

# THE QUALITATIVE DETERMINATION OF CLAY MINERAL GROUPS BASED ON COLOUR REACTION'

BY J. MEZŐSI

## PRELIMINARY REPORT

### INTRODUCTION, METHODS OF INVESTIGATION.

For the solution of many scientific and practical problems the exact knowledge of the mineral composition of clays is important. A common characteristic of clay minerals is that they mostly crystallise very difficultly, consequently, they usually occur as minute crystals (the diameter of their granule not exceeding 0.0002 mm in size).

Considering the importance of clay minerals, various methods were elaborated for their determination.

The more important ones are as follows:

1. *Optical method.* This method can only be used if the size of the granule components does not exceed the clayey fraction, i. e. they are at least 2 microns in size or larger. Kaoline is almost the only clay mineral which corresponds to this postulate. The bulk of the other clay minerals are about the size of colloids or still small. Hence the smallness of the grain sets a limite to the use of optical determination methods. Considering that the qualitative determination is already difficult the quantitative one is still more complicated. Apart from this the changes in the external conditions renders the application of the optical method still more intricate. Thus, for instance, at the determination of the value of the refraction index and of the magnitude of the double refraction such factors as temperature, pressure, the quality of the embedding liquid, wave length, etc. all play a role. Concerning the effect of the environment it should only be mentioned that, e. g. montmorillonites can take up water various cations etc. between their interlaminar layers which influence the refraction of light to a great extent.<sup>3, 48, 19, 20</sup>

2. *The electronmicroscopic and röntgenographic methods* of determination yield exact results, however, owing to the intricate and expensive equipment needed, their application is no easy matter so that these methods cannot be generally used.<sup>12, 14</sup>

3. A disadvantage of *the chemical methods* is that the analyses do not always furnish suitable results. In this respect the fact, that within

<sup>1</sup> Delivered as a lecture to the Geochemical Commission of the Hungarian Academy of Science at its Meeting in April 1954.

the same kind of mineral the chemical composition varies very much, that certain ions can substitute one another to a great extent, as well as the base exchange capacity, the variations of the water content, the great adsorption ability, etc.<sup>4, 14</sup> must all be taken into account.

4. The examinations carried out by means of *differential thermal analyses* supplement the X-ray examinations. The disadvantage of this method is that its exactness depends upon many factors: fineness of the pulverization, the impurities, etc. Thus the data reported by the different authors cannot be compared at first hand, whereas in the case of the results obtained with X-ray examinations this is possible. Hence by differential thermal investigations for each apparatus a comparison curve must be previously prepared from the pure substance. This method was elaborated in Hungary by Mrs. A. Földvári. With her method quantitative determinations within an error range of 0.5 per cent can also be performed.

5. It is known that the interlaminar adsorption of the montmorillonoid group which can be brought about by an excess charge can alter the interlaminar distance in a characteristic manner. As organic molecules can also be built in organic complexes may form, too. On this basis already some time ago *colour methods* were elaborated for the montmorillonoid groups. Initially aniline and azo dyes, later amines were used for the investigations.<sup>1, 2, 5, 9, 10, 11, 13, 15, 16</sup> Other workers carried out experiments with benzidine.<sup>16, 21</sup> The mechanism involved at the colouration of the clay surfaces,<sup>21</sup> as well as the relation between the ionic substitution of montmorillonites and swelling were examined.<sup>2, 21</sup> The different types of colour tests were in the first place used for the determination of the montmorillonoid group.

Of the investigations reported particularly the results published by Hauser and Leggett<sup>10</sup> are valuable. In their work all the organic substances involved at the colouration of clays are listed in tables. The experiments were carried out with Wyoming bentonite, hence their results are only valid for montmorillonoid groups. As they established that certain compounds do not exhibit colour reactions (certain anilines, aliphatic amines, saturated cyclic amines, nitrobenzene, heterocyclic nitrogen compounds, furthermore organic compounds where there are no amine groups on the benzene ring did not show colour reactions; the acetyl group, bound to the nitrogen, NO<sub>2</sub>, SO<sub>3</sub>, H, acetyl, Br, OH inhibited the colour reaction, the methoxyl and ethoxyl groups lightened the colour) the investigations were, of course, continued with those groups of compounds where colour formation could be observed.

The colouration produced by the organic compounds examined by Hauser and Leggett could not always be precisely identified. The authors obtained with orthotoluidine on bentonites in alkaline medium a yellow and in acid medium a pink colouration. Bosazza<sup>1</sup> and the author, however, observed in alkaline medium a green, in a neutral one a bluish green and in acid medium an orange yellow colouration.

Hambleton and Dodd<sup>9</sup> carried out their experiments with para-aminophenol with which compound Hauser and Leggett could not detect a colour reaction. This procedure is, however, very

uncertain, as for instance when HCl was added dropwise into the alcoholic solution of para-aminophenol — according to the prescription published by the former two authors — and then left to dry, a bluish lavender colour appeared which according to them is characteristic for the montmorillonoid group. It is, however, also probably that the purity of the compound influences to a great extent the colour production and unfortunately no chemically pure para-aminophenol was available to the author of this paper.

#### EXPERIMENTAL RESULTS.

The respective compounds were also examined as to what colour they show in alkaline or acid medium and as to whether the produced colour does not interfere with the colouration of the complex compounds formed on the clay samples. If the compound exhibited in acid or alkaline medium without the addition of any other substance a colour reaction it was not further examined as the colour would as it is have caused an interference.

Concerning the concentration of the solutions — but for the one para-aminophenolic examination — the author could not find any reference in the literature. Thus to obtain the most suitable colour intensity solutions of 10, 1 and 0.1 per cent were prepared. In the case of caoline, when benzidine was used, no essential difference could be found between the solutions of 1 and 0.1 per cent. On increasing the concentration the undissolved (?) benzidine on the surface of the suspension interfered. With montmorillonite when a solution of 10 per cent was used the result was the same as with caoline, a solution of 1 per cent yielded a fine Berlin-blue colour, one of 0.1 per cent a somewhat less distinct colour. With illite a solution of 10 per cent furnished a pale blue colouration, on using a solution of 1 and 0.1 per cent the colour became still lighter.

Of orthotoluidine also solutions of 10, 1 and 0.1 per cent were prepared. In the case of the caoline group if a solution of 10 per cent was used the surface resembled that observed with benzidine. With a solution of 1 per cent a turquoise green colour appeared, with a solution of 0.1 per cent the colour faded somewhat. In the case of montmorillonite with a solution of 10 per cent like in the latter case no proper colouration could be detected, whilst on using a solution of 1 per cent the colour of the suspension became greenish blue, with one of 0.1 per cent a lighter colour was produced. With the illite group the colour resembled that of caoline when solutions of varying concentration were used.

Solutions of 10 and 0.1 per cent were prepared from diphenyl amine. However, in this case, considering that the reaction runs down more rapidly in a hydrochloric acid medium, the addition of different concentrations of HCl was also attempted. For all three mineral groups the diphenyl amine concentration proved to be the most suitable, if a solution of 1 per cent was used, whereas the variation of the hydrochloric acid concentration did not influence essentially the course of the reaction. For all further experiments HCl was used in a solution of 10 per cent.

The series of experiments revealed that for these compounds a solution of 1 per cent proved to be the most suitable concentration.

Earlier authors who have dealt with this problem were of the opinion that only certain fractions of the substance are suitable for the determination. They examined the resulting colouration on single granules under the microscope. The author of the present paper, on the other hand, pulverised in all his experiments the substance to be examined in a mortar. In every case a solution of 1 per cent was prepared from the respective organic compounds and a suspension of the substance to be examined was made with this solution in small white coloured porcelain dishes. In this manner the colour reaction could be easily observed with the naked eye. As far as possible the compounds used for the experiments were always pure chemically.

The composition of all substances used for the experiments, as well as their structure are all known on the basis of previous investigations, they represent characteristic samples of the different clay mineral groups. The samples occurred at the following deposits: the caoline at Zettlitz, the montmorillonite at Gönc and the illite at Füzérradvány. The samples were furnished by Mrs. Földvári the head of a department of the Geological Institute and the author wishes to express his sincere gratitude to her for her kindness. The author is also very much obliged to the Hungarian Mining Research Institute for providing the substances needed for the experiments, they were made available from the following places. Gönc, Mád, Komlóska, Istenmezeje and Nagytétény.

With various organic compounds the following results were obtained:

BENZIDINE (4,4' diamino-diphenyl).

Weil, Malherbe and Weiss<sup>21</sup> consider the blue reaction of benzidine to be an oxidation-reduction mechanism.

Some authors are doubtful as to the utility of benzidine, amongst others only a paper published by Page<sup>15</sup> should be mentioned. On the other hand, the investigations of Siegl<sup>16</sup> and other authors proved that it is suitable for the determination of montmorillonite, particularly in a neutral medium. Hauser and Leggett,<sup>10</sup> mainly on the basis of the investigations of Stern, also find it appropriate for the determination of the montmorillonites. On using it for the minerals of the caoline group Bosazza<sup>1</sup> did not obtain a colour reaction either in a wet or in a dry state, with montmorillonite and illite (!) on the other hand, he observed a Berlin-blue colouration. He mentions that the caoline which he examined, though it contained a considerable amount of ferrous and ferric iron, did not show any colour reaction. With the exception of Bosazza<sup>1</sup> all investigators did not take the pH values into consideration.

The author of this paper the colours produced during the reaction by the means of the UNESMA<sup>22</sup> colour scale.

Our investigations have proved that benzidine is suitable for the determination of montmorillonite groups through the colour reaction the latter can be well distinguished from the caoline- and illite groups. After standing for a fairly long time the reaction also runs down if a dry solid reagent is added to the clay sample. The deepness of the blue

sample deposit	p <sub>H</sub> 1—2		p <sub>H</sub> 6 7		p <sub>H</sub> 9—10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	no changes	white light yellow (11 ga) border	light blue (17 ca)	light blue (17 ga) fading gradually finally white	no changes	no changes
montmoril- lonite Gönc	green (24 la)	darker green (24 pg)	Berlin blue (15 pa)	dark blue (15 pi) changing gradually green, yellow, finally white	light ochre yellow (2 pc)	light brown (3 lg)
illite Füzér- radvány	no changes	no changes	light blue (16 ca)	light blue (17 ga) fading gradually finally white	no changes	no changes

colouration shows to a certain extent how much of the montmorillonite group is contained in the respective clay. In such cases the characteristic Berlin-blue colouration is somewhat diluted. The mixture of mineral groups contain every transition colour from the light blue of caoline or illite to the characteristic Berlin-blue of montmorillonite. A disadvantage of using benzidine for the investigations is that the caoline and illite groups cannot be differentiated from each other.

In the course of drying the colour gradually changed from blue to green and yellow, becoming finally colourless. If water was added to the substance after it had been dried it soon took up its original colour. Weil, Malherbe and Weiss<sup>21</sup> only obtained a weak colour reaction with montmorillonite and caoline, the intensity of the colour also only increasing slowly, whereas at the experiments of the author of this paper the colour reaction took place rapidly under the conditions described above.

ORTHO-TOLUIDINE (ortho-aminotoluene).

Häuser and Leggett<sup>10</sup> also carried out experiments with the homologues of aniline ortho-, meta- and para-toluidine. They obtained with ortho- and meta-toluidine in the case of bentonite in alkaline medium a yellow colour and in acid medium an orange one, whereas with para-toluidine a pink colouration only in proportion to the amounts appeared in alkaline medium.

sample deposit	p <sub>H</sub> 1-2		p <sub>H</sub> 6-7		p <sub>H</sub> 9-10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	no changes	light yellow (10 ca)	light green (20 ca)	the green (20 ga) colour fading gradually (20 ca)	no changes	no changes
montmoril- lonite Gönc	yellow (2 na)	orange becoming gradually darker (3 pa 4 pa)	bluish green (18 pa)	bluish green (18 pa) turning after being kept for a fairly long time orange (3 pa)	dark green (24 ng)	brown (3 pi)
illite Füzérrad- vány	no changes	light yellow (1-ca)	light green (20 ca)	light green (20 ca)	no changes	no changes

The author of the present paper only carried out experiments with ortho-toluidine, the result are summarised in the following table.

The table shows that ortho-toluidine is very suitable, particularly in a neutral medium, for the determination of montmorillonite. It also yields the corresponding values in alkaline and acid medium, but only for montmorillonite. The differentiation of the caoline and illite group is also difficult in this case. If montmorillonite is mixed with illite or caoline the characteristic green colour is diluted and in proportion to the amount of the mineral groups all colours from a light greenish blue to the dark greenish blue of pure montmorillonite can be produced.

Bosazza<sup>1</sup> also accomplished experiments with ortho-toluidine. It is interesting that he did not obtain any colour reaction with any of the minerals of the caoline group. With bentonite and montmorillonite he did not either achieve any results. In the course of the examinations of the author illite showed only a weak colour reaction, whilst Bosazza<sup>1</sup> could only detect a dirty green colouration in the case of this mineral group.

The author let ortho-toluidine undergo reactions with ferrous and ferric compounds. In the case of ferrous compounds there was no change of colour, in that of ferric ones the solution showed a green colour. Thus ferric ions certainly play a significant part in the production of colour reactions.

DIPHENYLAMINE

Hauser and Leggett<sup>10</sup> obtained with montmorillonite both in acid and alkaline mediums a blue colouration, however, they do not describe the experimental conditions. Bosazza on the other hand, only succeeded in observing a dirty green colouration with activated Fullers earth, whereas in the case of caoline-, montmorillonite- and illite groups in moistened and dry no colouration could be observed.

The results of the experiments of the author are illustrated in the following table:

sample deposite	p <sub>H</sub> 1—2		p <sub>H</sub> 6—7		p <sub>H</sub> 9—10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	light green (23 ga)	green (24 le) fading gradually	no change	white with a light bluish border (17 ca) light blue (16 ga)	no change	no change
montmo- rillonite Gönc	green (21 na)	green (23 pi) fading gradually	green (23 nc)	green (23 nc) becoming gradually darker (23 pi)	no change	no change
illite Füzér- radvány	grass green (23 na)	light green (22 ca)	no change	white becoming gradually light blue (16 ga)	no change	no change

With an alcoholic solution of 1 per cent of diphenylamine a suspension was prepared in a neutral medium the reaction taking place very slowly, the colouration only appeared after the substance had dried. In acid medium the reaction ran down relatively quickly, about within an hour. The experiments show that particularly in acid medium the montmorillonite group can be well distinguished from the caoline- and illite ones, respectively. However, this procedure has also the disadvantage that the caoline and illite groups cannot be differentiated from each other, furthermore that in the case of a caoline-montmorillonite mixture neither the lighter green colour of caoline, nor the darker green one of montmorillonite can be distinctly detected, but that in proportion to the mixture transition colours appear.

## DIMETHYLANILINE.

It belongs to the tertiary amines.

This organic compound was only examined by Hauser and Leggett<sup>10</sup> on Wyoming bentonite. The author of the present paper did not only examine caoline and illite but also extended his experiments to montmorillonite. When the pulverised substance was mixed with the reagent the substance of all three mineral groups turned light green resembling the colour of dimethylaniline. The colours could only be distinguished, in the course of the drying of the substance caoline turning brownish green, montmorillonite dark green and illite light green. When the substance was dried the colours changed, caoline showed a light green colouration, montmorillonite no change of colour and illite became colourless. After being kept for some time, first caoline and illite, later also montmorillonite exhibited a blue and eventually a pink colour already previously observed.

\*

The disadvantage of the examination methods used so far is that they are only suitable for proving the presence of montmorillonite and for the distinction of montmorillonite from caoline and illite groups. However, they do not render possible the establishment whether caoline or an illite group, or a mixture of these clay mineral groups is involved. For this purpose the author performed experiments with several groups of organic compounds, among others with phenols. The latter have — as is known — an acid character and combine with alkalies to form salts. The acid character becomes more pronounced if not only a hydroxyl radical, but a nitro radical is also substituted. The following compounds proved to be suitable: para-dioxybenzene (also called hydrochinone), used for photography, para-methylaminophenol (methol) and para-methylaminophenol-sulphate. A solution of 1 per cent was also prepared from these compounds for the experiments. Experiments with pure substances yielded the following results at pH 6—7.

On using a solution of 1 per cent of paramethylaminophenol and paramethylaminophenolsulphate montmorillonite turned immediately light green. This colour gradually faded. With para-dioxybenzene at first no change could be observed in either group, later after standing for a fairly long time the green colour of montmorillonite faded completely and the colour of the substance to be examined showed at the most a light greenish tint. At the same time caoline also began to undergo a change, with para-methylaminophenol and para-methylaminophenol sulphate a greenish brown, with para-dioxybenzene a pink colouration could be observed. This reaction ran down relatively slowly lasting about one day. In alkaline medium on the action of any of the three reagents the liquid above the substance turned brown. This could be seen in the case of all three samples. Caoline and illite remained colourless, whereas the whole of the montmorillonite took up a greenish brown colour (2pc). In acid medium the light green colour of montmorillonite disappeared at once, gradually, however, it after all changed again to a green colour



reagent		caoline	montmorillonite	illite
para-dioxybenzene (hydrochinone)	wet	gradually pinkish brown (6 pg)	no change	no change
	dry	reddish brown	no change	no change
para-methylaminophenol (methol)	wet	gradually brown (2 ng) greenish	light green (24 ic) fading gradually	no change
	dry	brownish green (1 pu)	colourless	no change
para-methylaminophenol- sulphate	wet	gradually greenish brown (2 ng)	light green (24 ic) fading gradually	no change
	dry	brownish greenish (1 pn)	colourless	no change

later displaying a bluish tint (19ne). Caoline and illite, on the other hand, do not change either in a wet or a dry state and do not show any colour reaction. If pure caoline and illite were mixed in a ratio of 1 : 1, the suspension prepared from a solution of 1 per cent. of para-methylaminophenol sulphate was at first — as long as it was wet — colourless eventually it turned greenish brown which colour also persisted when it was dry. A mixture of caoline and montmorillonite 1 : 1 behaved in the same way. A mixture of montmorillonite and illite 1 : 1 did not show any change whether it was wet or dry. Control experiments were carried out with bentonite from Istenmezeje it was pulverised and a suspension prepared not either showing any colour reaction. According to the data reported in the literature bentonite from Istenmezeje consists of 85 per cent montmorillonite and 12 per cent illite. The fact that the clay minerals are not pure could already be established in the course of the examinations with benzidine, inasmuch as a deep Berlin blue colour could not be observed. This method makes it obvious that only the caoline group undergoes an essential change, hence it is easy to distinguish it from montmorillonite and illite. These two latter groups, on the other hand, can be readily differentiated with any of the methods using amines.

An experimental series was devised to keep the different clay mineral types at various temperatures for an hour in order to observe at

which temperatures they undergo a colour reaction. As the action of benzidine is very rapid and intensive a suspension of a benzidine solution of 1 per cent was prepared from samples heated to different temperatures, of course, the heated sample was first cooled to room temperature.

The following results were obtained:

temperature C°	caoline		montmorillonite		illite	
	wet	dry	wet	dry	wet	dry
110	characteristic		colour reactions			
200						
500	greenish grey not characteristic	no changes	15 pa (green)	15 pa	characteristic colour reaction	
600	no changes	no changes	green (15 pa)	15 pa		
700	no changes	no changes				
800	—	—	no changes	no changes	—	—
900	no changes	no changes	no changes	no changes	no changes	no changes

The experiments proved that relatively the caoline group is the most sensitive to changes of temperature, a sample heated to 500° C and subsequently cooled did not any more show a characteristic colour reaction. If we compare this with the values obtained by means of differential thermal analysis reported in the literature<sup>7, 8, 12</sup> it can be established that in the case of most caolines at a temperature of 500—550° C an endotherm change results depending upon which of the members of the caoline

group are present. The separation of the hydroxyl radicals results in the decomposition of the crystal lattice. Hence it is obvious that such samples do not exhibit a colour reaction.

In the case of montmorillonite a bentonite sample from Istenmezeje first heated to 500° C and 600° C and then cooled, showed instead of the characteristic Berlin-blue colouration a dark green one (15 pa). Another sample heated to 700° C exhibited the same colour, the only difference being that when benzidine was used for the suspension of the pulverised sample its colour was of a lighter tint. Both wet and dry suspensions prepared from a sample heated to 800° C and still higher temperatures no longer showed any colouration. The curves plotted on the basis of the differential thermal analyses reported in the literature show that the decomposition of the crystal lattice and the separation of the OH radical of the various members of the montmorillonite family occurs at different temperatures: with nontronite at 450—500° C, with montmorillonite at 600—700° C and with hectorite at 700—900° C. It may therefore be assumed that probably it is possible to determine the mineral species within a montmorillonite group more exactly. In this respect bentonite from Istenmezeje was examined, the presence of montmorillonite could undoubtedly be established in it, however, it stands to question what cause the appearance of the dark green colour instead of the blue one of benzidine.

Although the OH radical of the illite group separates at a temperature range of 200—600° C the crystal lattice persists, at the most the lattice constants increase to a small extent. The structure disintegrates gradually the complete decomposition only taking place at 800—900° C. On heating, the illite showed a light greenish blue colour reaction till the temperature reached 700° C above it both wet and dry suspensions prepared from this substance did not undergo any further change. After standing for some time the green colour turned gradually greenish blue.

The experiments point to the fact that within all three mineral groups a colour reaction only takes place as long as the structure is intact, if the structure disintegrates a colour reaction does not take place any more. It will be attempted to extend the method of examination not only to render possible a quick and certain determination of pure substances, but also of mixtures. We shall try to establish which compounds are more reactive those of acid or those of alkaline character, furthermore to what extent the colour reaction is sensitive to the changes of the pH and finally to examine the substance yielding a colour reaction under the microscope. It would also be useful to extend the investigations to the determination of soils. However, in this case it must be taken into account that their darker colour will cause difficulties.

Later it will be possible to control and supplement the results through comparing them with the values obtained with the differential thermal analyses. It seems also desirable to examine the complex compounds forming at the colour reactions more closely.

An advantage of the method is that the different clay mineral groups can be readily determined in the areas of occurrence rendering the investigation of these kinds of crude substances far easier. Another important field of research is oil mining where the quick determination of the clay

mineral groups is also a significant factor. If the method can be improved it may under certain conditions also be suitable for the identification of the geological strata.

#### REFERENCES:

1. Bosazza V. L.: On the adsorption of some organic dyes by clays and clay minerals. *Amer. Mineral.* 29. 1944. 235—241.
2. Buzágh Aladár: Bentonit szolok és bentonit gélek sajátságairól. *Magyar Kémiai folyóirat.* 56. 1950. 7—10.
3. Correns C. W.: Bestimmung der Brechungsexponenten in Gemengen feinkörniger Minerale und von Kolloiden. *Fortschritte der Min. Krist. und Petr.* 14. 1929. 26—27.
4. Engelhardt W.: Über silikatische Tonminerale. *Fortschritte der Min. Krist. und Petr.* 1937. 21. 276—340.
5. Faust G. T.: Staining of clay minerals as a rapid method of identification in natural and beneficiated products. *U. S. Bureau Mines R. I.* 3522, 21, (1940).
6. Foster Margaret: Geochemical studies of clay minerals. II. Reaction between ionic substitution and swelling in montmorillonites. *Amer. Mineral.* 33. 1953. 994—1006.
7. Földváriné, Vogl Mária: Agyagásványok differenciális termikus vizsgálata. *Földtani Közlöny.* 1951. 91—96.
8. Földváriné, Vogl Mária: Magyar bauxitfajták ásványos összetételének vizsgálata differencialtermikus elemzéssel. *M. T. A. Műszaki Tudományok Osztályának Közleményei.* V. 3. 1952.
9. Hambleton W. W. and Dodd, Ch. G.: A qualitative color test for rapid identification of the clay mineral groups. *Economic Geol.* 48. 1953. 139—146.
10. Hauser E. A. and Leggett M. B.: Color reactions between clays and amines. *Jour. Amer. Chem. Soc.* 62. 1940. 1811—1814.
11. Hendricks S. B. and Alexander L. T.: A qualitative color test for the montmorillonite type of clay minerals. *Jour. Amer. Soc. Agronom.* 32. 1940. 455—458.
12. Jasmund K.: Die silicatischen Tonminerale. Monographien zu „Angewandte Chemie“ and „Chemie Ingenieur-Technik“. Weinheim, 1951.
13. Marshall C. E.: Mineralogical Methods for the Study of Silts and Clays. *Zeitschrift für Kristallographie*, 90, 1935. 8—34.
14. Nemezc Ernő: Az agyagásványok kristályszerkezete és röntgenvizsgálata. *Földtani Közlöny* 1953. 182—196.
15. Page J. B.: Unreliability of the bensidin colour reaction as a test for montmorillonite type of clay minerals. *Soil Science*, 51. 1941. 133—140.
16. Siegl W.: Über den Nachweis von Montmorillonit mit Benzidin. *Neues Jahrbuch für Mineralogie, Geol. und Paleont. Monatshefte.* 1945—48. Abt. A. 40—42.
17. Tittel Oszkár: A bentonit, mint öntödei segédanyag. *Bányászati és Kohászati Lapok* 1949. 490—495.
18. Vendel Miklós: Ein Verfahren zur Bestimmung der Lichtbrechung silicatischer Tonminerale vom Montmorillonit—Nontronittyp. *M. Kir. József Nádor Műszaki és Gazdaságtudományi Egyetem Bánya és Kohómérnöki osztályának közleményei.* Sopron. 1943. 330—343.
19. Vendel Miklós: Zur Bestimmung der Lichtbrechung silicatischer Tonminerale. *Chemie der Erde*, 15. 1945. 325—370.
20. Vendel Miklós: Szilikátos agyagásványok meghatározása. *Bányászati Lapok* 1951. 14—17.
21. Weil H., Malherbe and Weiss J.: Colour reactions and absorptions of some aluminosilicate. *J. Chem. Soc.* 1948.
22. Unesma: 24 Farbefaeln. Leipzig, 1933.