Chapter 6
Sample Preparation Techniques for Clay Minerals

There is no *single* way to prepare materials for X-ray diffraction analysis. Preparation techniques depend on (1) supplies and equipment available; (2) purposes of analysis, e.g., whether qualitative or quantitative identification is the goal; (3) the material itself; and, probably most important, (4) your sense of organization and habits, your goals, your understanding of the principles of X-ray diffraction, and your ingenuity. You must design and execute suitable procedures because they are so dependent on the characteristics of the sample and what you want from the sample. When someone said "research is 90% tedium," sample preparation may have been what he or she had in mind. We discuss several methods of preparation, keeping in mind that we may be addressing neophytes and that the laboratory facilities available may be limited. We have borrowed heavily from Brown and Brindley (1980), Jackson (1969), and Bish and Reynolds (1989).

This chapter may seem pedestrian—a bit like giving instruction on typing or driving or other subjects that might seem unscientific. But unless you make good samples that produce clean, intense diffraction patterns, all the world's theory and creativity cannot be usefully applied to the interpretation of XRD results.

Our discussion is directed toward the treatment of common types of clay minerals in sedimentary rocks. We show no flowcharts because, although they are nice devices for summary, they usually are so complicated that they are intelligible only to those who do not need the information in the first place.

The most important point to be made here is that *there must be a single method of preparation for a given set of samples if X-ray diffraction data are to be compared within the set,* particularly for quantitative analysis. However, treatment of different sets of samples may vary up to the point at which they are exposed to the X-ray beam, because each set may present characteristics and preparation problems of its own. For example, carbonates present different problems than tills, and shales require a different treatment than sandstones.

Procedures for preparing samples for X-ray diffraction fall into two groups: one in which perfectly random orientation of the grains is the goal, and one in which perfect orientation of the clay mineral flakes parallel to the substrate is the goal. Neither goal will be met, but we try.

EVALUATING THE SAMPLE

We assume you have at hand a representative sample, one you have taken carefully at the outcrop with specific questions in mind. The first step is a preliminary assessment. Split out 1 to 2 g, crush it in a mortar, and grind it as a paste with water or propanol. Dry the sample and load into a sample holder as a randomly oriented powder (see subsequent discussion on preparation of random powder mounts). Note that we crush by impact (as gently as will do the job) rather than by grinding, and we accomplish further reduction in grain size by wet grinding. Aggressive dry grinding can cause changes of phase, and in extreme cases, can lead to strains on the crystal structure that cause XRD line broadening or even the production of X-ray amorphous material. The X-ray diffraction tracing from a randomly ordered powder will give you a rough idea of the proportion of clay and nonclay minerals. All clay minerals diffract from the 020 and 110 spacing. These spacings are very nearly the same dimension for all of them. The intensity of this combined peak (they diffract at approximately the same Bragg angle) is used by many workers to estimate the amount of clay minerals relative to the nonclay minerals. This preliminary tracing will also be the basis for designing subsequent steps.

Certainly the nonclay minerals will be of interest, but most of them, when present, mask some of the 00*l* reflections of the clay minerals. In addition, the weak 00*l* clay mineral intensities produced by such a sample means that you will not be able to do much identification of specific clay minerals with this preparation.

For many studies, you will know enough about the samples to eliminate the random powder XRD reconnaissance and proceed directly to a separation of the clay minerals.

The most common nonclay minerals are quartz, feldspars, carbonates, gypsum, pyrite, zeolites, and iron oxides (either amorphous or crystalline). Organic matter also can be present. Most of these minerals can be separated from the clay minerals by extracting a fine enough particle-size fraction, leaving the nonclay minerals in the coarser residue, but not always.

Good orientation of the clay minerals requires that nonplaty minerals such as quartz be removed, for their equant crystal shapes destroy the preferred orientation we are seeking. In addition, the clay minerals must be dispersed into individual colloidal particles in the suspension before you prepare the sample, because in the flocculated condition they produce submicroscopic polymineralic aggregates within which the orientation is poor to random. All this preparation must be accomplished with a minimum of chemical and physical damage to the clay minerals present. The rule is *do as little as possible to the sample before presenting it to the X-ray beam*. Use chemical treatment only as a last resort, and use as little physical treatment as possible because there is always the danger of changing, in some unanticipated way, these fragile phyllosilicates with large, reactive surfaces.

In what follows, we have tried not to present suggestions as recipes, but as general guidelines. The suggestions, those that appear as recipes and otherwise, must be adapted to your problem, your lab, and your skills.

DISAGGREGATING THE ROCK

Rock samples that require different treatments can be categorized as: (1) Friable sandstones and moderately to poorly lithified shales; (2) silica-cemented sandstones, flint clays, and well-lithified (siliceous) shales; (3) limestones and dolomites; (4) gypsum-anhydrite rocks; and (5) unconsolidated materials such as till, soil, and modern sediments. The first serious mistake, and one that is all too commonly made, is to pulverize the sample with a grinder, shatter-box, or ball mill. This reduces the coarse-grained, nonclay minerals to the clay-size range from which they can never be separated. The samples must be crushed, not ground, with some device such as a large iron mortar and pestle. The purpose of this operation is to increase the specific surface area of the grains so that the following procedures are more effective. Stop when the grains average a few millimeters and don’t worry about the inevitable presence of some larger grains. Ten grams of starting material is just about right for most clastic rocks, with perhaps 20 g for carbonates and evaporites.

Separating Clay Minerals from Clastic Rocks

Suppose that the sample is some sort of sandstone or shale. The next step is a preliminary disaggregation in an industrial-grade Waring® blender, perhaps after an overnight soak. The home kitchen-grade device will fail so quickly that it is not cost-effective. For a mix of 200 mL of distilled water and ~10 g of crushed rock, give it 2 to 3 min at full power. Quickly decant the obvious fine fraction and transfer it to a plastic container for ultrasonic treatment. If the rock is hard or silica-cemented or both, the blender treatment is ineffective and should be eliminated.

Ultrasonic disaggregation is a crucial contributor to good preparations. The best instruments are the horn-type devices that produce 100 or more acoustical watts at the transducer tip. If you use one of these devices, be certain that suspensions are always irradiated in plastic containers because the horn tip will quickly punch a hole in a glass cup or beaker if it contacts it. In addition, glass becomes crazed by exposure to the ultrasonic energy, with the result that a beaker will suddenly crumble, usually when you are treating a valuable sample for which only small amounts are available. Wear ear plugs or enclose the instrument in a sound-dampening box or both. Irradiate the sample for a few minutes (1 min at 300 W is nominal), allow it to settle for a minute or so, and decant the fines to a centrifuge cup. Much longer irradiation times are not advisable because the ultrasound causes some exfoliation of clay mineral crystallites and, you will notice, quickly heats the sample. If you are dealing with well-cemented clastic rocks, it may take hours in the ultrasonic instrument to separate enough material for a good preparation. The way to accomplish this separation is to irradiate for 3-5 min, decant off the fines, add more water, irradiate again, etc. This procedure ensures that liberated crystallites spend only short periods exposed to the ultrasound. In the end, you will finish with a very large volume of water that contains only small amounts of clay, but, as we will see, there are easy ways to concentrate such a dilute suspension.

Separating Clay Minerals from Carbonate Rocks

Carbonate rocks, or clastic rocks with significant carbonate contents, need to have the calcite or dolomite removed. Removal is accomplished by using a method tested by Ostrum (1961). He found that clay minerals can be extracted from carbonate rocks without affecting them if acetic acid ≤0.3 molar is used, and if the process is closely watched so that the sample is rinsed as soon as all the carbonate has been dissolved. The carbonate itself serves nicely as a buffer if closely monitored. As long as the sample is effervescing, carbonate is being dissolved and that controls pH. Heating will speed up the reaction and may be necessary to dissolve dolomite. Watch the sample carefully for at least $^1/_2$ h to make certain that the increased reaction rate due to heating does not cause sufficient effervescence to result in sample loss. Such loss can be a mess to clean up. For samples with large amounts of calcite, have a pan of water cooled with ice in case the reaction becomes too violent. If it does, you may place the beaker in the pan of cold water to cool it. Then proceed with the digestion at a lower temperature. Jackson (1969) recommended heating the crushed sample and using a sodium acetate-acetic acid solution buffer at pH 5.

In spite of the results reported by Ostrum (1961), mixed-layered clay minerals, particularly the ordered ones commonly found in soils, may be damaged by high temperature and low pH. Although we can find no written mention, palygorskite and sepiolite are quite acid soluble. So, be cautious. Try to find a way to test the clay minerals before and after exposure to acid and heat.

Separating Clay Minerals from Sulfate Rocks

Clay minerals can be extracted from gypsum-anhydrite rocks by dissolving the sulfates in the sodium salt of ethylenediaminetetraacetic acid (EDTA), an alternative method for carbonate rocks because it works about as well as acid for the removal of calcite and dolomite but is somewhat slower. (To extract gypsum or anhydrite from argillaceous rocks, water may do the trick. They dissolve in amounts of about 0.2 g per 100 cc of water.) The following procedure is summarized from Bodine and Fernalld (1973).

Per one liter of solution, dissolve 74.45 g of reagent-grade disodium EDTA in 800 to 900 mL of water and adjust the pH to about 11 by carefully adding sodium hydroxide pellets. Dilute to 1 L to produce a 0.2 M EDTA solution. Add 20 g of crushed rock to about 600 mL of reagent and boil for 4 h. Centrifuge and discard the supernatant. Wash the insoluble residue repeatedly by centrifugation until dispersion. The high pH of the reagent may, for some samples, prohibit flocculation and thus make it impossible to separate the insoluble residue from the EDTA. If calcium is added to promote flocculation, calcium sulfate will precipitate, and if the pH is lowered, the acid salt of EDTA will precipitate and mix with the insoluble residue. In this situation, the best procedure is to separate and wash the insoluble residue in its dispersed condition by ultracentrifugation if available. Bodine and Fernalld (1973) have demonstrated that this treatment has no deleterious effects on the simple clay minerals, but research is needed to ascertain whether or not it is entirely safe for mixed-layered clay minerals.

Separating Clay Minerals from Unconsolidated Materials

Unconsolidated materials are the easiest to work with and often require only dispersion by ultrasound or the Waring® blender and removal of salt by centrifugation. Some samples may contain carbonates that must be removed (see preceding section), or else the solubility will keep the Ca ion activity in solution high enough to inhibit full dispersion of some of the clay minerals. Organic matter and iron oxides can present real problems, and if they occur together with highly disordered mixed-layered clay minerals, you will have to face the fact that there is no ideal way to proceed. Treatments to eliminate organic matter and iron oxides may alter the mixed-layered clay minerals. Yet if these substances are not removed, the diffraction patterns may be so poor that you will not be able to make acceptable interpretations. Our tendency in such situations is to use smear mounts on porous tiles and run the samples while they are moist, as with peelers, as discussed below. (If you suspect smectite is

Box 6.1. Glacial Deposits of the North American Interior

Resolution of the broad features of the stratigraphy of the glacial deposits covering the interior of the North American continent and distinguishing one till unit from another rest on a database of the clay mineralogy of approximately 150,000 samples, run in duplicate, and prepared by first soaking overnight, then disaggregating with a milk shake mixer, another period of standing for flocculation, a decanting, adding more water and a few grains of Calgon®, and then a pouring off those that seemed too concentrated. Then samples were stirred, allowed to settle for 15 min, and using an eyedropper, a portion was drawn from the top half cm and deposited on a glass slide that had been cleaned with a bit of spit. The slides dried on the lab bench, and were then placed in an ethylene glycol atmosphere to be run after two days. The intensities of the peaks are adjusted according to a set of empirically derived factors and tabulated. There is the art in all this of the good cook or the butcher who picks up exactly the amount of hamburger you request. Herbert Glass of the Illinois State Geological Survey created this database, and continues to add to it. He is a cook's cook. The details of his method were presented by Hallberg et al. (1978).

present in the sample, glycol may be added to the paste.) The intrinsically poor diffraction pattern is made acceptable by using step-scanning procedures with long count-time intervals or by recording the pattern at slow goniometer and strip-chart speeds in conjunction with long time constants (see Chapter 2, p. 49).

CHEMICAL PRETREATMENTS

Removal of Iron Oxides

If you are using a Cu (atomic number 29) target X-ray tube, fluorescent X-rays from Fe (atomic number 26) are a problem because they produce a high background that can mask peaks. Iron oxides also cement particles together and thus inhibit dispersion of the clay mineral particles. You can overcome the problem of fluorescence from Fe by placing a crystal monochromator in the beam path just in front of the detector. The monochromator diffracts the diffracted beam through the spacings of a crystal, commonly graphite, so that only the l.54 Å CuKα radiation is diffracted at an angle that allows it to enter the detector. The problem can also be solved by using an Fe tube, but the monochromator is less expensive, solves the problem equally well, and eliminates the trouble of changing and aligning tubes.

Fe oxides can be removed chemically. The most commonly used treatment is the citrate-bicarbonate-dithionite (CBD) method (Jackson, 1969, p. 44). Jackson notes that the method he recommends also removes calcite and phosphates. This method can change the X-ray diffraction response of mixed-layered clay minerals, and it is not recommended unless it is absolutely necessary to remove very large amounts of Fe oxides.

Removal of Organic Materials

Organic matter can produce broad X-ray diffraction peaks, increase the background, and inhibit dispersal of other minerals if present in significant amounts (a few percent). The organic matter can be removed chemically. The solutions used are strong oxidizing agents, so you must be alert to possible changes in the clay minerals. Commercial bleach (Chlorox™, Purex™, etc.) is NaOCl (sodium hypochlorite) and seems quicker, cheaper, and safer (for your health) than the frequently recommended hydrogen peroxide.

The following procedure is recommended. Treat with 10 to 20 mL of NaOCl that has been adjusted to pH 9.5 with HCl just before treatment. Heat the mixture in a boiling-water bath about 15 min. Centrifuge at 800 rpm for 5 min and decant and discard the supernatant. Repeat the procedure until organic material is sufficiently removed, as evidenced by a change in sample color to white, gray, or red. The procedure can oxidize ferrous iron in octahedral sites, causing a change in silicate layer charge and altered clay mineral diffraction characteristics. Do not use this method unless you must, and then do so with the full realization that mixed-layered clay mineral identifications are suspect.

A sample that is predominantly organic matter, such as coal, requires that the organic material be removed by low-temperature ashing. This technique, described by Gluskoter (1965), treats the sample in an atmosphere of electronically excited oxygen at a temperature at or slightly above 100°C. The procedure oxidizes the organic material in the sample. Possible effects on clay minerals have not been documented.

Saturating the Clay Minerals with Different Cations

Clay minerals adsorb anions and cations and hold them in an exchangeable state. The X-ray diffraction characteristics of the air-dried and the ethylene glycol-solvated states of smectites depend on the type of cation that is held in the exchange sites. Saturation with Mg and solvation with glycerol is standard for tests for differentiating vermiculite from smectite (see Chapter 5, p.160).

Techniques for exchanging cations are relatively simple. Treat the clay minerals with a l M solution of the chloride of the univalent cation of choice or a 0.1 M solution of the divalent cation of choice. An exchange reaction will occur; cation A, adsorbed on the clay mineral, will be replaced by cation B from the solution containing excess B cations. The clay mineral will become saturated with B cations if it is separated from the solution 3 to 5 times, replacing the liquid each time with a fresh solution containing an excess of B cations. For the last step, wash the clay minerals with deionized water and then with a 50/50 ethanol/water mixture[1] until essentially all chloride ions are removed, for the absence of chloride ions means that the cations from the salt solution have also been removed. There is a simple test for this. Prepare a small amount (10 mL) of $AgNO_3$ solution and keep it in a light-proof dropper bottle. (To make the bottle light-proof, etch the bottle and dip it into the liquid material used for making plastic handle grips on pliers.) A drop or two of $AgNO_3$ will cause the precipitation of AgCl if there is even a very small amount of Cl anion present (the solubility product of AgCl = 1.8×10^{-10}). If all Cl anions, as cation indicators, cannot be removed this way, final washings should be done by dialysis. To do this, put the clay mineral suspension in semipermeable dialysis tubing (available from hospital or biological lab suppliers) and immerse in a large volume of warm, deionized water. Gentle stirring is helpful, and the water should be changed about four to five times the first day or until no more Cl is detected.

Cation saturation can also be accomplished very simply if you use the Millipore® transfer method for sample preparation (see p. 215).

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[1] The ethanol-water mixture is used to minimize hydrogen ion substitution for the other exchangeable cations, i.e., to stop hydrolysis.

PARTICLE-SIZE SEPARATION

At this point we have a suspension in which, ideally, the particles are single crystals. One of the important reasons for washing the suspension free of salt is that if there is enough dissolved salt in the suspension, it will cause flocculation. Suspensions must be washed free of salt by centrifugation before particle-size separations are performed. Balance the centrifuge cups and spin them for a few minutes at 2,000 rpm. If the suspension has flocculated, the supernatant liquid after centrifugation will be crystal clear. Decant the water and discard it. Redisperse the suspension in another 200 mL of distilled water by means of ultrasound and repeat the centrifugation. After three or four of these washings, the supernatant will show some turbidity that may be extreme or only a faint opalescence. This condition indicates full or incipient dispersion, and that process should be completed by the addition of a suitable dispersing agent.

Dispersing agents all have one feature in common—they produce a buffered pH from neutral to high. The most effective ones also have phosphate ions that promote dispersion, presumably by the adsorption of the phosphate ions on clay edges where they reverse normally positive edge charge and thus help prohibit flocculation. Sodium pyrophosphate is our choice, although you may want to try other sodium phosphates if you encounter particularly recalcitrant sample. You don't want to add too much dispersing agent, or you can actually promote flocculation because of an increase in ionic strength. About 10^{-3} to 10^{-4} M is suitable, and for 200 mL of suspension, that is about equal to 20 to 30 mg of the reagent. Take about half a "pinch" of the powder, and you will see that this is just about right. Such an approximate measure is good enough, and you need not go to the trouble of weighing the powder that is added to each suspension. Add the reagent and disperse by ultrasound. Let it stand a few minutes and gently stir the surface with a rod or spatula. Notice that the streamlines stand out, just as they do when you stir aluminum paint (that is, if you've ever stirred aluminum paint). This effect is caused by the orientation of the clay mineral crystals in the stream lines with reflection of light from their cleavage faces, and signifies that dispersion is good and that the suspension is suitable for particle-size separation. Seldom will dispersions be good enough to see this effect, but it is a goal.

With the sample well dispersed, you may now split the sample into a number of size fractions. For different samples, you will have to move to smaller sizes to get below the grain size of quartz and feldspar. Other reasons for making a series of size fractions will become clear in the discussions of polytypes and the dating of various size fractions in Chapter 10; the smaller the size fraction, the more it is dominated by polytypes of diagenetically formed clay minerals.

Before we move on to the next subject, we make a few comments about difficult samples. Some materials resist dispersion, even after repeated washing by centrifuge and the addition of normal peptizing (dispersing) agents. If this happens, try adding 20 to 30 mg (per 200 mL) of sodium carbonate; it often works wonders. We have been able to disperse numerous samples of palygorskite and some materials rich in opaline silica only by this procedure. If you're faced with dispersing a flint clay, Bohor and Triplehorn (1993, p. 6) suggested a three to four week soak in water and dimethyl sulfoxide (DMSO).

The next step is the separation of the clay-size fraction, which we take here to be the < 2 µm equivalent spherical diameter (< 2 µm e.s.d.). Particle-size separations are based on Stokes's law, and it applies strictly to spherical particles, which platy clay minerals are not. So when we say that a clay mineral crystallite is 1 µm, we mean that it settles at the same velocity as a 1 µm sphere of equal density. Intuitively, you know that a leaf will fall through air more slowly than a ball of the same volume, so you won't be surprised that the maximum diameters of "1 µm" clay crystallites are a good deal more than 1 µm.

Below a particle size of about 20 µm, particles settling in a fluid approximately obey Stokes's law, which is a numerical expression that describes a particle being pulled by gravity but whose fall is resisted by a viscous fluid. The balance between these two forces results in a terminal velocity V_T (i.e., no longer accelerating) that is inversely proportional to the viscosity of the liquid η and proportional to the force of gravity g (in cm/sec^2). It is also directly proportional to the difference in density between the particle and the liquid (d_p - d_l) and the particle diameter squared, D^2, in square centimeters (i.e., the size of the surface resisting movement through the fluid). The equation for Stokes's law is

$$V_T = g(d_p - d_l)D^2 / 18\eta \tag{6.1}$$

Stokes's law can be put into a more useful form by using the relation velocity = distance/time ($V = h/t$), and the height h of the cylinder in which we have a dispersion as the distance in the relation $V = h/t$. Hence,

$$t = 18\eta h / g(d_p - d_l)D^2 \tag{6.2}$$

Equation (6.2) will allow you to figure the distance *h* a particle falls (in centimeters) during a given time interval *t* (in sec). Particles settling through a fluid in a centrifuge obey the same law except that the settling force is increased as a function of the speed and radius of the centrifuge.

Table 6.1. Settling times for gravity sedimentation of particles in water at 20°C[a]

Particle diameter (µm)	h	min	sec
50	—	—	22
20	—	2	20
5	—	37	30
2	3	50	

Data apply to a settling distance of 5 cm and a mineral density of 2.65 (Jackson, 1969).
[a]The viscosity of water is a function of temperature.

Table 6.2. Settling times for a specific centrifuge for sedimentation of particles[a]

Particle diameter (µm)	sp. g. mineral	Centrifuge speed (RPM)	time (min)
5	2.65	300	3.3
2	2.65	750	3.3
0.2	2.50	2400	35.4

[a]Data apply to 20°C, a distance of 15 cm from the centrifuge axis to the liquid meniscus, a 10-cm suspension depth, and 1 cm of sediment at the bottom of the centrifuge tube (Jackson, 1969).

Tables 6.1 and 6.2 give solutions of Stokes's law for normal gravity and for centrifuge sedimentation (Jackson, 1969). Table 6.1 gives the settling times for a standing cylinder, and Table 6.2 gives times for one centrifuge.

The data in Table 6.1 are easily modified for other conditions. Just remember that if you double the settling distance you must double the time [see Eq. (6.2)]. Notice that a lower specific gravity (sp. g.) is used for 0.2 µm clay particles (Table 6.2). This reduction in sp. g. is necessary to take into account the bound water at the mineral surface because very fine particles have very high specific surface areas and their absorbed water is no longer a negligible portion of their volume. Particle-size separations should be made as soon as dispersion is achieved, because some clay minerals flocculate slowly even though they were once well dispersed.

Normal gravity settling in tubes is not recommended because it takes too long. Centrifugation is the best method. If you have a 15-cm machine, spin for 3.3 min at 750 rpm (Table 6.2) and decant the supernatant liquid into a separate container. The supernatant is the yield of the process. All the particles in it are < 2 µm e.s.d., but the material in the bottom of the centrifuge cup is not entirely >2 µm. It contains a good deal of the < 2 µm suspension, so if sample size is limited and there is not yet enough clay in the yield or if you wish to measure the amount of the < 2 μm fraction, redisperse the sediment from the cup by ultrasound, centrifuge again, and add the supernatant to the yield from the first separation. Three separations are about all that are practical because that constitutes almost all the < 2 μm material in the suspension.

Minerals can be separated based on their Fe contents. Dispersions of the entire <2 μm portion of a sample or separate size fractions can be passed through a system with a reservoir, a tube filled with stainless steel wool passing through a Frantz Isodynamic Magnetic Separator™, and a pump. Clay minerals that contain iron can be separated from those that do not. It is not uncommon to separate an Fe-poor chlorite from an Fe-rich one. The details of this technique have been given by Tellier et al. (1988).

PREPARING THE ORIENTED CLAY MINERAL AGGREGATE

We now have a dispersed suspension of clay-size material. Let us proceed to the preparation of the oriented clay aggregate. The first step often required is the concentration of this material to a level that it is suitable for the various sample preparation procedures.

The easiest way to make the suspension more concentrated is to collect the clay by ultracentrifugation and then redisperse it in a small volume of water. Any of the available angle-head centrifuges capable of 20,000 rpm are suitable for this purpose. If such a centrifuge is not on hand, or if the volume of the suspension is large (>1 L), then the clay must be flocculated, collected by gravity settling, and washed to redispersion in a small volume of water. Make the suspension 0.1M with respect to $CaCl_2$ and do something else for a while. Calcium is a good ion to use because it will saturate the ion-exchange positions in smectites, producing a glycol solvated type that will give unambiguous diffraction characteristics. The floccules will settle after a few hours and the supernatant can be removed by means of a vacuum hose attached to a tap-water-driven aspirator. The concentrated suspension must be centrifuged, redispersed in water, centrifuged, etc., until dispersion is attained. Try to achieve a sediment concentration of 60 mg of clay per milliliter of liquid in the final suspension.

X-ray diffraction samples must be smooth, flat, long enough, thick enough, and should be mineralogically homogeneous throughout their depth or thickness. These characteristics are crucial for quantitative representation (Hughes et al., 1994), and acceptable limits of deviation from the ideal for each of them are discussed in Chapter 9. There is a bewildering array of sample preparation methods in use throughout the many laboratories that deal principally with clay science. We recommend that you become proficient with four: (1) the so-called glass slide method; (2) the smear method; (3) the

Millipore™ filter transfer method (Drever, 1973); and (4) the centrifuged porous plate (Kinter and Diamond, 1956). Table 6.3 summarizes, in order of ease of mastery, the strengths, weaknesses, and application for each method.

The Glass Slide Method

The glass slide method is best described as old faithful. It probably is the most commonly used routine method. Its only advantage, however, is its ease of application. Orientation is only fair, the aggregate usually is particle-size segregated with the finest material on the top, and the clay films are usually too thin for accurate diffraction intensities at moderate to high diffraction angles. Place a glass microscope slide (2.7 by 4.6 cm) in an oven at 90°C. It is a good idea to use a porous ceramic plate under the slide to catch any spills. Use an eye dropper to add the suspension so that the liquid covers the entire surface of the slide. You will be surprised at how much you can add without overflow. Four mL is easily possible on a standard slide (Fig. 6.1). Drying usually takes about 1 h at 90°C.

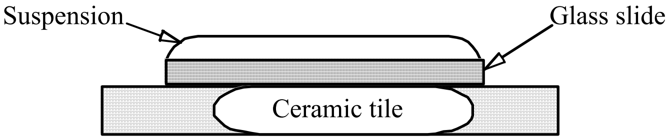

Fig. 6.1. Surface tension holds the suspension on a clean glass slide. The tile catches spills.

Some readers may object to the high drying temperatures recommended here. Poorly crystallized clay minerals, such as those found in soils, can be damaged by such high temperatures. Studies of hydrated halloysite, for example, require samples that have been dried at room temperature, or even to be run while wet. Most sedimentary rock clay minerals, however, are unaffected (as measured by X-ray methods) by temperatures near 100°C, and such temperatures greatly diminish sample preparation time. All the methods described above produce samples that can be dried at room temperature, if you require that option.

Glass substrates are not very useful for heat treatments because they soften unacceptably or warp at temperatures that are much above 300°C. Fused silica glass can be used, but it is expensive.

The Smear Mount Method

For identifying the constituents in a bulk sample and roughly estimating the quantities, the smear technique is a good compromise between time and skill required and the quality of the results. Done properly, phases should be represented in their true proportions, i.e., without segregation. Quarter the sample for a representative portion. For the quickest preparation, place about

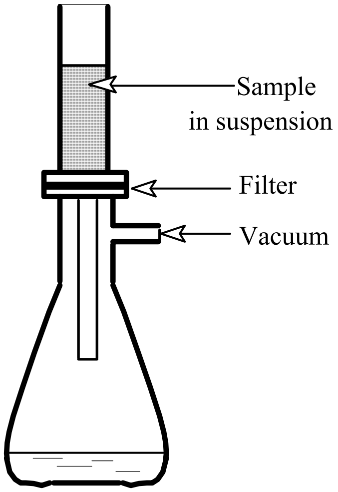

Fig. 6.2. Filtration apparatus.

half of the end of a microspatula (a few mm^3) of sample in a medium (~ 100 mm diameter) mortar and thoroughly grind until the material is smeared on the mortar. Brush the powder onto a labeled slide and add one or two drops of a dispersant solution to the powder, mixing with microspatula until a butter-like paste is formed. Sample material also can be collected from a dispersion by centrifugation. In this case, pour off the supernatant, mix the material in the bottom of the centrifuge tube, again to a butter-like paste. Smear by spreading the paste uniformly over the slide with the microspatula subparallel to the slide. Practice may be required to obtain a thin, even coating on the slide. You may find it helpful to hold the slide by attaching it to a vacuum hose while smearing. Preparation with a McCrone™ mill, i.e., micronizing the sample, as described below in the discussion about particle size and diffraction effects, will improve the precision of this technique. Virtually any size fraction can be smeared in this way. Some laboratories use the <16 µm size fraction as a way to "catch" all the clay minerals and also have a sampling of the nonclay minerals. However, samples with abundant kaolinite are not always as well sampled by this technique because kaolinite often occurs in vermicules up to 100 µm.

Table 6.3 Features of different sample preparations

Method	Advantage	Disadvantage	Level of skill required	Application
Glass slide	Quick	All	Low	Qualitative analysis
Smear slide	Quick, moderately homogenous	Most	Moderate	Clay and non-clay minerals
Filter transfer	Homogeneous aggregate	Fair intensities	Moderate	Quantitative representation
Porous plate	Best intensities	Inhomogeneous aggregate	High	Crystal structure studies

The Millipore® Filter Transfer Method

The filter transfer method produces only fair crystallite orientation, but the clay surface presented to the beam is likely to be representative of the proportions of the different minerals present. Therefore it is the recommended method for quantitative analysis of the size fraction being examined.

The method requires a vacuum filter apparatus, such as the one provided by the Millipore™ Corporation. The apparatus consists of a side-necked vacuum flask and a funnel reservoir clamped to a flat porous glass base. The filter separates the two pieces of the device (Fig. 6.2). The Millipore™

apparatus is the best we have seen because the junction between the permeable glass filter and the enclosing glass funnel has been ground to a flush joint. Other filter apparatus have a distinct ridge at this point that will be impressed into any sample prepared from such a device. You don't want any device that has a raised pattern on the glass filter plug unless you like sample surfaces that resemble waffles. We use the Gelman$^{\text{TM}}$ GA-6, 0.45 µm pore, 47 mm diameter Metricel$^{\text{TM}}$ filter, although others are doubtless equally useful. Insert the filter, add the suspension, and apply the vacuum.

We presume at this point that the application is quantitative analysis, so no particle-size segregation is acceptable. In other words, you cannot extend the filtration period beyond about 3 min or else the surface of the filter cake will be enriched in fine particles. Use the correction method for measuring μ^* described in Chapter 9 if, after this period, there is insufficient material on the filter to provide infinite thickness (the usual case). An alternative method is to stir the suspension in the funnel; stir just enough so that settling velocities are overcome. This keeps the suspension homogeneous. Then suction time can be as long as necessary to get a layer that is thick enough. To finish, be certain that liquid is still present in the funnel and then turn off the vacuum and bring the vacuum flask up to room pressure. This sequence is necessary because if air is drawn through the filter cake, it probably will not adhere properly to the glass substrate. Drain the excess suspension from the filter funnel, remove the wet filter, invert it, and carefully lay it face down on a glass substrate. Do this just as you would apply a decal onto an automobile windshield (Fig. 6.3). Start at one end and lower the filter surface sequentially in a smooth motion. Then invert the sample and examine the clay film through the glass. If there are any air pockets, which show as reflective (silver) areas, the sample is useless because it will fail to adhere to the glass at those points. You will have to try again and do better this time. In the original method, Drever (1973) recommends pressing the sample onto the glass by means of a roller. We do not use this procedure because it may produce a non-Gaussian particle orientation, which in turn produces an unknowable Lorentz factor.

Drying the sample-filter-glass slide combination correctly is crucial to a successful preparation. We place it in a oven at 50°C and check it frequently. It usually requires about 3 or 4 min to reach the critical point at which the filter must be stripped off. That point is reached when the filter surface shows opaque and translucent streaks. If you strip the filter too soon, the clay film may come off with the filter. If you wait so long that the filter surface is opaque and white, the filter is so brittle that you won't be able to remove it. But if you catch the filter with the correct moisture content and place the tip of your tongue precisely on the point of your upper, right canine tooth, you will have a well-oriented, smooth, and uniformly thick clay film centered on the glass slide.

Some may question the need to invert the clay film by transference from the filter to a different substrate, for it is this step that requires the most skill and causes most of the sample preparation failures. But it is the crucial one for good quantitative procedures because other methods (except for the smear method) invariably lead to particle-size segregations within the sample. Think of it this way. At first, flow rates through the filter are high because the filter has not yet been clogged with the sample. So long as the vertical movement of the liquid is fast compared with the settling rate of the coarsest particles, there can be no significant particle-size segregation. This condition applies for the sample portion nearest to the filter face. When the filter is inverted, the most particle-size-representative portion of the sample is presented to the X-ray beam, and the least representative (enriched in the finest sizes) becomes the bottom. Due to the logarithmic absorption of the beam in the sample, the surface of the inverted clay mineral film produces a disproportionately large proportion of the diffraction intensity, with the result that errors due to particle-size segregation are minimized.

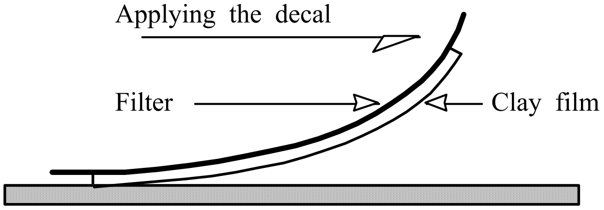

Fig. 6.3. Application of a wet clay film onto a glass substrate.

As mentioned before, cation exchange or saturation can be accomplished relatively simply with the Millipore™ method. When the sample has reached sufficient thickness, remove the vacuum, add a few milliliters of the exchange solution, draw it through the clay cake, and follow it with a few milliliters of distilled water. This procedure leaves the clay minerals homoionic and sufficiently salt-free for X-ray diffraction analysis. Cation saturation can be eliminated if the sample is known to be free of expandable clay minerals.

The Centrifuged Porous Plate Method

The porous plate method produces thick aggregates that have very high degrees of preferred orientation and therefore produce excellent diffraction patterns. Indeed, the best-prepared tiles produce integrated diffraction intensities comparable to those from single crystals. We have studied examples of illite/smectite and illite that give measurable intensities for $00l$ peaks out to the limit of 130° 2θ, corresponding to the illite 00,12. Unfortunately, the method suffers from particle-size segregation effects and is therefore useless for quantitative analysis. It is too skill intensive and too time consuming for routine qualitative studies, but it is the one indicated for crystal structure studies or the detailed characterization of pure clay minerals. It requires unglazed ceramic tile that has been cut into rectangles approximately 2.5 by 4.5 cm to serve as sample substrates.

You or your machine shop must prepare a sample holder assembly similar to the one in Fig. 6.4. Aluminum is a suitable fabrication material, although others are acceptable. The porous plate is faced with rubber gaskets above and below. Insert it into the assembly and tighten the screws to provide a liquid-tight seal for the whole apparatus. Put a pair of these assemblies into centrifuge cups on opposite pans of a laboratory balance, and add clay suspensions to each cup until they balance. Screw a threaded rod into the tapped hole in the top of each assembly to facilitate transfer to the centrifuge cup. Centrifuge the samples for about 10 min at 2,000 rpm. Remove the sample assemblies, decant any supernatant liquid, disassemble the apparatus, and dry the porous plate preparations in an oven below 100°C. Higher temperatures are undesirable because boiling of the pore fluids will destroy the uniformity of the aggregate. Many things can go wrong during this procedure, and we suggest that you practice on a suitable standard clay before you apply it to a valuable sample that may be in short supply.

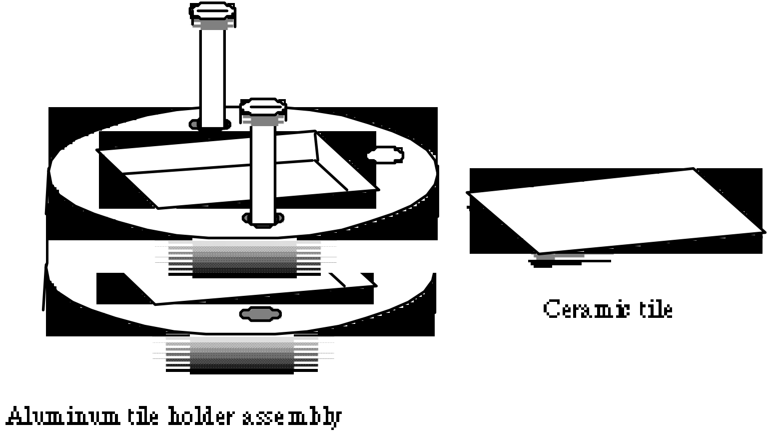

Fig. 6.4. Aluminum assembly for holding porous plates.

A strong advantage of this method lies in the character of the porous tile substrate. After the sample is prepared, dried, and analyzed, it can be carefully replaced in the centrifuge plate assembly, and the exchangeable cation can be changed by means of the simple expedient of centrifuging a small amount of a chloride solution through the clay film and porous plate. In addition, the ceramic tile is unaffected by high temperatures, so the substrate is an ideal one for the various heat treatments that can be essential for correct identification of some clay minerals, and clay films on ceramic tiles do not lose glycol as readily as films on glass slides do because the porous tile acts as a reservoir for glycol retention.

Dealing with Curlers or Peelers

The most vexing problem in sample preparation is the occasional encounter with a "peeler." Some materials, no matter how they are treated, shrink on drying with the result that the sample curls, breaks up, and separates from the substrate. This behavior is usually due to (1) the presence of angular grains, such as quartz, that destroy the preferred orientation of the clay mineral crystallites; (2) partial flocculation of the clay minerals during sample preparation, which also destroys preferred orientation; (3) a large particle-size range with the finest material on the surface of the clay film, leading to differential shrinkage during drying; and (4) the presence of gelatinous, hydrated colloidal material, such as some hydrated iron hydroxides and organic matter in soils. Samples that produce peelers often cannot be dealt with in any fashion that will produce good 00*l* diffraction patterns. The best that you can do is collect the material by ultracentrifugation as a first step. Then drain off the supernatant water. Using a spatula, smear the clay paste onto a dry unglazed ceramic tile. Capillary forces will draw the pore fluids into the plate quickly, leaving a moist but not wet clay film. Run this sample on the diffractometer before it dries and curls. If ethylene glycol solvation is required, stir into the wet paste some glycol before the sample is smeared onto the tile. This procedure will produce poor diffraction patterns, but they are better than nothing. For some reason, some expandable clay minerals do not respond normally to glycol solvation performed by this method, so be wary when you interpret the diffraction pattern.

MAKING THE RANDOM POWDER MOUNT

In the preceding sections we have described and discussed procedures for maximizing the preferred orientation of the flake morphologies of clay minerals. For three-dimensional diffraction studies you will need to see all (*hkl*) reflections of the mineral or minerals present, with the correct relative intensities of their reflections, which requires perfectly random orientation of the particles of the sample. However, the platy character of the clay minerals makes random orientation difficult to achieve. Most crystals break or cleave more readily along some planes than others. When packed as a powder, orientation of individual grains tends to be governed by the juxtaposition of faces formed by these preferential breakages, and this process works against the production of a randomly oriented aggregate. Sample preparations that have no preferred orientation are crucial for quantitative analyses of mixtures of clay and nonclay minerals and for interpretations of diffraction patterns of clay mineral polytypes (Chap. 10). Various procedures for achieving random orientation of the sample powder, some elaborate, some simple, have been suggested. Spray drying holds great promise, but to date a suitable commercial apparatus for this has not become widely available (Smith et al., 1979). Brown and Brindley (1980, p. 310), Brindley (1980, pp. 426-27), and

Bish and Reynolds (1989) review a number of other methods. A back-loading procedure was described in an earlier edition of this book, but recently we have had better results with side-loading.

One of the most important steps is to start with a powder of small and uniform particle size, 5 to 10 µm. Perhaps the easiest way to grasp the importance of particle size is to think about particle statistics. Picture two particles mounted on a slide that you're going to present to the X-ray beam. As the diffractometer moves through the arc in search of signals, the two particles may be oriented so that they will diffract from one, or even two, of their many spacings. However, two particles cannot, under any circumstances, provide a diffraction signal for all the spacings they contain. If you increase the number of particles to 100, your chances of getting diffraction from most of the spacings is much improved. However, the chances that the spacings will yield diffraction signals in proportion to the real distribution of spacings are pretty slim. For any sort of quantitative determination, precise, i.e., repeatable, relative intensities are very important. This sort of relative intensity will come only from the averaging of diffraction from millions to billions of individual crystal fragments. If you had a sample of quartz particles packed into a holder and its volume was 25 mm^3, and the particles were 10 µm cubes, how many particles would you have? How does about 25 million sound? And what if you were to double the size to 20 µm, or halve the size of the particles to 5 µm, how many would you have?

Klug and Alexander (1974, pp. 365-68) offered an example of the importance of particle size. Using powdered quartz, they did ten replicate analyses on each of four particle-size ranges and found these mean percentage deviations in peak intensity: ±18.2% for 15-20 µm powder; ±10.1% for 5-50 µm powder; ±2.1% for 5-15 µm powder; and ±1.2% for <5 µm powder. Hand grinding does not yield particles much less than 40 µm. You can see that using the material that passes through a 325-mesh screen, i.e., <44 µm, as is so often recommended, is going to give you poor precision. Small particles, and we recommend trying to get the narrowest possible size range centered at 5 µm, give you two other distinct advantages in addition to improved precision: (1) They decrease or eliminate the preferential absorption of the X-ray beam by minerals with heavy elements in them, a phenomenon called microabsorption (see Bish and Reynolds, 1989, p. 82); and (2) for whole rock samples, the nonclay minerals with good cleavage are far less likely to preferentially orient. You will need to use some kind of grinding device and grind your sample in water or alcohol. We like the McCrone™ mill.

The relative intensities of the set of peaks from a random mount for a given mineral are used in the Joint Committee on Powder Diffraction Standards (JCPDS) *Powder Diffraction File* system of identification, so if you wish to compare relative intensities for a series of peaks from one mineral, you will need a randomly oriented aggregate. Relative intensity is one of two criteria used to classify all diffraction patterns, the other being the size of the spacings. The thousands (probably 35,000 by now) of cards in the JCPDS file are subdivided into Hanawalt groups according to a range of spacing sizes responsible for the most intense peak. Within each Hanawalt group, compounds are arranged according to the size of the spacing responsible for the second most intense peak. This system was established by two papers, Hanawalt and Rinn (1936) and Hanawalt, Rinn, and Frevel (1938). Both of these historically important papers have been reprinted in the journal *Powder Diffraction*, Vol. 1, No, 1, March 1986. The Committee and the International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081-2389, publish in book form the minerals selected from all the compounds they catalog. The 1993 edition, *Mineral Powder Diffraction File Databook, Sets 1-42*, catalogs 3800 data cards representing 3200 minerals. An appendix has X-ray diffraction tracings of typical clay minerals because recognition of the clay minerals is often a "gestalt" process, i.e., the pattern just looks, in its entirety, like such-and-such clay mineral.

Deviation from perfect randomness can be tolerated for some problems. For others, it cannot. We recommend two methods, one for every day problems (side-loading of the sample holder) and one for those instances when as little deviation as possible must be achieved. The latter requires freeze drying and side loading.

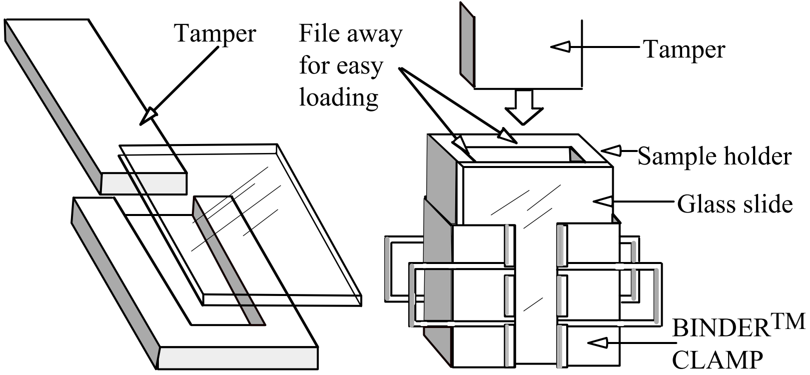

Fig. 6.5. Sample holder and accessories for side-loading method for a random powder mount.

Everyday random powder packs

For the every-day method, an example of the simple type of device used in most labs for side-loading is shown in Fig. 6.5. It is an advantage to have the side of the glass slide frosted, or rough on a microscopic scale, next to the powder. This helps prevent particles from orienting against the plane of the glass. The glass is held to the sample holder by a pair of Binder™ clips. These serve as legs so the assemble can stand upright. Different labs use different funnel-like devices to guide the powder into the holder. We have one machined from an aluminum cylinder that has a rectangular notch cut into the bottom that just fits over the top of the assembly shown in Fig. 6.5, and has a funnel machined into the top. It takes judgment and some practice to apply the proper amount of packing or tamping of the powder to fit it snugly between the glass plate and the bottom of the sample holder for enough adhesion that it won't fall out. If packed too hard, orientation will be introduced. Or, the tamping pressure may store some strain in the aggregate, so when the glass slide is removed, the surface of the powder may bulge upward, making it impossible to align a flat sample surface with the goniometer axis. If the powder is not packed enough, it may fall out of the holder. This method is appropriate for whole samples powdered to an appropriate grain size (as discussed above), or for size fractions of a sample.

Freeze-dried random powder packs

For circumstances in which deviation from perfect randomness must be minimized, freeze-dried clay suspensions that are side-loaded into specially designed sample holders (Fig. 6.5) have given us our best results. Freeze-drying equipment is readily available commercially. You will need a shell freezer which rotates rapidly in a freezing bath and a cylindrical vessel that contains the dispersed sample. This step in the process lines a cylindrical vessel with a concentric layer of ice that has the high specific surface area necessary for efficient evaporation in the freeze drier. A good place to start is with 200 mL of suspension containing 200 to 500 mg of sample. The frozen suspension is then attached to the freeze drier and pumped to dryness, which takes overnight. This may seem like a long time, but you can dry perhaps six samples at once, and drying in an oven is not a quick operation either.

The freeze-dried powder has an extremely low density and cannot be handled unless it is somewhat compacted. We attach a rubber stopper to a glass rod and whip the powder much like you whip eggs to scramble them or make an omelette. If your lab is in a dry climate, or if you work in winter when the relative humidity is low, an alpha-emitting probe is useful to combat the static electricity that makes the powder very mobile. (**N.B.** Remember our caution from Box 2.2, p. 29, that alpha particles do about 20 times as much damage to tissue as X-ray photons.) We use the same sample-holding assemblage as for the everyday random powder pack, as shown in Fig. 6.5. The procedure rarely produces a sample that is dense enough to produce good diffraction tracings without packing, so careful tamping is more important for freeze-dried samples than for those simply powdered. The carefully packed sample may be run in a chamber in which the atmosphere can be controlled. We stream tank N_2 through the chamber to prevent heated samples from rehydrating. (Chambers can be made relatively easily. We have seen pieces of 6 in. diameter Plexiglas™ tube, clear Nalgene™ buckets cut in half, etc., work effectively as chambers.)

The area of the sample well in the holder that will be exposed to the X-ray beam depends on the slit system you use and the lowest diffraction angles anticipated. The lowest-angle clay mineral *hkl* peaks are at about 19° 2θ ($CuK\alpha$), and for a one-degree divergence slit, the sample length should be about 2.5 cm for typical (20 cm) goniometer radii; this is shorter than that necessary for diffraction tracings that include the first-order peaks of the clay minerals. The depth should be 1 mm or greater for infinite sample thickness (CuKα) at diffraction angles up to 70°, which are the highest you will probably record. A full sample holder will require between 150 and 300 mg of powder, depending on how tightly it is compacted.

This all takes some practice, but we have found that it often yields aggregates that, judging by agreement between experimental and calculated diffraction patterns, are almost perfectly randomly oriented.

There are a few pluses and minuses. The sample suspensions must be washed free of salt because all the dissolved ions in the 200 mL of solution will be concentrated as crystals in a few hundred milligrams of powder. The method works poorly on Na-saturated expandable minerals, so Ca or Mg saturation should be routine. Pure Wyoming bentonite has so far resisted all our attempts to make a random powder--it always forms a leathery film of oriented crystals. But there is a way to deal with that is better than nothing. Cut the film into strips with scissors, roll them into tiny tubes, and put them in epoxy. The hardened epoxy surface can be ground flat to make a good sample surface. Of course, the diffraction pattern will contain the very broad maxima due to the epoxy, but that is easily dealt with by running a pattern from the pure epoxy, and then by means of a simple computer program, subtracting that from the clay mineral/epoxy data file.

An important plus is that the freeze-dried powder is very easily dispersed into suspension. Add water, a quick zap with the ultrasonic probe, and you have a stable dispersion suitable for making slides of oriented aggregates. Freeze-dried powders are in a good form for storage in your sample or standard library because they are easily studied as random powders or oriented aggregates, and need no further preparation for other studies such as chemical and isotope analyses.

ETHYLENE GLYCOL SOLVATION

Most clay mineral samples should be analyzed in an air-dried condition, an ethylene glycol-solvated condition, and after enough heating to collapse any expandable layers. If you are experienced and already know something about the mineralogy of the samples in a suite, you may elect to eliminate one or the other of these analyses, but that election should only rarely eliminate the ethylene glycol analysis because, otherwise, you risk a serious misidentification. The diagnostic adsorption of ethylene glycol by smectite was discovered by Bradley (1945).

The best general method of ethylene glycol solvation is to expose the sample to the vapor of the reagent for at least 8 h at 60°C. Use a large desiccator or a Pyrex casserole dish with lid, add 100 to 200 mL of ethylene glycol, insert some sort of a platform similar to the ones used in desiccators, and put the setup in an oven at 60°C. You will have to dedicate one oven permanently for this purpose. Place sample mounts face up on the platform and do not allow them to contact the liquid glycol. Label the sample slides with a diamond marker, because ethylene glycol is a good solvent and may remove identification marks that have been made with a felt-tipped pen. An ordinary pencil works well for ceramic tiles, if those are what you are using. After solvation, analyze the samples immediately. If the clay film is on a glass substrate, you have about 1 h to complete the analysis, because, for longer times, the glycol will evaporate away sufficiently to affect the expansion of clay minerals. Good procedure requires that you scan the low-angle region first, run the complete diffraction pattern, and repeat the low-angle scan. If the two low-angle scans are identical, you are assured that there has been no significant change in the solvation state during the analysis, and there frequently is. An alternative is to rig some sort of environmental chamber around the sample and place an open dish in the chamber with a few mm of glycol and a wick in it, or pass glycol-saturated gas through the chamber while running the glycolated sample (as mentioned in the section on freeze drying). Such chambers also are required when running samples that have been heated to keep them from rehydrating. In handling large numbers of samples, you might use a large desiccator with a few cm of glycol in the bottom kept at room temperature. Samples should stay in such a desiccator for at least two days.

Novich and Martin (1983) suggested two other methods: (1) while the sample is dispersed, mix glycol in the dispersion; and (2) saturate a laboratory tissue with ethylene glycol and leave the sample mounts face down on the tissue for about 8 h. For clay minerals that solvate with difficulty, this procedure may be carried out in a closed chamber at 60°C (Whitney and Northrop, 1987).

Ethylene glycol solvation is difficult to accomplish with random powders if they contain large amounts of smectite, for the smectite swells enough to displace the powdered mineral surface above the plane of the surface of the sample holder. The best method is the vapor technique described before. Simply place the random powder mount in an ethylene glycol atmosphere at 60°C for 12 h. The surface may swell above the surface of the aluminum plate and require pressing with a spatula. Unfortunately, such pressing will introduce some orientation of the clay minerals at the surface, but you will have a preparation that is sufficiently randomly oriented to serve well for the identification of the various clay mineral polytypes or to provide good 060 intensities.

There are several other special sample preparation techniques for reducing background, for enhancing peak intensities, and for dealing with very small amounts of sample. These are thoroughly covered by Bish and Reynolds (1989, pp. 93ff).

FINAL NOTE

Ś rodoń and Eberl (1980) made a plea in which we concur. When you write a report or submit a paper for publication, include the X-ray diffraction tracings in the form in which they came off of the diffractometer, not after they have been smoothed by a draftsperson. Such traces are data that can be reinterpreted in the future as more is learned about peak shapes, relative intensities, and other, as yet unrecognized features. Ś rodoń and Eberl have some other good suggestions, too, that you may want to look at.

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