Quantitative Mineralogical Analysis of Soil Clays[1]

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Abstract

Quantification of the components in the $< 2.0\mu$ fraction of soils is at best semi-quantitative in nature. Degree of crystallinity, particle size distribution, and chemical composition greatly affect results obtained from any quantitative study. It is best to use more than one diagnostic method to make quantitative estimations.

There is an increasing interest in agricultural and soil mechanics laboratories with respect to the different kinds of clay minerals in soils and their quantitative estimation. This is especially true for soils of countries in which practical experience on land reclamation, construction of buildings, roads, etc. is not yet available. Pedologists are interested in the kind and amount of clay minerals in soils for the study, characterization, and classification of soil profiles.

The complexity of the problem of quantitative determination of minerals in clays is recognized by all workers. This holds for studies of standard minerals and is an even greater problem with multicomponent soil clays. The purpose of this paper is to briefly review useful techniques and to comment on those found to be satisfactory for Indiana soils. Due consideration will be given to information gained relative to the efficiency of time spent.

Review of Literature

Konta (5) reported a comparative study by nine laboratories on the quantitative mineralogical analysis of a clay he supplied to each. The laboratories were free to use any technique or combination of techniques they desired. X-ray diffraction was used by all laboratories and is recognized as the most effective single method. This was supplemented by differential thermal analysis, infrared, chemical analyses, cation exchange capacity, and surface area measurements. From this study he concluded the results were only of a semi-quantitative rather than quantitative nature.

Mackenzie (7) concluded all clay mineralogical methods currently in general use can give quantitative data with some degree of accuracy. He has studied differential thermal analysis in greatest detail and stated, "Where applicable, the DTA method can give results of a good degree of accuracy and the relationship between peak area and amount of material is very nearly, if not perfectly, linear." However this has serious limitations because some minerals give peaks in such a close

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temperature interval that they can not be resolved, or they may give such small reactions that extremely high sensitivity and accuracy of recording are necessary. In addition, some minerals may give no thermal reaction in the usual 0-1000°C temperature range.

Van der Marel (12, 13) treated the quantification of soil clay minerals with x-ray, differential thermal analysis, infrared, cation exchange capacity, and chemical analyses. His conclusion, like the others, was that the quantitative determination of clay minerals in soils is a very difficult problem. Differences in the grade of structural ordering in the crystallites and an amorphous layer covering the clay particles were the two main factors he suggested which hinder quantitative analyses. In addition, amorphous organic and inorganic substances and variable crystalline composition of the clay mineral particles are further hindrances. Van der Marel has included a very complete bibliography as a part of his articles which would be most helpful for anyone contemplating further study in this area.

MacEwan (6) discussed another aspect of this problem which is usually not considered—the structural irregularities which are particularly liable to occur in soil clay minerals. Such iregularities may have a considerable effect on the intensities of x-ray reflections given by such minerals. This would be true of any type of interstratification, but is particularly true of random interstratification.

Recently selective dissolution followed by chemical analysis for dissolved components has been successfully used for quantification of soil clay components (1). They present flow-sheets for a system of quantitative mineralogical analysis of clays of soils and sediments that the Wisconsin group has developed over a period of years. They offer as best evidence of the accuracy of the system of analysis the consistent total recovery of nearly 100%. They conclude this is a significant measure of the specificity of this method.

Dixon (2) combined the differential thermal and selective dissolution analyses to measure amount of kaolinite and gibbsite in soil clays. He was interested in kaolinite and gibbsite, as they are important constituents in the soils of southeast United States. He reasoned that if these two major components can be accurately determined, the estimates of other constituents would be improved.

Results and Discussion

It was originally thought a detailed quantitative study of entire soil profiles might be enlightening as to the genesis of the soil clay minerals. Therefore it was of special interest to obtain a better estimate of the clay mineral components. The following discussion describes methods which the authors feel would provide a good evaluation of soil clays.

The Seventh Approximation (11) has established a scheme for the clay mineralogy classification of soils at the family level based on all materials $< 2.0\mu$ in size. Post and White (10) were the first to mention significant contents of amorphous materials in Indiana soils. Commonly the quartz content has not been estimated, though clearly

present as seen on the x-ray diffraction tracings. The earlier Indiana work included estimates of only layer lattice silicates; an average of 10% amorphous material was assumed in some of the determinations.

Table 1 presents part of the results of the selective dissolution analyses. (Refer to ref. 9 for the complete table.) Clearly the percent recovery, the only measure of accuracy for this method, is very poor. A number of factors probably have contributed to this error and will be discussed later. In the following discussion the minerals will be considered in groups according to the method of analysis.

Mica (Illite)

The term "illite" will be used as defined by Grim, et al. (3) as follows: "The term is not proposed as a specific mineral name, but as a general term for the clay mineral constituent of argillaceous sediments belonging to the mica group." This very adequately defines the variable nature of the micaceous minerals commonly found in Indiana parent materials. Post and White (10) using the 10 A/ 5 A peak height ratio for mica have concluded that the 10 A material found in the solum horizons has a full complement of potassium and is good muscovite; however the parent material mica often has a variable potassium content and more appropriately should be called illite.

The low potassium content-illite is readily weathered, as can be seen by the abrupt illite vermiculite transformation in going from the parent material to the lower B horizon (8, 9, 14, 15).

Mica and K-feldspars, the latter usually not present in the soil clay fraction, are the two major sources of potassium in the soil. Therefore a measurement of total K in the clay fraction should be an accurate measure of the mica content. Jackson (4) reported soil micas to contain about 10% K_2O. Thus, dissolution and determination of % K_2O and multplying this by a factor of 10 should be a good approximation of the % mica.

It is felt this mica determination for solum horizons is a reasonable quantitative measurement. The "illitic" character or parent material horizons with variable potassium contents does, however, decreases the specificity for these horizons. The x-ray diffraction tracings should always be checked for presence of feldspars.

Kaolinite and Amorphous Material

It appears from this work that the differential thermal analysis, perhaps combined with x-ray peak height measurements, should be used for quantifying kaolinite. Particle size and crystallinity do affect DTA and x-ray peaks, but perhaps a combination of the two compared to standard mixtures, would provide a reasonable estimate.

The question of amorphous material is problematical. In general, it is agreed amorphous materials are present but there is no completely satisfactory measurement technique available. The probability that the treatment will attack poorly crystalline or very small crystalline minerals must be considered. Alexiades and Jackson's procedure (1)

TABLE 1

Selective dissolution analyses on certain Pembroke soil horizons

Horizon	(inches)	(microns)	Quartz	Amorphous	Kaolinite	Mica "Illite"	Vermiculite	Montmorillonite	% Total Recovery
II B23t	28-36	2.0-0.2	.8	17.1	24.5	16.2	18.0	—	76.6
II B23t	42-48	2.0-0.2	1.7	12.5	30.6	19.2	22.2	—	86.2
II B23t	48-54	2.0-0.2	2.7	18.4	7.1	20.4	24.9	—	70.8
II B3-C	54-54.5	2.0-0.2	.9	18.7	12.0	20.4	22.8	—	73.9
II B23t	28-36	<0.2	—	25.5	33.8	12.6	20.6	—	92.5
II B23t	42-48	2.0-0.2	—	21.0	41.0	13.8	17.3	—	93.1
II B23t	48-54	2.0-0.2	—	29.0	12.7	14.8	19.8	—	76.3
II B3-C	54-54.5	2.0-0.2	.1	27.8	15.7	16.2	17.3	—	77.0
II R*	54.5+	<2.0	.9	3.9	—	58.8	9.1	.9	73.6

— Analyzed and found none.
* Analyses of insoluble residue.

which utilizes boiling for 2 minutes in 0.5 N NaOH as the extracting agent, is probably as good as any. The question of amorphous materials in Indiana soils has not been resolved and needs additional research.

Vermiculite-Montmorillonite

Alexiades and Jackson's (1) method is based on that part of the total initial cation exchange capacity lost on drying K-saturated samples at 110°C overnight.

Results obtained on Pembroke soil horizons were generally lower than expected from x-ray diffraction results. Probably the biggest source of error is the many washings involved in saturating 100 mgs of clay with the respective cations and then washing out the excess salt. The chance for loss of the very fine sample in decanting the supernatant washing liquids is great. Polyethylene tubes are not satisfactory in this determination as the clay tends to adhere to the sides and does not sediment smoothly to the bottom. As an example of this difficulty, in 16 Pembroke samples only 70 mgs of the original 100 mgs were recovered at the end of the procedure.

A serious error using cation exchange capacity to estimate the expansible clay minerals is the cation exchange capacity contribution by the other constituents, in particular, amorphous material. Alexiades and Jackson (1) have corrected for this in their calculations, but this is only a general correction factor. Also the presence of calcium carbonates in unweathered horizons would introduce a great error in the Ca^{++} analysis in the CEC determination.

Summary and Conclusions

It should be pointed out in all fairness to the selective dissolution technique that this was the first attempt to use this method. Some errors which contributed to the poor duplication experienced with this procedure could be due to poor technique. The percent total recovery was about 80%.

It appears very likely that, because of their low degree of crystallinity, small particle size, and/or chemical makeup, the kaolinite and vermiculite in the Pembroke soil horizons (9) in certain horizons are reacting with the extracting reagents and being measured as amorphous material. The selective dissolution method, like most others, was calibrated against "standard" minerals and "standard" average correction factors applied where it was found necessary.

In conclusion, the authors feel the following suggested procedure would provide a maximum for quantifying and characterizing Indiana soil clays on a routine basis.

1. In some cases there would be little advantage in fractionating the $<2.0\mu$ clay into two size fractions, especially for general characterization work. The nature of the study will determine this.
2. Saturation with a known cation prior to any analyses is always required. The Fe and organic matter removal usually would not be necessary.

3. Make two x-ray diffraction tracings per sample:

    (1) Mg-saturated ethylene glycol-solvated and (2) K-saturated, heated to 110°C overnight and glycolated. This should sufficiently characterize the sample. (Heating the K-saturated sample to 525°C may be necessary if the presence of chlorite is suspected.) The distinction between montmorillonite and vermiculite should be carefully considered as saturating cation, particle size, and the solvating organic molecule all effect the degree of expansion.

4. Make a differential thermal analysis of the Mg-saturated sample. Use this information and x-ray peak height measurements compared to standard mixtures to calculate kaolinite content. The true potential of DTA as an additional aid in Indiana soil clay investigation has not been recognized to date, mainly due to lack of an adequate instrument.

5. If no feldspars were noted by x-ray diffraction, run total K after dissolution of the Mg-saturated clay to calculate mica content.

6. Determine the amorphous content by selective dissolution analysis on the Mg-saturated sample. (At the present time the Al-Si colorimetric measurements are tedious. However Si and Al can be rapidly measured by atomic absorption. Amorphous Fe and free iron oxides after dithionite extraction can also be measured by this technique).

7. If the x-ray tracings show the presence of quartz and feldspars, these should also be determined by selective chemical dissolution.

8. Montmorillonite and vermiculite can be assumed to make up the balance. X-ray peak height checks should be used to quantify these two components.

After giving due consideration to step 1, steps 4 to 6 should be carried out to supplement the x-ray analyses of step 3. At best the results will still be semi-quantitative. However, this gives a truer picture of the clay composition and should provide useful information for interpreting weathering trends and genesis.

If time will not permit the characterization study suggested above, it is recommended that the relative amounts (Small, moderate, predominant) of montmorillonite, vermiculite, mica (illite), and chlorite be estimated from areas or peak heights of first order basal x-ray diffraction peaks. Kaolinite (and gibbsite, if present) could be estimated from the size of the respective DTA endothermic peaks as compared to standards. Amorphous material should also be determined.

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