QUANTITATIVE MINERAL ANALYSIS WITH A RECORDING *X*-RAY DIFFRACTION SPECTROMETER[1]

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ABSTRACT

A method of quantitative mineral analysis by means of a recording Geiger-counter *x*-ray spectrometer has been developed. It eliminates many of the difficulties of the photographic method and is applicable to a wide variety of mineral powders over a range of concentration from 100 per cent of the constituent being determined to a minimum of a few per cent. For quartz this minimum may be as low as one per cent. The method is particularly suited to rapid mineralogical analyses required in plant control or desired for research. It may be applied, as well, to individual samples under routine study. It is effective for slimes, coated and locked grains, and other systems difficult or impossible to identify by petrographic, spectrographic, or chemical methods. In addition the method is non-contaminating and non-destructive of the material being analyzed.

Working curves for quartz in a variety of base constituents have been derived and the logical extension to other minerals is pointed out. A detailed description of the technique developed for the use of this comparatively new instrument is given.

INTRODUCTION

X-ray diffraction has been developed in recent years into an indispensable tool in the field of mineral identification, particularly since complete commercial equipment has become more generally available. The powder method has proved especially valuable in the study of multicomponent mineral samples and those too small in particle size to permit identification by optical methods.

This technique, however, usually has been limited either to purely qualitative analyses or to quasi-quantitative estimates of the components in the more familiar mineral groupings or mixtures. Even here these estimates frequently can be reported only as above or below a certain minimum or maximum value. As the actual lower limits of detection for different minerals vary considerably, these limits are frequently uncertain.

An exception to these limitations has been the work done on the quantitative determination of quartz in mine dusts.[3,4] In this field the nature of the sample with regard to particle size and quantity available for

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[3] Clark, G. L., and Reynolds, D. H., Quantitative analysis of mine dusts, an *x*-ray diffraction method: *Ind. and Eng. Chem.*, Anal. Ed., **8**, 1, 39–40 (1936).

[4] Ballard, J. W., Oshry, H. I., and Schrenk, H. H., Quantitative analysis by *x*-ray diffraction: *U. S. Dept. Interior, Bureau of Mines*, R. I. **3520** (June 1940).

study has necessitated the development of a special technique to handle such material. This work has been broadened to include a more general analysis and the technique has been somewhat simplified and extended, by implication, to all crystalline materials.[5,6] However, the "internal standard" method in conjunction with the use of photographic film and densitometric records thereof has been retained.

Photographic Method—Its Limitations

Possibly one of the reasons that quantitative *x*-ray analysis has been of limited usefulness is that so many variables exist in the usual powder technique. These variables occur not only in the type of samples but also in their preparation and mounting, in the exposure and processing of the photographic film, and in the interpretation or densitometry of the patterns. Different samples often have dissimilar absorption characteristics, even with careful use of diluents; reproducible mountings of the prepared samples are difficult to achieve; differences exist in the scattering power of samples; and significant variations may occur in the total *x*-ray output from exposure to exposure, particularly during short exposures. All these factors tend to introduce unknown or uncontrolled variations into the final record. In addition, the complicated and often indeterminate effect of background density makes a reliable interpretation of a densitometric record of a photographic *x*-ray diffraction pattern even more difficult.

All of these possible variables must be considered in any technique of power diffraction analyses. The use of an internal standard eliminates some of these difficulties only partly and may be objectionable in itself, particularly if a further study of the material actually *x*-rayed is desired or when the time necessary to prepare numerous samples is an important consideration.

Geiger-Counter Method

The automatic recording Geiger-counter *x*-ray diffraction spectrometer[7,8,9,10] which is now commercially available* eliminates or minimizes

[5] Gross, S. T., and Martin, D. E., Quantitative determination of crystalline materials by *x*-ray diffraction: *Ind. and Eng. Chem.*, Anal. Ed., **16**, 2, 95–98 (1944).

[6] Ballard, J. W., and Schrenk, H. H., Routine quantitative analysis by *x*-ray diffraction: *U. S. Dept. Interior, Bureau of Mines*, R. I. **3888** (June, 1946).

[7] Friedman, H., Geiger-counter spectrometer for industrial research: *Electronics*, **18,** 132–137 (April 1945).

[8] Buhler, J. S., Engineering-design development of *x*-ray spectrometer: *Electrical Manufacturing*, **35,** No. 6 (June 1945).

[9] Buhler, J. S., Process quality control with *x*-ray spectrometer: *Instrumentation* **1,** No. 6 (Nov. 1945).

[10] Firth, F. G., The Geiger-Mueller *x*-ray spectrometer: *Colloid Chemistry* by Jerome Alexander, Vol. VI. 108–117 (1946), Reinhold Pub. Co., N. Y.

* Manufactured by the North American Philips Co., New York, N. Y.

many of the undesirable variables of the photographic method and consequently is more readily applicable to the quantitative analysis of a variety of mineral mixtures. This instrument completely eliminates the photographic record by substituting an automatically drawn curve representing intensity versus angle of x-ray diffraction. This is accomplished by recording on a standard strip-chart recorder the output of a special Geiger-counter tube which is mechanically driven through a 90° arc, the sample simultaneously being moved (at half speed) through a 45° arc. Through a collimating and filter system the counter tube receives the diffracted rays from the sample that is radiated by the x-ray beam similarly collimated, the intensity of the diffracted beam varying according to the usual Bragg relationship.

With this type of instrument the standardization of a technique for quantitative work becomes comparatively easy. The equipment, after a suitable stabilization period, provides a very steady output of x-radiation, stable operation of the Geiger-counter detection and amplification systems, and a reliable recording of the counter-tube output. The mounted sample has a comparatively large area under radiation, and the resulting diffraction may be considered to approximate a surface reflection condition which minimizes or removes many of the uncertainties due to variations in sample size, absorption, and scattering characteristics. The disadvantages of the photographic process and of the subsequent densitometric measurements are completely eliminated. A somewhat larger quantity of sample than is used in the camera technique, however, is necessary for best results. The technique of sample preparation, mounting, and examination, to be described, was developed in order to provide as reliable an analysis as possible with a minimum of effort and with the least contamination of the material to be studied.

Application of the Geiger-Counter Method

One application of a rapid method of quantitative mineral analysis would be to a series of samples taken from plant operations or from a research program involving numerous tests on which a control analysis is desired. Such a method should be equally satisfactory for individual or isolated samples under routine study. The method described herein is applicable to any mineral or crystalline material having a fairly strong diffraction maximum at a Bragg angle less than 45°. It will cover a range of concentration from 100 per cent to about one to five per cent, the lower limit depending, among other factors, on the effective intensity of the strongest diffraction maximum of the crystal being analyzed. The method is rapid, non-destructive and non-contaminating, practically independent of initial particle size, locked grains, or minor surface coatings and alterations.

Technique of Analysis

The specimen preparation consists merely of selecting a representative sample and grinding a sufficient quantity to produce about three cubic-centimeters volume of minus 325-mesh material. On difficultly comminuted material a somewhat larger particle size may be tolerated, but in any case all the material should pass a 200-mesh screen. The area of the specimen as mounted should at least equal the maximum radiated at the diffraction angle to be used for the analysis. For spectrometer angles, 2θ, down to about 10°, a surface $1'' \times \frac{1}{2}''$ is used.

The sample holders are made from any convenient plastic. Such holders can be prepared by cutting $\frac{1}{8}''$ sheet material into $1\frac{1}{2}''$ squares on which are cemented $\frac{1}{4}''$ strips of thin plastic, preferably about 1/32″ in thickness, to form an opening 1″ by $\frac{1}{2}''$ and thereby leaving a free area for handling. Such a mount can be held readily while being loaded and can be inserted accurately into the specimen clamping device of the spectrometer.

The depth of the specimen is controlled by the thickness of the narrow strips cemented on the mount base. Where the quantity of material is limited, either a thinner mount or one having a smaller area may be used. Care must be taken, however, to prevent any reduction in the intensity of the diffracted beam because of insufficient thickness or area under radiation. When several mounts are used in quantitative work, they should be as nearly identical as possible.

The packing of the specimen into the mount is the one point in the procedure where uncontrolled variations may occur. A considerable variation exists in the facility with which different materials may be mounted. Usually minerals which are neither platy nor fibrous give little trouble. The "sticky" powders and those tending to assume a preferred orientation require special care in handling.

The surface of the specimen is formed as uniform and flat as possible and in the identical plane of the edging strips by being worked with a small, thin-bladed spatula. This procedure usually involves packing down sufficient powder to consolidate it, followed by a series of pats and sweeps to produce a uniformly smooth surface. Any curvature of this surface in a horizontal plane, as mounted, will result in an undetermined increase in the focussing, and hence higher intensity, of the diffracted rays. This step involves a certain amount of practice before the best technique of obtaining the most satisfactory surface for different types of powders has been acquired.

After the mount is prepared and positioned in the specimen holder, the spectrometer arm carrying the counter tube is set at the desired starting point. This position may be marked on the record chart, which is then synchronized with the motor-driven spectrometer arm. Subsequent angles indicated on the chart corresponding to spectrometer positions may

be determined by counting divisions from the starting point knowing the chart and spectrometer arm driving speeds.

It has been found most satisfactory to drive the scanning arm at 1 r.p.m. and the recorder chart at 20 inches per hour. This results in each division line on the chart (having 3 divisions per inch) representing 1° (2θ) on the spectrometer scanning arm. Faster scanning and recording will not always give a reliable and uniform record, and a slower operation is unnecessarily time-consuming.

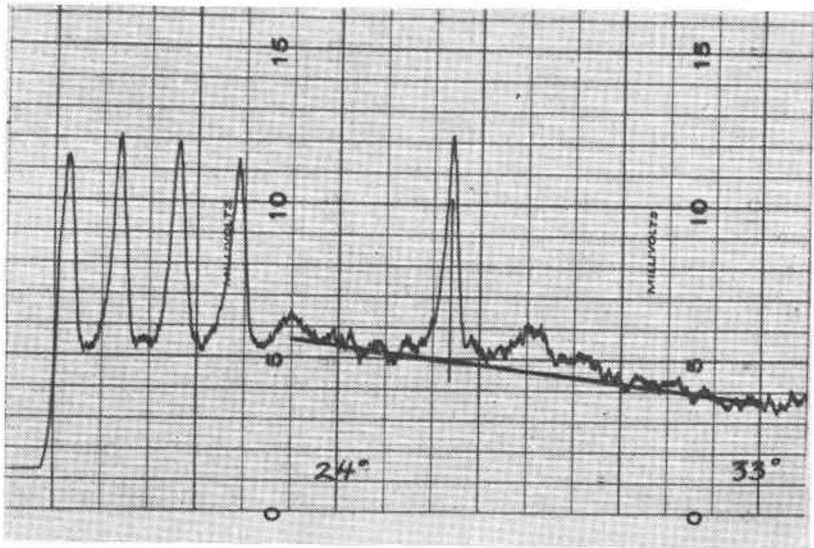

Fig. 1

A sufficient record should be obtained on both sides of the "line"[11] under consideration to enable a determination of the immediate background to be made. This is done by drawing a straight line connecting the average background both before and after the peak to be measured and noting the value indicated immediately under the peak. The actual value used is taken as the deflection above this background value. This is a necessary step as the background intensity will vary considerably for different materials and concentrations. However, its value may be directly substracted from the peak value to obtain a correct index of diffraction intensity, as there is only a direct linear relation between

[11] The word "line" will be used to denote the recorded maximum of diffraction intensity corresponding to a diffraction line or density maximum on a film record.

intensity and recorder deflection. This numerical value of line height is, under standardized conditions, a direct measure of the actual intensity of the diffracted beam from the specimen.

Since this measurement is obtained under dynamic conditions rather than as a time-integrated determination, as is the photographic method, it is subject to certain errors resulting from the random distribution, with time, of the *x*-ray photons, as they are emitted from their source, as they are diffracted by the specimen, and as they are detected and counted by the Geiger tube. Therefore, reruns on the same sample will produce slightly varying intensity values, even with the usual amount of damping in the recording circuit. Consequently, duplicate runs are always made. It was found that an average of five determinations on the same mounted specimen could be reproduced with considerable precision. Figure 1 shows a background determination, followed by four more repeated runs to complete the record of a single mount. The duration of the background determination is unusually lengthy in this case because of superimposed faint lines.

To reduce errors that may arise from the mounting technique, five different mounts of each sample are made, and the average value of line intensity is obtained for each mount. The over-all average of these values, 25 determinations in all, is taken as the measure of the desired line height of the sample. This does not necessarily mean that enough sample for five mounts is required. A new mount may be made using all or part of the material from a previous mount. A fresh surface is what is desired.

Specific Application: Quartz in Various Minerals

Quartz was selected as the first mineral to be analyzed by this method. It occurs frequently as an impurity in other industrial minerals, and its analysis by spectrographic methods is not possible in the presence of silicates and is frequently difficult by chemical methods. When it occurs in a very fine particle size or in "locked" or coated grains a petrographic analysis is likewise difficult.

Standard samples of quarts were prepared in concentrations varying from 1 to 80 per cent in pyrex glass, BeO (bromellite), bentonite, pyrophyllite, spodumene, albite, talc, NiO (bunsenite), galena, a pyrope-almandite-type garnet, and magnetite, respectively. The minus 325-mesh materials were weighted on an analytical balance and transferred directly to a small 250-mesh screen. Each mixture was brushed through this screen at least four times thereby providing a thorough mixing of the components. It had been determined previously that this method of mixing rapidly produces a homogeneous sample. These mixtures, in-including a 100-per cent quartz sample, were then run on the spectrome-

ter and the corresponding heights of the 3.35A quartz line determined.

The particular instrument settings for such a quartz analysis are as follows: The *x*-ray beam exit slit and the counter tube defining slit are both set at "medium" width and 6 mm. height. A nickel filter is used. The recorder coupling controls (furnished with the instrument), are set at a value of 8 for sensitivity or "amplitude" and at 5 for "damping." Operation at these dial settings give practically a full scale deflection for pure quartz.

The *x*-ray source and counter-tube units should be given about an hour warm-up period before any quantitative measurements are made. Satisfactory operating conditions are reached when the output of the *x*-ray tube and the voltage on the counter tube have dropped to their steady values. The power supply of the recording unit should also be turned on for a short time, although its warm-up period does not seem to be critical.

To determine the background under the quartz peak a record is usually made for 3 or 4° on both sides of the line. A single background determination for each mount is sufficient. For duplicate runs on the same mount, scanning may be started just before the quartz line begins and continued just past the peak. A manual resetting of the scanning arm will then repeat this record.

With practice, five runs on the same mount, including a base line determination can be made in from 5 to 7 minutes and a complete determination on five mounts of a single sample can be made in about 45 minutes. The relative ease of mounting some materials may decrease the time occasionally.

Working Curves

From the data obtained there has been drawn a series of curves, representing recorded height of the diffracted quartz line versus concentration of quartz for mixtures having *x*-ray absorption characteristics for copper radiation varying from the extremely low absorption of BeO to the high value of Fe_3O_4 and for a range of concentration from 100 to 1 per cent by weight of quartz in the base mineral. It was found that concentrations of quartz below 1 per cent could not usually be measured reliably, although in many mixtures, particularly in BeO, less than this amount could easily be detected.

In plotting these curves with a linear ordinate representing line height, it became apparent that for relatively low concentrations of quartz a logarithmic scale was not as suitable for the abscissa as a linear one. Consequently these curves were divided into two parts, from 100 to 10 per

cent quartz being plotted on a logarithmic scale, while amounts below 10 per cent were plotted on a linear scale.

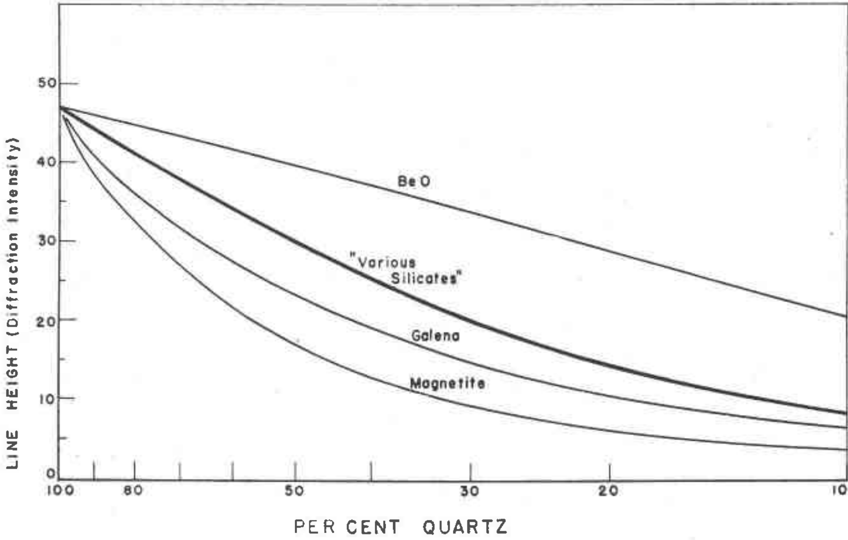

FIG. 2

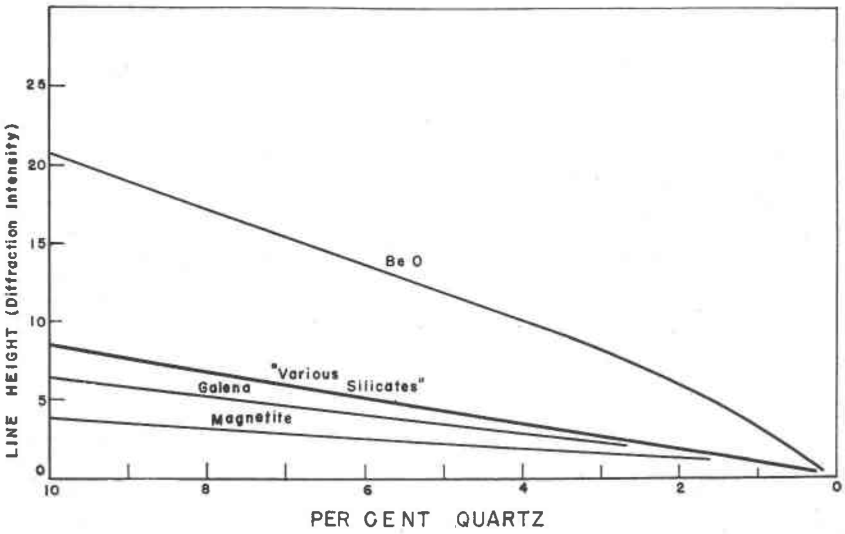

FIG. 3

The curves shown, Figs. 2 and 3, are only a few of those determined or possible within a family of curves covering the entire range of absorption characteristics exhibited by minerals. The heavy curve marked "Various Silicates" includes powdered pyrex glass, spodumene, talc, albite and bunsenite, while the bentonite clay curve is almost coincident. Although the curve for bromellite differs considerably, it probably represents the case of minimum absorption. It is certain that few minerals will have a characteristic curve between glass and BeO. Magnetite has one of the highest absorptions for copper radiation, although this value may not be the maximum possible. Its curve is much lower than that of galena or of the iron-bearing garnet studied.

Before a quantitative quartz analysis can be made on an unknown, a few representative curves similar to those shown in Figs. 2 and 3 must be obtained, using the particular apparatus and technique to be employed in future analyses. Thereafter for a quartz analysis of an individual sample or of a series of samples having similar matrix material it is only necessary to know the location of the working curve of that matrix material within the family of curves previously constructed. This can be determined by a measurement of one or two synthetic mixtures of the base material and a known amount of quartz. It might be determined merely from a knowledge of the composition of the base material. The amount of quartz to be used in a synthetic mixture should be either about 5 per cent or 25 per cent, depending on the probable range of quartz concentration in the samples to be studied. A measurement of the intensity of the quartz diffraction in these synthetic samples using the developed technique will then establish a point on the desired working curve within the family of such curves, and the complete curve may then be drawn through this point by a process of visual interpolation between the nearest bounding curves.

In practice it will be found that a large number of the more common minerals with low iron or heavy element content will possess very similar absorption characteristics and hence will have the same working curve within the limits of accuracy with which such curves may be determined. Therefore, an immediate analysis may be made on many samples of known constituents without the necessity of first running a synthetic mixture.

Accuracy of Analysis

The fluctuations in the measurements of line height used as an index of diffraction intensity necessitate taking five readings on each mount. Likewise the possible non-uniformity of mount surfaces requires a measurement of five different mounts of the same sample. Although these in-

dividual readings may vary among themselves by a full division or more (on a scale of 50), the averages of all 25 readings can be reproduced to within about one-half division, or with a precision of about one per cent. Translated into amounts of quartz, this means that an analysis is good to within 10 per cent of the value of the quartz determined in the high range (Fig. 2), and to within plus or minus one per cent quartz in the low range (Fig. 3).

Application to Other Minerals

In general, the technique developed for the analysis of quartz should be applicable to the analyses of other minerals. For example, rutile in ilmenite was found to produce a working curve similar to quartz in magnetite with slightly different coupling control settings. Likewise magnetite in ilmenite (with iron radiation), various other opaque minerals, and many systems difficult to handle by other methods can be analyzed by this means.

Discussion and Conclusion

The preparation of the mounts, the one step in which completely standardized conditions do not prevail, needs further investigation. Possibly some other method of mounting samples can be developed to improve the technique and reduce the time required for an analysis. A step in this direction may be in the use of the recently described rotating sample holder[12] designed to present a greater effective surface area to the *x*-ray beam and to reduce the effect of preferred orientation.

The recording Geiger-counter *x*-ray diffraction spectrometer produces diffraction patterns more suitable for quantitative analysis of a larger variety of minerals while using the same radiation, copper Kα, than does the usual powder camera technique. It produces a permanent record which may be measured conveniently and interpreted reliably and in less time than the photographic method. For non-destructive quantitative mineral analysis on uncontaminated samples, its facility of standardization and ease of operation make it an excellent analytical tool.

Acknowledgment

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[12] Champaygne, E. F., Rotating sample holder for *x*-ray diffraction studies: *Rev. Sci. Inst.*, **17,** No. 9, 345 (Sept. 1946).