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Determination of the Percentage of CO_2 in Soda

DECLARATION

This is to certify that the work herein described has never previously been submitted as a dissertation or thesis for any degree at any University.

(Signed) D.K. Craig

D.K. CRAIG

"DETERMINATION OF THE PERCENTAGE OF QUARTZ (S_1O_2) IN SAMPLES OF MINE DUST BY THE METHOD OF DIFFERENTIAL THERMAL ANALYSIS"

by

DOUGLAS KENNETH CRAIG

Submitted in partial fulfilment of the requirements for the degree of Master of Science in the Faculty of Science, University of the Witwatersrand, Johannesburg.

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xxx Thesis

THESIS TOPIC

"Determination of the Percentage of Quartz (S_iO_2) in Samples of Mine Dust by the Method of Differential Thermal Analysis"

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THE DETERMINATION OF THE PERCENTAGE OF QUARTZ (S_iO_2) IN SAMPLES OF MINE DUST BY THE METHOD OF DIFFERENTIAL THERMAL ANALYSIS

CHAPTER I

INTRODUCTION

1. REASONS FOR UNDERTAKING THE PROJECT

Crystalline quartz dust has been proved to be considerably more toxic than the other constituents of dust that occur in mine air. It is therefore of importance to know not only how much dust there is in the air that the miners breathe, but also how much of that dust is dangerous; that is, consists of quartz particles.

Routine dust sampling on the Gold Mines in the Transvaal and Orange Free State is carried out by means of an impinger-type instrument called the konimeter. This gives a dust "spot" on a glass slide which is ignited and acid treated before being assessed under a low-power microscope by methods that have been well defined. At the moment it is assumed that the result, expressed in number of particles per cubic centimetre of air sampled, gives a measure of the dangerous component of the dust. This may by no means be the case, as the particles that remain after treatment may be composed almost entirely of non-toxic materials. Much dust sampling is also carried out by means of thermal precipitation, but the method of assessment is in principle the same as that for konimeter samples and the same criticism applies.

It is therefore important that other methods be used to determine how the quartz content of the airborne dust varies from mine to mine, from place to place in one mine, and even from one dust generating mining operation to another. Methods of assessing the quantity of crystalline silica in any given dust sample depend on the physical and chemical properties of the quartz. They are such that they can, in general, be carried out only by laboratories that are especially equipped for the

/purpose .....

purpose, and not by the normal ventilation department on a mine.

The available methods may conveniently be divided into two groups, those that can be carried out only on fairly large samples (at least a tenth of a gram, and often more), and those that need only small samples.

(a) Bulk Samples

These are usually collected by means of electrostatic precipitation. Depending on the dust concentration in the air, a sample of 100 mgm takes about twenty minutes to collect.

(i) Chemical Analysis

There are various methods of determining the quartz content of a sample chemically, but they all require a large sample (at least a gram) and they are tedious and uncertain, especially for samples of particle size less than 2 microns.

(ii) X-Ray Diffraction Techniques

This is a useful method which requires only a small sample (say 100 mgm), but it requires expensive apparatus and a specially trained operator. There is also the possibility of other components of the dust, such as mica, interfering seriously with quartz results if present.

(iii) Differential Thermal Analysis

This method depends on the thermal effects of quartz when heated. It requires special apparatus but not nearly as expensive as X-ray diffraction equipment. The work does not require an especially skilled operator, and the method appears to be a useful and convenient one for samples of between 200 and 300 mgm.

(iv) Fusion Method

A bulk sample is redispersed for fusion at

/1500°C .....

1500°C and the resulting dust is collected on microscope slides by thermal precipitation. Analysis for quartz is then made by counting and sizing the particles that do not fuse (quartz). There are interfering substances, but these can be determined and allowed for. It is limited to particles with a diameter of more than half a micron, as the shape of smaller particles is indistinguishable. It is a fairly tedious method to apply.

(b) Small Samples

These samples are collected by means of thermal precipitation, so consist of strips of dust about 10 mm long and 1.5 mm wide on microscope slides. The volume of air sampled is about 100 cubic centimetres.

(i) Polarisation, Interference or Petrographic Microscope

The principles involved in these microscopic methods of identifying specific minerals in dust samples are well known, but they are all limited to particles with diameters greater than 1 or 2 microns.

(ii) Ordinary Light Microscopy

This method has been referred to above. The microscope slides are first ignited to a temperature of about 500°C in order to eliminate contamination due to moisture and organic matter, and are then acid treated to dissolve away any salts that may be present. After this treatment sections of each dust strip are counted under a medium power microscope and the number of particles per cubic centimetre of the air sampled is calculated. When it is desired to express the result in terms of mass or surface area, the particles are also sized.

/(iii) .....

(iii) Electron Microscope Studies

These require very expensive equipment, careful sampling techniques and a very experienced operator. Electron diffraction techniques can be used to identify quartz, but the results are qualitative rather than quantitative. As the examination of samples is very tedious, the electron microscope can be considered useful for research only.

(iv) Selective Staining of Quartz with a Tagged Compound

This is a new method which it is hoped to develop. The idea is to find a substance that will selectively stain quartz and to treat thermal precipitator samples with a radioactive isotope of that substance. If this turns out to be a compound, it would be possible to tag it. Measurement of the radioactivity level of the treated sample in a gas-flow counter would then give a measure of the projected surface area of the quartz in the sample.

(c) Remarks

An examination of the above possible methods of measuring the toxicity of the dust being breathed in by the miners reveals that there is at the moment no satisfactory method applicable to small samples. Of the bulk sample methods, X-Ray Diffraction techniques and Differential Thermal Analysis appear to offer the most convenient and rapid methods for determining the quartz content of airborne mine dust. The first of these methods has been used in the Research Laboratories of the Transvaal and Orange Free State Chamber of Mines for some years, but it has not been possible to check the results of the analyses carried out by any but the tedious and uncertain chemical methods. It was therefore decided that an attempt should be made to apply the method of Differential Thermal Analysis (hereafter

/referred to .....

referred to as D.T.A.) to the determination of the quartz content of dust samples.

This thesis gives a brief description of the work that has previously been done in this field, of the apparatus that has been developed in this Laboratory, of the calibration and other tests that have been conducted on this apparatus, and finally of the results that have been obtained. All the samples used in these tests were analysed by X-ray diffraction, this method being used as a standard for comparison of the results obtained on the D.T.A. apparatus.

2. PRINCIPLES OF THE D.T.A. METHOD

Differential thermal analyses makes use of the fact that when a substance is heated it may undergo one or more of several physical and chemical changes. These are usually accompanied by the evolution or absorption of heat. Both the temperature at which such a reaction occurs and the amount of heat invclved in the reaction are characteristic of the substance being heated. These heat effects may be caused by [24] (i) absorbed water, (ii) water of hydration, (iii) crystal water, (iv) dissociation of carbonates, (v) dissociation of sulphates, (vi) crystallographic inversions, and (vii) oxidations, and they can be used for both qualitative and quantative identification of minerals in samples.

The term "quartz" is reserved in this thesis for crystalline free silica (S_iO_2). This substance displays a small, but sharp, reversible thermal change associated with the latent heat of inversion of α and β quartz at about 573°C, and it is this change which is used in the D.T.A. method for the estimation of quartz.

The technique employed is this. The dust sample to be analysed and an inert powder (i.e. one that displays no thermal reactions in the range of temperatures in which wc are interested) are packed into two identical sample holders.

/A differential .....

A differential thermocouple (See Fig. 1) is introduced into these holders, which are mounted so as to be located at a fixed point inside an electrical furnace. It is desirable that the temperature distribution inside this furnace should be as uniform as possible. A separate thermocouple is used to record the temperature of the furnace, which is heated up at a suitable rate, usually between 5 and 20 degrees centigrade per minute. The unknown and the reference sample are at the same temperature until some thermal reaction takes place in the former, when its temperature either rises above or falls below that of the inert sample. When the temperature of the unknown sample is above that of the reference sample the change is said to be exothermic, when below endothermic. On heating, the $\alpha \rightarrow \beta$ crystal inversion of quartz gives rise to an endothermic reaction.

This difference in temperature between the dust sample and reference material causes a minute potential to develop across the differential thermocouple, its magnitude depending on the temperature difference obtained. This potential has to be amplified to a suitable level for accurate recording or observation. Many methods have been tried, but the most satisfactory appears to be by means of a stabilized D.C. microvolt amplifier feeding into an electronic recorder. The magnitude of the thermal effect is measured by either the peak height of the deflection from the base line or more commonly by the area under the peak. Calibration tests using samples of known quartz content enable these readings t be related to the percentage of quartz in the test sample.

3. HISTORY OF THE D.T.A. METHOD

(a) General

Thermal [40] as distinct from differential thermal analysis has been used in the investigation of various materials for many years. A thermocouple junction is embedded in the specimen, which is contained in an

/enclosure .....

Fig. I, 1. THE DIFFERENTIAL THERMOCOUPLE



----- Platinum - 10% Rhodium

------- Palladium - 40% Gold

a Test sample

b Inert sample

V_T Differential Potential due to temperature difference T between a and b

enclosure which can be heated or cooled at a constant rate. The specimen temperature is plotted against either time (t) or the inverse rate of temperature change (dt/dT), the latter being the more practical. Any small evolutions or absorptions of heat by the specimen reveal themselves as deviations from the smooth curve that would be obtained were the specimen thermally inactive. Le Chatelier (1887) appears to have been the first to have studied these peaks, the areas of which were proportional to the quantity of heat evolved or absorbed.

The differential thermal technique seems first to have been used by Roberts-Austen in 1899 in conjunction with metallurgical studies. Details of the historical development of the technique from that time will not be given here as they may be found in several text books and reviews devoted to D.T.A.[17, 32, 40, 56]. D.T.A. has been widely used in the study of industrial clays, the firing of clays and ceramics, the analysis of soils and the study of building materials, and has also been applied to metallurgy, geology and mineralogy. As we are concerned with the D.T.A. of quartz, only attempts to apply the method to the determination of this mineral will be considered. Other literature has been studied only in so far as the design of the apparatus and the effect of numerous variations in experimental technique are concerned.

(b) <u>D.T.A. of Quartz</u>

It seems that Fenner (1913) was the first to apply D.T.A. to quartz, but many workers have made brief references to the small sharp thermal peak obtained from the $\alpha \rightleftharpoons \beta$ quartz inversion in conjunction with work on other minerals. Tool and Insley were the next to study the silica minerals by thermal methods in 1938, but the

/first work .....

first work on quartz to be described in any detail was that of Berkelhamer (1) and (2) in 1944. The first of these papers concerns the design and construction of the apparatus that he used, and the second describes his work on the D.T.A. of quartz. In his introduction he states that:

> "Although usually termed 'quartz determination', chemical procedures actually detect the free silica. In studies concerning the silicosis hazards of industrial dusts, this is of little consequence, as all forms of free silica have been found exceedingly toxic."

This conclusion is not justified, since crystalline quartz has been proved considerably more toxic than amorphous silica, and chemical methods do not in general distinguish between these forms of "free silica".

I can also not support his statement that the detection of quartz by X-rays is not adversely affected by small particle size, but will leave discussion of this point until a later chapter. Berkelhamer proceeds to discuss the D.T.A. of quartz, pointing out that after calcination of the test sample at 950°C for 15 minutes, only cryolite with a reversible reaction at 565°C was likely to interfere with quartz results. He also says that a mixture of cryolite and quartz is uncommon in nature.

For evaluating the magnitude of the D.T.A. response, Berkelhamer developed a somewhat artificial construction whereby the area of only about one-third of the α-β quartz peak was measured. He used this technique to show that, within the limits of experimental error, the decrease in D.T.A. response with particle size for minus 100-mesh, 10 to 20, 5 to 10 and 1 to 5 micron (μ) fractions of quartz could be considered negligible. He

/also reports .....

also reports that whereas the first calcination of a test sample affected the response to a small extent (10% increase), subsequent calcination did not.

The most important of Berkelhamer's conclusions is the one that concerns the variation in magnitude of the alpha-beta inversion peaks for different varieties of quartz. He gives the following table:

TABLE I, 1

Peak areas for different varieties of quartz and chalcedony (all minus 100-mesh)

Sample	Sample Weight gm	Peak Area sq. mm	Total Silica per cent
Potter's flint	0.57	240	99.8
Glass sand	0.56	210	99.26
Rock crystal	0.55	172	99.6
Ferruginous sandstone quartz	0.57	163	96.5
Chalcedony	0.54	5	99.0

On examining the results given in this table, I must agree with Grimshaw and Roberts [20] who state on page 273 that:

> "Berkelhamer claimed that different types of quartzite rock showed widely different thermal effects for the same weight of test sample, but he apparently overlooked the probability that the actual content of quartz crystal may have varied widely from one rock to another."

In addition, for sample No. 4 the presence of iron could have caused the fusion of a certain percentage of quartz to silicates during the pre-calcination of the sample, thus lowering the D.T.A. response for quartz crystal. Berkelhamer nevertheless obtains fairly good agreement between the percentage of quartz by D.T.A. and the actual amount present in various prepared mixtures. He concludes that the D.T.A. method for the determination of the quartz content of a

/sample .....

sample is only useful if the apparatus can be calibrated with respect to the particular variety of quartz present, but that under these conditions, as little as 1 per cent quartz could be detected.

Faust [14] (1948) advocated the use of the highly reproducible $\alpha \rightarrow \beta$ quartz inversion temperature as a fixed point for calibrating the temperature thermocouple in D.T.A. apparatus. He found that the temperature at which the inversions started (573.3°C) was identical for specimens of quartz from widely distributed sources. He states that the straight portion of the D.T.A. curve of high quartz is always displaced above that of low quartz, and attributes this to the change in specific heat accompanying the inversion.

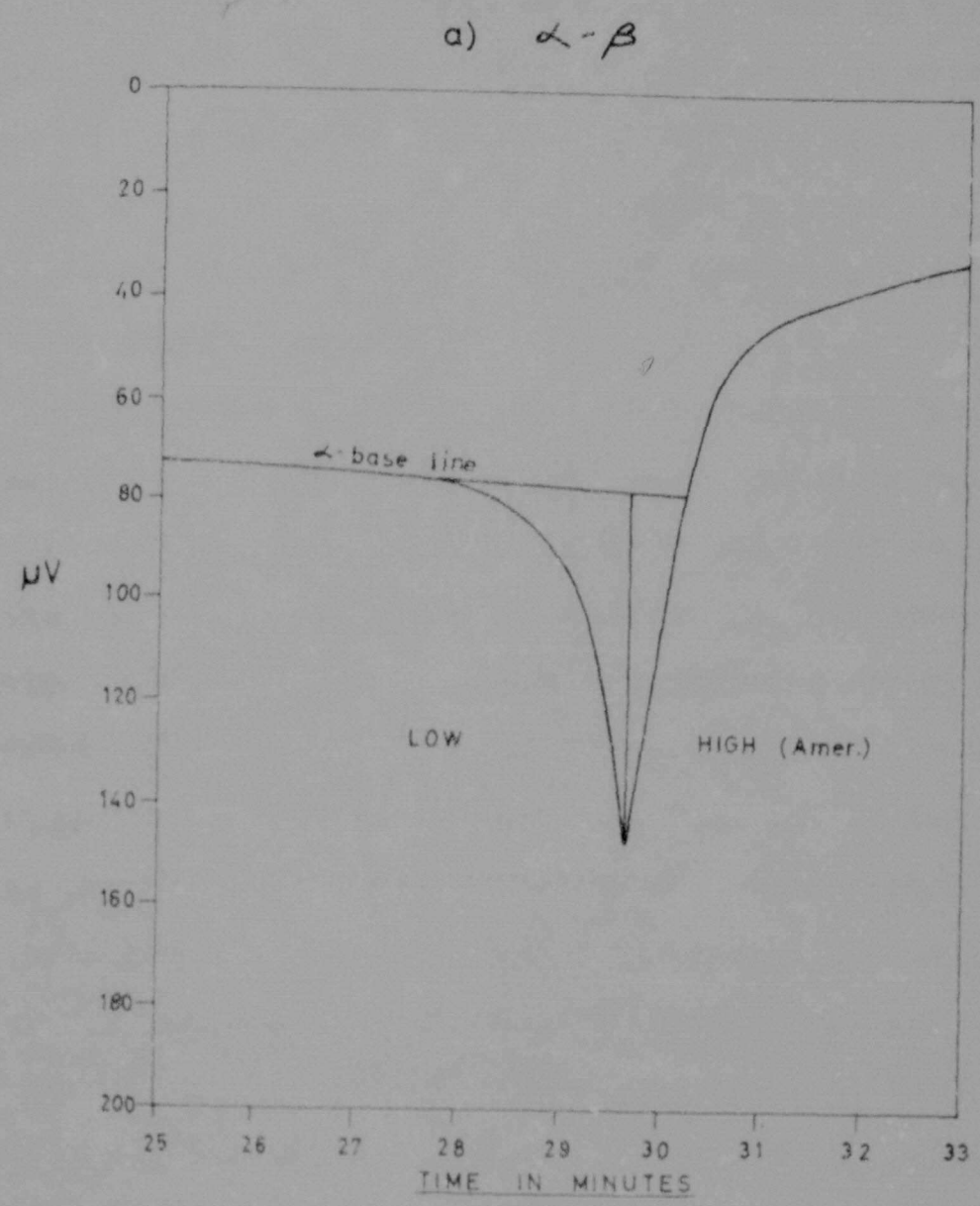
(It should be noted that the American terminology is different from that used elsewhere, α or "high" referring to the form stable above 573°C and β or "low" to that below 573°C. See Mackenzie, p. 275 [32] and Figure 1, 2).

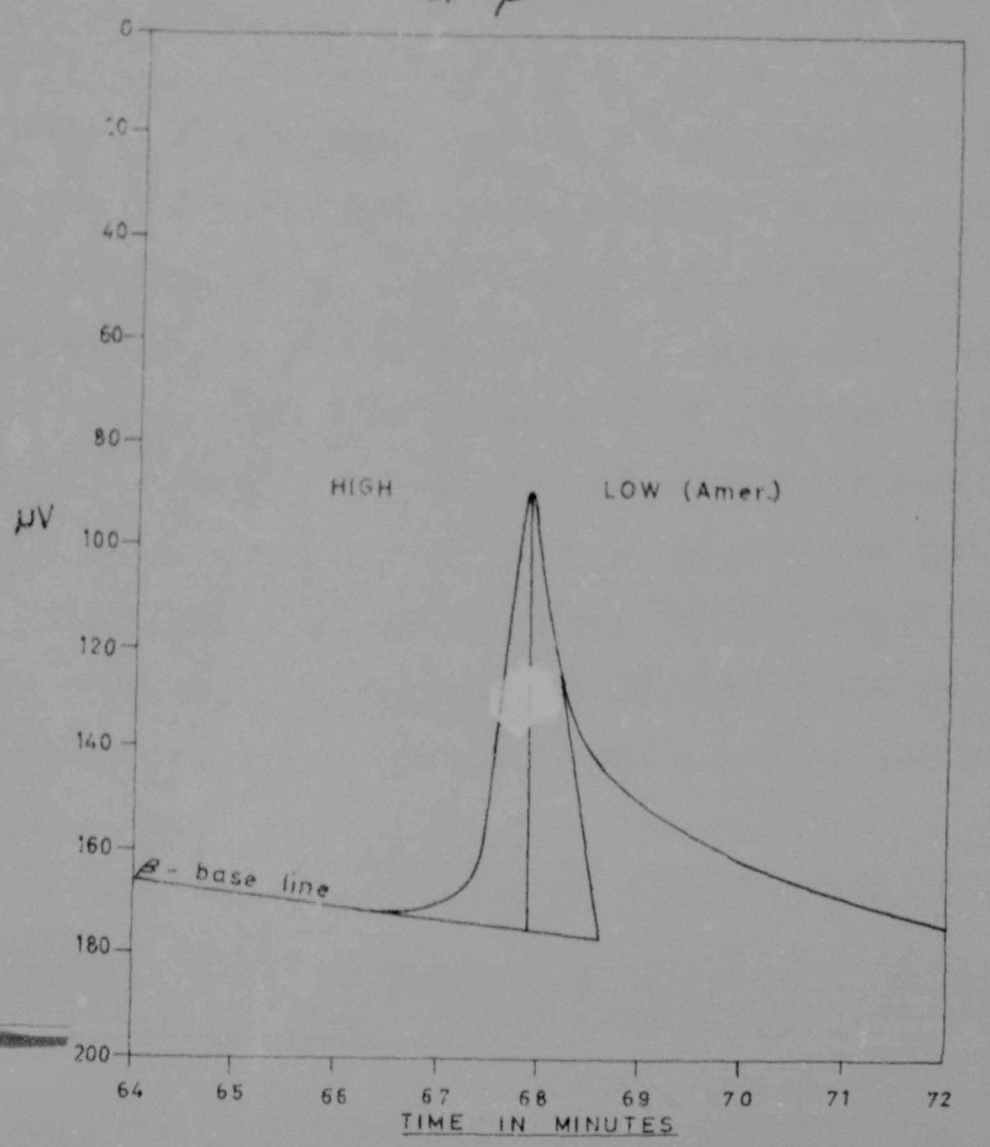
Faust also states that the area under the D.T.A. curve is proportional to the heat effect accompanying the inversion of quartz, but his most interesting comment in so far as the present work is concerned is in connection with the grain size of the quartz samples. He states:

> "Thermal analyses were made on samples of fairly uniform grain size and on heterogeneous mixtures. The maximum size tested was a sample of quartz crystals all of which measured about two millimetres in diameter, and the minimum size was a natural novaculite powder whose grain size was 25 microns and less. The heterogeneous mixtures of grains were prepared by grinding rock crystal to pass a 58-mesh cloth sieve. These samples all produced curves whose shape and character are fundamentally identical. (Page 341)".

/Reference .....

Fig. I, 2 TYPICAL QUARTZ D.T.A. PEAKS





The figures on the horizontal axis represent minutes after switching on furnace. The furnace was switched off 50 minutes later.

Reference to this statement will be made in a later chapter when the results of the present work on sized fractions of quartz are discussed. Suffice it to say here that the smallest fraction investigated by Faust is considerably larger than the largest particles that will reach the human lung.

Another point of interest in this paper by Faust is the weight of various samples of quartz given in Table 1, page 344. These show variations from 491.7 mgm to 752.8 mgm, and are presumably obtained by packing the specimens into identical sample holders by some standardised technique. He unfortunately does not give figures to show how the magnitude of the D.T.A. response varies, but in the light of the present work, this could be very significant.

Grimshaw and Roberts published several useful papers on the D.T.A. of quartz between the years 1946 and 1953 (18) (19) (20) (21) (22) and (44) and these two authors were also responsible for the chapter on "The Silica Minerals" in the book edited by Mackenzie in 1957 (32). This latter chapter is a review of the D.T.A. method as applied to quartz and will be referred to again. The following points of interest arise from the other papers. Firstly, they emphasize the fact that the temperature changes accompanying the thermal reactions in clay minerals are greater than that accompanying the $\alpha \rightarrow \beta$ quartz inversion by a factor of as much as 30. This makes accurate observations on quartz samples much more difficult to achieve, and with their equipment they obtained a deflection sensitivity of 10 cm per degree centigrade temperature difference. This compares rather poorly with the 10 inches per degree centigrade deflection sensitivity attained with the apparatus developed in the present work.

Grimshaw and Roberts discussed the packing of the test sample into the container, and found that the weight of

/different .....

different materials which could be packed into the same sample holder varied from 1.5 gm for pure quartz down to 0.8 gm for pure china-clay. They state that good reproducibility of packing for any one material could be attained with practice. Though they found such differences as did exist between packings to be insignificant they do not say whether or not they made any correction for mass when comparing one sample with another. This is strange, for the mass of material that is packed into a given sample holder assuredly has an effect upon the magnitude of the thermal response. This point will be discussed in greater detail in a later chapter, together with experimental results obtained in this work.

These authors proceed to discuss the continuous base-line drift obtained with their thermal curves and attribute it to the pronounced increase in specific heat of quartz as its temperature increases. This drift could only be eliminated by using as the inert sample a material with identical thermal properties to the test sample, an ideal that cannot be achieved in practice. They arbitrarily chose a base-line parallel to the zero line in much the same way as was initially done in the work to be described in this thesis. They measured the peak height of the response from this base-line and found that this varied fairly regularly with the heating rate. They did not consider their work up to this stage to be very satisfactory, and developed a new technique whereby they determined the D.T.A. response on the cooling cycle. They found the cooling rate to be highly reproducible, the reactions to be much more sharply defined and the drift much less as well as being very nearly constant for all mixtures containing more than 25 per cent of quartz.

Grimshaw and Roberts produced the base-line before the reaction occurred, and measured the peak height as the distance from the apex of the peak to this base-line. They

/found .....

found a linear relationship between this parameter of the D.T.A. response and the percentage quartz in the test sample without making any correction for the mass of the sample. However, where they have given the results of duplicate packings on the same sample, there is a 5% variation in the mass of the test sample and a 6% variation in the inter-packing D.T.A. response, although the two variations do not seem to be related. They suggest that the variation between the results on different samples is due to a change in the position of the thermocouple rather than to differences in the packing density. This argument could not be applied to the inter-packing variations that are shown to exist in the present work. They conclude their first paper [18] (1946) by saying that "the proportion of quartz may be estimated with an absolute accuracy of not less than ± 3 per cent, for mixtures containing 50 per cent of quartz or more ..... approximately ± 10 per cent for mixtures containing 25 per cent of quartz and ± 25 per cent where the proportion of quartz is less than 10 per cent" (Page 43).

In their 1948 paper [20] these same two authors came to the conclusion that the magnitude of the thermal effect was uninfluenced by the environment of the quartz, but that the drift in the thermal analysis curve was dependent on the nature of the diluent. It seems that the first of these two conclusions would only be valid if the "environment" did not consist of a material with a much higher thermal conductivity than quartz, in which case one would expect to obtain a broadening of the peak with a consequent reduction in height. Grimshaw and Roberts obtained fairly good agreement between the percentage of crystalline quartz in samples of quartz rocks from different sources as determined by D.T.A. and the Trostel and Wynne chemical method [11]. (See their Table I on page 273).

/Grim .....

Grim [17] (1950-51) in a review article on D.T.A. states that the upward shift in the base-line after the $\alpha \rightarrow \beta$ quartz inversion is due to a difference in the coefficient of thermal diffusivity. He states that

> "The matter of thermal diffusivity is very significant in the differential thermal method and has not yet been given the critical study that it deserves". (Page 1043).

This is a statement which the results of the present work seem to confirm, for the thermal diffusivity of a sample must change not only with changes of actual thermal properties while heating, but also with differences in the density of packing, differences in particle size distribution of the test sample and differences in contaminants in the test sample.

Unlike the worker so far cited, Grim finds that the magnitude of the D.T.A. response and the temperature at which it occurs both decrease as particle size decreases. He states that it sometimes happens that the degree of crystallinity of a material decreases as particle size decreases, and that this diminishes the intensity of reactions. Grim states that for reactions that begin and end abruptly, such as the $\alpha = \beta$ quartz transition, measurement of an area under the peak is simple, but he fails to describe by what method or how drift in and displacement of the base-line is accounted for.

Merjenberg and van Santen [35] and Nelson [40] also describe the application of D.T.A. to quartz determinations, the latter in quite a useful review article. It should be noted that the first of these two papers is in error in stating:

> "The fact is that quartz undergoes a structural change at approximately 573°C, developing heat in the process. Consequently the temperature of the quartz rises faster than that of the Al_2O_3, which is manifested by a peak in the curve."

/On the .....

Author Craig D K
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