# Determination of the composition of montmorillonite in the presence of natural admixtures

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## Received 9 February 1973

A method for the determination of the crystallochemical characteristics of montmorillonites present in natural specimens has been worked out. It is based on the transfer of the montmorillonite into an alkylpyridine complex which is subsequently extracted into a nonaqueous organic solvent. By using this method, the evaluation of the content of montmorillonite as well as of the total amount of admixtures is also possible. The factors influencing the accuracy of this method are discussed and the method itself is verified on four natural specimens of montmorillonite.

Purity and homogeneity of montmorillonite is the basic stipulation for correct determination of its crystallochemical formula [1-4] as well as of its physical properties as they can be considerably influenced by the presence of impurities.

The simplest and commonly used method for obtaining pure montmorillonite from natural bentonites is based on a sedimentation of the coarse fraction, while only the finest montmorillonite fraction is being used for further studies. Such method, however, works well only if the sample contains montmorillonite accompanied by coarse non-clay admixtures (quartz, feldspar and the like). In the case of more complicated mixtures containing simultaneously free oxides, hydroxides, and other clay components (kaolinite, illites, sericites, *etc.*) we are bound to encounter serious difficulties, or the above method fails completely. Also other separation methods fail in such cases, no matter whether they take advantage of different densities of montmorillonite and admixtures [5] or of peptization, or extraction [6-12]. Still, it happens quite frequently that only the crystallochemical formula of montmorillonite is of interest, without any necessity to separate it from impurities.

It is well known that clays can react with salts of quaternary organic bases forming the so-called organoderivatives [13-16]. The organic cation is firmly adsorbed onto the surface of clay particles, causing their hydrofobization and complete change in the character of the material. Such changes are most pronounced in montmorillonites, because the above reaction takes place not only on the external surface, but also on the interlayer faces [17]. The organoderivatives obtained in this way are wetted and also swell in organic solvents [18]. Other clay components (kaolinite, illites, halloysite and the like) are hydrofobized only to a small extent and the non-clay materials are not hydrofobized at all. Keeping this in mind, the described method rests on a conversion of the original specimen into an organocomplex and on the selective separation of the organomontmorillonitic portion.

# Experimental

## Starting materials

Montmorillonite from Fintice (Czechoslovakia). The sample contains even after sedimentation free  $SiO_2$  as determined by X-rays.

Montmorillonite from Kriva Palanka (Yugoslavia). No admixtures detected by X-rays. Montmorillonite from Lastovce (Czechoslovakia). Fine crystalline cristobalite detected

by X-rays.

Montmorillonite from Badín (Czechoslovakia). No admixtures detected by X-rays.

All above montmorillonites were prepared by sedimentation from natural bentonites. The cetylpyridinium bromide was used for the formation of the organomontmorillonitic complex, which was then separated from the aqueous suspension by means of an extraction by an organic, nonaqueous solvent. The precipitated, hydrofobic organomontmorillonite coagulates in water and goes into the organic solvent by which it is wetted and peptized during the extraction.

In order to find a suitable organic solvent, benzene, toluene, o-xylene, m-xylene, chloroform, carbon tetrachloride, and nitrobenzene were applied in turn, testing their ability to extract the montmorillonite portion alone. From among the tested liquids only the toluene did not coprecipitate the admixtures, which was confirmed by the X-ray diffraction.

# Working procedure

To homogeneous sample (10 g) of known chemical composition  $Na_2CO_3$  (0.5 g) was added and the mixture was gradually, under intense stirring, diluted with water, until the concentration of the suspension dropped under 1%. This suspension was then allowed to stand for 12-18 hrs, while occasionally shaken; afterwards 0.005 N solution of cetylpyridinium bromide (CPB; 2000 ml), *i.e.* 200 ml of the solution to each gram of the sample, was added slowly with vigorous stirring.

The organomontmorillonite precipitate that, together with coprecipitated admixtures, coagulates very rapidly was left to precipitate and the supernatant removed. The precipitate was then transferred into five 250-ml separating funnels, about 5 ml of toluene plus enough water was added into each of them and thoroughly shaken for 5 min. The mixture was allowed to separate and the lower portion discarded. Distilled water was added afterwards to the upper, remaining phase and the extraction was repeated. The whole extraction process was to be repeated 4-5 times. The resultant precipitated organomontmorillonite from all funnels was combined on a filter, dried, and chemically analyzed. It is very important to peptize the starting material very thoroughly, *i.e.* to avoid polymineral aggregates in the suspension. That is why the concentration of the suspension should be as low as possible, otherwise the separation of admixtures from primarily aggregated particles would be incomplete, leading to erroneous results. It is obvious that the coprecipitation of accessory minerals with the flocks of organomontmorillonite always takes place during the reaction with CPB, but this is irrelevant as they can easily be isolated from the organomontmorillonite by repeated extraction. provided they have been already separated from the montmorillonite particles beforehand by thorough peptization.

The amount of toluene used for the extraction should be low; this ensures the formation of only light "foam" of the organomontmorillonite in toluene, having large contact surface and facilitating the isolation of coprecipitated admixtures. An excess of toluene retards the extraction and can even cause a reversal of phases, *i.e.* the formation of a W/O emulsion which definitely prevents the separation.

## Calculations

As the atoms building the crystal structure of montmorillonite enter the organomontmorillonitic complex in the same proportions, it is possible to figure the crystallochemical formula of the original montmorillonite out of the chemical composition of the pure, extracted organomontmorillonite. But the widely used Kelley's method, which takes also the interchangeable atoms into the calculations, cannot be used here. As a matter of fact, the content of these atoms in the organomontmorillonite is lowered, since some of them have already been replaced by the organic cations that cannot be directly determined (they are included in the total loss on ignition). That is why the content of CaO in the organomontmorillonite is also lowered and does not correspond to the exchange capacity of ions. Supposing however, that the number of the tetrahedral and octahedral atoms per unit cell is equal to 8 and 4, respectively, it follows that

$$K = \frac{8}{\frac{\% \operatorname{SiO}_2}{M_{\mathrm{S}}} + X} = \frac{4}{\frac{\% \operatorname{Al}_2 \operatorname{O}_3}{M_{\mathrm{A}}} + \frac{\% \operatorname{Fe}_2 \operatorname{O}_3}{M_{\mathrm{F}}} + \frac{\% \operatorname{MgO}}{M_{\mathrm{M}}} - X}, \qquad (1)$$

where K is a reduction coefficient, X is the portion of atoms belonging to the tetrahedral coordination and  $M_{\rm S}$ ,  $M_{\rm A}$ ,  $M_{\rm F}$ , and  $M_{\rm M}$  are the grammole equivalents of the respective oxides.

The evaluation of X made it possible to determine the content of exchangeable cations from the deficit of positive charges (related to the percentage of CaO):

$$\chi + \frac{\% \text{ MgO}}{M_{\text{M}}} \cdot M_{\text{c}},$$
 (2)

where  $M_{\rm C}$  is the grammole equivalent of CaO.

The calculation procedure is illustrated in Table 1 on the sample from Lastovce. From the figures in column 3 it is possible to write down the crystallochemical formula of pure montmorillonite, which in this case reads

$$(Si_{7.52}Al_{0.48})(Al_{3.10}Fe_{0.48}Mg_{0.41})(Ca_{0.45})O_{20}(OH)_{4.4}$$

The chemical composition of the starting bentonite sample as well as of the pure organomontmorillonite extracted from it can be used, however, also for a quantitative determination of montmorillonite in the starting material. A look at Table 2 shows us how such a determination has been made for the sample from Lastovce. The lowest value in column 4 yields the coefficient, by which we have to multiply all the values of the column 3 in order to get the actual content of oxides constituting our montmorillonite (column 5). This coefficient in the case of the sample from Lastovce has the value of 0.51 - MgO. This figure corresponds at the same time to the percentage of montmorillonite in our sample. By subtracting the values of the column 1 and relating them to the total amount of all components (column 6), we obtain the content of individual admixtures (in percent) expressed in the form of oxides. By the summation of the values

## Table 1

Calculation of the crystallochemical formula of pure montmorillonite from Lastovce

	1	. 2	3
Ign. loss	36.02		
SiO <sub>2</sub>	40.32	0.67	7.52
Al <sub>2</sub> O <sub>3</sub>	16.22	0.319	3.58
Fe <sub>2</sub> O <sub>3</sub>	3.47	0.043	0.48
·MgO	1.51	0.037	0.41
CaO	2.24	0.040	0.45
	(1.65)		
TiO <sub>2</sub>	0.00		
K <sub>2</sub> O	0.00		
Na <sub>2</sub> O	0.00	_	
K <sub>2</sub> O Na <sub>2</sub> O	0.00		
	K = 11.25		
	X = 0.0425		

Originally determined content of CaO = 1.65%.

1. Chemical analysis of the organomontmorillonite; 2. equimolar ratios of individual oxides; 3. total amount of atoms per unit cell.

K is the reduction factor from equation (1).

# Table 2

Calculation of the content of montmorillonite and admixtures in the specimen from Lastovce

	1	2	3	4	5	6
SiO <sub>2</sub>	65.95	40.20	53.75	1.23	27.36	45.30
$Al_2O_3$	12.21	16.22	21.68	0.56	11.04	1.37
Fe <sub>2</sub> O <sub>3</sub>	2.40	3.47	4.64	0.52	2.36	0.05
MgO	1.03	1.51	2.02	0.51	1.03	0.00
TiO2	0.24	0.00	0.00	0.00	0.00	0.28
CaO	3.15	2.24	2.99	1.05	1.52	1.91
$K_2O + Na_2O$	0.15	0.00	0.00	0.00	0.00	0.17

Content of montmorillonite 50.9%.

Content of admixtures 49.1%.

1. Chemical analysis of the starting material; 2. chemical analysis of the pure extracted organomontmorillonite considering the re-evaluated content of CaO according to equation (2); 3. corrected chemical analysis of the organomontmorillonite regarding equal amount of the solid phase as in the starting material; 4. ratios of individual oxides in the starting material (column 1) to those in the organomontmorillonite (column 3); 5. actual content of the components of the montmorillonite; 6. percentage of admixtures expressed by their constituting oxides.

in column 5, related to the total amount of all components, we obtain the content of montmorillonite.

The sample from Lastovce contains about 51% of montmorillonite. The rest are admixtures, predominantly free SiO<sub>2</sub>.

#### **Other** results

The data for other samples investigated during this work are collected in Table 3.

The specimen from Fintice contains 73% of montmorillonite and about 25% of free  $SiO_2$ . This compares well with the result of a quantitative X-ray determination of  $SiO_2$  in the starting material. Other admixtures are present in negligible amounts.

#### Table 3

Phase composition of investigated specimens

	Fintice			Badín		Kriva Palanka			
	A	В	C	A	В	C	A	В	C
SiO <sub>2</sub>	60.75	42.55	24.6	45.81	38.37	27.8	50.43	44.12	3.77
$Al_2O_3$	12.92	12.68	1.03	13.35	3.77	13.8	16.50	15.33	0
$Fe_2O_3$	2.93	2.69	0.45	18.34	30.17	. 0	2.81	2.61	0
TiO <sub>2</sub>	0	0	0	0	0	0	1.00	0	1.24
MgO	2.80	2.94	0	0.61	0.35	0.49	3.30	3.08	0
CaO	2.48	2.12	0.56	3.15	2.99	1.64	5.70	2.92	3.19
$Na_2O + K_2O$	0.24	0.07	0.22	0.25	0.10	0.23	0.79	0	0.98
% montmorillonite			73			56.3			90.8

A. Chemical composition of the starting material in percent; B. chemical composition of the organomontmorillonitic complex in percent; C. content of admixtures — the phase composition of the sample in percent.

The specimen from Badín is a mixture of nontronite together with a considerable amount of free  $SiO_2$  and  $Al_2O_3$  that could not have been determined by X-rays. Apparently, they are present as amorphous phases, or they might form the amorphous allophane.

The specimen from Kriva Palanka contains 90% of montmorillonite and only a small amount of other admixtures.

#### Conclusion

The determination of the phase composition of bentonites calls for very accurate and correct chemical analyses. Even small deviations from true values, particularly for oxides present in low amounts, *i.e.* CaO, MgO, and sometimes also Fe<sub>2</sub>O<sub>3</sub>, cause considerable errors in their relative proportions as well as in their total amount relative to montmorillonite. The routine and thoughtless attitude to take the numerical results at their face value has thus to be discarded in favour of critical consideration of all sources of errors and their influence on final results. Of importance is also to take into the account the information gained from other identification methods (presence of minerals consisting of many oxides in certain proportions, *e.g.* kaolinite, illite and so on), if we wish indeed to judge properly the reliability of our findings. The method described yields also valuable information concerning the purity of montmorillonites, accompanying admixtures, and their qualities. It can be successfully used also in cases, when related identification methods (X-rays, i.r. spectroscopy, electron microscopy, and electron diffraction) are not sensitive enough or, when the admixtures are present in amorphous form.

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Translated by S. Durovič