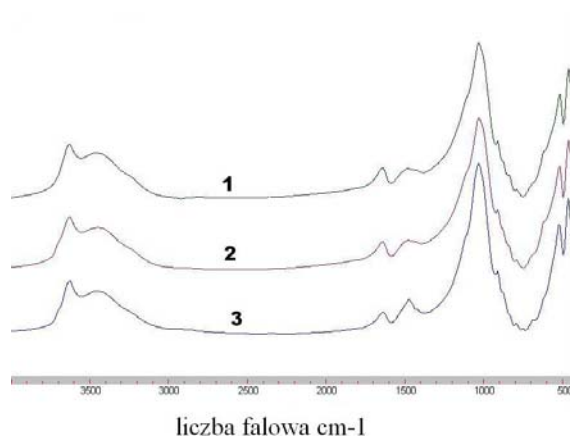


Fig. 1. FTIR spectra of tested bentonites – samples 1, 2, 3

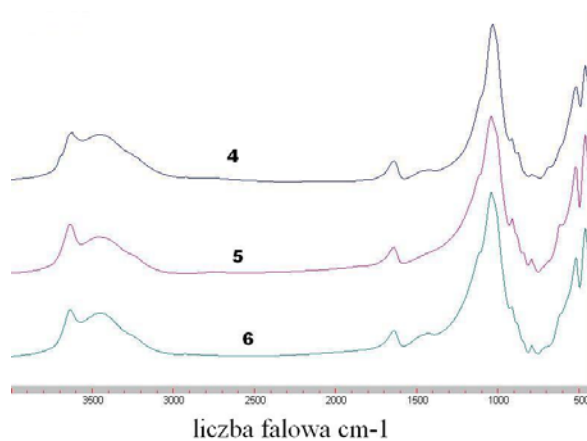


Fig. 2. FTIR spectra of tested bentonites – samples 4, 5, 6

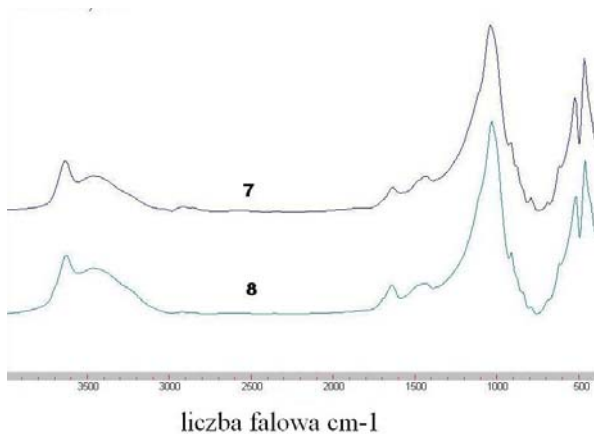


Fig. 3. FTIR spectra of tested mixtures: bentonite-lustrous carbon carrier – samples 7 and 8

Two methods of analysis of the obtained spectra were applied:

- Determination of the dependence in between the intensity of the analytic OH band occurring at a wavelength of app.  $3600\text{ cm}^{-1}$  and the intensity of the reference Si-O band at a wavelength of  $1040\text{ cm}^{-1}$ .
- Determination of the dependence between the surface area under the analytic OH band occurring at a wavelength of app.  $3600\text{ cm}^{-1}$  and the surface area under the reference Si-O band at a wavelength of  $1040\text{ cm}^{-1}$ .

Sample No 1 was assumed as the reference sample containing 100% of montmorillonite.

The method of calculating heights of the reference Si-O band and of the analytic band - related to vibrations of OH groups - is illustrated in Figures 4 and 5, while the method of determination the areas under bands of those vibrations is illustrated in Figures 6 and 7.

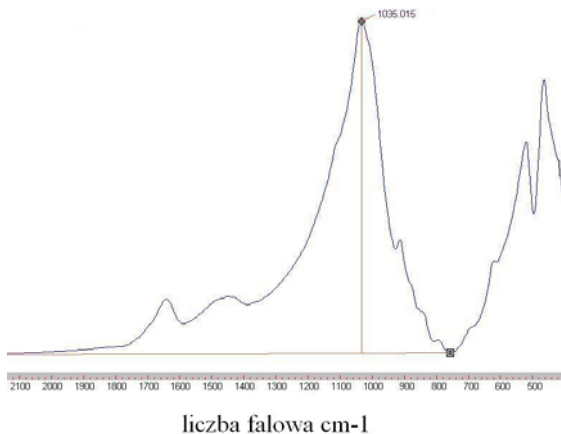


Fig. 4. Method of determination of the intensity (height) of the reference Si-O band

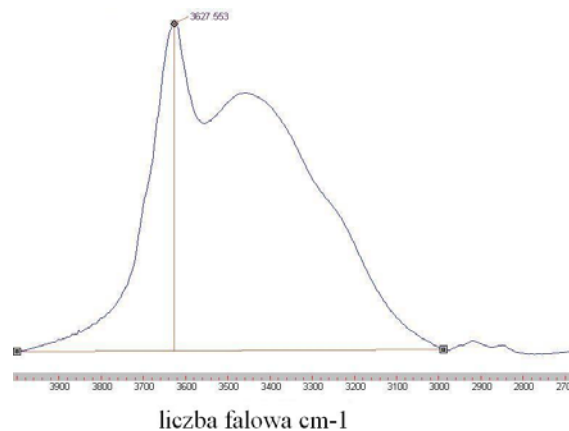


Fig. 5. Method of determination of the intensity (height) of the analytic OH band

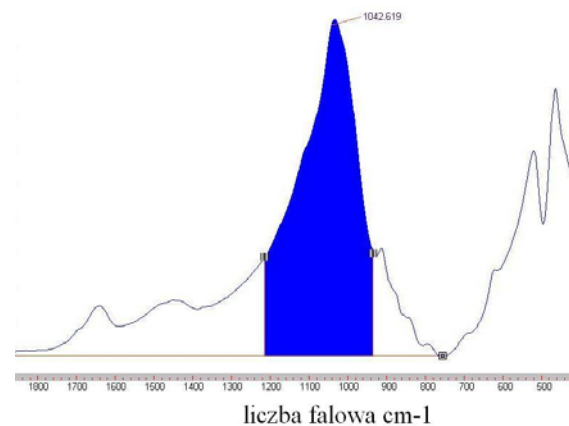


Fig. 6. Method of determination the surface area for the reference Si-O band

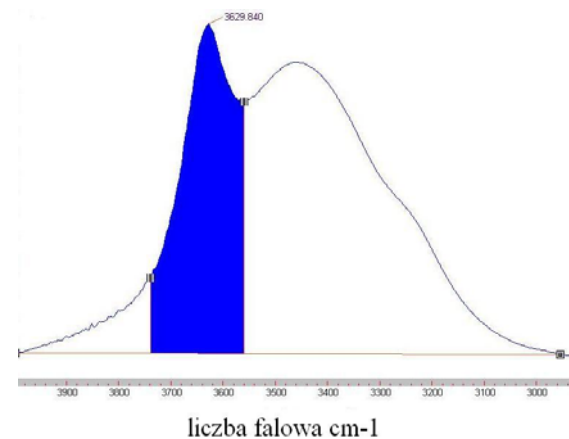


Fig. 7. Method of determination the surface area for the analytic OH band

The results of calculating the relation of the intensities of bands and surface areas under bands related to OH groups versus the reference Si-O band for the examined bentonites and mixtures

of bentonite with lustrous carbon carrier - are presented in Table 1. Each of the presented results constitutes the arithmetic mean from 3 measurements.

Table 1.  
Results of the measurements montmorillonite contents in bentonites

Sample number	Relation of the intensity Si-O/OH	Relation of the surface areas Si-O/OH	Methylene blue method mg/g	Copper complex method %
1	0,344	0,240	440	99
2	0,338	0,232	403	72
3	0,308	0,210	325	63
4	0,310	0,250	338	-
5	0,295	0,199	324	-
6	0,289	0,198	303	-
7	0,269	0,167	254	-
8	0,308	0,213	276	-

## 5. Conclusions

On the basis of the preliminary examinations of the application possibility of the infrared spectroscopy for the determination of a montmorillonite content in bentonites and in mixtures of bentonite with lustrous carbon carrier, it can be stated:

- There is a total conformity of mutual relations between the intensities of characteristic bands as well as the surface areas under those bands, and therefore it seems that both methods of the spectra interpretation can be taken into account.
- Comparison of results of the quantitative determination of the montmorillonite content obtained by the FTIR method with the results obtained by other methods, especially the methylene blue absorption method (compatibility of tendencies in the range of the montmorillonite content)

creates premises for the future application of this method under industrial conditions.

- Further investigations concerning a wider group of bentonite of a distinctly diversified montmorillonite content are necessary.

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