

THE HIGH-LOW INVERSION OF QUARTZ

YOETZ DEUTSCH, AMIR SANDLER, YAACOV NATHAN
Geological Survey of Israel
30 Malkhei Israel St., Jerusalem 95 501, Israel

ABSTRACT

DTA is one of the preferred methods used to determine quartz quantitatively. It is well known that for quartz of small particle size (less than $0.5\ \mu$) large discrepancies are found between X-ray and thermal results, raising doubts as to the reliability of the DTA method. However we show that the height of the DTA high-low inversion quartz peak is a function of both the amount of quartz in the sample and of the crystallinity index (CI) of quartz as defined by Murata and Norman [1].

DTA can be used in a routine manner for the quantitative determination of quartz for well crystallized quartz (CI above 8); for other cases, special curves with appropriate standards have to be prepared, and for poorly crystallized quartz (CI less than 3), DTA cannot be used.

INTRODUCTION

A quantitative determination of quartz in geological samples is frequently required. Sometimes there are practical reasons, such as in commercial clays or feldspar mined for ceramic use, or in dust samples collected for ecological purposes. In other cases the interest is mainly scientific, e.g. to interpret environments of deposition. In our case quartz had to be determined in clay (mainly palygorskite), feldspar (mainly albite) and porcelanite (mainly opal c-t) samples.

Standard methods of chemical analysis fail to differentiate between free and combined silica and between the various polymorphs of silica; hence physical methods are used for this purpose. X-ray diffraction (XRD) is the method most often used but it suffers from several drawbacks. There is an overlap between the most intense peaks of quartz and some clay peaks, making the XRD determination of small quantities of quartz in clay samples problematic. For accurate work, the mass absorption coefficient of the sample has to be determined. This can be done, by measuring the intensity of the Compton-scattered line, using X-ray fluorescence (XRF), or by carrying out a full chemical analysis, which makes the quartz analysis laborious. Finally the calibration curve for quartz by XRD is not linear.

Differential thermal analysis (DTA) has been used as an alternative to XRD for quartz determinations [2, 3]. The principle of the method is based on the use of the high-low quartz inversion at 573°C . The thermal inversion of quartz at about 573°C is not a new discovery in thermal analysis; it was already observed in 1889 by Le Chatelier [4], during laboratory experiments.

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21-25 August 1988.

This is a reversible rapid displacive inversion. The DTA method has many advantages, mainly: a) the matrix effect is very small; b) the possibility of using very small amounts of sample (down to 20 mg.); c) because the inversion is reversible, the same sample can be run a number of times and an average value measured; d) the cooling curve, in which there are no interfering peaks as in the heating curve may be used. Nevertheless, DTA also has drawbacks. It is less sensitive than XRD: concentrations lower than 3% cannot be measured and concentrations less than 1% cannot be detected. The main disadvantage is that quantitative determinations of quartz by different methods and particularly by X-ray and DTA have been found to diverge considerably [5, 6], raising doubts as to the accuracy of the DTA method in certain cases.

SAMPLES AND ANALYTICAL TECHNIQUES

Clay and feldspar samples were taken from outcrops and cores, the clay from the Nezer Formation, Upper Turonian, Negev [7] and the feldspar from an albitite in southern Sinai [8]; almost pure samples of palygorskite and albite were obtained by grain size and density separation. Standards were made by adding finely ground well crystallized quartz to the pure samples. Further samples were then taken from porcelanites from the Santa Cruz Mudstone, Miocene, California [9] and from cherts from the Mishash Formation, Campanian, Negev [10, 11], including some which had undergone metamorphism. These samples came from outcrops only. The thermal analysis was done with a Stanton Redcroft 781 apparatus using 30.0 ± 0.5 mg sample and various heating rates (5° , 10° and 20°C per minute). Five cycles were run per sample, the temperature limits varying with the heating rate, for the heating rate of 5°C per minute, the limits were 530° and 610°C . XRD was carried out with a Philips PW 1050/80 instrument.

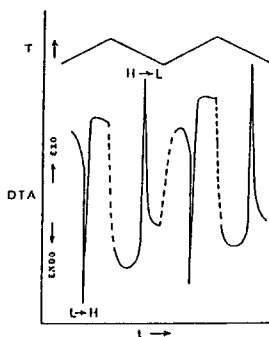


Fig. 1: DTA curve for a pure well crystallized quartz; Two cycles are shown.

RESULTS AND DISCUSSION

Fig. 1 presents an example of a DTA curve for a well crystallized quartz; calculations showed that the height of the peak gives as good an estimate of the quantity of quartz as the surface of the peak. The standard curves made for quartz in palygorskite and albite by addition methods are given in Fig. 2. Similar curves were prepared with calcium carbonate (calcite) and aluminum oxide. The results confirm that the matrix has a very small effect on the height of the DTA quartz peak. Furthermore, the amount of quartz found in the

clay and feldspar samples by DTA was in good accord with the chemical analysis and with the physical properties of these samples. On the other hand, the DTA results from the Santa Cruz Mudstone samples were not always in accord with the X-ray results.

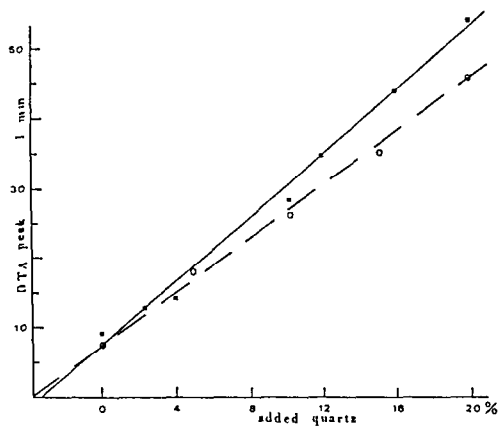


Fig. 2: Calibration curves for quartz determination; solid line, in albite; dashed line, in palygorskite.

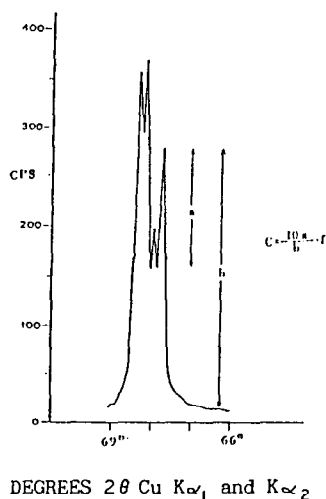


Fig. 3: Diffractogram of a well crystallized quartz. a and b are measured to obtain the crystallization index of the sample.

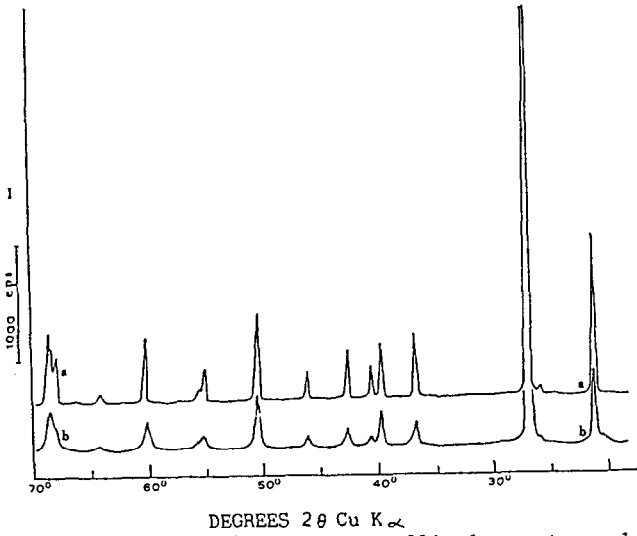


Fig. 4: Diffractograms of a) well crystallized quartz and b) poorly crystallized quartz.

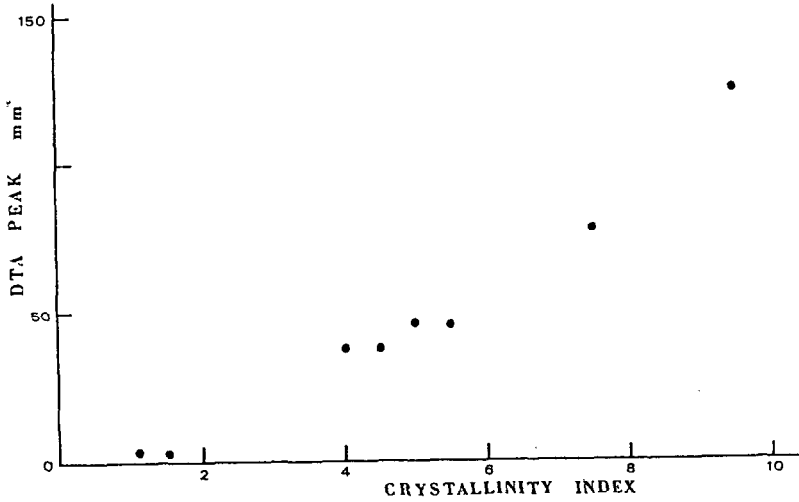


Fig. 5: Relationship between height of DTA peak and crystallinity index

In some cases they were noticeably lower, while in others they gave similar results. Two other noteworthy results from the Santa Cruz Mudstone samples are: 1) A very good correlation between the amount of quartz found by DTA and the clay content. 2) A great variability in the crystallinity index (CI) of quartz [1]. This index is derived from the intensity of the (212) at 2θ 67.4° (Fig. 3). Height a of this peak is divided by its height above background b and this quotient a/b is multiplied by 10 to convert the fraction into a number greater than 1.0. A scaling factor F is further used to express the crystallisation indexes (CI's) on a scale of one to ten. This is found by arbitrarily giving a CI of 10 to a supposedly perfect quartz. The quartz chosen by us was a pegmatitic quartz from Elat which gave the highest a/b ratio of all the measured samples.

In an attempt to understand the results obtained with the Santa Cruz Mudstone samples, cherts from the Mishash Formation were examined. In general these samples gave practically no peak in the DTA, e.g. samples which had 100% quartz by XRD showed less than 5% by DTA. In view of these results, which are both puzzling and known from the literature [2, 5, 6, 12], an X-ray study of the Mishash cherts was carried out. Careful comparison between the X-ray diffraction patterns of Mishash chert and well crystallised quartz showed two main differences. As expected, very different crystallinity indexes (Murata and Norman, 1976) were found, around 1 for the cherts and 9 for detrital Turonian sand. A big difference in the intensities of the diffractograms was also found (Fig. 4). Differences in the intensities of diffractograms of quartz of different grain size have been reported by Nagelschmidt et al. [13]. These results imply a relation between the crystallinity of quartz and the size of the DTA peak. To prove this assumption a set of Mishash cherts belonging to the Hatrurim Formation [14] which underwent thermal metamorphism, (different grades) were chosen. On each sample both crystallinity index and height of DTA peak were measured. Fig. 5 shows the relationship between them.

CONCLUSIONS

The number of samples examined in the present work is relatively small and therefore the following conclusions are tentative and have to be confirmed by further work, which is now under way. There is no contradiction between X-ray and DTA results, the height of the DTA peak is a function of both the amount of quartz in the sample and of its crystallinity index. DTA can be used for the quantitative determination of quartz for very well crystallised quartz (CI above 8 - this is quite common in geological samples) in a routine manner; for other samples special curves with appropriate standards have to be prepared and for quartz with a crystallinity index less than 3, DTA cannot be used. The function which links the amount of quartz to the height of the DTA peak is linear, whereas the function which links the crystallinity index of quartz to the height of the DTA peak appears to be quadratic. Two interesting uses may be made of the relationship between crystallinity and peak size: a) In samples with quartz of two provenances with big differences in crystallinity e.g. the Santa Cruz Mudstone with autigenic and detrital quartz, both can be quantitatively determined; b) In sedimentary formations which contain authigenic quartz and later underwent metamorphism, e.g. the Hatrurim Formation, DTA may give a good indication of the grade of metamorphism. Finally there might be a case for a redefinition of chalcedony to include only quartz with a crystallinity index [1] under 3 and which does not show the characteristic low-high inversion peak in the DTA curve.

ACKNOWLEDGEMENTS

We thank Ms. Dallilah El-Sabagh and Mr. Avi Burg for kindly providing the Santa Cruz Mudstone and the Mishash Formation samples respectively, Prof. Lisa Heller-Kalai for her critical reading of the manuscript and Ms. Beverly Katz for her careful editing.

REFERENCES

- 1 K. J. Murata and M. B. Norman, *Am. J. Science* 276 (1976) 1120.
- 2 L. H. Berkelhamer, *Rep. Invest. U.S. Bur. Mines*, No.3763 (1944)
- 3 R. W. Grimshaw, *Clay Minerals Bull.* 2 (1953) 2.
- 4 H. L. Le Chatelier, *C. R. hebd. Acad. Sci. Paris*, 108 (1889) 1048.
- 5 O. W. Floerke, *Schweiz. Mineral. Petrog. Mitt.* 41 (1961) 311.
- 6 W. Smykatz-Kloss, *Contr. Mineral. and Petrol.* 36 (1972) 1.
- 7 Y. K. Bendor and A. Vroman, *The Geological Map of Israel, 1:100,000 Sheet 17, Nizana, Geological Survey of Israel, Jerusalem* (1963).
- 8 R. Bogoch, T. Minster and D. Bahat, *Miner. Resour. Div. Rep. M. P. 550/73, Geol. Survey Israel, Jerusalem*, (1973) 18 pp.
- 9 J. C. Clark, Ph. D. thesis, Stanford Univ., Stanford, California, (1966) 184 pp.
- 10 S. H. Shaw, *Southern Palestine, Geological Map on a scale of 1:250,000 with explanatory notes. Govt. of Palestine, Jerusalem.* (1947)
- 11 Y. K. Bendor and A. Vroman, *The Geological Map of Israel, 1:100,000 Sheet 16, Mount Sdom, 2nd. Ed. Geological Survey of Israel, Jerusalem* (1960).
- 12 M. Fields, *Nature, Lond.*, 170, (1952) 366.
- 13 G. Nagelschmidt, R. L. Gordon and O. G. Griffin, *Nature, Lond.*, 169, (1952) 539.
- 14 S. Gross, *Geological Survey of Israel Bulletin*, 70, (1977) 80 pp.