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16. ABSTRACT

Part I of this report describes the work completed toward development of X-ray diffraction quantitative procedures during the period from March 1, 1964, to June 15, 1965. Part II is an outline of recommendations for future work. Work completed prior to March 1, 1964, is described in "Progress Report on Identification of Soil Minerals by X-ray Diffraction." (1) dated December 15, 1964. A General Electric XRD-5 diffractometer has been used for all work in this study.

This report covers the work accomplished during the period from March 1, 1964, to June 15, 1965, in developing an X-ray diffraction procedure for the quantitative determination of minerals. It also includes future proposed work.

The theoretical equations presented by Klug and Alexander in conjunction with Beer's Law form the foundation upon which this procedure is based. When the mass absorption is measured directly it is based upon a derivation of Beer's Law. This derivation relates the mass absorption of the sample to the properties of the sample and the aluminum foils.

The physical state of particle size and orientation were investigated. The particle size problem can be reduced by securing a motorized pestle and mortar and wet grinding the material. The orientation factor for most minerals may be resolved by using the ratios of three orthogonal diffraction peaks.

By adding a strong diffractor to the sample an indirect measurement of the mass absorption was accomplished, although, reproducibility was not good. However, the results obtained from measuring the mass absorption directly are reproducible and the accuracy is favorable. The average deviation varies from a high of 12% to a low of 2%. Better results can be obtained by securing some new equipment and more accurately measuring the aluminum foil standards.

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PROGRESS REPORT ON QUANTITATIVE DETERMINATION OF SOIL BY X-RAY DIFFRACTION

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September 1965

MATERIALS & RESEARCH DEPARTMENT

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

September 30, 1965

Lab Auth 225218

Mr. L. R. Gillis
Asst. State Highway Engineer
Division of Highways
Sacramento, California

Dear Sir:

Submitted for your consideration is:

PROGRESS REPORT

on

QUANTITATIVE DETERMINATION OF SOIL

AND AGGREGATE 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
J. Puleo

Very truly yours,

JOHN L. BEATON
Materials and Research Engineer

cc: LR Gillis
JF Jorgensen
AC Estep
CG Beer-4

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ATTACHMENTS

QUANTITATIVE DETERMINATION OF SOIL AND AGGREGATE MINERALS BY X-RAY DIFFRACTION, MATERIALS AND RESEARCH PROJECT NO. 225218

Part I of this report describes the work completed toward development of X-ray diffraction quantitative procedures during the period from March 1, 1964, to June 15, 1965. Part II is an outline of recommendations for future work. Work completed prior to March 1, 1964, is described in "Progress Report on Identification of Soil Minerals by X-ray Diffraction,"(1) dated December 15, 1964. A General Electric XRD-5 diffractometer has been used for all work in this study.

SUMMARY

This report covers the work accomplished during the period from March 1, 1964, to June 15, 1965, in developing an X-ray diffraction procedure for the quantitative determination of minerals. It also includes future proposed work.

The theoretical equations presented by Klug and Alexander in conjunction with Beer's Law form the foundation upon which this procedure is based. When the mass absorption is measured directly it is based upon a derivation of Beer's Law. This derivation relates the mass absorption of the sample to the properties of the sample and the aluminum foils.

The physical state of particle size and orientation were investigated. The particle size problem can be reduced by securing a motorized pestle and mortar and wet grinding the material. The orientation factor for most minerals may be resolved by using the ratios of three orthongonal diffraction peaks.

By adding a strong diffractor to the sample an indirect measurement of the mass absorption was accomplished, although, reproducibility was not good. However, the results obtained from measuring the mass absorption directly are reproducible and the accuracy is favorable. The average deviation varies from a high of 12% to a low of 2%. Better results can be obtained by securing some new equipment and more accurately measuring the aluminum foil standards.

Lastly, a log of k values and standard patterns should be compiled to be used for later reference.

PART I - WORK COMPLETED

Various approaches to the quantitative determination of soil and aggregate minerals have been used in the field of X-ray diffraction such as chemical analysis, method of addition, peak integration, standard charts, and the internal standard method. After examining these techniques and their combinations, it was decided to attempt to measure the mass absorption of the total sample using Beer's Law, and then use the values obtained in the following equations.

THEORETICAL EQUATIONS

The theoretical equations used for quantitative diffraction are based on those presented by Klug and Alexander(2). Assuming that the sample is a uniform mixture of "n" components with a particle size small enough that extinction and so-called micro-absorption effects are negligible, and of such thickness as to give maximum diffracted intensities, then the total intensity of X-rays diffracted by the ith component of the mixture by some selected plane (h k l) is given by:

$$I_i = \frac{K_i\, x_i}{\rho_i\left[x_i\,(\mu_i - \mu_m) + \mu_m\right]} \qquad (1)$$

Where: I_i = the diffracted intensity of the ith component in cps

K_i = depends upon the nature of the ith component and the geometry of the diffraction apparatus

x_i = the weight fraction of the ith component

ρ_i = the particle density of the ith component in gm/cm^3

μ_i = the mass absorption coefficient of the ith component

μ_m = the mass absorption coefficient of the matrix (the combined mass absorption coefficient for all the other components in the sample except the ith component)

μ_T = mass absorption for the total sample (all components)

let: $k_i = \frac{K_i}{\rho_i}$

Then: $\mu_T = x_i\,\mu_i + (1 - x_i)\,\mu_m$

$$\mu_m = \frac{\mu_T - x_i\,\mu_i}{1 - x_i}$$

$$I_i = \frac{K_i}{\rho_i} \cdot \frac{x_i}{x_i\,\mu_i + (1 - x_i)\,\dfrac{\mu_T - x_i\,\mu_i}{1 - x_i}}$$

$$I_i = \frac{k_i\, x_i}{\mu_T} \qquad (2)$$

$$k_i = \frac{I_i\,\mu_T}{x_i} \qquad (2a)$$

$$x_i = \frac{I_i\,\mu_T}{k_i} \qquad (2b)$$

The diffracted intensity for a particular (h k l) plane of a mineral is proportional to the weight fraction present divided by the mass absorption of the total sample. The mass absorption coefficient for any sample can be found by using Beer's Law where the fraction of parallel monochromatic (single wavelength) X-rays that pass directly through the sample unchanged in direction or wavelength is:

$$\frac{I}{I_o} = e^{-\mu_T \rho_T t} \qquad (3)$$

where: I = the intensity of X-rays transmitted through the sample in cps

I_o = the original incident beam intensity in cps

e = the Napierian base

μ_T = the mass absorption coefficient for the total sample

ρ_T = the density of the total sample in gm/cm^3

t = the sample thickness in cm

k_i can be found by substituting in equation (2a) if x_i is known. For a pure mineral $x_i = 1.00$.

THE PROBLEM OF PARTICLE SIZE

As stated in the first Progress Report, particle size has the greatest single effect on reproducibility of peak heights on an X-ray diffraction pattern. Ideally, a uniform particle size of 5 microns should yield the maximum intensity without line broadening problems and give 1% - 2% reproducibility. Experimental results of Klug and Alexander indicated this was true for quartz.

Several methods were explored in an attempt to obtain a satisfactory particle size. Dry grinding was tried, using tungsten carbide balls with a Spex Mixer Mill, Catalog No. 8000, manufactured by Spex Industries, Inc. This was unsatisfactory because there was no control on particle size and caking of material prevented efficient grinding. Wet grinding using stainless steel balls and methanol was effective in reducing particle size, but there was little control over uniformity and average size. An electric mortar grinder Model MG-2 manufactured by Torsion Balance Company was tried. This dry grinding method proved ineffective because of caking of clays. Wet grinding with the MG-2 was not tried.

Next a Selective-Uniform Particle Size Grinder, Photos 14 - 16, p. 35, manufactured by the Pitchford Manufacturing Corp. was tried. Five trial samples were sent to the manufacturer for grinding. They were montmorillonite, muscovite, fibrous serpentine, quartz, and a combination of the four minerals. Microscopic examination of the

ground samples indicated a favorable range of particle size was obtained. Less than five minutes was required to grind 10 grams of each of the above mentioned samples.

This grinder dry grinds using a tungsten carbide vial with slits on the sides of the vial that are covered by a 508 mesh screen. As the material is ground, it is blown through the screen, thereby controlling the particle size. Gulf Research and Development Co. in Harmarville, Pennsylvania, has been using this equipment to grind rock samples. However, they use a 450 mesh screen. They can process 30 to 40 samples daily.

It was considered more important to obtain a uniform particle size of 21 microns than to obtain a 5 micron size within a wide range of particle sizes. Rotation of the sample was considered as a possibility to improve reproducibility of the quantitative results from the larger size particles.

The Pitchford Selective-Uniform Particle Size Grinder appeared to be the best means of obtaining a uniform particle size and was, therefore, purchased. Although there was some delay in the delivery of the equipment, even more time was required to solve the mechanical difficulties inherent with this grinder.

The original tungsten carbide vial was too brittle and readily chipped, necessitating replacement. It was found that approximately 0.5 grams of material from a 10 gram charge was not recovered. Some of the lost material was caught in the collector system and some coarse material remained in the vial and never ground. Since the grinder removes the softest material first, the fraction left in the vial is the more resistant material; thus, a completely representative sample is not obtained. An operational skill must be developed to prevent clogging of the screen and to determine the proper grinding time. If the sample is completely ground, some tungsten contamination will result. Clogging of the screen by soil and aggregate samples has not been a real problem. The ground product is then mixed by the equipment and has proven satisfactory. However, the grinding of pure materials to check absorption theories has created problems in both clogging and mixing. With some material the screen clogs quickly and requires ultrasonic cleaning. Eight hours was required to obtain 20 grams of Fe_2O_3 even though the grinder has a 10-gram capacity. Equipment clean-up was a problem. Al_2O_3 has a tendency to form balls when ground. Consequently poor mixing of Al_2O_3 with Fe_2O_3 was experienced.

During a recent conference with Dr. Robert Rex of the California Research Corporation, he described a Fisher motorized pestle and mortar in which he grinds his samples using butanol. Dr. Rex has used a Pitchford grinder, but feels the wet grinding method he now uses has several important advantages.

It appears that particles when wet ground in a pestle and mortar reach a certain minimum particle size and then go into suspension, preventing further particle size reduction. The range in particle size is 1 to 16 microns. Two hours of grinding time are required per sample, however, only 15 minutes of operator time is necessary per sample. Mineral phase changes which may be produced by heat in the dry ball grinders would be eliminated. Finding a suitable grinder and time spent on the Pitchford grinder occupied at least two months.

MEASURING THE MASS ABSORPTION

Indirect Method

The first attempt to obtain the mass absorption coefficient for a sample was made using the following procedure. To the sample, 50% by weight of a high intensity diffractor was added. Then the diffracted intensity for the main peak of the high intensity diffractor was used to calculate the absorption of the composite sample. This procedure was tried in order to eliminate two problems inherent in the internal standard method; that of interference with the interpretation of the diffraction pattern because of secondary peaks from the internal standard used, and the problem of sample dilution.

First, a strong diffractor had to be found with a main peak that would not interfere with a diffraction peak of the common minerals. Much searching was done to find a suitable d-spacing. There are no tables available listing good diffractors except for those materials used as analyzing crystals. The best found was the 4.38 Å peak of pentaerythritol $C(CH_2OH)_4$. An example of an absorption determination is given below. The sample is mixed with 50% pentaerythritol (PET) and prepared using the backpack method described in the first progress report.

$$I_{PET_{100\%}} = 33{,}000 \text{ cps} \qquad \mu_{PET \text{ theoretical}} = 7.25$$

using equation (2a)

$$k_{PET} = \frac{I_{PET}\,\mu_{PET}}{x_{PET}} = \frac{33{,}000\ (7.25)}{1.00} = 240{,}000$$

using equation (1) and simplifying and solving for μ_m where μ_m is the original sample mass absorption and μ_{PET} is the PET mass absorption

$$\mu_m = \frac{x_{PET}\ (k_{PET} - \mu_{PET}\ I_{PET})}{I_{PET}\ (1 - x_{PET})}$$

if $x_{PET} = 0.50$ and $I_{PET_{50\%}} = 5{,}000$ cps then

$$\mu_m = \frac{0.50\ [240,000 - 7.25\ (5,000)]}{5,000\ (1 - 0.50)} = 40.8$$

To minimize the error in finding the absorption, a plot, Fig. 10, p. 28, of I_{PET} for pentaerythritol versus μ_T of the total sample using various percentages from 10 to 90% were made. It was found that 70% gave a steep average slope in the range of absorption values from μ_T = 20 to 100. This is the range normally expected from common minerals unless they have high iron content. For example, μ_T = 227 for pure magnetite.

When the sample was prepared by the briquette method, also described in the first progress report, reproducibility of absorption values was very poor. A manual count was made for the 4.38 Å peak three times: each time with the briquette rotated 120°. The range was 60,000 to 77,000 cps with an average of 67,000 cps; better than ±10% error. The 100% increase in intensity of the briquette from the back pack is primarily due to preferred orientation. The ±10% error is probably due to large particle size and differences in degree of preferred orientation within the same briquette. The nature of the sample may encourage or discourage preferred orientation.

Direct Method

It was decided to try to measure the absorption directly because the direct absorption technique is independent of orientation.

The same sample can be used for diffraction and absorption measurements when using the direct absorption technique. To achieve maximum random orientation for quantitative diffraction, a back pack is needed.

The thickness-density factor of the sample is critical in this method. The sample must be thin enough to allow sufficient intensity of CuK_α X-rays to be transmitted through the sample to keep the counting error low. However, the sample must be thick enough to hold together and to achieve maximum diffracted intensities.

Back pack holders were made of aluminum because they are nonmagnetic, noncorrosive, and nonfluorescent with CuK_α radiation. Aluminum can also be held to closer tolerances than plexiglas with less warping. The inside dimensions are 5.08 x 1.43 x 0.164 cm. Instead of using a glass slide to support the back pack in measuring the mass absorption, a piece of Magic Mending Tape was used. This tape is a very low absorber of CuK_α radiation. When a diffraction scan is run, a glass slide is used as a backup plate and then removed for the absorption measurements. For detailed back pack fabrication procedure see p. 15.

The absorption set-up consists of using a Cu target X-ray tube operated at 35 KVP and 22 MA, a 1° beam slit with a beam shutter assembly placed on the end of the beam slit holder to hold the aluminum foils and back pack, a LiF analyzing crystal, a MR soller slit, a 0.1° detector slit, a scintillation counter, pulse height selector and scaler.

The beam shutter assembly was designed and built to help solve the problem of shifting tube alignment caused by thermal expansion. In the first hour and one-half after the X-ray tube was energized the 2 θ angle for CuK_α using a LiF crystal shifted about 0.035° which caused a 10% change in intensity. In order to keep the 2 θ angle stabilized, the tantalum shutter was incorporated so that samples could be changed without turning off the X-ray tube.

After the X-ray beam passes through the beam slit it passes through a selected number of aluminum foils. These foils reduce the CuK_α intensity to the optimum counting level (10,000 cps) when the beam reaches the detector. After passing through the foils, the beam passes through the back pack sample and hits a LiF analyzing crystal. This crystal diffracts only CuK_α radiation and orders to the detector. These orders are filtered out by using a pulse height analyzer. After the count is taken the back pack is replaced by a sufficient number of aluminum foils to match the original count rate. When the count rate is low (below 450 cps) it needs to be matched as closely as possible because the electronics cease to have a linear response. The reason for this is not clearly understood. A plot of the natural log of intensity versus number of Al foils, Fig. 9, p. 27, is linear from about 8000 to 450 cps and reasonably linear to 150 cps. If the fraction of $\frac{I_o}{I}$ is kept very close to 1.00, count rates as low as 70 cps have given satisfactory absorption values.

The mass absorption "μ_T" is found by experimentally measuring I and I' and using the following equation:

$$\mu_T = \left[\ln \frac{I'}{I} - \mu_{Al}\, \rho_{Al}\, (t_{Al} - t'_{Al})\right] {}^{1}\!/\!_{\rho_T t} \qquad (4)$$

where: μ_T = mass absorption of unknown sample

I' = intensity of CuK_α passing through sample plus foils in cps

I = intensity of CuK_α passing through foils in cps

μ_{Al} = mass absorption of aluminum foils

ρ_{Al} = density of aluminum foils in gm/cm^3

t_{Al} = thickness of foils in cm used with sample

t'_{Al} = thickness of foils in cm used for obtaining second count

ρ_T = density of unknown sample in gm/cm^3

t = thickness of unknown sample in cm

The development of this equation is given in Fig. 2, p. 20.

EXPERIMENTAL RESULTS

Mass absorptions for 11 samples were determined experimentally. These samples ranged from 100% $CaCO_3$ - 0% LiF to 0% $CaCO_3$ - 100% LiF in 10% increments. The theoretical mass absorption of the samples ranged from 11.7 to 76.0. A correlation of the theoretical values and the experimental values is shown in Figure 3, p. 21. The deviation from the theoretical is 2.

The diffraction peak intensities were found by scanning at 2° per minute. This was the slowest speed that would be practical in routine work because scanning from $2\theta = 2$ to 65° would require 30 minutes. The following components and settings were used to obtain the diffraction peaks.

1. X-ray tube, operated at 35 KVP, 22 MA and 3° target angle
2. 1° beam slit
3. MR soller slit
4. 0.2° detector slit
5. 0.25 time constant
6. scintillation counter

It is desirable to reduce the number of variables in equation 2b in order to calculate the weight fraction of the ith component. To do this, samples can be prepared with varying percentages of this i^{th} component. The resulting "k" values can then be plotted versus the percentages of the ith component (see Fig. 5). A straight line curve is then drawn through the points.

From the resulting curve the value of "k" from the fifty percent level is used. Instead of using the peak height above background the peak area above background was used (Fig. 12, p. 30). This area was continuously recorded by a disc-integrator. For the $CaCo_3$-LiF series, the experimental μ_T was used. The density (1.2 to 1.6 gm/cm^3) of samples containing 50% Fe_2O_3 or greater proved to be too high, resulting in a very low count rate. Therefore, the theoretical μ_T was used in the computations. The "k" value for a particular component was obtained from the curve drawn (see Fig. 5) through the individual "k's" for the varying percentages. A density of 1 gm/cm^3 for a pure Fe_2O_3 sample has given satisfactory absorption results.

The wt. fraction results of the component seem to reflect both random and systematic errors. The range in error obtained from test data was ±10% for $CaCo_3$, ±15% for LiF, ±5% for Fe_2O_3, and ±20% for Al_2O_3. Table No. 1, p. 16, presents both the corrected and uncorrected quantitative results for absorption assuming that the quantity present is proportional to the intensity only. This data demonstrates why absorption corrections are needed.

Several factors may contribute to the error in quantitative determination. Some of these factors are particle size, mixing, orientation, counting error, and equipment errors. Use of a motorized pestle and mortar should reduce particle size, improve mixing, and encourage random orientation. It appears that the degree of orientation changes with concentration. Dr. Rex suggests that possibly an orientation correction can be applied by comparing the ratios of peak area intensities of three orthongonal or nearly orthongonal planes.

Table No. 2, p. 17, lists the results of six back packs containing a mixture of 50% $CaCO_3$ and 50% LiF. The purpose of this series was to evaluate the reproducibility of the method. The maximum range relative to the mean was ±5% for the $CaCO_3$ and ±21% for the LiF. The mean number of total counts for the $CaCO_3$ was 23,100 and 14,200 for the LiF giving a possible counting error of ±1.5% and ±2% respectively at a 95% confidence level. An explanation for the great difference in range of reproducibility is that the LiF may be much more sensitive to orientation.

It is interesting to note that if the theoretical mass absorption is used, instead of the experimental, the weight fraction is improved .03-.04 (3-4%). With improved aluminum foil standards the experimental mass absorption may also be improved.

Indication of back pack density uniformity is shown by Table 3, p. 18. Mass absorption measurements were taken at two other positions (1/8 in. left and 1/4 in. left of the central position) across the face of the fabricated $CaCO_3$ - LiF series, in order to determine changes in density.

The results are listed in Table 3. The difference in mass absorption measurements between the three positions varied from 0 to .5. This indicates that the present sample fabrication method is adequate.

The experimental results of this study appear promising in establishing a procedure for quantitative X-ray analysis of minerals in soils and rock. Further work is necessary to refine this procedure.

PART II

PROPOSED WORK OUTLINE

The following is a proposed detailed work outline for the continuation of the research project from July, 1965. Four phases are proposed:

Phase I	Purchase a motorized pestle and mortar with auxiliary equipment. A Tem-Pres tube mount may be required. Prepare standard Aluminum foils. Attempt to improve reproducibility by using the aforementioned new equipment.
Phase II	Determine how the mean experimental quantitative results compare with the theoretical values.
Phase III	Attempt to reduce equipment errors by modifying and supplementing the present equipment.
Phase IV	Compile a log of k values and standard patterns.

Phase I - Equipment

The purchase of a Fisher motor-driven pestle and mortar with a mullite vial is proposed. A vapor hood is needed to safely vent the butanol vapors as the mineral slurry is heated for butanol removal following grinding.

The X-ray tube should be checked for alignment stability. To do this the tube geometry will be carefully aligned after a two-hour warm-up period by taking readings for 2 hours using 20 layers of approximately 0.001 inch thick pure aluminum foil. The X-ray tube will be operated at 35 KVP, 22 MA, and 3° target angle, and a MR soller slit, 1° beam slit, LiF crystal in the sample holder set on the CuK_{α} peak, 0.1° detector slit, and a NaI scintillation counter will be used. The shield with a 3/8-inch diameter hole will be placed over the detector to prevent stray radiation from reaching it. Using a 20 second counting time, the counting error will be less than $\pm 0.5\%$ for an 8000 cps peak. To check the stability of the tube geometry a series of peak profiles will be plotted. This will be done by taking 20 second counts from $2\theta = 44.89°$ to 44.98° in 0.01° increments. A profile will be taken every 10 minutes for two hours and then plotted. The effect of poor stability can be seen by realizing that the CuK_{α} is measured by setting at one 2θ value. If the peak shifts, then the intensity could rise and then fall, or just fall with time depending on which side of the peak the 2θ value was. The tube alignment always moves in the same direction. This change in tube alignment is relatively unimportant in diffraction when scanning, because the net effect is a very slight shift in the 2θ value for the peaks.

If the tube is not stable then a Tem-Pres tube mount should be purchased which rigidly holds the front of the X-ray tube to the goniometer. This allows the rear of the tube to expand freely but keeps the tube target geometry constant. The mount can be purchased from Tem-Pres Research, Inc., State College, Pennsylvania.

When satisfactory tube stability has been obtained, then the thickness of each aluminum foil can be indirectly determined. Pure aluminum foil approximately 0.001 inch thick will be purchased. A chemical analysis will then be run to determine the purity. A large, accurately measured sheet will then be weighed. Assuming a density of 2.699 grams per cubic centimeter, the average thickness can then be determined. Five 0.5 x 2.0 inch pieces will be cut from the sheet and used together as a standard foil having an assumed thickness equal to the average thickness multiplied five times. Thus, the standard foil has an assumed density (ρ), an adjusted mass absorption (μ_{Al}), and an assumed thickness in cm (t). The thickness of a single foil with respect to the standard foil (five foil) can be found using the equation:

$$\ln \frac{I_{single\ foil}}{I_{Standard\ foil}} = \mu_{Al}\rho_{Al}(t_{Std}-t_{single}) \qquad (5)$$

Comparison of a single foil to a standard of five foils will minimize the effect of the counting error. The ratio of intensities when comparing a single foil to a single foil is very close to 1.0. Near 1.0 the natural log approaches zero very rapidly so that a $\pm$0.25% counting error could be magnified 25 times or more. Using five layers rather than one, the ratio is close to 4. If the counting error is $\pm$0.25%, the thickness can be determined to $\pm$1%. It should be noted that the counting error is always for a 95% confidence level, meaning that 95 times out of 100 the true value will fall somewhere between $\pm$0.25% of the reading.

At least two-hundred fifty-five 0.5 x 2.0 inch foils will then be made, followed by a comparison of each foil with the standard five foil using a 100 sec count. This will reduce the counting error to $\pm$0.25%. After the relative thickness has been determined, the foils will be made into 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, and 60 foil standard packets.

Using a series of packets of varying numbers of foils, and knowing the relative thickness, the non-linear correction for the detector system can be found by plotting the natural log of the intensity ratio of I/I_o for each number of soils versus thickness.

The initial counting time should be long enough to obtain a counting error of ±0.25% for a 20-foil packet, and then as the number of foils increases the counting time should be increased to maintain a ±0.25% error. The total counting time should not exceed 400 sec., however, as the results will not justify the time. The correction will be the number of cps that need to be added to each intensity to produce a straight line.

Phase II - Comparison of Experimental and Theoretical Values

Hopefully the reproducibility error in diffracted peak intensity and the random and systematic errors in measuring mass absorption will have been reduced in Phase I. The purpose of Phase II will be to determine how closely the experimental mean quantitative values agree with the theoretical values.

Five back packs will be made for each concentration of $CaCO_3$-LiF mixtures of 0, 30, 50, 70, and 100%. The experimental mean concentration values will then be compared to the theoretical values to determine what differences exist and whether they are random or systematic. If samples with a large concentration of one material give higher experimental values than the corresponding theoretical values, and conversely if samples with a low concentration of a particular mineral give lower experimental value than their corresponding theoretical values, this may indicate problems with changing degrees of orientation as a function of concentration. If this is the case, data from Phase I concerning particle size and shape may help explain what is occurring. If orientation is a major factor, its influence will probably be different for each material.

The degree of orientation for a particle will be explored to determine if it is constant for a given concentration regardless of the other minerals in the mixture. This can be done by mixing minerals with various crystal shapes such as needles, disks, cubes and spheres with $CaCO_3$.

If the degree of orientation is affected by the other constituents, a possible approach in reducing the error is to try and correct for orientation by comparing the ratios of three orthongonal or nearly orthongonal diffraction peaks. The ratios should remain constant regardless of concentration provided the degree of orientation remains constant. This solution may not be feasible for many minerals because three orthogonal planes of sufficient diffractive intensity may not be available. This procedure should be tried with several minerals to cover the range in particle shape and size.

Phase III - Reduction of Equipment Errors

If problems of reproducibility arising from mixing, grinding, and orientation can be sufficiently controlled through Phases I and II then additional equipment components should be considered as a means of further refinement of quantitative measurements.

A major improvement would be the installation of a LiF monochromator between the detector and the diffraction sample. This monochromator would eliminate 99% of the background and remove all of the high background at low 2 θ angles. The diffraction peaks would be cut in half, but operation of the X-ray tube at 50 KVP rather than 35 KVP should off-set much of the decrease. Present operation of the X-ray tube above 35 KVP produces a false peak at 6° = 2 θ resulting from excitation of iodine in the NaI crystal of the scintillation counter. This will not occur when a monochromator is used.

Use of a high intensity tube will produce about 50% more CuK_{α} when operated at 50 KVP and 32 MA. In addition to the purchase of a high intensity tube, a Tem-Pres tube mount could be installed to improve alignment stability.

To improve the linearity and stability of the electronics and increase the range of linearity with less than 1% deviation from 0 to 15,000 cps, several components are needed; a sealed Xeonon Proportional Counter, a linear amplifier and pulse height selector, a preamp, and a kit to modify the high voltage power supply for the detector. A constant potential unit which produces a constant wave pattern could be installed to stabilize the X-ray intensity.

Phase IV - Compilation of k Values and Standard Patterns

Once the quantitative procedure is standardized and the error reduced to its practical limit, a list of k values for different minerals can be accrued along with the expected range of error. The range of error will be a function of how strong a diffractor a mineral is, since the counting error is a function of total counts. The range of error will also reflect the degree of isomorphic substitution and crystallinity.

APPENDIX A

REFERENCES

(1) Adams, P. M., "Progress Report on Identification of Soil Minerals by X-ray Diffraction," California Division of Highways, Materials and Research Department.

(2) Klug, H. P., and Alexander, L. E., "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials," Wiley, New York, 1954.

APPENDIX B

BACK PACK SAMPLE PREPARATION

Steps

1. Set up Syntron vibrating unit as shown in Photo 1, p. 31. Note: Mount vibrator on separate foundation from back pack frame holder. As the back pack stack is being filled it must not vibrate since this may encourage preferred orientation.

2. Position the back pack stack beneath the recess in the plexiglas insert (see Photo No. 3, p. 31). Then cover the back pack stack with a cover sheet.

3. Place 3 grams of the ground material in the recess and distribute it in such a fashion (see Photo No. 4, p. 32) that it will result in the back pack stack being uniformly filled.

4. Remove the back pack cover sheet.

5. Turn on the Syntron vibrator assembly (which has been previously adjusted for a satisfactory vibration rate) and fill the back pack stack.

6. Slide the filled stack from under the screen.

7. Remove excess of powder from top frame with razor blade (see Photo No. 5).

8. Remove frame #3.

9. Remove excess powder from frame #2 as previously stated.

10. Remove frame #2.

11. With an alcohol-cleaned photographic glass press plate, gently press the powder remaining above frame #1 into frame #1. (See Photo No. 8).

12. Remove excess powder from frame #1 being careful to preserve a smooth finish on this surface (see Photo No. 9).

13. Carefully place a strip of "Magic Mending" tape over this exposed face.

The sample is now ready for the diffraction phase.

APPENDIX C

TABLE No. 1

Table of Experimental Results
$CaCO_3$ - LiF Series and Fe_2O_3 - Al_2O_3 Series

	$CaCO_3$						LiF						Fe_2O_3			Al_2O_3		
	$k_{2.09}$ = 5,280**			$k_{3.03}$ = 29,700**			$k_{2.01}$ = 18,800**			$k_{2.32}$ = 13,100**			k = 122,000***			k = 67,500***		
Theoretical %	% Exp. c	dev.	% Exp. unc.	% Exp. c	dev.	% Exp. unc.	% Exp. c	dev.	% Exp. unc.	% Exp. c	dev.	% Exp. unc.	% Exp. c'	dev.	% Exp. unc.	% Exp. c'	dev.	% Exp. unc.
10	10.4	+.4	42.2	10.1	+.1	38.2	11.5	+1.5	2.3	9.5	-.5	1.6	8.5 (9.3)*	-1.5	35.7	-	-	-
20	22.0	+2.0	70.9	19.9	-.1	59.6	32.1	+12.1	7.0	18.1	-1.9	3.3	19.7 (21.6)*	-0.3	60.2	18.1	-1.9	4.2
30	27.9	-2.1	75.0	26.6	-3.4	66.4	35.5	+5.5	8.5	33.5	+3.5	6.8	31.2 (30.2)*	+1.2	74.4	35.7	+5.7	9.2
40	46.5	+6.5	84.6	38.4	-2.6	77.4	34.1	-5.9	10.0	39.9	-.1	9.7	41.4 (38.6)*	+1.4	81.5	48.8	+8.8	14.2
50	46.5	-3.5	101.0	47.6	-2.4	81.1	52.6	+2.6	17.9	48.9	-1.1	13.8	49.2	-0.8	82.4	49.8	-0.2	16.7
60	51.2	-8.8	80.5	57.6	-3.4	84.2	56.6	-3.4	22.9	65.5	+5.5	22.1	58.8	-1.2	85.4	52.6	-7.4	20.8
70	70.6	+.6	91.4	80.6	+10.6	97.2	57.5	-12.5	28.8	68.5	-1.5	28.7	71.6	+1.6	92.0	66.6	-3.4	31.9
80	77.5	-2.5	91.4	83.6	+3.6	92.0	63.3	-16.7	37.9	81.8	+1.8	40.9	80.6	+0.6	92.8	61.5	-18.5	37.6
90	92.1	+2.1	101.0	95.6	+5.6	97.6	88.9	-1.1	67.2	100.2	+10.2	63.5	93.8	+3.8	97.8	63.1	-26.9	53.0
100	112.4	+12.4	108.1	115.1	+15.1	103.7	84.2	-15.8	101.6	94.4	-4.6	95.4	106.6	+6.6	101.6	69.0	-31.0	93.4
Ave. dev.		4.1			4.7			7.7			3.1			1.9			11.5	

* = using experimental μ
Exp. = experimental
dev. = deviation of experimental (corrected) from theoretical %
c = corrected for absorption (experimental)
c' = " " " (theoretical)
unc. = uncorrected for absorption
** = 5,000 cps range dial setting
*** = 2,000 " " " "

TABLE NO. 2

REPRODUCIBILITY STUDY

Sample - .50 $CaCO_3$ and .50 LiF

	$CaCO_3$ $k_{3.03}$ = 113,100 *				LiF $k_{2.01}$ = 74,200 **			
BP#	I_{area}	μ_T	x	x'	I_{area}	μ_T	x	x'
3	1293	40.1	.470	.502	788	40.1	.426	.466
6_1	1272	40.2	.464	.494	844	40.2	.457	.499
7_2	1243	39.9	.439	.482	777	39.9	.418	.459
8_3	1264	40.7	.456	.490	617	40.7	.338	.365
9_4	1350	40.5	.484	.524	940	40.5	.513	.556
10_5	1294	40.3	.464	.502	750	40.3	.407	.444
Mean	1286	40.3	.464	.494	786	40.3	.427	.465
Overall Range	107	0.8	.045	.042	323	0.8	.175	.191

x = wt. fraction of said component
x' = wt. fraction of said component using theoretical μ_T (43.9)
I_{area} = intensity in cps as obtained from the strip chart using the disc-integrator
1 - 5 = sequence of testing

* = see fig. 5
** = see fig. 7
$x_i = \frac{I_i \mu_T}{k}$ equation no. 2b

TABLE NO. 3

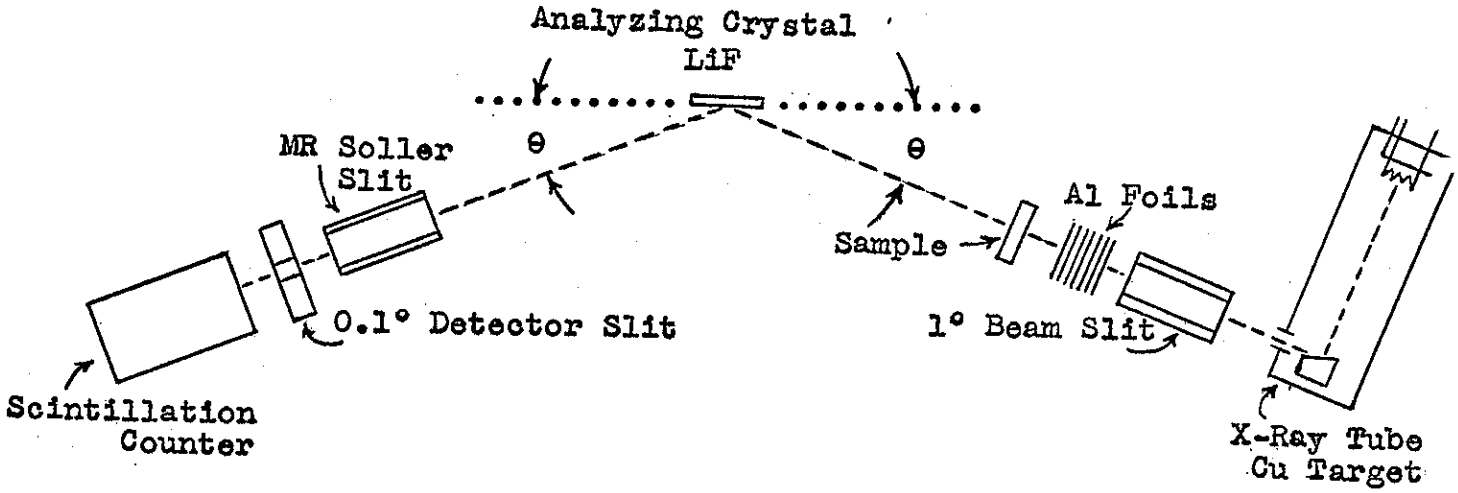
MEASURING THE DENSITY ACROSS THE FACE OF THE BACK PACK FOR UNIFORMITY

Values in terms of mass absorption

LiF - $CaCO_3$ Mixture

BP No.	1/4" lt.	1/8" lt.	Center
1	11.1	11.1	11.1
2	28.0	27.9	27.9
3	40.1	40.1	40.1
4	52.9	53.0	53.2
5	75.0	75.0	74.9
6	40.1	40.1	40.2
7	39.7	39.7	39.9
8	40.9	40.8	40.7
9	40.0	40.2	40.5
10	40.7	40.4	40.3

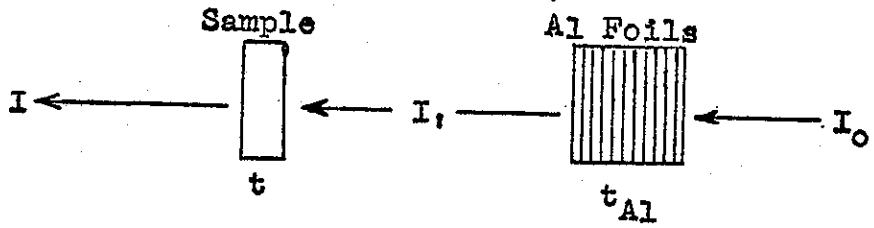
METHOD OF OBTAINING MASS ABSORPTION
DIRECT



X-Ray Path $2\theta = 44.94$

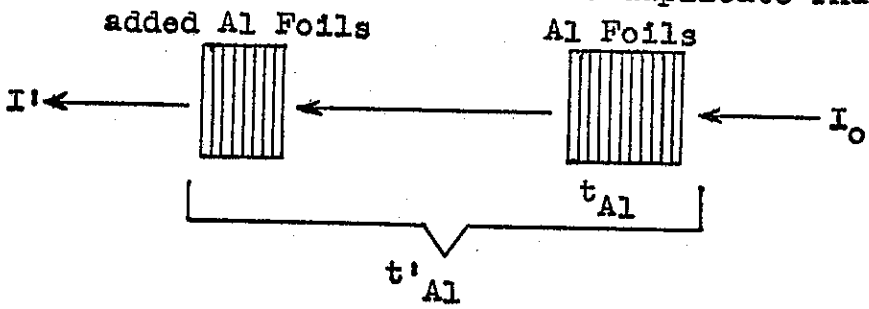
Phase I

(as shown above)



Phase II

(replace sample with additional Al Foils to duplicate Phase I count)

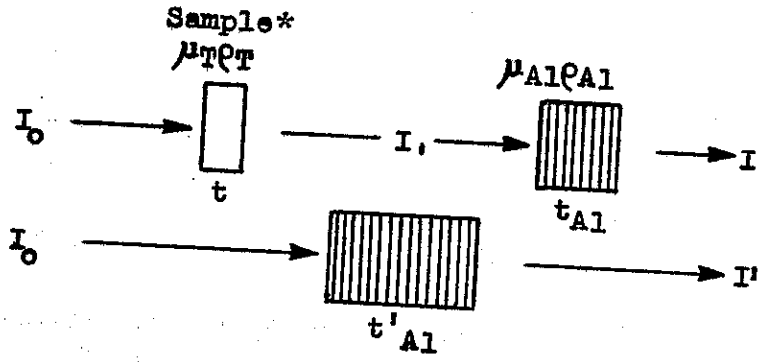


I' must be close to I so that $\frac{I}{I'} \cong 1$

then by substituting in 4. (see page 7),

$$\mu_T = \left[\ln\frac{I'}{I} - \mu_{Al}\,\rho_{Al}\,(t_{Al} - t'_{Al})\right]\frac{1}{\rho_T t} \qquad 4.$$

Fig. 1



$$I_1 = I_o\, e^{-\mu_T \rho_T t}$$ Beer's Law

$$I = I_1\, e^{-\mu_{Al} \rho_{Al} t_{Al}}$$

$$I = (I_o\, e^{-\mu_T \rho_T t})\, e^{-\mu_{Al} \rho_{Al} t_{Al}}$$

$$I_o = I\, e^{\mu_T \rho_T t + \mu_{Al} \rho_{Al} t_{Al}}$$

$$I_o = I'\, e^{\mu_{Al} \rho_{Al} t'_{Al}}$$

$$\frac{I'}{I} = e^{\mu_T \rho_T t + \mu_{Al} \rho_{Al} (t_{Al} - t'_{Al})}$$

$$\ln \frac{I'}{I} = \mu_T \rho_T t + \mu_{Al} \rho_{Al} (t_{Al} - t'_{Al})$$

$$\mu_T = \left[\ln \frac{I'}{I} - \mu_{Al} \rho_{Al} (t_{Al} - t'_{Al})\right] \frac{1}{\rho_T t} \qquad 4.$$

*For derivation purposes the sample was placed before the Al foils but in practice the sample is placed after the Al foils (see Fig. 1)

Fig. 2

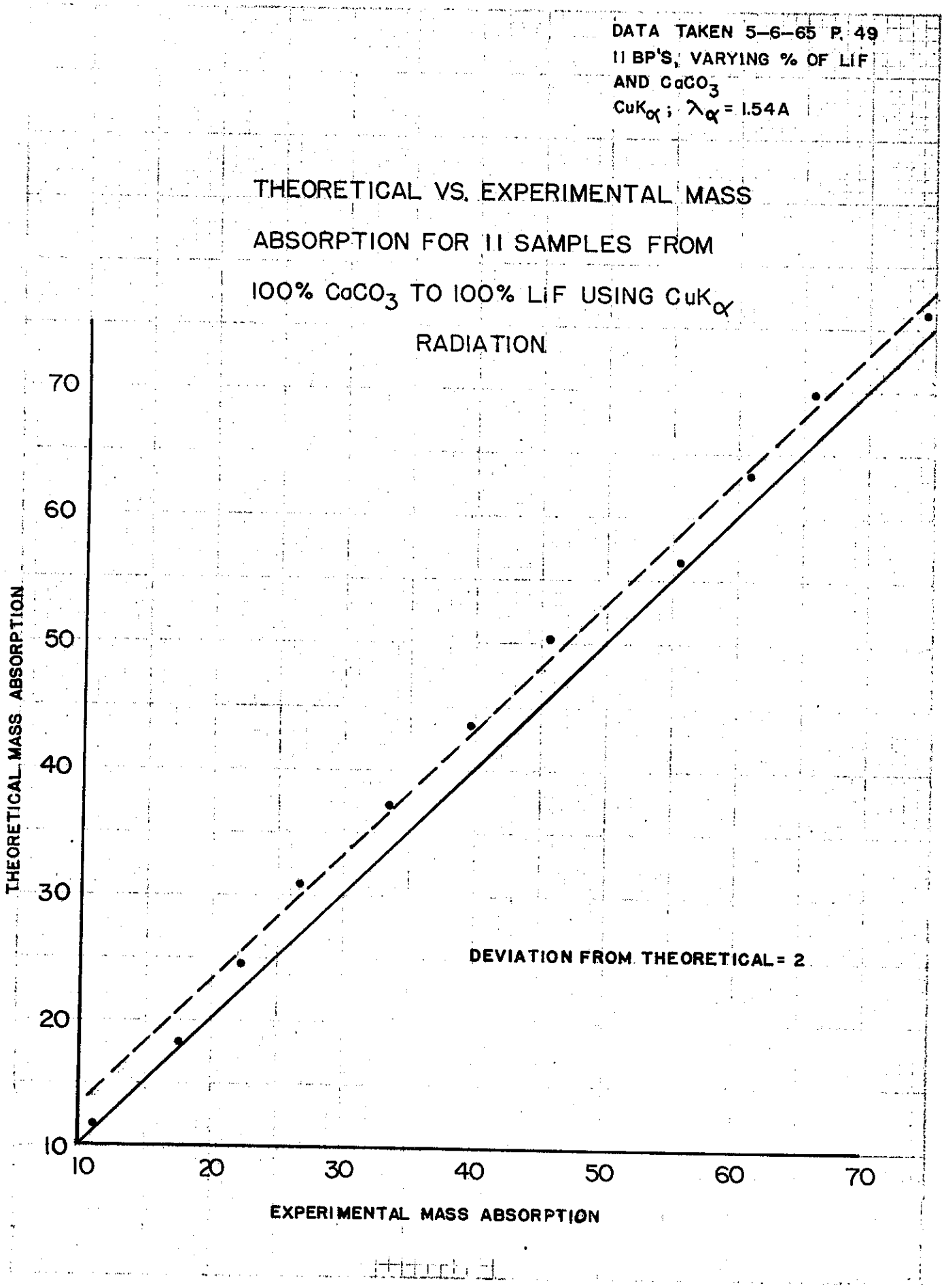


Fig. 3

ALCOA WRAP: 5-10-65

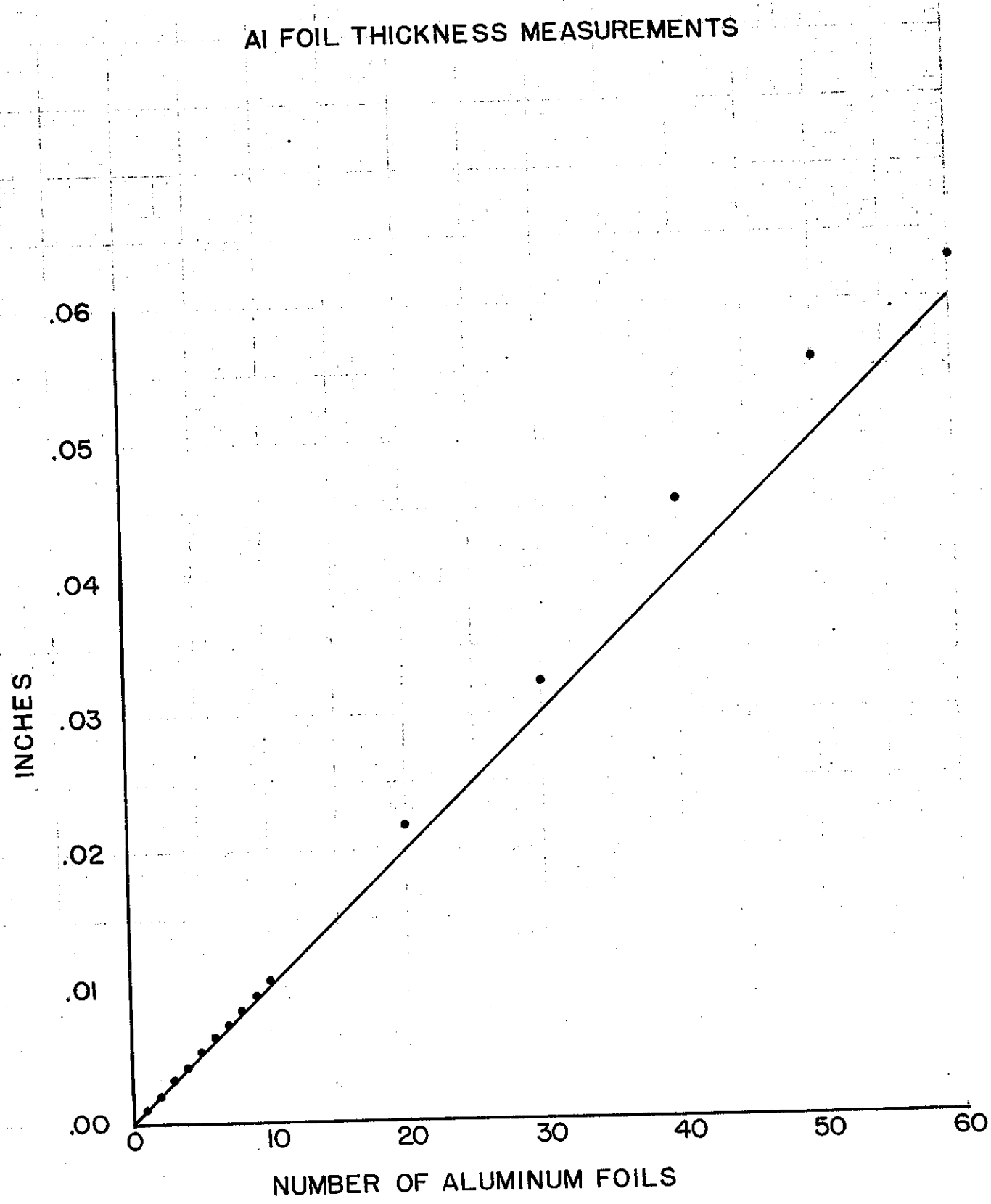


Fig. 4

METHOD OF OBTAINING "k" VALUES

FOR $CaCO_3$ AT DIFFERENT RANGE DIAL SETTINGS

$\lambda = 3.03$ Å
$CaCO_3$-LiF

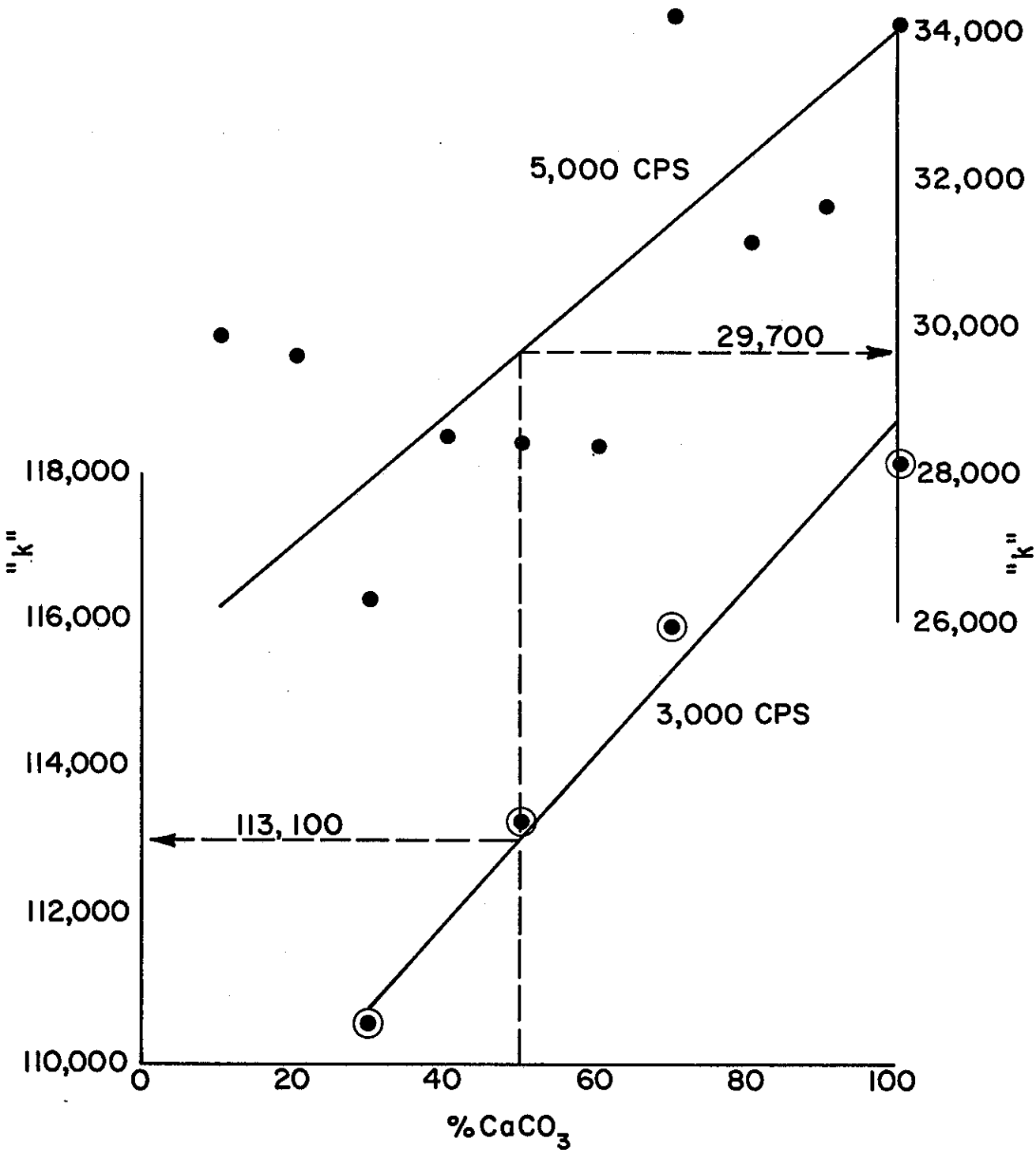


Fig. 5

METHOD OF OBTAINING "k" VALUES

FORMULA : $k_i = \frac{I_i \mu_T}{x_i}$

MIXTURE : $Al_2O_3 - Fe_2O_3$

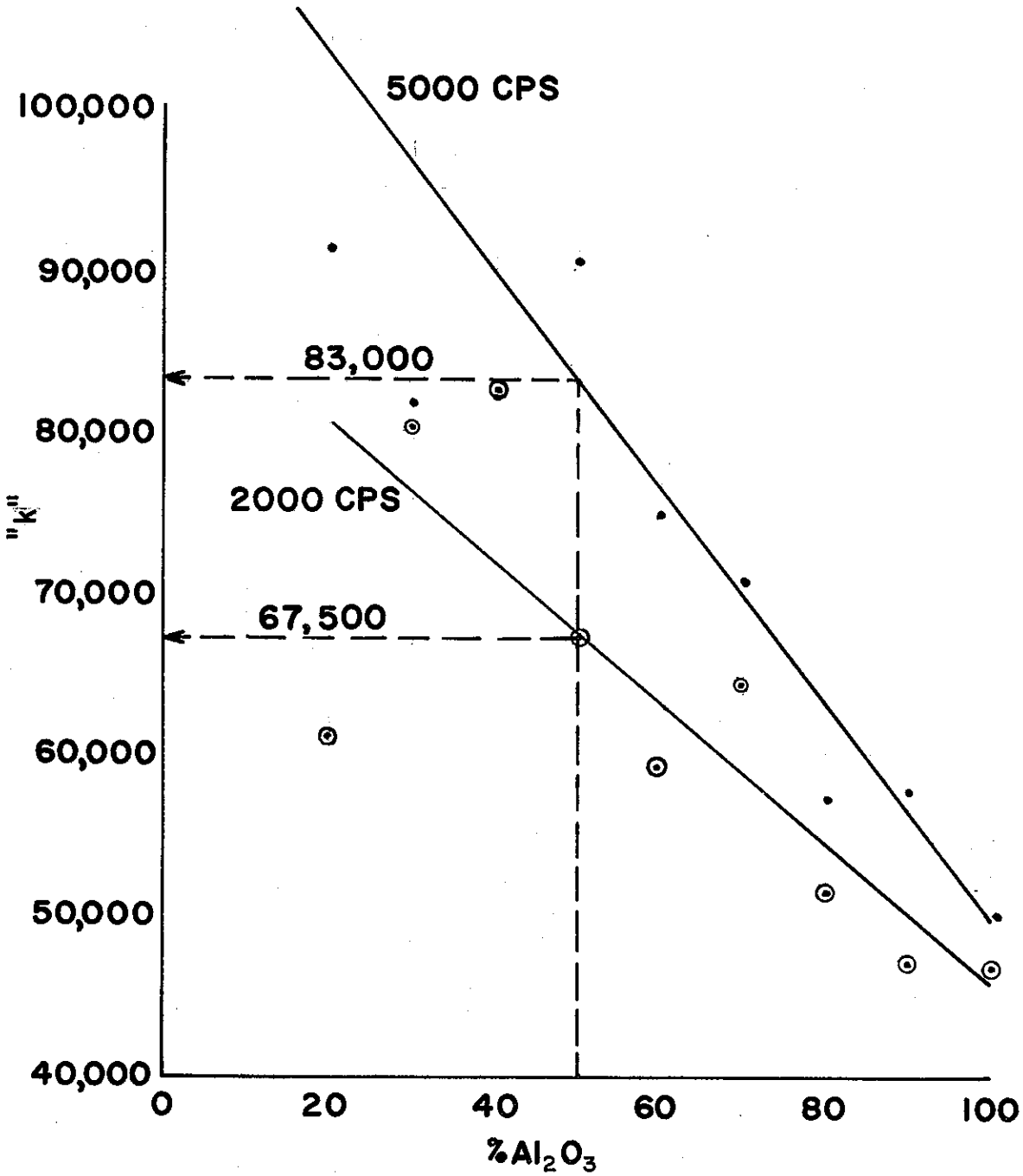


Fig. 6

METHOD OF OBTAINING "k" VALUES

FOR LiF AT DIFFERENT RANGE DIAL SETTINGS

$\lambda = 2.01$ Å
$CaCO_3$-LiF

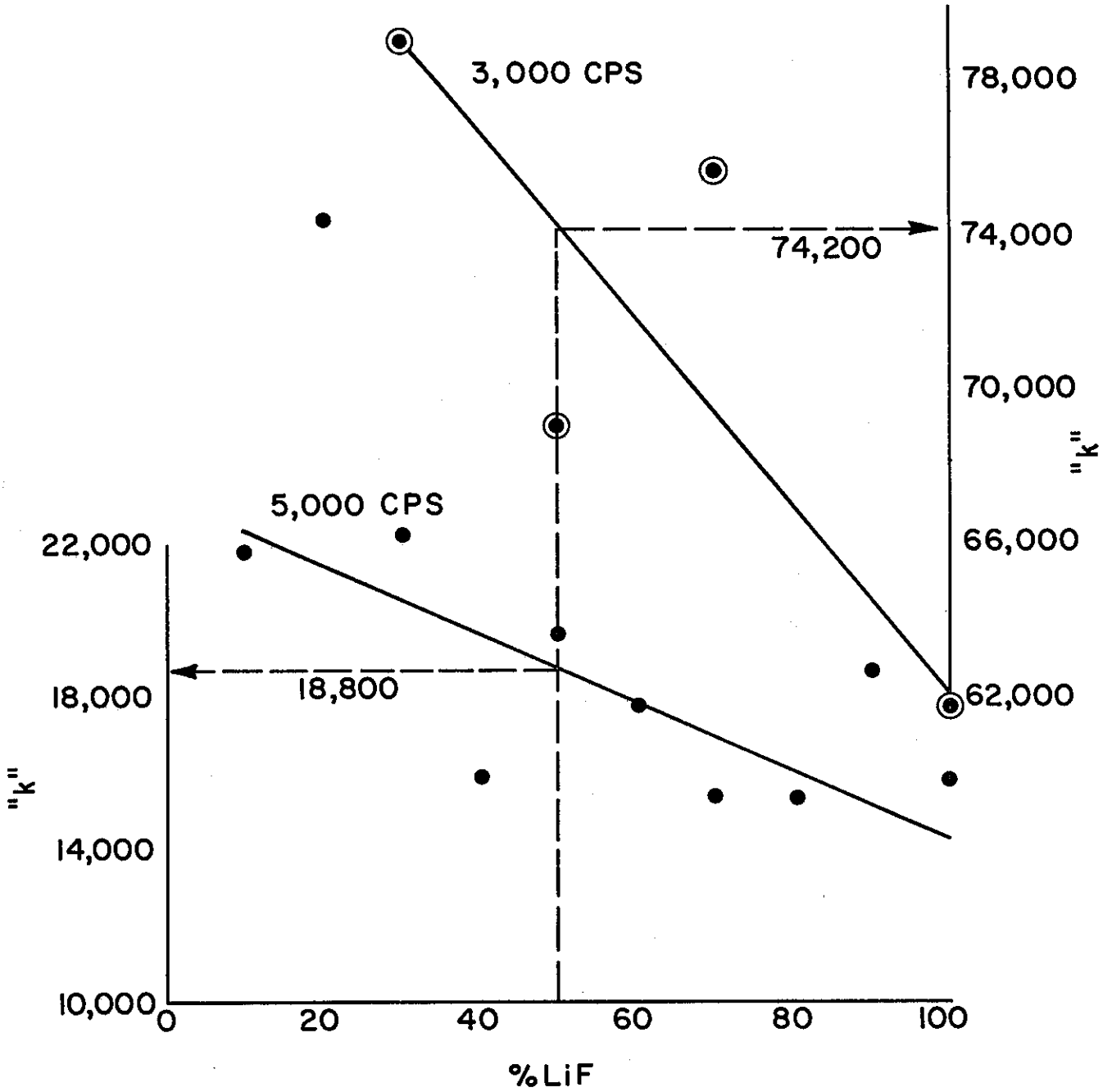


Fig. 7

METHOD OF OBTAINING "k" VALUES

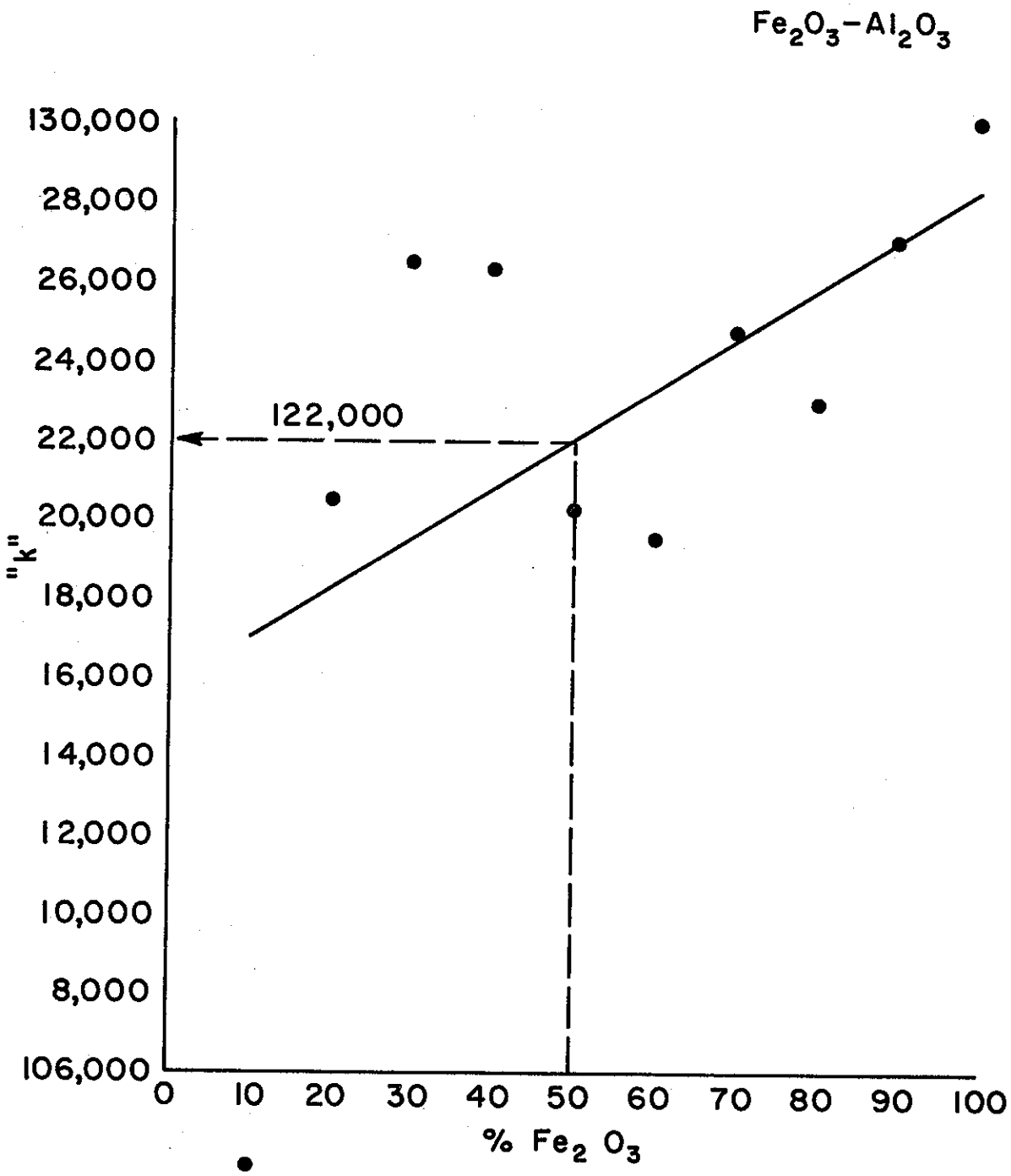


Fig. 8

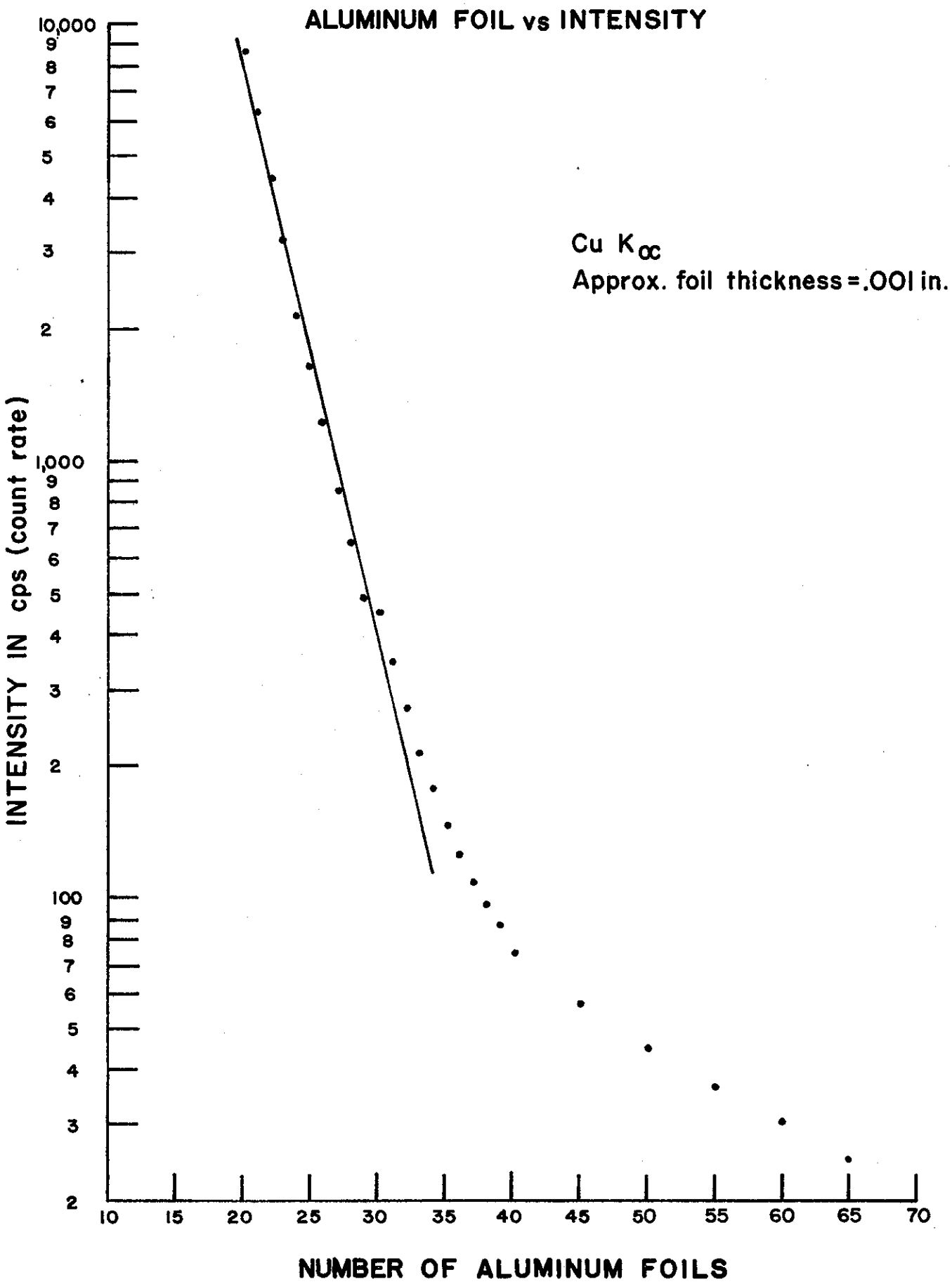


Fig. 9

INTENSITY vs MASS ABSORPTION
FOR VARIOUS % OF PENTAERYTHRITOL
IN THE SAMPLE

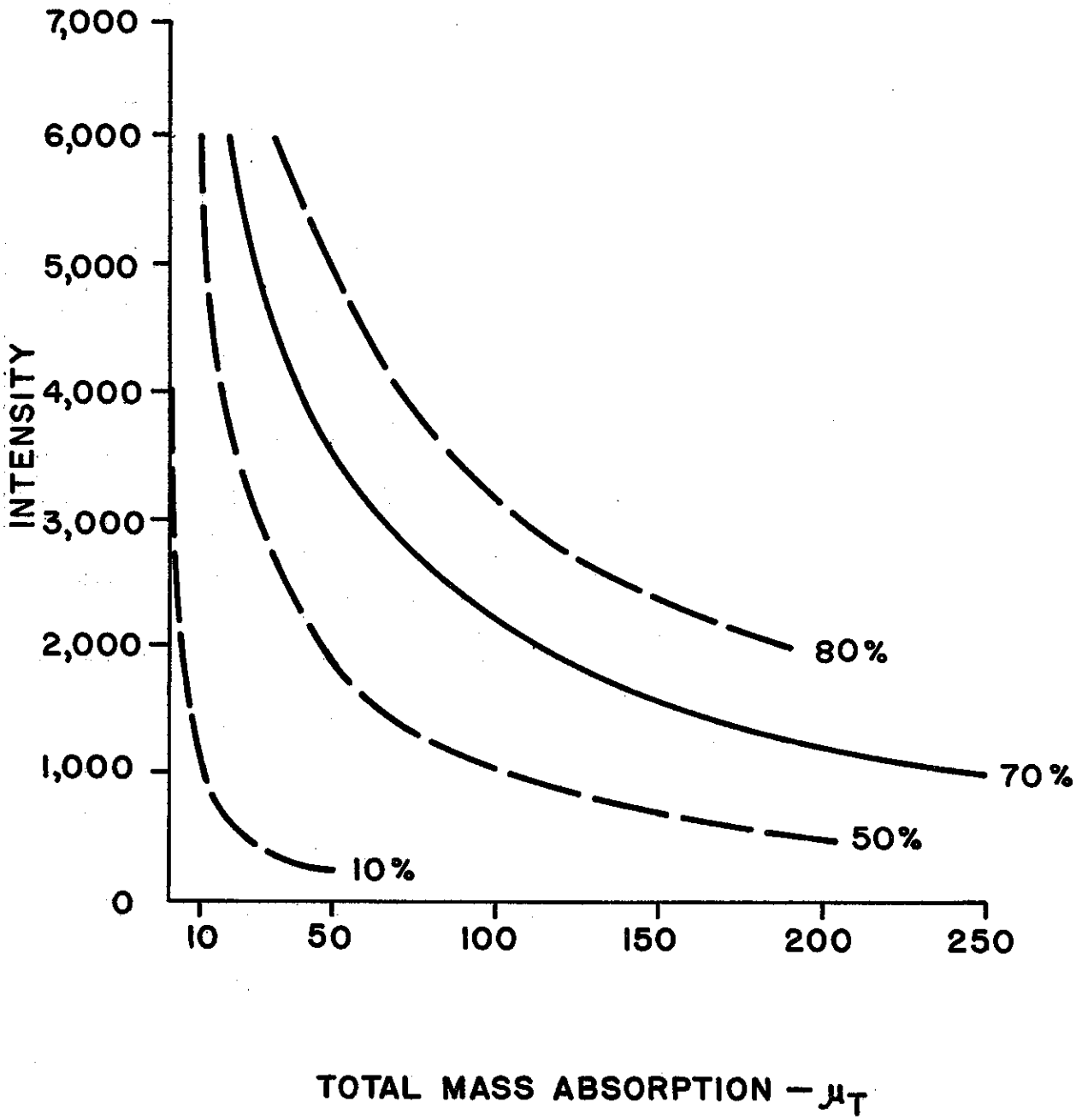


Fig. 10

X-RAY OPERATIONAL ARRANGEMENT

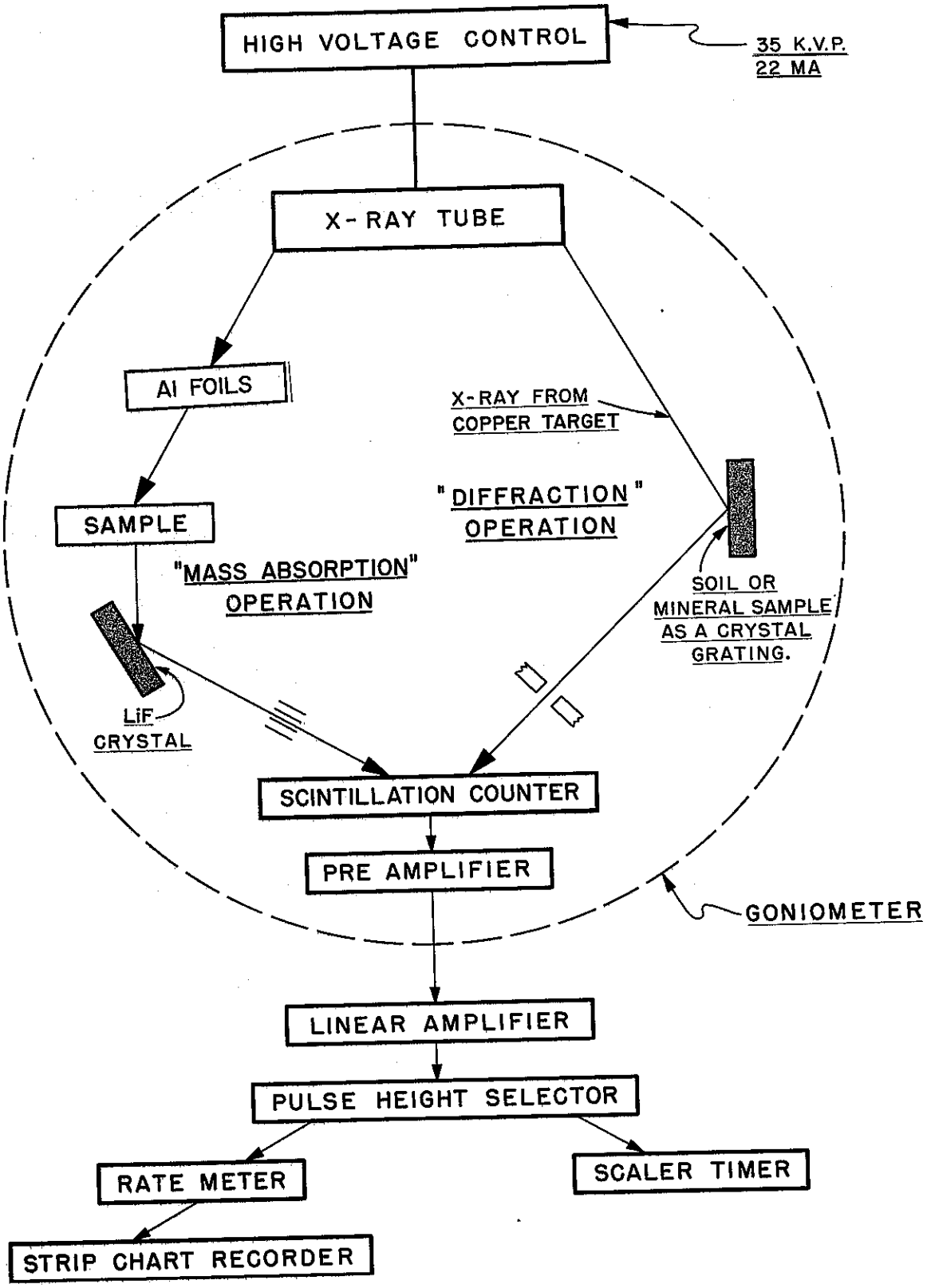


FIG. 11

BP #6 3rd run @ 5000 cps, .0035 Ni filter, 0.5 TC, 50% CaCO & 50% LiF

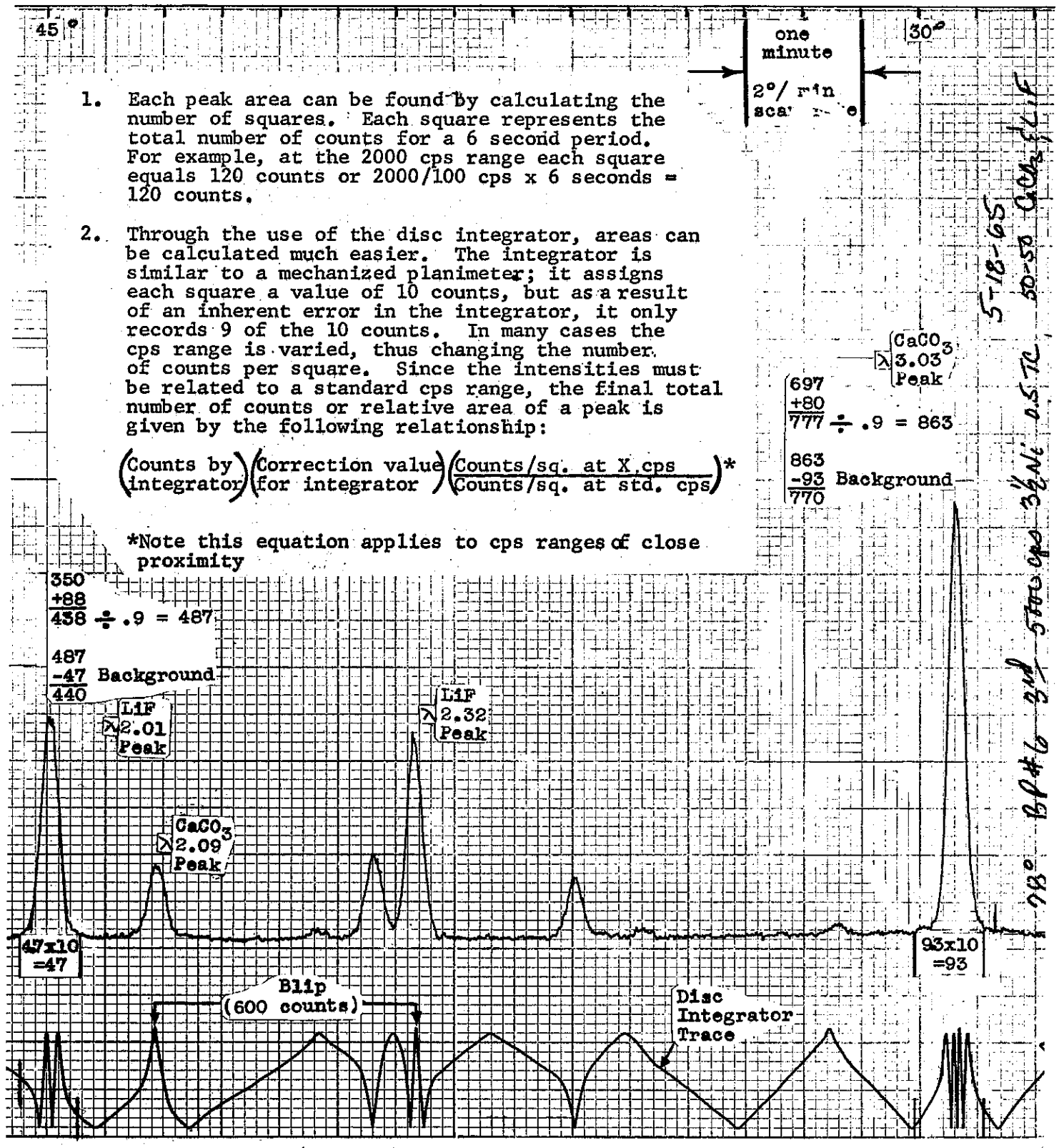


FIG. 12

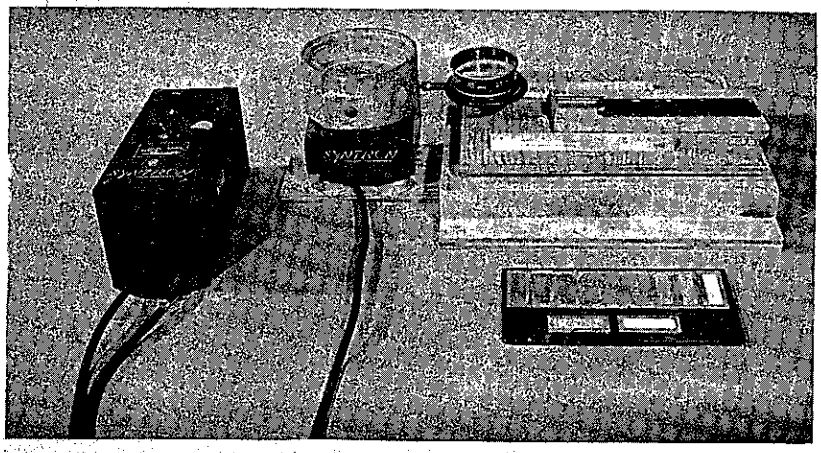


Photo No. 1

Back pack preparation assembly. A Syntron vibratory parts feeder supplies the energy to the screen.

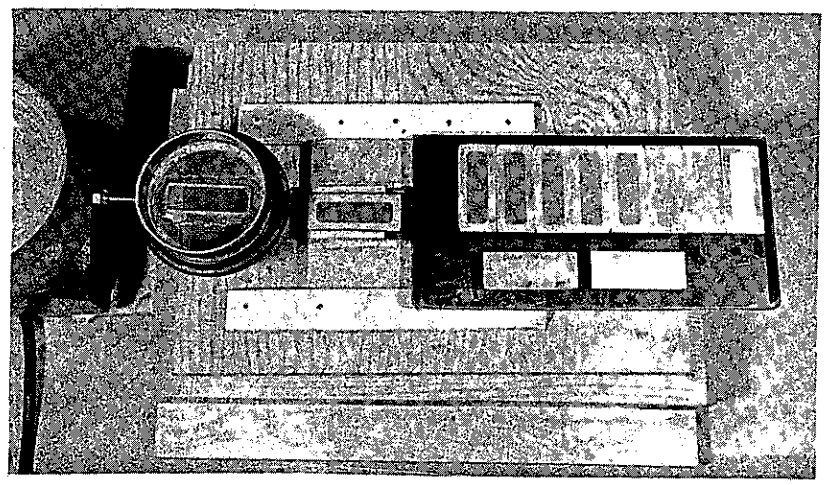


Photo No. 2

Slotted plexiglass insert mounted in a 3-inch 20-mesh sieve.

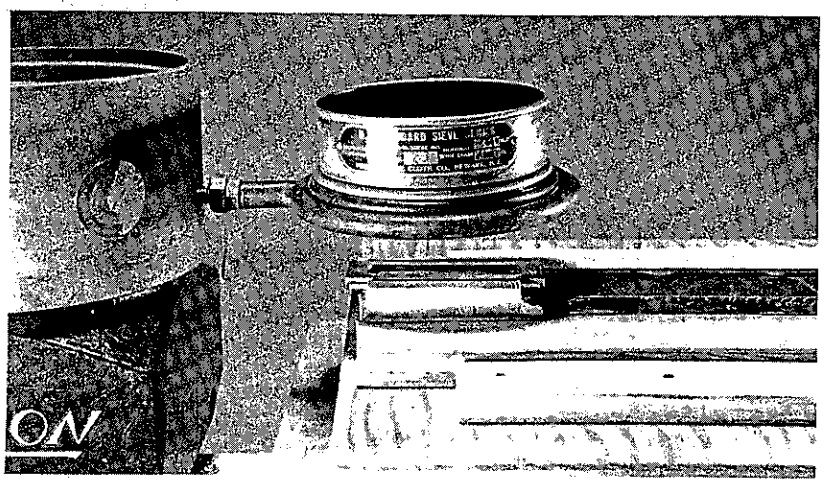


Photo No. 3

Close-up view illustrates the relative position of the back pack stack beneath the vibrating sieve.

Back Pack Fabrication Sequence

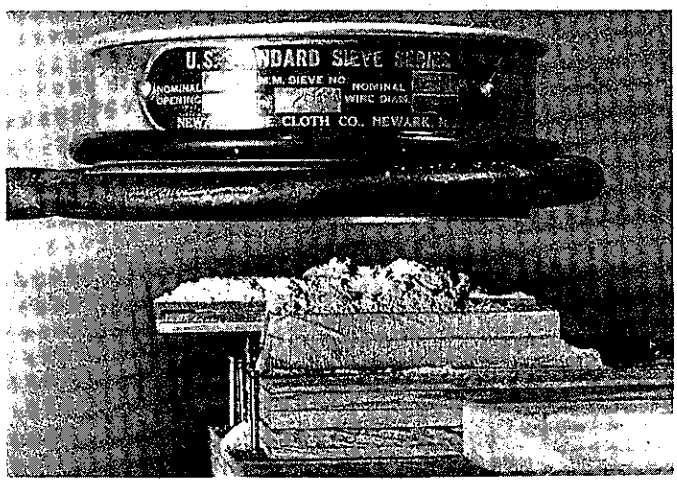


Photo No. 4
Back pack frames filled with powder

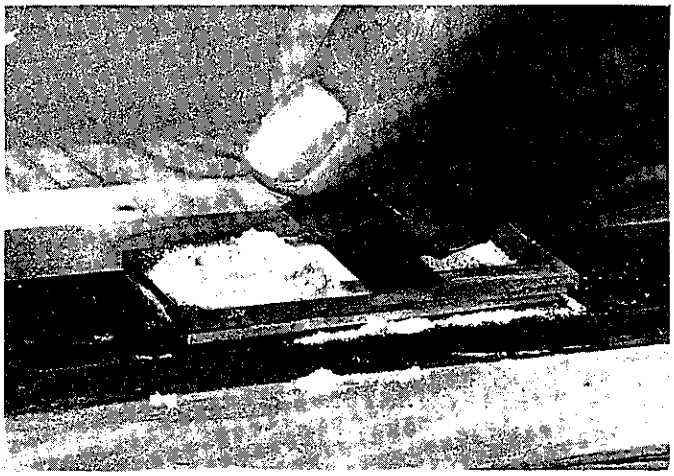


Photo No. 5
Removing powder from top of frame #3

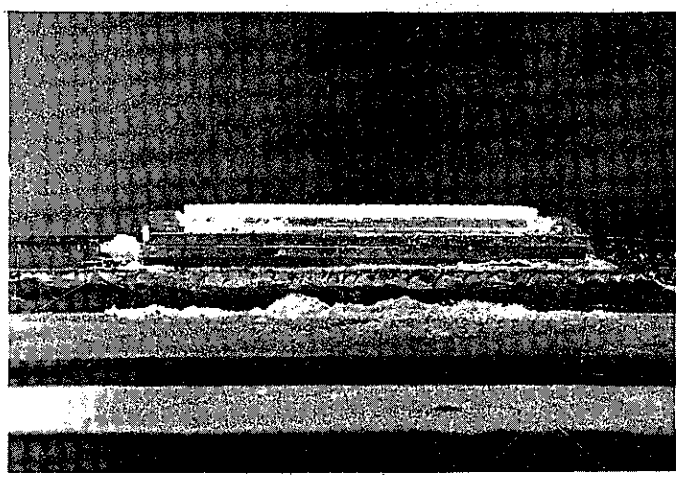


Photo No. 6
After frame #3 is removed

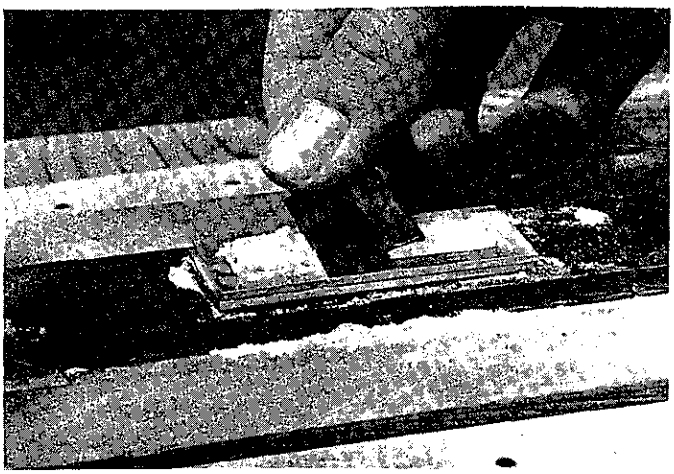


Photo No. 7
Removing excess powder from top of frame #2

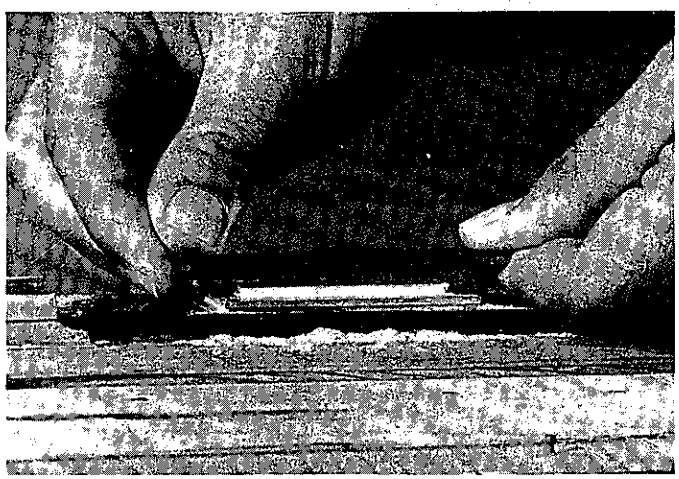


Photo No. 8
After frame #2 is removed and before powder is pressed into frame #1

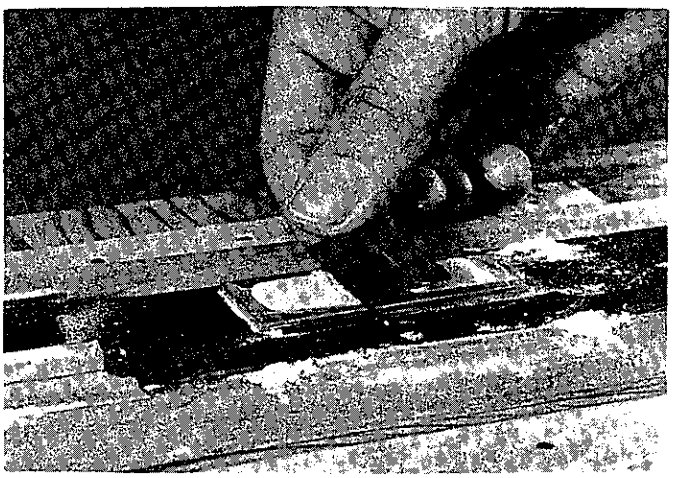


Photo No. 9
Excess pressed powder removed from sample holder frame #1

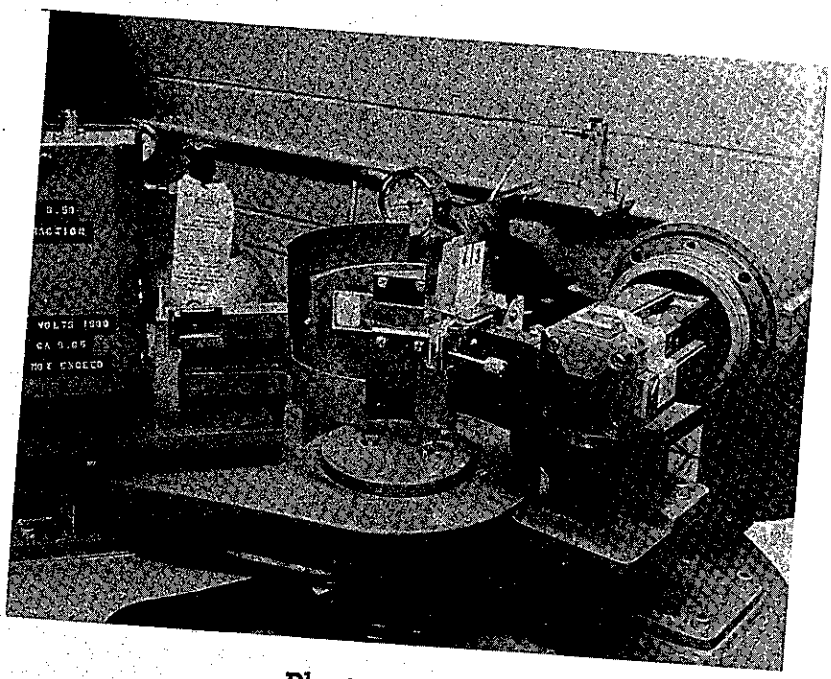


Photo No. 10

View of Goniometer set up for measuring the mass absorption directly.

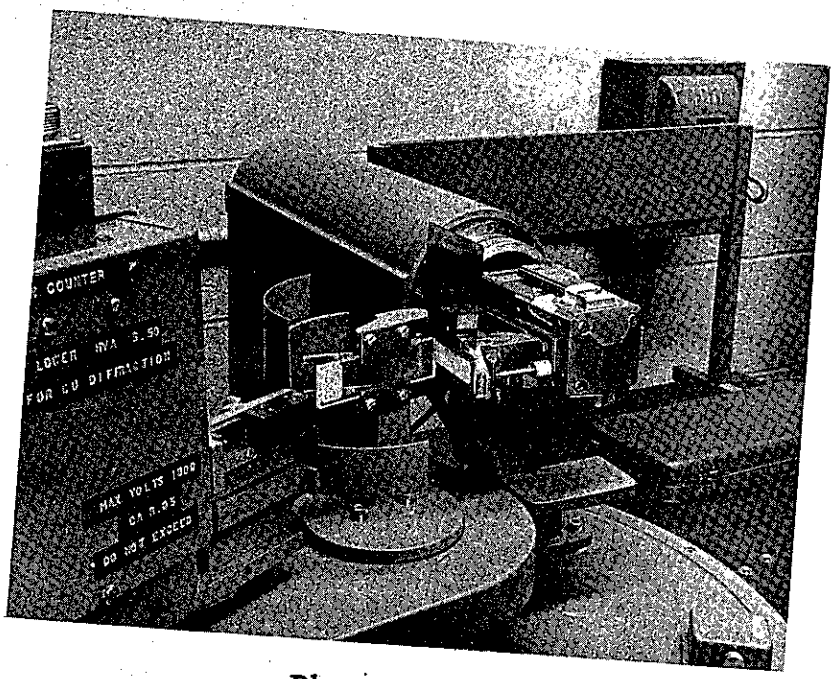


Photo No. 11

Back pack sample mounted in path of x-rays for mass absorption measurement. Note LiF analyzing crystal.

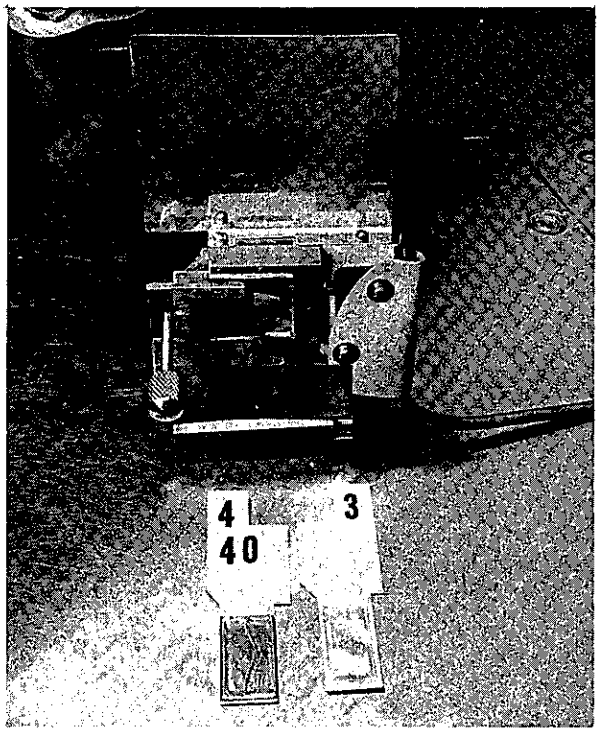


Photo No. 12

Beam shutter assembly showing a tantalum shutter in the open position.

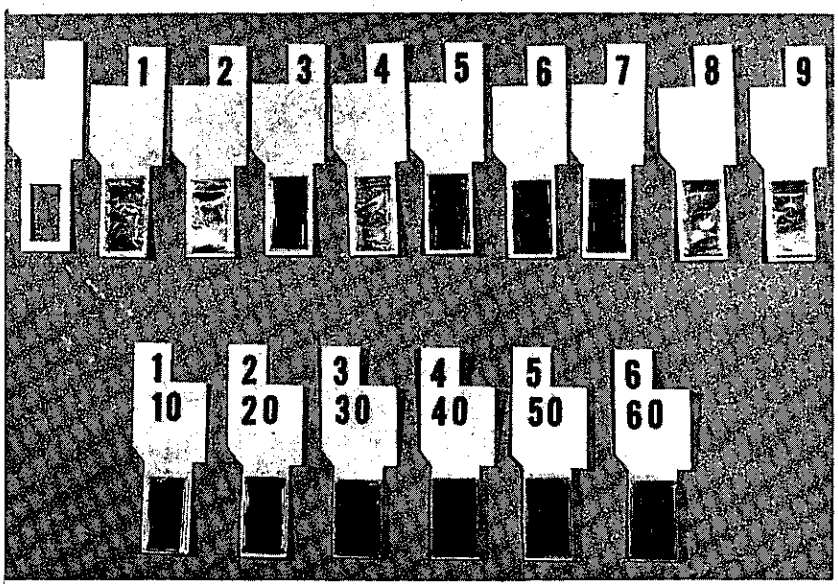


Photo No. 13

Aluminum foils mounted on holders.

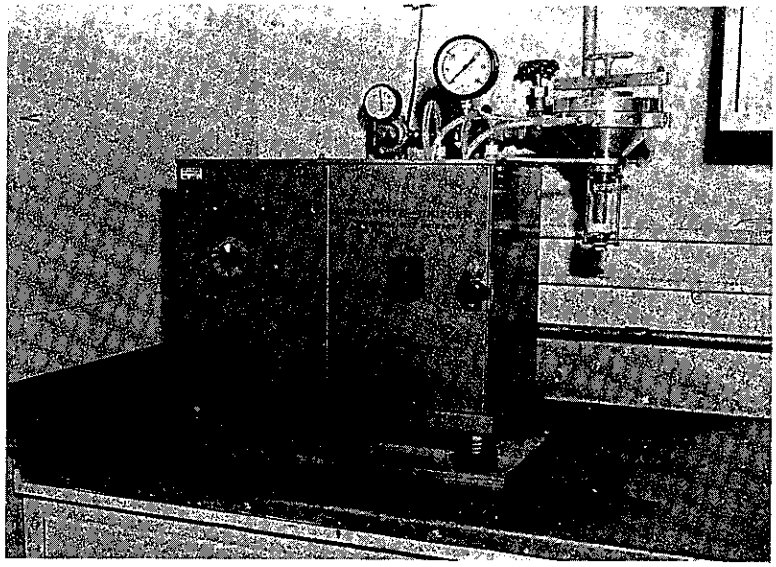


Photo No. 14

Pitchford Manufacturing Corp's Selective-Uniform Particle Size Grinder combines oscillatory motion of the grinding cylinder with pulsating air as the transporting media and screens for size control.

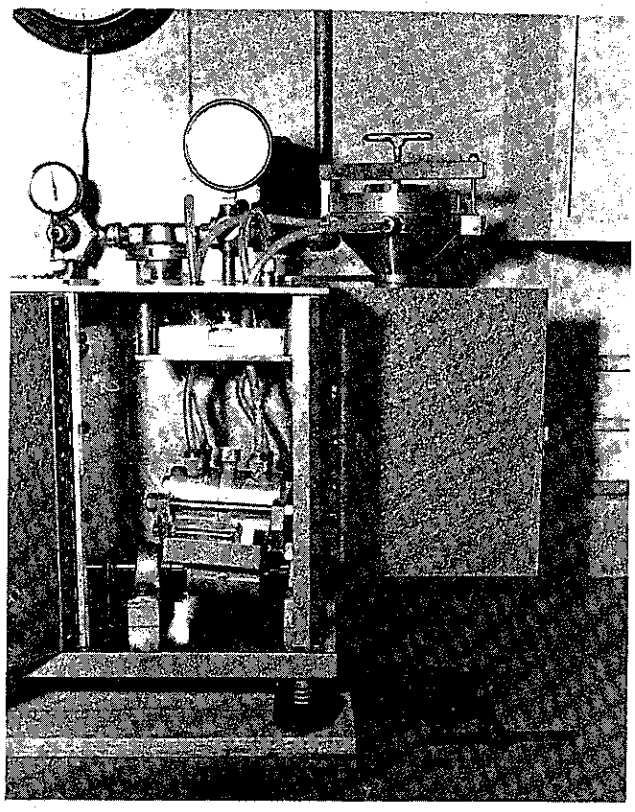


Photo No. 15

View showing grinding area. Note sample bottle in shaker frame. Used to mix powders.

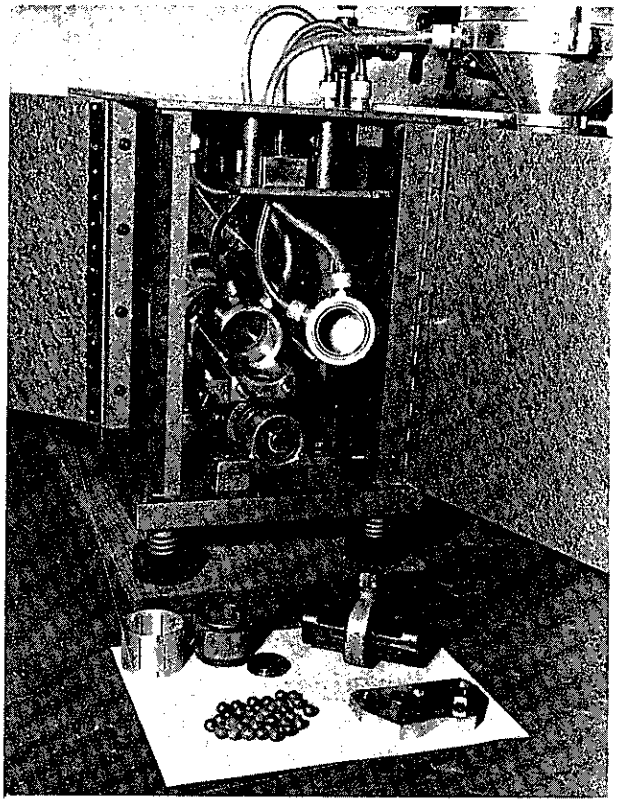


Photo No. 16

Tungsten carbide vial and grinding balls, 508 mesh screen, etc.