APPENDIX 1

Target: CuKα; Filter: Ni; Range 400cps for clay fractions and 100cps for bulk mineralogical analysis; Goniometer speed: 1° of 20 angle per minute; Scan angle: 2° to 30° for clays, and 2° to 70° for bulk samples. The clay fractions were separated by International Pippette Method (Jackson, 1958), and separately run on X-ray diffractometer as untreated, glycol treated (12 hours at 65°C) and heat treated (25°C, 110°C, 300°C and 550°C) (Jackson, 1958). The minerals and their proportions were determined from the diffractograms after Griffin (1971) and Carrol (1974).

X-RAY DIFFRACTION TECHNIQUES FOR MINERAL IDENTIFICATION AND MINERALOGICAL COMPOSITION

PREPARATION OF SAMPLES

To ensure detection of mineral species in clay sample by X-ray diffraction analysis, it is distinctly advantageous to concentrate the individual species as much as possible. It is possible by fractionation of samples according to particle size.

REMOVAL OF FLOCCULATING AND CEMENTING AGENTS

Common cementing agents in soils include alkaline-earth carbonates, organic matter, oxides and hydroxides of iron, oxides of manganese, and amorphous silica and alumina. Removal of these materials is of advantage not only from the stand-point of obtaining efficient dispersion of soil particles prior to size fractionation, but also from the stand-point of improving X-ray diffraction quality from segregated samples. Unless removed, these cementing agents may (1) prevent effective dispersion and ultimate segregation of minerals particles, (2) act as diluents, thus reducing diffraction intensity of crystalline species present, (3) prevent efficient orientation of layer-silicate species during preparation of an oriented aggregate specimen, (4) cause attenuation of the
primary X-ray beam, and (5) cause an increase in the general level of scatter of X-rays from the sample being analyzed.

SATURATION OF EXCHANGE COMPLEX

Principles: Since different cations may retain different amounts of water of hydration (Barshad, 1950; Norrish, 1954; Mielenz et al; 1955), it is imperative that a day sample prepared for diffraction analysis be homoionic to ensure that expansion as a result of hydration will be uniform within all crystals of a species. Also, since clay samples are commonly analyzed after drying in air, it is advisable to exchange-saturate the clay with a cation which will minimize changes in interlayer water adsorption due to fluctuation in relative humidity. Calcium (Ca), which allows relatively uniform interlayer adsorption of water by expandable layer-silicates, and potassium (K), which specifically restricts interlayer adsorption of water by vermiculite, are most commonly used for exchange saturation (Hellman et al 1943; Mac Ewan, 1946; Walker, 1957).

Formation of a stable, two-layer water complex between plates of air-dried. Ca saturated members of the montmorillonite and vermiculite series results in an interatomic spacing of approximately 14 Å, between (001) planes. This spacing which results from expansion of the layers, allows the distinction of these species form the nonexpanding 2:1 layer-silicates, the interatomic spacing of which is approximately 10 Å.

Detection of nonexpendable 14 Å. Chlorites (2:2 layer-silicates) which may be present requires further diagnostic tests for positive differentiation from 14 Å. vermiculite. Vermiculite will collapse to an essentially nonexpanded structure (10 Å) when saturated with K (Barshad, 1948), whereas chlorites will be unaffected. The difference in behavior of these species when saturated with K is utilized as a means for their differentiation.

Rich and Obenshain (1955), Tamura (1955), and Klages and White (1957) have found that some soil vermiculites contain nonexchangeable interlayer aluminum (as a hydroxy complex) which inhibits lattice contraction on saturation with K. Heating a K-
saturated sample at 500°C. For 2-hours will destroy the hydroxy complex and permit contraction of the vermiculite layers. The heat treatment will not affect chlorite.

As many as four K-saturated samples and two Ca-saturated samples may be required for the complete succession of analysis, depending upon the mineral species present and the manner of presentation of the sample to the X-ray equipment. The procedure for exchange saturation with Ca or K is the same for all preparations regardless of subsequent treatments. It is usually convenient to prepare sufficient Ca- and K-saturated samples to allow the maximum number of analyses that may be necessary.

METHOD

REAGENTS

1. Calcium chloride IN (CaCl₂)
2. Methanol, 50 % and 95 %.
3. Potassium chloride (KCl), IN.

PROCEDURE

To saturate the clay with Ca, transfer an aliquot of dispersed clay suspension containing approximately 25 mg. of clay in to a centrifuge tube. Add sufficient 1N CaCl₂, centrifuge the tube for 5 minutes at 1,500 revolution per minute (rpm), and decant and discard the clear supernatant liquid. Complete the exchange saturation by washing the sample four times with 1N CaCl₂. To affect each washing, add approximately 10 ml of salt solution, mix the suspension thoroughly, centrifuge the suspension, and decant the supernatant liquid. After exchange saturation is complete, remove excess salts from the sample by washing (centrifugation and decantation) once with distilled water and once with 50 % methanol and 95% methanol.

To saturate a sample of clay with K, transfer an aliquot of dispersed clay suspension containing approximately 25 mg. of clay to a 15-ml centrifuge tube, Add enough 1N KCl to the suspension to flocculate the clay. Centrifuge the suspension, and discard the supernatant solution. Wash the sample four times (centrifugation and decantation) with 1N KCl to complete saturation of the clay with K. Remove excess
salts from the sample by washing once with distilled water and with 50% and 95% methanol.

**SOLVATION WITH GLYCEROL**

**METHOD**

Preparation of a glycerol-solvated random powder sample

**REAGENTS**

1. Benzene,
2. Glycerol,
3. Benzene-ethanol, 10 to 1 by volume and 200 to 1 by volume.
4. Benzene-ethanol-glycerol, 1,000 to 100 to 4.5 by volume.

**PROCEDURE**

To prepare a glycerol-solvated, random powder sample, add 10 ml. of 10-to-1 benzene-ethanol to a Ca-saturated sample. Mix the suspension thoroughly, centrifuge it for 5 minutes at 1,500 rpm, and decant the supernatant liquid. Repeat the benzene-ethanol washing once. Wash the sample three times with 10 ml portions of the ternary mixture of benzene, ethanol, and glycerol to effect solvation the clay with glycerol. Wash the sample once with 200-to-1 benzene-ethanol solution to remove most of the excess glycerol. Resuspend the sample in benzene and transfer the mixture to a large watchglass. After evaporation of the benzene, the sample is ready for analysis as a Ca-saturated, glycerol-solvated, random-powder sample.

To prepare a glycerol-solvated, oriented-aggregate sample, add approximately 2 ml of distilled water and 2 drops of glycerol to a Ca-saturated sample as described above. Thoroughly mix the suspension to ensure complete dispersion. The sample is ready for mounting as an oriented aggregate.

**MOUNTING**

**WEDGE METHOD FOR RANDOM ORIENTATION**

Powder samples are frequently mounted in a specially designed metal wedge (Jeffries and Jackson, 1949). To form the mount, place a small quantity of sample on a
clean glass slide, and gently push it in to the recess of the wedge with a spatula or with the edge of another glass slide. Carefully smooth the surface of the mounted sample, so that it forms a sharp edge flush with the tip of the wedge.

GLASS-PLATE METHOD FOR ORIENTED AGGREGATES

Oriented aggregate specimens may be formed directly from Ca-saturated, K-saturated, Ca-saturated, glycerol-solvated samples as prepared above.

Add sufficient water to the sample (or samples) to make a suspension of approximately 2-ml volume. Thoroughly mix the suspension to ensure complete dispersion. Extract the suspension with a pipette, and carefully transfer it to a glass microscope slide (2.6 by 4.6 cm) resting on a level surface. Add as much suspension to the slide as can be held by film tension. The total amount of clay per slide should be between about 15 and 25 mg. Allow the suspension to dry completely on the slide before the sample is analysed.

X-RAY EXAMINATION OF SAMPLES

PROCEDURE

Clay samples prepared for analysis should be examined in the following order for most efficient identification and differentiation of species: (1) Ca-saturated, air-dried sample; (2) Ca-saturated, 60°glycerol-solvated sample (3) K-saturated, heated sample (25° C, 110°C, 300°C and 550°C.).

EXAMINATION WITH DIRECT-RECORDING SPECTROMETER

Place a sample in the sample holder provided on the instrument, and position the Goniometer to start its angular scan. The practical lower limit for most analyses for 2θ is two degrees. The upper limit for 2θ is dictated by the geometry of the Goniometer system (maximum allowable is 180°) and the mineral assemblage in the sample. Start the Goniometer in synchronism with the chart recorder, and scan through the desired angular range.