

## COMPARISON BETWEEN MOUNTING TECHNIQUES FOR CLAY MINERALS AS A FUNCTION OF QUANTITATIVE ESTIMATIONS BY X-RAY DIFFRACTION

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**ABSTRACT.** - Many mounting techniques are currently used in clay mineralogical studies which qualitatively give the same results. However, when estimations of the amount of the different clay minerals have to be made, important differences occur between the different methods.

In this paper, it is shown why a specific procedure has been followed to estimate the clay mineral amounts and how these results can be compared with chemical data.

Preparation is such that a stable clay suspension is obtained after a very mild physical pretreatment without the use of chemicals so that the clay minerals could be studied as they occur *in situ*. Samples for X-ray diffraction are prepared with the suction method and specific correction factors were applied on the peak areas above the background of X-ray patterns of the <2  $\mu\text{m}$ -fraction.

### INTRODUCTION.

Mounting techniques are a point of discussion when estimations of the amount of the different clay minerals have to be made on the X-ray diffraction measurements of the <2  $\mu\text{m}$ - fraction. While the accuracy of a method is often unknown in clay mineral analysis, attention should at least be paid to the precision of the analysis. Hereby, a difference has to be made between :

- the repeatability which is the agreement of successive measurements with the same method, and which normally does (may) not give problems;
- the reproducibility which is the agreement between different mounting techniques.

This paper intends to discuss the reproducibility of three techniques and the problems related to the estimation of the clay minerals content. Two methods (sedimentation and smear) are well known and are discussed in many papers amongst which the paper by GIBBS (1965) remains a valuable contribution. The third method (suction) is rather recently developed and will be compared and evaluated. The

estimation problem was clearly encountered during a statistical treatment of chemical, physical and mineralogical data of the Boom clay, as relative values could not be used and "more absolute" values were required.

### MATERIALS AND METHODS.

For this comparison, a representative sample (THPR1) of the grey Land van Waas clay (Boom clay, Rupelian) was used. A detailed chemical, physical and mineralogical analysis was carried out. The results of some important parameters with their analysis method are summarized in Table 1.

For the clay mineralogical analysis, the following procedure has been followed. The dried (<40°C) and crushed (<1 mm) clay was dispersed in demineralized water by applying a mild physical pretreatment : ~24 h shaking and ~10 min ultrasonics (45 kHz). No chemicals were added. A stable suspension was obtained after repeated washing by which the soluble salts were removed and flocculation was prevented. A few drops  $\text{NH}_3$  were finally

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added to increase the suspension stability. The <2 μm equivalent spherical diameter fraction was separated by pipetting off. This was repeated several times until the starting suspension was nearly free of <2 μm-particles in order to have a representative <2 μm-suspension. Settling times were determined using Stokes' law. Finally a stable clay suspension was obtained with a concentration of ~60g/l. It is recommended to start from the same clay suspension for an adequate comparison of the different methods.

For the sedimentation mounts, 0.5 ml, 1 ml and 1.5 ml suspension were successively pipetted on a glass slide (2.8 x 4.8 cm). When more than 1.5 ml was used, the clay film began to curl after drying.

For the smear mounts, the method described by LARQUE & WEBER (1978) was used. A 1.5 ml-aliquot was centrifuged. The clay was then smeared out in a central groove (1.1 x 3.0 cm) of a glass slide (3.0 x 4.5 cm).

For the suction mounts, a refinement of the method of Drever (1973) was applied. It was presented on a workshop of the 19 th Annual Meeting of the Clay Minerals Society. This method is analogous to the method of BRUSEWITZ (1982). 1.5 ml, 2 ml, 2.5 ml, 3 ml and 3.5 ml suspension were used to suck off. The filtered clay cake is transferred to a glass slide of 2.8 x 4.8 cm.

The samples were X-rayed using Fe-filtered CoKα-radiation at 30 kV and 20 mA. Scanning speed was 1°(2)/min and chart speed was 10 mm/min. The range varied from 400 cps for the smear and suction slides to 1000 cps for the sedimentation slides. Normal patterns were obtained after equilibration at 52 % relative humidity. All mounts were glycolated by the vapor method : 24 h in a desiccator under vacuum at room temperature. Calculations were made on these patterns. The samples were finally heated at 500° C during 1 h.

Peak areas were measured by "weighing" the surface on an analytical balance since the amount of a clay mineral is more closely related to the peak area than to the peak height. Peak heights were also measured because the use of peak areas is not generally accepted and/or applied.

## RESULTS.

The main clay minerals in the Boom clay are :

- illite with its maximum at ~10Å;
- swelling clay minerals (smectite and illite-smectite interlayers) which give a peak at ~17Å after glycolation and disappear after heating;
- kaolinite with its maximum at ~7Å which disappears after heating.

The presence of (degraded) chlorite is shown by a very small peak at ~14Å after heating. This accessory mineral, however, is left out of consideration.

TABLE 1.  
ANALYSIS RESULTS & METHODS

| PARAMETER                      | %                     | ANALYSIS METHOD  |
|--------------------------------|-----------------------|--|
| quartz                         | 34.1                  |  |
| microcline                     | 10.0                  | X-ray diffractometry<br>(WEBER <i>et al.</i> , 1973)   |
| plagioclase                    | 5.4                   |  |
| calcite                        | 0.3                   | calculated from CO <sub>2</sub> -content<br>(evolved gas analysis)   |
| pyrite                         | 1.4                   | calculated from S-content<br>(combustion method) after<br>subtracting an amount of S<br>equivalent to the water soluble<br>sulfates (turbidimetric deter-<br>mination) |
| <2 μm                          | 51.4                  | sedimentation analysis<br>(% <2 μm = Σ% clay minerals)   |
| Σ                              | 102.6                 |  |
| organic C                      | 1.8                   | Walkley & Black-method (ALLISON,<br>1965)  |
| pH                             | 7.0                   |  |
| Al <sub>2</sub> O <sub>3</sub> | 16.4                  | emission spectrometry  |
| total specific<br>surface      | 142 m <sup>2</sup> /g | calculated from equilibrium<br>moisture content (VAN DER VELDEN,<br>1978)  |
| >63 μm                         | 2.0                   | sieving  |

TABLE 2.  
RESULTS OF THE CLAY MINERAL ANALYSIS USING DIFFERENT  
MOUNTS AND CALCULATION METHODS (in %)

|               |        | swelling clay<br>minerals | illite | kaolinite |    |
|---------------|--------|---------------------------|--------|-----------|----|
| SMEAR         | 1      | 36                        | 30     | 34        |    |
|               | 1.5 ml | 2                         | 42     | 22        | 36 |
|               | 3      | 29                        | 46     | 25        |    |
| SEDIMENTATION | 1      | 48                        | 26     | 26        |    |
|               | 0.5 ml | 2                         | 57     | 20        | 23 |
|               | 3      | 41                        | 43     | 16        |    |
| SEDIMENTATION | 1      | 47                        | 26     | 27        |    |
|               | 1 ml   | 2                         | 55     | 20        | 25 |
|               | 3      | 39                        | 43     | 18        |    |
| SEDIMENTATION | 1      | 48                        | 25     | 27        |    |
|               | 1.5 ml | 2                         | 55     | 19        | 26 |
|               | 3      | 40                        | 41     | 19        |    |
| SUCTION       | 1      | 38                        | 31     | 31        |    |
|               | 1.5 ml | 2                         | 42     | 26        | 32 |
|               | 3      | 28                        | 51     | 21        |    |
| SUCTION       | 1      | 38                        | 31     | 31        |    |
|               | 2.0 ml | 2                         | 47     | 23        | 30 |
|               | 3      | 32                        | 47     | 21        |    |
| SUCTION       | 1      | 38                        | 31     | 31        |    |
|               | 2.5 ml | 2                         | 45     | 22        | 33 |
|               | 3      | 31                        | 46     | 23        |    |
| SUCTION       | 1      | 38                        | 31     | 31        |    |
|               | 3 ml   | 2                         | 48     | 22        | 30 |
|               | 3      | 33                        | 46     | 21        |    |
| SUCTION       | 1      | 37                        | 32     | 31        |    |
|               | 3.5 ml | 2                         | 48     | 20        | 32 |
|               | 3      | 34                        | 43     | 23        |    |

1 = height measured from clean glass slide;  
2 = peak area;  
3 = peak area after correction : swelling clay minerals/3,  
illite/1 and kaolinite/3.

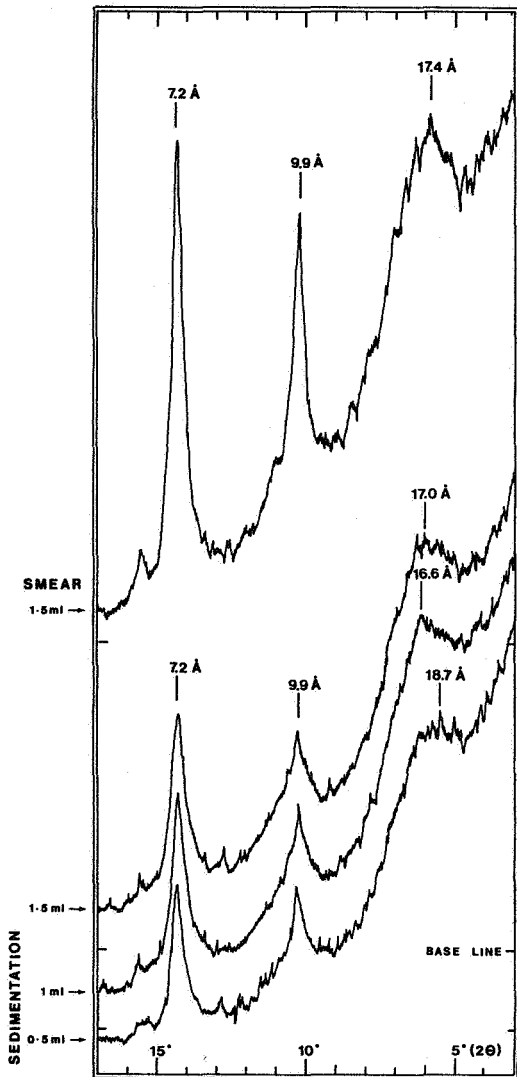


Figure 1 - X-ray patterns smear and sedimentation mounts.

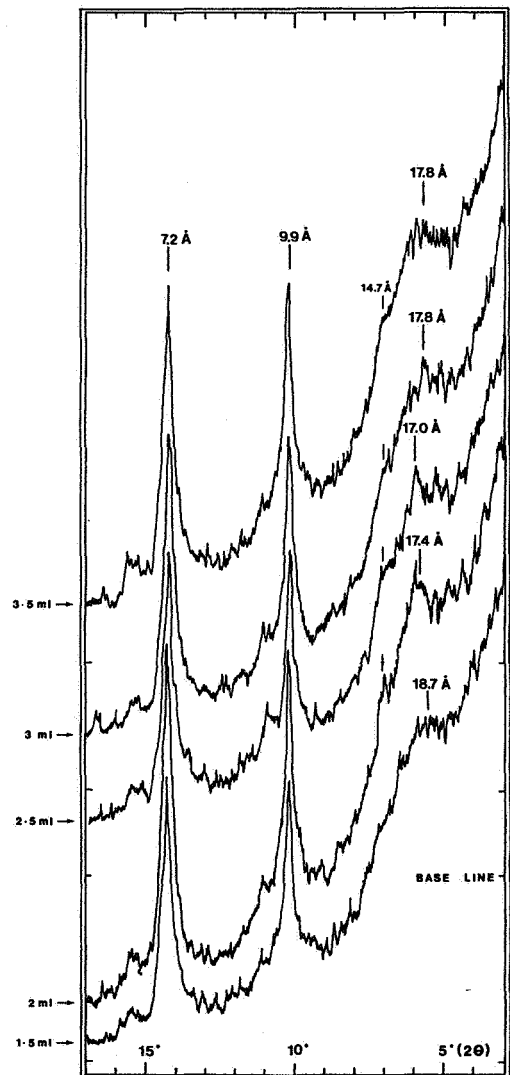


Figure 2 - X-ray patterns suction mounts.

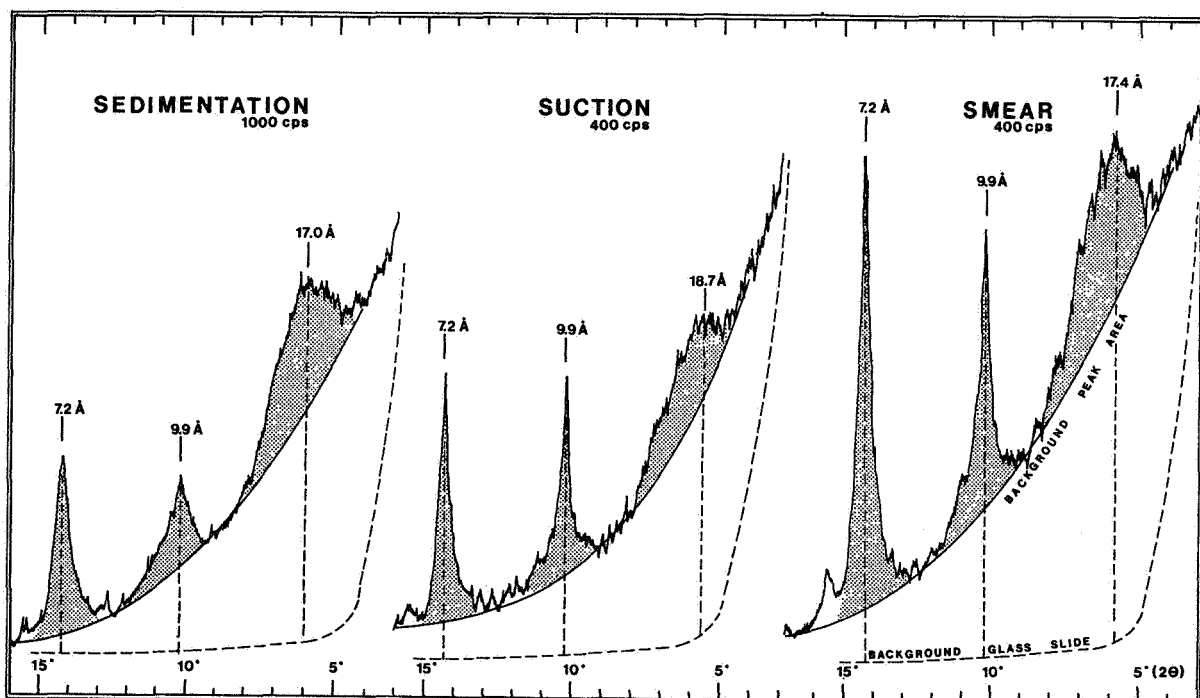


Figure 3 - Calculation method.

The X-ray patterns are presented conformable to the suggestions of SRODON & EBERL (1980). In Figure 1, the patterns of the smear and sedimentation slides are given, and in Figure 2 the patterns of the suction slides.

In Table 2, the results according to the different calculation methods are given. To avoid any confusion, the calculation method is shown in Figure 3.

#### DISCUSSION.

The importance and/or influence of grain size, mounting technique, peak area *vs.* height, background and correction factors on the estimation of the amount of the different clay mineral will successively be discussed.

< 2  $\mu\text{m}$ .

Although this topic was not investigated in this study, it will be discussed for the sake of completeness. The <2  $\mu\text{m}$ -fraction is traditionally chosen as a grain size limit for routine analyses, mainly because this fraction is almost free from non-clay minerals (the separation of this fraction is indeed more a phase separation than a real grain size separation) and capable to produce oriented X-ray mounts in order to enhance the (001) basal reflections. Moreover, this limit has also a sedimentological significance because it separates the lutum fraction (<2  $\mu\text{m}$ ) from the silt fraction (2-63  $\mu\text{m}$ ). Owing to this, it is possible to link physical data (*e.g.* grain size and total specific surface) with mineralogical data. The choice of this limit depends also of the field of interest. For petrographers, the 5  $\mu\text{m}$ -limit suffices, while pedologists frequently prefer 1  $\mu\text{m}$ . However, by using other grain size fractions, different amounts for the clay minerals will be found because the different clay minerals have no identical "diameters". Swelling clay minerals tend to be concentrated in the smaller grain size fractions, while kaolinite frequently occur in the >2  $\mu\text{m}$ -fraction. Depending on which size fractions are studied, other proportions will be obtained. Also for detailed clay mineralogical analyses, it is desirable to examine other fractions *e.g.* <1  $\mu\text{m}$  and < 0.2  $\mu\text{m}$ .

It is well known that by the separation of a grain size fraction by chemical and physical pretreatments and by settling procedures, the first errors can be introduced. Especially when estimations have to be made, attention has to be paid to the representativity of the sample. This can be done *e.g.* by repeated pipetting or sucking off the <2  $\mu\text{m}$ -fraction from the clay suspension until the supernatant liquid is almost clear after the calculated Stokes' law times.

In this comparative study, the influence of chemical and physical pretreatments on the dispersion degree of a clay suspension and on the X-ray diffraction patterns will not be treated. In agreement with others, it is the author's opinion that only a mild pretreatment can reveal qualitative and quantitative information on the clay minerals as they occur *in situ* and, consequently, as they have to

be used in clay mineralogical studies of geological materials. This can probably not be generalized for the study of soils. For the influence of chemical pretreatment, one is referred to *e.g.* McKYES *et al.* (1974) and BREWSTER (1980) and for the influence of physical pretreatment to *e.g.* CICEL & KRANZ (1981).

Also the influence of separation techniques is out of the scope of this study because it can be assumed (TOWE, 1974) that the quantitative distribution of clay minerals in fine-grained sediments is essentially independent of the size fractionating procedure.

#### MOUNTING TECHNIQUE.

Because this is the main topic in this paper, it will be discussed in detail. It is clear from Figure 1 and 2 and Table 2 (values peak area), that distinct differences exist between the different methods. Some striking features are :

- high values for swelling clay minerals with the sedimentation method (which is also indirectly expressed by the need to use another range *i.e.* 1000 cps);
- sharp peaks for the different clay minerals with the smear method;
- intermediate (between sedimentation and smear) values for the suction method;
- higher and even more distinct peaks with an increasing amount of clay on the glass slide which, however, does not influence the percentages.

With the sedimentation method, it is well known that due to different settling, mineral segregation occurs resulting in a mineralogically zoned clay film. At low  $2\theta$  angles, due to a lower penetration depth, the incident beam diffracts only from the upper surface layer of the sample, mainly composed of swelling clay minerals. It explains the high values for the swelling clay minerals.

With the smear method, sharper peaks are obtained, because a clay paste is smeared out while the supernatant liquid is poured away. This liquid is always slightly coloured, even after several washings, due to the presence of amorphous material, colloids, organic matter, ... which can obscure the diffraction peaks. This obscuring effect is probably present in the case of the sedimentation and suction mounts. In the first method, a suspension aliquot is used which contains besides clay particles, also amorphous material, colloids, organic matter, ... Even in the suction method, where a suspension aliquot is sucked off, the obscuring components occur in the clay film although these very fine particles should, theoretically, pass through the filter with a pore size of 0.45  $\mu\text{m}$ . The sucked off liquid, however, is always clear.

The oriented clay film has to be sufficiently thick so that the incident X-rays cannot produce diffraction effects from the substrate. Moreover, the depth of penetration of the beam increases with increasing  $2\theta$ . In the case of a thin sample, this results in a gradual decrease in intensity with increasing  $2\theta$  compared to the intensities of the same peaks derived from an infinitely thick clay layer. This explains the increase of peak intensities

with increasing clay amount. For a 2.8 x 4.8 cm slide, 200 mg clay is required! Therefore, the analyst is advised to determine the clay suspension concentration in order to know if sufficient clay will be on the slide.

Each method, however, has its advantages and disadvantages. For the three mounting techniques, they are summarized below.

#### SEDIMENTATION METHOD.

##### Advantages :

- easy, quick and cheap method (no special equipment is required);
- thin films prepared by sedimentation give the best orientation;
- suitable for small samples;
- great sensitivity for the detection of small amounts of smectite.

##### Disadvantages :

- grain size fractionation resulting in mineral segregation;
- clay cake curls and cracks after heating;
- difficult to obtain an "infinite" thickness;
- long drying time;
- peptizing agents (its use, however, is absolutely not recommended) or other residual salts can crystallize during drying, disturb orientation and produce interference peaks.

#### SMEAR METHOD.

##### Advantages :

- easy and quick method (little equipment);
- good orientation;
- sharper and higher peaks on glycolated patterns;
- better resolution of the peaks;
- easy to obtain infinite thickness.

##### Disadvantages :

- no control of clay thickness (thickness variations);
- clay cake curls (already during drying) when too thick;
- uneven surfaces (can be avoided with adapted method of CROUDACE & ROBINSON, 1983);
- more sample is required;
- special glasses are necessary;
- lower repeatability (in comparison with suction and sedimentation), probably due to a different degree of orientation and amount of clay for duplicate slides.

#### SUCTION METHOD.

##### Advantages :

- excellent orientation;
- quick method (probably the fastest method available);
- very flat surface, uniform thickness;
- also suitable for small samples (filters with  $\phi$  25 mm exist);
- high repeatability due to a constant sample geometry;
- membranes (re-usable) and glass slides are stock items and need no cutting or shaping.

##### Disadvantages :

- more equipment is required.

As can be seen from this summary, as well as from the results of this comparative study, it is clear that for routine analyses where large series or samples have to be examined in a rather short time period, the suction method gives the best solution and can therefore be recommended.

#### PEAK AREA VS. HEIGHT.

Peak areas were measured to estimate the amounts of the different clay minerals. Since reflections of the basal planes occur over a small but appreciable angular range, particularly in the low angle region, a summing of observed intensities over a sequence of angles surrounding each maximum is highly desirable (JOHNS *et al.*, 1954). The broad peaks are not only due to small crystal size and low angle effects, but also to the presence of mixed-layers which also have to be estimated. Moreover, even in the quantification of non-clay minerals, with peaks occurring in higher angle regions, peak areas are calculated by integrating over  $1^\circ(2\theta)$  (WEBER *et al.*, 1973). Therefore, peak areas are preferred.

Peak heights are still used because they can easily be measured and correspond sometimes better with other data, *e.g.* with cation exchange capacity values (SCAFÉ & KUNZE, 1971). It is also true, as mentioned by BRINDLEY (1980), that measurements of peak heights are not so sensitive for errors made by the estimation of the background than measurements of peak areas.

#### BACKGROUND.

In the low angle region, diffraction peaks are superimposed on a sharply decreasing background. As summarized by van der GAAST & VAARS (1981), the background is caused by :

- incoherent radiation (Compton diffusion, fluorescent radiation and temperature-diffuse scattering);
- apparatus-dependant factors (incident beam and air scattering);
- total reflection.

Background effects are also influenced by the Lorentz-polarization factor, the absorption factor and the atomic scattering factor.

Reflections, caused by coherent radiation, result not only from the (001) reflections of the clay minerals but also from :

- diffraction by small particles, amorphous material, ...;
- micro-pores;
- crystal defects,

which cannot strictly be regarded as background. They often are regarded as such because they cannot be distinguished from the real background.

The sum of these effects gives rise to a hyperbolic shaped curve which has to be subtracted from the pattern. The background curve is frequently drawn by running a clean glass slide. With this method, however, only peak height can be measured. But as already discussed, the use of peak areas is preferred to the use of peak heights. Therefore, the background has to be drawn as illustrated in Figure 3. Using this method, the different peaks are clearly separated on the glycolated pattern and peak areas can exactly be determined.

## CORRECTION FACTORS.

Peak areas of different clay minerals cannot directly be compared due to differences in mass attenuation coefficients, structure factor, ... Also because the intensity is a function of the Lorentz-polarization factor for each reflection angle, the use of correction factors is necessary. In comparing different clays, one has to pay attention on the mass attenuation coefficient which differs for the different samples due to different proportions of the clay minerals. Mass attenuation coefficients vary from about 30 for kaolinite and 50 for illite to values as high as 100 for iron rich clays. Because in this paper only one clay has been examined, this problem can be left out of consideration.

The correction factors used by VANDENBERGHE (1978) for the Boom clay are applied on our results and correspond well with chemical data. On an average, montmorillonite contains 18 %  $Al_2O_3$ , illite 27 %  $Al_2O_3$  and kaolinite 40 %  $Al_2O_3$ . When the results of the suction method (3.5 ml) are taken (34 % swelling clay minerals, 43 % illite and 23 % kaolinite), it can be calculated that the clay minerals ( $\Sigma=100$  %) contain together 26.9 %  $Al_2O_3$ . Taken into account that the  $<2 \mu m$ -fraction (51.4 %) is mainly composed of clay minerals, it can be calculated that the  $<2 \mu m$ -fraction contains 13.8 %  $Al_2O_3$ . This value corresponds very well with the value of rest- $Al_2O_3$  (13.6 %) which can be attributed to the clay minerals. Rest- $Al_2O_3$  is obtained by subtracting the  $Al_2O_3$ -content in microcline and plagioclase from the total  $Al_2O_3$ -content.

## CONCLUSION.

From the comparison of three mounting techniques, it can be concluded that the suction method can be recommended due to its many advantages, once the equipment is available. It is a quick and reproducible method for the study of large series of samples. Moreover, it has been shown that for a representative sample of the Boom clay, the amounts of the different clay minerals obtained :

- by preparing the mounts with the suction method;
- by using the  $<2 \mu m$ -fraction for the X-ray mounts;
- by determining the peak areas above the background;
- by applying specific correction factors, correspond very well with chemical data.

It is hoped that this paper has its value among many others, mainly in emphasizing the many difficulties of quantitative work in this field, but also that a forest of information may not have been lost in the trees of experimentation (TOWE, 1974).

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## REFERENCES.

- ALLISON, L. E. (1965) - Organic carbon. In : Methods of soil analysis, *American Society of Agronomy*, Wisconsin, USA. 90 : 1366-1378.
- BREWSTER, G. R. (1980) - Effect of chemical pre-treatment on X-ray powder diffraction characteristics of clay minerals derived from volcanic ash. *Clays and Clay Minerals*, 28 : 303-310.
- BRINDLEY, G. W. (1980) - Quantitative X-ray mineral analysis of clays. In : G. W. BRINDLEY & G. BROWN (Editors), *Crystal structures of clay minerals and their X-ray identification*. *Mineralogical Society London*, pp. 411-438.
- BROWN, G. & BRINDLEY, G. W. (1980) - Chapter 5 - X-ray diffraction procedures for clay minerals identification. In : G. W. BRINDLEY & G. BROWN (Editors), *Crystal structures of clay minerals and their X-ray identification*. *Mineralogical Society London*, pp. 309-310.
- BRUSEWITZ, A. M. (1982) - A filtering device for oriented XRD mounts. Note. *Clay Minerals*, 17 : 263-264.
- CICEL, B. & KRANZ, G. (1981) - Mechanism of montmorillonite structure degradation by percussive grinding. *Clay Minerals*, 16 : 151-162.
- CROUDACE, I. W. & ROBINSON, N. D. (1983) - A simple, rapid and precise smear method for the preparation of oriented clay mounts. Note. *Clay Minerals*, 18 : 337-340.
- DREVER, J. I. (1973) - The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peel technique. *American Mineralogist*, 58 : 553-554.
- GIBBS, R. J. (1965) - Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. *American Mineralogist*, 50 : 741-751.
- JOHNS, W. D., GRIM, R. E. & BRADLEY, W. F. (1954) - Quantitative estimations of clay minerals by diffraction methods. *Journal of Sedimentary Petrology*, 24 : 242-251.
- LARQUE, Ph. & WEBER, F. (1978) - Technique de préparation des minéraux argileux en vue de l'analyse par diffraction des rayons-X. *Notes techniques de l'Institut de Géologie, Université Louis Pasteur, Strasbourg*. 33 pp.
- McKYES, E., SETHI, A. & YONG, R. N. (1974) - Amorphous coatings on particles of sensitive clay soils. *Clays and Clay Minerals*, 22 : 427-433.

- SCAFE, D. W. & KUNZE, G. W. (1971) - A clay mineral investigation of six cores from the Gulf of Mexico. *Marine Geology*, 10 : 69-85.
- ŚRODOŃ, J. & EBERL, D. D. (1980) - The presentation of X-ray data for clay minerals. Note. *Clay Minerals*, 15 : 317-320.
- TOWE, K. E. (1974) - Quantitative clay petrology : the trees but not the forest. *Clays and Clay Minerals*, 22 : 375-378.
- VANDENBERGHE, N. (1978) - Sedimentology of the Boom clay (Rupelian) in Belgium. *Verhandeling Koninklijke Academie Wetenschappen, Letteren & Schone Kunsten, België - Klasse der Wetenschappen*, XL(147), 137 pp.
- VAN DER GAAST, S. J. & VAARS, A. J. (1981) - A method to eliminate the background in X-ray diffraction patterns of oriented clay mineral samples. *Clay Minerals*, 16 : 383-393.
- VAN DER VELDEN, J. H. (1978) - Evenwichtswatergehalte en specifiek oppervlak van kleien. Onderzoeksvorschriften. *Rapport CTI-TNO, Apeldoorn*, 13 pp.
- WEBER, F., LARQUE, Ph. & FEURER, R. (1973) - Mise au point d'une méthode d'analyse minéralogique quantitative par diffraction des rayons-X. *Analysis* 2(1).

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