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AN ELECTRICAL TECHNIQUE FOR CHARACTERIZATION OF RESPONSE PARAMETERS OF DTA SAMPLE HOLDERS*

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ABSTRACT

Of the many parameters essential to the description of the performance of differential thermal analysis (DTA), two of the most important are also the most difficult to accurately measure. These are energy sensitivity and response time of the transducer system consisting of the sample-reference masses, their holders and the temperature sensors. The interaction between these two parameters is the chief difficulty in measurement of either, since the usual means of measurement is to analyze a known standard under dynamic conditions.

This paper describes a simple electrical means to measure both energy sensitivity and response time without interaction. The equipment required is within the means of any laboratory having DTA, and a well equipped laboratory will normally already have most of it.

INTRODUCTION

Efforts have been under way in our laboratory for many years to find a simple and reliable means of comparing the performance of DTA transducer systems. As a manufacturer it is desirable to characterize this performance for quality control and design purposes. A comparison between different geometries can give the user a valuable insight into the difficult task of deciding which of the available geometries will give the best performance and reproducibility on a specific type of sample.

The analogy between electrical current flow is well defined by Gebhart[1] and others. Applying this analogy to the isolated cup DTA sample holder suggests a simple electrical calibration technique consisting of introducing a measured amount of electrical power into the sample cup and measuring as a response the change in its temperature. Since the DTA system is designed and calibrated to do this, the only additional equipment required is a heater small enough to fit in the sample cup, a stable electrical power source and a method for measuring the power supplied to the heater. The energy sensitivity is then calculated by relating the temperature change at

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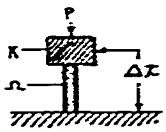
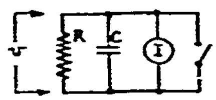
equilibrium to the input power. The response time is determined by measuring the time constant in an electrical sense. That is the time required for the exponentially-changing variable to reach 63.2% (or 1/e) of its equilibrium value.





$T = \Omega K$ $T = RC$

EQUIVALENT QUANTITIES

Time, seconds	T ——— T		Time, seconds
Thermal resistance	Ω ——— R		Resistance, ohms
Heat capacity	K ——— C		Capacitance, farads
Power	P ——— I		Current, amperes
Temperature	t ——— v		Potential, volts

Fig. 1. Hypothetical isolated DTA sample holder and its approximate electrical analog circuit; in both cases the time, T, is the time required for the dependent variable (t or v) to reach 1/e or 63.2% of its final value.

EXPERIMENTAL

Fig. 1 shows a hypothetical isolated cup DTA sample holder, its approximate electrical analog and a tabulation of equivalent quantities for the two systems. Experimental data supports the early assumption that a minor deviation from precise equivalence is the approximation that the heat capacity of the stem upon which the cup is supported is a lumped instead of distributed quantity. This results in a slight reproducible departure of the response from a first-order exponential. Fig. 2 is a photograph of the heater used. It is a miniature 1,000-Ω, 1% metal-film resistor of commercial manufacture*.

RESULTS AND DISCUSSION

The power was calculated from measurement of the voltage across the 1,000-Ω heater by:

$$P = E^2/R$$

For the purposes of this paper, the resistance of the heater and applied voltage was measured within ±0.1% with a digital multimeter. The temperature differential was read out on the strip-chart readout of a model D6000 Deltatherm DTA unit calibrated to within ±0.5%. The sensitivities calculated have an estimated probable error of less than 3%, the response times less than 7%. Power inputs to the heater of up to 25 mW were used. This represented a maximum of 5 V across the 1,000-Ω heater. Power inputs were adjusted to keep the maximum temperature differential within a 5°C full span of a 10" strip-chart recorder.

*Available as type CE-1/20, 1K 1% metal-film resistor from American Components Inc., Conshohocken, Pennsylvania.

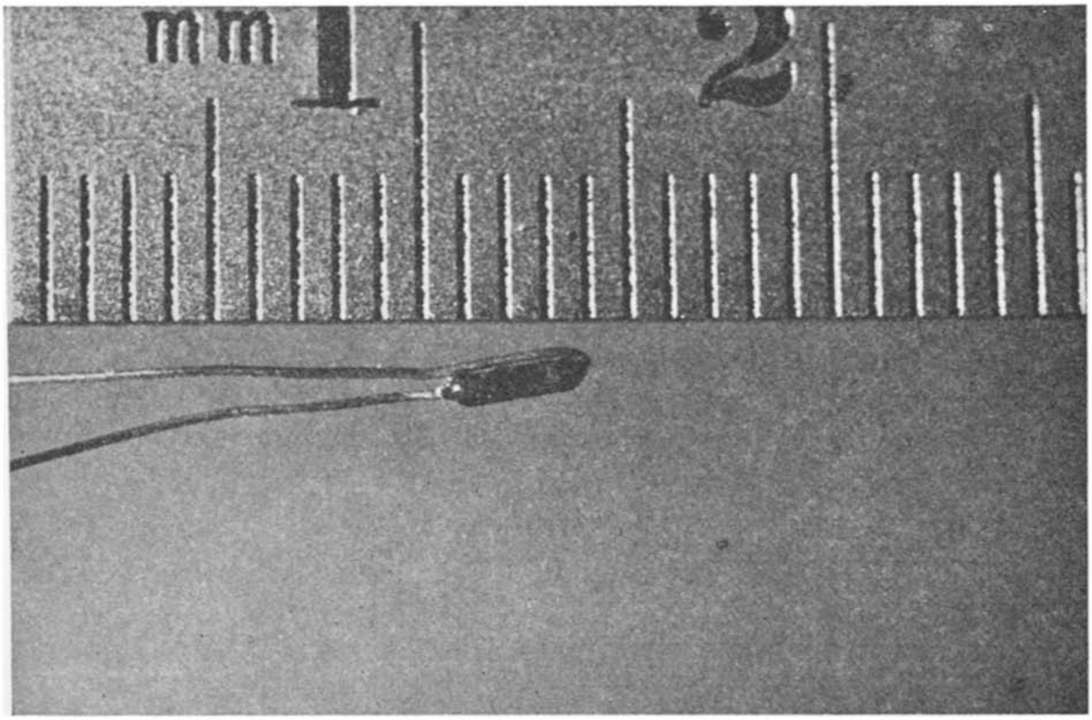


Fig. 2. Photograph of heater employed.

The thermal resistance, Ω, of the heat leak is defined by $\Omega = l/kA$ where l is length, A is cross sectional area and k is the thermal conductivity of the heat leak. This is assigned arbitrary units of °C/mW so that the value can be calculated directly. This is directly related to the DTA sensitivity for slow reactions. The total heat capacity, K is defined by $K = Mc_p$ where M is the mass and c_p is the specific heat of the body. The units would be mWsec/°C and can be calculated from Ω and T. This has little meaning to the user of DTA, however, compared to the response time, which is measured directly.

Fig. 3 shows an actual chart and the measurements made. The thermal resistance, Ω, is calculated by dividing Δt by P, and is 0.147°C/mW for this example. The time constant, T, is measured directly as 26.2 sec. It should be noted that 5 time constants are required to reach a point closer than 1% to the equilibrium value. A good rule of thumb is to use a duration at least 7–10 times the time constant.

The isolated-cup configuration of DTA sample holders is the only one that is reasonably analogous to this simple case. It is felt that for other less well-defined configurations this test can still give useful data. For example, the more traditional configuration of a bare thermocouple surrounded by the sample in a cavity in a relatively massive block would require an extremely complex electrical analogue. From the experimental work done, it is felt that in this case the calculated thermal resistance has little meaning relating to actual sensitivity, but is still useful for comparisons. The time constant is felt to be valid for all cases.

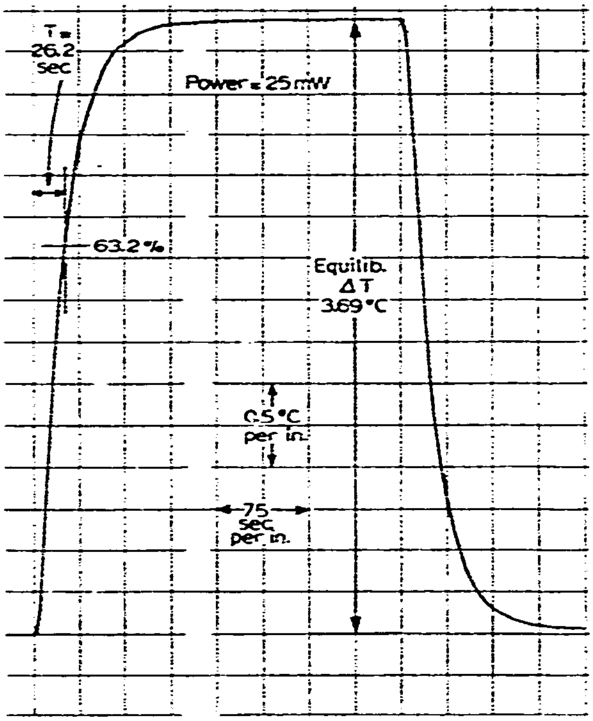


Fig. 3. DTA cell response curve.

Fig. 4 shows four DTA sample configurations and the measured thermal resistances and time constants. The thermal resistances values in cases (C) and (D) were found to not reproduce at all well as heater position with respect to the thermocouple was varied, but the time constant values were much less affected. The values given are with the heater in good thermal contact with the thermocouple junction and surrounded with alumina powder. The comparison between thermal resistances in cases (C) and (D) verifies DTA sensitivity comparisons obtained by running samples with relatively slow reactions. Faster (sharper peaked) reactions exhibited an even further reduction in the peak height shown by (D) compared to (C). This was attributed to lag due to the larger thermal mass of the sheathed thermocouple. The time-constant data verify that assumptio-.

Since the miniature heater used has a maximum rated temperature of 150 °C, all measurements were taken within a few °C of room temperature. It is a well known phenomenon that the energy sensitivity of an isolated-cup DTA sample holder decreases with increasing temperature. This is due to an increase in the thermal conductivity k in most materials with increasing temperature. This results in a reduced thermal resistance, Ω, and reduced energy sensitivity. Performance comparisons at room temperature of different sample cup geometries fabricated of the same or similar materials will still be valid at elevated temperatures because the temperature dependent parameters will exhibit the same changes. For high-temperature com-

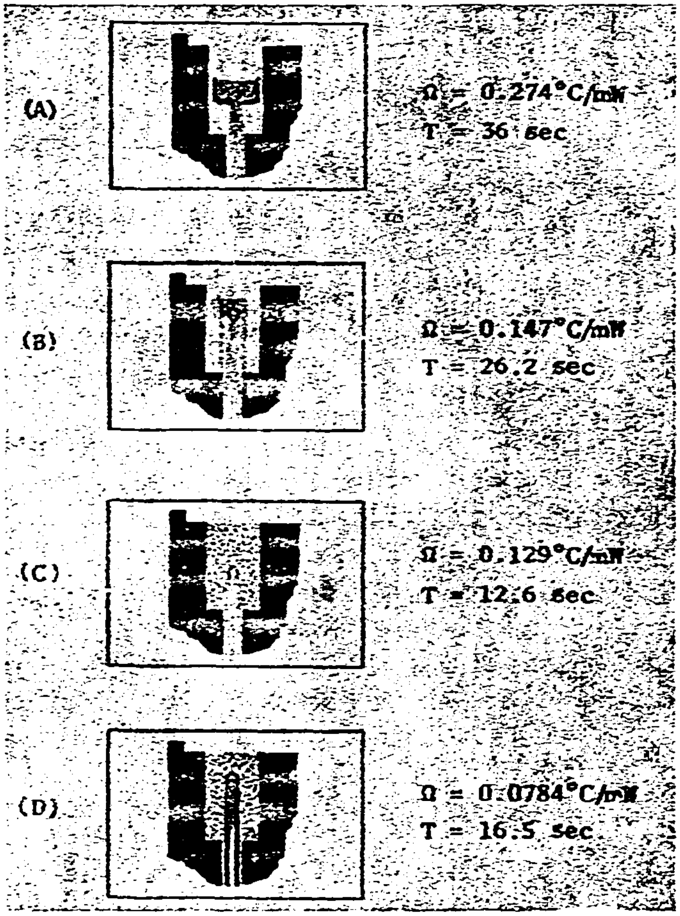


Fig. 4. Sample-holder configurations.

parisons on systems made of different materials, the application of this technique could be accomplished by fabricating a miniature heater which would withstand the temperature range of interest.

REFERENCES

1 B. Gebhart, *Heat Transfer*, McGraw-Hill, New York, N. Y., 1961, Chapter 13.