THE DETECTION OF QUARTZ IN CLAY MINERALS BY DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

Differential thermal analysis (DTA) has proven to be a sensitive, specific and relatively rapid technique for the detection of small amounts of free crystalline quartz in clay minerals. The method utilizes the thermal transition representing the reversible alpha–beta crystal inversion of quartz at 573 °C. On heating, the latent heat of inversion gives rise to an endothermic reaction; on cooling, an exothermic transition is obtained. The mineral is first calcined at approximately 800 °C for the purpose of inducing irreversible thermal transitions characteristic of that mineral and its impurities. The cooling curve then shows a flat baseline, thus improving detectability for quartz.

With the use of standard prepared samples of quartz in talc, the minimum level of detection of quartz by DTA was determined to be 0.5% by weight. If sample preparation and experimental parameters are standardized, DTA provides a definitive technique for detection of quartz in clay minerals.

The method has also been applied for the detection of quartz in industrial dust and in respirable particle size material such as might be taken from personnel air samplers.

INTRODUCTION

The natural abundance of silica leads to its frequent occurrence in clay mineral deposits, if only in trace quantities. Quartz, the most common polymorph of free silica, has been associated with respiratory diseases as a result of the inhalation of airborne mineral dusts. For this reason, a sensitive and specific method for the detection and quantitative estimation of small amounts of free crystalline quartz is of paramount importance. This has been a popular topic in the literature, much of it contradictory with respect to determination of the optimum method. In the case of clay mineral investigations, this analysis of free silica in the silicate matrix provides a

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unique challenge for bulk material as well as industrial dust. The analytical methods extant for this purpose include spectrophotometry, X-ray diffraction, infrared spectroscopy, and DTA.

The lengthy chemical procedure involves a selective phosphoric acid digestion of silicate mineral, followed by the spectrophotometric determination of free silica. Talvitie[1], who played a major role in the application of this method to the determination of quartz in industrial dust, indicated the need to critically control the digestion time in an attempt to avoid dissolving the quartz along with the silicate matrix, recommended the use of correction curves to compensate for this loss of quartz, and suggested that the incompletely dissolved silicate phases be identified by polarized light microscopy[2]. Although refinements have been proposed for the experimental procedure[3], the results can be unreliable.

X-ray diffractometry, commonly used as an analytical technique in mineralogy, has been applied extensively to quartz determination. Recent work has involved the analysis of both settled dust collected near an industrial operation and respirable dust ($<10 \mu m$ airborne particulates) taken from the entire occupational environment[4-7]. Typically, the respirable dust is deposited on a membrane filter of some kind along with an internal standard such as fluorite to compensate for matrix absorption effects. The filter is then inserted directly into the specimen holder of the X-ray diffractometer and quantitative determination of quartz is accomplished by measurement of either diffraction peak height or area. Methods utilizing this technique quote accuracy of about $\pm 30\%$ of the quartz present[8]. Difficulty is encountered in applying X-ray diffraction to the determination of quartz in clay minerals. Many minerals in the group show diffraction peaks at the same or very similar interplanar spacing as that of the strongest peak of quartz (0.334 nm). The problem is further compounded in attempting to use another quartz peak which might be free from interference. The relative intensity of the second strongest quartz reflection is only about one third that of the strongest, thereby greatly reducing the sensitivity of the method. Self-absorption by elements such as iron in the matrix has been found to cause significant attenuation of quartz peak intensity. In addition, some clay minerals have diffraction peaks which interfere with those of materials normally employed as internal standards.

The use of infrared spectroscopy for quartz determination involves a characteristic double band in the quartz spectrum at 12.5 and 12.8 μm. Generally, the halide pellet technique is employed for both bulk and dust samples. The feasibility of determining the quartz content of dust by concentrating it directly on an infrared-transparent filter has also been investigated[9]. Spectral response, however, is significantly affected by particle size and distribution. As in the case of X-ray diffraction, numerous clay minerals show interfering bands in the region of the quartz doublet. The analysis of a large number of dust samples taken from granite sheds[10] revealed that approximately 27% of the samples yielded unsatisfactory infrared scans because of inability to define either the peak at 12.5 μm or a satisfactory baseline. These problems were attributed to particle size or interference by materials used in the granite industry. In several recent studies[6,7], workers have employed both infrared

spectroscopy and X-ray diffraction for the analysis of quartz in dust samples in order to compare results.

Quartz undergoes a well-known thermal transition representing a reversible alpha–beta crystal inversion at 573 °C. On heating, the latent heat of inversion gives rise to an endothermic reaction; on cooling, an exothermic transition is obtained. In an often-quoted study of 250 samples of quartz by Keith and Tuttle[11], using DTA, it was found that natural quartz showed a range in its inversion temperature of 38 °C. More than 95% of the natural quartz samples investigated, however, underwent the phase transformation within 2.5 °C of the usual temperature. The range of inversion these workers observed was believed to have been caused by the solid solution of small amounts of other ions in the quartz. This definitive thermal transition suggested DTA as an analytical technique for quartz determination. For this purpose, most workers have assumed that natural quartz will always invert at 573 °C.

Numerous studies have shown that the intensity of the quartz peak is affected substantially by its particle size distribution. In addition, Dempster and Ritchie[12] reported that the accuracy of a quantitative DTA method fell off in the analysis of finely ground samples. This was shown to be a grinding effect, in which a layer of modified silica on the ground material yielded no thermal transition. For this and other reasons, DTA has not been recommended for the quantitative determination of quartz. The estimation of quartz content by DTA requires strict control of experimental parameters such as geometry of the sample holder, packing technique, and particle size of the material. Craig[13] has studied the effects of these and other variables in the determination of quartz in airborne mine dust by DTA. He concluded that an accurate and reliable quantitative DTA method might be feasible if optimum experimental parameters could be fixed.

Weiss et al.[14] evaluated the DTA method and studied the effect of particle size on peak height. The quartz crystal inversion was found to be reversible on heating the sample to over 800 °C, and no other material was found which had a transition peak at 573 °C. Their work suggested that the most accurate analysis of unknown samples was possible only after particle size determination. In a critical comparison of analytical methods for quartz determination in clay materials, Rowse and Jepson[15] found DTA to be superior to X-ray diffraction and chemical analyses in terms of experimental precision for clays containing as much as 4% by weight quartz. The sample was heated initially to 700 °C for the purpose of inducing irreversible thermal transitions characteristic of that mineral and its impurities. The cooling curve then showed a flat baseline, thus improving detectability for quartz. This experimental technique has been applied in the present study.

For the reasons previously described, X-ray diffractometry and infrared spectroscopy are non-specific techniques for the detection of quartz at low levels in clay minerals. DTA has been investigated as a test method for this purpose. The emphasis has not been on the development of a precise quantitative method, but rather on developing specific methodology for detection at the lowest possible level.

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A Robert L. Stone differential thermal analyzer (Model RC-202C) with high temperature powder sample holder (Model SH-8BE2) was employed. This sample holder, made of nickel or stainless steel, utilizes an exposed-loop differential thermocouple which protrudes into the sample and reference cavities. This direct immersion of the thermocouple into the mineral sample provides optimum sensitivity for the detection of thermal transitions characteristic of trace mineral components. The sample cavity is packed with about 150 mg of the mineral, and a heating rate of $10°C \, min^{-1}$ is used with a static air atmosphere. The quartz used to prepare standard samples was analyzed by X-ray diffractometry. No impurities were detected. All bulk mineral samples, the quartz standard, and the alumina used as reference material were minus 325-mesh particle size. Standard samples were prepared by dry mixing with a Spex mixer/mill.

RESULTS AND DISCUSSION

The application of this technique to the detection of quartz in some common clay minerals was investigated. Figure 1 shows a partial DTA curve for the mineral pyrophyllite, an aluminum silicate. It has a soft, slippery feel very similar to talc and is used in some areas of the world for the same purposes as talc. When this sample was run under normal sensitivity (40 μV full scale differential temperature gain), an intense transition was obtained at 573°C. The concentration of quartz in this particular sample of pyrophyllite was estimated to be between 20 and 25% by weight.
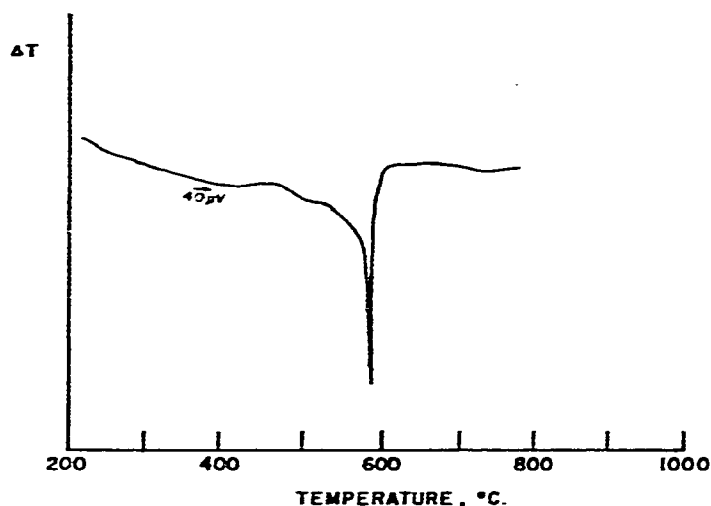

Fig. 1. Partial DTA curve showing the detection of quartz in the mineral pyrophyllite.

Figure 2 is a DTA curve for the mineral muscovite, a potassium aluminum silicate. It was run under normal sensitive conditions, and the dehydroxylation peak

is shown at approximately 930°C. A trace of quartz, perhaps 1 to 2% by weight, was detected (1). Although the sample was heated to 1000°C, the cooling curve (2) was recorded in order to demonstrate the appearance of the exothermic transition as the quartz was converted back to the alpha form.
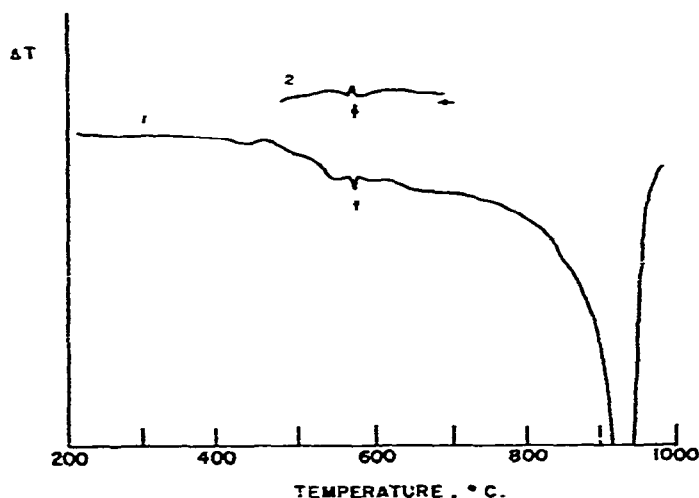

Fig. 2. DTA curve for muscovite (1) and partial cooling curve (2) showing the detection of quartz.

Figure 3 is a partial DTA curve for the mineral bentonite, or montmorillonite, a substituted aluminum silicate commonly found. It often occurs interbedded with shales, limestones and sands, and may contain considerable enrichment of silica[16]. The irreversible exotherm which occurred between 400 and 500°C is attributed to
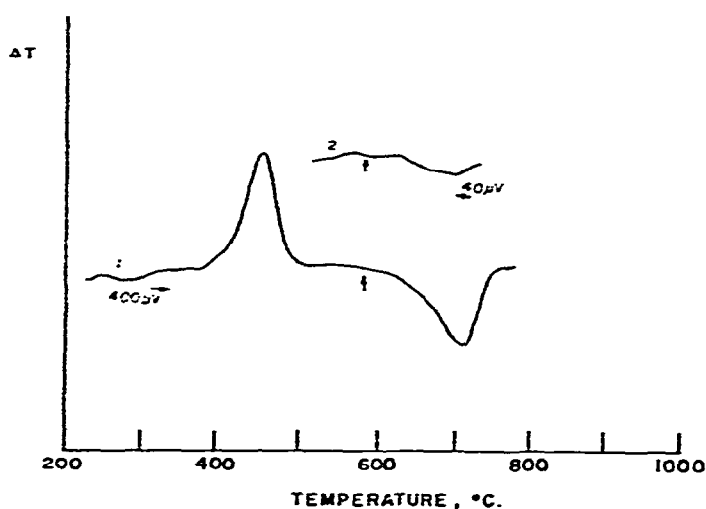

Fig. 3. Partial DTA curve (1) for bentonite and cooling curve (2), in which no quartz was detected (arrow at 573°C).

stress imposed on the material during milling. The intensity of the dehydroxylation endotherm at 700°C was such that it was not possible to record the curve at normal sensitivity in an attempt to detect quartz. The sample was run at 400 μV gain to 800°C (1) for the purpose of inducing this irreversible thermal transition. The cooling curve (2), then run under normal sensitivity, did not show the presence of quartz. The arrows at 573°C indicate where the quartz thermal transition would occur.

Figure 4 shows partial DTA curves for kaolinite, another very common and widely used aluminum silicate mineral. In this mineral, quartz is frequently found as an impurity. Curve (1) represents the DTA curve for kaolinite run under low sensitivity
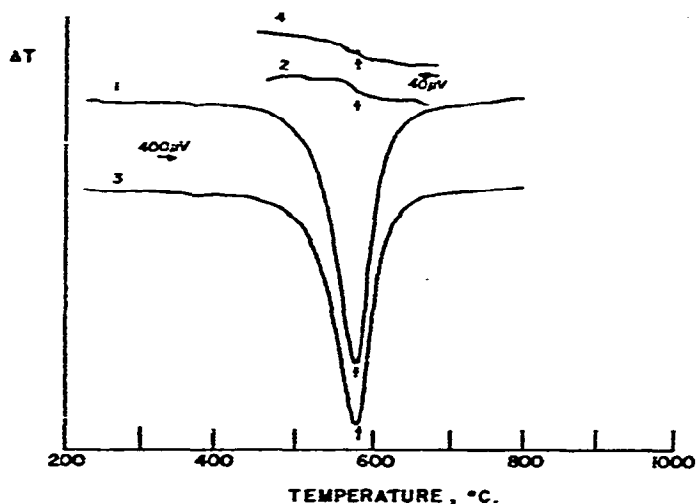

Fig. 4. Partial DTA curve (1) for kaolinite and cooling curve (2), in which no quartz was detected (arrows at 573°C). Partial DTA curve (3) and cooling curve (4) for the same sample of kaolinite to which 0.5% quartz was added.

due to the intensity of the dehydroxylation peak at about 570°C. At normal sensitivity, the region of the quartz transition would occur in such a sharply sloping baseline that traces of quartz could not be detected. Curve (2) represents the cooling curve for that sample of kaolinite run at normal sensitivity. It did not indicate the presence of quartz. Approximately 0.5% by weight of quartz was then added to another portion of this sample, and DTA curve (3) was obtained. Here the quartz was not detectable, but the cooling curve (4) did show the presence of quartz. Verification of the quartz at this level was often achieved by running an additional heating curve. We would consider 0.5% by weight as the minimum level of quartz detection by this technique.

Figure 5 represents the partial DTA curve (1) obtained for some material denoted as industrial grade talc. Analysis by X-ray diffraction and DTA indicated that the material actually consisted of about 5% muscovite and 95% chlorite minerals. No talc was detected. The intensity of the chlorite dehydroxylation peak at 630°C made the detection of quartz impossible. The cooling curve (2) of this material after

being calcined at 800°C did not indicate the presence of quartz, using normal gain sensitivity. On adding 1% by weight of quartz to the sample, the quartz was detected in the cooling curve (3) after calcination.
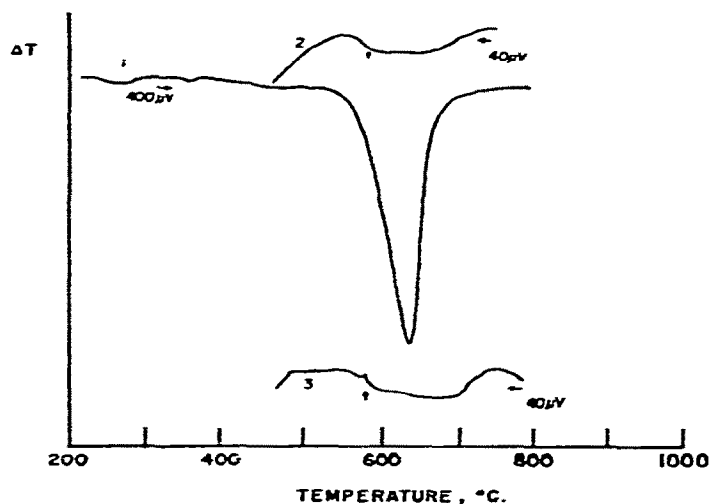

Fig. 5. Partial DTA curve (1) for an industrial grade talc and cooling curve (2), in which no quartz was detected (arrows at 573°C). Partial cooling curve (3) for the same material to which 1% quartz was added.

The DTA curves in Fig. 6 represent partial runs for a cosmetic grade talc, which normally contains 90% or more of the mineral species talc. Curve (1) was obtained when 1% of quartz by weight was added to that talc. It is detectable on the shoulder of the chlorite impurity endotherm in the initial heating curve and more
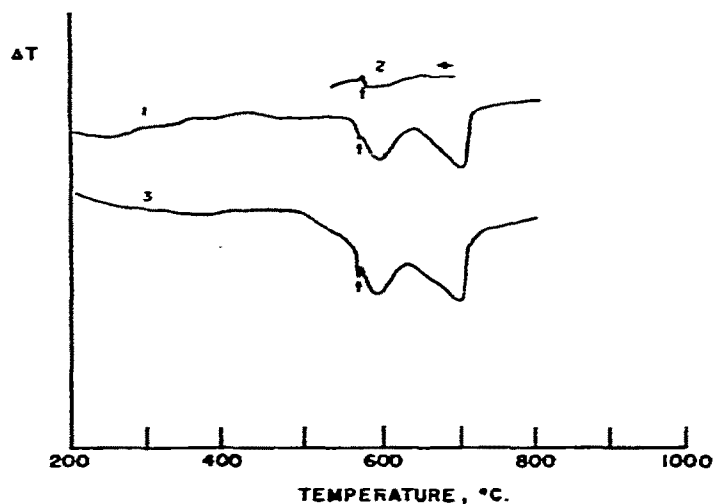

Fig. 6. Partial DTA curve (1) for a cosmetic grade talc and cooling curve (2), showing detection of the 1% quartz added. Partial DTA curve (3) for the same talc to which 2% quartz was added.

readily detectable in the cooling curve (2) for that sample. Curve (3) represents the addition of 2% quartz. It is easily detected at this level. The endotherm with peak temperature at 700°C is due to the presence of about 0.5% by weight dolomite.

A cosmetic grade talc was selected for the preparation of standard quartz-mineral samples for determination of the minimum detectable level. We selected, in Fig. 7, a talc which showed a reasonably flat baseline in the area of 573°C, and again the limit of detection was 0.5% by weight. Cooling curves were not required because no interfering mineral impurities were present. The endotherm with peak at 530°C
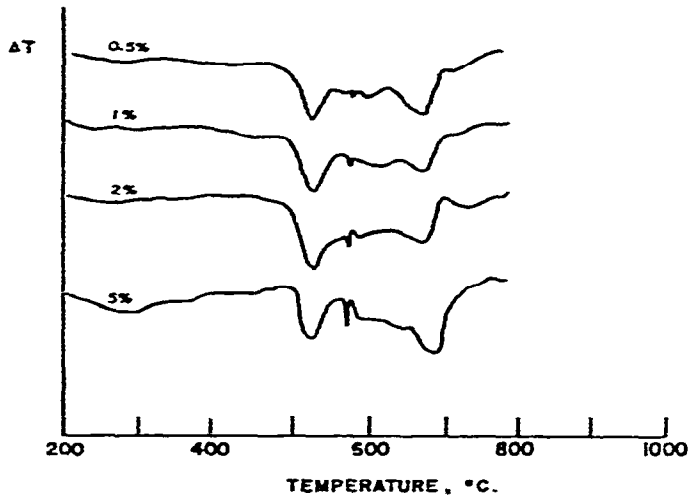

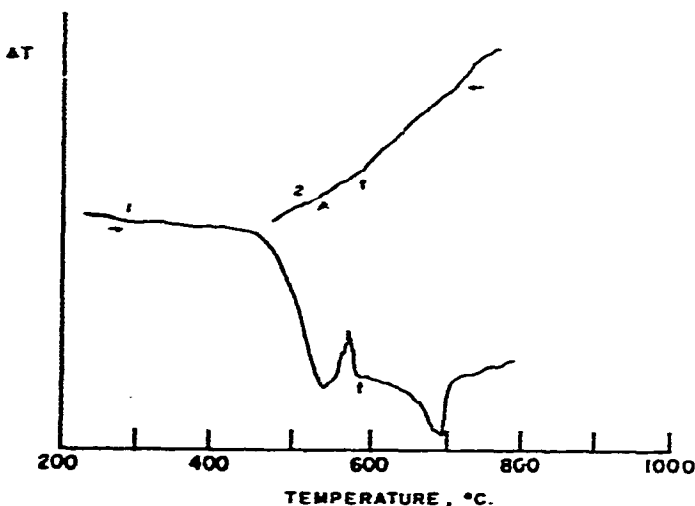Fig. 7. Partial DTA curves for 0.5, 1, 2, and 5% by weight quartz in cosmetic talc standard samples.

Fig. 8. Partial DTA curve (1) for a commercial sample of talc baby dusting powder and cooling curve (2).

represents approximately 0.5% by weight magnesite. If clay mineral samples to be analyzed are ground to minus 325-mesh particle size, then the particle size distribution should closely approximate that of the prepared standards. Quantitative estimation of quartz content is then feasible, by comparison of peak intensity with that of the standard curves.

The partial DTA curve (1) in Fig. 8 was obtained for an off-the-shelf sample of talc baby dusting powder containing no additives. It shows a reproducible and irreversible jagged exotherm in the area of interest for quartz. This extraneous peak has been attributed to physical stress imposed on the mineral as a result of milling and processing. It represents another example of the need for a cooling curve in some instances in order to detect traces of quartz. The cooling curve (2) did not indicate the presence of quartz.

It has been determined that the finer the quartz dust, the greater its pathogenicity. In an effort to determine the sensitivity of the DTA method for detection of respirable quartz in industrial dust, standard quartz of various particle size distributions was added to cosmetic talc at a 1% by weight level. As shown in Fig. 9, the thermal transition for quartz of less than 2 μm particle size was difficult to detect on heating and only slightly more evident in the cooling curve shown directly above it. For the analysis of respirable clay mineral dust, it was concluded that quartz of less than 8 μm particle size could be detected at a minimum level of 1% by weight.
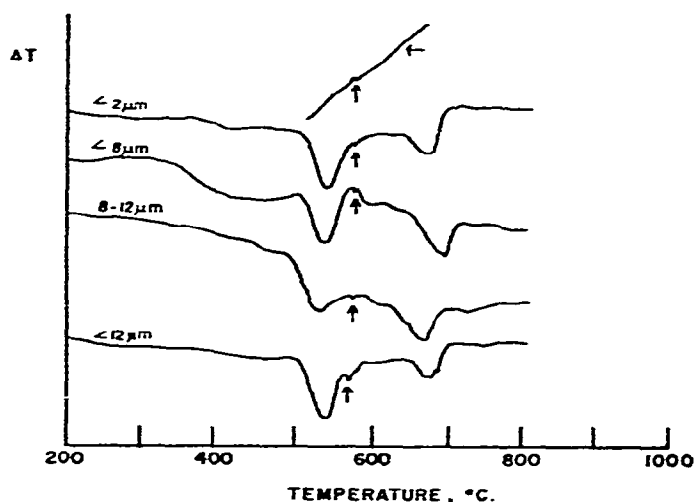

Fig. 9. Partial DTA curves for quartz of various particle size distributions at a 1% level in cosmetic talc.

Figure 10 shows the partial DTA curve (1) for a sample of 25 mg cosmetic talc of 5 μm mean particle size to which 1% of less than 8 μm particle size quartz was added. This represents the minimum quantity of sample required for the sample holder described, using the "sandwich" packing technique. The sample cavity is

partially packed with calcined alumina, the mineral sample is placed directly around the exposed differential thermocouple, and the remaining portion of the cavity is filled with alumina. Here, the quartz was detectable only by means of the cooling curve (2). In ten samples of this standard which were analyzed, all cooling curves showed the quartz exotherm. The sharp spike detected at 583 °C on the shoulder of the chlorite endotherm is the alpha–beta phase transformation of potassium sulfate, added as an internal temperature reference standard. It is useful in this work because of the close proximity of its thermal transition to that of quartz[17]. The potassium sulfate was present at a 2% by weight level, an insufficient quantity for its less intense exothermic transition to be detected in the cooling curve.
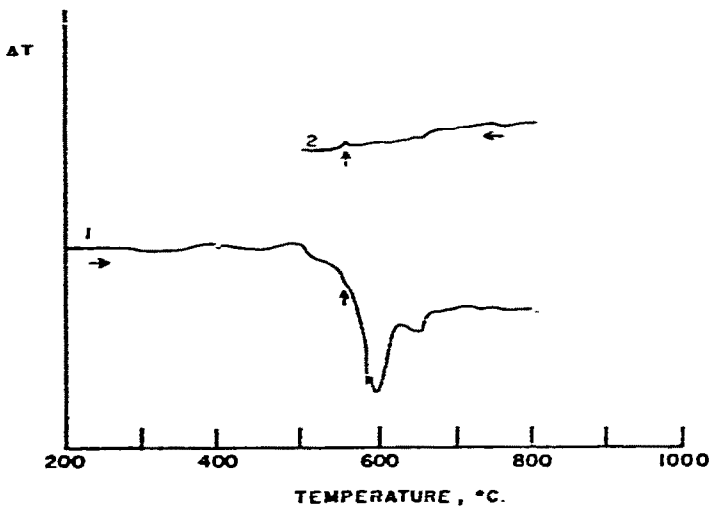

Fig. 10. Partial DTA curve (1) for 25 mg. respirable particle size talc to which 1% <8 μm particle size quartz was added, and cooling curve (2).

DTA curve (1) in Fig. 11 was obtained for a sample of dust taken from the floor of the finishing room of an industrial plant. It shows a very intense exotherm, probably due to carbonaceous material, with peak at approximately 475°C. The slope of this exotherm in the region of 573 °C prevented detection of traces of quartz. The cooling curve (2) run at normal sensitivity, however, did not indicate the presence of quartz.

DTA curve (1) in Fig. 12 was obtained for a sample of settled dust which was collected from the top of a duct in a fabric products plant. Again, a very intense exotherm occurred through the temperature region of the quartz inversion. This sample, after calcining at 800°C and recording the cooling curve at normal sensitivity, did not show quartz. One percent by weight of quartz was added to another portion of the dust. The cooling curve (2) obtained for the calcined material indicated the presence of quartz. In DTA curve (3), the same sample was reheated to confirm detection of quartz.
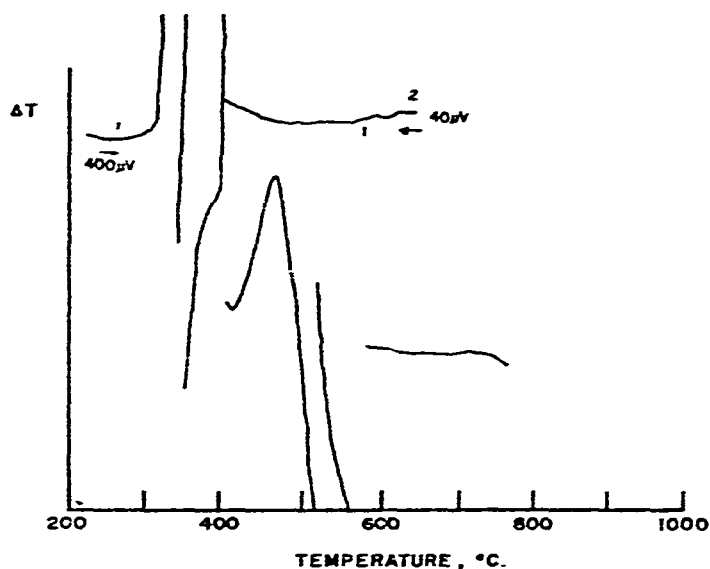
Fig. 11. Partial DTA curve (1) for a sample of dust from an industrial plant and cooling curve (2).
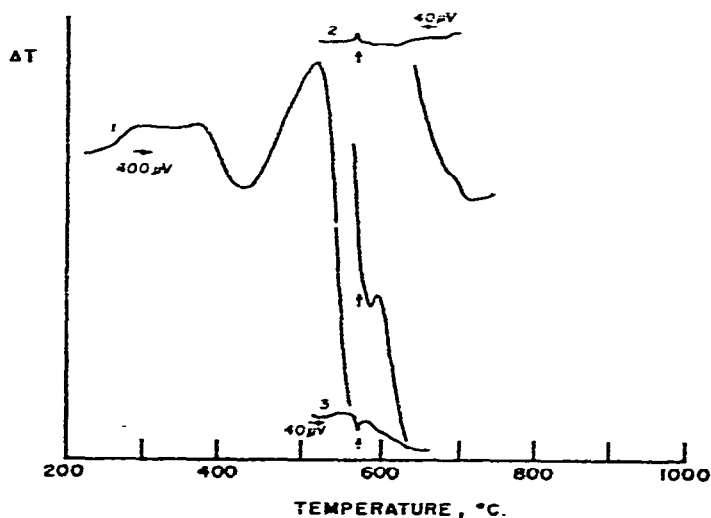

Fig. 12. Partial DTA curve (1) for another sample of industrial dust to which 1% quartz was added, and cooling curve (2). DTA curve (3) obtained by reheating.

The advantage of the DTA method lies in the specificity of the determination over that attainable by X-ray diffraction or infrared spectroscopy for samples of silicate minerals. A drawback with respect to dust analysis is that with the type of sample holder described, the minimum quantity of sample which can be analyzed is 25 mg. DTA appears to be a viable, specific and reasonably sensitive technique for the detection of quartz in clay minerals as well as in dust from the occupational environment, where these ores are being milled, processed and bagged.

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