THE PROCEDURE AND SIGNIFICANCE OF CHEMICAL AND MINERALOGICAL TESTS ON SOILS .

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Two different approaches can be used to determine the properties of soils involved in a problem of soil mechanics. The first approach consists of subjecting each soil in question to standard engineering tests, in the field or laboratory or both, to determine properties such as permeability, shear strength and compressibility. The second approach consists of two basic determinations: the nature of component parts of the soil and the detailed geological history of the soil since its deposition or residual formation. In this second approach, the engineering properties would be predicted from the knowledge of the properties of individual components and the history of their association and development.

The first of the above approaches is now in common use. It has the disadvantage of usually requiring many tests for every problem. While the development of knowledge to the stage where the second approach will be feasible now seems far in the future, the use of a modified form of the second approach to supplement the first is practical at the present time. In other words, the number of required engineering tests may be substantially reduced if physical properties of the soil in question can even be approximately predicted from the results of chemical and mineralogical tests. In fact, the use of identifying and classifying tests is a limited, but very practical, form of this modified approach. Also, the use of some parts of the second approach along with the first helps one to develop judgment and a "feel" for soil behavior.

It must be emphasized that the relation of mineral and chemical composition to the engineering behavior of a soil is known only slightly. Much research is needed to define more clearly this relationship. As this reservoir of knowledge is increased, the value of the tests presented in this paper will likewise increase. Although some of the tests are still in the development stage, it is felt that some form of these tests will eventually become standard for the more completely equipped soil mechanics laboratories. The different tests are presented herein as separate determinations, but it should be emphasized that to a certain extent they are interrelated. For example, for best interpretation of the results of a differential thermal analysis, the results of tests for certain chemicals, the ion exchange capacity, and the nature of the exchangeable ions should be known.

In the following pages, an attempt is made to present the significance and procedure of the more important chemical and mineralogical soil tests. The material for this paper was obtained from a study of pertinent literature and from research in the soil mechanics laboratory of the Massachusetts Institute of Technology. Many of the tests were developed by agricultural scientists

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and thus had to be modified for use in soil mechanics. Likewise, some of the chemical tests were developed by chemists interested in precise chemical analysis and they, in turn, had to be modified. Therefore, it is felt that the contribution of this paper lies in the development and modification of these tests for the engineer of soil mechanics.

The tests which are described in the following pages are:

1. Identification of soil minerals
2. Determination of the hydrogen-ion concentration of soil
3. Detection of deleterious substances
4. Determination of exchange capacity and exchangeable bases

IDENTIFICATION OF SOIL MINERALS

The determination of minerals in the coarser grained soils is not presented herein for two reasons, namely, the actual determination normally does not present a major problem and, in general, the engineering properties of cohesionless soils are not greatly affected by the nature of the mineral.

It was originally thought that the complete study of the component parts of a soil entailed only the determination of the chemical elements present. It was soon discovered that knowledge of what elements were present was not enough, but the structural arrangement of these elements must be known. From the viewpoint of many geologists, clays are soils composed of the so-called clay minerals—they being basic units built of unique atomic arrangements. It must be pointed out that many natural soils may have a large proportion of grains in the clay size range which still are not clay minerals.

In soil mechanics there seem to be three important clay mineral groups: kaolinite, illite, and montmorillonite. These groups consist of essentially the same chemical elements, but the structural arrangement of these elements is different. While there remains much to be learned about the engineering properties of the clay mineral groups, some qualitative data are available on these properties. Kaolinite is the least active of the clay minerals: it has the highest permeability, the lowest water adsorption, and the lowest compressibility of the three clay minerals. Montmorillonite is at the other extreme, having the lowest permeability, the highest water adsorption, and the highest compressibility. The illite group is between these extremes; some of the illites approach the kaolinites, while others approach the montmorillonites. Only a little is known quantitatively on the properties of mixtures of the clay minerals. Practically nothing is known of the engineering properties of bodies which are not clay minerals but are in the colloidal size range.

There are three methods available for the identification of the clay minerals or other minerals of "clay size" particles: the differential thermal analysis, X-ray diffraction, and the electron microscope. The differential thermal analysis seems to be the most practical of the three methods for use in a soil mechanics laboratory for qualitative and semiquantitative mineral determination, although the results may often be very difficult to interpret. Therefore, only the differential thermal analysis will be discussed here.

DIFFERENTIAL THERMAL ANALYSIS

The differential thermal analysis consists of heating at a uniform rate the soil in question and an inert substance from around 100 C. to over 1000 C. During the heating, changes in structure of the soil occur which result in the release or imbibition of heat. Since the inert substance does not undergo any structural change, the difference in temperature

between the soil and the inert standard, as measured by a differential thermo-couple, is a measure of the thermal change in the soil. Each pure mineral has a unique curve of thermal change *versus* temperature.[2] The apparatus is not described here because detailed descriptions are available in the literature (21).[3]

Test Procedure:

Analyzer Calibration.—Before the minerals in a given fine-grained soil can be identified, the analyzer must be calibrated by separately obtaining stand-

temperature can throw the early portion of the thermal curve off by driving off more water than is desired or possibly causing the grains of the soil to break down. If the specimen tested is a clay, no fractionation is necessary; but if the specimen has coarser grains present, all material coarser than the No. 200 sieve should be removed.

The dried specimen is next put in the sample holder. During the filling, care should be taken to keep the thermo-couple centered. The amount of speci-men used for the test and the void ratio obtained should be similar to that
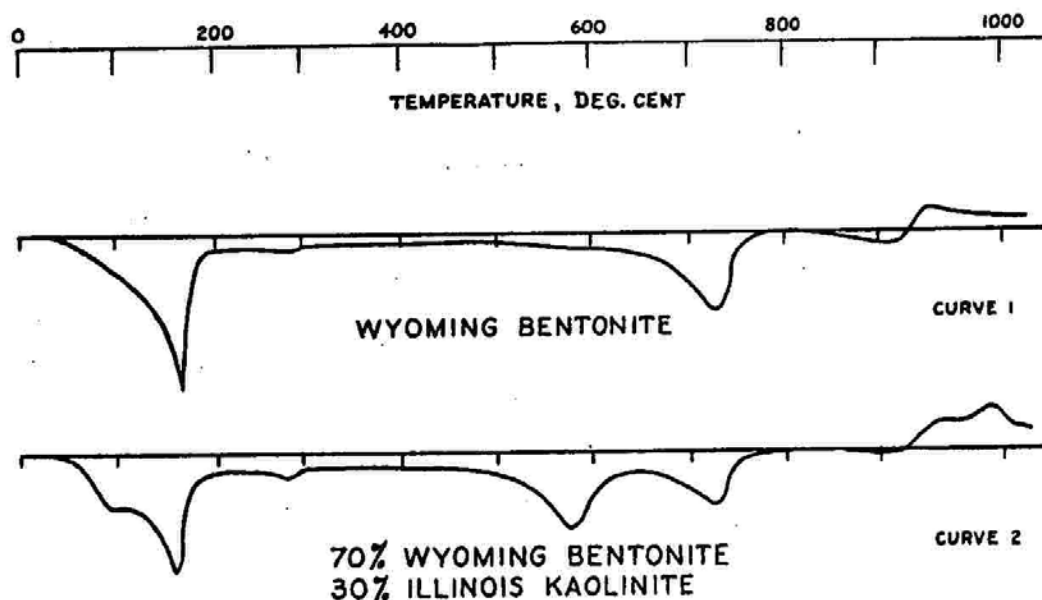

FIG. 1.—Differential Thermal Analyses.

ard thermal curves for each unique component whose recognition is desired. Each component is tested by the pro-cedure described below for subsequent testing of a soil of unknown components.

Sample Preparation.—The specimen to be tested should first be dried at a temperature of 50 C.[4] Drying at high

of the inert material used as a standard. This desired condition can be approxi-mately obtained by using the same arbitrary standard procedure for all packing.

Sample Heating.—The furnace is next placed around the holder and heating at a uniform rate is started. A continuous record of the thermal reactions is made by the electronic recorder.

Interpretation of Results.—There are two things to be determined from the thermal curve: the different minerals or impurities present and the approximate amount of each. The minerals are identi-fied by the characteristic temperatures

[2] Substances other than minerals possess unique ther-mal curves; therefore, the differential thermal analyzer may be used to identify more than the mineral. Work is being done on the thermal analysis of organic substances by the Massachusetts Institute of Technology, Geology Department and on the thermal analysis of building mate-rials by the M. I. T. Engineering Construction Depart-ment.

[3] The boldface numbers in parentheses refer to the bibliography appended to this paper, see p. 11.

[4] Current research indicates that it may be necessary to prepare some specimens much more carefully. If or-ganic matter is present in the soil, it may be desirable to remove it before testing.

at which the thermal changes occure For example, kaolinite has two tell-tal. changes, an endothermic reaction in the neighborhood of 575 C. and an exothermic reaction in the neighborhood of 950 C. The proportion of any given mineral in the tested soil is approximately equal to the ratio of the area under the curve of the tested soil divided by the area under the standard curve of the pure mineral. This interpretation of the results can best be shown by an actual example (Fig. 1).

Example.—Curve 1[5] is the thermal curve for a Wyoming bentonite; curve 2 is the thermal curve for an artificially prepared mixture of 70 per cent bentonite and 30 per cent kaolinite. If curve 2 were that of an unknown soil, the presence of bentonite and kaolinite would immediately be recognized from the characteristic temperature at which thermal changes occurred.

A semi-quantitative analysis[6] of curve 2 depends on the approximate relationship, from the theory of thermal reactions, that the amount of reactive mineral is proportional to the area enclosed by a bump on the curve. Thus the proportion of bentonite in the sample of curve 2 is equal to the ratio of the area under the curve in the 700 C. range in curve 2 to that in curve 1. The value of the ratio (multiplied by 100), 70 per cent, agrees with the predetermined proportion of bentonite.

DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF SOIL

Hydrogen-ion concentration (pH) of a soil is not a fundamental property characterizing and defining its engineering behavior. It is true, however, that there are significant correlations between the pH of various soils and the weathering processes and weathered products which define the soil, even in terms of engineering properties. Agricultural chemists have used to great advantage the correlations between pH and the properties of soils as classified by them.

Although pH determinations must take a modest position beside such determinations as that of the mineral constituents of soil, which purports to determine the soil properties by defining its components, it must be conceded that among chemical tests for a soil, determination of the soil reaction (pH) stands as important in its own right. Highly acid soils are injurious to steel and cement alike, and it has often been reported that highly alkaline soils are very detrimental to the adequate setting of cement. Furthermore, the interpretation of the results of other soil chemical tests, such as the tests for exchangeable bases associated with the soil, is facilitated by knowledge of the soil pH. M.D. Catton concluded from a study of about three hundred soil samples, that "if organic content is 5000 ppm. or over, the soil will also be acid. It does not show that if the soil is acid it will have a high organic content" (10).

For the development of a suitable method of determining pH in soils, we are indebted to the agricultural chemists who have long been interested in this problem. Both electrometric and colorimetric procedures for measuring pH have been in common use, the former being used for soil suspensions, the latter more commonly with soil extracts. While new colorimetric procedures are steadily being developed and suggested for use, especially in cases where precision may to some extent be sacrificed for economy of time and money, the electrometric procedures have already developed to the point of general ac-

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[5] Curves 1 and 2 were obtained by Kulp and Lambe with the analyzer of Kerr and Kulp (21).
[6] The above example was selected to illustrate the principle of qualitative and semi-quantitative analysis. It is not to be inferred that the analysis of any given unknown soil will be as easy and definite as the example.

ceptance. The present discussion will, therefore, focus on electrometric methods of determining pH, although it is emphasized that for many cases some specific colorimetric procedure may prove quite adequate and may be selected for various practical reasons.

Electrometric measurement of pH in soils is analogous to measurement of pH in solutions. An electrode, the potential of which is a direct function of hydrogen-ion concentration, is immersed in a solution or suspension, connected with another standard half-cell (usually the calomel) and the electromotive force of the cell is measured potentiometrically. The definition of pH properly applies to aqueous solutions; in the case of two- or three-phase systems such as soils some question may be raised as to the meaning of the term "pH." However, the term as used in soils refers to the reading obtained using some electrode scheme on a commercial instrument, such as a "Beckman pH meter"; the reading if made with due precautions is indicative of the acidity or alkalinity of the soil.

Apparatus:

The apparatus consists of two essential components: the electrode and electrode vessel, into which the sample is placed, and the measuring equipment including a standard half-cell, a potentiometer and a galvanometer. The commercial units are compactly arranged providing the standard assembly of potentiometer, galvanometer, and standard half-cell, and providing some specific electrode scheme; as a result, usually, upon placing the sample in the electrode vessel, by merely turning on a switch or two, the pH may be read directly on a dial. Retention of this facility is greatly favored: hence the measuring assembly utilized in commercial units will be assumed herewith. The questions lie in

the selection of electrode scheme and in the treatment of the soil samples prior to and during testing for pH.

Soil Sample:

It is widely recognized that a variety of factors affect readings of pH in soils: variations of the amount of carbon dioxide in the system, the use of distilled or tap water, drying the soil sample, variations of the soil-water ratio, grinding of the soil sample, and even extended storing of soil samples at constant water content—all these factors contribute in some way to modification of the pH of the soil. These various effects will not be discussed individually but are merely mentioned in order to emphasize the point that since we are interested in determining the pH of the soil *in situ*, there are some definite precautions that must be observed in making pH measurements on soil samples.

Fresh samples should be used, if possible; the soil should not be dried or ground; if possible, the pH reading should be taken with the soil at its natural water content; if it is necessary to increase the water content of the sample, boiled distilled water should be used. If the *in situ* pH of the soil is not determined, the determination of the pH of a sample is of little value unless the conditions of test are specified.

A variety of samples at low natural water contents may make it necessary to increase the water content considerably before a suspension is obtained on which pH measurements can be made. Standardization of samples to a soil-water ratio of 1:5 has been suggested, recognizing that the pH thus determined is different, but not widely so, from the pH of the soil at natural water content. "When a more accurate idea of the pH at low moisture contents is desired, this can be obtained by extrapolation of the graph connecting

the hydrogen-ion concentration determined at three soil-water ratios (preferably 1:5, 1:25, 1:125). Plotting the pH values against the log of the soil-water ratios lends itself best to this treatment," (39).

More recently the use of the glass electrode has been adapted to pH readings in soils at lower water contents. Consequently, in the field of agriculture the recent trend is toward standardization with the use of soil samples at the moisture equivalent, as a convenient lower limit at which pH readings are still reliable.

Electrode Scheme:

Four major electrode schemes have been developed and used to some extent over the years, but gradually the use of the glass electrode in connection with a commercial pH meter, has superseded the others in view of its reliability coupled with several advantages of practicability.

A discussion of the hydrogen, quin-hydrone, and antimony electrodes will not be within the scope of this brief paper. With some modifications they have been very successfully used in many instances. The advantage of the glass electrode, however, is that no great refinements are necessary. It is well adapted to use with soil samples even at rather low moisture contents. At low water contents, precautions have to be observed of compacting the soil sample so as to make close contact with the glass electrode.[7] At higher water contents, in soil suspensions, some agitation scheme is necessary in order to keep the soil in homogeneous suspension.

DETECTION OF DELETERIOUS SUBSTANCES

In a soil there may exist some substances which have deleterious effects on the soil itself or on structural materials placed adjacent to the soil. One substance which has a pronounced effect on the engineering properties of soils is organic matter. Some organic matter by its very nature tends to lower the strength and increase the compressibility of the soil. For example, peat which is dervived to a large extent from trees, leaves, small plants, etc., is very compressible and weak in shear strength. Also organic colloids can be absorbed by the soil in base-exchange reactions and other reactions (17). These adsorbed organic colloids greatly reduce the ability of the clay to imbibe water, thus reducing the swelling tendency of the clay and simultaneously reducing the shear strength of the soil at a given water content. Only a little is known of the magnitude of the effect of adsorbed organic colloids on the engineering properties of clays.

Substances in soils which may have serious effects on adjacent structural materials are sulfides, sulfates, carbonates, and organic matter. These substances may cause their damage either by being in actual contact with the structural materials, from their position in the soil, or by supplying reactable materials to the flowing ground water to form acids, bases, or salts.

The common structural materials used for pavements, piles, foundations, and walls are steel, wood, concrete and stone. The deleterious effects of the above named substances on wood and most sound masonry are so small that they need not be considered any further. Since steel is injured by acids, all of the substances must be considered as they are all potential acid producers. Piles driven into soils containing significant amounts of these potential acid producers may require special treatment such as an acid-resistant coating or some type of cathode

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[7] As mentioned earlier, water contents below a convenient lower limit should be avoided, since various sources of error arise, including difficulties due to the abnormally high electrical resistance involved.

protection. Steel is not attacked by hydroxides.

Concrete can receive injurious effects from all of the above listed substances. The presence of organic matter can prevent cement from setting. The nature of attack of the sulfides, sulfates, and carbonates can be either chemical corrosion or crystal formation. Acids, bases and aggressive salts can actually chemically attack concrete; the degree of this attack depends on the concentration of the active substance as well as the type of aggregate used in the concrete mix. For example, certain aggregate constituents such as opal are seriously attacked by hydroxides. Crystal formation due to the evaporation of alkali-laden water from the surface of concrete may cause disintegration somewhat analogous to that caused by the freezing of water.

From the above brief discussion, one can see that it is desirable to have short, simple, chemical tests to detect the presence of sulfides, sulfates, carbonates, and organic matter in soils. The following simple tests have been selected for the detection of the presence of minute quantities of the above components. These tests, called "spot tests," are only qualitative as they are described. Based on the results of "spot tests" a complete quantitative analysis of the soil may be desired. Such a quantitative analysis may be time-consuming and may be of only small additional value until more is learned of the limiting concentrations that may be permitted with regard to the safety of the particular foundation. It must be remembered that the dangerous concentration of these substances may depend largely on ground water conditions.

Procedure:

Sulfides (15).—Add to the soil in question a few drops of azide-iodine solution. The formation of tiny bubbles of nitrogen indicates the presence of a sulfide in the soil. The stable azide-iodine solution is prepared by dissolving 3 g. of sodium-azide in 100 ml. of 0.1 N iodine solution.

In making this test it is helpful if a microtest tube is used; it should be held so as to get a background of strong light to aid in seeing the minute nitrogen bubbles.

Soluble Sulfates (31).—Add to the soil in question about 4 ml. of 5 N hydrochloric acid and stir; next add a little barium chloride solution. The formation of barium sulfate, which is a white precipitate, indicates the presence of a soluble sulfate. The hydrochloric acid is added to prevent the formation of barium carbonate or barium sulfite both of which are white precipitates.

It should be noted that the above test is only for soluble sulfates, but since these are the ones whose presence in soil is of interest, the test is sufficient for sulfate determination.

Carbonates.—Add a few drops of 5 N hydrochloric acid to the soil in a test tube which is equipped with a U-shaped delivery tube inserted in barium hydroxide. After heating the tube containing the soil, the formation of a white precipitate in the barium hydroxide indicates the presence of a carbonate in the soil.

In this test it is desirable to use microtest tubes and a capillary tube for the delivery tube to increase the sensitivity of the test. Often the application of heat is not needed.

The barium hydroxide must be stored carefully to prevent its reacting with the carbon dioxide in the atmosphere to form barium carbonate. This reaction can be prevented by venting the barium hydroxide solution through a drying tube containing crystals of sodium hydroxide.

Organic Matter.—Add a few drops of concentrated sulfuric acid to the soil contained in a test tube with a stopper and a U-shaped delivery tube inserted in barium hydroxide. Heat the soil and acid; the formation of a white precipitate in the barium hydroxide indicates the presence of organic matter. The above test is based on the sulfuric acid and heat oxidizing any organic matter present to free carbon dioxide which reacts with the hydroxide to form the insoluble barium carbonate. The same microtest tube set-up used for the carbonate test is used here. Since the above described test would also be positive for any carbonates present, it is essential to test the soil for carbonates before testing for organic matter. If there are carbonates in the soil they must be removed by the addition of hydrochloric acid (see previous test) before the organic test is made.

DETERMINATION OF EXCHANGE CAPACITY AND EXCHANGEABLE BASES

The importance of the exchange capacity of clays in determining engineering properties of clay soils has been justly recognized. The correlation between the engineering properties of clays and the type of clay mineral of which the clays are composed has already been pointed out. Further, it is known that the exchange capacities of the clay minerals similarly fall into the typical pattern noted for the other properties of the clays; montmorillonites have high exchange capacities, while the illites, and kaolinites have moderate and low exchange capacities. It might thus be stated, *a posteriori*, that there are definite trends of correlation between the exchange capacity and the engineering properties of clays.

However, the moment a few generalizations have been made with respect to such a correlation, it must be recognized that the nature of exchangeable base present cannot be disregarded. Recognition of exchange capacity entails recognition of the possibility of exchanging the adsorbed bases (cations); hence one speaks of a sodium-montmorillonite, calcium - montmorillonite, magnesium - kaolinite, and so forth, in each case specifying the exchangeable cation adsorbed by the clay. Most natural clays are not homoionic, that is they contain more than one type of exchangeable cation. But the distinction in properties between several homoionic varieties of a clay permits the estimation of the properties of heteroionic clay bodies. For instance, it is known that a sodium-clay tends to have a higher liquid limit, plasticity index, and swelling capacity, than a corresponding calcium-clay; this is similarly true of montmorillonites, illites and kaolinites, but quite naturally the differences in properties are most marked in the case of clays with high exchange capacities. If the properties of a sodium-clay and the corresponding calcium-clay are well established, the properties of a heteroionic clay composed partly of sodium-clay and partly of calcium-clay can be estimated to be intermediate.

It is not the purpose of this paper to elaborate on the ideas presented in the above paragraph, for soil mechanics literature has already disseminated those concepts. The above paragraphs are merely intended to emphasize the importance and significance of determinations of exchange capacity and exchangeable bases associated with a soil.

Test Procedure:

The limitations of space that must be imposed on this presentation make it necessary to present a summary outline procedure for determining exchangeable bases and total exchange capacity. It

will not be possible to discuss the selection of the procedure recommended or the details of all the steps involved. The procedure is outlined for what appears to be the most complicated general case, namely, a saturated clay with the cations K^+, Na^+, Ca^{++}, Ba^{++}, Mg^{++}, Fe^{++}, Fe^{+++}, and Al^{+++} present both as exchangeable ions adsorbed on the clay particles and as free ions in the solution composing the pore liquid.

The proposed logical sequence of testing are outlined in the following steps:

1. Determine the water content of the clay: this determination is necessary for the subsequent computation of the dry weight of clay used and the volume of liquid in which it is dispersed.

2. Simultaneously place a given weight of the wet clay (computed to give about 10 to 25 g. of dry clay) into a 250-ml. heavy-duty centrifuge bottle. Add a known volume (about 200 ml.) of dioxane, stopper the bottle and shake well to disperse the clay; addition of clean glass beads helps the dispersion on shaking. Then centrifuge at 2000 rpm. or higher.

3. Extract the clear supernatant liquid for analysis of cations present as soluble salts in the pore liquid. Aliquots of the solution are used, and computations are based on the assumption that the concentration of a particular ion is the same throughout the total volume of liquid. Analyze for Na^+ and Ca^{++} quantitatively; then detect the presence of other ions by qualitative spot tests; finally, if desired and justified by the indications of the qualitative tests, analyze quantitatively for some of these ions.

4. To the clay sediment in the centrifuge bottle add a known volume (as much as possible) of neutral N ammonium acetate solution. Shake and disperse the clay thoroughly, and re-

centrifuge. The clear supernatant liquid now contains all of the cations present in the pore liquid, in quantities that may easily be computed from the results of step 3; further it contains all of the replaceable ions originally associated with the clay, except for Al^{+++} which may not be replaced adequately by NH_4^+, and Fe^{+++} which, although replaced, has formed an insoluble precipitate with the acetate.

5. Use the supernantant solution from step 4 for quantitative analyses of Na^+ and Ca^{++}, and qualitative and quantitative analyses of the other ions as described in step 3.

6. To aid the replacement of Al^{+++} ions by NH_4^+ ions, add ammonium phosphate to the clay batch and shake well. The clay should now be essentially saturated with NH_4^+ ions; further, insoluble ferric acetate and aluminum orthophosphate will be precipitated.

7. Wash the clay, and iron and aluminum precipitates, with distilled water; this is best done by leaching, passing water through under suitable pressure.

8. Transfer the washed clay, and precipitates, back to a centrifuge bottle, noting the volume of water associated with the clay. Add a known volume of $5\ N\ H_2SO_4$ and stannic sulfate solution. Shake well, then centrifuge.

9. The clear supernatant solution is used for the determination of the total exchange capacity, and for the quantitative estimation of the exchangeable Fe^{+++} and Al^{+++} ions associated with the clay. One aliquot is used for the quantitative determination of NH_4^+ by the standard Kjeldahl procedure: the exchange capacity is very readily computed from this determination. Another aliquot is used for the estimation of exchangeable Fe^{+++} and Al^{+++}. For this determination it may be sufficiently satisfactory to separate the two ions by filtration after addition of an excess of

NH_4OH reagent, subsequently estimating the ions by ignition to the oxides.

10. The use of a check should not be neglected. The sum of the milliequivalents of the exchangeable bases must be equal to the exchange capacity, within experimental error.

The above procedure can naturally be simplified in certain cases, although as now proposed it is not unduly refined for engineering purposes. For the analyses involved in steps 3 and 5, the following suggestions may be helpful, although it is strongly recommended that more detailed study be given to the matter.

Qualitative Spot Tests:

Fe^{+++} 1. Put a drop of the test solution (acidify if necessary) on a white spot plate. Add a drop of potassium ferrocyanide solution. Formation of a prussian blue indicates Fe^{+++}.

Fe^{++} 2. Put a drop of test solution (acid) on a white spot plate. If solution is red, decolor by adding a few crystals of potassium fluoride in a paraffin-lined depression. Add a drop of α-α'-dipyridyl solution (2 per cent in alcohol). A deep red soluble complex cation indicates Fe^{++}.

Ba^{++}
Ca^{++}
Sr^{++} 3. Put several drops of neutral or slightly acidic test solution on a black spot plate. Add indicator solution (lead sulfate dissolved in acetic acid solution of ammonium acetate). Cloudiness, or white precipitate indicates presence of this group.

Ba^{++} 4. Put a small quantity of solid tetra-hydroxyquinone and potassium chloride on a white spot plate. Add a drop of test solution and a drop of water. A brown color (appearing first near undissolved reagent) which turns to red upon addition of 0.1 N HCl indicates Ba^{++}.

Al^{+++} 5. Remove any iron present by precipitation with NaOH. Then add a drop of test solution to alizarin paper (quantitative filter paper soaked in a saturated alcohol solution of alizarin, dried, stored in stoppered bottle). Hold over dish of NH_4OH until spot turns violet. Dry in oven. A change to red color indicates Al^{+++}.

K^+ 6. Dissolve a small quantity of sodium cobaltinitrite in a drop of water on a black spot plate. Add neutral or slightly acid test solution. A yellow crystalline precipitate indicates potassium.

The sensitivity of the test can be increased by adding a drop of silver nitrate solution, but before this is done, a drop of the test solution should be added to a drop of silver nitrate alone to find whether halides or NH_4 salts or other interfering salts are present in the test solution. These produce a thick white precipitate which would obscure the cobaltinitrite test.

Mg^{++} 7. Place a drop of neutral or slightly acid test solution on a white spot plate. Add a microdrop of N potassium hydroxide followed by a microdrop of iodine solution. (N iodine in 20 per cent KI solution.) Stir until the solution becomes brown from free iodine. After 1 min. add potassium hydroxide until solution becomes lemon yellow. If Mg^{++} is present, brown flecks are clearly visible in the yellow solution.

NH_4^+, Al^{+++} and such ions as form colored hydroxides under test conditions interfere.

Quantitative Tests:

1. *Sodium.*—Use a suitable aliquot part of the solution and evaporate it carefully to a small volume, then add more than ten times the volume of zinc-uranyl-acetate reagent and allow to stand 30 min.: finally, gravimetrically filter the precipitate by suction, washing with small portions of the reagent, absolute alcohol, and ether. The weight of sodium is equal to 0.01495 times the weight of the precipitate (3).

2. *Calcium, Magnesium, possibly Barium, also Potassium.*—Use a suitably large aliquot part of the solution, concentrate it by evaporation and add a large excess of a saturated solution of ammonium oxalate. The precipitate of calcium oxalate is separated and washed with water by suction filtration, dried and weighed.

The filtrate from above is used for the quantitative estimation of magnesium,

if desired. Evaporate it to dryness expelling ammonium salts, then dissolve it in dilute HCl and then precipitate magnesium ammonium phosphate as follows. Acidify the solution with 5 ml. concentrated HCl, add methyl red indicator, and add a 5- to 10-fold excess of the precipitant, a saturated solution of diammonium phosphate. Then add ammonia water (sp. gr., 0.90) slowly, while stirring, to neutralization. Stir for 5 min. or until the precipitate is well formed, then add a little excess ammonia water, stir for 10 min. Filter the precipitate after it has stood overnight, and then wash with water containing 3 per cent by volume of ammonia water. Ignite the wet filter paper and precipitate in a weighed platinum crucible at approximately 1000 C. to constant weight. The magnesium pyrophosphate is weighed.

Barium can further be obtained from the magnesium filtrate by precipitation as the sulfate.

After elimination of such ions as calcium, magnesium, and barium, as indicated above, the filtrate can be analyzed for potassium.

Evaporate to dryness, expelling ammonium salts. Dissolve in water and add twice the perchloric acid required to convert the salts into perchlorates. Evaporate to dryness with special attention to driving off all the excess perchloric acid; cool the beaker, rinse the inside with a little water and repeat the evaporation and heating. Dissolve the residue by adding 95 ml. of 95 per cent ethyl alochol and heating if desired. Chloroplatinic acid, 0.2 g. dissolved in 5 ml. of 95 per cent ethyl alcohol, is added to this solution, preferably hot, and after a few minutes digestion and vigorous stirring, the mixture is cooled to 0 C. and allowed to stand with frequent stirring at this temperature for over an hour. The precipitated solution is filtered through a sintered-glass crucible, the potassium chloroplatinate is washed with several portions of cold absolute alcohol, to free from sodium perchlorate. It is then dried and weighed.

The above discussions of the differential thermal analysis for mineral structure, the determination of soil pH, the identification of admixed chemicals, and the determination of base-exchange capacity with the concomitant analysis of the exchangeable ions associated with the soil complex have of necessity been summarized in view of the authors' intent to emphasize the perspective of the method of testing delineated. In conclusion it may be said that it is hoped that the field of soil mechanics will rapidly advance towards filling in the details, thereby simultaneously broadening the perspective, to the advancement of our understanding of soil behavior.

Acknowledgement:

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