

Analysis of Clays and Soils by XRD

I. Introduction

Proper sample preparation is one of the most important requirements in the analysis of powder samples by X-ray diffraction (XRD). This statement is especially true for soils and clays that contain finely divided colloids, which are poor reflectors of x-rays, as well as other types of materials such as iron oxide coatings and organic materials that make characterization by XRD more difficult. Sample preparation includes not only the right sample treatments to remove undesirable substances, but also appropriate techniques to obtain desirable particle size, orientation, thickness, etc. Several excellent books are available that deal with appropriate sample preparation techniques for clays and soils (Jackson 1979, Brindley and Brown 1980, Moore and Reynolds 1989, Bish 1992, Iyengar 1997)

II. Sample preparation

1: Drying:

Soils and clays are dried before they are ground and separated into various particle sizes.

2: Grinding:

Analysis of powders by XRD requires that they be extremely fine grained to achieve good signal-to noise ratio (and avoid fluctuation in intensity), avoid spottiness and minimize preferred orientation. Reduction of powders to fine particles also insures enough particle participation in the diffraction process. The recommended size range is around 1-5 μM (Klug and Alexander 1974, Cullity 1978, Brindley, 1980), especially if quantification of various phases is desired. For routine qualitative evaluation of mineral components, the samples are usually ground to pass through a 325 mesh sieve (45 μM). Grinding is accomplished either through hand grinding or in a mechanical grinder. The effects of excessive grinding include lattice distortion and possible formation of an amorphous layer (Beilby layer) outside the grains.

III. Pretreatments:

The ground soil and clay sample may require certain pre-treatments before they can be analyzed by XRD. This step is to remove undesirable coatings and cements, either to improve the diffraction characteristics of the sample or to promote dispersion during size fractionation. Relatively pure clay samples may not require any of these pre-treatments. Soil samples, on the other hand, will require most of these treatments. The pre-treatment can be grouped into the following:

Removal of soluble salts and carbonaceous cements

Removal of organic matter

Removal of sesquioxide coatings

Removal of oil contamination:

IV: Size separation:

Size ranges: Minerals occur in various size ranges. The USDA system of size classification is shown below:

Very Coarse Sand	2.00 - 1.00 mm
Coarse Sand	1.00 - 0.50
Medium Sand	0.50 - 0.25
Fine Sand	0.25 - 0.10
Very Fine Sand	0.10 - 0.05
Coarse Silt	0.05 - 0.005
Fine Silt	0.005 - 0.002
Clay	< 0.002

It is often necessary to fractionate soil and clay samples to one of these size ranges to elucidate and quantify specific mineral species present.

Coarse size fractions are obtained either by wet or dry sieving through a standard set of sieves. The fine fractions, starting from very fine sand, are separated by a combination of wet sieving and gravity or centrifugal sedimentation.

Optimum size: What is the optimum size range to study clay minerals?. This choice depends on the types of clay mineral present. Generally, samples are separated to less than 2 or 5 micrometers to examine various clay minerals. Figure 1 shows the XRD patterns for four different size fine fractions from a sandstone rock. In this sample, kaolinite and mica was present even in 5 -50 μM range, and the detectability of smectite increased with a decrease in size range examined.

Separation Techniques: The dispersed sample is wet sieved through 325 mesh sieve (~ 50 μM) to separate very fine sand. The suspension or centrifuge method is then used to separate other fine (clay and silt) fractions either by gravity sedimentation or centrifugation. The settling times required to separate various size ranges are based on Stokes' law and are presented in extensive nomographs and tables by Jackson (1979).

V. Slide preparation and Analysis:

Two important criteria to keep in mind while preparing slides for XRD analysis are the amount of sample and orientation of crystallites.

Amount of sample: The amount of sample should be enough to produce an "infinitely" thick sample (Brindley 1980, Moore and Reynolds 1989). Infinitely thick sample is defined as that thickness of the sample that yields optimum diffracted intensity. Increasing its thickness (by adding more sample) will result in a negligible increase in diffracted intensity.

Orientation of crystallites: The type of mounts normally employed are dictated by the nature of crystallite orientation required and can be grouped into random or oriented mounts.

a: Random Mounts:

Random mounts are preferred when mineralogy of a whole soil or clay is required. In this type of mount, particles are packed to assume different orientations and insure reflections from various hkl planes. Types of random mounts available include: Spray drying, Front-loading, Rear-loading, Side-loading or drifting, and Vaseline coated. These methods are described elsewhere.

b: Oriented Mounts:

Several methods are available to prepare oriented mounts. Some of the methods available include: Slurry Mount, Centrifuge on tile, Suction on Millipore

Ion Saturation: Why ion saturation? The (001) spacing from an oriented clay depends on the type of cations in the interlayer region. In nature, clays and soils are saturated with various types of cations including Na^+ , Ca^{2+} , Mg^{2+} , K^+ . It is easier, for proper identification, to make them monoionic.

Glycolation: For identification of expandable clay minerals, several organic reagents are used for intercalation. The most commonly used solvents are ethylene glycol (EG) and glycerol.

Heat Treatment: Clay mounts on ceramic substrates, Si crystals, silver membranes or certain glass substrates can be heated to various temperatures for the identification of mineral species. The temperatures normally used are 120 - 150 C (overnight), 300 C (4 to 5 hrs) and 550 C (4 to 5 hrs).

VI. References:

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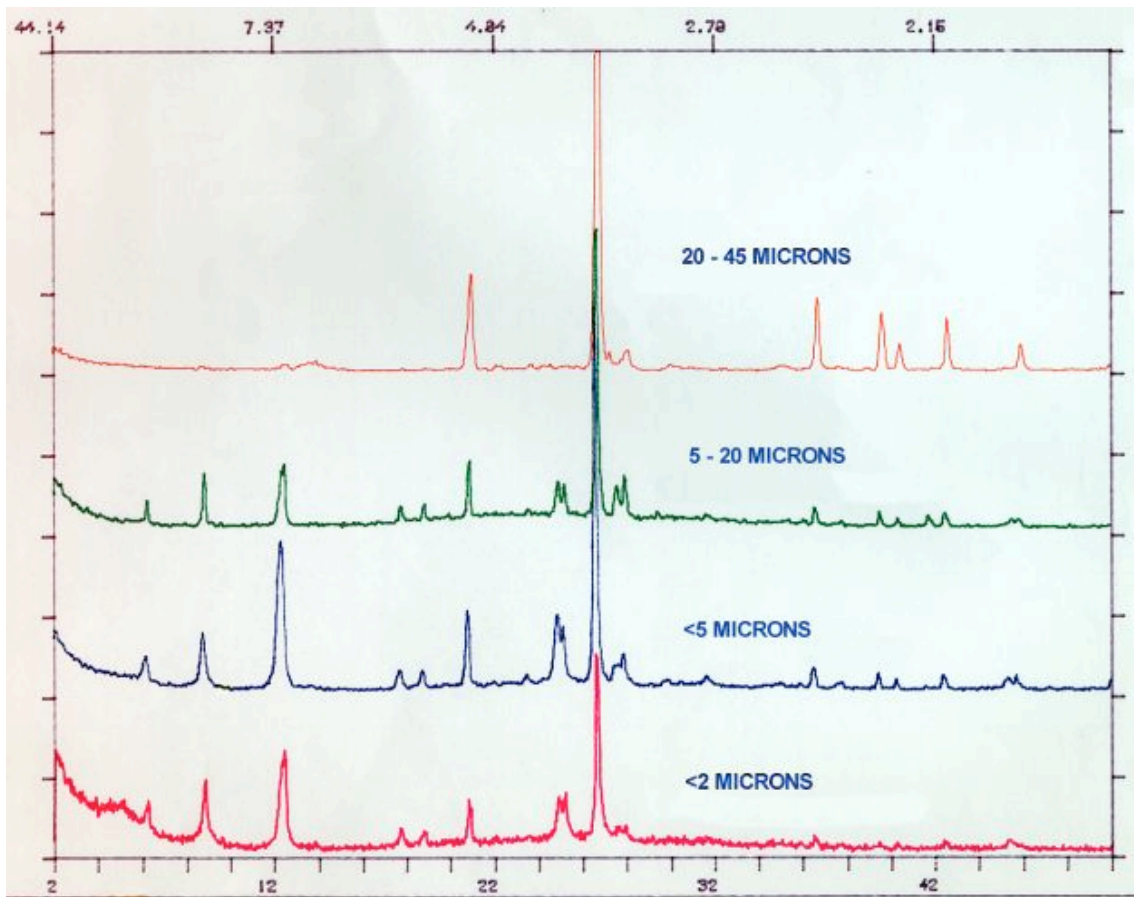


Figure 1. Composit view of the various size fractionations performed on sample 2555.6.