IMPROVED DIFFERENTIAL THERMAL ANALYSIS APPARATUS

J. Laurence Kulp and Paul F. Kerr,
Columbia University, New York, N. Y.

Abstract

A modification of the multiple type differential thermal analysis apparatus permits automatic pen or dot recording with a sensitivity equal to that of the galvanometer-photographic recording methods. The increased sensitivity is accomplished through the use of a stable d.c. preamplifier. With a dual furnace assembly virtually continuous operation alternating between multiple and single recording may be accomplished.

Although a wide variety of apparatus has been employed in applied differential thermal analysis, there are fundamentally four essential parts common to all experimental arrangements: (1) specimen holder, (2) furnace, (3) rate-of-heating controller, and (4) differential thermocouple recorder.

Specimen holders are ordinarily made either of pure nickel or of stainless steel. The latter material has slightly less thermal conductivity than nickel but has proved more durable. Since the rate of heat flow in stainless steel is about a hundred times that of most minerals, the slight increase in thermal conductivity obtainable by employing nickel is not sufficient to compensate for the use of less stable material. The sample holder, itself is designed with the container holes for powdered minerals spaced symmetrically relative to the axis of the furnace.

The furnaces are ordinarily of the electric resistance type, either commercial or home wound and may be mounted either horizontally or vertically. It is believed the latter is preferable since vertical mounting allows closer geometrical control, greater facility in centering the specimen holder in the furnace after placing the furnace around the holder, and also mechanical rigidity.

The rate of heating has been controlled in a number of ways. The applied voltage may be changed manually or automatically by means of a *variac* or by more precise program controllers.

The differential thermocouple voltage may be recorded by manual observation, galvanometer-photographic recording or by the use of an electronic amplifier coupled with a pen or dot recorder. About two years ago a multiple differential thermal analysis unit was developed which included an automatic program control of the heating rate combined with a 6-point electronic recorder (Kerr and Kulp, 1948). Since the description of this apparatus, a number of improvements have been made which make possible not only the original multiple feature, but high sensitivity for a single sample as well. The most significant development has been the installation of a d.c. preamplifier which gives a dot record curve comparable in sensitivity and stability with the best galvanometer-photographic recording devices. The sensitivity with the new arrangement is adequate for a wide variety of mineralogical studies.

At present the apparatus consists of the controlling and recording assembly plus two furnaces each with a sample holder. One unit uses a single sample and records through the d.c. preamplifier to the Speedomax recorder with high sensitivity. The second unit employs a multiple sample holder (six holes) and records with moderate sensitivity directly via the Speedomax. The furnaces are run alternately, one heating while the other cools. In a normal day it is feasible to obtain thermal curves for three samples with high sensitivity and eighteen samples at moderate sensitivity. Since the time required for cooling and loading about equals the time required for an analysis, the program controller and recorder may be kept essentially in constant operation. The specific improvements will be discussed below.

Specimen Holder Block

In recent developments both an improved multiple sample holder and a single sample holder have been constructed. The plan view of an

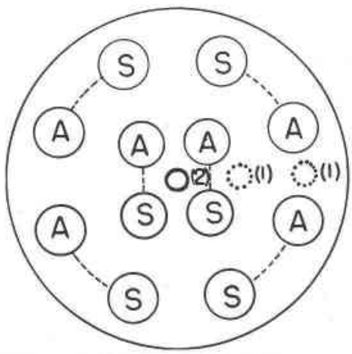

Fig. 1. Modified stainless steel holder for multiple differential thermal unit.

improved holder of (18-8) stainless steel for multiple differential thermal analysis is shown in Fig. 1 (drawn to $\frac{1}{2}$ scale). "*A*" refers to the recess for the inert alundum while "*S*" refers to the recess for the specimen. The holes for an "*A*"-"*S*" pair are centered symmetrically parallel to a vertical axis with identical radii. The dashed lines indicate the connecting differential thermocouple. The holder is drilled from a $1\frac{3}{4}''$ cylindrical stainless steel block and is $1''$ thick. The sample and alundum recesses are $\frac{1}{8}''$ in diameter and $\frac{1}{2}''$ deep. This arrangement makes it possible for the thermocouple head to be above or below the center of the sample by as much as $\frac{1}{8}''$ without appreciably changing the heat flow to the head, since the heat flow is primarily determined by the closest distance from the head to the stainless steel wall. Furthermore, this simplifies centering the thermocouple head in the hoizontal plane so that it coincides with the central vertical axis of the hole. Thus, the geometrical arrangement is essentially reproducible and the baselines of the thermal curves show few irregularities due to thermal gradients and the sensitivity of a particular thermocouple head becomes quite constant over a series of runs.

The multiple specimen holder is held in place by a stainless steel collar attached to a vertical alundum tube. The latter is V-clamped to a universal vice which fits a track on the table. This assembly facilitates the centering of the specimen holder block after the furnace has been lowered to surround the block and supporting alundum tube. A $\frac{1}{4}''$ thick disk with the same diameter as the sample block supported on $\frac{1}{8}''$ long pins is placed over the sample holes as a shield against direct furnace radiation.

The small holes indicate the positions of the temperature recording thermocouples (1) and the temperature controlling thermocouple (2). The former is placed in the block at the same height and on the same radius as the thermocouple head within the sample. The temperature controlling thermocouple is brought through both the block and the lid into the open space of the furnace directly exposed to the furnace coils. This arrangement has been found to give a highly linear heating rate.

Although it has not been constructed, it is believed that a multiple specimen holder for twelve specimens is feasible, if such a number of samples of a routine nature may be required for a particular problem. In such a case the description would be essentially the same as above except that a furnace of larger diameter would be required. The recording and controlling equipment now available should be adequate for a twelve-sample apparatus.

In the case of high sensitivity, still more precise symmetrical location of the sample in the block is required. Figure 2 shows plans and elevations drawn to $\frac{1}{2}$ scale of the specimen holder used. The top section of the block *I* is $1\frac{3}{4}''$ diameter and the sample holder $\frac{3}{8}''$ diameter. The symbols have the same meaning as in Fig. 1. The block is also supported in the manner described above and has a comparable lid.

In order to provide long life and to allow precise spot welding, Pt-Pt10%Rh thermocouples B.S.×22 are used. The desired placement of the thermocouple head at the center of the sample and the alundum is obtained by accurately spot welding a measured length of Pt10%Rh wire to two long pieces of pure Pt wire. The centering in the vertical direction is fixed as the block is machined in such a way that the thick-

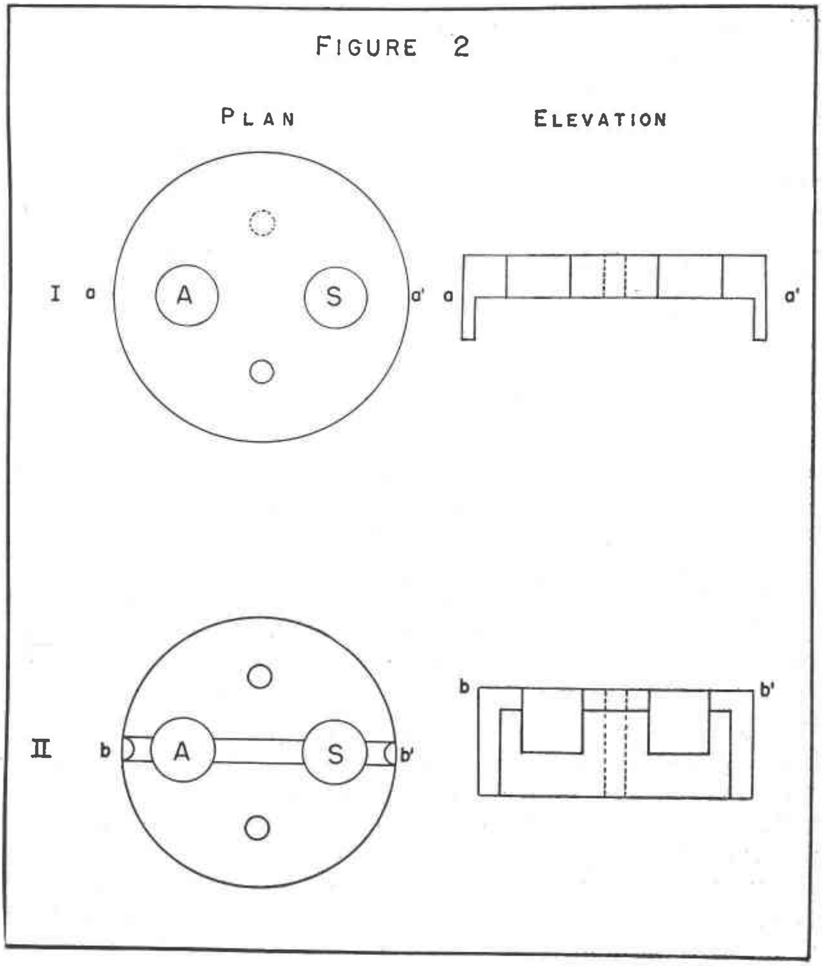

FIG. 2. Stainless steel holder for single differential unit of high sensitivity.

ness of sample above and below the trough in which the thermocouples lies is the same. The slightly larger sample hole radius compared with the multiple unit has been found desirable for this application.

FURNACE

No essential change has been made in the furnace except to remove the alundum tube which prevents direct radiation from the resistance coils to the specimen holder. This change permits more effective control of the heating rate and eliminates drag at the top of the heating range. Although the coils are relatively thick ($\frac{1}{8}''$ diameter) and although they are separated by about $\frac{1}{2}''$ this does not cause any noticeable gradient in the sample block.

PROGRAM CONTROLLER

The Leeds and Northrup Micromax Program Controller described in the earlier paper has required no major modification. Heating rate control begins at room temperature and although there is an initial lag in the sample temperature, by the time a temperature of 100° C. is reached in the sample, the heating rate becomes essentially linear at $12\frac{1}{2}$ degrees per minute. The heating rate indicator which the actual thermocouple temperature should follow has been arranged to move continuously at a uniform rate of $12\frac{1}{2}$ degrees per minute in contrast to the previous method of intermittent movement which only *averaged* $12\frac{1}{2}$ degrees per minute.

RECORDER

The six samples in the multiple unit are recorded on the six point Speedomax mentioned in the previous paper. This Speedomax is being converted at the present time to a sixteen point recorder of the same speed (2.5 seconds between points) and range (full scale 3.0 millivolts) which will have twelve of the sixteen points on the differential couples and the other four on absolute temperature. This will make it possible to run twelve samples at one time with moderate sensitivity and in addition will offer the great advantage of having the actual temperature printed on the same sheet with the differential curves. Further, if desirable, up to four different temperatures of the samples from different portions of the block may be printed simultaneously.

The high sensitivity differential thermocouple (Pt-Pt10%Rh) is connected by a screw junction to a shielded cable which leads directly into the d.c. amplifier preamplifier of the "chopper" type especially built by Leeds and Northrup on an experimental basis to be coupled to the Speedomax. Soft solder joints were found unsatisfactory causing considerable "noise" in the highest sensitivity record. Hence clean screw connections were employed. The d.c. amplifier has the following arbitrary sensitivity scales: 50, 100, 200, 500, 1,000, and 2,000. The table below gives the approximate range of the Speedomax chart for the various settings on the amplifier.

Amplifier Scale	Approximate Full Range on Speedomax	Amplification
not in circuit	1500 microvolts	× 1
2000	800	2
1000	400	4
500	200	10
200	40	20
100	20	40
50	10	80

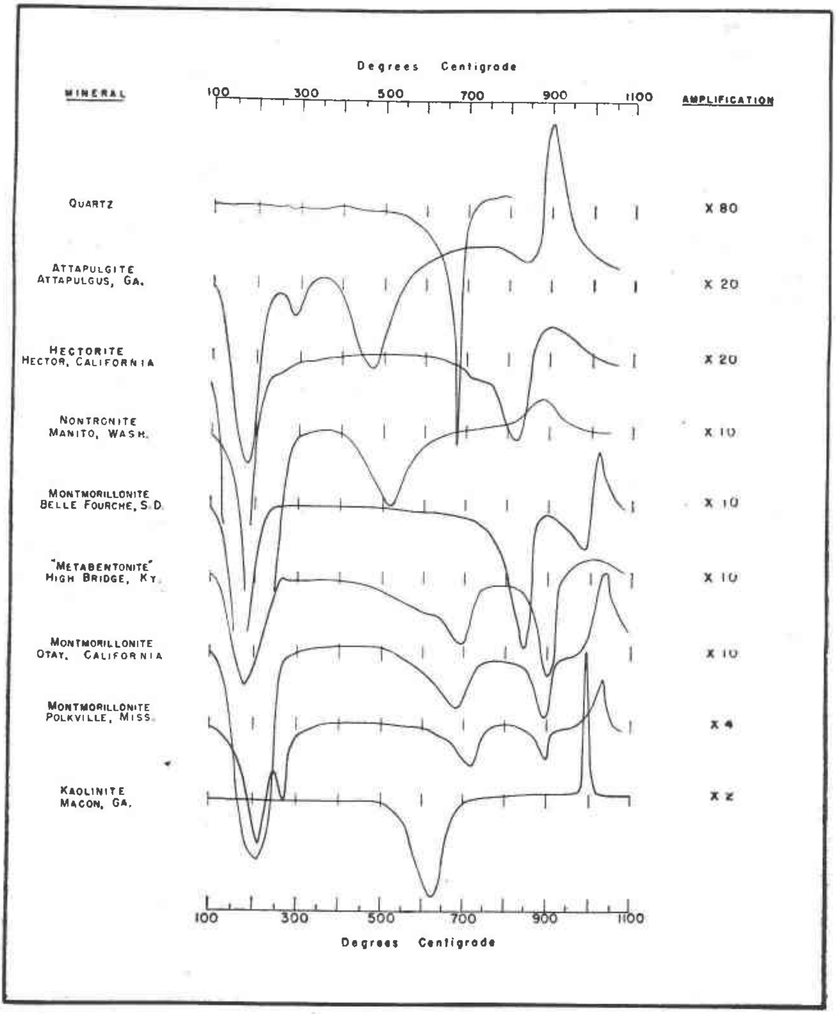

FIG. 3. Representative differential thermal curves at amplifications ×2 to ×80.

A personal communication from Dr. Ben B. Cox of Gulf Research and Development Laboratory indicates that his laboratory has developed with the cooperation of Leeds and Northrup, an automatic rotating switch that will reproducibly and rapidly switch voltages on the order of microvolts or less. This may make it possible to accomplish multiple thermal analyses with an increased sensitivity. On account of the precise geometrical requirements involved in any type of multiple sample holder, it appears that as yet, in order to achieve highest sensitivity and at the same time stability of the base line, a single sample type may be essential.

Figure 3 shows a set of representative thermal curves taken at different amplifications. Comparison of such curves with curves in the literature demonstrates the adequacy in quality and sensitivity of the differential thermal curves produced by this apparatus.

A versatile differential thermal analysis apparatus is now available which combines the features of multiple analysis, direct non-photographic recording, maximum sensitivity useful with the method, and simple operation. Such apparatus with one program controller and one recording outfit plus two furnaces, permits continuous operation of the controller and recorder.

Acknowledgments

The developments outlined in this paper have been made possible through assistance derived from Project 49, Clay Mineral Standards, of the American Petroleum Institute.

References

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