STATE OF CALIFORNIA
HIGHWAY TRANSPORTATION AGENCY
DEPARTMENT OF PUBLIC WORKS
DIVISION OF HIGHWAYS

PROGRESS REPORT

# IDENTIFICATION OF SOIL MINERALS BY X-RAY DIFFRACTION

64-10

MATERIALS & RESEARCH DEPARTMENT

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State of California
Department of Public Works
Division of Highways
Materials and Research Department

December 15, 1964

Project W.O. R-23521

Mr. J. L. Beaton
Materials and Research Engineer
Division of Highways
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Dear Sir:

Submitted for your consideration is:

PROGRESS REPORT

on

IDENTIFICATION OF SOIL MINERALS

BY X-RAY DIFFRACTION

Study made by ..... Foundation Section
Under general direction of ..... Travis Smith
Work supervised by ..... M. L. McCauley
Lab work and report by ..... P. M. Adams

Very truly yours,

Travis Smith

Travis Smith
Assistant Materials and
Research Engineer - Foundation

Attach.

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## SUMMARY

This research project, utilizing X-ray diffraction techniques, was initially established to develop a routine procedure for identification of the common minerals found in soils, especially clay minerals. The project has been broadened to include identification of minerals and their altered products found in aggregate and rock. In the future the emphasis will be placed on developing routine quantitative procedures for the types of samples mentioned above.

To date the following has been accomplished:

(1) A routine procedure for identifying minerals has been developed. A 5-gram briquette is prepared and scanned using an X-ray diffraction unit. For clays the briquette received two auxiliary treatments - glycerine solvation and heating. The procedure requires 2 hours per sample. Mineral concentrations as low as 5% can usually be detected.

(2) A study of the X-ray machine variables was conducted. This resulted in finding how to gain the maximum intensity from the General Electric X-RD5 X-ray unit and yet retain satisfactory resolution of the diffraction peaks.

(3) Standard charts have been prepared for 15 common minerals to aid in semiquantitative work. (These charts are not included in this report.)

(4) A knowledge of the many problems involved in quantitative work has been gained.

To finish this project, routine quantitative procedures need to be developed. The following areas will be covered:

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(1) Solve the problem of reproducibility in sample preparation. This is essential before quantitative work can proceed. Reduction of the maximum particle size to 20 micron will help considerably.

(2) Evaluate the effect of variations in crystallinity and chemical composition of a mineral on its diffracted intensity.

(3) Develop a method of determining the mass absorption value for a sample.

## INTRODUCTION AND PURPOSE

In March, 1963, a study was initiated to develop a procedure for identifying both clay and non-clay minerals in soils by using X-ray diffraction. Previously this department examined soils using differential thermal analysis and microscopic techniques. However, these techniques need to be supplemented by X-ray diffraction information especially in the area of clays. Without X-ray information often the particular type of clay can not be identified or the presence of a clay mineral is missed completely. The accurate knowledge of the minerals present in a soil or an aggregate has several important applications. For example, mineral composition affects the physical properties of a material. Also, the potential for further degradation of a material may be indicated.

The purpose of this paper is to present a routine method that has been developed for identifying soil minerals by X-ray diffraction of a powder briquette. The sample preparation, X-ray machine operation, and interpretation of this method will be discussed in detail. Other topics that will be covered are:

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general background information on X-ray diffraction, quantitative procedures, other methods of sample preparation, X-ray machine variables and X-ray machine maintenance.

The purpose of discussing these latter items is so that when the project is continued the person will not need to duplicate the time-consuming work of the author. Of necessity the discussion is limited to the narrow field of soil mineral qualitative and some quantitative techniques using a General Electric XRD-5 Diffractometer.

## GENERAL INFORMATION ON X-RAY DIFFRACTION

General information on the principles of X-ray diffraction will be brief. The reader should consult "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" by Klug and Alexander if more information is desired.

X-ray diffraction is the coherent scattering or bending of X-rays when they hit a crystalline material. This bending or diffracting occurs in a predictable manner according to Bragg's Law. X-rays are electro-magnetic waves like light except X-rays have a much shorter wavelength and are of a higher energy level. X-ray diffraction will only occur with a crystalline material. Such a material has the atoms arranged in a set geometric pattern and a set spacing between each atom.

To illustrate the principle of diffraction consider a clay which has a set distance between two layers of atoms, as in Figure 1. An X-ray can be pictured as a sine wave. It will hit an atom in the top layer making an angle of $\theta$ with respect to the layer and will be diffracted at the same $\theta$ angle. This is similar to light where the angle of incidence equals the angle of re-

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flection. At one specific angle of $\theta$ an X-ray parallel to the first X-ray will hit an atom in the layer below and this diffracted wave will be <u>in phase</u> with the diffracted wave from the top layer giving twice the amplitude. However, if $\theta$ is just above or below this critical $\theta$ angle complete destructive interference will result. There will be no peak. By knowing the wavelength of the X-rays and the critical $\theta$ angle, the spacing between the two layers or d-spacing can be found from Bragg's Law. It is:

$$n\lambda = 2d \sin \theta$$

Where n is any integer
$\lambda$ is wavelength of X-rays in Angstrom units
d is d-spacing in angstrom units
$\theta$ is angle at which the X-rays hit the sample face

NOTE: One angstrom or $1A = 1 \times 10^{-10}$ meters

In the G.E. XRD-5 diffraction unit ideally all the X-rays are produced having the same $\lambda$ and are focused on a sample as parallel rays by means of mechanical slits. The same is then rotated at a constant angular velocity with respect to the X-rays hitting it. Likewise, the detector is rotated at the same angular velocity with respect to the sample to pick up any X-rays that are diffracted from the sample. The detector counts the number of X-rays much like a geiger counter. In fact, in some cases a geiger counter is used. From the detector through complicated electronic circuitry the X-ray intensity is converted into electrical pulses which are recorded on a chart. This chart moves at a constant rate of speed showing the intensity of diffracted X-rays versus the $\theta$ angle. The result is a diffraction pattern or series of peaks at various $\theta$ angles.

Each crystalline material has its own diffraction pattern. However, depending on the percentage of material present and the type of sample preparation, the relative heights of the peaks will

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change but their θ angles are usually unaffected. Most diffraction tables will list the height of peaks and their θ angles for a particular material by its d-spacing and relative intensity with the highest peak being given a value of 100.

Production of X-rays

X-rays are produced when fast-moving electrons hit a target. A high-speed electron may strike the target and displace a tightly bound electron deep in an atom near the nucleus, thereby ionizing the atom. When a certain inner shell of an atom has been ionized in this manner, an electron from an outer shell may fall into the vacant place, with the resulting emission of an X-ray characteristic of the atom or target material involved. An atom has a series of electron shells surrounding the nucleus. The number of shells and the number of electrons in each shell depends on its atomic number. However, the energy level of an electron depends primarily on what shell it is in. The shells are called K, L, M, N -- with the inner most shell being called the K shell. The energy level of an electron increases from the K to the L shell. Thus, the farther away from the nucleus the higher the energy level of the electron.

When an electron is displaced from the K shell usually an electron from the L shell will replace the lost electron but since the energy level of the L shell electron is higher than the electron it is replacing, the difference in energy must be given up. This parcel of energy is called an X-ray. The difference between the energy levels of the K and L shell electrons is constant for any one element but varies according to the atomic

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number. Thus, each element emits X-rays with a characteristic amount of energy. This energy is directly related to the wavelength of the X-ray.

X-ray Tube

Basically in an X-ray tube high speed electrons from the filament bombard the target emitting X-rays. For soil mineral identification a Coolidge type X-ray tube with a Cu target is the most useful. A schematic is shown in Figure 2. Normally a Cu diffraction tube is operated at 50 kilovolts and 16 milliamperes. The potential or voltage between the filament and target determines the maximum speed of the electrons hitting the target. The intensity of X-rays or number produced per unit time is controlled by the tube voltage, current, and filament heater voltage. The tube is evacuated in order to give the electrons a path to the target unobstructed by air molecules. The X-rays leave the tube through a window made of 10 ml beryllium foil which will allow a large percentage of X-rays to pass through unaltered.

An X-ray tube is very inefficient in that 98% of all the electrical energy supplied to it, is dissipated in the form of heat. Most of this heat is generated in the target. The target is cooled by circulating water through the core.

In practice the X-rays produced do not all have the same wavelength. The distribution of $\lambda$ versus intensity of radiation is shown in Figure 3. There are two reasons for this wide range in $\lambda$ produced. First, the L shell has two sub-shells, each with a slightly different energy level. Thus, an electron from the

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first sub-shell in the L shell may replace the displaced electron in the K shell emitting $K\alpha_1$ radiation. If, however, an electron from the second sub-shell in the L shell should replace the displaced electron, $K\alpha_2$ radiation would be emitted. The $K\alpha_2$ radiation has slightly more energy and would, therefore, have a slightly shorter wavelength. Also, it is possible for an electron from the M shell to replace the displaced K shell electron. This would cause $K\beta$ radiation and since the energy difference is considerable between the K and M shells the X-ray would have a considerably shorter wavelength. However, the chances are best that an electron with the energy level nearest the energy level of the displaced K shell electron will fill the vacancy. Thus, the relative intensity will diminish in the following order: $K\alpha_1$, $K\alpha_2$ and $K\beta$. The wavelengths of $K\alpha_1$ and $K\alpha_2$ are so close that for most practical purposes they are called $K\alpha$. Later on it will be seen that $K\beta$ radiation can be filtered out. These three intensity peaks of radiation are referred to as "characteristic radiation." This name is used because the value of $\lambda$ for each of these peaks depends on the target material.

The second reason for the wide range in wavelength is that many of the high speed electrons from the filament instead of colliding with an inner electron of an atom of the copper target may be slowed down in passing through the strong electric field near the nucleus of the atom. These electrons in slowing down give off energy in the form of X-rays. The wavelengths of the X-rays are a function of the change in speed of the electrons. This results in a continuous spectrum of wavelengths. The mini-

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mum wavelength depends on the applied voltage of the tube. This continuous band of varying wavelengths is called "white radiation."

Path of X-ray

The path of the X-rays from the X-ray tube to the detector is shown in Figure 4. From the target, X-rays are emitted in all directions. However, the only useful X-rays are those that pass through the beryllium window. The X-rays then go through a beam slit which, by its size, controls the amount of radiation that can hit the sample, the size of the beam, and allows only parallel X-rays to pass through. If there is crystalline material present in the sample the X-rays will be diffracted and received by the detector after going through a soller slit, a detector slit, and a filter. In actual operation the sample is rotated at a constant rate causing the $\theta$ angle to change. Likewise the detector, filter, soller and detector slits are rotated at a $2\theta$ angle to keep an angle of $\theta$ with respect to the sample.

The function of the soller slit is to control resolution. Resolution is the sharpness of a peak or the angular width of a peak. For example, if two diffraction peaks are displaced by a very small $\theta$ angle and the resolution is poor the two peaks will appear as one. The soller slit is a mechanical device to allow only the X-rays diffracted from the sample at $\theta \pm$ a small fraction of $\theta$ to go to the detector.

The X-rays after leaving the soller slit go to the detector slit which controls the amount of radiation that can go to the detector. Next a filter is used to remove $CuK_\beta$ radiation. Usually the filter is made from a material having an atomic

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number of one less than the target material in the X-ray tube. For $CuK_\beta$ radiation a 0.7 mil Ni filter is normally used. This sill remove 98% of the $K_\beta$ radiation. The filter works on the principle of absorption which will be discussed later.

From the filter the X-rays go to the detector or counter. There are two general types of counters. One type is a gas filled counter tube. When the X-rays hit the gas it is ionized. The amount of ionization is related to the number of incoming X-rays. This ionization creates an electrical pulse which is recorded on a chart. The second type is a counter with a crystal that will phosphoresce when hit by X-rays. A sodium iodide crystal is commonly used and will change incoming X-rays to visible light. The intensity of visible light is amplified by a photomultiplier tube and then recorded on a chart.

The electrical circuitry between the counter and the chart will be discussed later under the section entitled "X-ray Machine Variables."

Background Radiation

Even if a sample contains no crystalline material the chart recorder will make a trace similar to Figure 5. Theoretically no diffraction is taking place and thus the trace should show nothing. However, the area under this curve represents background. This background can be caused by several things. First, the electrical circuitry will produce some electrical noise. This noise shows as a constant background regardless of the $\theta$ angle or type of sample. This background is of low intensity (5 to 10 counts per second). The measure of intensity for X-rays

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is counts per second (cps). This is directly proportional to the number of X-rays received by the detector. The main peak from a strong diffractive material may be 10,000 cps or more.

At low 2 θ angles the X-rays may miss the sample entirely and go straight from the tube to the detector. This is the reason for the initial high background that may be as high as 1500 cps or more at 2 θ = 2°. This depends on the beam slit used.

Secondary fluorescence can contribute a constant background at any 2 θ angle. This occurs when the energy of the X-rays is sufficient to displace an electron in the K or L shells of an atom in the sample and cause secondary X-rays to be emitted that are characteristic of the atom. These secondary X-rays are emitted in all directions and thus will be picked up by the detector at any 2 θ angle. $CuK_{\alpha}$ radiation has sufficient energy to excite iron in a sample. This secondary fluorescence can add 200 cps or more to the background depending on the percentage of iron present.

The absorption of X-rays is an important property of a sample if quantitative results are desired. If all elements would absorb the same number of X-rays, then the intensity of diffracted X-rays would be directly proportional to the quantity of crystalline material present provided the particle size and crystallinity were the same. However, this is not the case, the absorption varies with the elements in the sample. For example, a 10% concentration of quartz may give a main peak height of 500 cps if mixed with 90% cristobalite which has the same absorption value as quartz. However, a 10% concentration of quartz would only

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give a peak height of 100 cps if mixed with 90% $Fe_2O_3$. This drop in apparent intensity results from many of the CuK$\alpha$ X-rays that would normally be diffracted by the quartz being absorbed by the iron.

The absorption coefficient "$\mu$" depends on the element, density, and the wavelength of the radiation hitting it. However, the mass absorption coefficient "$\mu/\rho$", where $\rho$ is the density, is only dependent on the element and $\lambda$. It is independent of the physical and chemical state of the material. The crystalline form or what elements it has combined with have no effect either provided the particle size is small enough. A plot of $\mu/\rho$ versus $\lambda$ for platinum, as shown in Figure 6, reveals sharp discontinuities in the absorption. These discontinuities are referred to as the critical absorption edges of an element. These absorption edges mark the point where an incoming X-ray possesses sufficient energy to eject an electron from one of the shells. X-rays with a $\lambda$ a little shorter than the absorption edge will eject an electron and are thus absorbed. However, as $\lambda$ continues to become shorter, ionization is less likely and the X-ray will simply pass on through the atom unabsorbed. For a $\lambda$ just a little longer than the absorption edge, the absorption drops off sharply because the X-rays do not possess sufficient energy to displace an electron. But as $\lambda$ becomes longer it approaches the critical absorption edge for the next outer shell. The mass absorption coefficient[1] increases with the 4th power of the atomic number of the element.

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[1] Tables of mass absorption coefficients and critical absorption edges are found in Appendix I of "X-Ray Absorption and Emission Analytical Chemistry" by H. A. Tiebhafshy, H. G. Pfeiffer, E. H. Winslow, and P. D. Zemany (1960).

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$CuK_{\alpha}$ radiation with $\lambda$ = 1.54A falls just short of the K absorption edge for iron with $\lambda$ = 1.74A. This is the reason why iron affects the background so much when using Cu radiation.

Another factor contributing to background is the effect of white radiation. White radiation contains a continuous band of wavelengths from $\lambda$ min., determined by the applied tube voltage, to $\lambda$ max. determined by what will penetrate the beryllium window, nickel filter and not be absorbed by the air before reaching the detector. Shorter wavelengths are referred to as hard radiation and the longer wavelengths as soft radiation. The intensity of white radiation is only a fraction of the characteristic radiation but since it covers the spectrum it can cause small secondary fluorescence to occur in many of the elements present in a soil sample. Also if crystalline material is present, diffraction can occur over a wide range of 2 $\theta$ values because of the range in wavelengths available. Normally with the use of a pulse height selector the effects of white radiation can be filtered out. The pulse height selector will be discussed later under the section entitled "X-ray Machine Variables."

In summary, the background results from four factors: (1) electrical noise, (2) direct X-rays at low 2 $\theta$ angles, (3) secondary fluorescence, and (4) white radiation.

## RECOMMENDED METHOD OF SAMPLE PREPARATION

A recommended method for preparation of soil samples for routine identification is presented in this section. In this method 5 grams of passing No. 200 sieve material is made into a briquette then scanned using an X-ray diffractometer. This is

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followed by two auxiliary scans, one after glycerine solvation and the other after heating to 500°C. This method is recommended because of the simplicity, relative speed, and results obtainable. It requires about 2 hours per sample including interpretation. Satisfactory identification can be obtained for most common minerals if they are present in 5% concentration. However, this method is not satisfactory for quantitative results.

Sieving and Grinding

Five grams of material passing the No. 200 sieve is required to make a briquette. This material should be air dried. If the material is wet it may be dried in a 100°C oven for 2 hours or dried in a 50°C vacuum oven for 30 min. Heating above 110°C may permanently change the material.

Normally only the passing No. 200 sieve portion of a soil is to be X-rayed. If there are clay lumps present these should be broken up by using a rubber pestle. Next, only enough soil should be placed on a 3" diameter No. 200 sieve to yield approximately 5 gm. of passing No. 200 material. This material should be sieved thoroughly to separate all the passing No. 200 material. (Shake the sieve and then empty the pan; repeat until no more material appears in the pan.) After sieving, pour the passing No. 200 material into a 2-oz. paper cup and give a quick preliminary mixing with a squared off spatula before weighing out the 5 gm for the briquette.

The above procedure is recommended to help obtain a representative sample. In sieving, the finer particles are more likely to come through first. Thus, segregation of particle size may result. Also there may be mineral segregation because many

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minerals have a certain minimum particle size. For example, feldspar and amphibole commonly occur in the coarser fractions of the passing No. 200 (74 micron opening) material while clays all pass the 2 micron. Thus, the sieved material will tend to segregate with the clay first and feldspar last. For quantitative work it is essential to obtain a representative sample.

If grinding of a sample is required there are three methods available. If the sample is relatively soft a porcelain pestle and mortar may be the best. If the sample is hard, for example, quartz, a steel pestle and mortar may be the fastest, however, iron impurities will be introduced from the mortar. If impurities cannot be tolerated a tungsten carbide ball mill can be used. For mica that is flaky and difficult to grind fine a ball mill is best.

This department has a ball mill called a Spex Mixer Mill, Cat. No. 8000 manufactured by Spex Industries, Inc. To operate this mill fill the tungsten carbide vial 1/3 full of material and add 2 one-quarter inch diameter tungsten carbide balls. (NOTE: this material must be broken up by hand to passing a 1/8" sieve before placing in the vial.) Grind for 10 minutes, sieve, return the material retained on the No. 200 sieve and regrind. If, after grinding, a sample appears fine enough to pass a No. 200 sieve but will not, as can be the case for serpentine, a long bristle brush can be used on the sieve. This brush should be used only when necessary since the brushing may force coarser particles to go through the sieve than will go through by shaking.

In order to obtain a representative sample is is important that all the material put in a mortar or ball mill be ground to

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passing the No. 200. If any correlating is to be done with the differential thermal analyzer (DTA), the sample for both the DTA and X-ray should be sieved or ground at the same time using 7 instead of 5 grams.

Mixing

Mixing is important in order to obtain a uniform sample. Uniformity is desired in both particle size and mineral type. If a material is not well mixed before making a briquette, a different diffraction pattern will result when the briquette is rotated. The intensity of peaks will change making quantitative work impossible. Reasonably good results have been achieved by mixing a sample on a smooth sheet of 8½ x 11" paper with a spatula. Approximately 1 milligram of lamp black is added to the 5 gm. sample to serve as a mixing control. The sample is then mixed until a uniform color is achieved. Usually 2 to 3 minutes is satisfactory.

Normally 5 gm. of passing No. 200 material makes a briquette of satisfactory thickness. However, if a material has a very low density 4 gm. of material is enough.

Briquette Making

A 1" diameter by approximately 3/16" thick briquette is made by exerting 15,000 psi on 5 gm. of passing No. 200 material placed in a mold. For every soil tried to date the briquette has been firm enough to place in the sample holder on the X-ray machine with only a backing plate to distribute the force of the spring clips on the back of the briquette. For some ground aggregates and pure minerals the briquettes made could not be handled without falling apart. When this happens the back-pack method should be used - see the section entitled "Other Methods

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of Sample Preparation."

The mold is shown in Figure 7. All parts are made of hardened steel. The side of each spacer that touches the sample is polished.

The procedure for making a briquette is as follows:

1. Place mold on 3" x 5" piece of tin plate.
2. Drop into the mold the 1/2" thick spacer with the polished side up.
3. Place 3" diameter No. 60 sieve on top of the mold.
4. Place approximately 1/10 of the mixed sample on the No. 60 sieve directly above the 1" dia. hole in the mold.
5. Lift sieve off the mold until it is not touching then tap lightly until a thin layer of material covers the 1/2" spacer.
6. Return the material left on the sieve to the pile of material remaining on the mixing paper.
7. Pour all the remaining material into the mold and level off with a spatula.
8. With small magnet place 1/4" spacer into mold on top of the sample with the polished surface downward followed by the rod.
9. Apply 15,000 psi with a hydraulic press. Leave full pressure on for 5 seconds after creep has ceased (15,000 psi is equivalent to 10,000 pounds on the Materials and Research Department Pasadena hydraulic press.)

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10. Release the pressure, turn the mold upside down, and with the large spacer ring push the briquette out of the mold, bottom first.

11. Handle with care since some briquettes will be fragile. Blow off loose powder and lightly brush the edges with a small analytical balance brush.

12. Scribe an "X" on the surface not to be X-rayed. (Side touching the 1/4" spacer).

The reason for using a No. 60 sieve to put the first layer of material on the 1/2" spacer is to try and obtain a homogeneous and randomly orientated sample. Also since the bottom of the sample is compacted less than the top the chances of preventing preferred orientation are improved by using the bottom side.

When handling the briquette the surface to be X-rayed should not be touched at <u>any</u> time. Especially, the surface should not be brushed as this will cause preferred orientation.

<u>Cleaning Procedures</u>

In cleaning the mold, sieves, and other tools it was found helpful to use two cleaning towels. The first towel was used to do the rough cleaning and the second towel was used to do a final cleaning on any part that comes into direct contact with the sample. A bottle brush is useful on cleaning the mold and a soft brass brush works well on cleaning the No. 200 stainless steel sieve. The polished surface on the 1/2" spacer is especially critical. Since the X-rays only penetrate 1/64" below the surface of a briquette, any foreign matter left on the polished surface can influence the diffraction pattern even though only a very small percentage relative to the total 5 gm. sample. The polished

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surface can corrode very easily and therefore should be washed only with pure alcohol. Normally 1 to 2% of any crystalline material is not sufficient to give any detectable diffraction peaks, however, for any quantitative work it is necessary to minimize sample contamination.

## RECOMMENDED X-RAY OPERATIONAL PROCEDURE

In this section the operational procedures for running X-ray diffraction scans on a routine sample briquette will be discussed, including specific settings and the hazards involved.

In general, the operation of X-ray diffraction equipment is relatively safe, however, there are some hazards. This unit is not like a commercial or medical X-ray unit. The X-rays produced in a diffraction unit are directional and soft. They only travel in a narrow beam that is well shielded wherever scatter may occur. Still, a person can get a serious radiation burn if he should get in the way of the beam. Soft radiation can be more dangerous than hard radiation. Hard radiation will pass through the human body but soft radiation is stopped by the skin and causes a burn. The operator should be very careful because the burn can occur almost instantaneously and the person probably will feel no pain at the time to indicate that he has his hand in the beam.

The following operational procedure applies to a General Electric XRD-5 X-ray diffraction unit. In order to obtain a diffraction pattern for a routine briquette sample the following settings should be used on the X-ray unit:

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1. Cu diffraction tube - CA7 Coolidge
2. 1° beam slit
3. MR soller slit
4. 0.2° detector slit
5. 0.00035" thick Ni foil filter
6. SPG 3 scintillation counter
7. HVA = 6.50 volts (approx. 1.4 kilovolts on the power supply)
8. Time constant = 1 second
9. Δe in
10. Δe = 4.0 volts
11. E = 5.0 volts
12. Range = 5000 cps
13. Target angle = 3°

After checking item Number 7, the cooling water valve, the main power switch, and the machine should be turned on. A 20-minute warm-up period should be allowed for the electrical circuitry before the X-ray tube is used. If the HVA - high voltage adjust, is much higher than 6.50 volts damage could result in the counter tube. Then the rest of the items can be checked while the machine is warming up. Next the chart recorder should be calibrated. (See the General Electric operating instructions) If the X-ray tube or target angle has been changed or the X-ray table moved then the alignment of the X-ray machine should be checked after the 20-minute warm-up period. (See the General Electric operating instructions)

Then set the 2 θ angle on the gonimeter to 1.995°. Clean

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the sample holder with an analytical balance brush. Slip in a 1/8" x 1" x 1¼" backing plate between the spring clips and the front of the sample holder. This backing plate is to distribute the load of the clips on the back of the briquette. Then slip in the briquette carefully and center laterally in the holder. Cleaning of the sample holder after each briquette has been removed is important in order to prevent contamination of one sample with another and to preserve the system of geometry. If the briquette does not set flush with the front of the holder then at low 2 θ angles more X-rays can pass directly in front of the sample and thus raise the initial background level. Also, the d-spacings of the peaks may shift because the geometry of the system has changed.

For a routine sample four separate charts or scans will need to be run. The first two charts are with the briquette untreated.

1. 2 θ = 2 to 60° at 4°/min scan rate
2. 2 θ = 2 to 14° at 2°/min scan rate

Then the briquette is carefully removed from the sample holder and glycerine solvated with an atomizer containing one part glycerine and one part distilled water. The briquette should be sprayed just enough to wet the surface and then allowed to dry for 5 min. or until the surface appears dry again before X-raying. If the briquette is not X-rayed within 30 min. after it has been glycerine solvated the treatment should be repeated. One chart is made with the briquette glycerine solvated.

3. 2 θ = 2 to 14° at 2°/min scan rate

The briquette is again carefully removed from the sample holder and placed in an aluminum foil disk. The sample is put in a 100°C

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for 10 min. followed by 1 hour in a 500-550°C oven. If the briquette is not placed in the 100°C oven it will quite often crack in the 500°C oven. Then the briquette is removed from the oven and allowed to cool so that it may be handled; usually 5 min. is sufficient. Next the briquette is returned to the sample holder and X-rayed. If the briquette is not X-rayed within 1 hour after removing from the furnace it should be reheated. One chart is made with the briquette heated.

4. 2 θ = 2 to 14° at 2°/min scan rate

The first scan is used primarily to identify the non-clay minerals and to estimate their quantities. The other three scans are for identifying what clay minerals are present. Several of the clays have the same d-spacing so that auxiliary treatments by glycerine solvation and heating are required to distinguish between them.

Much of what will be said in the following paragraphs will be a repeat from the general operating instructions but they are included so that techniques for minimizing hazards can be emphasized. Before turning on the X-ray tube the goniometer should be checked. The 2θ angle should never be less than 1.95°. A 2 θ less than this will allow direct radiation to hit the scintillation counter and damage it. After the briquette is placed in the sample holder the scatter shield should be placed in front of the sample holder. Then the appropriate scan rate should be set on the goniometer. Next, the KVP dial for the X-ray tube should be set on 35 kilovolts and the MA on position No. 1. This last step is very important. An X-ray tube can only take a set maximum amount of energy before damage will result because of excessive heat.

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This maximum energy is a function of both kilovolts and milliamperes. For the Cu diffraction tube the operating limit is 50 KVP and 16 MA or 35 KVP and 23 MA. An X-ray tube will take an overload for a short time but this will shorten its life. A tube normally lasts 2000 hrs. and costs $700. For running routine soil briquettes the settings of 35 KVP and 22 MA (not 23 MA) will be used. The 22 MA just provides an extra margin of safety. Using any tube voltage higher than 35 KV will cause a false peak to occur at the same place as montmorillonite. This false peak is caused by a peculiar characteristic of the scintillation counter.

After the KVP is set on 35 and MA on position No. 1, turn on the chart recorder and the X-ray tube. Next turn the MA switch to position "B" and adjust the MA on the dial to 22.0 milliamperes with the adjusting screw labeled "B" just to the left of the dial. Tap lightly on the dial since the needle may stick. Readjust the KVP to 35 if it is needed. The adjusting of the MA may be required every time the X-ray tube is turned on because the switch does not seem to make the same degree of contact consistently. If at any time while adjusting the X-ray tube voltage or current one of the following things should happen turn off the X-ray tube <u>immediately</u>. It means that one of the settings is wrong and damage to the equipment could result if not <u>immediately</u> corrected. They are: (1) the rate meter goes off scale, (2) the pen on the chart recorder goes off scale, (3) the MA goes above 23, and (4) the KVP goes above 35. After the X-ray tube is off check all the settings and try again.

When the X-ray tube voltage and current is adjusted, if the chart pen is below 3.5 on the scale turn the range from 5000 to

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2000 cps. Allow the X-ray tube 30 seconds warm-up time before beginning an actual scan. When the recorder pen reaches a heavy transverse line on the chart paper turn the goniometer button to increase. Warning - if by accident the goniometer button is turned to decrease shut off the X-ray tube immediately. This is to prevent damage to the scintillation counter caused by too many X-rays hitting it. If the range is set on 5000 cps then after the scan has begun and the pen has dropped to 3.5 turn the range to 2000 cps. Then mark the initial 2 θ angle on the scan and label it in ink with sufficient information to identify the briquette, treatment, and any unusual X-ray machine settings. After the scan is run all the settings should be clearly marked on the chart so that someone else may reproduce your work. At the proper 2 θ angle 14 or 60° turn off the X-ray tube, goniometer, chart recorder, and return the MA to position No. 1. While the scan is being run it is best to stay 3 feet away from the machine when possible to minimize exposure to possible scatter radiation.

List of Hazards

1. Putting fingers in the X-ray beam
2. Having HVA read more than 6.50 volts
3. Going below 2 θ = 1.95° while X-ray tube is on
4. Forgetting to put scatter shield in place
5. Exceeding 35 KVP or 23 MA

A brief step by step X-ray operational procedure will be given below:

1. Check that HVA = 6.50 volts and that the tube is a CA-7 Cu diffraction tube

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2. Turn on the water, throw the main power switch, and press the machine on button
3. Check on settings given on page 19
4. After 20 min. warm-up time calibrate the chart recorder
5. Check alignment, if necessary
6. Set 2 $\theta$ = 1.995° and the proper scan rate
7. Clean the sample holder and insert the backing plate
8. Insert the briquette
9. Place scatter shield in front of the sample holder
10. Put KVP at 35 and MA on position No. 1
11. Turn on the chart recorder
12. Turn on the X-ray tube
13. When the chart pen responds put MA on position "B" and adjust to 22.0 milliamperes
14. Allow tube 30 seconds warm-up time then turn goniometer to increase
15. Turn cps range to 2000, if necessary
16. Label chart
17. When scan is finished turn off the X-ray tube, goniometer, chart recorder, and turn MA to position No. 1.

## METHOD OF INTERPRETATION

Explaining how to interpret a diffraction chart is difficult. Interpretation is mainly learned from experience. In theory the problem is relatively easy but in practice there are many complicating factors involved especially in soil mineral identification. A diffraction chart indicates what crystalline materials are present in an unknown sample by giving a series

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of diffraction peaks each with an intensity (peak height) and 2 θ angle (d-spacing). The problem is to find minerals of known intensity and d-spacing that will account for all the diffraction peaks. This problem is greatly complicated if there are several minerals in a sample giving twenty or more peaks. Sometimes all the peaks for a mineral do not occur or the relative intensity of peaks is incorrect.

There are several tools that can be used in conjunction with X-ray diffraction to simplify and confirm the identification of the minerals present in a soil sample. They are:

1. DTA - Differential Thermal Analysis - By this method several minerals and organic materials can be identified. This simplifies interpretation because the diffraction peaks for these minerals can be immediately identified.
2. Some minerals may be expected if the locality from which the soil comes is known.
3. Some minerals may be expected from knowing that certain minerals can degrade into other minerals.
4. Some minerals may be expected because of their common association with other minerals.
5. Petrographic Analysis - By this method many minerals can be identified. An additional advantage is that only one grain may be sufficient for identification where the X-ray usually requires 5% concentration before a mineral can be detected.

It should be noted that none of the above tools, including

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X-ray diffraction, is adequate by itself to identify all the minerals present in a soil. The X-ray is the best single tool but quite frequently one or more of the other tools must be used too.

Clay Mineral Interpretation

The interpretation will be considered in two parts - clay minerals and non-clay minerals. Before the mechanics of clay mineral identification can be discussed some background concerning the nature of clays is in order. Also the factors that can influence the shape of a diffraction peak will be mentioned.

The word "clay" has two meanings. The first refers only to particle size - any particle under 2 micron. The second refers to layer silicate minerals that usually are under 2 micron in size. The latter meaning will be used in this paper.

There are several families of clay minerals. The more common types found in soils are: montmorillonite, vermiculite, chlorite, and kaolinite. All of these clays are layer silicates containing oxygen, hydrogen, aluminum and silicon. The differences between these clay families and the clays within each family are caused by the arrangement of the atoms to form different types of layers. Also there are differences caused by isomorphic substitution for the silicon and/or aluminum, iron, magnesium or potassium. This isomorphic substitution can change the size of the layer and its net charge. This net charge can have a profound effect on how the clay acts - whether or not the clay is expansive. Normally a clay particle is made of a series of layers stacked on top of each other. The particle is a disk with its length and width twenty to fifty times greater than its

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thickness. This explanation has been very brief. The reader should consult a book on clays. Two good books are "Clay Mineralogy" by R. E. Grim and "The X-ray Identification and Crystal Structures of Clay Minerals" edited by G. Brown.

Montmorillonite is the most important clay family. Montmorillonite has the ability to absorb a great deal of water. In fact, water can increase its volume by 100% from the completely dehydrated to the completely hydrated state. This occurs because the montmorillonite layer possesses a net negative charge on its surface which attracts or absorbs water between each layer. The d-spacing can go from 10A to 20A. Normally if the montmorillonite has only been air-dried the main peak or distance between two layers will be 14.7A. If the montmorillonite is moist the spacing will shift to between 14.7 and 20A. After heating for 1 hour at 500°C the absorbed water and free water will be driven off giving the lowest d-spacing of 10A. Other clays do have water in between the layers but this water is held tightly so that under normal conditions little or no expansion or contraction will occur.

In order to interpret a diffraction chart properly a knowledge of what the shape of a diffraction peak may indicate is necessary. Normally a diffraction peak is fairly sharp and represents an atomic distance between two layers of atoms in a crystal. Sometimes a crystal giving a strong peak will have reflections associated with it. These reflections are called orders. These orders usually have less intensity than the main peak and a d-spacing of 1/2, 1/4, ---- of the main peak. This

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occurs because of the "n" in Bragg's Law - $n\lambda = 2d \sin \theta$. Here $\lambda$ and $\theta$ remain constant but n can vary. If n = 1 the d-spacing is for the main peak. If n = 2 the d-spacing is for the 1st order. If n = 3 the d-spacing is for the 2nd order. Chlorite is a good example of a mineral having two orders of the 14A peak. However, many minerals, even though they have strong diffraction peaks, do not exhibit orders.

A broad peak can indicate three things. It may indicate the presence of two diffraction peaks being so close together as to appear as one wider than normal peak. A broad clay peak will quite often indicate small particle size. As the particle size decreases below 2 micron the diffraction peak will broaden at the base and the peak height will drop. A broad clay peak may also indicate poor crystallinity or that two or more clay minerals are interstratified. These latter two items will be discussed later.

The identification of clay minerals is made difficult in that several clays have one or more d-spacings the same as other clays or as some non-clay minerals. However, by auxiliary treatments of glycerine solvation and heating these clays can usually be distinguished one from another. A step by step procedure will be presented for clay mineral identification followed by a procedure for interstratified clay minerals.

Identification of Clays

I. Examine the $2\theta = 2$ to $14°$ scan for the untreated briquette. The following peaks may occur:

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| | |
|---|---|
| 14-15A | Montmorillonite or vermiculite |
| 13.5-15 | Chlorite |
| 9.9-10.1 | Mica |
| 9.2-9.4 | Talc |
| 9.1-9.2 | Pyrophyllite |
| 8.4-8.5 | Amphibole |
| 7.6 | Gypsum |
| 7.1-7.3 | Serpentine or chlorite |
| 7.1-7.2 | Kaolinite |
| 6.3-6.45 | Feldspar |

II. If a 14 or 7 a peak occurs examine the 2 θ = 2 to 14° scan for the glycerine-solvated briquette.

a. If 17.8 A peak occurs then montmorillonite is present.

b. If 14 A peak remains then chlorite and/or vermiculite is present.

III. If a 14 or 7 A peak persists after glycerine solvation examine the 2 θ = 2 to 14° scan for the heated briquette.

a. If 14 A peak remains then chlorite is present.

b. If 14 A peak disappears then vermiculite is present.

c. If 7 A peak remains and there is no chlorite present then there is serpentine present.

d. If 7 A peak disappears and there is no chlorite present then there is kaolinite present.

NOTE: Upon heating, both vermiculite and montmorillonite will collapse to 10 A.

IV. If chlorite is present examine the DTA chart to see if serpentine and/or kaolinite are present.

Other peaks can occur between 2 θ = 2 to 14°. These may result from interstratification. Interstratification is when a single particle is made of a stack of clay layers of more than one clay mineral, for example, chlorite and montmorillonite. Two types of interstratification exist. Regular interstratification occurs

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when the layers regularly alternate between one clay type and another. The resulting d-spacing is the sum of the two individual layer d-spacings with a 1st order being quite frequently present. Random interstratification occurs when there is no regular alternation between layers. The resulting d-spacing is an approximate average of the d-spacing for the individual layers involved. Sometimes more than two types of layer silicates may be interstratified, however, the interpretation in such cases is very difficult if not impossible without using several auxiliary techniques. A mixture of two types of layer silicates is different from an interstratification because each particle contains only one type of layer silicate.

A list of d-spacings for identifying the type of interstratified clay, provided there are only two kind of clay interstratified, is given in Table I. These d-spacings are idealized. In practice the d-spacing for the main peak of an air dried montmorillonite depends on the absorbed ion. Usually the absorbed ion is calcium or magnesium which gives a 14.7 A peak. However, potassium gives a 12 A peak and sodium a 12.6 A peak. Potassium and sodium montmorillonites should not be confused with a randomly interstratified montmorillonite-mica because the glycerine solvation treatment will yield a 17.8 A peak and the interstratified montmorillonite-mica will be nearer a 14 or 15 A peak. Montmorillonite is the only common clay whose d-spacing is significantly affected by the type of absorbed ion.

When a random interstratification is found in a sample some idea of the relative percentage of the two components can be

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found by noting where the peak falls within the given range. For example, a randomly interstratified chlorite-vermiculite after heating should have a peak between 10 and 14 A. If the peak occurs at 12 A or half-way in between, the chlorite and vermiculite are present in approximately equal portions. If the peak is at 13 A there is more chlorite than vermiculite.

A few other notes on clay mineral identification need to be given. If a 12.1 A peak occurs and is unchanged by any treatment then it is a mineral called sepiolite. A peak between 4.45 to 4.60 indicates the presence of layer silicates. If this peak is strong and yet very little clay is indicated by the peaks on the $2\theta = 2$ to $14°$ scans check for the presence of halloysite. The DTA may be able to confirm halloysite. Or a strong 4.45 to 4.60 peak and no strong peaks on the $2\theta = 2$ to $14°$ scans may indicate a clay having poor crystallinity. Usually glycerine solvation will decrease the peak heights to some extent. This should be expected.

Non-Clay Mineral Interpretation

To help in identifying non-clay soil minerals Table II has been prepared showing the d-spacings for the common soil minerals found in California. Only the peaks that are likely to occur for a 20% concentration of a mineral are given. Also the relative intensity of peaks for each mineral is given with No. 1 signifying the most intense peak. If a mineral occurs in a small enough percentage, only the most intense peak will be visible. However, if there is considerably more than 20% of a mineral present then the complete set of d-spacings for the mineral should be consulted. Sources for the d-spacings of common minerals is found in Table III.

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It is probably easiest to identify the clay minerals first by use of the three 2 θ = 2 to 14° scans. Then the 2 θ = 2 to 60° scan is used to identify the other soil minerals present. Mark the d-spacing on the 2θ = 2 to 60° scan for any peak that is clearly above the background hash. Label all the peaks that represent clays previously identified. If a DTA has been run and shows some minerals to be present label the peaks that represent these minerals. Then using Table I begin at the largest d-spacing and work downward to identify the remaining peaks. If a peak indicates that a mineral might be present check to see if the No. 1 peak for that mineral occurs. If the No. 1 peak is not evident, it is unlikely that the mineral is there. If the No. 1 peak is present, look for the other peaks of lesser intensity. Note the relative intensity of the peaks. Do they agree with the values given in Table I? There may be superposition. If there are two minerals present that have one peak in common the intensity of that peak will be the sum of the two. Thus, the intensity will appear stronger than normal. Also there may be preferred orientation. This is when the individual crystals line up parallel to the front surface of the briquette instead of being randomly placed. When this occurs the main peak intensity will usually be enhanced and the intensity of the minor peaks will drop.

The d-spacing for the peaks may not agree with any d-spacings listed in Table I. The d-spacing can be off ±0.02 A or more. This discrepancy can be caused by several factors: (1) the chart speed can cause a lag; (2) interpolation error, (3) slight changes in chemical composition will result in changes in the size of the crystal lattice. This latter reason is why the d-spacings for

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feldspar are listed as broad ranges.

Table I represents a compilation of several investigators' works. In surveying the literature, the investigators do not agree exactly on the d-spacing and relative intensity of the peaks for the same mineral. There are several possible reasons for this. First, the samples may have been slightly different chemically. Second, the method of sample preparation was different. Third, the method of recording the diffraction patterns was different - powder camera vs diffractometer. This makes interpretation on the basis of other investigator's work difficult. To the extent that relatively pure soil minerals are present, it is helpful to run a series of standard charts using the same sample preparation techniques and diffraction equipment that is used in running unknown soil briquettes. These standard charts can then be used instead of Table I.

Frequently there are two possible mineral interpretations. Which mineral should be chosen? Usually an auxiliary tool should be tried. For example, heating at 500°C for an hour can differentiate gypsum from other minerals in that it is completely destroyed and thus all its diffraction peaks will disappear.

If the background in a scan is abnormally high the presence of free iron or an iron-rich mineral should be suspected.

Even with the information and procedure outlined the identification of soil minerals can be difficult and many times minor peaks cannot be identified at all. It is best when interpreting a diffraction pattern to show when there is only weak evidence for a mineral by including the word "maybe." If the interpretation

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agrees with the knowledge of the geology of the area from which the sample was taken and the DTA, chances are that the interpretation will be satisfactory.

## QUANTITATIVE PROCEDURES

Quantitative work on soil minerals is very difficult. At best quantitative work is only semiquantitative because of the many variables involved that cannot be controlled.

Ideally, the amount of a mineral present is directly related to its peak height on a diffraction pattern. But in practice there are several other variables besides amount of a mineral that affect the peak height. These variables are (1) particle size, (2) crystal imperfection, (3) chemical composition, (4) crystal orientation, and (5) matrix effect.

Particle Size: When particles are larger than 10 micron in diameter poor reproducibility may result because there are too few crystals in all possible orientations. If a soil sample ranges from 74 micron (passing No. 200 mesh) to less than 1 micron the very small particles may be hidden by the larger ones resulting in underestimation of the small particles present. On the other hand, if the particles are less than about 1 micron the intensity of the diffraction peak will decrease and become broad at the base because there are too few crystal planes in each particle to effectively cancel out all diffraction at angles other than the critical angle $\theta$. Thus, for very small particles the diffraction intensity decreases with decreasing particle size.

Particle size has the greatest single effect on reproducibility of peak heights on an X-ray diffraction pattern. As the particle

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size becomes smaller the reproducibility will improve and, therefore, the quantitative results will improve.

Crystal Imperfection: The intensity of diffracted X-rays is strongly affected by the condition of the crystals. The extent of discontinuities present in a crystal and the degree of weathering influence the diffracted intensity. If a pure mica sample were ground up its intensity would probably be twice that of an equal percentage of highly weathered mica found in a soil.

Chemical Composition: Chemical variations within the same mineral variety will change the absorptive power and thus influence the diffraction intensity. A good example is montmorillonite-nontronite. These minerals both have the same d-spacings but montmorillonite gradually grades into nontronite by increasing the iron substitution for silica. Iron absorbs CuK$\alpha$ radiation six times better than silica so that the intensity for nontronite is less than an equal percentage of montmorillonite.

Crystal Orientation: Crystal orientation is influenced primarily by the method of sample preparation and in the case of clays by the disk-like shape of the particles. Crystal orientation falls within two extremes. There is complete random orientation and complete preferred orientation. In random orientation the crystal planes are placed at all angles with respect to the surface of the sample. In complete preferred orientation one crystal plane is placed parallel to the surface of the sample. The results of orientation can be seen by looking at the relative intensity of the diffraction peaks. As the sample becomes more preferably orientated the relative intensity will shift with the main peak usually being enhanced considerably and the minor peaks losing intensity.

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For quantitative work a randomly orientated sample is required. A sample with preferred orientation will not give the correct percentages of the minerals unless the particles are all spherical.

Matrix Effect: The intensity of diffracted radiation from a given percentage of a mineral depends on the absorptive power of the whole sample. This is the matrix effect. If the sample contains a high iron content the percentage of radiation available to diffract from the mineral will be less than if the iron were not present. The scatter and background will increase.

There are many methods used to obtain semiquantitative results but they are all plagued with the above five variables. In some methods some of the variables can be controlled but in no method yet devised can all the variables be controlled.

In addition to controlling the five variables there are other problems. What should be used as a standard? Is there a pure montmorillonite? Is there a method for telling the amount of amorphous material in a sample?

With these problems in mind five quantitative methods for soil analysis will be presented. These are by no means an exhaustive list. It should become evident that a combination of methods will probably be required to obtain adequate results.

I. CHEMICAL METHOD: Determination of the chemical composition of a sample can be helpful. The amount of muscovite in a sample is proportional to the amount of potassium oxide provided that no other sources of potassium are present in the sample. Any alkali salts can be removed by washing. Any potassium ions can be removed from a soil by washing with magnesium acetate. Other common minerals that contain potassium are biotite and alkali

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feldspars.

The main difficulty with using data from a chemical analysis is that many of the soil minerals do not have a set chemical composition. The crystal structure remains constant but the degree of isomorphic substitution can vary over a wide range. Also many of the soil minerals have a similar chemical composition with different crystalline arrangements.

II. METHOD OF ADDITION: In this method a known amount of a pure soil mineral is added to a sample and the corresponding increase in peak height caused by the addition is measured. By calculating backwards the percentage of the soil mineral present in the sample can be determined. However, this method assumes that the pure soil mineral added has the same chemical composition, particle size, and degree of crystal imperfection as the mineral in the sample. This assumption could be grossly inaccurate.

III. METHOD OF PEAK INTEGRATION: In this method the area under a peak is found and used as an indication of the amount of a mineral present. This method is simple and relatively fast. It is hoped that this method may give satisfactory quantitative results for montmorillonite within a ±2% range for concentrations less than 25%. This is neglecting the variations that can be caused by differences in chemical composition and crystallinity. Using the peak area rather than peak height will compensate for peak broadening caused by fine particle size. However, if the montmorillonite is interstratified or there are other minerals present giving a 14A peak the method is of little value. Standards are required.

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The author has done some work in setting up standards for montmorillonite. Cement was used as a matrix since it has similar absorption properties as a non-iron rich soil. Various percentages of a standard montmorillonite from Little Rock, Arkansas, were mixed with cement and made into briquettes. A 100 second count was taken at $2\theta = 4°$ and 8°. Using a scan rate of 2°/min. the area between $2\theta = 4°$ to 8° was integrated using the scaler. This was done twice, once in each direction. The background was considered to have a straight line variation between $2\theta = 4$ and 8°. Any cps over the average cps of the background between $2\theta = 4$ to 8° was considered montmorillonite. Instead of integrating with the scaler a planimeter could be used to measure the area.

IV. METHOD OF STANDARD CHARTS: This is the quickest and easiest method for making a semiquantitative estimate of the minerals present. Standard charts for each mineral at 5, 10, 25, and 100% concentrations need to be prepared. The mineral should be mixed with an amorphous material possessing absorption properties similar to common soils. Ground glass has been used. The same preparation and the running of the diffraction pattern should be done the same way as for a regular soil sample. However, there is the problem of suitable standards. When pure minerals are ground and used as standards the intensities are frequently much higher than would be yielded by an equal amount in a natural soil. The difference is probably caused by differences in crystallinity. Differences in the mass absorption of the soil are not accounted for in this method.

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V. INTERNAL STANDARD METHOD: In this method a known amount of a pure crystalline material is added to the sample to serve as an internal standard. Its main peak should be such that it does not interfere with any peak in the sample. Then in order to eliminate the matrix effect the main peak height of a mineral is compared with the peak height of the internal standard. Standards need to be run to correlate the ratio of the mineral to internal standard peak heights to the concentration of the mineral present in a sample. One disadvantage of the method is that the sample is diluted, thus, requiring greater concentration of a mineral if it is to be detected. Probably minerals with less than 10% concentration cannot be seen. This is one of the most widely used quantitative methods.

In concluding, all the above methods have problems in controlling at least one of the five variables. This is why the second phase of this research project is to develop a relatively simple and quick method for performing routine quantitative analysis on soil and aggregate samples. The problems of quantitative work will be dealt with much more thoroughly in the next report at the completion of the project.

## OTHER METHODS OF SAMPLE PREPARATION

There are many ways in which a sample can be prepared for X-ray diffraction analysis. The proper choice of sample preparation is governed by what information is desired and the exactness of the information.

In any sample preparation, particle shape and orientation play an important part. Orientation refers to how the crystal faces are lined up with respect to the surface of the sample.

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The shape of a particle is influenced by cleavage and crystal structure. Many minerals form particles that are not round spheres. For instance, clays are disk-shaped so that if the surface of a sample is smoothed off with a glass slide the clay particles will tend to orient parallel to the surface. This orientation can be advantageous or not, depending on what is being sought. Parallel orientation will enhance the main diffraction peak of a clay and thus make it easier to identify. Also a smaller percentage of clay will be detected than if the sample were randomly orientated. However, for quantitative work this parallel orientation of the clay may hide other soil minerals and indicate a higher percentage of clay present than is actually there.

Several sample preparation methods will be presented along with the advantages and disadvantages of each one.

Front Pack Method: In this method a powder is placed in a shallow cavity and the surface leveled off by a glass slide. This method is the quickest and requires 1 gm or less of material. However, preferred orientation frequently results and there is little control over reproducibility. If a sample has 25% of its particles greater than 50 micron, the clay or less than 2 micron fraction seems to filter down into the sample while it is being packed into the shallow cavity. This results in the clay intensity being lower than it should be.

Back Pack Method: In this method a 1/8" x 1" x 2¼" plexiglas holder with a ½" x 2" slot cut out of the middle is used. A glass slide is taped on the front of the holder thus making a cavity. This cavity is packed with a powder sample from behind. After

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the powder is leveled off, a second glass slide is placed on the back of the holder and the front slide is removed. This exposes a smooth powder surface that has never had a glass slide drawn across it as in the front pack method so that preferred orientation is less likely to occur. Two and one-half grams of material is required. Particle size is not so critical and reproducibility is satisfactory.

Briquette Method: In this method a 1" diameter briquette is made from a 5 gm powder sample using 15,000 psi pressure. This method has a great advantage in time saved for clay mineral identification because the same briquette can be glycerine solvated and later heated. However, in the back pack and front pack methods the sample must be removed and repacked between each treatment. Sometimes the glycerine solvation can be done without removing the sample from the back pack holder. The skill of the operator is less important for the briquette method than the two previous methods. The effects of particle size and orientation seems comparable to the back pack except that the peaks at low 2 θ angles show some enhancement. In some instances with pure minerals the enhancement has been considerable, 100% or more indicating definite preferred orientation was present. The briquette method does require that the material possess sufficient adhesion to stay together. This has been no problem for soils however some powdered aggregates would not make a briquette and so the back pack procedure was used instead.

Chemical Method: This is a method for separating the passing 2 micron material from the rest of the sample. The sample is first dispersed by removing the natural cementing agents from

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the soil along with any organic material. Then by centifuging, the soil is separated at the 2 micron size. A full explanation of the method and techniques can be found in "Soil Chemical Analysis - Advanced Course" by M. L. Jackson. This method has the advantage of concentrating the clay minerals so that much smaller quantities of clay can be detected - less than 1% of the original sample. But the time involved is two or three times greater than the other methods.

Binder Method: In this method a glass slide is sprayed with acrylic and immediately a powdered sample is sprinkled on and the excess blown off. The slide is built up with several layers of acrylic and powder. This is another way to improve random orientation. 0.5 gm is usually enough. Reproducibility could be a real problem with this method.

A comparison of the sample preparation methods discussed is presented in Table IV. This comparison is general and applies primarily to clays. It is solely based on the opinion and experience of the author.

## X-RAY MACHINE VARIABLES

In operating an X-ray diffraction unit there are many variables that influence the peak intensity, background level, and peak resolution on a diffraction pattern. These variables will be discussed in this section. The remarks made may apply only to a General Electric XRD-5 diffractometer.

X-ray Tube: X-ray diffraction tubes differ as far as the type of target material, thickness and type of window, tube efficiency, and power input.

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Presently, a General Electric CA-7 Coolidge copper diffraction tube is being used. This tube has a 0.010" beryllium window which transmits 94% of the radiation that strikes it. For soil mineral identification work a copper target diffraction tube is the standard.

If a sample contains a large percentage of iron some investigators have suggested using an iron target diffraction tube to eliminate the high background caused by the secondary flourescence of the iron when a copper target is used. This was tried using a relatively pure iron pyrite sample. The background was cut by a factor of four but the peak height above background was no greater than when using the copper tube. The reason for the lack of improvement in the peak height above background is that the total output intensity from the iron tube is only one-half that for the copper tube. Also the absorption by the air, counter tube window, and the common elements in soils is greater since the characteristic radiation for iron is softer than for copper.

Kilovolts and Milliamperes: All X-ray tubes have a maximum power limitation as well as maximum and minimum voltage requirements. This power limitation is needed to prevent the target material from melting since 98% of the input power is dissipated in the form of heat. Less than 2% becomes useful radiation.

Power input in watts = volts times amperes

The intensity of the characteristic radiation produced is the most important criterion for an X-ray tube. It is found by the following formula:

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$$I = Ai\ (V - V_k)^{1.5}$$

Where: I is intensity in cps

A is constant

V is applied voltage in KV

$V_k$ is critical voltage in KV

i is tube current in MA

The critical voltage or excitation potential is the minimum energy that an electron must possess in order to dislodge an electron from the K shell of the target material. For copper the critical voltage is 8.86 kilovolts. In other words, if the applied voltage across a copper tube is less than about 10 KV, no $CuK_{\alpha}$ radiation will be produced. Only white radiation can result.

This formula indicates that the tube should be operated at the maximum voltage in order to yield the maximum intensity and that the tube current should be as high as the input power limitations permit. If the maximum peak height to back ground ratio is desired the applied tube voltage should be 3 to 3.5 times the critical voltage or 30 to 35 KV.

For a CA-7 copper diffraction tube 50 KV and 16 MA should be used to obtain the maximum intensity. Operating a little below the maximum is conducive to longer tube life. However, there are times when operating the tube at 50 KV is undesirable. This will be explained later. The maximum power input for the copper tube is 800 watts and the minimum voltage is 10 KV.

For the CA-7 iron diffraction tube the maximum power input is 400 watts, maximum voltage is 50 KV, and the minimum voltage is 10 KV.

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Target Angle: The target angle is the angle that the target in the X-ray tube makes with the beam slit. If the target angle is zero then no X-rays will reach the beam slit. However, as the target angle increases the area exposed to the beam slit increases and thus the intensity increases. This increase in intensity versus target angle is parabolic. At 3° the intensity is 82% of maximum, at 6° 93% of maximum, and at 10° 99% of maximum.

As the intensity increases with increasing target angle the resolution decreases. Resolution refers to the angular width of a diffraction peak. The better the resolution the narrower and sharper the peak will be. It will be easier to distinguish from the background and less likely to overlap another diffraction peak. For general diffraction a target angle between 3° and 6° gives a good compromise between intensity and resolution.

Beam, Soller, and Detector Slits: The beam slit assembly controls both the horizontal and vertical widths of the X-ray beam hitting a sample. It is placed between the X-ray tube window and the sample. It consists of two parts - a collimater and two vertical slits. The collimator is the stack of horizontal plates within the beam slit assembly that controls the vertical divergence of the X-ray beam. The two vertical slits control the horizontal angular width of the X-ray beam. As the beam slit angle increases the intensity per unit area will decrease some but the total intensity will increase considerably because the X-ray beam strikes a much larger portion of the sample. At $2\theta = 10°$ the X-rays from a 1° beam slit will cover a 1" long portion of a sample; X-rays from a 3° beam slit will cover a 3.5" long portion and the total intensity will have

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increased by more than 100%. It should be noted that as the 2 θ angle increases the portion of the sample hit by X-rays will decrease but the total intensity will remain constant for the same beam slit. At 2 θ = 45° only a 0.25" of a sample will be hit by X-rays if a 1° beam slit is used. A graph of 2 θ angle versus sample length required to keep the total intensity constant for various beam slit angles is shown in Figure 8.

The size of the beam slit also limits the 2 θ angle at which a scan can be started. The larger the beam slit is the more X-rays at low 2 θ angles will completely miss the sample and go directly to the detector causing very high background. With a 1° beam slit the scan may begin at 2 θ = 2° but no diffraction peaks will be detected before 2 θ = 3.5°. With a 3° beam slit the scan may begin at 2 θ = 7°. The latter 3° beam slit would be entirely inadequate for clay minerals because the important peak at 14.7A occurs at 2 θ = 6°. The practical maximum d-spacing that can be detected using a 1° beam slit and copper radiation is 25 angstroms.

The soller and detector slits work together to control the radiation received by the counter or detector. The soller slit has a collimator much like the beam slit to control vertical divergence. The detector is a narrow vertical slit to control the horizontal divergence. The smaller the detector and the more plates in the soller slits the better the resolution will be, however, the intensity will drop.

In summary, the three slits, beam, soller, and detector, work in combination with each other to control the vertical and horizontal divergence and the intensity of the X-ray beam. Their

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effects are interdependent. Changing any slit may make the machine operate totally unsatisfactorily. For a soil powder sample a 1° beam, MR soller, and 0.2° detector slits seem to give the optimum balance between intensity, resolution, and initial background.

Filter: The function of a filter is to remove $K_B$ radiation. This simplifies the interpretation of diffraction charts by eliminating the diffraction peaks caused by $K_B$ radiation. The filter material should have an absorption edge just short of the $K_B$ line for the target material. Usually this is an element with an atomic number of one less than that of the target material. For Cu $K_B$ radiation a nickel filter is used.

The effectiveness of a filter can be determined by using the following formula:

$$\frac{I}{I^\circ} = e^{-\mu x} = e^{-\frac{\mu_M}{\rho}\rho x}$$

Where: $I/I^\circ$ = fraction of intensity transmitted

$e$ = Napierian base

$\mu$ = Linear absorption coefficient

$\mu_M$ = Mass absorption coefficient

$\rho$ = Density in $g/cm^3$

$x$ = Thickness of filter in cm.

The ratio of cu$K\alpha$ to Cu $K_\beta$ radiation before filtering is approximately 5.4 to 1. The standard nickel filter is 0.0007" thick and will remove 98% of the $K_\beta$ and reduce the $K\alpha$ radiation by 50%. Thus, after filtering the ratio of $K\alpha$ to $K_\beta$ is 135 to 1. This means that a 2700 cps $K\alpha$ diffraction peak is necessary before a 20 cps $K_\beta$ peak will be visible.

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Counters: At present the laboratory has two types of counters manufactured by General Electric. One is a SPG4 Proportional Counter and the other is a SPG3 Scintillation Counter.

The proportional counter is a gas filled counter with PR10 gas which is a mixture of 10% methane and 90% argon. This gas continually flows through the counting chamber. When an X-ray hits the PR10 gas, the gas is ionized in proportion to the energy of the incoming X-ray and transmits a corresponding voltage to the recorder.

For each counter there is an efficiency curve. This is a plot of the ability of the counter to detect X-rays versus the wavelength of the X-ray. The proportional counter is only 40% efficient for Cu K$\alpha$ (1.54A) radiation. The efficiency drops off rapidly for any radiation with a wavelength less than copper. For FeK$\alpha$ (1.94A) radiation the counter efficiency is 55%. The proportional counter is not very sensitive to white radiation. This results in low background, however, this advantage is overridden by its low efficiency for CuK$\alpha$ radiation and, therefore, it is not used for identification of soil minerals.

The scintillation counter has a thallium activated sodium iodide crystal that phosphoresces when hit by an X-ray. This crystal produces visible light with an intensity proportional to the energy of the X-ray. This light is then converted into a voltage by a photomultiplier tube and sent on to the recorder.

The scintillation counter is 95% efficient for CuK$\alpha$ radiation and has the same efficiency for harder white radiation. A diffraction pattern made using a scintillation counter will have

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a higher general background than one using a proportional counter but the efficiency is 2.5 times greater. When the applied voltage on the X-ray tube is 50 KV and the scintillation counter is used a false peak will occur. This peak usually occurs at about $2\theta = 6°$ which is where montmorillonite would be found. From running diffraction patterns on many different pure minerals it was found that the location of the false peak and its intensity are related to the location of the main diffraction peak and its intensity. In fact, if there are two or more very strong diffraction peaks there may be two or more false peaks. A completely satisfactory explanation for the false peak has not yet been found. It does not appear at all with the proportional counter. It may be caused by secondary florescence of the iodine in the sodium iodide crystal in the counter because when the applied tube voltage is less than the excitation voltage for iodine no peak appears.

In order to avoid the false peak the applied voltage on the copper X-ray tube must be kept at 35 KV or below. Dropping the KV from 50 to 35 caused at 30% drop in the X-ray intensity. To compensate for this a 0.00035" nickel filter is used instead of the usual 0.0007". This gives a net gain of 10-15% intensity over using 50 KV and a 0.0007" nickel filter. Using a filter only one-half as thick does not remove the $CuK_B$ radiation as effectively but still a diffraction peak must exceed 1000 cps before the $K_B$ peak is visible. The background level is increased but the peak height above background is still considerably better than when using the proportional counter.

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Pulse Height Selector: The pulse height selector allows an input voltage of a certain range to produce an output pulse. It is an electronic filter. Each X-ray will produce a voltage proportional to its wavelength or energy level. $CuK_{\alpha}$ radiation produces a certain voltage and white radiation produces a continuous spectrum of voltages. The "E" value on the pulse height selector prevents any X-rays that produce less voltage than "E" to be registered. Then "$\Delta E$" supplies a window. Any voltage between E and $E + \Delta E$ will register as an output pulse. This selector, however, is not 100% efficient so that a small portion of white radiation will be received. For general diffraction with $CuK_{\alpha}$ radiation values of $E = 5$ volts and $\Delta E = 8$ volts are used.

Rate Meter: The rate meter indicates the number of counts per second (cps) that the counter is receiving after the filtering process by the pulse height selector. This is an instantaneous reading. The number of cps that will cause full deflection on the rate meter is set by the "cps range" dial. Rather than giving a true instantaneous reading the rate meter gives a value averaged over a number of seconds. This averaging time is set by the "time constant" dial. This averaging will tend to smooth out fluctuations in the background and may smooth out small peaks if the time constant is too large.

For a soil powder sample a 2000 cps range and 1.0 second time constant is used. A continuous recording of the rate meter is made by the chart recorder and is called a diffraction pattern.

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Above 10,000 cps the rate meter ceases to be linear and above 100,000 cps the peak will appear as a double peak. This double peak is really only a single peak with a depression in the middle because the cps have exceeded the capacity of the scintillation counter.

Scaler: The scaler counts each output pulse from the pulse height selector. The scaler has a timer connected with it that can be read to the nearest one-hundredth of a second. The scaler can be used in several ways (1) to count for a preset length of time, (2) to count for a preset number of counts and register the time required to obtain the counts, and (3) to count manually where the operator may stop the counting at any time. This is frequently used to integrate peaks for quantitative work. A peak is scanned at a slow angular rate and the scaler will count the total number of cps under the peak.

The counting error for the scaler is equal to the square root of the total number of counts. Error is introduced because of the production of X-rays is random and there is fluctuation in the voltage and current supply to the tube. The error can be made a small as desired by increasing the count time. NOTE: The ones digit on the scaler has been omitted so that a zero should always be added to a scaler reading.

Scan Rate: The scan rate is the rate at which the goniometer is being turned in degrees per minute. Normally for identification of non-clay minerals a 4°/min. scan rate is used. It gives fairly sharp peaks which are easy to distinguish. A scan rate of 2°/min. is used if the d-spacing needs to be determined more accurately and for clay mineral identification where shifts in d-spacing

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caused by auxiliary treatments need to be seen. The resolution is no better than at 4°/min. but the distance between peaks is magnified. Also there is a slight gain in peak intensities. Decreasing the scan rate will cause a small displacement of the diffraction peaks. The peaks will appear at a lower 2 θ angle because the rate meter requires a finite time to respond to the diffracted X-rays.

High Voltage Adjust (HVA): When an X-ray hits a counter, a voltage proportional to the wavelength is produced. However, the degree of amplification of this voltage is a function of the high voltage potential placed across the counter tube. This high voltage is adjusted by the HVA knob. Because there is always some fluctuation in the high voltage from the power supply, it is desirable to pick a high voltage in a region where the effects of this fluctuation will be a minimum. This is found by plotting high voltage versus cps for a strong diffraction peak. The plot will have a plateau in it. The voltage used should be in the middle of this plateau. For the scintillation counter and CuK$\alpha$ radiation a HVA setting of 650 or approximately 1.4 KV on the power supply is best.

Alignment: In order to obtain maximum intensity, the beam slit must be directly in line with the detector slit when 2 θ = 0°. Being out of alignment by 2 θ = 0.3° can reduce the intensity that the counter will receive by 25% or more. This alignment should be checked every time the X-ray tube is changed or the goniometer table is disturbed. For the procedure see the General Electric Manual.

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## X-RAY MACHINE MAINTENANCE

The general approach for X-ray equipment trouble shooting is presented in this section along with some specific examples. For detailed instructions on repair and maintenance see the General Electric Manual.

The X-ray machine is made up of several individual electronic units and put together to form the whole. Thus, if the machine ceases to function properly the first step is to locate the unit or units in which the malfunction is occurring. Then with the aid of trouble shooting charts and circuit diagrams trace down the trouble.

General Warning - This machine can be very dangerous. A person without electronic repair experience and a knowledge of the circuitry should not poke around in the machine. When the machine is on there is much high voltage about. Even after the machine is shut off sizeable shocks can be obtained by discharging capacitors. Also a person could make the troubles worse. The equipment is expensive to replace. However, all of the breakdowns to date have been of a nature where a careful reading of the trouble charts without prior electronic experience has resulted in remedying the troubles. These were such things as cleaning a relay, replacing fuses, untangling cables which were causing inductance, and replacing tubes.

It is helpful in pinning down a trouble to be familiar with the flow chart for the counting and recording equipment. It is as follows: power transformer → power supply → counter → pulse height selector → scaler and rate meter → rate meter to chart recorder.

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EXAMPLES

1. If the X-ray machine will not go on when the button is pressed check the water valve. There is a safety pressure switch. If the machine is not receiving water it will not go on or if the water stops when the machine is on it will automatically shut itself off.
2. If the X-ray machine is on but the X-ray tube will not function, check the safety micro-switch on the X-ray tube cover.
3. If the scaler shows more than 10 cps when the X-ray tube is off the trouble is usually located before the scaler. Check and make sure that the counter cables are not wound around each other. This will produce inductance and cause a high noise level from the counter. If the cables are okay check the cable connnections. A little dust or dirt can cause noise too. Carbon tetrachloride is a good cleaner.
4. If the scaler and rate meter show a high cps - 25 or more, and the X-ray tube is off, check the relay in the power supply. Flipping the power switch off and on may suffice, if not, clean the relay by closing the relay (with the machine <u>off</u>) and draw a piece of paper between the contacts.
5. If a unit ceases to work check the fuses. (Turn off the machine while checking.) If a fuse is blown and after being replaced it blows again then the trouble is something more than an old fuse.

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About twice a year the machine requires routine maintenance. There are fans and gears that should be oiled. The power relay should be cleaned. The whole machine should be vacuumed to remove the accumulation of dirt and dust. See the General Electric Manual for details.

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TABLE I

D-SPACING FOR INTERSTRATIFIED CLAYS

I. Vermiculite-montmorillonite or Chlorite-montmorillonite

a. Regular Interstratification

| | Peak in Angstroms |
|---|---|
| Untreated sample | 14 |
| Glycerine solvated | 14 + 18 = 32 and 1st order at 16 |
| Heated sample | |
| Vermiculite-montmorillonite | 10 |
| Chlorite-montmorillonite | 14 + 10 = 24 and 1st order at 12 |

b. Random Interstratification

| | |
|---|---|
| Untreated sample | 14 |
| Glycerine solvated | between 14 and 18 |
| Heated sample | |
| Vermiculite-montmorillonite | 10 |
| Chlorite-montmorillonite | between 10 and 14 |

II. Chlorite-mica

a. Regular Interstratification

| | |
|---|---|
| Untreated sample, Glycerine solvated, Heated sample | 10 + 14 = 24 |

b. Random Interstratification

| | |
|---|---|
| Untreated sample, Glycerine solvated, Heated sample | between 10 and 14 |

III. Montmorillonite-mica

a. Regular Interstratification

| | |
|---|---|
| Untreated sample | 10 + 14 = 24 |
| Glycerine solvated | 10 + 18 = 28 |
| Heated sample | 10 |

b. Random Interstratification

| | |
|---|---|
| Untreated sample | between 10 and 14 |
| Glycerine solvated | between 10 and 18 |
| Heated sample | 10 |

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| IV. Chlorite-vermiculite | Peak in Angstroms |
|---|---|
| a. Regular Interstratification | |
| Untreated sample | 14 |
| Glycerine solvated | 14 |
| Heated sample | 14 + 10 = 24 |
| b. Random Interstratification | |
| Untreated sample | 14 |
| Glycerine solvated | 14 |
| Heated sample | between 10 and 14 |

| V. Vermiculite-mica | |
|---|---|
| a. Regular Interstratification | |
| Untreated sample | 14 + 10 = 24 |
| Glycerine solvated | 14 + 10 = 24 |
| Heated sample | 10 |
| b. Random Interstratification | |
| Untreated sample | between 10 and 14 |
| Glycerine solvated | between 10 and 14 |
| Heated sample | 10 |

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TABLE II

D-SPACING FOR COMMON SOIL MINERALS

| d-spacing "A" | Mineral & Relative Intensity |
|---|---|
| 14-15 | Vermiculite (1) |
| 13.5-15 | Chlorite (2 or 1) |
| 12.1 | Sepiolite (1) |
| 9.9-10.1 | Mica (1) muscovite and biotite |
| 9.6-20 | Montmorillonite (1) in various stages of hydration |
| 9.2-9.4 | Talc (1) |
| 9.1-9.2 | Pyrophyllite (2) |
| 8.4-8.5 | Amphibole (only 1) |
| 7.6 | Gypsum (1) |
| 7.1-7.3 | Serpentine (1) antigorite and chrysotile |
| 7.1-7.2 | Kaolinite (1) |
| 7.0-7.2 | Chlorite (1 or 2) |
| 6.3-6.45 | Feldspar |
| 5.0 | Muscovite (3) |
| 4.83 | Gibbsite (1) |
| 4.72 | Bayerite (1) |
| 4.7-4.9 | Chlorite (4) |
| 4.45-4.60 | Kaolinite, montmorillonite, muscovite, pyrophyllite, serpentine and vermiculite |
| 4.35 | Bayerite (2) |
| 4.34 | Gibbsite (2) |
| 4.29 | Gypsum (2 or 3) |
| 4.27 | Quartz (2) |
| 4.15 | Goethite (1) |
| 4.05 | Cristobalite (1) |

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| d-spacing "A" | Mineral & Relative Intensity |
|---|---|
| 4.0-4.2 | Feldspar |
| 3.8-3.9 | Feldspar |
| 3.79 | Gypsum (4) |
| 3.73-3.75 | Feldspar |
| 3.73 | Ilmenite (3) |
| 3.67 | Hematite (3) |
| 3.64-3.67 | Feldspar |
| 3.59-3.64 | Serpentine (2) |
| 3.57-3.58 | Kaolinite (2) |
| 3.52-3.58 | Chlorite (3) |
| 3.51 | Anatase (1) |
| 3.44-3.48 | Feldspar |
| 3.36 | Biotite (2), phyrophyllite (3) |
| 3.35 | Quartz (1) |
| 3.3 | Muscovite (2) |
| 3.14 | Cristobalite (2) |
| 3.1-3.25 | Feldspar (often two lines), hornblende |
| 3.10 | Talc (2), pyrite (5) |
| 3.06 | Gypsum (3 or 2) |
| 3.05 | Pyrophyllite (1) |
| 3.03 | Calcite (1) |
| 2.97 | Magnetite (2) |
| 2.95-3.00 | Feldspar |
| 2.95 | Maghemite (2) |
| 2.89 | Dolomite (1) |
| 2.85 | Cristobalite (3) |

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| d-spacing "A" | Mineral & Relative Intensity |
|---|---|
| 2.82-2.87 | Chlorite (5) |
| 2.81-2.89 | Feldspar |
| 2.75 | Ilmenite (1) |
| 2.73 | Hornblende |
| 2.71 | Pyrite (1) |
| 2.69 | Hematite (1), goethite (2) |
| 2.55 | Ilmenite (2) |
| 2.53 | Magnetite (1) |
| 2.51-2.55 | Feldspar |
| 2.51 | Maghemite (1), hematite (2) |
| 2.49 | Cristobalite (4) |
| 2.45 | Goethite (3), quartz (5) |
| 2.42 | Pyrite (2) |
| 2.40-2.42 | Pyrophyllite (4) |
| 2.38 | Anatase (3), gibbsite (3) |
| 2.34 | Kaolinite (3) |
| 2.28 | Quartz (6) |
| 2.22 | Bayerite (3) |
| 2.21 | Pyrite (3) |
| 2.19 | Dolomite (2) |
| 2.10 | Calcite (3) |
| 1.99-2.00 | Biotite (3), muscovite (4) |
| 1.91 | Calcite (2) |
| 1.89 | Anatase (2) |
| 1.87 | Ilmenite (5) |
| 1.84 | Hematite (4) |

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| d-spacing "A" | Mineral & Relative Intensity |
|---|---|
| 1.83 | Pyrophyllite (5) |
| 1.82 | Quartz (3) |
| 1.78 | Dolomite (3) |
| 1.72 | Ilmenite (4) |
| 1.69 | Hematite (5) |
| 1.63 | Pyrite (4) |
| 1.62 | Magnetite (3) |
| 1.60 | Maghemite (3) |
| 1.54 | Quartz (4) |

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This table was compiled using the above sources and X-ray data obtained by the author.

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TABLE III

SOURCES FOR D-SPACINGS OF COMMON MINERALS

| | Page No.(1) | Card No.(2) | | Page No. | Card No. |
|---|---|---|---|---|---|
| Alunite | 478 | | Ilmenite | 386 | |
| Anatase | 475 | | Jarosite | 478 | |
| Ankerite | 476 | | Kaolinite | 111 & 113 | |
| Antigorite | 121 | | Labradorite | | 3-0499 |
| Apatite | 482 | | Maghemite | 386 | |
| Augite | | 3-0623 | Magnesite | 476 | |
| Bayerite | 384 | | Magnetite | 386 | |
| Biotite | 238 | | Metahalloysite | 114 | |
| Calcite | 476 | | Montmorillonite | 192 | |
| Cassiterite | | 5-0467 | Mullite | 485 | |
| Chamosite | 123 & 124 | | Muscovite | 238 | |
| Chlorite | 288, 290 & 291 | | Olivine | 486 | |
| | | | Palygorskite | 352 | |
| Chrysotile | 118 | | Penninite | 292 | |
| Corundum | 384 | | Pyrite | 475 | |
| Cristobalite | 474 | | Pyrophyllite | 475 | |
| Cryolite | | 1-1273 | Quartz | 473 | |
| Diaspore | 384 | | Rutile | | 4-0551 |
| Dickite | 115 | | Sepiolite | 340 | |
| Diopside | | 2-0656 | Sericite | | 2-0056 |
| Dolomite | 476 | | Serpentine | 120 & 125 | |
| Enstatite | 486 | | Siderite | 386 | |
| Feldspars | 480, 483 & 484 | | Sillimanite | 485 | |
| | | | Spinel | 486 | |
| Forsterite | | 4-0768 | Talc | 475 | |
| Gibbsite | 384 | | Tridymite | 474 | |
| Goethite | 386 | | Vermiculite | 319 | |
| Gypsum | 477 | | | | |
| Hematite | 386 | | | | |

(1) "The X-ray Identification and Crystal Structure of Clay Minerals" edited by Brown.
(2) ASTM card file

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TABLE IV

COMPARISON OF SAMPLE PREPARATION METHODS

| Sample Preparation Method | Sample Size in Grams | Preparation Time for 3 Treatments | Degree of Random Orientation | Reproducibility | Intensity Above Background |
|---|---|---|---|---|---|
| Front Pack | 1 | 15 min. | Poor | Poor | Poor - fair |
| Back Pack | 2½ | 14 " | Satisfactory | Fair | Satisfactory |
| Briquette | 5 | 8 " | Fair - Satisfactory | Fair - Satisfactory | Satisfactory |
| Chemical | 2 | 3 hrs. | parallel | Fair - Satisfactory | Good |
| Binder | ½ | 20 " | ? | ? | Poor - fair |

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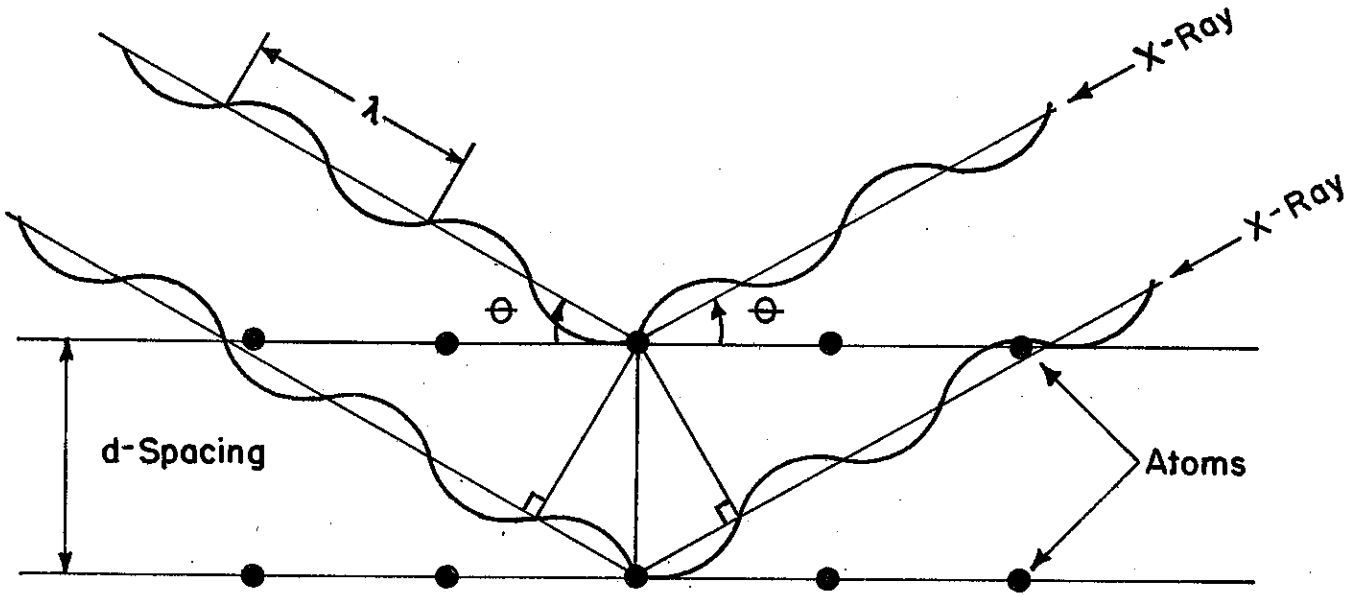
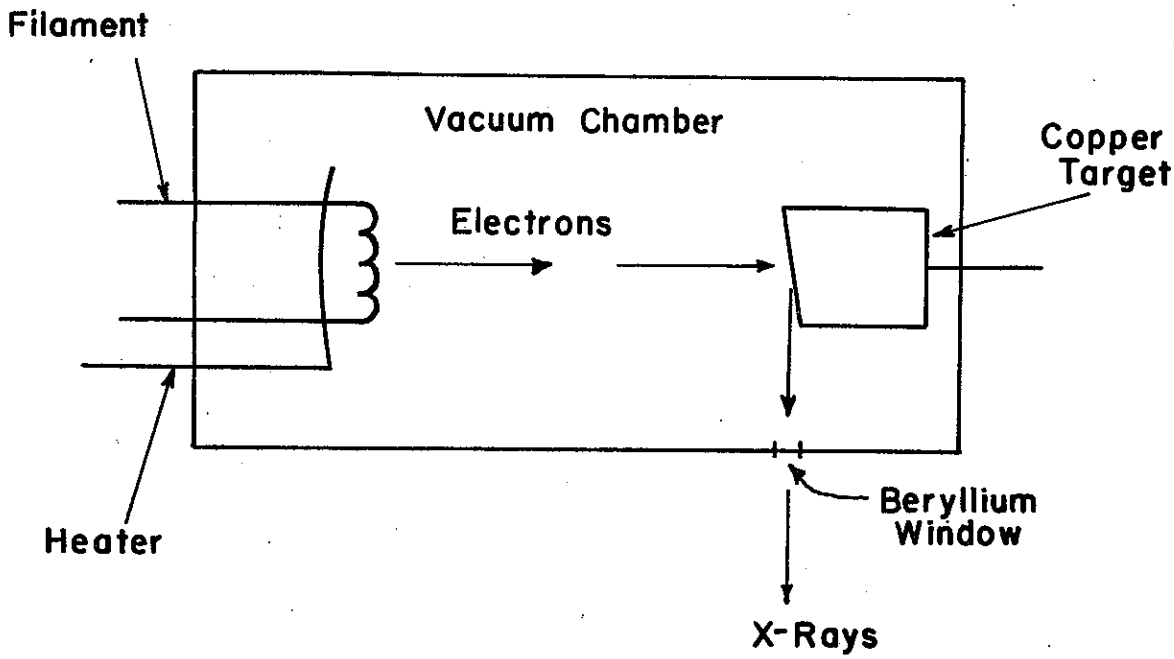



DIFFRACTION OF X-RAYS

FIGURE 1




X-RAY TUBE SCHEMATIC

FIGURE 2

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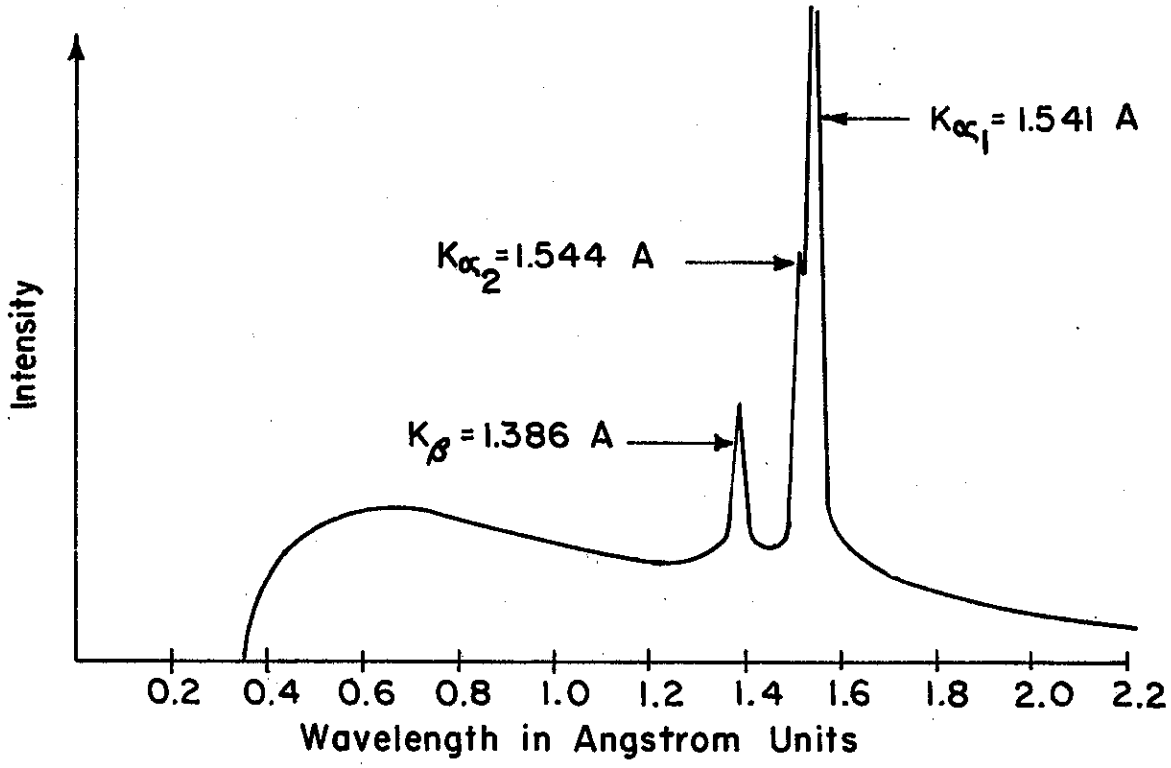
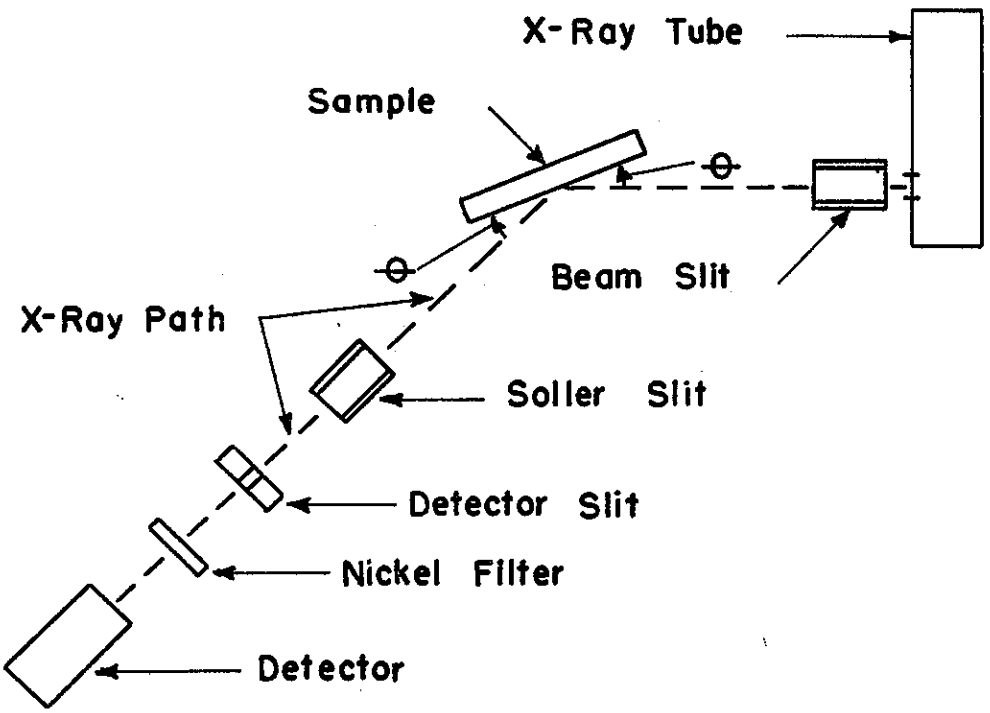



COPPER RADIATION INTENSITY CURVE

FIGURE 3




X-RAY PATH

FIGURE 4

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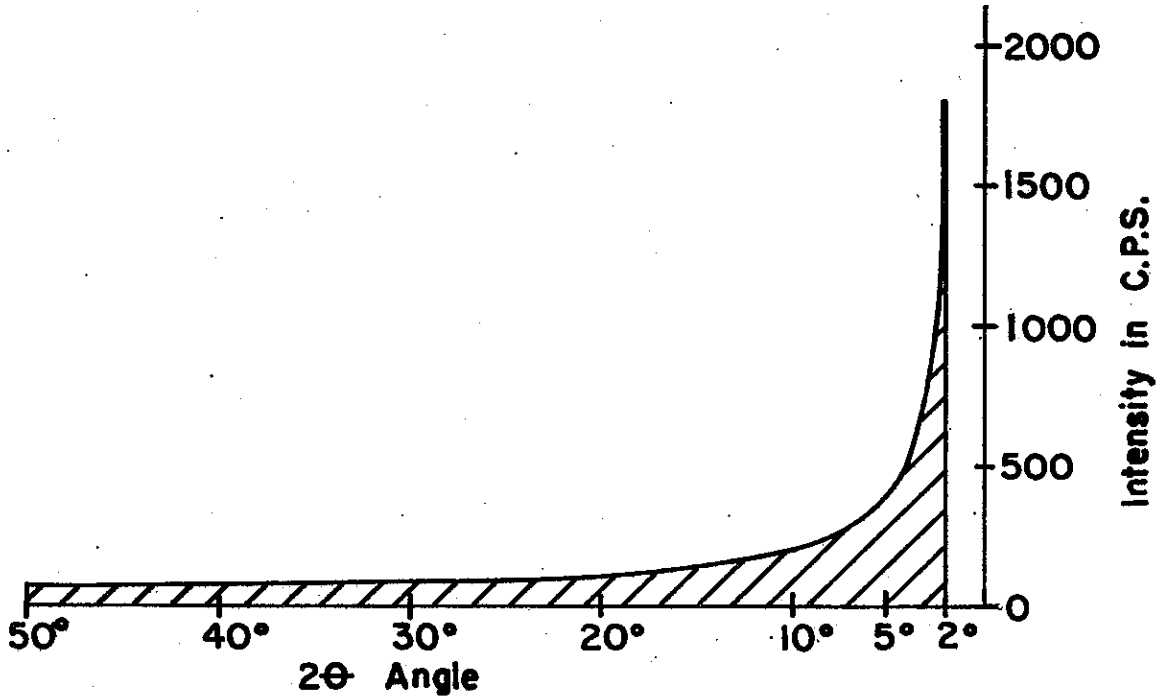
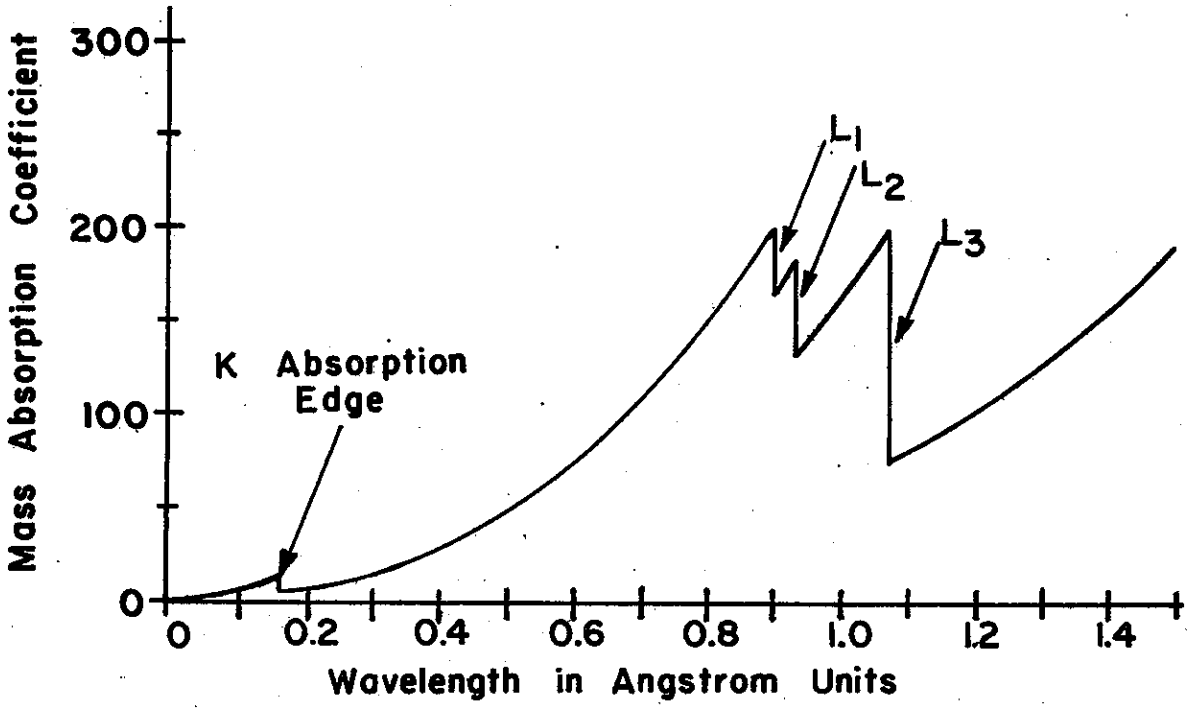



DIFFRACTION CHART SHOWING BACKGROUND
( DIFFRACTION PEAKS OMITTED )

FIGURE 5




MASS ABSORPTION VS. λ FOR PLATINUM

FIGURE 6

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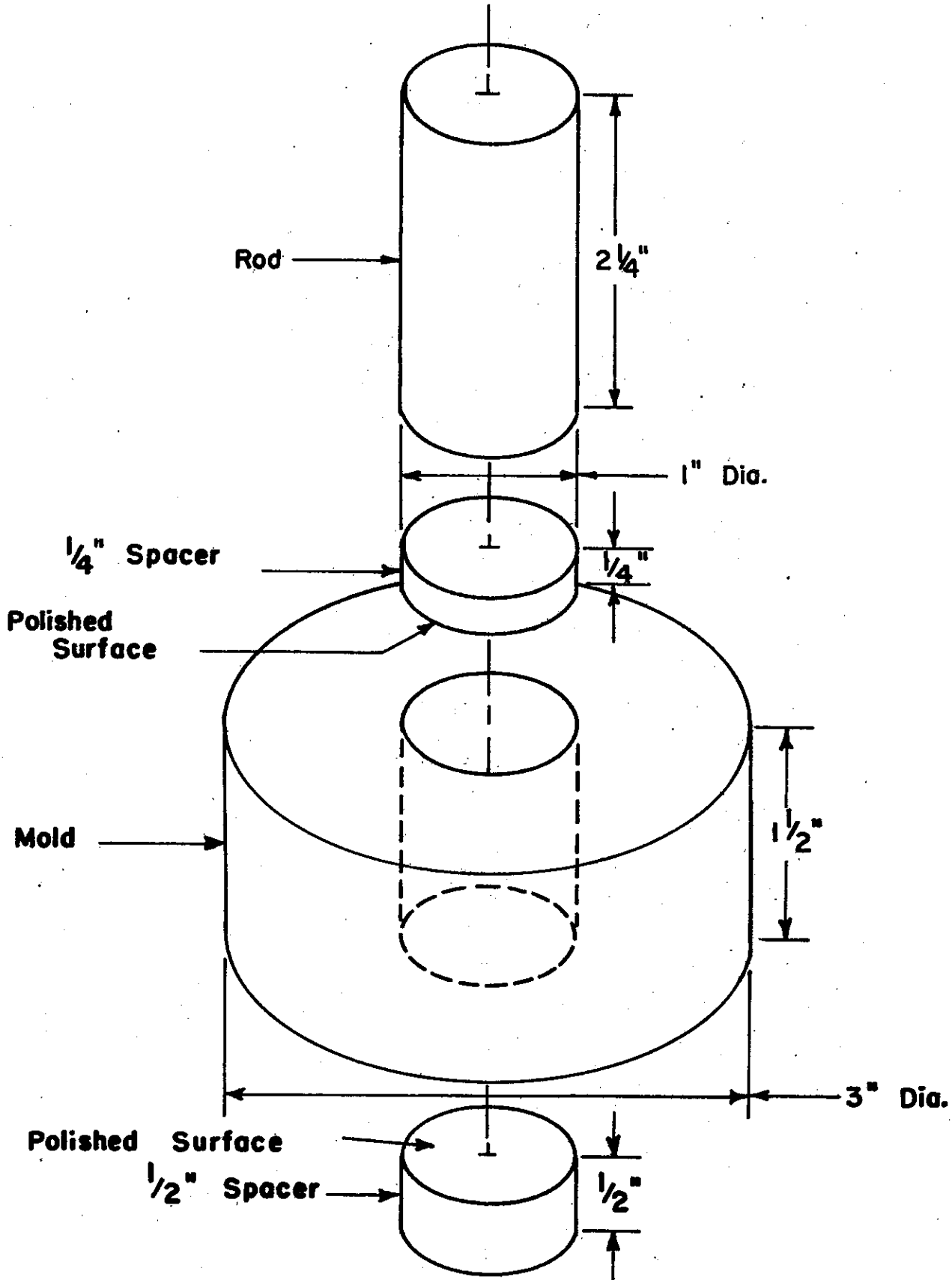


BRIQUETTE MOLD ASSEMBLY

FIGURE 7

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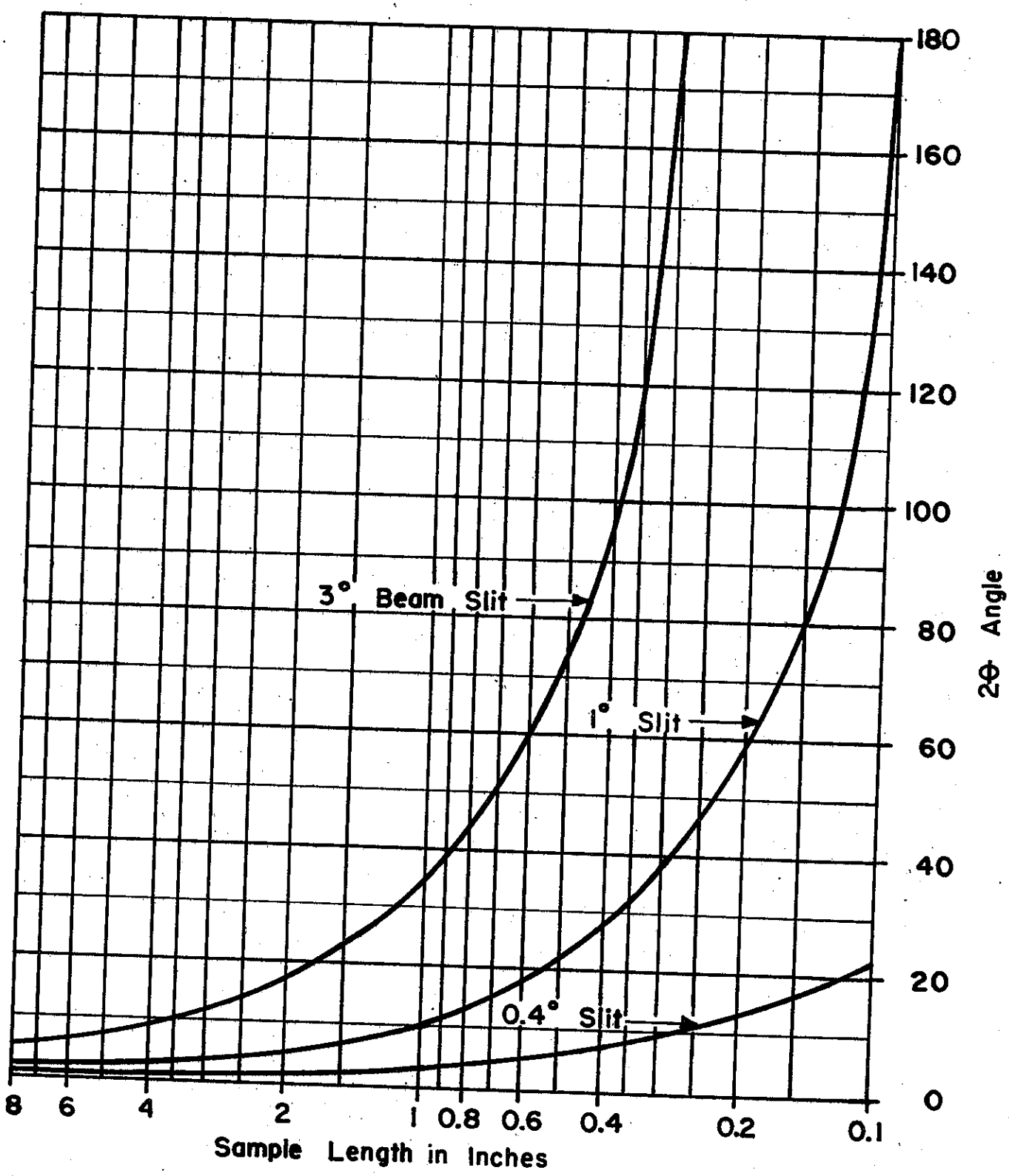


SAMPLE LENGTH VS. 2θ ANGLE

FIGURE 8

Based on figure in General Electric XRD-5 instruction manual.

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