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THE DETERMINATION OF QUARTZ IN CLAY MATERIALS

A CRITICAL COMPARISON OF METHODS

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The quartz contents (maximum, 4 wt.%) of four clay materials and a tourmaline were determined by differential thermal analysis, by X-ray diffraction and by chemical analysis. The results are used to make a critical comparison of these three methods. DTA gives a better precision than X-ray diffraction analysis. The chemical method is judged unreliable in that feldspar and mica, present as minor components, are recorded in part as quartz.

Differential thermal analysis (DTA), X-ray crystallographic analysis and chemical analysis have been widely used to determine quartz in clay materials [1–10]. The major emphasis has been directed to the analysis of mixtures containing upwards of 10 wt.% quartz. In this paper, we make a critical comparison of the above methods. The greatest amount of quartz in the substances analysed (four clay materials and one tourmaline) was only 4 wt.%.

Materials

The quartz used for calibration was of Norwegian origin; it had been ground to give a material finer than 50 μm (20 wt.% below 5 μm). Calculations based on published work [11] showed that the amount of amorphous material present was unlikely to exceed 2%.

Table 1

Approximate mineralogical compositions and particle sizes of the five materials

Sample	Approximate mineralogical composition (wt.%)					Particle size
	Kaolinite	Mica	Feldspar	Quartz	Tourmaline	
A	94	5	<1	1	0	−10 μm with 75 wt.% − 2 μm
B	75	23	<1	0	0	−300 mesh with 50 wt.% −10 μm
C	61	30	2	4	3	a 5 μm to 50 μm fraction
D	0	100	<1	Trace	0	100 wt.% − 2 μm
E	0	0	<1	5	95	100 wt.% − 10 μm

Five materials were examined; these included three kaolins (samples A, B and C), a ground biotite (sample D) and a ground tourmaline (sample E). Their approximate mineralogical compositions (X-ray diffraction) and particle size ranges are shown in Table 1. Artificial mixtures of quartz with each material were prepared by mixing the components in a Wig-L-Bug mechanical mortar (Crescent Dental Mfg. Co., Chicago).

Differential thermal analysis

A Mettler Recording Vacuum Thermoanalyser was used for the DTA work. Experiments were made in flowing air (100 cm^3 at S.T.P. per min) which had been dried over anhydrous magnesium perchlorate. The DTA sample holder is shown in Fig. 1; it had been machined from alumina and was used without crucibles.

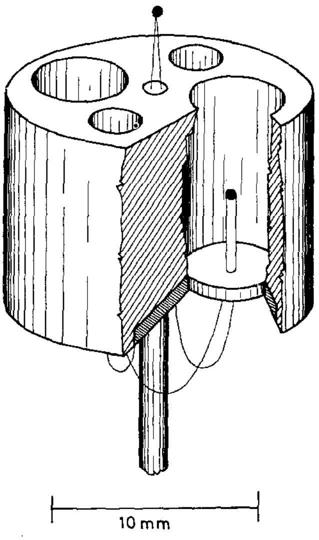

Fig. 1. The block DTA—TG sample holder with the crucibles omitted

The sample and reference material (calcined alumina) were each packed by hand into the cylindrical wells of the block. The sample weights were reproducible to ±1.0%. Both the temperature and differential thermocouples were of platinum: 10% rhodium-platinum (their locations are shown in Fig. 1): the emf from the differential thermocouple was amplified by a factor of 500 (maximum sensitivity) and fed to a recorder (an input of 2 mV gave a full scale deflection of 20 cm).

For a determination, the sample was first heated at the maximum available rate (greater than 15°/min) to 700° [12]. This dehydroxylated the kaolinite. The DTA curve was then recorded at a cooling rate of 10°/min; the cooling mode was chosen for convenience since the sample was already above the quartz $\alpha-\beta$ transition temperature of 573°. A representative trace is shown in Fig. 2. Experiments established that prolonged heating at 700° produced no change in the dimensions of the subsequent quartz inversion peak; likewise the small slope of the base line was unaffected by extended heating at 700°.

Various geometrical constructions (eight in number) were used to define both the height and the area of the quartz inversion peak measured on sample B and five of its mixtures with quartz (up to 10 wt. %).* Statistical analysis showed no one method to be better than the others. Accordingly, the method of peak height construction shown in Fig. 2 was adopted for convenience.

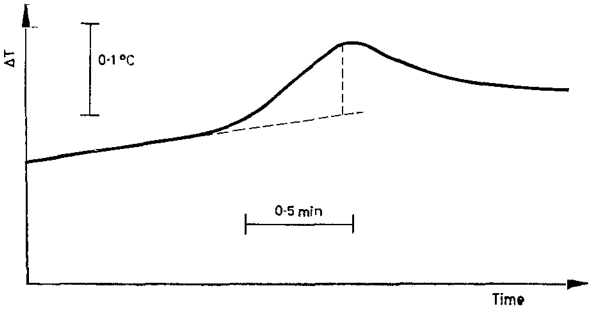

Fig. 2. DTA cooling curve for a mixture composed of sample B and added quartz (q = 0.04). The method of peak height construction is illustrated

In determining the quartz content of a sample, five mixtures containing known amounts of added quartz up to about 10 wt. % were made up as described above. A part of each mixture based on sample B was taken for X-ray analysis. Each mixture including the sample with no quartz addition was examined by DTA.

Now the weight fraction x of quartz in a mixture composed of a weight $(1-q)$ of unknown and a weight q of added quartz is

$$x = q + x_0(1-q), \tag{1}$$

where x_0 is the weight fraction of quartz in the unknown. If peak height h is proportional to the weight fraction of quartz in the mixture,

$$h = B\{q(1-x_0)+x_0\} \tag{2}$$

where B is some constant. The data for each mixture, when plotted according to Eq. (2), gave good straight lines. Values of B and x_0 together with their standard errors are given in Table 2. The precision in the measured quartz con-

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* There is some theoretical justification for the use of peak area rather than peak height as the working parameter; see for example, reference [13].

Table 2

Determination of quartz contents by DTA and by chemical analysis

Sample	DTA		Chemical analysis
	B, °C	x_0	x_0
A	2.15 ± 0.05	−0.002 ± 0.003	0.0094, 0.0092, 0.0090, 0.0084
B	2.26 ± 0.07	0.003 ± 0.002	0.024
C	2.03 ± 0.07	0.035 ± 0.003	0.052, 0.050, 0.050, 0.050
D	1.98 ± 0.05	0.001 ± 0.002	0.0036, 0.0024, 0.0020
E	2.34 ± 0.04	0.037 ± 0.002	0.234, 0.177, 0.122

tent can be judged from data for sample C; here x_0 is equal to 0.035 and the relative standard error is about ±10%. There are three sources of error: sample packing, peak height construction and measurement, and instrumental reproducibility. It is possible to account for the observed errors in terms of these three sources.

X-ray diffraction analysis

Sample B and its mixtures with known quartz additions were analysed by X-ray diffraction (Philips PW 1010). Each sample was ground as slurry in water to a −5 μm particle size [14] before examination. Diffraction patterns were recorded at a scanning rate of 0.5° (2Θ) per min using CuK_α radiation with a vertical goniometer (Philips PW 1050). The three most intense peaks arising from the (101), (100) and (112) planes and corresponding to spacings of 3.34 Å, 4.26 Å and 1.82 Å were used for analysis. With pure quartz, their relative heights are 100, 35 and 17 respectively [15]. Peak heights H were measured for each mixture after correcting the base line where necessary for adjacent peaks from other minerals. Each set of data was fitted by the method of least squares to the empirical relation

$$H = C\{q(1-x_0)+x_0\}, \tag{5}$$

where C is some constant and x_0 is as above. The calculated values of x_0 were 0.024 ± 0.002 (3.34 Å), 0.003 ± 0.010 (4.26 Å) and −0.005 ± 0.007 (1.82 Å) compared with the value 0.003 ± 0.002 determined by DTA. The value of x_0 for the 3.34 Å spacing is widely disparate from the other two. Furthermore, the relative errors in the values of x_0 for the 4.26 Å and 1.82 Å spacings are quite large. There are two principal sources of error: interference from other minerals* and

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* Till and Spears [7] suggested that interference could be eliminated by calcining the specimen at 900° for 3 h before examination. This approach was investigated here. Reference to Fig. 3 shows that whilst the interference from kaolinite was eliminated, that from mica was little altered.

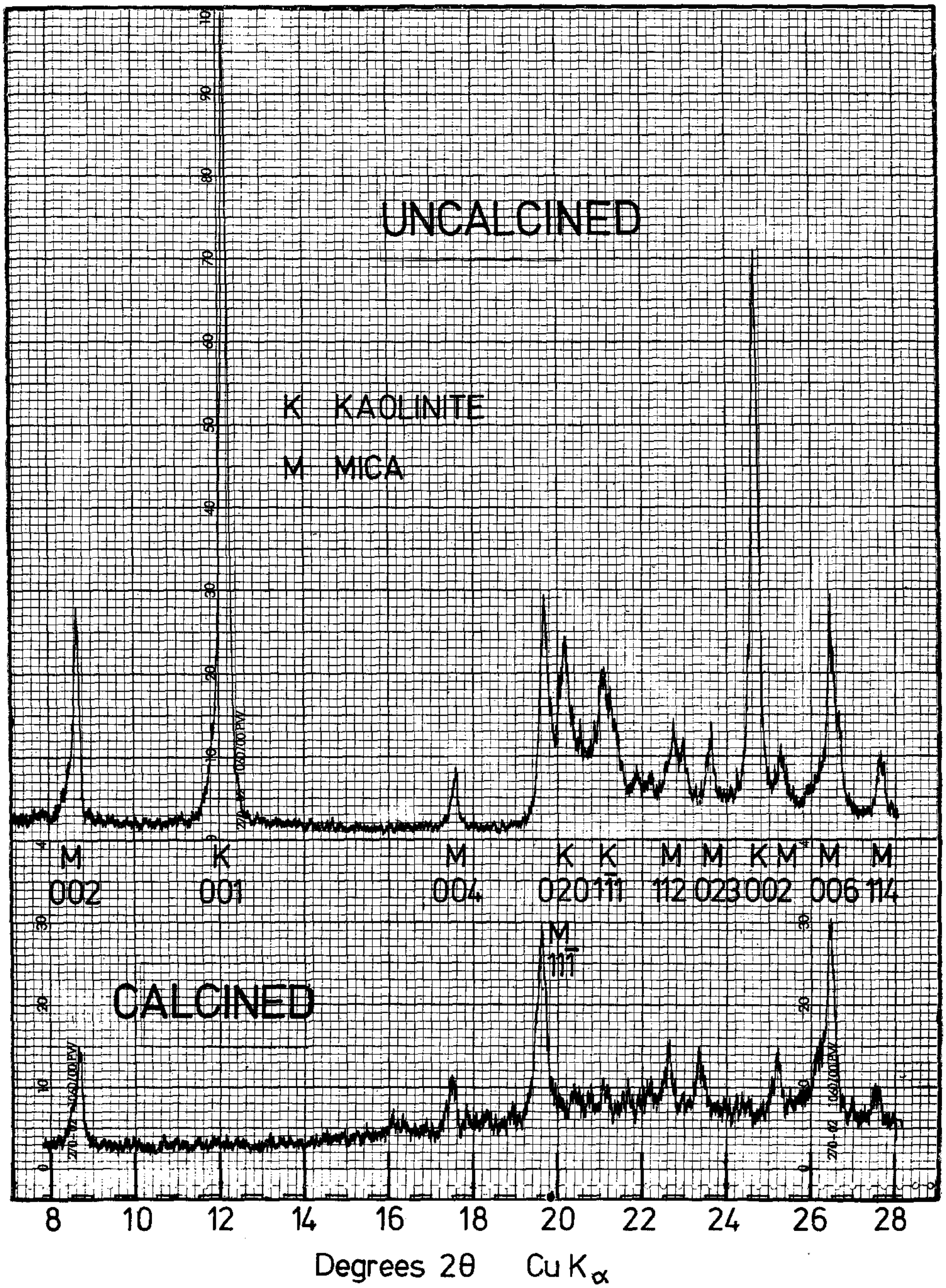

Fig. 3. X-ray diffractometer records for sample B before and after calcination at 850° for 3 h

peak height reproducibility. This latter point was illustrated by ten replicate measurements using the mixture with x equal to 0.1 and without disturbing the specimen; relative standard errors in the peak heights were 8.7% (4.26 Å), 2.6% (3.34 Å) and 12.2% (1.82 Å).

Chemical analysis

In the method described by Trostel and Wynne [10], the clay mineral is fused with potassium pyrosulphate and then extracted with hot sodium hydroxide solution. The unattacked minerals (considered in the original paper to be quartz and feldspar) are recovered and weighed.

This procedure was applied to the five samples and gave the results shown in Table 2. The reproducibility between repeated determinations is considered acceptable except for biotite (sample D) and tourmaline (sample E) which was only partially attacked during the fusion. It is evident from Table 2 that chemical analysis always indicates a higher quartz content than does DTA. The discrepancy could be attributed to feldspar. To test this, the residue from sample C was analysed by X-ray diffraction: the approximate composition was 45 wt.% quartz, 10 wt.% feldspar together with a significant amount of mica (any metakaolinite present would escape detection). We conclude that feldspar was either unattacked or attacked in part and that only 85 to 90 wt.% of the mica had reacted.

The possible loss of quartz through solution in the hot caustic soda solution was considered by Trostel and Wynne [10] but not examined quantitatively. In this work, three mixtures containing added quartz ($x = 0.1$) were prepared: these contained the standard ground quartz (-50 μm), a -2 μm quartz fraction and a 15 μm to 20 μm quartz fraction. The two fractions had been prepared from the standard ground quartz. Each mixture was analysed. There was a detectable loss of quartz from the mixture containing the added 15 μm to 20 μm quartz fraction (x fell from 0.10 to 0.098) and a significant loss from the mixture containing the -2 μm quartz fraction (x fell to 0.054). In experiments with the -2 μm quartz fraction alone, it was established that such loss arose in two ways: by chemical attack of the quartz to give soluble silicate and by passage of fine quartz through the filter paper during the washing stage.

Discussion

The present work has emphasized the experimental difficulties in measuring relatively small amounts of quartz (up to about 4 wt.%) in clay materials.

Chemical analysis [10] by selective dissolution is not advocated. Feldspar, mica and tourmaline are only partially attacked. Quartz can be lost both physically and through chemical attack.

Analysis by X-ray diffraction was applied to only one of the clay materials (Sample B) and its mixtures with added quartz. The values of x_0 obtained using the three strongest diffraction lines were widely disparate (0.003, 0.024 and

-0.005) and the precision in two of them was poor. The results confirmed the serious interference from other minerals. We would judge 1 wt. % to represent the lower limit of detection of quartz by this method. The more time-consuming differential thermal analysis emerges as the superior method in that it gives the best experimental precision: typically a relative standard error of about 10% on an x_0-value of 0.04.

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Résumé — On a déterminé la teneur en quartz (4% en poids au maximum) de quatre argiles et d'une tourmaline en se servant de l'analyse thermique différentielle, de la diffraction de rayons X et de l'analyse chimique. On a utilisé les résultats pour faire une étude critique des trois méthodes. L'ATD donne une meilleure précision que l'analyse par diffraction X. L'analyse chimique présente peu de sûreté car le feldspath et le mica, présents à l'état de constituants mineurs, interviennent en partie comme le quartz.

Zusammenfassung — Der Quarzgehalt (max. 4%) von vier Tonmineralien und von Turmalin wurde durch Differentialthermoanalyse, Röntgendiffraktion und chemische Analyse bestimmt. Die Ergebnisse ermöglichten einen kritischen Vergleich der drei Methoden. Die DTA ist genauer als die Röntgendiffraktion. Die Chemische Analyse ist unzuverläßlich, da kleinere Mengen an Feldspat und Glimmer ebenfalls teilweise als Quarz erfaßt werden.

Резюме — Методами дифференциального термического анализа, рентген-диффракции и химического анализа определены трумалин и содержание кварца макс. 4 вес % в четырех образцах. На основании полученных результатов проведено критическое сравнение этих трех методов. Найдено, что метод ДТА более надежен, чем рентген — диффракционны анализ. Химический метод ненадежен, если присутствуют в виде микрокомпонентов фельдспат и мика, т.к. они регистрируются как кварц.