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The Routine Mineralogical Analysis of Clay-Bearing Samples

U.S. GEOLOGICAL SURVEY BULLETIN 1563




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The Routine Mineralogical Analysis of Clay-Bearing Samples

By HARRY C. STARKEY, PAUL D. BLACKMON,
and PHOEBE L. HAUFF

U.S. GEOLOGICAL SURVEY BULLETIN 1563

*A description of the equipment and
procedures used for the mineralogical
identification of geologic samples
that contain clay minerals*



UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

	Page
Abstract	1
Introduction	1
Equipment and apparatus	2
X-ray diffraction apparatus	2
Centrifuge and stopwatch	3
Ultrasonic generator	3
Electron microscope	3
Porous tiles	3
Tile preparation apparatus	4
Filter candles	7
Procedures	8
Crushing and splitting	9
Disaggregation and dispersion	11
Sand removal	11
Separation of silt and clay	11
Quantification of clay-size material	15
Oriented aggregates	16
Randomly oriented mounts	17
X-ray diffraction patterns	17
Rapid sample processing	18
Mineral identification	18
Quantitative estimates	19
Supplemental procedures	21
Physical concentration	21
Chemical determinations	22
Removal of organic material	22
Carbonate removal	23
Iron oxide removal	24
The Greene-Kelly lithium test	24
Determination of amorphous material	24
Distinguishing between kaolinite and chlorite	25
Acknowledgments	26
References cited	26

ILLUSTRATIONS

	Page
PLATE 1. Flow sheet for clay mineral identification	In pocket
FIGURES 1-7. Diagrams showing:	
1. Method of mounting oriented aggregate tiles on X-ray diffractometer	5
2. Apparatus for preparing oriented aggregates on porous ceramic tiles	6
3. Modification of Buchner funnel to be incorporated into apparatus for preparing oriented aggregates	7
4. Specifications for a rubber gasket to fit the modified Buchner funnel	8
5. Removal of water from clay-water suspensions	9
6. Flow sheet for sample treatment procedures	10
7. Diagram of radial measurements necessary for calculations of centrifuging times	12

TABLE

	Page
TABLE 1. Chart showing representative centrifugation times for various particle-size separations	14

THE ROUTINE MINERALOGICAL ANALYSIS OF CLAY-BEARING SAMPLES

By HARRY C. STARKEY, PAUL D. BLACKMON, and PHOEBE L. HAUFF

ABSTRACT

The procedures used for the routine identification of samples containing clay minerals involve the separation of the samples into micrometer- (μm -) size fractions: sand ($>62\ \mu\text{m}$), silt ($2\text{--}62\ \mu\text{m}$), and clay ($<2\ \mu\text{m}$). The sand is removed by wet sieving, and the silt and clay sizes are separated by centrifugation. The principal method of mineral identification is X-ray powder diffraction analysis of randomly oriented powders of the total sample and of the various fractions, and of oriented aggregates of the clay-size fraction, air-dried and after prescribed treatments. Supplemental procedures are mentioned but are not described in detail, and an extensive bibliography is supplied so that the investigator may obtain more detailed information about these supplemental procedures, and about alternative methods of treatment.

INTRODUCTION

Much of the work on the mineralogy of sedimentary rocks by the U.S. Geological Survey in Denver, Colo., involves the identification and semiquantitative estimation of the amounts of minerals present in samples that contain clay minerals. Many geologists are interested in accurately identifying discrete clay mineral species because the clays may be important indicators of weathering conditions, decomposition, and depositional environments. This paper is designed to assist the geologist in identifying the common clay minerals. It discusses the routine methods used in this U.S. Geological Survey laboratory and lists some advanced techniques for clay mineral identification.

These methods enable the reader to make semiquantitative estimates of the relative amounts of the various minerals present. We report results as parts in ten rather than as percent. Many factors in addition to the amounts of mineral present may affect the intensity of diffraction peaks, especially clay mineral diffraction peaks; therefore, percentage estimates may be misleading. Some of these factors are: (1) degree of ordering (Azároff and Buerger, 1958), (2) crystallite size (Klug and Alexander, 1954), (3) preferred orientation (Klug and Alexander, 1954), (4) isomorphous substitution within the mineral structure (Brown, 1955), and (5) masking by other minerals, organic matter, or amorphous material. Mineral content reported as parts in ten rather than as percent gives a good indication of the relative

amounts of the minerals present without giving misleading impressions of the degree of accuracy of the analyses.

A flow sheet (pl. 1) based on the treatments used in clay mineral identification is provided to facilitate identifications. The references listed on the flow sheet furnish information on the more-detailed identification of the clay minerals, on the genesis of clays, on the type of environment in which they are found, or on the physical and chemical data of the clays.

Although some samples may require more extensive procedures than those described here, the methods given in this paper should prove adequate for routine identification. The supplemental procedures and the references cited should be consulted for those samples that require more than the routine procedures for identification.

EQUIPMENT AND APPARATUS

Some of the equipment listed here is essential and the rest is desirable. Where use of alternative equipment is possible, we will mention the other equipment although it may require more time to use and be slightly less desirable.

X-RAY DIFFRACTION APPARATUS

The basic tool for clay mineral analysis is the X-ray diffraction unit with a vertical scan goniometer and a strip chart recorder. The vertical scan goniometer is desirable because the sample is mounted horizontally in the specimen holder. Samples in a horizontal scan goniometer must be mounted vertically, which requires more packing pressure so the finely ground material doesn't fall out, but the extra pressure may cause unwanted preferred orientation.

A desirable accessory to the goniometer is the focusing monochromator, which greatly reduces the fluorescence of iron-rich samples when copper radiation is used; it also eliminates the need for a beta-peak filter and usually produces a greater peak intensity. In this paper all radiation mentioned will be copper $K\alpha$ unless otherwise specified.

The strip chart recorder should be one on which the baseline can be raised and lowered, and on which the pens may be changed readily. Several patterns must be made of each oriented aggregate following various diagnostic treatments. After one pattern is run the pen can be changed, the baseline raised, and another pattern run, stacking one above the other for easy comparison. Four or five pens, each containing a different colored ink should be sufficient. If the baseline cannot be changed on the recorder, the patterns can be run on separate pieces of chart paper. This method uses more chart paper, which is difficult to handle and store.

CENTRIFUGE AND STOPWATCH

These two items are used together. The stopwatch is used to measure the centrifuging time. The centrifuge should be a large floor model with a tachometer. It should have trunnion cups large enough to hold 250-mL (milliliter) centrifuge bottles. Smaller centrifuges with trunnion cups can be used but the reduced capacity will greatly increase the time spent centrifuging.

The centrifuge is used to separate the silt and clay after the sand has been removed from the sample. This separation depends on the speed at which the centrifuge is operated, the viscosity of the liquid which in turn depends on the temperature, the density of the particles, and the centrifuging time, which must be measured to the nearest second.

ULTRASONIC GENERATOR

An ultrasonic generator is desirable but not essential for the disaggregation and dispersion of the samples. Although a probe- or a tank-type unit will work well if the samples are allowed to soak for several hours, or overnight, in distilled water before treatment, the probe is more powerful and therefore faster and more efficient. If an ultrasonic unit is not available, the disaggregation and dispersion can be accomplished by using a mechanical stirrer similar to a milkshake stirrer. The ultrasonic unit, however, does a more thorough job, especially on samples that are somewhat indurated.

ELECTRON MICROSCOPE

If available, an electron microscope, either transmission (TEM) or scanning (SEM), may be a valuable tool in identifying those clay minerals that have a distinctive morphology. The SEM is especially helpful in studying the relationships between fine-grained minerals. Where the electron microscope may be of value in mineral identification, the morphology of that mineral is noted on the flow sheet (pl. 1).

POROUS TILES

We use smooth, unglazed porous ceramic tiles with dimensions of approximately $40 \times 17 \times 3$ mm (millimeter) for making oriented aggregates of the clay-size fractions. The dimensions of the tiles may be varied to fit the goniometer specimen holder of the particular X-ray equipment being used. The tiles are cut from unglazed ceramic bathroom tiles that have a quartz-feldspar composition. The crystallinity of the tile is poor enough that the diffraction peaks at lower angles than the 20.85° 2 θ quartz peak do not show up on the diffraction pattern even when the amount of clay on the tile is extremely thin.

The quartz peaks at 20.85° and 26.64° 2θ can be used as an internal standard from which to measure the positions of the other peaks. However, a pattern of the tile should be available to determine whether any particular peak has been produced by a sample or by the tile.

These tiles may be stored with the sample on them for future reference. If the samples are not to be kept, the tiles can be cleaned by boiling in hydrochloric acid, washing thoroughly to remove all traces of the acid, and gently rubbing the surfaces of two tiles together to remove any remaining sample. The tiles then may be rinsed and reused.

Porous tiles are preferable to glass slides (which may be used if the tiles are unavailable) for the following reasons: (1) Smectites tend to curl off glass slides more than from tiles (Kinter and Diamond, 1956). (2) Differential settling is more likely to occur on glass slides producing mineral segregation (Stokke and Carson, 1973). (3) Glass slides may warp when heated to 550°C or higher (Drever, 1973). (4) Glass slides may crack when removed from furnace to cooler room temperatures or when placed on an unheated surface while still hot. (5) If the amount of sample on a glass slide is quite thin, the broad hump due to the amorphous glass will show up on the diffraction pattern between 18° and 32° 2θ . (6) Clays can be treated chemically while on the porous tiles by drawing solutions through the sample by vacuum.

Glass slides do have a couple of advantages over the porous tiles. Better preferred orientation can be obtained because of the smooth glass surface, and no additional apparatus other than a pipet is required to prepare the slides.

The ceramic tiles that we use are not wide enough to fit into the goniometer specimen holder and still project far enough out into the beam for full exposure, so a spacer tile of the same thickness as the specimen tile is placed behind the sample-coated tile to align it in the X-ray beam (fig. 1). This arrangement also reduces the amount of sample, which may be moist after glycolation, that might adhere to the specimen holder. If any of the sample does adhere to the specimen holder, it will be near the front where it can be easily removed. If it is not removed succeeding samples will be improperly aligned.

TILE PREPARATION APPARATUS

An apparatus (fig. 2) for sedimenting clay samples on porous tiles can be built from common laboratory equipment. The top of a small Buchner funnel (No. 1 size, 65 mm outside diameter) is cut off at the upper surface of the perforated plate as shown in figure 3, and

the surface of the cut is ground until it is even with the surface of the perforated plate. Next, a rubber gasket is cut to fit the top of the perforated plate. Two oblong holes (10×30 mm) are cut in the gasket with about 1 cm (centimeter) of space between them as shown in figure 4. The gasket is placed on top of the perforated plate of the cutoff funnel. A light film of stopcock grease on the bottom of the gasket gives a better seal, decreasing air leakage and increasing the efficiency of the apparatus.

A hole large enough to accommodate the stem of the Buchner funnel is made in a No. 9 rubber stopper. The modified Buchner funnel with the gasket attached is inserted into the rubber stopper which, in turn, is inserted into the neck of a 2000-mL filter flask that has been filled about three-fourths full of water. The water makes the apparatus more stable and reduces the amount of air to be evacuated. The surface of the gasket is made level and the filter flask is connected to the vacuum line, which always should contain a drying tube to prevent water vapor from reaching the vacuum pump.

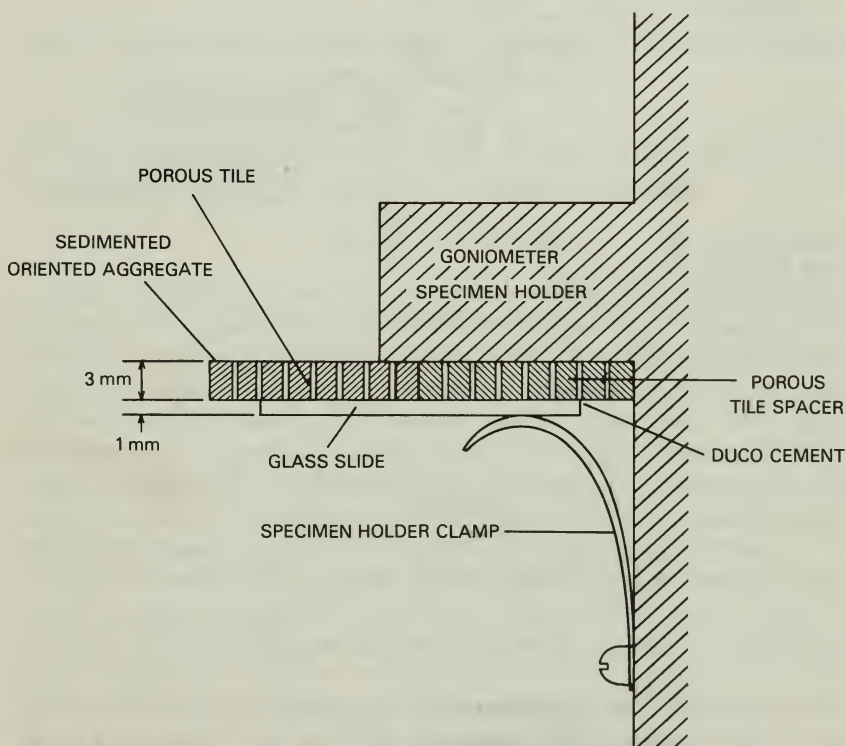


FIGURE 1.—Method of mounting oriented aggregate tiles on X-ray diffractometer.

To deposit samples onto the porous tiles, a tile is placed over each hole, and the vacuum is turned on. Duplicate slides are prepared by placing about 1 mL of a thin clay slurry on each tile. Because smectites are more prone to crack, curl, or peel off the tiles than are the other clay minerals, the smectite slurry should be made thinner than other clay minerals, the smectite slurry should be made thinner than other

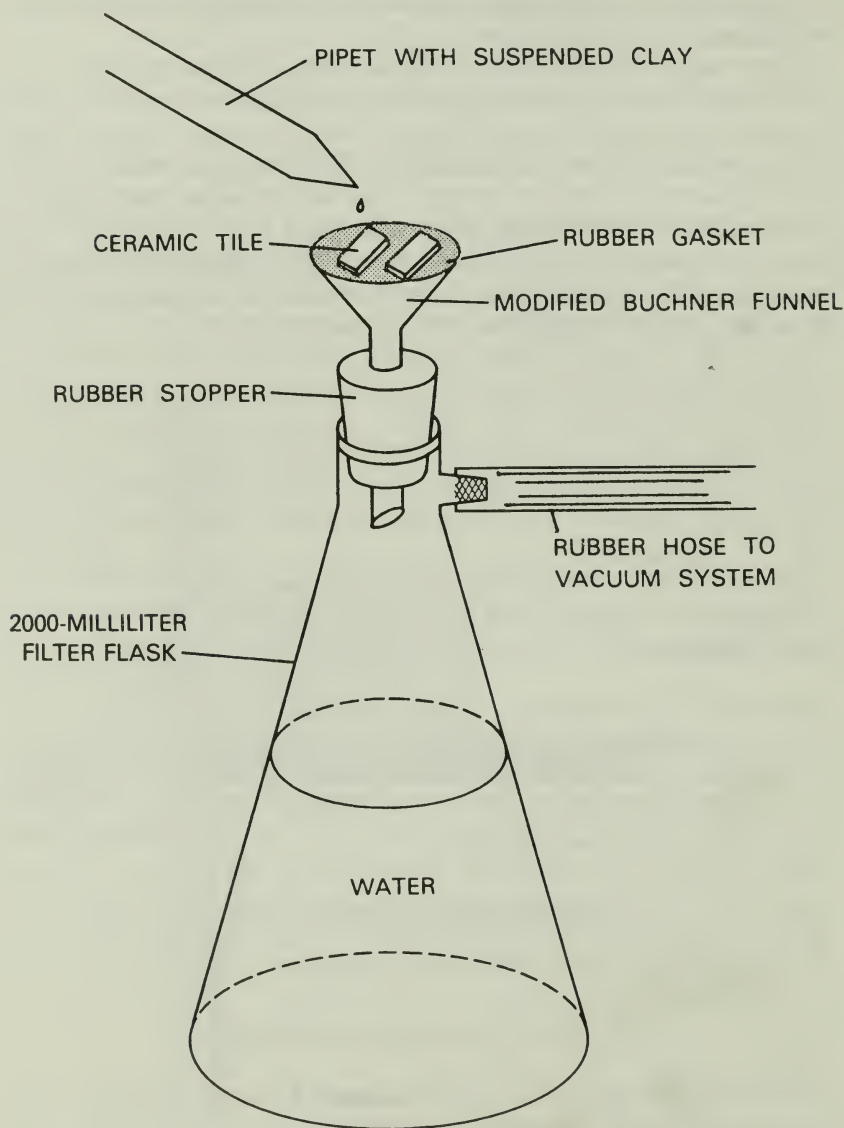


FIGURE 2.—Apparatus for preparing oriented aggregates on porous tile.

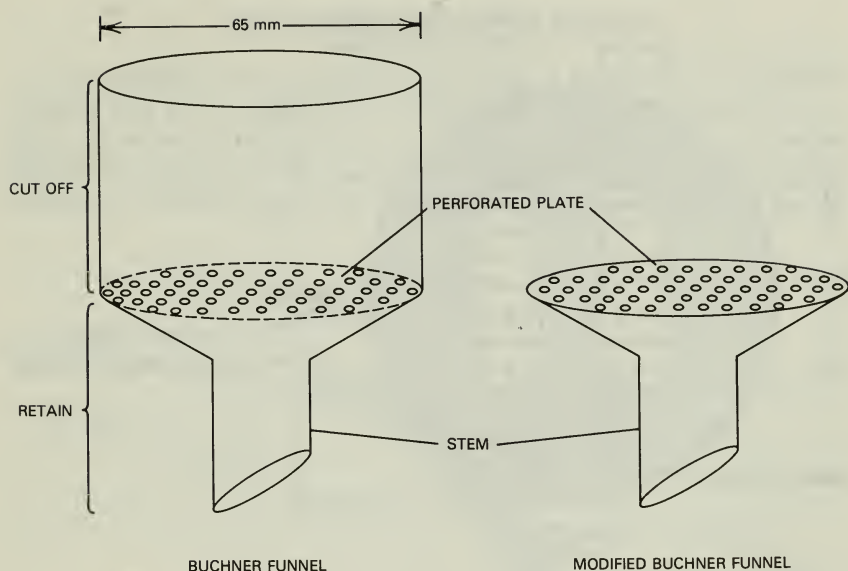


FIGURE 3.—Modifications of Buchner funnel to be incorporated into the apparatus for preparing oriented aggregates.

slurries. Several layers of the smectite slurry are deposited on the tiles. Better adhesion is obtained with several thin coats.

FILTER CANDLES

Large quantities of water must be removed from the clays after separation from the silt by centrifugation. Water is removed by using the filter candle arrangement shown in figure 5. The clay and water suspension is poured into a 1000-mL Berzelius beaker and a bacteriological filter candle is immersed in the suspension. This candle is connected by pressure tubing to a three-way stopcock which, in turn, is connected to a regulated air line and to a vacuum line. The vacuum line is connected to a vacuum pump through a reservoir that collects the water to keep it from getting into the vacuum pump.

When the stopcock is turned so the vacuum line is connected, the vacuum draws water from the slurry. This causes clay to collect on the filter candle, until the clay becomes thick enough to significantly impede the flow of water. The stopcock is then turned 180° to close the vacuum line and open the air line that is regulated so that the air pressure does not blow the pressure tubing off the candle or off the glass stopcock. The air pressure causes the clay to slough off the filter candle. In some instances, a rubber policeman may have

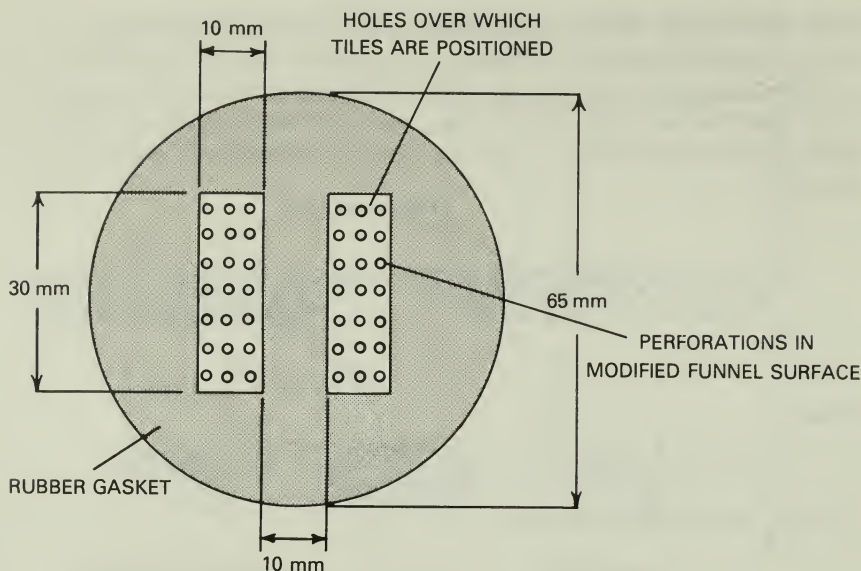


FIGURE 4.—Specifications for a rubber gasket to fit the modified Buchner funnel.

to be used to remove all the clay from the candle. Then the stopcock is again turned 180° and the removal of water is resumed.

PROCEDURES

The general procedure in analyzing samples containing clay minerals is outlined in figure 6. The samples are separated into sand ($>62\ \mu\text{m}$ (micrometer)), silt ($2\text{--}62\ \mu\text{m}$), and clay ($<2\ \mu\text{m}$) sizes. The clay minerals are concentrated in the clay-size fraction. This concentration allows for easier identification of the clay minerals because better orientation can be achieved and small amounts of clay can be detected that might otherwise be missed. The size separation tends to concentrate the heavier minerals in the silt-size fraction, which makes them easier to detect, especially if they are present in small quantities. There is also the added benefit of having a weight for each fraction and, as some minerals are concentrated in particular fractions, estimates of the relative amounts of the minerals present can be more reliable.

Randomly oriented preparations of each fraction as well as of the whole sample are analyzed by X-ray powder diffraction. X-ray patterns also are made of oriented aggregates of the clay fractions both before and after diagnostic treatments.

CRUSHING AND SPLITTING

If the sample, as received, is indurated, it is crushed to particles of about 3–5 mm in diameter so that representative portions can be taken. A subsample of about 2 g (grams) is used for X-ray powder diffraction analysis of the total sample. Information from this analysis is useful in determining which supplementary procedures may be re-

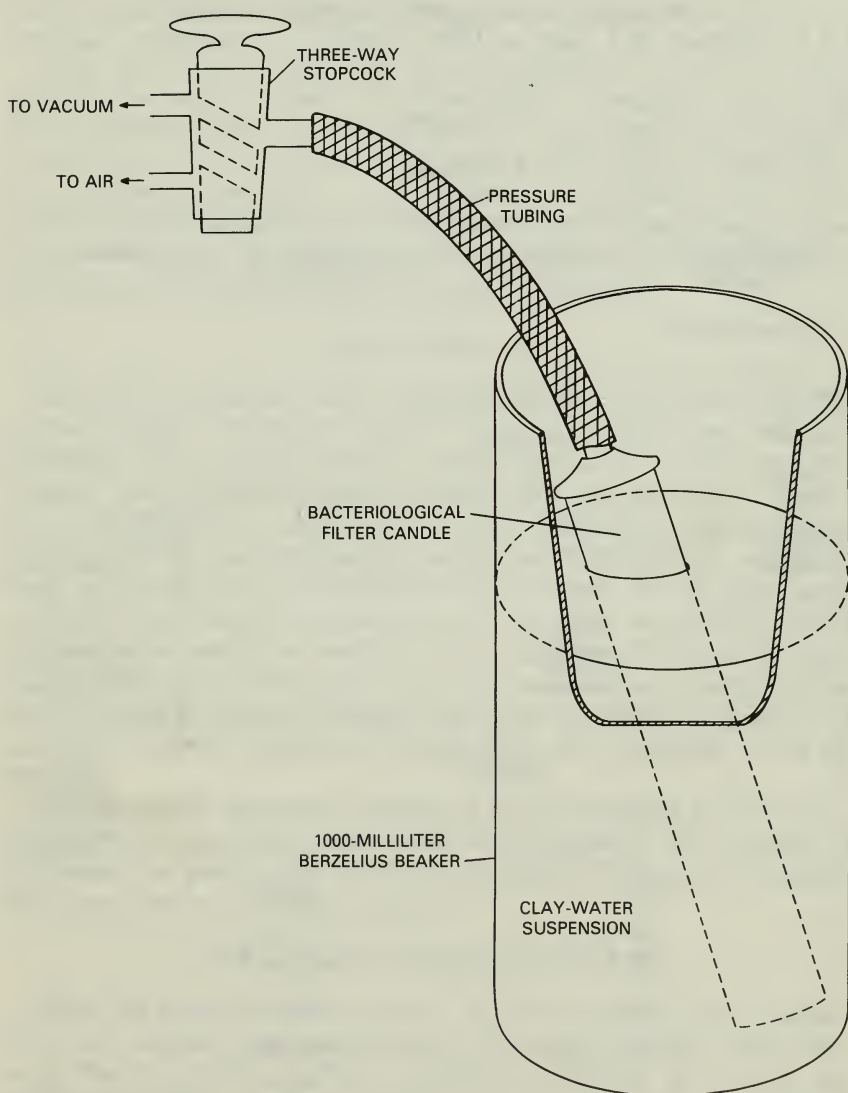


FIGURE 5.—Removal of water from clay-water suspensions.

quired. This X-ray pattern also may show the presence of soluble salts that are removed during fractionation.

A second subsample, usually about 25–30 g, is weighed out. Smaller or larger amounts are used if the sample appears to be unusually clay-rich or clay-poor. A sample of this size should provide enough clay-size material for routine analysis, for supplemental procedures if necessary, and for reference material.

A third subsample of about a gram is weighed separately, heated for a minimum of 1 hour at 110°C, cooled in a desiccator, and re-

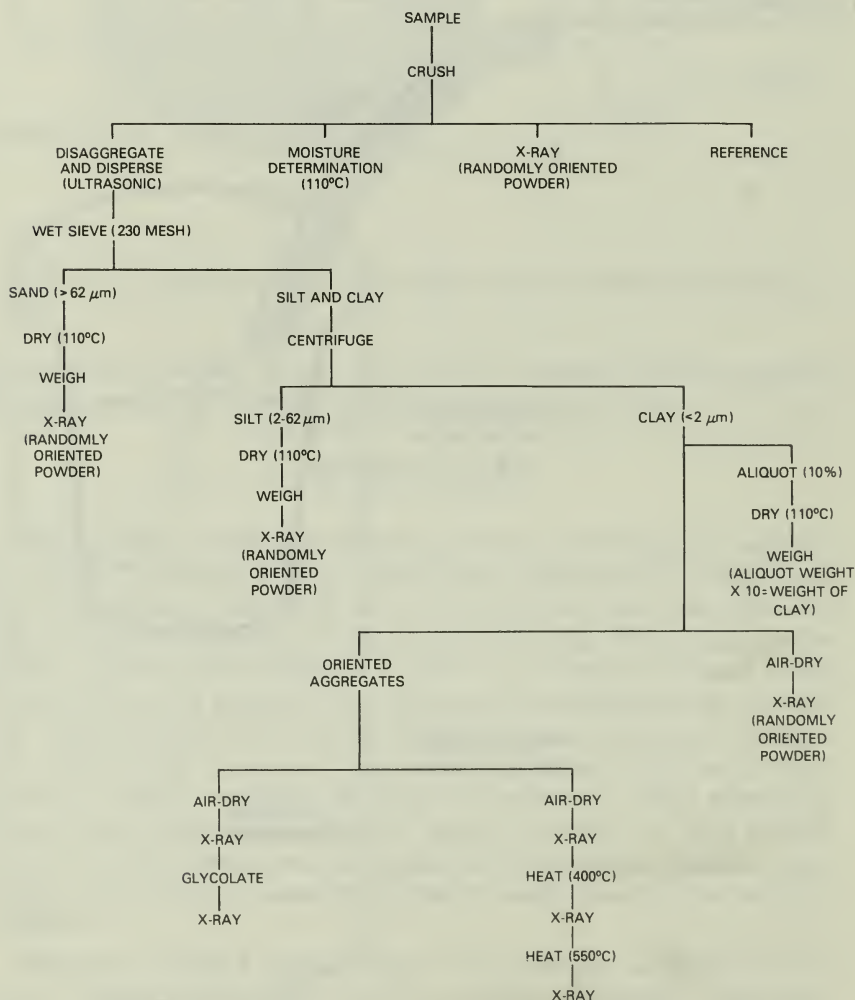


FIGURE 6.—Flow sheet for sample treatment procedures.

weighed to determine the percentage of moisture loss. This percentage is deducted from the weight of the second subsample because the weight of samples containing clay minerals may vary with changes in the relative humidity in the laboratory. Therefore, the sample for fractionation and the sample for moisture determination are taken at the same time.

DISAGGREGATION AND DISPERSION

After the correct weight has been established for the 25- to 30-g sample, the sample is softened by soaking it overnight in about 200 mL of distilled water. The sample is then disaggregated and dispersed ultrasonically for 5–15 minutes, depending on its state of induration. If an ultrasonic generator is not available, a mechanical stirrer can be used. If the sample is so well-indurated that it is not disaggregated by the treatment, the sample may have to be crushed lightly, preferably with a rubber pestle, and the treatment repeated.

SAND REMOVAL

After the sample has been disaggregated and dispersed, it is wet-sieved through a 230-mesh sieve to remove the sand-size ($>62\ \mu\text{m}$) particles. The sand-size fraction which is retained on the screen is washed with distilled water to remove any fine particles adhering to it. Brushing the sample with a typewriter eraser brush or any brush of similar flexibility while washing with the distilled water will help to separate any fine material from the sand. Do not apply much pressure when using the brush or the screen may be stretched which could produce erroneous results in future samples. Care must be taken to clean the brush thoroughly after each use to remove particles that have worked up into the bristles. The water and finer materials ($<62\ \mu\text{m}$) are collected together and retained for the separation of the silt and clay.

The separated sand-size material is then oven-dried at 110°C in a preweighed evaporating dish, cooled in a desiccator, and weighed to determine its percentage of the whole sample. The sand is retained for X-ray powder diffraction analysis.

SEPARATION OF SILT AND CLAY

After the sand has been removed, the silt and clay, now in suspension, are separated by centrifugation. The centrifugation, essentially a settling technique, operates according to Stoke's law. As in any settling technique, various assumptions are made that may lead to error in separating the silt and clay. In any particular set of circumstances, some of the errors introduced by these assumptions are:

(1) The density of most geologic samples is assumed to be 2.65, although some of the minerals in a sample will have a greater density and some will have a lesser density. (2) The particles are assumed to be spherical when in reality they may be of any shape; clay minerals are usually platelets having two long dimensions, although some are fibrous with only one long dimension. (3) Constant and reproducible acceleration and deceleration of the centrifuge are assumed but may not be attained at all times. (4) About a centimeter of silt is assumed to be in the bottom of the centrifuge bottle when the separation of the silt and clay is complete, but inasmuch as the silt content may vary from sample to sample, this ideal is not always achieved. These variables generally cannot be controlled but uniform procedures produce comparable results.

If the clays have flocculated before centrifugation, repeated washings usually will bring them into suspension. If washing does not deflocculate the clays, a small amount of sodium hexametaphosphate (about 0.25 g) added to the suspension usually will do so. We do not recommend adding any chemical to a sample unless absolutely necessary because chemical determinations of the sample or one of its fractions may be needed later.

Centrifuge bottles of 250-mL capacity are used in separating the silt from the clay. Smaller containers may be used but will require a longer overall centrifuge time and the use of several tubes or bottles for each sample in order to keep the amount of silt collected in the bottom of the container from becoming great enough to affect the settling time.

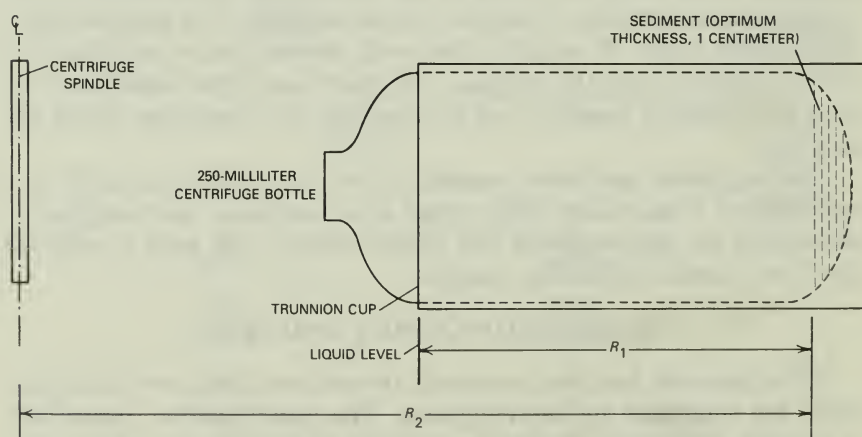


FIGURE 7.—Diagrams of radial measurements necessary for calculation of centrifugation times. R_1 , initial distance of particle from rotation; R_2 , final distance of particle from axis of rotation.

The formula for calculating the centrifugation time to settle any size particles in any liquid (Hathaway, 1956) is:

$$T = \frac{\frac{R_2}{\eta \log_{10} R_1}}{3.81 r^2 N^2 (\rho - \rho_0)} + \frac{2(t_a + t_d)}{3}$$

Where T = total time (in seconds),

$*t_a$ = time of acceleration of centrifuge (in seconds),

$*t_d$ = time of deceleration of centrifuge (in seconds),

η = viscosity in poises,

R_1 = initial distance of particle from axis of rotation (in centimeters) (see fig. 7),

R_2 = final distance of particle from axis of rotation (in centimeters) (see fig. 7),

r = radius of particle in centimeters,

N = angular velocity in revolutions/second ($\frac{RPM}{60}$),

ρ = density of particle in grams per cubic centimeter, and

ρ_0 = density of medium in grams per cubic centimeter ($H_2O = 1$).

*acceleration and deceleration assumed to be constant.

A typical calculation for centrifuging time is as follows:

$$R_1 = 12.95 \text{ cm}$$

$$N = 600 \text{ RPM} = 10 \text{ revolutions/second}$$

$$R_2 = 22.10 \text{ cm}$$

$$\rho = 2.65$$

$$\log_{10} \frac{R_2}{R_1} = 0.2322$$

$$\text{For clay fraction } (< 2 \mu\text{m}), r = 1 \times 10^{-4}$$

$$t_a = t_d = 30 \text{ seconds}$$

Find viscosity in poises from handbook for each degree Celsius it is practical to use: for 16°C , $= 0.011111$

$$T = \frac{0.2322}{3.81 \times 10^{-8} \times 10^2 (2.65 - 1.00)} + \frac{2(30 + 30)}{3}$$

$$T = \frac{609 \times 10^4}{1.65} + 40$$

$$T = 0.011111 \times 36909 + 40$$

$$T = 450 \text{ seconds} = 7 \text{ minutes, } 30 \text{ seconds, at } 16^\circ\text{C}.$$

Table 1 is a typical chart of centrifuging times constructed from the radii just given.

A chart similar to table 1 should be constructed for the centrifuge to be used and for the temperature range expected in the laboratory. Because a density of 2.65 is assumed for most geologic samples and the centrifuge speed is constant, the only variable to consider is the viscosity of the water, which is temperature-dependent.

The filled and balanced centrifuge bottles are placed in the centrifuge which is then set so that the desired speed will be reached in 30 seconds with the tachometer engaged. These settings must be determined by trial and error for each centrifuge. A table should be made to show the settings necessary to reach a given speed in 30 seconds, and to show the centrifuge settings at which a given speed can be maintained. A stopwatch is started at the same time as the centrifuge. When the 30 seconds have elapsed and the centrifuge has reached the desired speed, the centrifuge is reset so that the desired speed can be maintained. These settings must be adjusted if the number of bottles being used is less than the capacity of the centrifuge. When the time listed at $T-t_d$ (total time minus the time of

TABLE 1.—*Chart showing representative centrifuging times for various particle-size separations*

Temp. °C	T Min, s	$T-t_d$ Min, s	Temp. °C	T Min, s	$T-t_d$ Min, s
16	7, 30	7, 00	28	5, 48	5, 18
17	7, 19	6, 49	29	5, 41	5, 11
18	7, 09	6, 39	30	5, 36	5, 06
19	6, 59	6, 29	31	5, 29	4, 59
20	6, 50	6, 20	32	5, 23	4, 53
21	6, 42	6, 12	33	5, 16	4, 46
22	6, 34	6, 04	34	5, 11	4, 41
23	6, 25	5, 55	35	5, 06	4, 36
24	6, 17	5, 47	36	5, 01	4, 31
25	6, 09	5, 39	37	4, 56	4, 26
26	6, 02	5, 32	38	4, 51	4, 21
27	5, 55	5, 25	39	4, 46	4, 16

NOTES

T , total time in the centrifuge in minutes (min) and seconds (s)

Temp. °C, temperature in degrees Celsius

$T-t_d$, time to commence deceleration

To obtain less than 5- μ m particle size, use 240 RPM centrifuge speed

To obtain less than 2- μ m particle size, use 600 RPM centrifuge speed

To obtain less than 1- μ m particle size, use 1200 RPM centrifuge speed

Assumed density of particles=2.65

deceleration) is reached, the power to the centrifuge is shut off and the brake gently applied so as to bring the centrifuge to a complete stop in 30 seconds without agitating the water and sediment. This braking, too, must be determined by trial and error.

When the centrifuge has stopped, the supernatant liquid is decanted into a 1000-mL Berzelius beaker. These tall beakers allow more of the suspension to come into contact with the filter candle. The centrifuge bottle is refilled with distilled water, shaken, centrifuged again, and the supernatant added to the beaker. The process is continued until the supernatant liquid in the bottle is sufficiently clear that one's fingers can be seen plainly through the liquid.

When centrifugation is complete, the clear supernatant liquid is poured into the beaker as before. The silt is transferred from the centrifuge bottle to a preweighed evaporating dish, dried at 110°C, cooled to room temperature in a desiccator, weighed, and saved for X-ray analysis.

QUANTIFICATION OF CLAY-SIZE MATERIAL

After the silt has been removed by centrifugation the clay will be suspended in a large volume of water. This water must be removed to obtain a weight for the clay-size fraction. If the clays are dried out completely, however, they will be difficult to resuspend so that oriented aggregates can be prepared. Thus, most of the water must be removed, an aliquot of the suspension taken for drying, and some of the clay kept in suspension for the preparation of oriented aggregates.

As soon as the first batch of the supernatant liquid from the centrifugation is poured into the 1000-mL Berzelius beaker, the process of removing the water can begin. The bacteriological filter candle (fig. 5), connected to the air and vacuum lines, is placed in the suspension of clay and water. Care should be taken to wet the entire surface of the filter candle with water to prevent air from entering the system. The stopcock is turned to connect the vacuum and water removal begins. Supernatants from later centrifugations can be added at any time.

A clay filter cake forms on the filter candle, gradually slowing the flow of water. Therefore, the stopcock occasionally is turned 180° to allow air to enter the system so that the clay will slough off the filter candle. These procedures are repeated until the centrifugation is complete and the volume of the suspension has been reduced to less than 500 mL. If only a small amount of clay is in the suspension, the volume of the suspension can be reduced further. The clay-water slurry in the beaker is stirred mechanically until uniform.

The uniform slurry is transferred to a 500-, 250-, or 100-mL volumetric flask, depending upon the amount of material, and brought to volume with water. The flask is shaken thoroughly and a 10-percent aliquot of the slurry is withdrawn by pipet and transferred to a pre-weighed evaporating dish, dried at 110°C, cooled in a desiccator, and weighed. The weight obtained is 10 percent of the total weight of the clay-size fraction.

About 5–10 mL of the remaining slurry is transferred from the volumetric flask to a test tube and is retained for making the oriented aggregates. The remainder of the slurry is returned to the Berzelius beaker and most of the water is withdrawn by the filter candles, after which the sample is transferred to a large evaporating dish, air-dried, and used for a randomly oriented powder. If a 100-mL volumetric flask was used, the slurry can be transferred directly to an evaporating dish and air-dried. Heat should not be used because it makes the clay difficult to grind.

ORIENTED AGGREGATES

Many methods of preparing oriented aggregates of clay minerals have been described. Gibbs (1965) compared seven commonly used preparation techniques and concluded that the three acceptable techniques were: (1) smear-on-glass slide, (2) powder press, and (3) suction-on-ceramic tile; we recommend technique 3. Drever (1973) described a filter-membrane technique which produces uniform mounts rapidly. Although excellent orientation is achieved by this method, the end product is mounted on a glass slide, which may be subject to warping when heated to 550°C.

Duplicate oriented aggregates should be made of each sample; one to be used for the glycolation treatment and one to be used for the heat treatments. Some investigators use only one slide or tile, treat it first with the ethylene glycol, and then heat it. This procedure generally presents no problem but some samples may retain ethylene glycol even after being heated (Tettenhorst and Roberson, 1973).

That portion of the sample that was retained in a test tube to be used in preparing oriented aggregates is stirred or shaken to produce a uniform suspension. We use an ultrasonic probe immersed in the suspension for this purpose. A vortex stirrer will work well also.

To make the oriented aggregates, the porous ceramic tiles, on the underside of which is written the sample number, are placed over the openings on the rubber gasket of the apparatus for preparing oriented aggregates (fig. 2). First, about 1 mL of distilled water is sucked through the tiles to wet the surface so that the clay suspension spreads evenly to give a more uniform slide. Then, with an automatic

pipet, 1 mL of the suspension is deposited on each of the tiles and the vacuum applied. When the water has been sucked through the tiles, the vacuum is released and the tiles removed to air-dry. If the sample curls off the tile as it dries, the oriented aggregate should be remade after thinning the suspension by the addition of more distilled water. The oriented mounts are remade in the same way as before, but several 1-mL aliquots of the thinned suspension are deposited on the tile and the water is sucked through after each aliquot. Several thin layers of the suspension will adhere better than one thick one.

RANDOMLY ORIENTED MOUNTS

A number of methods for making randomly oriented mounts have been described in the literature. We use a method that requires no special equipment but gives good results when used with care. The samples are ground to a powder (<240 mesh) and mounted in an aluminum holder that has a hole passing clear through it. To the front of the holder a glass slide is taped to cover the hole. The opening in the holder is then filled from the back, care being taken to fill the hole completely with a minimum of pressure. The excess sample is removed without disturbing that which is in the hole and a second glass slide is taped to the back of the holder. The holder with glass attached is turned over and the glass slide is removed from the front of the mount. The smooth sample surface is then X-rayed.

X-RAY DIFFRACTION PATTERNS

Following is a list of the X-ray diffraction patterns that are made routinely for each sample:

Randomly oriented powders (2° – 66° 2θ)

Chart 1. Total sample—black

Chart 2. (a) Sand-size fraction—blue

(b) Silt-size fraction—red

(c) Clay-size fraction—black

Oriented aggregates (2° – 28° 2θ)

Chart 1. (a) First air-dried tile—black

(b) Treated with ethylene glycol vapor—green

Chart 2. (a) Second air-dried tile—black

(b) Heated to 400°C —red

(c) Heated to 550°C —blue

The colors listed are those we use to distinguish the various patterns. Any colors are acceptable but their use should be consistent.

The (a) pattern is run first and then the baseline is raised, the pen changed, and the other patterns are run above it on the same chart.

For the oriented aggregates of chart 1, the air-dried sample is X-rayed and then the sample is treated with ethylene glycol by a vapor-pressure method (Brunton, 1955) in which the tile containing the sample stands in a desiccator containing ethylene glycol for a minimum of 4 hours at 60°C. The sample must be X-rayed again immediately after removal from the desiccator (Kunze, 1955).

For the oriented aggregates of chart 2, the air-dried sample is X-rayed, the sample is heated at 400°C for a minimum of one-half hour and X-rayed again. The sample is reheated, this time at 550°C for a minimum of one-half hour, and X-rayed again. After each heating the sample should be X-rayed as soon as the tile has cooled enough to be handled safely.

RAPID SAMPLE PROCESSING

A shorter method of identifying the clays may be used. Because the sample is not separated into fractions in this shorter method, minerals present in small amounts, which ordinarily would be concentrated in the separation, may not be identified and the quantitative estimations of the minerals present will be compromised.

A portion of the total sample is ground and an unoriented mount is X-rayed. The resulting pattern is then used for the identification of the nonclay minerals and quantitative estimations of their amounts.

A separate portion of each sample is treated ultrasonically for from 5 to 15 minutes in a test tube and then is allowed to settle for about 10 minutes. The fine material is then withdrawn from the top of the suspension and is used to prepare oriented aggregates on porous ceramic tiles. These tiles are treated and X-rayed in the same manner and sequence as the oriented aggregates of the clays previously described. Amounts of the total clays are estimated by subtracting the amounts of the nonclay minerals from the total sample, and amounts of the individual clays are estimated using procedures described later in this paper.

MINERAL IDENTIFICATION

The X-ray diffraction mineral patterns may be identified by comparison with a pattern "sieve" similar to the one illustrated by Shepard and Gude (1968) or they may be identified by comparison with a file of standard X-ray powder diffraction patterns of the more commonly found minerals. The standard patterns are placed above that of the unknown sample and the diffraction peaks belonging to the standard mineral are identified in the unknown. Each peak and its intensity relative to the other peaks of the mineral should be marked on the pattern of the unknown because a peak actually may represent

reflections from two or more minerals. Reference to the powder diffraction file compiled by the Joint Committee of Powder Diffraction Standards (JCPDS file) commonly will produce an identification of any peaks unaccounted for after all the standard patterns or sieves have been used.

The method just described will identify the nonclay minerals, and in conjunction with the flow sheet (pl. 1), the more common clay minerals. The 001 spacing of a clay mineral from the diffraction pattern of the air-dried aggregate is matched to one of the spacings in the left-hand column of the flow sheet. The d -spacings obtained after the various diagnostic treatments are compared with those listed in the appropriate succeeding columns. When a complete match is found, the name of the mineral is read on the right. Further information can be had from the references that apply to the mineral (references are numbered) to the right of the mineral name.

QUANTITATIVE ESTIMATES

Quantitative estimates of mineral abundance in samples containing clay minerals, especially the estimates of the amounts of the clay minerals themselves are subject to error. Several papers (Johns and others, 1954; van der Marel, 1966; Pierce and Siegel, 1969; Carroll, 1970; Schultz, 1964, 1978) have been written about the quantitative estimation of clay minerals in general. All these authors pointed out problems encountered in estimating quantities of minerals in samples containing clays and one or more of their papers should be consulted before any attempt is made to make such estimates.

The weights of the various fractions contained from the separation procedures can set some limits on the amounts of some of the minerals present, and weighing the samples both before and after any chemical treatment or physical separation of the sample may give a more accurate value for one or more of the minerals. If infrared, differential thermal, or chemical data are available to supplement the X-ray powder diffraction data, better estimates can be made for some minerals.

Artificial mixtures of minerals can be prepared that are similar in composition, crystallinity, and particle size to the samples under investigation. X-ray diffraction patterns are made of these mixtures run at the same instrument setting as the unknown samples. From these patterns calibration curves can be constructed based on intensities of the various diffraction peaks or the areas under the diffraction peaks. These curves are better for estimating the amounts of nonclays than for estimating the amounts of clays, but clays should be included in the mixtures to more closely approximate the composition of the unknown.

Whenever possible, several calibration curves, based on different diffraction peaks, should be constructed for each mineral because the strongest peaks cannot always be used for quantitative estimations due to the presence of peaks of other minerals in the same position, or close to the same position. As an example, in trying to estimate the amount of quartz in a sample, the investigator may find that the intensity of the main quartz spacing at 3.34\AA is increased by a mica peak that almost coincides with it, and the second most intense spacing at 4.26\AA is increased because of a potash feldspar peak that has a similar spacing.

The estimates of the nonclay minerals are made from the patterns of the randomly oriented mounts by comparing the peak intensities of the minerals of interest with the calibration curves. If the sample has been separated carefully, this procedure should account for all the minerals in the sand-size fraction, most of the minerals in the silt-size fraction, and some of the minerals in the clay-size fraction. Mineralogical identification also should be made from the pattern of the randomly oriented total sample as well as for each fraction, because water-soluble minerals may have been removed from the sample during fractionation.

Calibration curves produced from the diffraction patterns of standard minerals also may be used in estimating amounts of some well-crystallized clay minerals such as kaolinite, mica, and chlorite, but if the kaolinite is partially disordered or the chlorite or mica has started to weather their peaks cannot be compared to the calibration curve with any degree of accuracy.

The amounts of the various clays are estimated by determining the ratios of the peak heights or areas under the peaks and then calculating the amounts from these ratios. The methods used by us are those described in succeeding paragraphs.

Johns and others (1954) stated that the intensities for illite must be multiplied by a factor of four in order to be comparable to the montmorillonite peak after glycolation. They determined the intensities by making a series of measurements from the baseline to the curve of the peak, which is similar to measuring the peak areas. We use the peak areas for our calculations. Schultz (1964) found that this factor, when based on the peak heights for illite and montmorillonite, was about 4 or 5 in the Pierre Shale and used the value of 4.5 in his calculations. We use a factor of 4.

Schultz (1955) stated that the peak areas of the 001 spacings of illite and kaolinite are comparable on a 1:1 basis. In a later paper (Schultz, 1960) he pointed out that this comparison was valid for disordered kaolinites but that well-crystallized kaolinites had peak areas twice as strong. A judgment must be made as to the condition of

the kaolinite before a comparison can be made between the kaolinite and illite peaks.

Elverhøi and Rønningsland (1978) made semiquantitative estimates of kaolinite and chlorite by comparing the intensities of their peaks at 3.58Å and 3.54Å, respectively, and drawing a calibration curve. They found that the calibration curve was nonlinear and that per unit weight the kaolinite peak intensity was twice that of chlorite. They based their intensity measurements on peak area rather than peak height. This method can be supplemented by chemical treatments, described later, for kaolinite-chlorite identification.

Isomorphous substitutions within the structures of both micas and chlorites can cause appreciable changes in the intensities of their X-ray diffraction reflections (Brown, 1955). Poor crystallinity, indicated by a broadening of the peaks, also may reduce the peak area. Weathering may cause a broadening of the peaks, asymmetry of the peaks, or loss of intensity. All these factors require interpretation on the part of the investigator and, as Schultz (1964) pointed out, "Inconsistency of interpretation has the greatest effect on the determination of clay minerals."

SUPPLEMENTAL PROCEDURES

Although we recommend using as few chemical treatments as possible because of possible unwanted side effects (Grim, 1968, p. 211; Brewster, 1980; Johns and Kurzweil, 1979), at times certain components must be removed from a sample in order to get a better picture of the rest of the sample. Also, certain diffraction peaks may be indicative of two different minerals and supplemental tests must be made to resolve the ambiguities. Some of the more common treatments will be given in the following paragraphs.

PHYSICAL CONCENTRATION

Occasionally only one possible X-ray diffraction peak of a mineral is visible which gives a doubtful identification. Concentration of the mineral by further particle-size fractionation may reveal sufficient peaks for a positive identification.

Heavy liquids may be used to separate minerals according to their specific gravities. Bromoform, diluted with acetone, can be used to obtain several fractions of minerals with differing specific gravities. This separation is useful because pyrite, hematite, magnetite, and other heavy minerals commonly are present in small amounts and some of their smaller diffraction peaks may be hidden by the peaks of other minerals. Care should be taken to work with heavy liquids in a fume hood at all times.

Magnetic separation and concentration of some sand and silt-size minerals can be made with a hand magnet or a Franz separator.

CHEMICAL DETERMINATIONS

Some of the methods listed here for removing one particular component may be harsh enough to remove or damage other components as well. These methods are included because the investigator may want to remove several components so that the remaining minerals will be concentrated for easier identification. Weighing a sample both before and after chemical treatments will contribute to the accuracy of the estimations.

REMOVAL OF ORGANIC MATERIAL

Small amounts of organic material will not appreciably affect X-ray diffraction peaks but large amounts may affect their intensity. Several methods of removing unwanted organic matter have been used in the past. Langeveld and others (1978) compared the effectiveness of eight methods of organic matter removal but they tried each of these methods on only one sample. They recommended a bromine oxidation method or a sodium hypobromite method.

Troell (1931) described a method of removing organic matter by the use of sodium hypobromite, and Anderson (1963) described a method using sodium hypochlorite in which the sample is treated repeatedly over a water bath for 15-minute periods. He stated that X-ray diffraction patterns of samples so treated have a generally higher peak for 14Å minerals.

A common method of removing organic matter from geologic samples is the use of 20–30 percent hydrogen peroxide with gentle heating on a steam bath, but this method of treatment has some unwanted side effects. The strong oxidizing action of the hydrogen peroxide may remove all the pyrite in a sample if the particle size is small enough. If the particles are larger they may not be removed entirely but the amount will be greatly reduced with prolonged treatment. Oxidation of organic matter with hydrogen peroxide in the presence of calcium-bearing minerals such as calcite or gypsum can cause precipitation of whewellite, a calcium oxalate monohydrate (Jones and Beavers, 1963), or weddellite, a calcium oxalate trihydrate (Martin, 1954; Jones and Beavers, 1963). Douglas and Fiessinger (1971) pointed out that some clay minerals may be degraded by lowering of the pH during hydrogen peroxide treatment. They recommend using a buffer such as sodium acetate to stabilize the pH.

During the hydrogen peroxide treatment the sample should be stirred frequently to reduce frothing. If frothing does occur and

threatens to overflow the top of the beaker, a jet of water or of alcohol from a wash bottle will reduce the froth quickly.

Any of these methods can be used but care should be exercised in using any method of chemical removal of organic matter because of the strong oxidizing properties of the solutions. The use of rubber or plastic gloves is strongly recommended to prevent injury. We recommend the use of sodium hypochlorite because it is efficient, has less destructive effect on the clay minerals, and is safer to handle.

CARBONATE REMOVAL

Small amounts of noncarbonate minerals in limestones or dolomites can be identified more easily if the carbonates are chemically extracted by one of the methods described here. Also, carbonate cements in geologic samples may interfere with the size fractionation and should, therefore, be removed. Various methods have been proposed for the removal of carbonates and most of them require the use of an acid.

Grim and others (1937) suggested placing the sample in 2 liters of distilled water and adding hydrochloric acid a few drops at a time until the limestone was dissolved. Jurik (1964) placed 50 g of sample in a 1500-mL beaker full of molar hydrochloric acid overnight and then heated below the boiling point for 2 hours. Ellingboe and Wilson (1964) used a 10-percent solution of hydrochloric acid at room temperature for 24 hours, which they hoped would have minimal effect on pyrite and clay minerals.

The acetic acid removal of carbonates was suggested by St. Clair (1935) as a means of obtaining a more complete mineral suite, and Gault and Weiler (1955) recommended acetic acid because it was less violent than was hydrochloric acid. Treatment with acetic acid (less than 0.3 molar) or hydrochloric acid (0.11 molar) at room temperature was recommended by Ostrom (1961) on the grounds that the weaker the acid solution the greater the possibility that the clay minerals would be unchanged.

Ray and others (1957) tested the solubility of hectorite in mixtures with hydrochloric, acetic, and formic acids, and exchange resins and concluded that the hectorite was attacked by all but the resins.

The acids in all of the methods just listed may attack small particles of chlorites or smectites, especially hectorite or saponite.

Ethylenedinitrilotetraacetic acid (EDTA) was suggested by Hill and Runnels (1960), Glover (1961), and Bodine and Fernald (1973); however, EDTA will remove some magnesium from the octahedral layers of hectorite and saponite.

The method that appears to be the least destructive to clay minerals is Jackson's (1956) method using acetic acid with a sodium acetate

buffer of pH 5. This method can be adapted readily for small or large samples and appears to have a minimal effect on clay minerals.

Any of these methods may be used depending on the information desired, the amount of carbonates, the size of the carbonate crystals, and the clay mineral content. We have used all the methods at various times. The investigator must bear in mind the possibility of removing other minerals along with the carbonates.

IRON OXIDE REMOVAL

The presence of iron oxide coating on clays can be a problem if a focusing monochromator or iron target X-ray tube is not used. The iron in the iron oxide coatings fluoresces with other types of radiation and, depending on the amount of iron present, can produce a very high background that can mask peaks and distort the pattern. If neither a focusing monochromator nor an iron target X-ray tube is available, the iron oxide may have to be removed in order to obtain a usable X-ray pattern. Mehra and Jackson's (1960) method using a dithionate-citrate solution buffered with sodium bicarbonate effectively removes iron oxide with little effect on the iron-bearing clay minerals that may be present. It is also faster than many previously used methods.

THE GREENE-KELLY LITHIUM TEST

Montmorillonite can be distinguished from trioctahedral smectites and beidellite by using Greene-Kelly's (1955) lithium test. An oriented aggregate sample is saturated with 3*N* (normal) LiCl and heated overnight at 200°C. In montmorillonite the Li^+ is said to enter the vacant octahedral sites and neutralize the charge created by the substitution of Fe^{+2} or Mg^{+2} for Al^{+3} within the octahedral layer, thus making the montmorillonite nonexpanding when treated with glycerol. In beidellite, on the other hand, the layer charge is caused by the substitution of Al^{+3} for Si^{+4} in the tetrahedral layer where there is no place for the Li^+ (Schultz, 1978). In trioctahedral smectites the layer charge may originate in either the octahedral or tetrahedral layer but nearly all the octahedral sites usually are occupied so there is no place for the Li to enter. The beidellite and the trioctahedral smectites, therefore, will expand when treated with glycerol.

DETERMINATION OF AMORPHOUS MATERIAL

The presence of amorphous material in samples containing clays causes difficulties in identifying minerals and in estimating the amounts present. If the material is amorphous iron oxide it can be removed by the buffered dithionate-citrate method mentioned earlier.

Amorphous iron oxide usually is present in small amounts but its fluorescence under copper radiation can produce a high background.

Samples from volcanic tuffs or tuffaceous sediments may contain amorphous silica present in amounts of as much as 100 percent. Smectites commonly are associated with, and formed from volcanogenic materials. Amorphous silica produces a broad diffraction band between 19° and $32^\circ 2\theta$ on diffraction patterns. This hump masks smaller peaks and also makes quantitative estimation difficult. Hashimoto and Jackson (1960) have devised a method to determine the amount of amorphous silica in a sample. In their method, a weighed sample is placed in a nickel beaker and boiled in 0.5N NaOH, quenched in ice water, and the supernatant is removed by centrifugation. The sample is then dried in an oven, cooled, and reweighed. The weight loss is assumed to be the weight of the amorphous material, although a few weight percent may be dissolved from the edges of some clays.

DISTINGUISHING BETWEEN KAOLINITE AND CHLORITE

Chlorite generally can be distinguished by its 001 spacing of 14\AA that increases in intensity when heated to 550° – 600°C and by the presence of the 003 peak at 4.7\AA . However, if a kaolin mineral is present and the chlorite is predominant the presence of the kaolin is difficult to determine, as is the quantity of each, especially if the kaolin is poorly crystalline.

The 001 peak of kaolinite and the 002 peak of chlorite appear at about the same position on the X-ray diffraction pattern; they each have a spacing of about 7.15\AA . Often the diffraction peaks of other minerals in the sample make the companion peaks of the chlorite and kaolinite impossible to see. Therefore, there can be a doubt as to whether one mineral or the other is present, or both.

The disappearance of the peak at 7.15\AA when the sample is heated to 550°C has been accepted as a criterion for the identification of kaolinite, but most poorly crystallized soil chlorites in recent sediments and serpentines also may show a loss of intensity of that peak when heated. If both the chlorite and kaolinite are well crystallized, there may be a detectable resolution of the 004 chlorite peak and the 002 kaolinite peak at 3.55\AA and 3.58\AA peak, respectively. However, these peaks are not always clearly defined, and the 004 peak of some chlorites also produces a spacing near 3.58\AA .

Boiling a sample in 2N hydrochloric acid for 30 minutes has been used by some to distinguish between kaolinite and chlorite; chlorite is decomposed by this treatment whereas kaolinite is not. Because other minerals may be destroyed or damaged by this treatment, a separate portion of the sample should be tested in this manner.

Andrew and others (1960) and Wada (1961) described a method for distinguishing between kaolinite and chlorite by grinding the sample with potassium acetate to expand the kaolinite lattice. We have modified the procedure somewhat. A weighed portion of the sample is ground for 15 minutes with 1.5 times as much potassium acetate and allowed to stand overnight in an atmosphere of 70-percent relative humidity, which can be attained in a closed desiccator containing a sulfuric acid-water solution with a density of 1.25. The moist sample is then smeared on a porous tile and an X-ray diffraction pattern is made. After being X-rayed, the tile is placed on the vacuum apparatus for making oriented aggregates (fig. 3), and three 1-mL aliquots of 6*N* ammonium nitrate are sucked through the sample. The sample is dried for two hours at 110°C and X-rayed again. It is then placed on the vacuum apparatus again and washed three times with distilled water, dried overnight at 70-percent relative humidity and a final X-ray diffraction pattern made.

The approximate 001 spacings for kaolinite after each treatment are: (1) after $\text{KC}_2\text{H}_3\text{O}_2$ treatment—14Å, (2) after NH_4NO_3 treatment—11.6Å, and (3) after H_2O wash—7Å for kaolinite and dickite and 10Å for halloysite.

This method does not always expand all kaolinites. Jackson and Abdel-Kader (1978), recognizing this difficulty, developed a method of grinding the sample with cesium chloride and then treating it with hydrazine and dimethylsulfoxide. This method is rather long but can be used if the results of other methods are inconclusive.

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