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RAPID XRD ANALYSIS OF QUARTZ IN AIRBORNE DUST SAMPLES USING COMPUTER CONTROL*

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Abstract—The objectives of adding computer control to the X-ray diffraction analysis developed for assessing quartz in airborne dust samples collected in mines were two-fold. First, to minimize counting time: samples with a lot of quartz required scanning of the peak over 3° 2Θ for a short counting time, whereas samples with little quartz required a longer counting time over a narrower scan. Thus both required feedback control to reduce average sample analysis time. Second, interference was frequent and variable even in one mine: to control this it was desirable to analyse on two or more diffraction lines. The computer control was set up to run each sample on up to four diffraction lines, stopping when any pair of lines gave results agreeing within the limits of error chosen.

The addition of computer control had two effects: first it reduced greatly the manual effort required to check for and avoid interference, and secondly it reduced counting time per line per sample. In total the effect was about a tripling of throughput on routine mine dust samples with a reduction in requirements for technician skill and professional supervision. As many as 1300 samples have been analysed in a month.

In addition to the routine analysis program some options are available such as a high accuracy program which uses longer counting times, and a wide peak program which handles filters which are distorted so that part of the sample is not in the focal plane of the diffractometer. The wide program is also useful in investigating interference.

INTRODUCTION

QUARTZ in airborne dust in hard rock mines is usually the major component giving a potential health hazard. Thus its control is a major requirement and the analysis of quartz in airborne dust samples is a substantial task. The requirement for mines in Canada is for the analysis of some 10 000 routine samples a year. The Elliot Lake Laboratory of the Energy Mines and Resources Canada has developed a technique for sampling and assessing airborne dust in mines using personal size-selective samplers, with gravimetric assessment both before and after ashing: X-ray diffraction is used for determination of the quartz fraction of the dust (KNIGHT, 1978, 1986). The analysis is carried out directly on the layer of airborne dust collected on silver membrane filters (LEROUX and POWERS, 1969). The thin film technique suggested by BRADLEY (1967) is used. Before the addition of computer control the system was capable of analysing fewer than 500 samples in a month. After the addition throughput reached 1300 per month, with much less professional supervision.

While this program was being developed the XRD equipment manufacturers

*This paper was originally presented at the Fourth Symposium on Electron Microscopy and X-ray Application to Environmental and Occupational Health Analysis at State College, Pennsylvania, in 1980. It now appears that the proceedings were not published, and since the approach is still of interest the paper has been updated for submission to *The Annals*.

introduced computer control, but the manufacturers' programs that this author has seen are not interactive, in that they use preset analytical setting for each batch of samples. The program described in this report changes sampling time and scan width according to the sample response and in addition it checks for interference. This leads to a considerable saving in machine and professional supervision time.

In accordance with the method described by BRAGG (1967) the area under the quartz peak is measured. In the original system this was done with a modified version of the computer program, developed by KEMPER and VAN KEMPEN (1970) for α-spectroscopy, and used off-line. Experience with this program demonstrated that the technique of integrating the count while scanning over width of the peak, which is usually recommended, was desirable. However, it was clearly preferable to limit the width of the scan, particularly on mine samples with little quartz, for four reasons:

(1) on many samples peaks due to interfering minerals are found near those due to quartz. The effect of interference on light samples can be reduced by determining the background as close to the peak as possible and rejecting adjacent peaks;

(2) on very light samples of pure quartz (less than 5 μg per filter or 0.013 μg mm^{-2}) it was also found that apparently random small peaks of counts occurred near the very small quartz peaks and that better correlation between the X-ray intensity and estimated weight of quartz was found by integrating over the minimum width and measuring the background close to the significant portion of the peak;

(3) counting in the outer regions where the peak does not rise significantly above the background (see Fig. 1) is non-productive as it does not contribute significantly to the peak area when the background is subtracted;

(4) it was also found, as expected, that the counting time per step required for analysis increased with decreasing amounts of quartz.

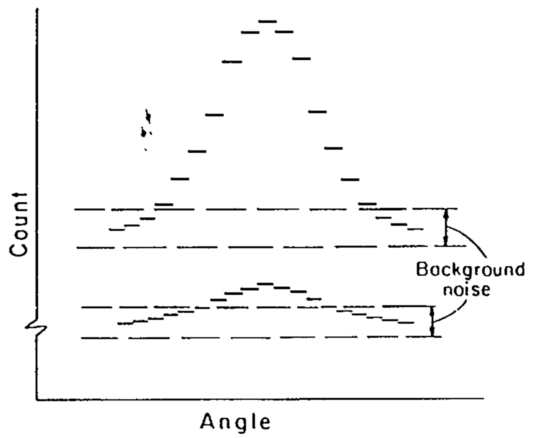

FIG. 1. Comparison of smoothed strong and weak peaks showing effective narrowing of weaker peak in presence of statistical background fluctuation.

Thus computer feedback control could save considerable time by counting the heavier quartz samples for a shorter time only, and the lighter samples for a narrower scan width. Also the control of interference showed considerable promise with multi-line analysis.

Using the strongest quartz line interference has been found on about 30% of the samples analysed. The use of up to four diffraction lines and the requirement for agreement between any pair of lines reduced interference to less than 5%. Computer feedback control which stops the analysis when agreement between a pair of lines is reached reduces the average number of lines analysed from four to about 2.5. The previous system of manual refeeding of samples required an excessive amount of technician time, skill and professional supervision to avoid errors due to interference and seriously restricted throughput: interference problems have been reviewed in a recent paper (KNIGHT, 1989).

DESCRIPTION OF THE SYSTEM

The X-ray diffractometer and accessories were supplied by Philips Electronics in 1970. The significant components are: vertical goniometer with automatic sample changer (35 samples); high intensity X-ray tube with cobalt target; graphite monochromator in diffracted beam; and scintillation detector and stepping motor with controller (PW 1935). The computer is a DEC PDP8 supplied by Digital in about 1972 for other research and passed on to the X-ray laboratory in 1978. The interface was built in the laboratory (KNIGHT and TIRRUL, 1982). The connections used are a 17-bit BCD output for the go-to-angle command together with a 1-bit start command and a 1-bit return signal when command completed; a 1-bit signal advances the automatic sample changer with a 1-bit sample changer busy signal return; counting is controlled by a 3-bit output; reset, start and stop with timing by the internal computer clock; a 24-bit BCD six decade signal returns the XRD count.

A 4° diverging slit is used to obtain the maximum count rate. The receiving slit is about 0.1° 2Θ wide and the step size used in scanning is 0.1° 2Θ. The alternative of narrower slits and better resolution was considered in order to reduce interference effects but because of filter distortion and the very small proportion of dust samples on which it would have been useful it was not used.

SOFTWARE DESCRIPTION

The computer programs were written in-house in Fortran II with the input and output signals to the diffractometer written in a symbolic machine language (SABR). The SABR language can be inserted into Fortran text. Because of limitations of the 16k memory on the PDP8 computer the program has had to be written in four parts and the output and input descriptions kept as short as possible: they are therefore difficult to understand. The programs are described and listed in an internal report available from CANMET (KNIGHT, 1988).

In addition to the routine analysis program, some options were found desirable and made available:

(1) high accuracy—the peaks are analysed for about a four times longer counting

time than routine. This option is used in calibration and in some experimental field work;

(2) wide peak—the peak width and the scan width used in assessing shoulders and adjacent peaks are increased. This option is used for analysing dust deposits on filters which are distorted and therefore do not lie in the focal plane of the diffractometer, and also for integrating over close multiple peaks;

(3) all lines—analyses all four quartz and/or crystobalite lines, i.e. it does not stop after agreement between a pair of lines is found. This option is used in calibration and when high accuracy analyses are required.

The programs when loaded into computer memory for running occupy about 13k of the 16k 12-bit memory available on the PDP8 computer.

ANALYTICAL PROCEDURES—OUTLINE

An outline of the analytical steps and decision procedures used in analysing each diffraction peak are:

(1) peak count—the peak region from peak centre $-0.5°$ to $+0.5°$ 2Θ is counted in 0.1° steps for a short time each (Fig. 2). The curvature of this is examined:

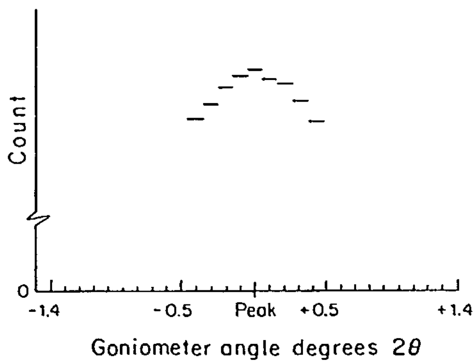

FIG. 2. Counting peak region—nine steps [showing normal result when quartz present—condition 1(a)].

(a) If it has a statistically significant higher centre than extremes it is taken as a positive quartz presence and the analysis is continued at this counting time (Fig. 2).
(b) If the curvature is such that the extremes are significantly higher than the centre then interference is inferred and no further analysis is carried out on this line.
(c) For lesser curvatures the peak region is recounted for a period three times longer and added to the previous values. The curvature is re-examined:
 (i) if (a) above, then analysis continues using the four times longer count time;
 (ii) if (b) above, then interference—no analysis;
 (iii) if (c) above, quartz (analyte) undetectable—returns zero quartz present.

(2) Complete counting peak region and check that maximum count step is within the error width of the quartz peak. This includes an allowance for increased peak width caused by distortion of the filter displacing the dust from the focal point of the

goniometer. If not within error band interference is assumed and the peak rejected (Fig. 3).

(3) Shoulder identification—a temporary background, a sloping straight line, is defined by the two extreme pairs of counts; then the rest of the peak is counted alternating from side to side until, on each side, the peak edge, or shoulder is found. The edge is defined as the count not being significantly less than the continually redefined temporary background line (Fig. 4).

(4) The background at each side is then counted step by step. As each count is added it is checked that it is not significantly higher than the developing background line (Fig. 5).

(a) If higher, the step is considered to be the start of an interfering peak and omitted from background. Further counting on that side is stopped.

(b) If not higher, stepping is continued until the background width on one side equals half the peak width.

(c) Shoulder position refinement—the background counts are re-examined starting at the outer edge to detect the start of the rise to the peak.

(5) Following the analysis of each line the control is returned to the main program, which tracks the quartz lines, to check whether the second line agrees with the first within the limits of error, which are:

$$\pm 20\ \mu g \text{ per filter} \pm 12\% \text{ of mean quartz value.}$$

If agreement, the results from the two lines are averaged and the normal program passes on to next analyte or next sample; if no agreement, the third line is analysed and agreement between third and first or third and second checked, and so on.

(6) If no agreement is found after analysing all four quartz lines the program plots the counts against the angle for the four lines so that the possible interferences can be readily observed. The analysis of all four lines is then repeated; occasionally a system fault has been found and, in unattended analysis, the repetition can ensure that no system problem occurred before a time-consuming manual approach is initiated.

DISCUSSION

The computer-controlled X-ray diffractometer has been very successful in the assessment of the quartz content of airborne dust samples collected in mines. During the course of the studies some 20 000 samples have been analysed for quartz and a few hundred for other minerals. Some 30% of the samples have been found to show evidence of interference on at least one quartz diffraction line. Some 5–10% of the samples have not been analysed satisfactorily for a number of reasons:

(1) dust deposit damaged after collection;

(2) dust sampler not loaded or operated satisfactorily;

(3) absorption effects in the sample matrix. Heavy samples are subject to significant error and it is not easy to correct for the absorption effects; while there is a correction program included using the absorption loss of the silver line (the filter is a silver membrane) through the dust deposit this is only approximate because of tarnishing of the silver layer and the limited memory available for data storage and computation. This has not been considered significant in the overall assessment of any mine in that most such samples have been over the target value and such places are classified as

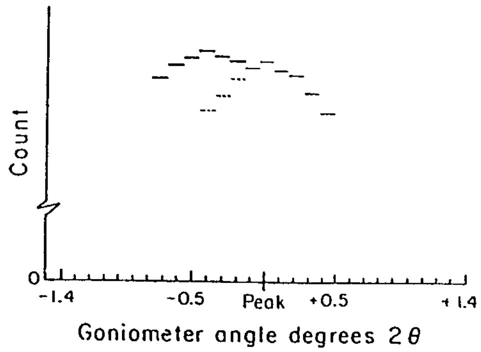

FIG. 3. Complete peak region and check for interference (showing maximum outside error region for quartz peak—line rejected because of interference).

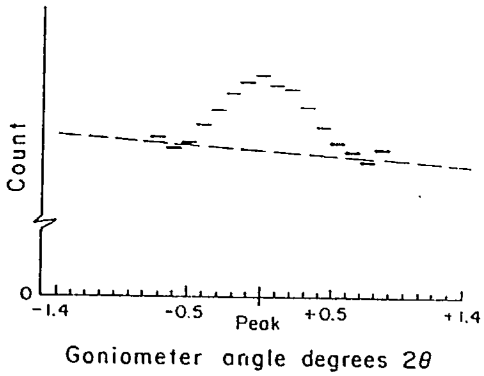

FIG. 4. Find shoulders (showing temporary background line and that last count on each side is not significantly less than background).

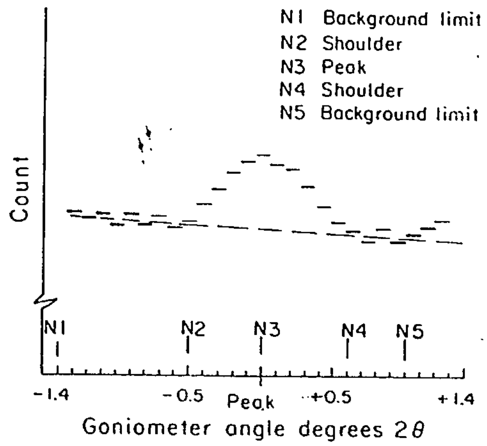

FIG. 5. Finish counting background. (A stop at a close peak is shown on the right-hand side. The peak descriptors, N1–N5, found by the program are shown.)

requiring improved dust control. However, the contribution to exposure of a few workers may have been significant;

(4) interference has so far led to significant uncertainty in the analyses obtained on the samples from two mines (KNIGHT, 1989). Some uncertainty has occurred on a small proportion of samples from other mines.

The major advantage of the computer control of the X-ray diffractometer together with the programs has been the ability to let a technician undertake the routine analyses with a minimum of supervision to control the effects of interference. I would not be satisfied with any system that uses, without checkup, only one or two quartz diffraction lines. The four lines used, those with Miller indices 1,0,0; 1,0,1; 1,1,2 and 2,1,1, have not all been found to be subject to interference by any one mineral. The variability of interference between samples even from one mine leads to difficulties in selecting one line free from interference for use on its samples. The second advantage is the reduction in time required to analyse samples, which is obtained by on-line control of counting and scanning width. The third advantage is the improvement obtained in the analysis of field samples with little quartz by rejection of areas close to peaks when assessing background with the narrower scan.

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