A NEW METHOD OF DIFFERENTIAL THERMAL ANALYSIS EMPLOYING MULTIPLE THERMOCOUPLES

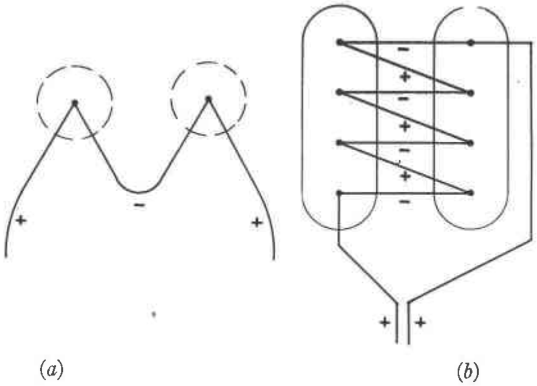
WILLIAM LODDING AND EDWARD STURM, *Bureau of Mineral Research, Rutgers University, New Brunswick, N.J.*

ABSTRACT

A method is described which permits the investigation of thermal reactions too small in magnitude to be detected by ordinary methods of Differential Thermal Analysis. The *e.m.f.* generated by thermal reactions can be multiplied by placing a number of thermocouples in series. Peak amplitudes in thermograms are increased by a factor directly related to the number of differential couples employed.

INTRODUCTION

Differential Thermal Analysis is employed in the analysis and study of minerals which upon heating undergo endothermic or exothermic reactions at characteristic temperatures. In this technique, a differential thermocouple is used (see Fig. 1*a*). One junction is inserted into the test material, while the other junction is placed in a substance which is thermally inert within a given temperature range. The inert and sample materials are heated simultaneously at a constant rate. Endothermic or exothermic reactions taking place in the sample material produce a temperature difference between sample and inert substance, causing an *e.m.f.* in the differential thermocouple. By means of a recorder, these temperature differences can be plotted against the temperature. Endothermic and exothermic reactions register as deviations from the base line.



(*a*) (*b*)

FIG. 1. Schematic diagrams of a dual differential thermocouple (*a*) and a multiple differential thermocouple (*b*).

Reactions accompanied by the liberation or absorption of energy, such as decomposition, loss of structural or absorbed water, or phase changes, are recorded as peaks above or below the base line. In order to detect thermal reactions of small magnitude, a *D-C* voltage amplifier is frequently placed in series between the differential thermocouple and the recorder (Kerr, *et al.*, 1949).

Electronic amplification of the weak signal generated by a differential thermocouple has been carried to a practical limit (Rowland, 1955). A full-scale sensitivity range of 50 microvolts has been used by some workers. However, because unavoidable noise is amplified along with the signal generated by the heat of the reaction, investigators rarely attempt to work in high sensitivity ranges.

The method described here results in an increase of the primary *e.m.f.* generated by the temperature difference accompanying the diagnostic chemical reactions. This is achieved by employing several thermocouples connected in series (see Fig. 1*b*). The total *e.m.f.* generated by the multiple thermocouple is directly related to the number of differential thermocouples used.

Multiplication of the original *e.m.f.* within the first stage of the system, rather than amplification in the second stage is proposed here. The stronger signal thus obtained can then be amplified by means of a *D-C* voltage amplifier. The advantage of increasing the primary (frequently small) *e.m.f.* over amplifying a weak signal lies in the reduction of the influence of noise and drift. An amplifier increases the *e.m.f.* due to the latter as well as the signal.

METHOD

The *e.m.f.* developed by a single differential thermocouple can be multiplied a number of times by employing several series-connected thermocouples (Fig. 1*b*). The amplitude of the peaks recorded is directly related to the number of couples making up the assembly. Fig. 3 (*a*) shows a thermogram of quartz obtained with a single couple. Fig. 3 (*b*) shows a thermogram of the same sample of quartz tested with a multiple thermocouple of four units. The peak amplitude of the latter is four times larger than the former. A greater factor of multiplication of peak amplitude may be obtained by using a multiple thermocouple consisting of more units. The principle of multiple thermocouples has been used in calorimetry (Roth and Becker, 1935), in radiation thermopiles (Gier and Boelter, 1941) and others.

One of the difficulties encountered in the standard dual-differential thermocouple assembly is the necessity of accurately centering the couple terminals and equalizing the sizes of the beads. This has to be done in

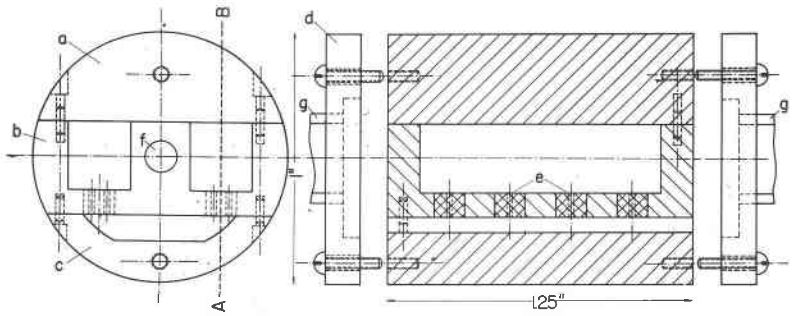


FIG. 2. Specimen-holder for a four-unit multiple differential thermocouple. The line *A-B* refers to the cross-section shown on the right.

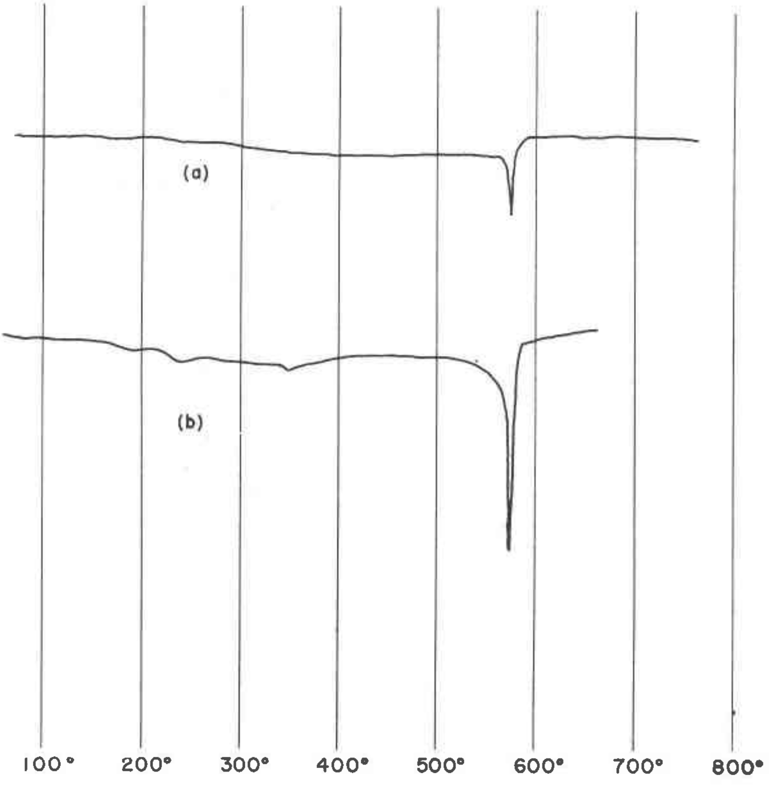


FIG. 3. Thermograms of quartz, (*a*) with conventional unit, (*b*) with multiple differential thermocouple.

order to obtain a straight base line. In the multiple couple assembly, centering of terminals and equalizing of bead sizes is not as critical. Asymmetrical tendencies caused by differences in bead sizes or unequal positioning of the terminals have the tendency to cancel each other out when several units are employed. Further, the larger size of the sample (the cavities hold 1 mm. of sample each or about 1.3 grams) tends to minimize the effects of non-homogeneity and stratification in the sample proper.

The increase in peak amplitude resulting from the increased *e.m.f.* causes the peak slopes to be steeper and thus facilitates the determination of the temperature of reaction. Quantitative work, involving the measurement of areas under peaks (Bramao, *et al.*, 1952), is also facilitated because of the greater ease of determining areas under large peaks.

It is believed that multiplication of the primary *e.m.f.*, as proposed here, will permit investigation of thermal reactions which, because of the difficulties mentioned above, could not be measured heretofore. If the four-unit multiple thermocouple shown in Fig. 1*b* is used in conjunction with a *D-C* voltage amplifier, the full range of sensitivity of 50 microvolts could be extended to 12.5 microvolts. Because, as mentioned above, drift of the base line and unwanted signals due to asymmetry of the dual-thermocouple are almost eliminated in a multiple assembly, the increased *e.m.f.* fed into the amplifier is due to the signal generated by the thermal reaction.

APPARATUS

Figure 2 shows a specimen holder which was designed for use with a four-unit multiple thermocouple. The holder consists of five parts machined from scale-resistant stainless steel.

The central segment (*b*) contains the wells for the sample and the inert substance. The hole (*f*) in the center of the segment (*b*) serves as cavity for the single thermocouple which controls the furnace temperature recorder. Four holes in the bottom of the wells serve to hold short pieces of two-hole porcelain insulator tubes (*e*). The latter support the individual thermocouples. The thermocouples were welded after the wires had been inserted in the insulator tubes. Segment (*c*) is hollowed out to permit space for the wires leading to and connecting the thermocouple terminals. The space also permits the adjustment of the terminals by manipulating the wires leading to them. Segment (*a*) serves as cover to the wells and completes the circular cross-section of the assembled specimen-holder. Small, tapered pins help to align the three segments. The disk-shaped end-plates (*d*) which are of the same diameter as the specimen-holder, complete the assembly. Two quarter-inch diameter tubes (*g*) support and position the specimen-holder in the furnace. The tubes contain two-hole porcelain insulators for the lead wires of the thermocouples. One of the stainless steel tubes can also be connected to a gas supply line if an analysis is to be made in controlled atmosphere (Stone, 1951). The tube on the opposite end then serves as an exit tube for the gas.

REFERENCES

BRAMAO, L., CADY, J. G., HENDRICKS, S. B., AND SWERDLOW, M. (1952), Criteria for the characterization of kaolinite, halloysite, and a related mineral in clays and soils: *Soil Sc.*, **73,** 273–287.

GIER, J. T., AND BOELTER, L. M. K. (1941), The silver-constantan plated thermopile: *Temperature* (*Am. Inst. Phys.*) 1284–1292.

KERR, P. F., KULP, J. L. AND HAMILTON, P. K. (1949), Differential thermal analysis of reference clay mineral specimens: *API Proj.* **49,** *Prelim. Rep. 3,* Columbia University.

ROTH, W. A., AND BECKER G. (1935), *Zeits. physik. Chem.*, **174,** 104–114.

ROWLAND, R. A. (1955), Differential thermal analysis of clays and carbonates: *Bull.* **169,** *Div. of Mines, Cal.* (*Proc. First Nat. Conf. on Clays and Clay Technology*).

STONE, R. L. (1951), Differential thermal analysis of clay minerals under controlled thermodynamic conditions. *Bull.* **146,** *Eng. Exp. Sta., Ohio State University.*

Manuscript received May 19, 1956.