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THE DETERMINATION OF QUARTZ IN SEDIMENTARY ROCKS USING AN X-RAY DIFFRACTION METHOD

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Abstract—An X-ray diffraction method for determining quartz in sediments is described which is both rapid and precise, with a coefficient of variation of 1·9 per cent. Samples are ignited at 950°C prior to X-ray analysis. This removes the interference of clay peaks, increases the relative intensity of the quartz peaks and reduces the initial matrix variation of samples. The peak area ratio of quartz (4·26Å) to an added standard boehmite (6·18 Å) is measured. Quartz content is obtained from a working curve constructed using similar rocks of known free silica content, which were analysed by the method of Trostel and Wynne (1940).

INTRODUCTION

METHODS available for quartz determination in sediments fall into two main groups. Firstly, chemical methods which are usually precise but time consuming, and secondly X-ray diffraction methods which are generally more rapid but less precise. The advent of more rapid methods of whole rock analysis, particularly X-ray fluorescence has led to much larger numbers of samples being analysed in research projects. Consequently more rapid but precise methods of analysing sediments for their other chemical components are also required.

The widely used method of Trostel and Wynne (1940) for free silica involves a pyrosulphate fusion, dissolution of the fusion by alkalis, leaving free silica for gravimetric estimation. The method is precise, e.g. the coefficient of variation quoted by Trostel and Wynne (1940, p. 19) is about 1 per cent, and also accurate as was shown by analyses of synthetic mixtures (Trostel and Wynne, *op. cit.*, p. 21). However, the method takes about 8 hr per batch of analyses. The overall time per sample may be reduced by running several batches together, but this is not always possible as it may require a monopoly of laboratory space and equipment, particularly platinum ware. Furthermore, the analysis does require care, so it is advisable to run duplicates.

Alternatives to the above method in the past were mainly X-ray diffraction techniques. Griffin (1954) used boehmite (γ-alumina monohydrate) as an internal standard. Measuring peak areas of the quartz 1·82Å line and the boehmite 1·86Å line, he obtained a coefficient of variation of 6·5 per cent. Calvert (1966) used alumina as an internal standard and measured the peak height ratios of the 3·34Å quartz line to the 3·47Å alumina line. He quotes a coefficient of variation of "less than 10 per cent".

More recently Chester and Green (1968) have developed a rapid method employing i.r. spectroscopy. They report a coefficient of variation of 4·7 per cent. Unfortunately not all workers have i.r. facilities.

The X-ray diffraction method described here is both rapid and precise (coefficient of variation 1·9 per cent).

DEVELOPMENT OF THE METHOD

In X-ray diffraction analysis of quartz shales, choice of a quartz and internal standard line is difficult. Griffin (1956, p. 5) chose the quartz 1·82 Å line with the boehmite 1·86 Å line. Boehmite was used because its mass absorption coefficient for CuKα X-radiation is similar to that of quartz and the clays found in typical shales. However, the quartz 1·82 Å line is not very intense, and the boehmite 1·86 Å line is one of a doublet not completely resolved by the diffractometer. The strongest quartz line, (101) at 3·34 Å, which would give the lowest detection level for quartz, cannot be used because a strong mica line, (024) and (006) at 3·32 Å, lies directly beneath it. Similarly, the quartz 4·26 Å line lies near the clay mineral and mica peaks ($11\bar{1}$) and (110) at 4·47 Å and is affected by its spread, as seen in Fig. 1A. This 4·26 Å line gives a detection limit of about 2 per cent quartz, and would be suitable for use with the boehmite 6·18 Å peak, if interfering peaks could be eliminated. This problem was overcome by igniting samples at 950°C for 3 hr prior to analysis. Figure 1B shows that interference is

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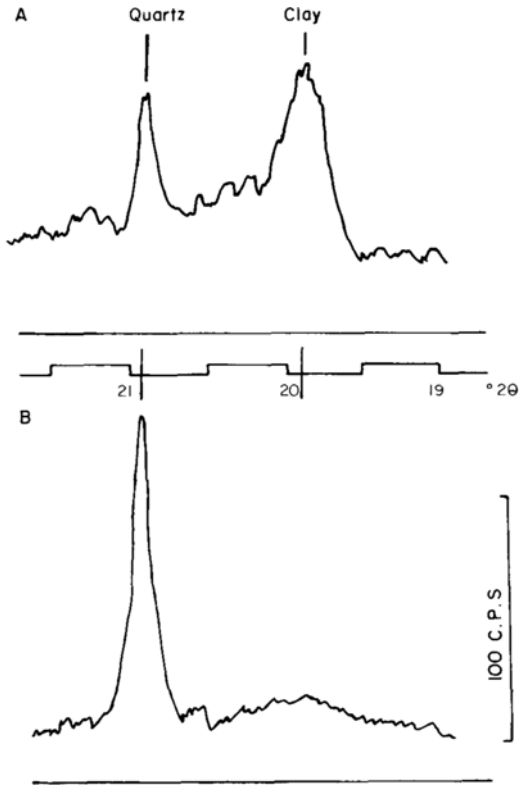


Fig. 1. X-ray diffraction trace from 19 to 21½°2θ of shale sample. A. Before ignition; B. After ignition at 950°C.

eliminated and the base line can be drawn with more confidence. The loss on ignition also increases the relative proportion of the quartz and hence the peak intensity, as can be seen in Fig. 1B. Another advantage of ignition is that some of the initial matrix variation between samples is reduced. The loss of organic matter is particularly important in this respect. Table 1 shows that the ignition loss can be determined with precision.

Grinding of samples for quartz determination also presents a problem since quartz X-ray peak intensity varies with grain size (see Brindley, 1961, p. 507: after Gordon and Harris, 1956). The work of these authors shows that reproducible results can be obtained if the grain size is kept constant, preferably about 15μ. In the present work it was hoped to achieve a constant grain size by hand grinding in an agate mortar to a talc-like consistency after the sample had first been mechanically crushed and ignited. The coefficient of variation of 1·9 per cent was determined on separately ground samples and thus shows that a comparable grain size was achieved for samples containing approximately the same amount of quartz. There is a possibility that samples containing different amounts of quartz may not be reduced to the same grain size. In part this is due to the cushioning effect of the clay minerals and organic matter, which is greatest in the fine grained sediments where the quartz content is lowest. This effect is reduced by ignition. To overcome these difficulties a working curve was constructed using Coal Measure rocks of known free silica content as standards. The free silica was determined by the method of Trostel and Wynne (1940) and the samples were chosen to cover the range of lithologies exhibited by the unknowns.

Table 1. Replicate ignition loss determinations on a sample

	Ign. loss (%)	
	36·49	
	36·57	Standard error = 0·15
	36.88	Coefficient of
	36·62	variation = 0·4 per cent
	36·70	
Mean	36.65	

PROCEDURE

All samples were treated in the following manner. 110°C oven dried samples were ground in a Tema crusher to pass 200 mesh (76μ). About 2 g of samples was ignited in a shallow 1½ in. diameter silica dish at 950°C for 3 hr. Ignition loss was accurately determined. Samples were further ground by hand to a talc-like consistency in an agate mortar. Great care was taken to ensure reproducibility of grinding. 0·9 g of the sample was mixed with 0·1 g of boehmite (5μ "Cera Hydrate" sold by the British Aluminium Company). The mixture was placed in a plastic tube and homogenised on a Wig-l-Bug for ½ min. The sample was then packed into an aluminium holder using a backfilling technique and scanned in a Philips 2 kW X-ray diffraction unit under the following conditions:-

Cu Kα ← Ni filtered radiation
1, 0·1, 1 ← degree slits
35 kV, 26 mA.

A maximum chart speed of 1200 cm/hr and a scan rate of ½°2θ/min. was employed to spread the peaks for accurate area measurements. The sample was scanned from 13·5–15·5°2θ and 20–22·5°2θ, so that the area under the boehmite 6·18 Å and the quartz 4.26 Å peak could be measured with a polar planimeter.

A working curve was constructed by plotting the

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ratio of quartz (4·26 Å)/boehmite (6·18 Å) peak areas (R) against percentage free silica in the ignited, chemically analysed samples. The graph is shown in Fig. 2, which uses the data from Table 2. A least squares curve fitting procedure was computed and successive polynomial fits were tested, till further orders made no significant difference. A quadratic fit was found to be satisfactory for these samples:-

$$Y = 0{\cdot}0317 + 0{\cdot}0201\,X + 0{\cdot}000305\,X^2$$

where X = quartz percentage in ignited sample

Y = Quartz(4·26 Å)/Boehmite(6·18 Å) peak area.

Table 2. Data for the quartz working curve

Free silica in ignited sample (%)	Quartz/boehmite peak area ratio
4·59	0·135
9·48	0·271
13·47	0·341
15·07	0·441
17·68	0·492
18·38	0·533
22·73	0·515
23·35	0·771
23·97	0·653
27·48	0·747
33·59	1·013
40·69	1·351
41·05	1·333
45·55	1·576
45·57	1·631
49·13	1·829
49·17	1·785
49·17	1·802
52·51	1·931
56·56	2·110
56·56	2·162
62·92	2·457
71·44	3·015

The quartz content of unknown samples was then determined by the same procedure, using the working curve. Table 3 shows the results of replicate determinations on separately prepared sub-samples from a single rock sample. The coefficient of variation obtained was 1·9 per cent.

Table 3. Replicate quartz determinations on an unknown

	Quartz (%)	
	9·00	Standard error = 0·17
	9·25	Coefficient of
	8·93	variation = 1·9 per cent
Mean	9·06	
	24·43	Standard error = 0·26
	24·95	Coefficient of
	24·61	variation = 1·0 per cent
Mean	24·67	

DISCUSSION

Following Draper and Smith (1966, Chap. 3) residuals were plotted against fitted points. Only

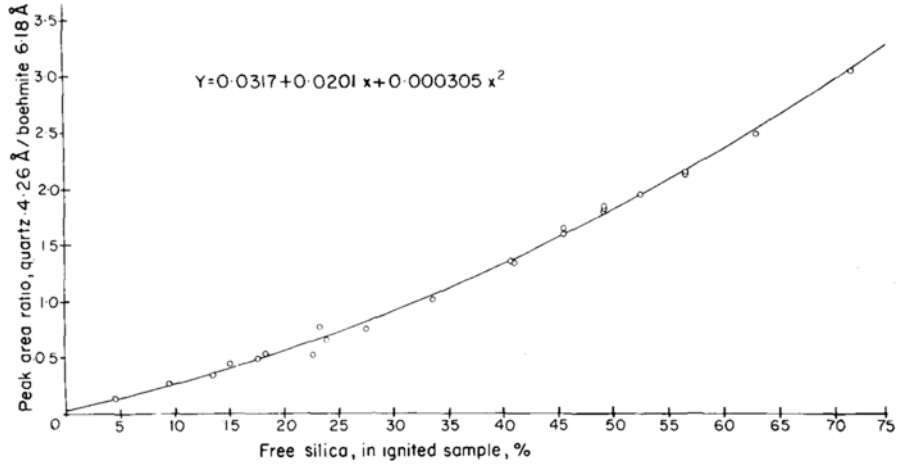


Fig. 2. Working curve relating quartz/boehmite peak area ratio to quartz content of the ignited samples.

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two points (quartz contents of 22·73 and 23·35 per cent) fall outside the main band of residuals. However, their residual values are not sufficiently different from the main band of points to merit exclusion of the points. The remainder of the residuals fall in an even band, which is of the same order of size for both high and low quartz values. This suggests that the quadratic fit is satisfactory and that no unexplained parameter is affecting the quartz determination.

Trostel and Wynne (1940, p. 19) point out that the pyrosulphate fusion does not dissolve amorphous silica. Therefore while the X-ray method is determining crystalline silica the chemical method is determining total free silica, namely crystalline and amorphous silica. This could lead to trouble in constructing a working curve if standards contained much amorphous silica. In the present study the fact that the quadratic fit is good and that the line nearly passes through the origin suggests that the amount of amorphous silica present is negligable. In addition, during the ignition to 950°C any amorphous silica would be converted to cristobalite (Calvert, 1966, p. 574). This mineral has a main peak at 4·04 Å (21.98°2θ in the CuKα radiation) which would have been picked up in the present study. A similar area ratio for cristobalite/boehmite could then be used to determine amorphous silica, if suitable standards were available.

The ignition to 950°C was found to have no effect on the quartz in the samples. An X-ray diffraction record of a sample of pure Belgian quartz sand before and after such ignition showed no change in quartz peak-shape or peak-height. Though clay minerals present in the sample are almost wholly decomposed by the ignition at 950°C, no new crystalline phases (e.g. cristobalite or mullite) have appeared at this temperature.

CONCLUSIONS

A precise X-ray diffraction method (coefficient of variation is 1·9 per cent) for determining quartz in sediments has been developed. Sample preparation is straightforward and can be performed on large batches of samples. Actual X-ray analysis is very economical of machine time, requiring only 7 min per sample.

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Résumé—On décrit ici une méthode rapide et précise de diffraction par rayons X permettant de déterminer la présence de quartz dans les sédiments, avec un coefficient de variation de 1,9 pour cent. Les échantillons sont allumés à 950° avant l'analyse aux rayons X. Ceci détruit l'interférence des pics d'argile, accroît l'intensité relative des pics de quartz et réduit la variation initiale de matrice des échantillons. On mesure le rapport de la zone de crête du quartz (4,26 Å) par rapport à un boehmite standard d'apport (6,18 Å) La teneur en quartz est obtenue à partir d'une courbe de travail construite en utilisant des rocs similaires d'une teneur connue en silice libre, qui one été analysés par la méthode de Trostel et Wynne (1940).

Kurzreferat—Eine Röntgendiffraktionsmethode zur Bestimmung von Quartz in Sedimenten wird beschrieben, die sowohl schnell als auch präzise ist. Der Variationskoeffizient beträgt 1,9%. Die Proben werden bei 950°C vor der Röntgenanalyse geglüht. Dies beseitigt die Interferenz der Tonpeaks, erhöht die relative Intensität der Quartzpeaks und verringert die ursprüngliche Grundmassenvariation der Proben. Das Verhältnis der Peakflächen des Quartzes (4,26 Å) und eines zugesetzten Normalböhmiten (6,18 Å) wird gemassen. Der Quartzgehalt wird an Hand einer Arbeitskurve festgestellt, die unter Anwendung ähnlicher Gesteine mit bekanntem Gehalt an ungebundener Kieselerde entwickelt wurde; diese Gesteine wurden nach der Methode von Trostel und Wynne (1940) analysiert.

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Резюме—Описан быстрый и точный метод рентгенометрического определения кварца в осадочных породах с коэффициентом вариации 1,9%. Образцы предварительно прокаливаются при 950°С, что исключает появление пиков от глинистых минералов, увеличивает относитеьлную интенсивность пиков кварца и уменьшает начальные фоновые различия образцов. Измеряется отношение площади пика кварца (4,26 А) к площади пика добавленного к образпу бёмитового стандарта (6,18 А). Содержание кварца определяется по рабочей кривой, построенной с использованием аналогичных пород, содержащих определенное количество кремнезема; эти породы анализировались по методу Тростела и Уайнна (1940).

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