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SINGLE THERMOCOUPLE DIFFERENTIAL THERMAL ANALYSIS WITH APPLICATION TO QUANTITATIVE LOW LEVEL DETECTION OF FREE CRYSTALLINE QUARTZ

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ABSTRACT

A new method of differential thermal analysis involving a digital multimeter has been developed and applied to the quantitative detection of free crystalline quartz at low concentration levels. In this method the ultimate reference material, the sample itself, is used and only one thermocouple is required. The method is made differential by computer analysis of the resulting temperature–time curve. In this manner DTA curves free of many drift effects normally associated with conventional DTA are obtained.

With this method the detectability limit for quartz has been lowered from the generally accepted value of about 1% to less than 0.25%. The relationship between silica level and peak area was found to fit a quadratic function with an error of about 0.2% SiO_2. The method could have important application in the general field of conventional DTA.

INTRODUCTION

Since its inception by Roberts-Austen[1], the method of differential thermal analysis has always been characterized by a two-thermocouple system. With the instrumentation generally available, this method was more sensitive to minute temperature changes in the sample than the single thermocouple method of thermal analysis introduced earlier by Le Chatelier[2]. Because of inherent differences in heat capacity, heat leakage, density and thermal conductivity between the sample and reference material, considerable baseline drift can occur in DTA causing major interpretation problems particularly when quantitative results are required. Although this difficulty can be minimized by using small samples, the capability of the instrument in detecting low level transitions is thereby diminished.

In this paper a new variant of differential thermal analysis is presented where the ultimate reference material, the sample itself, is used. The actual experimental

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procedure is thus simplified greatly, being reduced in effect to single thermocouple thermal analysis. The method is made differential by computer analysis of the resulting temperature–time curve. In this analysis the cooling curve is determined from all data points except those in the region of the thermal effect which are omitted. Then the deviation of all data points (thermal effect included) from the predicted baseline when plotted against sample temperature yields the desired DTA curve free of many drift effects normally encountered with the conventional (two-thermocouple) method.

This method has been applied to the quantitative detection of small amounts of free crystalline quartz in alumina based on the heat effect associated with the α–β transition of quartz. Because of the industrial and medical significance of quartz, methods involving chemical[3-6], X-ray[7, 8], DTA[9-11], infrared spectroscopy[12, 13], microscopic[14], or a combination of these[15-22], have been reported for the analysis of free quartz. In previous DTA work[11, 19], the limit of detection of free quartz was set at about 1%. By adding up to 10% quartz, Rowse and Jepson[22] have determined free quartz in clay minerals with a standard error of 0.2–0.3% quartz using DTA. The purpose of this paper is to introduce a new DTA method and to apply it to the quantitative detection of free crystalline quartz.

EXPERIMENTAL

Materials

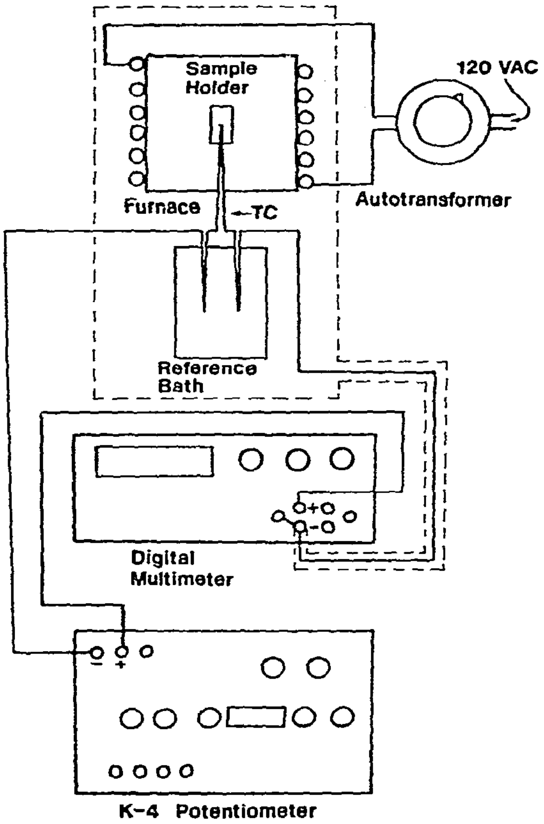
The samples were prepared from 99.9% pure Al_2O_3 with particle range 1/3 to 1/2 μm (Alcoa designation XA-139) and 99.89% pure SiO_2 (Grade 398 SILCOSIL, Ottawa Silica Company with 99.2% passing 325 mesh). These materials were weighed to within 0.1 mg in the correct proportions (weight percent basis) to yield 0.3 g samples. Each sample was dry mixed thoroughly before using.

Apparatus

The apparatus consisted of a Dana Series 5800 digital multimeter, a Leeds and Northrup Type K-4 potentiometer, a sample holder, reference bath and a well insulated resistance furnace controlled manually by an autotransformer. The apparatus is shown schematically in Fig. 1.

The range of the multimeter was extended to 27 mV using a 16 mV bucking potential from the potentiometer. The meter resolution was 0.1 μV and the reading rate was 4 sec^{-1}. The sample holder was constructed of a machinable glass ceramic (Corning Macor) into which a platinum liner 0.0254 mm thick was inserted. A chromel–alumel thermocouple constructed from 0.254 mm diameter wires was used and the arrangement of sample holder with thermocouple is shown in Fig. 2.

The thermocouple reference junctions were made by twist connections with solid, untinned copper wire (Belden). The reference junctions were located in separate 6 mm ID glass tubes which had been sealed at one end and filled to a height of about 40 mm with vacuum oil. The glass tubes were in turn placed into a well lagged bath



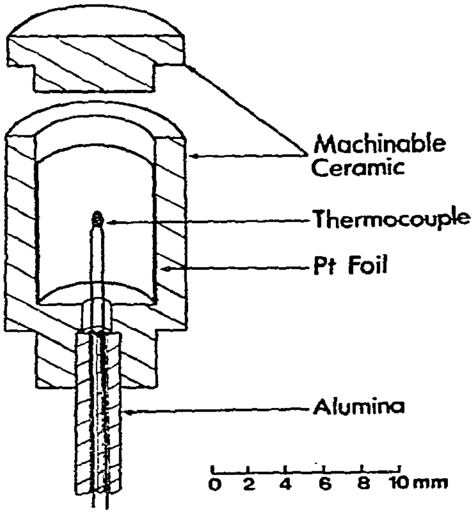


Fig. 1. Schematic diagram of single thermocouple DTA apparatus.

Fig. 2. Sample holder and thermocouple arrangement.

consisting of a 70 mm diameter, 305 mm high Dewar flask filled with distilled water and further insulated with a 100 mm thickness of styrofoam chips. The bath operated at room temperature and required no maintenance. During the course of an experiment (with room temperature at 25 ± 1 °C), the temperature drift of the bath was about 0.003 °C as monitored by a calorimetric, mercury-in-glass thermometer. The resolution of the temperature measuring system was 0.0025 °C and all measurements were made using guarded circuitry.

Procedure

The entire sample of 0.3 g was lightly packed into the sample holder. The sample was heated to about 660 °C, held for 1 h and allowed to cool at about 5 °C min^{-1} in air at 1 atm (static) with furnace power off. All data between 627 and 533 °C were obtained via a video taping system yielding about 5000 readings. The data were reduced to every eighth measurement. A value representing a 10 sec interval was then obtained by averaging five of these measurements taken consecutively. The values were subsequently used as data points in the analysis of the cooling curves.

RESULTS AND DISCUSSION

Baseline regression

Cooling curves were obtained for 0.3 g samples ranging from 0.1 to 4.0% SiO_2 using the experimental conditions described previously. Differential thermal data were obtained by the removal of a section of the cooling curve containing readings detectably influenced by the quartz inversion, in order to obtain a reference curve. The reference, which can be interpreted as the ideal cooling of the sample if no inversion took place, could then be expressed as a simple mathematical relationship between the thermocouple output and time. Cooling curve data for 11 runs were obtained from 25 to 21 mV (627 to 533 °C). The removal of data from 23.3 to 22.3 mV (587 to 564 °C), about 24 data points, was found to be near optimum for reducing scatter in the calibration curve obtained for the entire experiment. This point is considered further in the discussion of peak area. The DTA curves were then obtained by subtracting the reference curve values from the actual data for the entire data set. Typical curves are shown in Fig. 3. The peak maximum was at 576 °C (573 °C is the generally accepted α–β transition temperature). The baseline is indicated by dashed line segments.

Several mathematical forms were used for the reference regression, including polynomials from degree 2 to 8 and several exponential functions. A cubic equation of the form $mV = A + Bt + Ct^2 + Dt^3$, where t is time, gave good results. The coefficients obtained for each run are shown in Table 1. Higher order polynomials

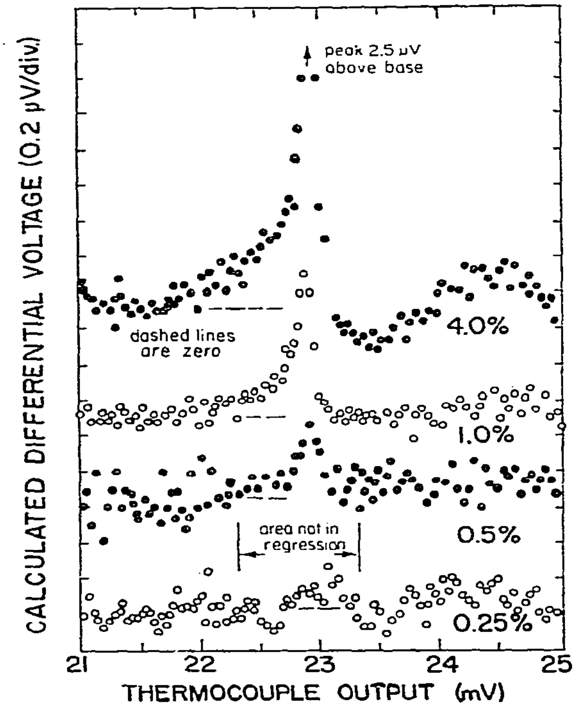


Fig. 3. Examples of single thermocouple DTA for various quartz levels.

TABLE 1

REGRESSION DATA FOR REFERENCE CURVES $mV = A + Bt + Ct^2 + Dt^3$

Run	*% SiO_2 added*	*A*	*B*	*C*	*D*	*Standard error*[a] *(μV)*	*Scatter*[b] *(μV)*
1	4.0	24.9861	−0.03565	4.24×10^{-5}	-3.81×10^{-8}	0.09	0.06
2	4.0	24.9860	−0.03548	4.13×10^{-5}	-3.72×10^{-8}	0.10	0.05
3	2.0	24.9863	−0.03510	4.14×10^{-5}	-3.67×10^{-8}	0.11	0.08
4	2.0	24.9863	−0.03544	4.09×10^{-5}	-3.59×10^{-8}	0.10	0.09
5	1.0	24.9858	−0.03525	4.20×10^{-5}	-3.85×10^{-8}	0.10	0.05
6	1.0	24.9856	−0.03453	3.96×10^{-5}	-3.53×10^{-8}	0.11	0.09
7	0.5	24.9864	−0.03516	4.05×10^{-5}	-3.48×10^{-8}	0.12	0.11
8	0.5	24.9859	−0.03456	3.90×10^{-5}	-3.35×10^{-8}	0.10	0.08
9	0.25	24.9863	−0.03447	3.92×10^{-5}	-3.49×10^{-8}	0.10	0.09
10	0.25	24.9869	−0.03481	3.97×10^{-5}	-3.48×10^{-8}	0.10	0.08
11	0.1	24.9859	−0.03527	4.07×10^{-5}	-3.71×10^{-8}	0.11	0.11

[a] $[(mV - mV\text{ predicted})^2/\text{number of data points} - 1]^{1/2}$.

[b] Standard error for short section of baseline.

and simple exponential functions did not significantly improve the fit for all runs. The scatter in the baseline measured from a short section of cooling curve (about 25 data points, compared with about 90 for the entire curve) was compared with the standard deviation of the regression to evaluate both the regression and the noise inherent in this particular experimental design. The standard deviation of the cubic fits varied from 0.08 to 0.12 μV (see Table 1). In some cases, (runs 2 and 5, Table 1), the scatter of the baseline was as low as 0.05 μV. The regression error could be reduced to that level by using a seventh order polynomial, but the coefficients thus obtained were not consistent with each other, and the application of such a large increase in complexity for modelling did little for the other runs. Apparently some external conditions not under control were influencing the exact form of the cooling curve, producing "rolls" in the baseline (see 4% curve, Fig. 3). This type of baseline "drift" could be artificially eliminated using higher order functions, but the lack of reproducibility in the present experiment did not warrant it.

Several runs (7, 11) were exceptionally noisy with scatter > 0.1 μV. An example of a noisy region is shown in Fig. 3 in the 0.5% curve at low mV levels. Noise of this level could tend to obscure peaks at the lowest silica levels, and the general problem of the variation in scatter could be troublesome for further efforts to lower the detection limit.

Peak area

The peak area was calculated by simple summation of the differences between the regressed reference curve and the data points, including the peak area data. The peak area obtained in this way was somewhat dependent on the particular data

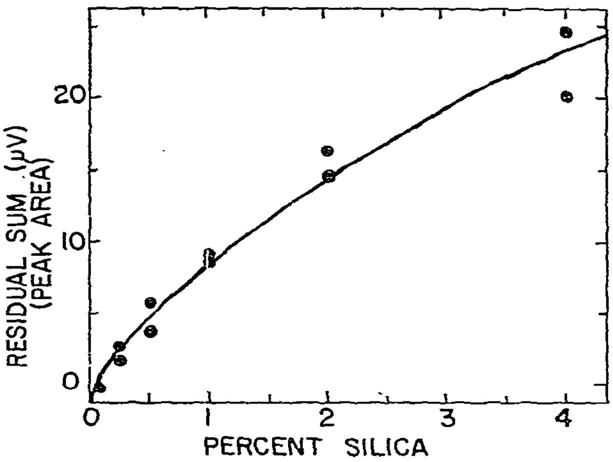


Fig. 4. Peak area calibration curve.

removed to find the reference curve, but the effect was only serious if the area removed was not made broad enough. This was primarily a function of the appearance of the "shoulder" on the low temperature side of the peak (see Fig. 3). In general, the computed area began to decrease if the peak width, centered about 23 mV (580°C), was made smaller than about 0.75 mV (18°C). The computed peak area also was observed to change slightly if the peak area was made too wide. In this case "rolls" in the baseline were included in the computation of area. Although peak area is influenced by sample thermal conductivity, this effect is believed to be small under the conditions of these experiments.

The selection of the "best" peak area removal was accomplished by means of a least squares fit of a quadratic equation for the percent silica as a function of peak area. In each regression, the peak area center and the area width were specified for all the levels of silica. The center and area width were varied to establish the best method of peak removal for determination of the reference curve. Except for narrow peak area width, or in cases where the peak area was larger than half the data span, the error in the calibration curve did not vary appreciably. It was also found that the use of higher order polynomials did not significantly affect the overall error. The best fit is shown in Fig. 4.

The use of peak height rather than peak area as the dependent variable showed about the same relative degree of scatter. It is hoped, however, that the use of peak area would have advantages for comparisons of materials with different peak shapes. The peak shape for different quartz minerals is not the same, though the energy of transformation should be reasonably constant.

GENERAL CONCLUSIONS

The method of digital thermal analysis, combined with the use of a regression of the cooling curve with the peak area removed to obtain the reference curve, has been shown to be capable of a sensitivity for quantitative DTA in this system greater than previously reported. The detectability limit for SiO_2 has been lowered from about 1 %[11, 19] to better than 0.25 % in a relatively unrefined system.

A host of experimental parameters were not optimized (or even varied) including sample and furnace arrangement, number of data points and choice of electronic components. Full automation of the data acquisition system will allow rapid investigation of such parameters.

The level of silica as a function of peak area was found to fit a quadratic equation with an error of about 0.2% SiO_2. The largest errors were at high (2–4%) SiO_2 levels. Although this was not substantially better than using peak heights, the peak area method can eventually be extended to a range of different quartz materials with various peak shapes. The effect of the type of matrix material on the peak area and shape of the reference curve would have to be evaluated. The inclusion of more impure form of quartz with broader peaks would require larger peak area removal and more data points for reference calculation.

With additional improvements in electronic instrumentation (at least one digital voltmeter now on the market is capable of 0.01 μV resolution at 140 mV) and refinement of other experimental techniques, the detectability limit should be considerably lowered. It is not unreasonable to suppose that conventional DTA can be done by this method if noise induced by heating elements can be suppressed and control functions can be made smooth. This method, as applied to the general field of conventional DTA, could have considerable importance.

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