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NO. 16 OF 1968

THE QUANTITATIVE DETERMINATION OF QUARTZ BY
MEANS OF X-RAY DIFFRACTION METHODS

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1. INTERNAL STANDARD METHOD

When a certain component, in a mixture with other components, has to be determined in a sample, one cannot directly compare line intensities of the component with the line intensities of the pure component, prepared under identical conditions as the sample (e.g. ground to the same degree of fineness), because of the absorption effects of the matrix pertaining to the sample.

The method generally used is the internal standard method as described by Klug and Alexander¹⁾. The method consists of mixing a known amount of the internal standard with a known amount of the sample and measuring the ratio of the quartz line intensity and the internal standard line intensity in the sample prepared in this manner. By using this internal standard method, the absorption effect of the sample matrix on the intensity of the quartz line is similar to that on the intensity of the internal standard line. Another advantage is also that this method should eliminate the effect of the degree of tamping of the sample into the cavity of the sample holder.

STANDARDIZATION CURVE

As suggested by Klug and Alexander Fluorite, CuF_2 , was chosen as the internal standard for the determination of the standardization curve for quartz. Fluorite has a line at $3.16\overset{\circ}{\text{A}}$ which is in the vicinity of the $3.34\overset{\circ}{\text{A}}$ line of quartz. Klug and Alexander suggested calcite, CaCO_3 , as a diluent, but the authors have found that with the $\text{Co K}\alpha$ radiation the tail end of the $3.03\overset{\circ}{\text{A}}$ calcite line interfered with the $3.16\overset{\circ}{\text{A}}$ fluorite line. For this reason it was decided to use $^{27}\text{Al}_2\text{O}_3$ instead of fluorite. Klug and Alexander used $\text{Cu K}\alpha$ radiation, but because the samples studied contained iron, it was decided to use $\text{Co K}\alpha$ radiation to prevent any iron fluorescence resulting from $\text{Cu K}\alpha$ radiation.

/The three

The three components are weighed in the proportions as suggested by Klug and Alexander (page 420 of the reference). The mixing of the components is performed in a Retsch automatic agate mortar for 1 hour, the mixture being kept moist continuously with a small amount of benzol. The three components used are first ground to pass a 325-mesh sieve because it is important that their grain size should be the same. The quartz used was a clear, colourless, natural crystal, powdered to pass a 325-mesh sieve.

The sample holders used for the quartz determination are made of steel and consist of 3 plates with a sample cavity of 2.5 x 2.5 x 0.1 cm. The filling of the sample cavity is in accordance with the procedure described on page 301 of "X-Ray Diffraction Procedures"¹⁾, but instead of using Scotch tape the sample holders are supplied with small screws. The small sieve suggested by Klug and Alexander was not used but the sample was carefully tamped into the cavity, care being taken to prevent preferential orientation of the fluorite crystals.

On determining the intensities of the quartz and fluorite lines, the integrated intensities rather than the peak intensities are determined. The reason for this is that one must bear in mind that there can perhaps be a line broadening effect due to small crystallite size of the sample. The method of determining the integrated intensities are as follows:

The scanning of the peak is started at a uniform and appropriate speed from a position in the background region, a little distance away from the peak, then through the peak region and again to a position in the background region on the other side of the peak. The two positions in the background region must be at about equal distances from the peak. The time, as well as the total accumulated counts, are taken during a complete scan from the one background position to the other. The counter tube is then kept stationary in the two background positions and the count is accumulated in each case for half the time taken for scanning the peak. The sum of the two background counts is then subtracted from the total peak count and the result is taken as the integrated intensity of the peak.

/After

After determining the integrated intensities of the quartz and the fluorite lines in the different sample mixtures, the standardization curve of grams of quartz per one gram of fluorite is plotted against the quartz/fluorite intensity ratio as in Figure 1. The determination of each intensity ratio is repeated several times by each time emptying the sample holder cavity and refilling again with sample mixture. The average intensity ratio is then used for plotting the curve. The quartz determination in an unknown sample is obtained by merely mixing the sample with the required weight of internal standard and determining the intensity ratio under the same conditions as for the curve. Because the intensity ratio is most accurately determined when the two intensities are approximately equal, the procedure followed was to make a direct comparison of the intensity of the quartz line in the unknown with the intensity of the quartz line of a pure quartz sample and thus to obtain an approximate value of the quartz content of the sample. The amount of internal standard necessary to give a ratio of about unity is then calculated. This amount is mixed into the sample and the accurate determination of the ratio is made. The weight of the unknown per one gram of fluorite is read from the graph and the unknown per cent is obtained by calculation.

EXPERIMENTAL CONDITIONS

The following experimental conditions were applied during the intensity measurements:

Co K α radiation;

General setting 35 kV, 12 mA;

Proportional counter settings;

1) Attenuator 1 x 10;

2) Discriminator on differential;

3) Counter voltage approximately 1930 volts;

4) Base line 11.6 V, channel 6.8 V;

Aperture (fixed) 2.4 mm;

Counterslit 1.0 mm;

Iron filter in front of counterslit;

Scanning speed $\frac{1}{4}^\circ$ /minute.

/The proportional

The proportional counter is supplied with a constant temperature plate through which water at 20°C is passed. From time to time, between measurements, the pulse height analyser was adjusted for maximum pulse rate by keeping the base line and channel voltages constant and making small adjustments to the counter voltage.

The sample holder device is supplied with an oscillation attachment for oscillating the sample through an angle of $\pm 1^\circ$. This serves to increase the number of reflecting crystal planes, resulting in a reduction in error of the intensity measurement.

From time to time, as the proportional counter gets older, the half width of the cobalt radiation peak must be checked according to the standard procedure prescribed by the manufacturers.

2. ADDITION METHOD

Sometimes it may happen that one cannot apply the internal standard method due to the interference of a line of some component present in the sample, either with the 3.34Å quartz line or with the 3.16Å fluorite line. For example, illite, which has a line that coincides with the 3.34Å line of quartz, may be present in the sample. In this case the addition method which is not as accurate as the internal standard method can be applied.

The method consists of the addition of a known amount of the pure substance which is to be determined, in this case quartz, to a known amount of the sample. Mixing must also be thorough as in the case of the internal standard method and the sample, as well as the pure quartz, must be finely ground (minus 325 mesh).

Using the same experimental conditions and filling technique of the sample holder cavity, the integrated intensities of some other suitable quartz line in the sample before the addition of quartz and in the sample after the addition of quartz are measured. The quartz content of the sample is then calculated according to the following formula:

$$\frac{x}{m} = \frac{I_1 y}{I_2(m+y) - I_1 m}$$

/Where

where

- I_1 = integrated intensity before addition of quartz
 I_2 = integrated intensity after addition of quartz
 x = unknown weight of quartz in sample
 y = weight of quartz added to sample
 m = weight of sample to which a known weight of quartz is added

This method is only applicable where there is a relatively low percentage of quartz present in the sample (up to about 20%). Where high amounts are present one can perhaps first dilute the sample by mixing with some substance having lines that do not interfere with the quartz line to be measured. In practice it was found, however, that when applying this dilution factor the experimental error of the addition method is exaggerated to such an extent that the results obtained were not of acceptable accuracy.

Experimental results and a discussion are presented in Fuel Research Institute Technical Memorandum No. 41 of 1968, which forms a sequel to this memorandum.

(SIGNED) J.H. COPEMAN
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W.T.E. VON WOLFF
CHIEF RESEARCH OFFICER

PRETORIA.
 January 13, 1969.
 /TW

REFERENCE

1. Klug, H.P. and Alexander, L.E., X-Ray Diffraction Procedures, John Wiley and Sons, London, 1959.

FIG. 1.

INTERNAL STANDARD STANDARDISATION CURVE.

I. = Intensity

