

CONTRIBUTION TO QUANTITATIVE DETERMINATION OF LAYER SILICATES BY CHEMICAL METHOD*

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INTRODUCTION

The layer silicate minerals of sedimentary basins are of great importance both in theoretical and practical respect. Great attention has been directed to their study in the last decade in consequence of their role in the genesis, migration and exploitation of petroleum.

For the sake of rendering possible the study of distribution and history of evolution of layer silicates in the sedimentary basins, first of all some analytical problems had to be solved. The most general method for the quantitative and qualitative analysis of crystalline layer silicate minerals is the X-ray diffraction analysis. It seems to be, however, advantageous to compare the data obtained by X-ray diffractometry with results of other methods.

From this point of view attention has to be turned to the chemical method proposed by ALEXIADES and JACKSON [1966] for quantitative determination of clay minerals, amorphous material, quartz and feldspar in soils and sediments, respectively.

PRINCIPLES OF THE CHEMICAL METHODS

The method according to ALEXIADES and JACKSON [1966] was developed for quantitative determination of the following minerals: montmorillonite, vermiculite, mica, kaolinite, dickite, chlorite, talk, quartz, feldspar and amorphous material.

The single steps of the method are based on measurements of ion exchange capacity, selective dissolution in NaOH, fusion by sodium pyrosulfate and on determination of ignition loss of samples.

The single steps of this complicated method are comprised in a flow sheet shown in *Fig 1*, constructed on the basis of own experiences.

The preparation means suspending the pulverized core samples in water and their fractionating. A pretreatment has to be made before analysis to remove carbonates, organic matters and iron oxides. This procedure is made with NaOAc solution, $\text{Na}_2\text{S}_2\text{O}_4$ solution and H_2O_2 . Then the samples are washed with KCl or NH_4Cl depending on what component is to be determined, to form monocationic K- or NH_4 -minerals. Before chlorite determination ions in exchange positions are replaced by K^+ because of the slight hydration of this ion. The determination of mica, quartz and feldspar is based on that of the K^+ ion, therefore, they cannot contain any K^+ in exchange positions, thus the saturation is carried out by NH_4^+

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ions. Before vermiculite and montmorillonite determinations samples have to be saturated by Na^+ for it can be exchanged easily and completely by K^+ or Mg^{2+} . At the determination of amorphous material or kaolinite K^+ or NH_4^+ may be used for saturation.

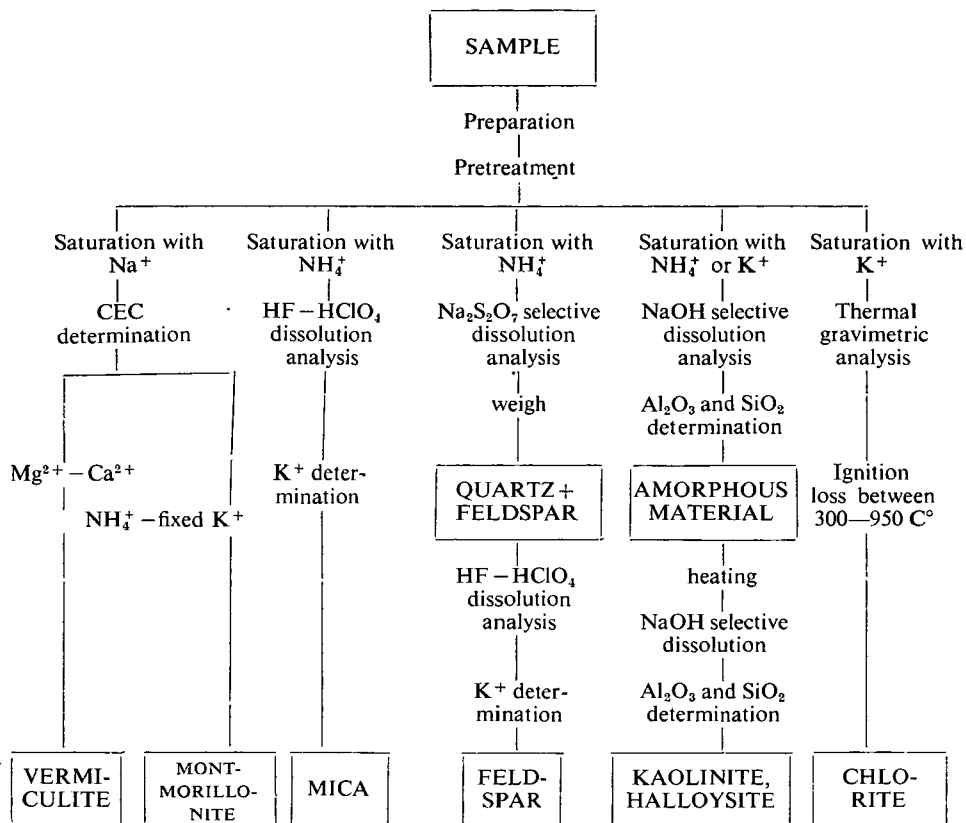


Fig. 1. The steps of the chemical method

Vermiculite determination is based on the high charge density of vermiculite and its K^+ fixing capacity [ALEXIADES and JACKSON, 1965]. The total cation exchange capacity (CEC) of the samples is measured by $\text{Mg}^{2+} \rightarrow \text{Ca}^{2+}$ ion exchange.

Ca^{2+} in the MgCl_2 solution is determined as follows: dilute 10 ml aliquot to 200 ml, add 20 ml of 6% NaOH solution and 1,5 ml of Eriochromblue SE indicator to it, stir the solution and titrate it with 0,05 M Komplexon III.

After CEC determination by Ca^{2+} , the samples are saturated by K^+ and heated to 110°C overnight to dehydrate and collapse the layers of vermiculite and to fix K^+ . The non-fixed K^+ is replaced by NH_4^+ . The concentration of K^+ is measured by flame photometry. The amount of vermiculite can be calculated from the difference of the two CEC measurements taking into account that the interlayer charge of vermiculite amounts to 154 meq/100 g.

Montmorillonite determination is carried out by CEC determination, too. The CEC is measured by $\text{NH}_4^+ - \text{K}^+$ cation exchange. The CEC of montmorillonite is

105 meq/100 g. The amount of amorphous material has to be considered in the calculation if its $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is > 3 . In this case also the montmorillonite-like components are dissolved in NaOH consequently this part of the sample would be counted as amorphous material and as montmorillonite, too.

The determination of *mica* of sedimentary rocks is based on its K_2O contents. The sample saturated with NH_4^+ is submitted to $\text{HF}-\text{HClO}_4$ dissolution. After this procedure K^+ is measured by flame photometry. The K_2O contents of generally dioctahedral micas are 10 per cent. The K_2O contents of feldspar are subtracted from the total K_2O of the samples.

The amount of *quartz* and *feldspar* is determined after $\text{Na}_2\text{S}_2\text{O}_7$ fusion. In this way the other, layer silicate minerals are decomposed by removing octahedral cations, so they become soluble in NaOH solution. SO_3 formed during the fusion of $\text{Na}_2\text{S}_2\text{O}_7$ means an acid treatment for the layer silicate minerals at high temperature and makes them soluble.

The weight of the insoluble residue gives the amount of quartz together with feldspar. The K^+ contents of the residue are measured after having dissolved it in $\text{HF}-\text{HClO}_4$.

During fusion by $\text{Na}_2\text{S}_2\text{O}_7$ there is an ion exchange, K^+ in feldspar is replaced by Na^+ from $\text{Na}_2\text{S}_2\text{O}_7$. Boiling in 0,5 n NaOH solution results some loss in the amount of quartz and feldspar. Both effects depend on the grain size. The losses coming from these effects have to be corrected by a factor (KIELY and JACKSON, 1965). The grain size influences the value of the correction factor. The calculation is based on the 16,9 per cent K_2O content of feldspar.

There is no ion exchange if the fusion is carried out by $\text{K}_2\text{S}_2\text{O}_7$. In this case the K^+ -excess can falsify the results of the determination. Another problem in connection with $\text{K}_2\text{S}_2\text{O}_7$ is that the solubility of the K-silicate minerals, formed during the fusion, is less than that of the Na-silicates.

The determination of *amorphous material* and *kaolinite* is based on dissolving monocationic (K or NH_4) minerals in NaOH solution after a short boiling (2,5 min). Amorphous material dissolves while the crystalline phase is not damaged.

Si and Al concentrations are measured in NaOH solution. Calculating the amount of amorphous material and kaolinite contents the SiO_2 and Al_2O_3 and water contents are taken into consideration.

Si determination was made according to RAINWATER and THATCHER [1960] with some modifications because the determination in this case was carried out in NaOH solution. Si determination:

Pipet 4 ml aliquot of sample into 50 ml volumetric flask. Add 15 ml of 0,6 n HCl and 5 ml of 5 per cent NH_4 molybdate. Let it stand for 5 minutes, then add 5 ml of 17 per cent Na_2SO_3 , mix, dilute to volume and let it stand for 30 minutes before measuring. Measuring was made with a "Spektromom 360" spectrophotometer at 700 nm wavelength. When calibration curve was determined only 10 ml of 0,6 n HCl was added.

The Al determination was carried out according to SNELL and SNELL [1951].

Transfer 10 ml aliquot of sample to a 50 ml volumetric flask. Adjust the acidity to 0,7 ml concentrated hydrochloric acid. Dilute to about 30 ml and add 5 ml of 0,1 per cent Alizarin S solution. Add 2 ml of 1:2 ammonium hydroxide and mix. Let it stand for 10 minutes and add 10 ml of 1:2 acetic acid. Mix, dilute to volume and let stand for 20 minutes before measuring. Measuring was made with a "Spektromom 360" spectrophotometer at 490 nm wavelength.

Kaolinite is determined as amorphous material because the crystal structure of kaolinite is destroyed at 525 C° and so it becomes soluble in NaOH solution. The calculation of kaolinite contents depend on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio < 2 indicates free alumina or dissolved interlayer aluminium. In this case only the SiO_2 contents are considered. Kaolinite has 46,5 per cent SiO_2 contents in average.

When $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is > 3 , 2:1 layer silicate minerals were dissolved. The kaolinite contents are calculated on the basis of Al_2O_3 . The theoretical Al_2O_3 contents are 39,5 per cent in kaolinite.

When $\text{SiO}_2/\text{Al}_2\text{O}_3$ is between 2 and 3 the calculation is on the basis of average of SiO_2 and Al_2O_3 contents.

The *dickite* can be determined in the same way. The *dickite* becomes amorphous at 625 °C.

Chlorite is determined by thermal gravimetric method [ALEXIADES and JACKSON 1967]. K^+ -saturated samples are used for hydration of K^+ ion is minimum. The chlorite contents are calculated on the basis of the total ignition loss (OH water) of the samples between 300 °C and 950 °C. The water allocated to the minerals present other than chlorite, is subtracted from the total ignition loss. A correction is applied for the weight gain of FeO present and oxidized by heating to 950 °C. A 14 per cent OH water is attributed to the chlorite.

FeO determination: 0,3 g sample is dissolved in H_2SO_4 —HF under CO_2 atmosphere, for 10 minutes, at 130 °C, in Pt crucible. Then it is put into 100 ml saturated boric acid and titrated with 0,01 N KMnO_4 solution.

REMARKS IN CONNECTION WITH DATA OBTAINED BY CHEMICAL METHODS

After obtaining experiences on the applicability of the method outlined above using relatively well identified layer silicates and other minerals, respectively, core samples from Makó-trench were analyzed. The amount of layer silicate minerals, quartz and feldspar were determined by the chemical method and X-ray diffractometry. The samples were ground in a ball mill, so that grain size should be under 60 μm . The time of grinding was short to avoid destroying crystal structure of clay minerals [JUHÁSZ, 1969].

The powdered samples were then suspended and the fractions of grain size $\cong 20 \mu\text{m}$ were separated. Experiments were carried out with these fractions.

The composition of 17 core samples from Makó-1 borehole is shown in Table 1.

Some problems, however, arose during the experiments. and calculations.

When vermiculite is determined its CEC is calculated as the difference of two CEC values measured in two different ways, but the CEC numerical value depends on the way of determination, namely what kind of ions are used for saturation.

The total CEC of the samples is determined by $\text{Mg}^{2+} \rightarrow \text{Ca}^{2+}$ ion exchange. The non-fixed K^+ is replaced by NH_4^+ . The latter ion exchange means the CEC of the other than vermiculite minerals. These two CEC-s are not commensurable, so their difference must not be considered as the CEC of vermiculite.

The 10 percent K_2O contents for mica given in the literature may be questionable because only muscovite has 10 per cent K_2O . The K_2O contents of illite are smaller than that of the muscovite [HOWER and MOWATT, 1966]. Illite does not form discrete phases in many places, but it is rather a mixed-layer illite-montmorillonite. Illite is considered as an end member of the illite-montmorillonite series [HOWER and MOWATT, 1966].

TABLE I

Minerals present in the core samples from Makó-1 borehole

	Quartz	Albite	K-feldspar	Amorphous material	Kaolinite	Chlorite	Mica—Illite	Montmorillonite	Vermiculite	Total
I	19,6	2,3	1,0	7,7	4,6	11,7	22,1	24,1	0,0	96,1
II	18,0	3,6	0,8	7,3	0,0	18,3	26,9	15,8	0,0	88,7
III	10,1	2,1	0,5	9,6	4,9	12,7	27,3	21,1	0,0	88,3
IV	22,0	3,6	1,5	5,2	5,4	11,8	25,5	20,7	0,0	95,8
V	20,6	1,9	0,9	5,9	3,5	18,4	24,5	12,5	0,0	88,2
VI	21,0	1,9	1,1	3,7	18,8	3,3	24,3	13,8	0,0	87,9
VII	19,6	4,9	1,2	9,8	1,7	22,8	25,6	0,0	0,0	85,6
VIII	13,8	5,3	2,2	4,5	2,9	20,1	28,6	14,2	0,0	91,6
IX	16,8	3,1	1,8	2,7	0,9	20,7	26,2	15,2	2,5	87,4
X	20,2	4,0	1,3	2,6	0,0	27,8	25,3	16,3	0,0	97,5
XI	11,5	3,9	1,1	4,7	0,0	29,9	27,6	8,1	0,0	86,5
XII	17,4	4,4	0,6	4,6	1,9	21,6	26,9	5,8	0,0	82,2
XIII	19,6	3,2	0,8	16,2	0,0	25,4	26,4	1,0	0,0	82,4
XIV	19,4	3,8	0,4	9,1	0,0	17,8	28,8	8,9	0,0	89,1
XV	13,5	2,3	0,2	0,6	0,0	22,0	26,2	19,0	2,6	83,3
XVI	23,0	6,8	1,3	1,2	0,3	24,4	28,2	10,2	0,0	95,4
XVII	16,9	3,7	0,4	0,5	0,0	24,4	31,6	11,1	0,0	88,6

TABLE 2

*SiO₂/Al₂O₃ molar ratio of the amorphous material and quartz contents
in the pulverized non fractionated samples*

	I	II	III	IV	V	VI
SiO ₂ /Al ₂ O ₃	8,2	8,6	13,0	19,0	11,4	20,9
Quartz	20,6	23,9	38,1	39,7	50,6	42,9

These samples come from the Makó-2 borehole.

According to the previous fact the mica contents in core samples containing not only muscovite but illite and mixed-layer illite-montmorillonite cannot be calculated on the basis of 10 per cent K₂O contents.

Calculating the feldspar contents, different factors are taken into consideration for the fractions of different size. The samples analyzed contained particles in every size below 20 μm. Instead of complete grain size analysis we determined correction factors using a feldspar standard of grain size ≅ 20 μm. The loss coming partly from Na⁺ → K⁺ ion exchange, partly from the solubility of feldspar was corrected by these factors.

Considering the ion exchange, both K⁺ and Na⁺ contents of feldspars were measured and calculated, respectively. The Na₂O content measured after Na₂S₂O₇ fusion and the data of X-ray diffractometry suggested the presence of albite not only that of microcline as it was in the paper referred [KIELY and JACKSON, 1964]. So we calculated with 16,9 per cent K₂O contents for K feldspar [KIELY and JACKSON, 1964]

TABLE 3

*SiO₂/Al₂O₃ molar ratio of the amorphous
material and quartz contents
in the ≤ 20 μm size fraction*

	SiO ₂ /Al ₂ O ₃	Quartz
I	4,5	19,6
II	5,8	18,0
III	8,4	10,1
IV	6,5	22,0
V	8,5	20,6
VI	2,7	21,0
VII	9,6	19,6
VIII	5,2	13,8
IX	2,1	16,8
X	1,5	20,2
XI	3,8	11,5
XII	6,6	17,4
XIII	22,4	19,6
XIV	4,7	19,4
XV	0,4	13,5
XVI	1,2	23,0

and 10,7 per cent Na_2O and 1,0 per cent K_2O for albite was taken into account as mean values of data of albite analyses comprised in a handbook by HINTZE [1893].

The reliability of the determination of amorphous material was proved by a pure kaolinite sample. The sample heated to 600°C became amorphous tested by X-ray measurements and it dissolved completely in NaOH solution.

The fine grain size fraction of samples has large quantities of amorphous material. It is difficult to say whether the observed great quantity of amorphous material is due enrichment is caused by the partial damage of the crystal structure of layer-silicates during the preparation.

The data obtained by chemical method differ from those by X-ray diffractometry. It can be attributed to the presence of much amorphous material.

To obtain data comparable with that of the X-ray diffractometry the chemical analyses were carried out in pulverized non fractionated samples from Makó-2 borehole. The data obtained in two different ways coincided well. The amount of amorphous material was less than it was in the $\leq 20\ \mu\text{m}$ size fraction of fractionated samples.

In spite of this the pulverized and non fractionated samples are not suitable for chemical analysis because of their badly defined grain size. The value of CEC and the calculation of feldspar depend on the grain size. Another problem is that these samples contain quartz in large quantities and the SiO_2 contents can dissolve in NaOH solution, as it is shown in Table 2.

The same data of the $\leq 10\ \mu\text{m}$ size fraction of the samples from Makó-1 borehole are denoted in Table 3.

It seems that the adaption of the chemical method is more suitable in clay fraction of samples than in the average samples without separating their clay fraction..

CONCLUSIONS

Comparing the X-ray diffraction and chemical data concerning the determination of the mineral composition of sedimentary rock samples. it seems that both methods have advantages and disadvantages. The joint adaption of the two methods means a good possibility of the determination of clay minerals, amorphous material, quartz and feldspar. For example, the determination of amorphous material can be carried out quickly and exactly by chemical methods but X-ray diffractometry is not suitable for it. The question whether samples contain discrete phases of illite, montmorillonite, vermiculite and chlorite or mixed layer structures of them, can be answered only by X-ray diffractometry. The latter method is faster than the chemical method, but the advantage of the chemical method is that constituents can be determined in very small quantities, too.

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