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Determination of the percentage of quartz (SiO2) in samples of mine dust by the method of differential thermal analysis

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On the heating cycle, quartz absorbs heat in changing from the α to the β crystalline form, giving rise to an endothermic, not exothermic, reaction. Their deflection sensitivity of 2 cm per $1^{o}C$ temperature differential seems to be very low indeed on an apparatus specifically designed for quartz determinations. In the light of this they seem to have gone to inordinate lengths in so far as electrical shielding is concerned. None of the precautions they mention has been found to be necessary in the apparatus that has been developed in the present work, even though this is more than twelve times as sensitive.

Nelson, in his review article, discusses in some detail the various anomalous results that have been reported in D.T.A. tests on supposedly pure quartz samples from widely differing sources. Berkelhamer (2) was the first to report these in 1945, but Grimshaw and Roberts (18) & (20) disagreed with his results. Subsequently these anomalies have been discussed, or further ones reported, by Keith and Tuttle (29), Fields (15) and McDowall and Voce (34) (1952), Nagasawa (37), Grimshaw (22) and Lewcock and Wylde (3) (1953), Nelson (40) (1955), Nagelschmidt (39) (1956), Mackenzie (32) (1957) and finally, Smothers and Chiang (56) in 1958. Clelland, Cumming, Dempster and Ritchie, in a series of papers written separately and collectively (8), (9), (10), (11) and (12), discuss the presence of a high-solubility layer on the surface of finely-ground silica, its removal by hydrofluoric acid etching, and its regeneration by purely mechanical grinding. This point is also taken up by Nagelschmidt (38) with respect to X-ray diffraction analyses of finely-ground quartz particles before and after etching.

The work of Clelland and his collaborators will be discussed before the above-mentioned anomalous D.T.A. results for quartz since it may have some bearing on them. These workers demonstrated (8) and (12) the presence of a high-

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solubility layer of amorphous silica on finely-ground quartz particles, and mentioned that caution appeared to be necessary when using D.T.A. methods for percentage quartz determinations. They state that the accuracy of the method appears to fall off markedly as particle-size diminishes, and that this is actually due to the presence of a layer of modified silica not estimated by D.T.A. They state further that the measured quartz content by D.T.A. can be restored to 100% by etching with hydrofluoric acid. They give the following interesting table:

TABLE I, 2

Quartz Content of Finely-Ground Quartz Dusts, Measured by D.T.A. Before and After Etching

Dust	Etching Treatment	Quartz Content by D.T.A. %	
		Before Etching	After Etching
Loch Aline sand dust (about 5-10 microns)	40% HF (5 min)	88	100
Rock-crystal dust (about 2.4 microns)	20% HF (10 min) followed by 40% HF (5 min)	67	100
Loch Aline sand dust (< 1 micron)	10% HF (2 hours)	36	99

It is a pity that these results were not accompanied by a microscopic sizing of the samples before and after etching, and also that no analysis for quartz content by an alternative method was obtained.

In an abstract from a later paper [9], Clelland and Ritchie state:

> "It is shown that the high-solubility layer previously demonstrated on silicious dust-particle surfaces is not a surface layer of hydrated silica; and evidence

/is adduced .....

is adduced that it is a vitreous layer of the Beilby type, formed during the production of the dust by crushing and grinding. An important part of the evidence is the demonstration that prolonged grinding of quartz leads to a reduction in density. This reduction is attributed to partial conversion of dust particles to vitreous silica: no conversion to other crystalline modifications of silica could be detected. Further, when the high-solubility layer has been removed from silicious dust particles by solvents, it can be regenerated by a purely mechanical polishing process. The regenerated layer yields silica into aqueous media very largely in colloidal form".

Nagelschmidt (38) also found that the X-ray diffraction response of very fine quartz particles increased after these were etched with HF. He states (1952) that the toxicity of the amorphous layer still had to be investigated, but it has since been established * that it is considerably less than that of crystalline quartz. Clelland and Ritchie estimated that the mean thickness of this disturbed layer was between 0.11 and 0.15 microns. Their comment that the presence of this layer meant that D.T.A. was unreliable for estimating the quartz content of finely-ground dust scarcely seems justified. Rather does it give confidence that the method measures the actual crystalline quartz content of a sample.

The conclusion drawn from this work, namely that the decrease in D.T.A. response for quartz with decreasing particle size is due to an actual decrease in the crystalline quartz content of the sample rather than to particle size, may or may not be correct. It is quite

/possible .....

* Accepted at Pneumoconiosis Conference, University of the Witwatersrand, February, 1959.

possible that the etching treatment eliminated much of the really fine particles from the samples given in the table, and that the sample subjected to D.T.A. analysis after treatment was actually coarser than that before etching. The same argument could be applied to the work by Nagelschmidt, but this point will be taken up later in this thesis when experimental results are discussed.

We now return to the question of the various anomalous D.T.A. results for quartz that have been obtained by workers in many parts of the world. Keith and Tuttle [29] carried out an exhaustive series of D.T.A. tests on the inversion temperature of some 250 quartz specimens. They found that over 95 per cent of all natural specimens examined inverted on heating within a range of 2.5°C. They found some samples with inversion temperatures nearly 40°C different from the usual inversion temperature of 573°C. Synthetic quartz samples were found to undergo the inversion at temperatures scattered over 160°C, but Keith and Tuttle came to the conclusion that the observed variations were nearly all due to the presence of ions other than Si^{4+} and O^{2-} in solid solution in the quartz.

These authors unfortunately do not give any figures for the actual magnitude of the thermal inversions obtained for these 250 samples, but do state that it was unaffected by particle size within the range - 35 to + 200 - mesh grain size. They state that the inversion temperatures are influenced slightly by variations in hydrostatic pressure, and also by the state of strain of different zones of the same single crystal. They make only a brief reference to the fact that the height and shape of D.T.A. curves of natural quartz specimens are highly variable, but do not in any way relate this to the area under the peaks. Also, their samples were of widely varying grain sizes, and as this undoubtedly affects the thermal conductivity of the

/test sample, ...

test sample, differences in the height and shape of the resultant D.T.A. curves are bound to occur. It is suggested that as long as the quartz dust to be investigated all comes from the same geological source (as appears to be the case with our mine dust samples), there need be little concern over variations in the heat of inversion of different quartz samples tested.

Lewcock and Wylde [30] also report anomalous results, and in a table on page 233 of their paper give D.T.A. results in terms of peak heights for 10 samples that vary from 16 for agate to 150 for "native quartz". They do not report X-ray or chemical analysis results for the same samples, so there is no method of assessing their value. In the discussion on this paper, Shorter says on page 253:

> "Work has been carried out on the thermal analysis of industrial and mine dusts with a view to quartz estimation, but the marked dependence of the thermal effect on particle size, the thermal effect diminishing with increase in surface, rendered the method unpromising."

On the next page (254), Richardson says:

> "We have used the X-ray in the quantitative determination of quartz. We have ground quartz crystals from 1-2 μ to 0.2-0.5 μ in size and have found that the X-ray method gave a lower quartz value for the smaller size, but the results were considered to be better than those determined by the differential thermal analysis method. It is considered that the low value is caused by the formation of the disordered or Beilby layer formed on the surface of the quartz crystals during grinding."

In further discussion on this paper, several workers suggest that on cooling not all the β-quartz may revert

/to α-quartz .....

to α quartz as the temperature passes through the inversion point. Results to be given later in this thesis seem to make this very unlikely (see Chapter III, Table III, H1A). Unfortunately, none of the above workers give figures which can be compared directly with the experimental results of the present work, so no critical analysis of them can be made.

Two sets of workers from New Zealand, McDowall and Vose [34] and Fields [15] discuss anomalous properties of quartz discovered while examining various New Zealand clays. The former paper states that quartz appeared in two forms, the one with a normal α - β inversion at 573°C and the second for which the inversion was more sluggish than usual, occurring between 555 and 560°C. The abnormal form was usually concentrated in the sizes below 75 microns, and it displayed approximately half the normal thermal effect. They do not state how they measured the magnitude of the effect, but say that it gave a "normal" X-ray pattern. Fields described a form of quartz that gave 99.3% free silica by the Trostel and Wynne chemical method of analysis, about 100% by X-ray diffraction analysis, and yet less than 10% quartz by D.T.A. methods, even though the inversion was sharp and occurred at 573°C. He also does not state which parameter of the thermal peak he used to make his determinations. The dust was reported to have particle sizes between 2 and 20 microns.

Nagasawa [37] evaluated the differential thermal curves of twenty-one quartz specimens obtained from various mineral deposits in Japan. He standardized his samples by using particles which passed through a 150 but not through a 300 mesh screen, and employed a heating rate of 5°C a minute (stated to be fluctuating). Nagasawa states that:

/"the area .....

> "the area proportional to the heat of reaction is one enclosed by the curve plotted against the abscissa time, not temperature. When heating rates in runs are not identical, the comparison of the areas must be made on the curves of temperature versus time." (Page 160).

The method by which he completes the area he measures seems to be rather arbitrary, but the important point is that he obtains widely varying results for the different samples tested. His results show differences of from 15 to 45 units on the heating cycle, and from 21 to 57 on the cooling cycle. As Nagasawa did not examine the above samples by chemical or X-ray methods, it is quite possible that there were large variations in pure quartz content from sample to sample, so it is difficult to assess the value of his results.

Grimshaw (22) discusses the results of all the above workers in a paper published in 1953, and in particular the differences in results obtained by chemical, X-ray and D.T.A. methods. He finishes by asking the question:

> "Is the discrepancy between thermal analysis and X-ray measurements due to a quartz without an $\alpha \rightleftharpoons \beta$ transformation, or to a non-quartz mineral with a similar line structure to α-quartz?"

He is the first worker to cast any doubt on the validity of X-ray analysis results, and it is the present author's opinion that this aspect of the problem merits much closer investigation than it has received in the past.

Nagelschmidt (39) conducted a series of inter-laboratory trials on the determination of quartz in dusts of respirable size, using several chemical methods, X-ray diffraction and differential thermal analysis. The best reproducibility was obtained amongst the chemical methods, but after making allowance for the variability of the

/standards .....

standards used in the various laboratories, found that X-ray analysis gave nearly as good results as the best chemical method. D.T.A. results showed a wide scatter. He states that individual laboratories produced better results by various methods, including D.T.A.

Grimshaw and Roberts summarize the present position of D.T.A. as an analytical tool in quartz investigations very well in their chapter on "The Silica Minerals" in the book edited by Mackenzie (32). They give additional information to show that:

> "the gap between values as determined by X-ray and differential thermal methods has narrowed considerably during the last few years, and it seems likely that further improvements to both techniques will bring them into still closer agreement in the near future. It can at least be concluded that the value of differential thermal analysis for quartz determination is now real and no longer merely potential." (Page 287).

They emphasize the need for the strictest possible standardization of technique for quantitative analysis.

One further table given by Grimshaw and Roberts on page 285 of this book, and taken from the work of Dempster and Ritchie will be given here in the light of its possible future importance relative to the present work.

/TABLE I, 3 .....

TABLE I, 3

Results obtained by X-ray and Differential Thermal Methods for Quartz content of sized samples

Sample	Particle size (e.s.d.) μ	Quartz Content		S_iO_2 content by HF evaporation %
		X-ray %	D.T.A. %	
1. Untreated	10	100	100	99.6
2. Untreated Etched with HF	5-10	91 91	88 100	99.6
3. Untreated Etched with HF	2	78 100	67 100	99.9
4. Untreated Etched with HF	0.5-1.0	73 94	55 76	97.0
5. Untreated	< 1.0	39	39	93.0

It is unfortunate that these authors do not state whether or not the samples were sized again after etching with HF. However, this table will be discussed later in conjunction with experimental results obtained in the present work.

Smothers and Chiang (56) refer to most of the work that is mentioned above in their chapter on quantitative D.T.A., but their discussion is not critical. Among other things, they give on page 119 figures that show that the area under the quartz inversion peak does not remain constant with changes in the heating rate, but increases from 7 to 36 units as the heating rate increases from 6 to 21°C per minute. This seems to contradict the results of certain other workers, but although the increase is much larger, it does agree with experimental results that will be given later in this thesis.

4. SCOPE OF THE WORK TO BE DESCRIBED

Initially, the purpose of the present work was to develop a D.T.A. apparatus in order to have an alternative method to the X-ray diffraction equipment for assessing the

/percentage .....

percentage of quartz present in samples of airborne mine dust. A study of the literature relating to absolute quartz determinations has revealed a very real need for a critical investigation of such determinations. It has also shown that much of the work that has been published has given only very inadequate descriptions of the techniques used for making quartz assessments. Much of the reported work is contradictory, and some factors that seem to the present author to be fundamentally important in quantitative D.T.A. appear to have been completely disregarded by most workers.

The scope of the present work has therefore broadened to the extent that the author wishes to investigate all outstanding problems relating to the experimental determination of the <u>crystalline quartz</u> content of dust samples by the D.T.A. method. This is obviously impossible in a limited time, but as much as has been possible has been done, and indications will be given as to where further work should be tackled and as to how it can be done.

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

CHAPTER II

DESIGN AND CONSTRUCTION OF D.T.A. APPARATUS FOR THE ESTIMATION OF QUARTZ IN DUST SAMPLES

1. REQUIREMENTS OF THE PROJECT

As the D. T. A. method is to be applied specifically to the determination of the quartz content of samples of airborne mine dust, the requirements of the apparatus are somewhat different from those of one designed for more general work. In the first place, we need concern ourselves only with the temperature range from 500 to 650 degrees centigrade about the quartz inversion peak at 573°C; secondly, we have to work with a heat reaction of the order of 3 calories per gram of active material, giving rise under the most favourable conditions to a maximum temperature difference between the test and inert samples of about 3°C in contrast to differences of up to 80°C for the thermal reactions of substances like calcium hydroxide; thirdly, whereas most workers have had unlimited quantities of the test sample with which to work, samples for the present work are collected by electrostatic precipitation from the air, so a sample of mass 1 gram takes four times as long to collect as one of 250 mgm.

The specific requirements of the D. T. A. apparatus for this project are therefore as follows:-

(a) The rate of temperature change in the range from 500 to 650°C should be highly reproducible on both the heating and the cooling cycles. There is no necessity for it to be perfectly linear, although this would in certain instances be advantageous.

(b) The equipment must be sensitive enough in order to be able to measure five per cent of quartz in a sample. In other words, it must be able to measure

/differences .....

differences of temperature between the two sample holders of 0.15°C under the most favourable conditions.

(c) The sample holders must be designed to admit samples of the order of 300 mgm., say. This condition is naturally linked with condition (b), as a small sample will give rise to a smaller thermal reaction than a large one. Most previous workers have used sample weights of from 500 mgm. to 1.5 gm.

In addition to the above specific requirements there are the more general ones that the equipment should be reasonably robust and easy to operate, and that it should give a thermal response that is both highly reproducible and easy to assess. Before describing the apparatus that has been developed in this Laboratory, a review will be given of design criteria and of some of the D. T. A. equipment that has been described in the literature.

2. DESIGN OF FEATURES OF OTHER APPARATUS DESCRIBED IN THE LITERATURE

Mackenzie [32] states that there must be over a thousand D. T. A. apparatuses in current use, and as nearly all of them have been individually constructed, it is probable that no two are identical. It is obvious that the design of a particular apparatus is largely influenced by the application for which it is intended, and also by the individual preferences of the designer. Only the more common types of equipment will be discussed here.

The apparatus usually consists of four parts, the furnace, the sample and thermocouple holder, a heating programme controller and the differential temperature recorder. As many different systems and methods have been

/employed .....

employed by various workers, each of these four items will be examined in turn.

(a) Furnace

Webb[52] appears to be the only worker who has made a systematic survey and study of furnaces suitable for use in D.T.A. equipment, although Mackenzie and Mitchell[32] and Smothers and Chiang[56] in their respective books do include brief reviews of various systems that have been used.

A furnace usually consists of a ceramic tube of internal diameter about 50 mm. and length anything up to 400 mm. This may be either externally or internally wound with electrical resistance wire, the most common materials used for this purpose being nichrome, kanthal and platinum. The furnace core is surrounded by a metal container with a diamter of from 10 to 12 inches (250 to 300 mm.), the core being positioned by asbestos cement end-pieces. The space between the core and the container is filled with an insulating material such as vermiculite. This whole set-up may be either horizontally or vertically mounted. Both methods have been extensively employed. From the literature one does not appear to have any particular advantage over the other, although Mackenzie[32] claims that vertical mounting gives a larger zone of uniform temperature within the furnace.

Horizontally mounted furnaces have been used by Berkelhamer[1] Grim[17] Gruver[23] Nagasawa[37] and Pask and Warner[42], while vertical systems have been preferred by Boersma[4], Kerr and Kulp[26], Kracek[28] Merjenberg and van Santen[35] and Webb[50][52], to

/mention .....

mention only a few. Nichrome has generally been found to be a satisfactory heating element up to 1000°C, Kanthal to 1300°C and platinum for still higher temperatures. Internal winding of the heating element has been preferred by some workers as this gives rise to a smaller temperature lag between the furnace and the sample holder. It has the disadvantage that it increases electrical shielding problems, and many workers have found it necessary to introduce earthed metal shields between the furnace windings and the sample holder in order to eliminate A.C. pickup by the differential thermocouple. Longitudinal heating elements (globars) have also been used to overcome this problem. Many workers have made provision for controlling the atmosphere of their furnaces during D.T.A. runs, but this is of no consequence for the present work.

Webb[52] indicates that the requirements for a D.T.A. furnace are as follows:-

(i) "The characteristics of the furnace should be such that a uniform and reproducible rate of heating of up to 20°C per minute is attainable over the temperature range 25 - 1100°C.

(ii) The furnace should have a zone of uniform temperature sufficiently large to ensure that there are no excessive temperature gradients in the vicinity of the specimen holder and the furnace design should permit reasonably accurate and reproducible positioning of the specimen holder at the centre of the uniformly hot zone.

(iii) The design should permit the nature and pressure of the furnace atmosphere to be controlled." (Pages 31 and 32).

/He .....

He conducted a detailed series of tests to evaluate the performance of the furnaces designed. His experiments revealed that it is unnecessary to construct too elaborate a furnace as good results can be obtained with a fairly simple one.

(b) Sample and Thermocouple Holder

(i) Sample Holders

This aspect of D.T.A. instrumentation is quite the most important in determining the amplitude, shape and reproducibility of the thermograms obtained and has been extensively examined by various workers[32], [36], [42], [51], [52] and [56].

Webb[52] has made a very detailed study of the relative performance of the various types of holders, and this work should be studied if further details are required. He appears to be the only worker who has attempted a comparative examination of the curves yielded by different sample holders under more or less identical experimental conditions. Others[32], [56] have merely compared the results obtained by workers using the different types of holders in their own equipment. Only a few general remarks will be made here, together with a brief review of the literature in this connection.

Webb[52] states that D.T.A. sample holders can be divided into four categories, namely metal blocks, metal crucibles, ceramic blocks and special types. Metal blocks have been widely favoured, nickel being the metal most often employed, though steel, platinum and other materials have been chosen for special applications. Examples of

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this type of holder have been described by Boerama[4], Faust[14], Grim[17], Grimshaw and Roberts[19], Gruver[23], Kerr and Kulp[26], Keith and Tuttle[29], Merjenberg and van Santen[35], Nagasawa[37], Pask and Warner[42], van der Marel[49] and Webb[50], (51) and (52). Metal crucibles, usually of platinum, have been used by Gruver[23] and Kracek[28], and ceramic blocks by Grimshaw and Roberts[21] and Pask and Warner[42], who used one constructed of graphite for some special tests. Sintered alumina is most often used for this type of block. The special types of holders that have been used need not concern us here, and only those of Herold and Planje[25], whose sample holders themselves formed this differential thermocouple, and Boersma[4], who had his thermocouple junctions in cavities below the actual sample holders, merit consideration. Boersma claims that:-

> "The peak area then is solely dependent on the produced heat of reaction and on the calibration factor of the instrument which no longer contains any sample properties (e.g. volume and conductivity)"

However, it appears as if this method, and that of Herold and Planje, is likely to lead to a considerable loss of sensitivity, which could be important when small reactions such as the quartz inversion are being studied.

An annoying feature is that very few workers give actual dimensions of the sample wells, although they do state whether their thermocouples were introduced from above, the side or below.

/Kerr ...

Kerr and Kulp[26] used wells $\frac{1}{4}$ inch in diameter and $\frac{3}{8}$" deep. Pask and Warner[42] used wells of 3/16 inch diameter, with the depth tapering from $\frac{1}{2}$ inch at the sides to 9/16 inch at the centre. These authors investigated variations in response with varying hole diameters and of ratios of bulk block volume to the volume of samples. They found that the latter has only minor effects on the response, but that for a given heating rate, the size of the reaction peaks increase with an increase in the well size. They also state that for maximum resolution, the size of the sample should be reduced. Webb[52] investigated the effect of varying well diameters and depths in considerable detail, and his conclusions are of interest. He found that reproducibility and sensitivity improve with increasing well diameter, though resolving power decreases. Since all properties of a peak are most affected for small diameters, he recommends a diameter of at least 5 mm. In a personal communication with the author, Dr. Webb indicated that a ratio of 2 to 3 for well diameter to depth had been found to be suitable for most work.

In his tests, Webb[52] evaluated the relative performance of nickel blocks, alumina ceramic blocks, twin platinum crucibles and twin platinum crucibles in alumina. He found the peak area responses to be in the ratio 11.4 : 14.7 : 19.6 : 13.1 and the percentage deviation from the mean value for several determinations to be 1.2, 2.0, 3.7 and 7.8 respectively. In view of the very much greater reproducibility obtained from a nickel block sample holder, in addition to its ease of

/construction ...

construction as compared with other types, he decided to use this type in all his further work, despite the greater sensitivity attainable with platinum crucibles. An important point in relation to the above work is that, whereas the differential thermocouple entered through the bases of the wells in the case of the nickel block, for the platinum crucibles the junctions were introduced from above. Slight differences in the positioning of these junctions could perhaps have accounted for the threefold increase in the scatter of results as compared with those for the nickel block.

The following general considerations seem to be of importance in designing D.T.A. sample holders:-

(i) A material must be chosen which will not react with any of the constituents of the samples to be tested[32];

(ii) The size of the wells should be a compromise between the desire for a large heat effect from a large holder and a small temperature gradient through the sample for a small holder[42];

(iii) The sample should have a low thermal capacity in order that as large a temperature difference as possible should be developed between the test and the inert samples;

(iv) There should not be a large thermal gradient between the sample and the furnace otherwise temperature control becomes difficult;

/(v) ...

(v) The results obtained should be highly reproducible otherwise the method is useless for any but qualitative work;

(vi) The design should be such that the thermocouple junctions can be accurately positioned in the samples.

The above criteria are seen to be in some measure conflicting, those sample holders that yield the greatest sensitivity not necessarily giving the best reproducibility or the easiest temperature control. This conclusion is supported by Webb's results quoted above, and the system chosen for any particular apparatus will depend on the application.

(ii) Differential Thermocouples:

Mackenzie summarises the requirements of thermocouples for use in D.T.A. and also gives a review of the types that have been used. Smothers and Chiang[56] and Murphy[36] also discuss the same thing, and it will be only briefly referred to here.

Materials used may be divided into two classes, base metal and noble metal couples. The former, of which chromelalumel[1] and copper-constantan are the most common, give a much larger potential per unit temperature difference than the latter, are cheap, readily constructed and replaced, but are much more readily corroded and have a considerably shorter life. Noble metal couples yield a much smaller e.m.f., but have a much longer life and must be used for temperatures above 1,000°C.

/Platinum ...

Platinum versus platinum - 13% rhodium is the most commonly used material, but others such as gold-palladium versus platinum-rhodium[28] have been used for special applications.

Apart from the materials used and the positioning of the couples in the sample wells, the only other variables are the size of the thermocouple junction (bead) and the diameter of the wire. There seems to be some disagreement about the influence of the former on the D.T.A. response. Berkelhamer[1] reports that the bead size affects the slope of the base-line, while Webb[52] could detect no influence on either the base-line or on reproducibility for bead sizes ranging from 0.4 to 1.2 mm. in diameter. Smothers and Chiang[56] state that it should be as small as practicable in order to reduce the thermal capacity of the thermocouple. Webb also found no significant difference in thermograms obtained with difference in the bead size in the test and inert samples. Murphy[36] found that large beads gave more "significant" thermograms.

In so far as the thickness of thermocouple wires are concerned, Smothers and Chiang[56] report that one worker (Arens, whose work was not available to the present author) found no great difference in response using wires of diameters 0.2 and 0.5 mm. This is in direct conflict with the views of most other workers who have studied the problem. Large wires have a high thermal conductivity, and Boersma[4] has calculated that heat loss through the termocouple wires can reduce the

/peak .....

peak area of a D.T.A. response to less than 50% of its theoretical value. Sewell (personal communication via Dr. Webb) arrived at more or less similar conclusions, and recommends that if noble metal couples are used they should not be thicker than 0.32 mm. Webb[52] made a detailed study of the effect of wire diameters of 0.1, 0.2, 0.3 and 0.5 mm. diameter, and found that the thicker wire gave a peak area of approximately 30% less than the 0.1 mm. wire. Accompanying this reduction in response was a significant improvement in the reproducibility of results.

From the foregoing results it seems that in choosing the thickness of thermocouple wire a compromise must be sought between the desire for mechanical strength and reproducible results and for a low heat loss along the wires. Mechanical strength is important since most workers have found that positioning of the differential thermocouple junction in the test sample is very important from the point of view of reproducibility. The junctions should be centrally or at least axially, located in both the test and the inert samples.

(iii) Temperature Measuring Thermocouples:

This is not an aspect of D.T.A. instrumentation to which much attention has been paid in the present work, mainly because we are concerned solely with the magnitude of the quartz inversion response, known to occur at or very near to 573°C[29]. Mackenzie[32] states that:-

> "inaccuracy of temperature measurement is very seldom a source of error" (Page 39).

/He ...

Author Craig D K
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