QUANTITATIVE DETERMINATION OF QUARTZ IN SEDIMENTARY ROCKS BY X-RAY DIFFRACTION*

BY

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Abstract. The determination of quartz in sediments by an X-ray diffraction method is described. This method which is rapid and precise with a coefficient of variation of 0.5 %, measures the peak area ratio of quartz (3.34 Å) to an added standard alumina (3.47 Å). A working curve wass constructed using known quantities of quartz.

The rock samples before testing were ignited to 950° C in order to remove the interference from the clay peaks, increase the relative intensity of quartz peaks and reduce the initial matrix variation of the samples.

Σύνοψις. Εἰς τὴν παροῦσαν μελέτην περιγράφεται ὁ ποσοτικὸς προσδιορισμὸς τοῦ χαλαζίου εἰς τὰ ἰζήματα διὰ τῆς μεθόδου περιθλασιμετρίας ἀκτίνων X. Διὰ τῆς μεθόδου ταύτης, ἥτις εἶναι ταχεῖα καὶ ἀκριβὴς μὲ συντελεστὴ διασπορᾶς 0.5 %, μετρᾶται ἡ σχέσις μεταξὺ τῆς περιοχῆς μεγίστου (πίκ) τοῦ χαλαζίου (3.34 Å) πρὸς τὴν περιοχὴν μεγίστου προστιθεμένου στάνταρντ ὀξειδίου τοῦ ἀλουμινίου (Al_2O_3 - 3 47 Å). Χρησιμοποιώντας γνωστὲς ποσότητες χαλαζίου κατεσκευάσθη μία πρότυπος καμπύλη.

Τὰ δείγματα τῶν πετρωμάτων πρὸ τῆς ἐξετάσεως ἐπυρώθησαν εἰς 950° C πρὸς τὸν σκοπὸν ὅπως ἀπαλειφθῇ ἡ παρεμβολὴ μεγίστων (πίκ) τῶν ἀργιλικῶν ὀρυκτῶν, αὐξηθῇ ἡ σχετικὴ ἔντασις τῶν μεγίστων χαλαζίου καὶ ἐλαττωθῇ ἡ ἀρχικὴ κύμανσις τῶν δειγμάτων ὀφειλομένη εἰς τὴν δευτερεύουσαν μᾶζαν αὐτῶν.

1. INTRODUCTION

The methods available for quartz determination are of two categories: (a) chemical — which are usually precise but time-consuming, and (b) x-ray diffraction methods, which are generally more rapid but less precise.

The method of Trostel and Wynne (1940) for free silica determination is widely used. This involves a pyro-sulphate fusion, dissolution of

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the fusion by alkalis, leaving free silica residue for gravimetric estimation. This method, despite its precision (coefficient at variation 1%) is time-consuming. Griffin (1954) used boehmite as an internal standard and measured areas of the quartz 1.82 Å line and the boehmite 1.86 Å line, with a coefficient of variation of 6.5%. Calvert (1966) used, alumina as an internal standard and measured height ratios of the 3.34 Å quartz line to the 3.47 Å alumina line. The coefficient of variation was less than 10%. Till and Spears (1969) used the 4.26 Å for quartz which gives a detection limit of about 2% quartz, with boehmite 6.18 Å peak. They overcame the interference of other peaks (mainly of clay minerals) at these wavelengths by igniting the samples at at 950° C for 3 hours prior to analysis.

2. METHOD

For the present study of quartz determination in sandstones, (Koukis, 1974) alumina was used as an internal standard and the peak height ratio of the 3.34 Å quartz line to the 3.47 Å alumina line was measured. The interferences of the other peaks were also overcome by ignition of the samples at 950° C, prior to analysis, so the base line can be drawn with more confidence. Ignition increases the relative proportion of the quartz and hence the peak intensity, and some of the initial matrix variations amongst the samples are reduced. The loss of organic matter is particularly important in this respect (Till and Spears, 1969).

The grinding of the samples for quartz determinations presents a problem since quartz x-ray peak intensity varies with grain size. It was found (Brindley, 1961, p. 507), that reproducible results can be obtained if the grain size is kept constant, preferably at 15 μ. In order to achieve this in the present study the sample was first crushed and passed through 200 B. S. mesh. Then, after ignition, the sample was again ground by hand in an agate mortar, down to a talc-like powder. The estimated coefficient of variation of 0.497% was determined on three separately ground samples and thus shown a comparable grain size was achieved for samples containing approximately the same amount of quartz.

3. WORKING CURVE

If, as an example, the 40% quartz point is required for the working curve, then 0.4 g of quartz, 0.4 g of MgO and 0.2. g of Al_2O_3 are required e. g.

$$0.4\,g\ Qz + 0.2\,g\ Al_2O_3 + 0.4\,g\ MgO = 1\,g$$

The quantity of Al_2O_3 was kept constant or 0.2 g so that points up to 80 % quartz content can be defined in the working curve. These quantities are well mixed in a Wigi-Bug for about 5 minutes Then four slides are made with this mixture, and scanned in the x-ray diffraction unit under the following conditions :

Cu Kα ←— Ni filtered radiation
1° ←— degree slits
30 kV, 25 mA

The measurements were taken by the counting process and not by the chart because it was found to be much faster. Hence in each slide 5 measurements for the alumina and for the quartz peaks are taken, altogether 40 measurements for each sample, and for both peaks. The average ratio from the four slides is calculated. In the same way all the quartz/alumina ratios were defined in steps of 10 % from 10 % up to 70 % quartz. The data are presented in Table 1, from which the working

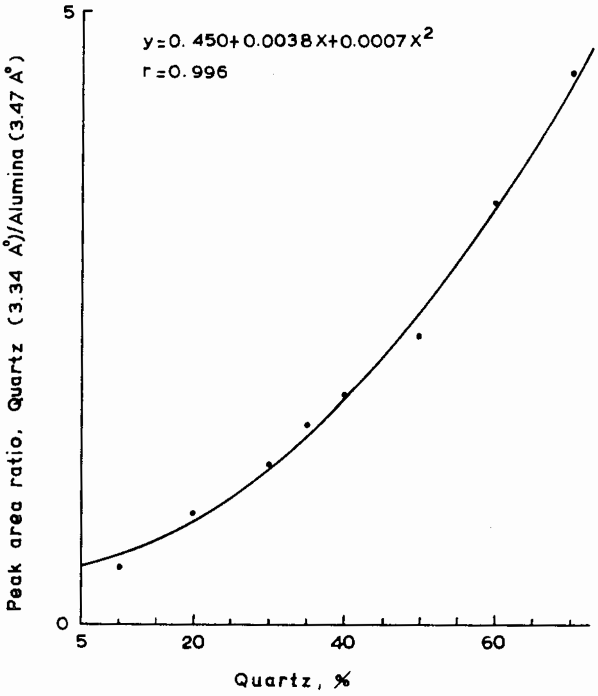

Fig. 1. Working curve relating quartz / alumina peak area ratio to quartz percentage.

curve was computed (Fig. 1). A least squares fitting curve was computed for the data with the following characteristics :

Order of the equation : 2
Goodness of fit : 0.992
Correlation coefficient : 0.996
Equation : $y = 0.450 + 0.0038\,x + 0.0007\,x^2$

where x = quartz % in the sample and y = quartz (3.34 Å) / alumina (3.47 Å) peak area ratio. The interception of the curve with the y-axis is justified if we take into account that in all these measurements the background was not excluded.

TABLE 1.

Data for the working curve.

Free silica %	Quartz / Alumina peak area ratio
10	0.464
20	0.901
30	1.300
35	1.590
40	1.849
50	2.320
55	2.783
60	3.390
70	4.463

For the determination of the quartz content of known samples, all the samples were treated under the same conditions as follows: the sample was dried in an oven at 110° C for about 3 hours, then ground in a Tema crusher to pass through 200 B. S. mesh. About 2 g of the sample was ignited in a shallow $1\,{}^1/_2$'' diameter silica dish at 950° C for about 3 hours. The ignition loss was accurately determined. Then the sample was again ground in an agate mortar to a talc-like consistency. Great care was taken to ensure reproducibility of grinding. Then 0.5 g of the ignited sample and 0.5 g of Al_2O_3 are mixed well in a Wigi-Bug for about 5 minutes and scanned as previously mentioned for the working curve.

The quartz / alumina peak area ration is applied to the working curve for the determination of the quartz percentage.

4. CALCULATION OF QUARTZ - ACCURACY OF THE METHOD

The percentage of quartz in the examined rocks is taken in two ways as follows : (a) % quartz in a volatile free base, directly from the working curve, (b) % quartz in the total sample given by the equation : % quartz = weight of sample x (1 — % of volatiles) x % of quartz from the working curve χ 100.

Replicate determinations were carried out on three separately prepared samples from the same rock (Table 2). The coefficient of variation obtained was 0.497 %.

TABLE 2.

Replication of quartz determinations.

	Quartz		
	56.098	St. Deviation	= 0.278
	56.053	Standard error	= 0.160
	55.595	Coefficient of variation	= 0.497 %
Mean	55.915		

5. DISCUSSION OF THE METHOD

The working curve gines a very satisfactory fit which suggests that no unknown factors affect the quartz determination. The advantage of constructing the working curve with known proportions of quartz is that it is not necessary for this to be estimated by another chemical method, which might give some errors. The second advantage is that all methods other than X-ray methods give total free silica, namely crystalline and amorphous, in contrast with the X-ray technique which gives crystalline silica. This, of course, suggests that in the examined samples no amorphous silica is included, a fact which is true since not any other peak was picked up.

Otherwise, taking into account that the possibly existing in the material amorphous silica is converted by ignition at 950^0 to Cristobalite (main peak at 4.04 Å — 21.98 2 in the Cu Kα radiation) another working curve had also to be constructed including Cristobalite/Alumina peak area ratio and using suitable standards.

Till and Spears (1969) have found that the ignition at 950°C has not any effect on the quartz in the samples (no change in quartz peak shape or peak height) by X-ray diffracting pure Belgian quartz before and after ignition. Also, observing the X-ray diffraction records of the present samples at this temperature no new crystalline phases have appeared.

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