THE DIFFERENTIAL THERMAL ANALYZER AS A MICRO-CALORIMETER*

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ABSTRACT

Calorimetric measurements of very small magnitude are made possible by a sensitive method of differential thermal analysis. The increased sensitivity of the technique is due to the use of a low-mass radiation-type furnace operated in a vacuum, and at high heating rates. Calibration of the instrument was accomplished by employing the well-known reaction of calcite dissociation as a standard.

INTRODUCTION

The technique of differential thermal analysis has been largely confined to the investigation of qualitative thermal characteristics of various mineral species. In particular, the clay minerals have been widely studied, and thermal analyses for these minerals are familiar to mineralogists, ceramists, and soil scientists.

Hitherto, the differential thermal analyzer has not been developed into a precise calorimetric tool. This paper describes a successful calibration of a differential thermal analyzer, so that it is able not only to detect, but also to measure heat changes as small as ten millicalories in magnitude. This device might well be termed a micro-calorimeter, and, as such, should be of interest to all physical scientists.

APPARATUS

The apparatus used in this investigation was essentially the same as that described by Whitehead and Breger.[1] The controller and recorder were unchanged, but the mass of the entire furnace housing was reduced so that its design is that shown in Fig. 1. As a result of these changes, the furnace was brought under closer temperature control, especially at high heating rates, and thermal changes, as recorded by the thermographic curves, became highly magnified.

THEORY OF METHOD

Cohn,[2] Macgee,[3] and Shorter[4] have described calibrations of differential thermal analyzers for use on ceramic bodies. All of these calibrations,

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* An investigation as part of a Ph.D. thesis by the author.

[1] Whitehead, W. L., and Breger, I. A., Vacuum differential thermal analysis: *Sci.*, **111**, 279–281 (1950).

[2] Cohn, W. H., The problem of heat economy in the ceramic industry: *J. Am. Cer. Soc.*, **7**, 475–488 (1924).

[3] Macgee, A. E., The heat required to fire ceramic bodies: *J. Am. Cer. Soc.*, **9**, 206–247 (1926).

[4] Shorter, A. J., The measurement of heat required in firing clays: *Trans. Brit. Cer. Soc.*, **47**, 1–22 (1948).

however, are on a macro scale, and entail a comparatively long and cumbersome procedure.

The method of calibration described here is simple. Briefly, it involved heating carefully weighed samples of a known reactive substance at a constant rate, through its reaction temperature range, and then relating the energy changes with the corresponding responses (areas) recorded by the thermographic curves.

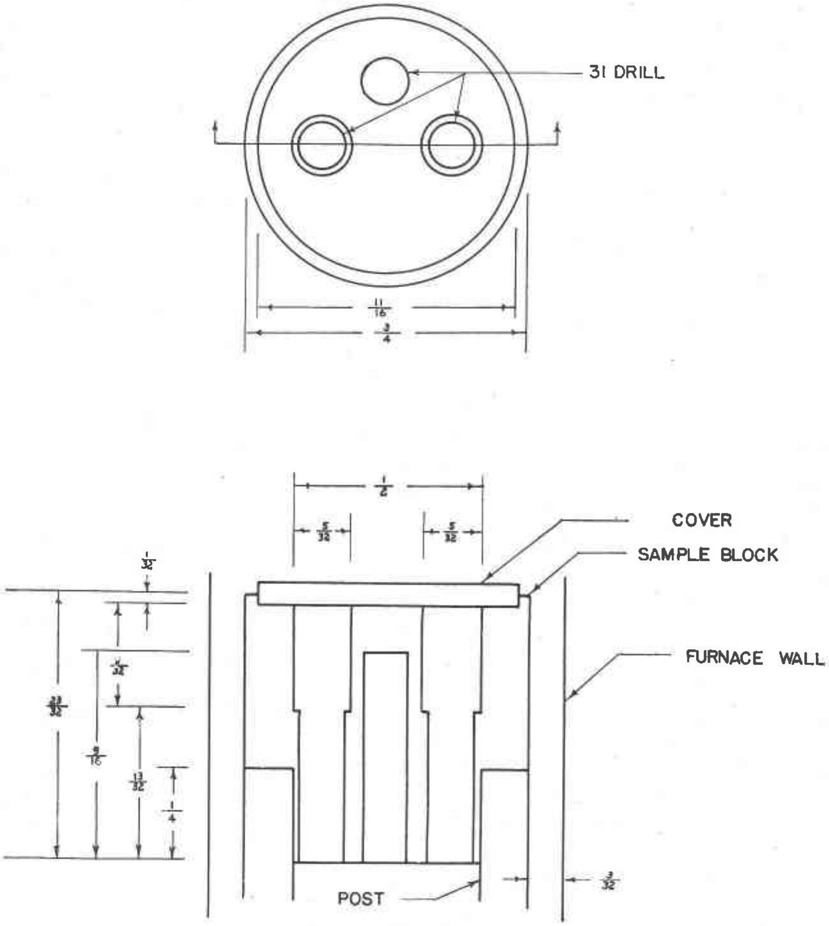

Fig. 1

The theoretical basis upon which this calibration was developed, was formulated by Speil[5] and is briefly reviewed here with the aid of Fig. 2,

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[5] Speil, S., Applications of thermal analysis to clays and aluminous materials: *U. S. Dept. of Int.—Bur. of Mines,* **R.I. 3764** (1944).

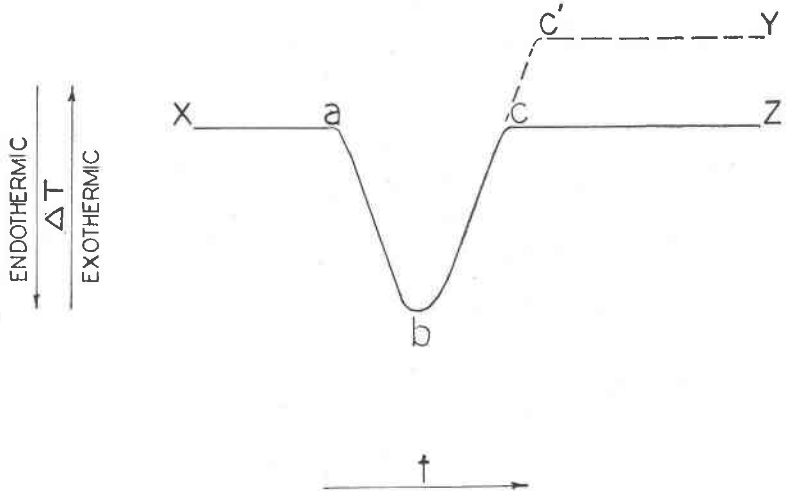

FIG. 2

a sample thermographic curve showing a reaction beginning at point *a*, and continuing towards point *c*.

$$\text{(Area) } abc \propto \int_a^c \Delta T dt = \frac{M(\Delta H)}{gk} \tag{1}$$

where,

M = mass of the reacting specimen
ΔH = specific heat of reaction
g = geometrical shape constant
k = thermal conductivity of the reacting specimen.

Equation (1) neglects the temperature gradient in the sample as well as some insignificant differential terms, and therefore is a close approximation. Transposing terms we get

$$\text{(Area) } abc \propto gk \int_a^c \Delta T dt = M\Delta H = Q \tag{2}$$

or,

$$\text{(Area) } abc \propto Q \tag{3}$$

where

$$Q = \text{heat of reaction.}$$

As an approximation, then, the area is a linear function of the heat of reaction as expressed by equation (3).

CALIBRATION

The reactive substance chosen for the calibration was $CaCO_3$ (calcite) which follows the reaction

$$CaCO_3+Q \rightarrow CaO+CO_2 \uparrow$$

beginning at a temperature of about 630° C. when heated statically. The values[6] for Q in the above reaction are very large and permitted samples smaller than the thermocouple head to be used. Later, the significance of these minute samples will be shown.

The dissociation of the $CaCO_3$ samples at a heating rate of 30° C per minute in an evacuated furnace produced the thermographic curves shown in Fig. 3, and the relation between the area and the heat of reaction, as described above, gave the linear plot of the same figure. The validity of equation (3) is demonstrated by the experimental evidence displayed by the linear plot. Table 1 is a summation of the experimental and calculated data of the calibration.

TABLE 1

Reactive Sample			Thermographic Response (Area in Sq. In.)
Sample	Weight (milligrams)	Heat of Reaction (millicals.)	
A	0.30	123	0.294
B	0.40	165	0.363
C	1.00	410	0.900
D	1.50	614	1.385
E	2.10	853	1.910
F	2.50	1015	2.283
G	3.00	1215	2.721

Measurements of areas were made with a planimeter and checked by means of a simple grid. The measurement of the areas, however, was the crux of the entire calibration since the area is not always clearly defined. In Fig. 2 the thermographic base-line X-Z is not linear in the general case. It is obvious that when a large sample is tested in the differential thermal analyzer, a major reaction is usually accompanied by a sharp change in the thermal conductivity and the specific heat capacity of the specimen. This results in a thermal gradient between the differential thermocouples that gives rise to a non-linear base-line. In Fig. 2 point *c* is often displaced towards *c'*, and the curve continues toward Y. In addition, slow heating rates (12° C. per minute) decrease the slope of *ab*

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[6] Smyth, F. H., and Adams, L. H., The system, calcium oxide-carbon dioxide: *Jour. Am. Chem. Soc.*, **45,** 1167–1184 (1923).

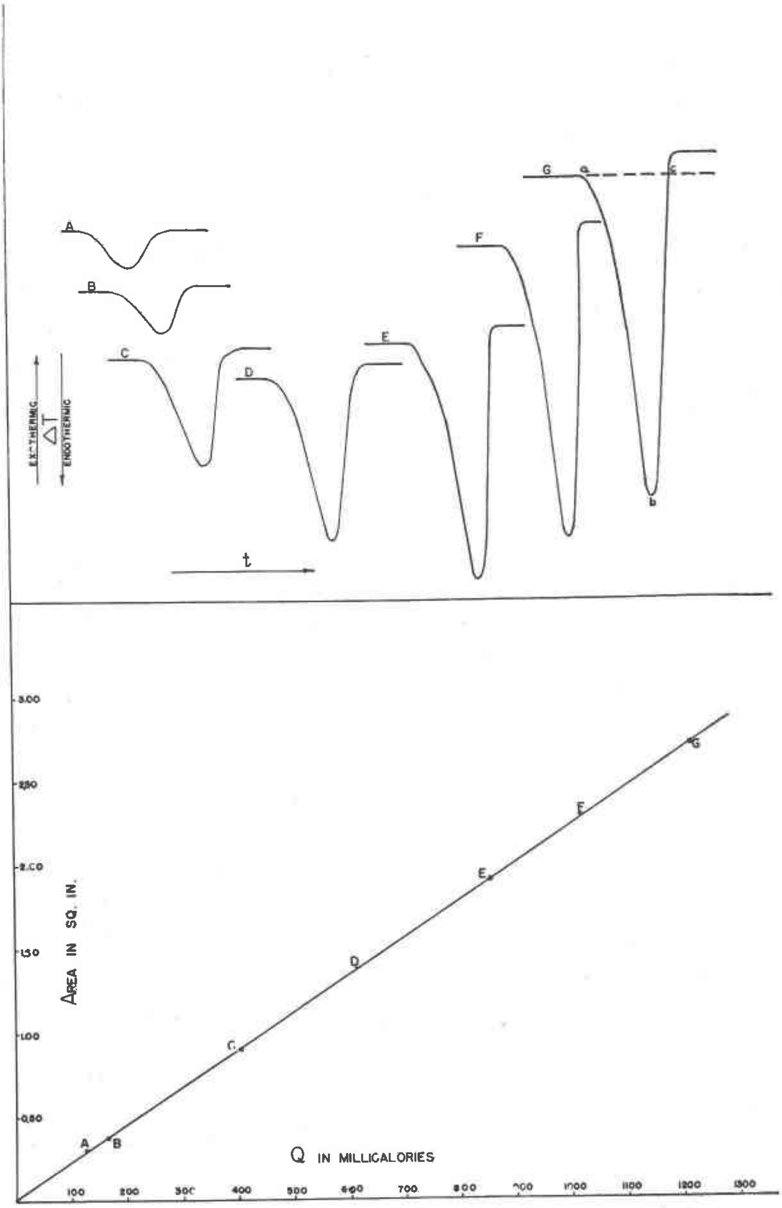
A
B
C
D
E
F
G
a
b
c
EXOTHERMIC
ΔT
ENDOTHERMIC
t
3.00
2.50
2.00
1.50
1.00
0.50
AREA IN SQ. IN.
A
B
C
D
E
F
G
Q IN MILLICALORIES
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300

FIG. 3

so that point *a* becomes unidentifiable. The work of Norton[7] and that of Berkelhammer[8] emphasize this fact clearly.

The difficulties of the non-linear base-line are largely obviated by reducing the mass of the furnace housing, employing high heating rates, (30° C. per minute), and testing small samples with large ΔH. The reacpoint *a*, Fig. 2, is sharply defined as the slope *ab* steepens, and the base-line deviation is reduced to a small magnitude. The method of area measurement adopted overcame this slight deviation as shown in Fig. 3, curve *G*. The base-line is merely extended from point *a*, the reaction origin, to point *c*, where the reaction is completed for all intents and purposes. The area measured is that enclosed by *abc*.

A standard procedure of analysis was established for this investigation and strictly adhered to. The use of uniform thermocouples, precise centering within the furnace wall, careful particle sizing, and uniform packing of samples are the important rules to be followed.

DISCUSSION

The results of this experiment justify the belief that a low-mass radiation-type furnace can render important service in investigations of this nature. The sensitivity of the instrument described was found to be 30 to 100 times that of instruments described in the recent literature,[5,7,8,9,10] and it should be mentioned that no amplification was needed to achieve these magnified thermographic curves.

The apparatus described here is an excellent tool in the range 300° C–1100° C. Below 300° C it cannot be used as a quantitative instrument because the mass of the furnace housing is too large to permit sensitive response and control at temperatures this low, especially at high heating rates which have been shown to be desirable in the higher temperature ranges. It is suggested that further diminution of the furnace housing to one having lower inertia may make calorimetric studies over a wider temperature range possible. The possible applications of such a quantitative calorimetric tool are numerous.

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[7] Norton, F. H., Critical study of the differential thermal method for the identification of the clay minerals: *J. Am. Cer. Soc.*, **22**, 54–63 (1939).

[8] Berkelhammer, L. H., Differential thermal analysis of quartz: *U. S. Dept. of Int.—Bur. of Mines*, **R. I. 3763** (1944).

[9] Faust, G. T., Thermal analysis studies on carbonates, I. Aragonite and calcite: *Am. Mineral.*, **35**, 207–224 (1950).

[10] Beck, C. W., An amplifier for differential thermal analysis: *Am. Mineral.*, **35**, 508–524 (1950).

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