

MINERALOGISCHE ONDERZOEKINGEN AAN KLEIEN EN KLEIMINERALEN

II. Quantitative X-Ray Analysis of Some Dutch Soils

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The application of the X-ray method of Debye-Scherrer-Hull is not only of importance for qualitative, but also for quantitative analysis: from the intensities of the reflections conclusions may be drawn as to the quantities of the constituents. That the difficulties are here greater than in qualitative examination appears from the fact that the number of applications of quantitative analysis is still small.

The methods, applied by various investigators in these examinations, have been described in detail in another paper [FAVEJEE (8)]. Of the methods mentioned there, only that one can be used for soil analysis which compares the intensities of the reflections on the clay-photographs with those

on the photographs of the pure constituents.

There is, however, in my opinion a serious objection to the way in which quantitative X-ray analysis has been applied by most investigators. They start from the assumption, whether implicit or not, that the quantity of a substance in a mixture is proportional to the intensities of its reflections on the X-ray photograph of that mixture.

Now, from experiments on synthe-

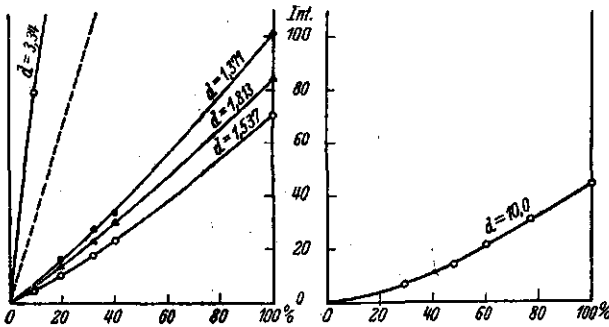


Fig. 1 Quartz.

Fig. 2 Muscovite.

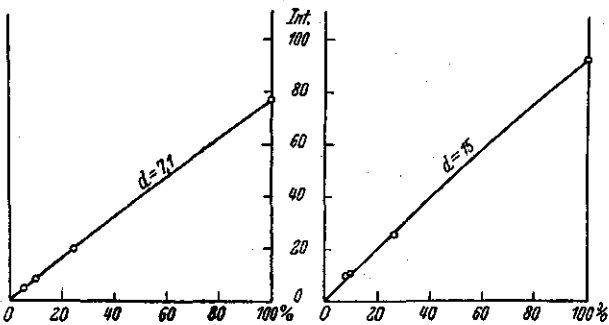


Fig. 3 Kaolinite.

Fig. 4 Montmorillonite.

tic mixtures [FAVEJEE (8)] it has appeared that in general this proportionality does not exist¹⁾. These mixtures were composed of quartz, muscovite, kaolinite and montmorillonite, as qualitative X-ray analysis has shown that the clay fractions of Dutch soils consist of these minerals [FAVEJEE (7), EDELMAN, VAN BAREN, FAVEJEE (5)]. The relationships between the quantity of each of these minerals in the synthetic mixtures and the intensities of its reflections are shown graphically in fig. 1-4 (the reflections are indicated by their spacing). Only for kaolinite and montmorillonite is the relation practically linear. For quartz and muscovite the deviations are very considerable: e.g. for the line $d = 3.34$ the percentage of quartz according to linear relationship would be 35%, whereas in reality it is only 13%. The line $d = 10.0$ of muscovite for instance would, according to linear relationship, give 25%, whereas in reality it is 40%.

Table I gives for a number of Dutch soils the compositions of their clay fractions, determined with the aid of these figures (the limits correspond with the exactness of the intensity measurement).

TABLE I

	Percentages				Total Amount
	Quartz	Muscovite	Kaolinite	Montmorillonite	
<i>Marine clays</i>					
Bellingwolde (Groningen)	29-34	27-30	9-11	5-6	70-81
Bijleveld (Zeeland)	17-20	32-36	6-7	6-7	61-70
Wieringermeer (acid clay)	15-18	28-31	5-6	3-4	51-59
Negenboerenpolder (Groningen)	12-14	33-37	6-7	15-18	66-76
„Kwelder” silt outside Negenboerenpolder (Groningen)	11-13	40-45	9-10	17-21	77-89
Poppendamme (Zeeland)	11-13	32-36	5-6	11-13	59-68
Panserpolder (Groningen)	9-11	36-40	5-6	10-12	60-69
Silt from seawater	8-10	27-30	6-7	4-5	45-52
Seasilt from the Wadden shallows	8-10	24-28	7-8	10-12	49-58
<i>River clays</i>					
Biesbosch (Noord-Brabant)	18-21	28-31	5-6	3-4	54-62
Echt (Limburg)	15-18	23-27	5-6	7-9	50-60
Hedel (Noord-Brabant)	11-13	32-36	5-6	3-4	51-59
Silt from Rhine-water	6-8	28-31	5-6	2-3	41-48
<i>Loam</i> (Eindhoven)	16-19	51-58	6-7	0	73-84
<i>Fuller's earth</i> (Limburg)	10-12	25-28	tr.	42-50	77-90

¹⁾ For mixtures of pyrolusite with braunite and of apatite with aluminium AGAFONOVA (1) likewise finds deviations from the linear relation.

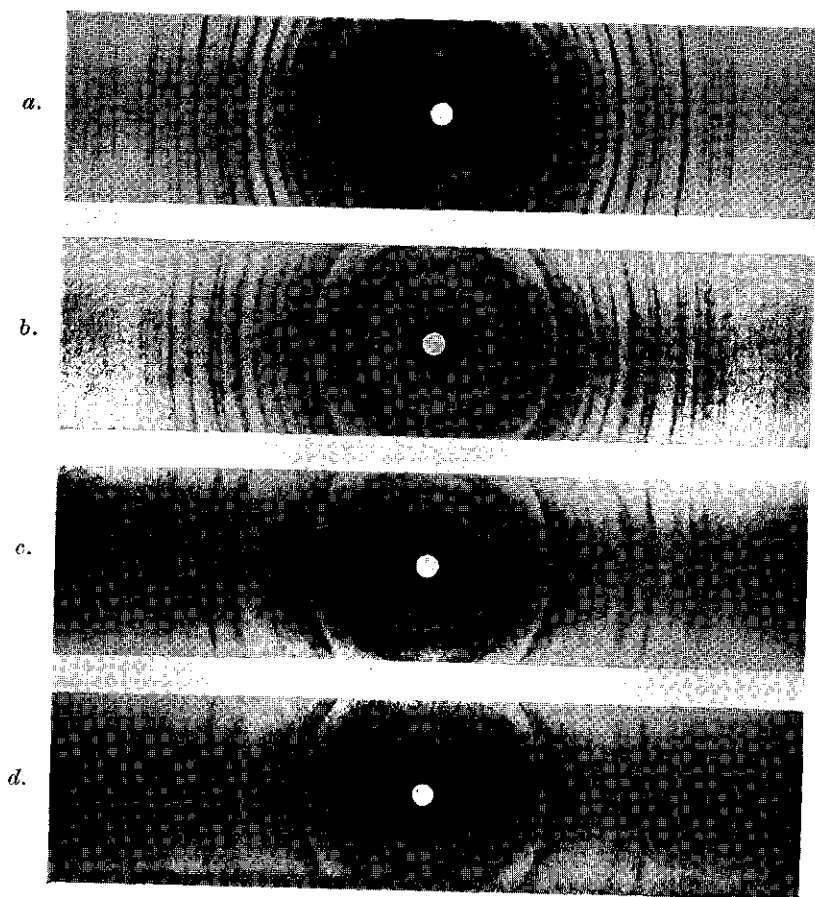


Fig. 5.

a. $8-2 \mu$ *c.* $0.16-0.06 \mu$
b. $2-0.16 \mu$ *d.* $< 0.06 \mu$

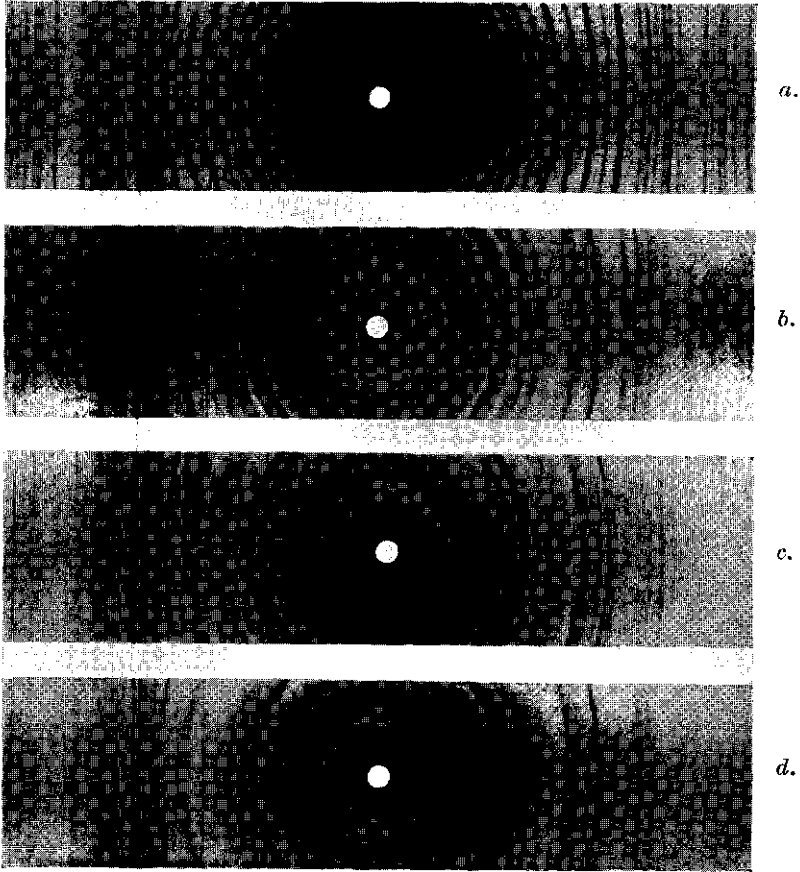


Fig. 6.

- | | |
|---------------------|---------------------------|
| <i>a.</i> Quartz | <i>c.</i> Kaolinite |
| <i>b.</i> Muscovite | <i>d.</i> Montmorillonite |

As regards this table, the following may be remarked:

1. The percentages of muscovite and kaolinite show some variation, but not to such an extent that, on the strength of these data, a relation may be assumed between the type of soil and the percentage of muscovite and kaolinite. As to the percentage of quartz it seems that young soils contain less quartz than old ones. The percentage of montmorillonite is, in general, greater in marine clays than in river clays. It is remarkable that the loam that was examined shows a deviation owing to the high percentage of muscovite and the lack of montmorillonite and that in the fuller's earth — which, as is well known, has a high percentage of montmorillonite — there is hardly any kaolinite.

It will be necessary to examine more samples, if for the Dutch soils it is sought to assume with more certainty a relationship between the type of soil and the mineralogical composition of the clay fraction.

2. When the quantities of the constituents are added up for every clay fraction, there appears in general to be a considerable deficiency, varying from 15-50%. Such deviations cannot possibly be due to inaccuracies in the method.

The question is therefore: To what must the deficiencies be ascribed?

An explanation, which on the strength of the old conceptions as to the nature of the clay material is very obvious, would be the presence of non-crystallized material. In this examination, however, it has not appeared that there are indications of the presence of quantities of non-crystallized material large enough to explain the deficiencies.

As the present writer presumed that the deficiency is caused by the presence of very small particles in the clay fraction, the composition was determined of some fractions ¹⁾, obtained by means of the centrifuge from the fraction $< 2 \mu$, viz. of a sample „Schwerer Tonboden” the fractions $2-0.16 \mu$, $0.16-0.06 \mu$ and $< 0.06 \mu$ (see Fig. 5) and of a sample of boulder clay the fractions $2-0.25 \mu$, $0.25-0.1 \mu$ and $< 0.1 \mu$. The way in which these fractions were prepared, their chemical composition and their properties are described by HISSINK, HOOGHOUTD and VAN DER SPEK (9).

From the X-ray analysis of these fractions (for the sake of comparison photographs are also given of the minerals quartz, muscovite, kaolinite and montmorillonite, see Fig. 6) it appeared that with decreasing particle-size:

- A. the qualitative composition changes;
- B. the diagrams of the minerals show changes;
- C. the deficiency in the total composition increases.

¹⁾ The author wishes to express his gratitude to Dr D. J. HISSINK, Director of the Soil Science Institute in Groningen, for putting these fractions at his disposal.

Moreover, it appeared that even the fractions $< 0.1 \mu$ and $< 0.06 \mu$ consist of crystalline material [in accordance with the results of NAGEL-SCHMIDT (10) and SCHLÜNZ (12)]; indications for the presence of considerable quantities of non-crystallized material were not found. However, that this presence may not be entirely excluded follows from the occurrence of a „gas-interference”, a corona round the primary beam on the photographs of the fractions $< 0.16 \mu$. That there is really question here of molecular dispersed material is shown by the fact that after treatment of the fractions with 0.05 N KOH this interference has disappeared. The diffuse blackening, the background, visible on most of the clay photographs, has not disappeared after this treatment; from this it may be concluded that the background is not caused by amorphous material [CORRENS (3) also arrives at this conclusion].

A. That the composition of the coarser fractions is dependent on the size of the particles is shown microscopically for particle sizes > 1 or 2μ by CORRENS and SCHLÜNZ (3, 4, 12) and VON ENGELHARDT (6). With decreasing particle size the percentage of quartz decreases, that of muscovite and montmorillonite increases (little can be found about kaolinite: SCHLÜNZ (12) finds in „Liaston von Dobbertin” that the quantity of kaolinite increases by decreasing particle size).

NAGEL-SCHMIDT (10) has examined the fractions $1-0.05 \mu$ and $< 0.05 \mu$ of „Mallisserton” by X-rays; he finds that the decrease of the percentage of quartz with decreasing particle size holds good also for fractions $< 1 \mu$; in the fraction $< 0.05 \mu$ quartz could not even be shown any more. For kaolinite (or halloysite) and for muscovite he finds no differences between the fractions $< 0.05 \mu$ and $0.05-1 \mu$. SCHLÜNZ (12) arrives at practically the same conclusions for „Liaston von Dobbertin”.

As regards quartz exactly the same has been found in the examination here described. Whereas the fractions of $2-0.16 \mu$ and $0.16-0.06 \mu$ contained respectively 15-20 and 2-3% quartz, this mineral was not present in the fraction $< 0.06 \mu$.

The percentages of muscovite and kaolinite show at first an increase with decreasing particle size, after that a decrease, as appears from the table below (for the sake of comparison with the coarser fractions the percentages of the fraction $8-2 \mu$ of „Schwerer Tonboden” are also given):

	<u>8-2 μ</u>	<u>2-0.16 μ</u>	<u>0.16-0.06 μ</u>
Muscovite	20	25-30	20-25%
Kaolinite	12-13	17-18	12-13%

For the boulder clay fractions similar results were found. To what extent the decrease for the fraction $0.16-0.06 \mu$ is real is discussed under B.

B. An examination of the photograph of the fraction $< 0.06 \mu$ gives the impression that it must be ascribed to montmorillonite. Yet there is a considerable difference to be seen, viz. that the basal interference has disappeared. Now this is entirely in agreement with what may be expected from such a mica-like material: When the particles of a crystallized material become very small, the interferences become less distinct: the intensities decrease [cp. BRENTANO (2)] and there appears broadening of lines. It would be possible that this decrease in intensity is only apparent, viz. that — with equal total intensity — only the peak intensity decreases owing to the broadening of the lines. That the total intensity actually decreases appears clearly from photographs of MgO [see RANDALL (11)]: the decrease is much stronger than would agree with the broadening of the lines. Moreover, even with the clay fraction $< 0.06 \mu$ the broadening of lines is small. It appears, that with decreasing particle size the phenomenon of decreasing intensity occurs sooner than the broadening of lines.

As the intensity of a reflection depends on the number of lattice-layers on which the primary beam is diffracted, the decrease of the intensity is not the same for all reflections. It is determined by the shape of the crystallites and by the size of the spacings. In micas the crystallites are plate-like, their size in the direction of the c-(pseudo-hexagonal) axis is small. Moreover, the spacing in that direction is great (20 Å; on the other hand ± 5.2 , respectively ± 9.0 in the direction of the a- and the b-axis). The number of reflecting lattice-layers in the direction of the c-axis is therefore small. With decreasing particle size the interferences caused by reflection on these planes (the (00l) interferences) will decrease in intensity first and then finally disappear altogether. To a lesser degree this also holds good for the (hkl) interferences; the prism interferences (hk0) are least sensitive to this. So according as the particle size decreases, the (00l) and the (hkl) interferences disappear; the prism interferences remain longest observable. This applies not only to montmorillonite, but likewise to muscovite and kaolinite.

From the above it may have appeared that the basal interferences of these minerals will disappear with very small particle size. The fact, therefore, that the quantitative determination of muscovite, kaolinite and montmorillonite was carried out with the aid of interferences whose intensities are dependent on the particle size, is the real cause of the deficiency in the total composition. Thus it is possible that the slight decrease in the percentage of muscovite for the fraction 0.16–0.06 μ (see table page 46) is due to the decrease of the particle size and not to the decrease of the real percentage.

Strictly speaking, for the quantitative determination of these minerals only those interferences should be used whose intensities are

least dependent on particle size, viz. the prism interferences. Owing to the analogous structure of these minerals, however, these interferences have practically the same spacings, so that the diffraction lines cannot be distinguished separately and are therefore of no use for intensity measurements.

C. In the sample „Schwerer Tonboden” the total composition for the fraction $8-2 \mu$ amounts to 86-94%; of $2-0.16 \mu$: 55-70%, of $0.16-0.06 \mu$: 35-40%. That of the fraction $< 0.06 \mu$ is still lower, but it cannot be expressed in figures owing to the lack of the basal reflections. The boulder clay fractions show similar results.

From this it appears that the deficiency increases with decreasing particle size, which corresponds entirely with the explanation of the deficiency given under B.

With very small particle size therefore the typical differences between the micas have disappeared. Yet it is still possible to recognize the minerals: From a very close comparison it appears that the prism interferences show some small differences in their spacings, and further the intensity relationship of these interferences in muscovite, kaolinite and montmorillonite, respectively, is not the same. Now it is of course not impossible that this intensity relationship also is influenced to some extent by particle size. This is certainly the case, when a prism interference coincides with a (00l) or a (hkl) interference (as these decrease in intensity with decreasing particle size). Without being able to attach too large a value to the intensity relationship (for this the structures of these minerals are not yet sufficiently known) it may be considered as an indication.

Thus, with the aid of these differences, it is yet possible, even if there are no basal reflections, to identify the minerals. The conclusion may thus be drawn that the fraction $< 0.06 \mu$ mentioned on p. 47, consist chiefly of montmorillonite.

The question now to be answered is:

For which minerals in the fraction $< 2 \mu$ is the difference between the quantity, determined in the way described here, and the real quantity of importance?

In answering this question the following must be taken into consideration:

1. The quantity of a mineral occurring in a certain fraction is connected with the particle size (cp. A).
2. According as for a mineral the size of the particles in the natural mixture (the clay fraction) differs more from that in the synthetic mixtures the difference between the percentage found and the real percentage is greater.

Quartz does not occur in very finely divided state (cp. A); so

the percentage of quartz as determined in the above described way will not considerably differ from the real percentage.

The percentage of muscovite increases with decreasing particle size, and in the fine fractions (0.16–0.06 μ , and, as appeared from an examination of boulder clay, also in the fraction $< 0.1 \mu$) it can certainly occur in considerable quantities. Therefore the particle size may have a great influence, especially in muscovite. For the preparation of the synthetic mixtures we started from ground muscovite $< 2 \mu$. As muscovite is very difficult to powder it is obvious to assume that the muscovite powder $< 2 \mu$ will contain comparatively little very fine material. Now when a synthetic mixture ($< 2 \mu$ with comparatively little fine muscovite) is compared with a clay fraction ($< 2 \mu$ with much fine material¹), the phenomenon of decrease of intensity as a result of very small particle size will occur exactly in muscovite, especially because the percentage of muscovite in the clay fraction is rather high (see Table I).

For kaolinite there are no indications of a considerable increase of the quantity with decreasing grain size in the fraction $< 2 \mu$. Moreover, the quantities are only small. For the synthetic mixtures the mineral purified by sedimentation is used; the original sample consisted for the most part of particles $< 2 \mu$. It is therefore not probable that the distribution of the particle size in this preparation deviates considerably from that of the kaolinite particles in the clay fraction, so that the real percentage of kaolinite will differ only little from the percentage found.

That the percentage of montmorillonite increases with decreasing particle size, may be considered as very probable: as has appeared, the fraction $< 0.06 \mu$ can even for a large part consist of montmorillonite. The high T-values given by HISSINK, HOOGHOUTD and VAN DER SPEK (9) for these fine fractions, agree with this. As in the case of kaolinite, also for montmorillonite the mineral purified by sedimentation was used for the preparation of the synthetic mixtures. Also in regard to montmorillonite the distribution of the particle size in these mixtures can be compared with that in the clay fractions, but in this case the possibility of a not inconsiderable difference between the percentage found and the real percentage will have to be taken into consideration, because particularly in the finest fraction the percentage of montmorillonite may be large.

From this quantitative examination it has appeared that the particle size plays an important rôle, as the intensities of the inter-

¹) According to HISSINK, HOOGHOUTD and VAN DER SPEK (9) the fraction $< 2 \mu$ sometimes consists for 33% of particles $< 0,05 \mu$.

ferences of the minerals are dependent on the particle size. Owing to this it will in general be impossible to obtain a total composition of 100%. The deficiency must in the first place be looked for in the quantity of muscovite and in the second place in the quantity of montmorillonite. It is improbable that the deficiency in the percentages of quartz and kaolinite is of any importance.

On the strength of the data obtained in this examination it is not yet possible to determine the differences between the percentages found and the real percentages of muscovite and montmorillonite; for this it will be necessary to establish for these minerals the relation between particle size and the intensities of their reflections.

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