

# Quantitative methods for quantification of montmorillonite content in bentonite clays

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**Abstract.** This article is devoted to the comparison of various methods for the quantitative determination of montmorillonite content in bentonite clays based on the adsorption of organic molecules and cations. The studies were conducted on samples of natural bentonite clays of the main Russian industrial deposits and the CIS: 10th Khutor (Republic of Khakassia), Zyryanskoe (Kurgan region), Dash-Salakhinskoe (Republic of Azerbaijan), Dinovavrovoe (Republic of Kazakhstan). All samples selected for the study are characterized by relatively high content of montmorillonite (more than 70 %). As reference values for the contents of montmorillonite, we used the data of X-ray diffraction analysis according to the Rietveld method. As the tested methods, the most common approaches were used both in the research and industrial sectors of Russia, based on the adsorption of a mixture of rhodamine 6zh and chrysoidine dyes (GOST 28177-89), adsorption of methylene blue dye and adsorption of copper (II) complex with triethylenetetramine (Cu-trien), as well as thermal characteristics after saturation with organic compounds.

The best convergence of the montmorillonite content values was shown by modified techniques based on the adsorption of methylene blue dye and the adsorption of the Cu-trien complex. Other methods are characterized by a large measurement error. A common problem with these methods is overs equivalent adsorption on highly charged alkaline bentonites and reduced adsorption on alkaline earth bentonites, as well as the presence of impurity minerals and amorphous phases capable of sorption in the composition of bentonite. The research results can be used to compare the results of the content of montmorillonite, cited by various authors in scientific publications and used in production.

**Keywords:** bentonite, montmorillonite, X-ray diffraction, adsorption, organic dyes

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## Introduction

Bentonite clays are valuable mineral raw materials. Due to its binding sorption and swelling properties and high thermal stability, bentonite has become an indispensable raw material in various industries. The most important areas of application for bentonite clay in Russia are (in order of consumption): metallurgy, where bentonite is used as a binder for pelletizing iron ore concentrate; in drilling, for the production of drilling fluids; in foundry, in the manufacture of sandy-clay molds for iron casting; in agriculture and medicine. In total, there are more than 200 areas of use for bentonite (Belousov, Krupskaya, 2019). The main

rock-forming components in bentonite clay are smectite-group minerals, in particular, montmorillonite (MMT). Commonly, it is the content of montmorillonite which is the determining factor when choosing raw materials for industrial needs.

Montmorillonite belongs to the class of layered aluminosilicates of the dioctahedral smectite group and is a 2:1 layer, consisting of Si-O tetrahedral networks joined in the middle with an Al-OH octahedral network (Drits, Kossovskaya, 1990; Guggenheim et al., 2006). Due to the isomorphic substitutions of Al<sup>3+</sup> for Mg<sup>2+</sup> and Fe<sup>2+</sup> in the octahedral networks (predominantly) and a small fraction of isomorphic substitutions of Si<sup>4+</sup> for Al<sup>3+</sup> in the tetrahedral networks, the montmorillonite layer has a negative charge of about 0.33–0.66 f.u., which is neutralized by exchange interlayer hydrated cations of Ca<sup>2+</sup> Na<sup>+</sup>, Mg<sup>2+</sup>, etc. Such a structure leads to the lability of the montmorillonite structure, makes the external and internal surfaces in crystallites available for adsorption

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and provides high swelling and high sorption capacity in relation to heavy metals, radionuclides and other anthropogenic components hazardous to human health. Currently, the most correct methodological approach for calculating the quantitative content of crystalline mineral phases in a mixture (rock, soil, material) is X-ray diffraction using the Rietveld method (Krupskaya, Zakusin, 2019; Zhou et al., 2018; Motoso et al., 2006; Srodon et al., 2001).

Analyzing the content of clay minerals is not a trivial task, it requires specialized equipment and the work of experienced analysts. The micron and submicron sizes of aggregates of clay particles, the complex structure of crystallites, the presence of mixed-layer formations and numerous impurities together make it difficult to diagnose clays. With the development of the instrumental and analytical base, the methods for monitoring the content of montmorillonite in bentonite clay have also improved. It should be understood, however, that most mining and processing plants and foundries date back to the middle of the twentieth century, and they often use old techniques that require neither expensive equipment nor highly qualified specialists in the diagnosis of clay minerals.

The main methods for determining the content of montmorillonite are associated with the calculation of the adsorption value of organic dyes. Despite the fact that these methods are outdated, have a large error and, in fact, determine the sorption capacity of montmorillonite, but not its actual content, they are still used at most Russian enterprises. These include the method for determining montmorillonite, described in GOST 28177-89 «Forming bentonite clays». In addition to industry standards, generally accepted methods include the assessment of the montmorillonite content by the value of the cation exchange capacity (CEC) of bentonite clay. The most common methods for determining CEC include methods for the adsorption of the methylene dye (MB) and triethylene tetramine complex of copper (Cu-trien) (Kahr, 1998; Kaufhold et al., 2002). In the literature, there are also more rare methods for the quantitative determination of montmorillonite that require specialized equipment, for example, thermogravimetric analysis of samples pre-saturated with ethylene glycol (Holtzer et al., 2009, 2011; Nieto et al., 2008).

The results of determining MMT using the above listed and similar methods depend on the structural features of a particular montmorillonite and the composition of impurities in bentonite clay, which, in turn, are associated with the geological conditions of formation and transformation, structural features and characteristics of the mineral composition in general. The presence in the rock of minerals such as zeolite, amorphous silica, cristobalite, calcite, as well as other clay minerals (vermiculite, kaolinite, halloysite,

palygorskite, etc.) significantly affects the adsorption rates and amount of organic dyes and, as a consequence, the results of measurements of the montmorillonite content. The main factors influencing the results of quantitative determination of montmorillonite by such methods are its (Kaufhold et al., 2002; Dormann, Kaufhold, 2009): cation exchange capacity; composition of exchangeable cations (ratio of alkaline and alkaline earth cations); total layer charge; layer charge density; mineral composition (the presence of impurities of other mineral phases which are able to adsorb organic dyes); the volume of micro and mesopores; the size of the clay particles; the presence of a pH-dependent charge, and as a consequence, the pH value of the clay suspension; and the presence of water-soluble salts.

The purpose of this article is to compare the main methods for determining the content of montmorillonite based on the adsorption of organic substances with the results of quantitative mineral analysis using the X-ray diffraction method, which is referenced as the most reliable and generally accepted method, as mentioned above. The paper presents the results of measuring the MMT content in bentonite clays and draws conclusions about the peculiarities of the identified differences.

## Materials and methods

Natural samples of bentonite from large deposits of Russia and the CIS countries, varying in their genesis, structural features and the composition of their interlayer complex, were selected as objects of research: 10<sup>th</sup> Khutor (Republic of Khakassia), Zyryanskoe (Kurgan region), Dash-Salahlinskoe (Republic of Azerbaijan), Dinovavrovoe (Republic of Kazakhstan). The bentonites of the Dinovavrovoe deposit are similar in composition and properties to the well-known bentonites of the Tagansky deposit (Krupskaya et al., 2017) and represent one bentonite-bearing province. The samples were selected in such a way that the content of montmorillonite (according to the data of X-ray diffraction analysis, as will be shown below) was sufficiently high and similar in all samples (Krupskaya et al., 2020).

### *Quantitative determination of mineral content by X-ray diffraction*

X-ray diffraction analysis (XRD) was carried out using an Ultima-IV X-ray diffractometer (Rigaku, Japan). The operating mode used was: 40 kV, 40 mA, copper anode, nickel filter, scan range 3–65°2θ, scan speed 3°2θ/min and step 0.02°2θ, fixed system of focusing slits. To speed up the survey and improve the quality of the experimental data, a new generation semiconductor detector, DTex/Ultra, was used: the scanning speed is 5°2θ/minute. The study of the composition of the sample was carried out using non-oriented preparations, which provides the maximum misorientation of particles. This

is necessary to obtain high-quality diffraction patterns for calculating the quantitative mineral composition (Krupskaya, Zakusin, 2019).

Diagnostics of the mineral composition were carried out by comparing the experimental and reference (from database PDF-2) diffraction patterns in the software package Jade 6.5 (MDI company). The quantitative determination of the mineral composition was carried out by the method of full-profile processing of X-ray pictures from non-oriented preparations (modified Rietveld method). The error in calculating quantitative grades by the Rietveld method is usually estimated at 2–3%. The determination error consists of the sum of the calculation errors for each phase and is given in mass percent. Meanwhile, for individual phases the determination error will differ and may range from 0.5 to 2–3%. The presence or absence of kaolinite was checked for by the presence of diagnostic absorption bands in the IR spectra of bentonites.

The method for calculating the content of clay and non-clay minerals in a mixture by the XRD method is generally recognized in global scientific community, as evidenced by the results of the international competition for quantitative analysis Reynolds Cup ([www.clays.org](http://www.clays.org); Omotoso et al., 2006) and was chosen as a reference, with the results of which all other calculations are compared.

#### *Quantitative determination of MMT content by thermogravimetric analysis (TG)*

The quantitative determination of the montmorillonite content was carried out in accordance with the method of F. Nieto (Nieto et al., 2008), based on the determination of the weight loss of bentonite samples saturated with ethylene glycol vapor. According to this technique, the most stable weight loss values are demonstrated by clay samples converted to the monocationic magnesium form. For this, natural samples are saturated twice with 1M MgCl<sub>2</sub> solution, followed by repeated washing to remove excess salts. The saturation with ethylene glycol (EG) is carried out at a temperature of 60°C for 3 days.

According to the authors of this technique (Nieto et al., 2008), the proposed method is inexpensive and easy to use. It can be used in addition to X-ray diffraction, including in the diagnosis of dioctahedral Al-smectite (montmorillonite) in soils. To obtain a quantitative relationship between weight loss and MMT content, the authors of the method prepared 8 artificial mixtures. By plotting the graphs of the dependence of weight loss in different temperature intervals, on the known value of the montmorillonite content, a conversion equation was derived for the interval of 100–450°C:

$$y = 3,96x - 4,05 \quad (R^2 = 0,96) \quad (1)$$

where, x is the weight loss of the sample (in mass %) in the temperature range from 100 to 450°C, and y is the montmorillonite content, in %.

The largest weight loss due to the desorption of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>3</sub>-CHO occurs up to a temperature of 300°C, after which the loss sharply decreases and practically ends at 450°C. For this reason, a limit of 450°C was chosen as the upper temperature limit. At this temperature, the desorption of CO<sub>2</sub> is almost completed, but the octahedral networks of aluminosilicates are still stable, since the loss of hydroxyls from the octahedral networks of most clay minerals lies in the temperature range of 500–700°C. Below 100°C, the weight loss corresponds to the loss of surface (atmospheric) moisture.

To stabilize the moisture values (Paterson, Swaffield, 1987) and standardize the experiment, the authors of this method proposed converting the MMT sample into a magnesium form and saturating it with EG vapor as much as possible.

TG analysis of the samples was performed on an EXSTAR TG/DTA 7300 (SII) instrument. The samples were heated in corundum crucibles at a constant rate of 10°C/min. To remove gases released during heating, the furnace space was purged with air dried by passing it through a column with silica gel at a volumetric air circulation rate of 100 ml/min. The weighed portion of the sample was 10–20 mg (accuracy up to 0.01 mg). During the analysis, the weight loss of the sample (TG curve) was determined simultaneously with the enthalpy change accompanying thermal reactions (DTG curve).

#### *Quantitative determination of MMT content by adsorption of rhodamine 6G and chrysoidine*

Determination of montmorillonite content by rhodamine adsorption method was carried out in accordance with GOST 28177-89 «Forming bentonite clays». The method is based on ion-exchange adsorption of fluorescent organic dyes, which causes coagulation of the clay particles. This technique is used at Russian iron-ore processing plants and foundries and does not require a preliminary conversion of MMT into a monocationic form.

This method is based on the adsorption of dye molecules on charged MMT surfaces. The cation of the dye chrysoidine has a higher molecular weight compared to the cation of rhodamine 6G and is more readily sorbed on the surface of montmorillonite, causing coagulation and coloring the resulting precipitate in red color. While the amount of chrysoidine cations is insufficient to fill all charged surfaces, the adsorption of rhodamine 6g cations occurs, in which case the tendency to adsorption is significantly lower. After the surface is completely filled with organic cations, the addition of a new portion of the dye mixture leads to an increase in the adsorption of chrysoidine and the displacement of rhodamine 6g cations, causing luminescence in the solution over the precipitate. Thus, the presence of weak luminescence of

the solution, simultaneously with the formation of the maximum volume of the precipitate, corresponds to the end point of the titration.

#### *Quantitative determination of MMT content by adsorption of methylene blue*

This technique is based on the determination of CEC in lumpy (natural, without additional processing) clay ( $CEC_{raw}$ ) and a fine ( $<0.5 \mu m$ ) fraction ( $CEC_{100\%}$ ), the content of montmorillonite of which is close to 100%. The montmorillonite content in the rock is defined as the proportion of  $CEC_{raw}$  over  $CEC_{100\%}$ .

Purification of bentonites and the preparation of a fine fraction ( $<0.5 \mu m$ ) were carried out by centrifugation (Sigma 3-18K centrifuge, 18000g). The montmorillonite content in the fine fraction was controlled by XRD and was found to be  $>96\%$  in all studied samples.

The method for determining CEC by the adsorption of the methylene blue (MB) dye is described both in Russian standards (GOST 21283-93) and in foreign literature (Kaufhold et al., 2002; Dormann, Kaufhold, 2009).

Due to the fact that the monovalent cationic dye is not able to completely displace the divalent cations of the exchange complex of montmorillonite under experimental conditions, in order to obtain adequate information, it is first necessary to convert the natural bentonite (and the fine fraction) into the monocationic sodium form, which is characterized by a greater lability of cations. This procedure also allows for a better selection of the clay fraction and increases its yield, which is a problem for calcium-magnesium varieties prone to aggregation of clay particles in suspension. Conversion to the monocationic form is carried out by repeated treatment of samples with 1M NaCl solution, followed by washing, to remove excess salt, in dialysis tubes. In order to minimize the contribution to CEC from

the pH-dependent active centers located on the lateral hydroxylated surface of clay particles, MB adsorption is carried out in an acidic medium.

#### *Quantitative determination of MMT content by adsorption of triethylenetetramine copper (II) complex*

This technique is similar to the above described method for MB adsorption, except that copper (II) triethylenetetramine complex (Cu-trien) is used instead of methylene blue dye. Currently, this method is most popular in world practice, which is associated with the high accuracy of determining the CEC values due to the more complete replacement of bivalent exchangeable cations of montmorillonite (Lorenz et al., 1999, Dohrmann et al., 2012). The main advantages of this method include its simplicity and low time consumption, which is an important factor for use in production. As in the previous case, to estimate the MMT content, a finely dispersed fraction ( $<0.5 \mu m$ ) was isolated from the preliminarily obtained monocationic  $Na^+$  form of bentonite.

## Research results

### *Mineral and chemical composition of studied bentonites*

Studies of the samples by X-ray diffraction showed that all the presented samples contain more than 70% montmorillonite (Table 1). Quartz and calcite are present in all samples as impurities. In addition, chlorite, feldspar and pyrite are present in the bentonite form 10<sup>th</sup> Khutor (10Kh) deposit and illite, kaolinite, feldspar in the sample from the Zyryanskoe (ZR) deposit. Bentonite from the Dash-Salahlinskoe (DS) deposit contains cristobalite and feldspar, and from the Dinozavrovoe (DIN) deposit – illite and pyrite. The obtained X-ray diffraction patterns of bulk samples are shown in Figure 1, the results of quantitative X-ray diffraction

Deposit	Sample	MMT	Il	Chl	Kaol	Q	Cr	PSh	Kts	P
Dinozavrovoe	DIN	73	1	-	-	22.5	-	-	2.3	1.2
Dash-Salahlinskoe	DS	73.9	-	-	-	3.7	5	13.8	3.6	-
Zyryanskoe	ZR	74.4	0.9	-	2.6	19.4	-	0.6	2.1	-
10 <sup>th</sup> Khutor	10Kh	73.0	-	1.2	-	14.2	-	8.6	3	-

Table 1. Mineral composition of bentonite clay samples, wt.%. Note: MMT – montmorillonite, Il – illite, Chl – chlorite, Kaol – kaolinite, Q – quartz, Cr – cristobalite, PSh – feldspars (potassium feldspars and plagioclase), Kts – calcite, P – pyrite.

Sample	LOI	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	S
DIN	8.00	1.50	3.81	16.71	61.15	0.14	1.43	0.70	0.16	6.35	0.02	0.04
DS	13.20	2.79	2.82	14.36	56.16	0.35	2.66	0.94	0.7	5.45	0.17	0.4
ZR	9.04	0.46	1.79	19.38	57.42	0.77	2.20	1.01	0.04	7.78	0.05	0.07
10Kh	7.64	1.04	2.96	18.10	61.71	1.01	2.24	0.74	0.09	4.23	0.14	0.11

Table 2. Chemical composition of rock-forming oxides, %. Note: LOI – loss on ignition.

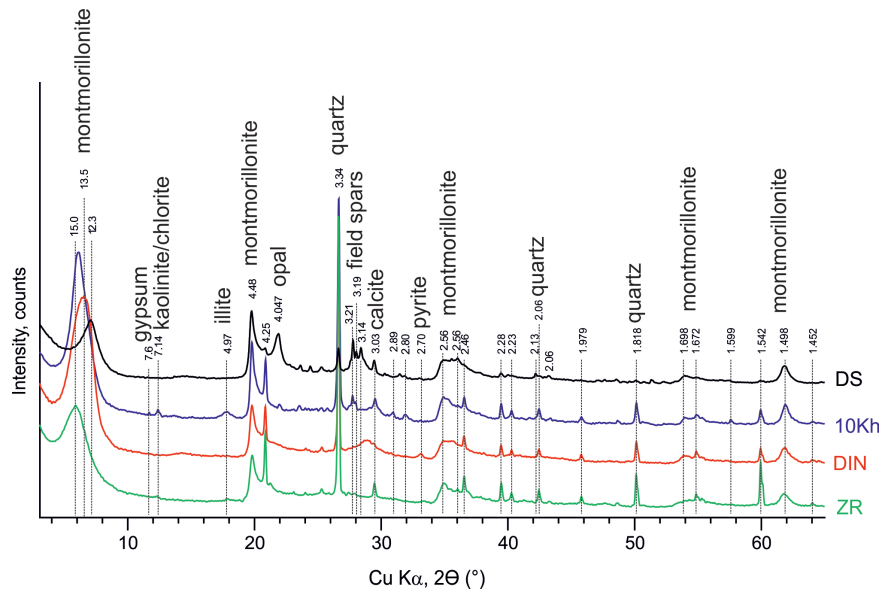


Figure 1. X-ray diffraction patterns of non-oriented preparations of the studied samples of bentonite clays. Deposit names: DIN – Dinozavrovoe; DS – Dash-Sahlinskoe; ZR – Zyryanskoe; 10Kh – 10<sup>th</sup> Khutor. Interplanar spacings are given in angstroms.

and chemical analyzes are presented in Tables 1 and 2, respectively. Montmorillonite was identified by a series of main diagnostic reflections corresponding to the following interplanar spacings (hkl): 12.3–15.0 Å (001), 4.97–5 Å (003), 4.48 Å (100), 2.56 Å (110), 1.69–1.7 Å (210), 1.492–1.504 Å (060).

In addition to calculating the montmorillonite content in bulk samples, this method was used to control the quality of the separated fractions <0.5 μm and monocationic forms.

*Determination of MMT content from thermal data*

Figure 2 shows the results of thermal analysis of clays prepared according to the above procedure. For all samples, the DTG curve shows two peaks in the temperature ranges 159–186 and 273–294°C. The first peak is due to the destruction of ethylene glycol (EG) molecules, the boiling point of which is 197°C. The second maximum is associated with the desorption of more tightly bound EG molecules fixed in the interlayer space.

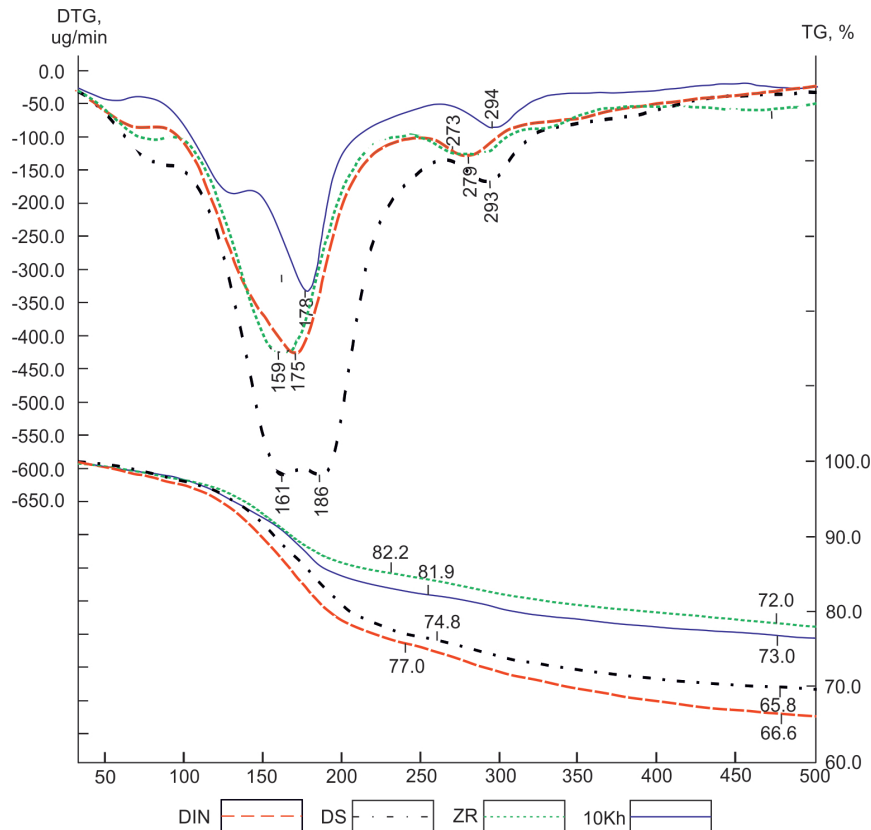


Figure 2. Results of thermal analysis

Calculated according to equation (1), the MMT content turned out to be overestimated for all studied samples (Table 3). The largest overestimation of the MMT content was obtained for DS and DIN samples, which is most likely associated with the peculiarities of the charge density distribution on the surface of montmorillonite particles in these samples, as well as with the possible presence of indistinguishable XRD of amorphous Fe, Si, and Al oxides, which can make contribution to a maximum at 250–300°C. The values of the montmorillonite content of more than 100% obtained for these samples indicate the unsuitability of this formula for calculating the MMT content in bentonite clays of other deposits.

It can be assumed that this technique could indeed be used to calculate the content of montmorillonite with the condition that the samples must have the same origin and structural features (layer charge, CEC, etc.). For example, if they are sampled from the same deposit or formed in specific facies settings. In that event, in each specific case, it is necessary to select the working temperature range and estimate the calculation formula anew.

The high convergence of the results of X-ray diffraction analysis and thermal analysis for 8 samples presented in the work of F. Nieto (Nieto et al., 2008) is due to the fact that the studied samples are artificially prepared mixtures based on the same smectite, for which the calculation formula really turned out to be true.

Thus, the main disadvantage of the method for determining the content of montmorillonite from the data of thermal analysis is the impossibility of using the same calculation formula for bentonite from different deposits. In addition, the use of the method requires a

rather large amount of time.

It should be noted that in order to verify the correctness of the results obtained by different methods, it is necessary to compare them with XRD data in order to assess the presence of other minerals with high sorption properties, the purity of fine fractions, and to identify the structural features of montmorillonite that can affect the calculation results.

*Method for determination of MMT content by adsorption of rhodamine 6g and chrysoidine*

Based on the detailed description of the procedure given above, it follows that this method gives no distinction between the montmorillonite content and the CEC value. This situation, in fact, means that the intrinsic cation exchange capacity of the monomineral phase of montmorillonite is equal to 100 meq/100 g, which is not true in the overwhelming majority of cases. The second source of error is associated with the specifics of sample preparation. To disperse particles in an aqueous environment, a polyanionic inorganic polymer, sodium tripolyphosphate, is used as a peptizing agent, which itself can chemically interact with organic cations and also partially change their composition. In addition, the technique involves the use of Na<sub>2</sub>-EDTA, which partially binds divalent cations, increasing the degree of ion exchange of organic dyes. Along with this, the technique involves the use of potassium hydroxide, which further complicates the interpretation of the results, since potassium is the strongest known coagulant of clay particles and has a very high adsorption capacity, which can compete with organic cations. All of these factors can make the interpretation of the results very difficult.

Sample	Method 1		Method 2		Method 3		Method 4			Method 5		
	In lump sample, %	Faction, %	Weight loss in the range of 100–450, %	MMT content, %	Dye volume, ml	MMT content, %	CEC, mg-eq/100g	CEC <sub>(100%)</sub> , mg-eq/100g	MMT content, %	CEC, mg-eq/100g	CEC <sub>(100%)</sub> , mg-eq/100g	MMT content, %
DIN	<b>73.0</b>	96	28.8	<b>110.0</b>	3.6	<b>89.7</b>	93.8	110.5	<b>84.9</b>	88.1	106.3	<b>82.9</b>
DS	<b>73.9</b>	96	28.9	<b>110.0</b>	3.8	<b>90.9</b>	87.7	110.0	<b>79.7</b>	80.4	99.3	<b>81.0</b>
ZR	<b>74.4</b>	96	23.0	<b>87.0</b>	2.2	<b>52.3</b>	64.1	87.5	<b>73.3</b>	55.1	89.9	<b>61.3</b>
10Kh	<b>73.0</b>	96	21.1	<b>79.6</b>	3.0	<b>72.5</b>	63.1	89.0	<b>70.9</b>	73.5	101.9	<b>72.1</b>

Table 3. The results of comparing the determination of the content of montmorillonite in bentonite clays by different methods. Methods: 1 – Measurement of the montmorillonite content according to the results of the XRD by the Rietveld method; 2 – Determination of MMT content based on the results of thermal analysis of samples after saturation with ethylene glycol (Nieto et al., 2008); 3 – Determination of MMT content by adsorption of rhodamine 6G and chrysoidine dye – GOST 28177-89; 4 – Determination of MMT content by adsorption of MB (Kaufhold et al., 2002; Dormann, Kaufhold, 2009). 5 – Determination of the MMT content by adsorption of Cu-trien (Lorenz et al., 1999., Dohrmann et al., 2012);

The experiments carried out showed an overestimated content of montmorillonite in the DIN and DS samples, namely 89 and 90%, respectively, compared with 73 and 73.9% (Table 1). The higher the particle charge and the proportion of sodium cations in the exchange complex, the stronger the super-equivalent adsorption of organic dyes. On the other hand, the ZR sample showed underestimated results in comparison with XRD, which is apparently associated with a significant content of calcium and magnesium cations in the MMT exchange complex, a low CEC value, and also with the presence of films of iron oxides and hydroxides on the particle surface. The outer surfaces of particles containing ferrous films can act as active sorption centers and reduce the access of large organic cations to the interlayer space and the surface of MMT crystallites. The best agreement between the results of determining the MMT content by this method and the XRD data is observed for sample 10Kh (Table 3).

In addition to the above disadvantages, it is worth noting the difficulty of determining the equivalence point when titrating samples, which, as practice shows, has a rather strong effect on the measurement results.

#### *Determination of MMT content by adsorption of methylene blue*

The methylene blue cation is easily sorbed on the surface and in the interlayer of smectite minerals. At the initial stage, MB cations are adsorbed on the outer surfaces of the clay particles, and then these organic dye molecules begin to replace the cations in the interlayer space of montmorillonite. The end of the substitution reaction for interlayer cations and the appearance of free MB cations in the solution are considered to be the equivalence point in the titration. In addition to the exchange reaction, MB cations can be adsorbed on the surface of particles in a super-equivalent manner, due to polar and hydrophobic interactions, and also due to the high tendency of dye molecules to aggregate.

It was found that in the presence of divalent cations existing in the interlayer space, the adsorption of the MB dye decreases. The amount of adsorption of MB will depend on certain experimental conditions, such as the concentration of the dye and the duration of adsorption. On the other hand, for alkaline varieties of bentonites and finely dispersed fractions, the CEC values can be significantly overestimated, which is more typical for minerals with a high charge density. Studies of the mechanism of adsorption of MG showed that for a correct diagnosis of smectite, it is necessary to know the dependence of the CEC value on pH to take into account the so-called 'variable charge' associated with the adsorption of cations on hydroxyl groups (Bujda'k, Komadel, 1997; Lagaly, 1993).

The conducted experiments showed a high convergence of the results with the XRD data for alkaline

earth bentonites (ZR, 10Kh), with an average error of 2-3%. However, for the samples of alkaline bentonites (DIN, DS) the values turned out to be overestimated.

Among the negative factors, it's worth mentioning the need for preliminary conversion of lumpy clay and fine fraction into sodium form, which significantly complicates the process of sample preparation.

#### *Determination of MMT content by adsorption of triethylenetetramine copper complex*

As noted above, the method for determining CEC by adsorption of Cu-trien differs from other methods by a high ability to replace divalent metal cations in the interlayer space of montmorillonite due to the fact that the copper complex has a high selectivity with respect to negatively charged adsorption sites on the basal surfaces of MMT. This method does not imply the need to convert the samples into the monocationic sodium form; however, the inaccuracy in assessing the MMT content may be associated with incorrect fractionation of the samples. As in the case of the adsorption technique using the MB dye, the MMT content is estimated by comparing the CEC values of the bulk sample and the fine dispersed fraction. It is necessary that the fraction be representative, and consist of practically pure montmorillonite. Therefore, for the preparation of the fraction, just as in the case with MB, it is necessary to convert the sample into the monocationic form. Other disadvantages of the method are associated with obtaining inaccurate CEC values for initial samples that contain water-soluble salts, gypsum, and carbonates. These inaccuracies can be associated both with the reactions of copper cations with carbonates and specific adsorption of amine, and with a change in the pH of the samples in the presence of carbonates and hydroxides.

These problems can be eliminated using fairly simple techniques described in (Dormann, Kaufhold, 2009) and avoiding the influence of calcite and other carbonates on the determined CEC value. These laboratory techniques include the method of using a fivefold increase in the concentration of Cu-trien complex, which makes it possible to reduce the solubility of calcium carbonate by reducing the amount of water, as well as the method for determining the CEC of bentonites after saturation of the titrated dispersion with calcite. As shown in (Kaufhold et al., 2013), these approaches are most convenient to use when used in combination.

The results of determining the CEC and calculating the MMT content are presented in Table 3. As in the case with the determination of the MMT content by the adsorption of MB, the results of measurements on the sample from the 10th Khutor deposit showed a high convergence with the results of quantitative XRD, while the values of measurements on alkaline bentonites are higher. In the case of the Zyryanskoe

deposit sample, the MMT content determined by copper adsorption is somewhat underestimated. One of the reasons for this discrepancy may be specific reactions of triethylenetetramine with iron-containing active centers on the surfaces. Indeed, this sample is characterized by a high iron content (up to 10–11% in terms of iron (III) oxide), and iron cations in the form of hydroxo complexes and oxide nanoparticles are present on the surface of montmorillonite and are capable of specific reactions with triethylenetetramine, which changes the equilibrium in the system. In addition, the presence of oxide/hydroxide shells can hinder the penetration of large complex copper cations to certain surface areas in the interlayer space of montmorillonite.

### Discussion

The studies carried out make it possible to assess the capabilities of various adsorption methods in assessing the content of montmorillonite and to identify certain difficulties in their use.

The general problem of methods using cationic dyes is associated with the super-equivalent adsorption of the dyes on areas of the surface with a high charge due to the high tendency of dyes to aggregate, as well as to complication of the ion exchange reaction for montmorillonites containing polyvalent cations in the interlayer space and on the surface of crystallites (magnesium, calcium, iron, etc.). In most cases, this problem can be solved by preliminary converting the samples into sodium form, which is a rather laborious task.

However, as shown by the results of the present study, even after transferring the samples to the sodium monocationic form, alkaline bentonites demonstrate overestimated results in comparison with the XRD data. The Cu-trien adsorption techniques used in this work have good theoretical validity and are widely used in the scientific community. It can be assumed that such a significant difference in the results may be associated with the size of montmorillonite particles and texture features (the number and volume of micro/mesopores). As shown in previous works (Krupskaya et al., 2017), alkaline bentonite of the Tagansky deposit is characterized by the presence of natural nanosized particles of montmorillonite, which have low values of coherent scattering regions (1–2 nm versus 3–4 nm for ordinary montmorillonites). Such nano-sized phases can practically not contribute to the intensity of diffraction maxima, as a result of which somewhat underestimated values of the MMT content can be obtained when using XRD. At the same time, the presence of such nanosized particles will lead to the over-adsorption of MB and Cu-trien and, as a consequence, to an overestimation of the MMT content.

In addition to the capacity and composition of the exchange complex, an important role is played by the

presence of mineral impurities with a high sorption capacity, for example, zeolites, carbonates, amorphous phases and other clay minerals (vermiculite, kaolinite, halloysite, palygorskite, mixed-layer minerals, etc.), which can distort the results.

Thus, despite the apparent self-sufficiency of the considered methods, there is a need for additional studies and manipulations with samples, for example, the use of XRD, infrared, Mössbauer, atomic adsorption spectroscopy, etc. to analyze the composition and structure of montmorillonite, the presence of impurity phases, and control the quality of the fine fraction.

In view of the need to complicate traditional adsorption techniques in order to obtain adequate results on the MMT content, in some cases, there should be a clear understanding of the required accuracy of determining the MMT content and the expediency of such calculations. Thus, the chosen method for the determination of the content of montmorillonite is of great importance in carrying out research work, in geological exploration, as well as in some innovative applied areas of using bentonite clay, where the properties of the product and the amount of added chemical reagents depend on the content of montmorillonite.

When using bentonite in classical industrial areas such as metallurgy, foundry, drilling, etc., in most cases, the determining factor is the properties of the clay, and not the content of montmorillonite, because there is often no direct correlation between them (provided that the content is sufficiently high, over 50–60%). These properties are understood as specific physical indicators, the value of which determines the quality of the final product in certain technological processes and prescribed in the standards of this industry. For example, for pelleting iron ore the main properties of clay that affect the quality of the pellets are its swelling index, moisture content, and thermal stability. In the production of sandy-clay molds in the foundry industry, the main factors are the strength properties and the thermal stability of bentonite. In drilling it is rheological properties.

The presence of restrictions on the content of montmorillonite in industry standards does not always give a real idea of the quality of the clay, which is associated with the peculiarities of the composition and properties of a particular bentonite, which in turn are primarily determined by the structural and textural characteristics of montmorillonite, and to a lesser extent – by its content. An example is the international standard of the American Petroleum Institute (API, Specification 13A), which specifies the properties of the raw material, and does not specify content of montmorillonite.

As a result, the indicator of the content of montmorillonite is a reason for speculation, both on the part of the consumer and the manufacturer of bentonite



products. On the other hand, in a number of applications for bentonite, the content of montmorillonite is one of the key indicators, for example, as in the case of the development and creation of engineering safety barriers for the disposal of radioactive waste, where the content of montmorillonite is a limiting criterion for the use of clays in various disposal sites (Krupskaya et al., 2018; 2020; Kaufhold, Dohrmann, 2016; Ahonen et al, 2008).

### Conclusion

The studies carried out illustrate the possibilities and limitations of various methods for determining the content of MMT, used in both research and industrial sectors. Comparative analysis of the results showed good agreement between the results of X-ray diffraction analysis with the data on the adsorption of methylene blue dye in determining the content of montmorillonite in alkaline earth varieties of bentonite. The error was less than 3%. The difference in the results of the analysis of alkaline bentonites, apparently, is associated with the presence of nanosized particles of montmorillonite, which leads to the over-adsorption of dyes in the case of MB and, at the same time, can underestimate the values according to the quantitative XRD data. A similar situation is observed when using the method based on the adsorption of the triethylenetetramine complex of copper (Cu-trien); however, in this case, the measurement results were influenced by the presence of films of iron oxides and hydroxides on the surface of montmorillonite particles in the Zyranskoe bentonite sample, which led to a decrease in the MMT content in that specified bentonite. It was also revealed that in order to more completely replace the exchangeable cations in the montmorillonite interlayer, it is necessary to carry out a preliminary conversion of both lumpy clay and fine fractions into a sodium form, which significantly complicates and lengthens the study process.

The measured montmorillonite content according to the industry standard by the method of adsorption of the rhodamine 6G and chrysoidine dyes showed the greatest variations relative to the reference values according to the XRD data. At the same time, it was noted that for alkaline bentonites, there is a significant over-adsorption of the dye, leading to overestimated results (by 8–10%). On the other hand, the alkaline-earth sample of the Zyranskoe bentonite showed underestimated results, which is probably due to an increase of the tetrahedral charge and other structural features that would require a separate study. Measurements of the montmorillonite content in the bentonites of the 10<sup>th</sup> Khutor deposit by all methods showed the most comparable results with the XRD data.

The content of montmorillonite, determined by the method of thermal analysis, turned out to be overestimated in comparison with the reference values for all samples

of bentonite, which is primarily due to the impossibility of using the same calculation formula for bentonites of different genesis and with different structural features. The measurement error by this method was 17–30%. In addition, this method requires a significant amount of time spent on sample preparation and sampling and can hardly be recommended for mass use.

In general, when using the considered methods for the determination of montmorillonite associated with the adsorption of organic substances and complex cations, the sorption properties of a particular montmorillonite, the magnitude and distribution of the layer charge, the composition of the absorbed complex, micro- and mesoporosity parameters, and other structural and textural features of montmorillonite play an important role, and are directly related to the geological conditions of formation. Also, the results are significantly influenced by impurities of other minerals with a high sorption capacity, such as, zeolite, carbonates, other clay minerals (vermiculite, kaolinite, halloysite, palygorskite, etc.), as well as amorphous phases.

Thus, it can be concluded that determining the content of montmorillonite is not a trivial task. Each method has its own characteristics and limitations, which indicates the need for a clear understanding of the goals and objectives of each specific study. Of all the methods available to researchers for determining the content of montmorillonite, the most accurate is the X-ray diffraction method based on information on the individual crystal-chemical structure of mineral phases.

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