NOTES AND NEWS

PROBLEMS ASSOCIATED WITH HIGH SENSITIVITY OF RECORDING IN DIFFERENTIAL THERMAL ANALYSIS

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During recent differential thermal studies on soil clays and plant materials it became necessary to detect without ambiguity reactions accompanied by very small energy changes. This led to assessment of the factors influencing such measurements and the methods by which high sensitivity together with high accuracy might be obtained. Although such aspects have been considered by many authors, the relevant data are widely scattered in the literature.

Generally, increase in sensitivity may be achieved by (*a*) variation in sample size, (*b*) variation in heating rate, (*c*) increase in sensitivity of recording equipment, or (*d*) a combination of two or more of these techniques. Each possible method has advantages and disadvantages and the one adopted must, therefore, be related to both the apparatus employed and the type of work being undertaken. For the investigations carried out at the Macaulay Institute the following considerations apply:

Sample Size. Although peak size is not proportional to increase in sample weight, an increase in the size of the sample may, up to a point, prove advantageous provided the reactions in question are comparatively discrete; if the reactions occur over a relatively limited temperature range, however, this procedure may tend simply to coalesce the peaks. Since the thermal curves for soil clays often show multi-peak systems, the possibility of loss of resolution accompanying increase in sample weight militates against this procedure. It may also be precluded because the amount of material is limited or because separation of the material is laborious.

Heating Rate. Since the slower the heating rate the greater the degree of resolution of the peaks, a technique involving variation in heating rate has recently been successfully applied in an examination of gypsum (Dilaktorsky and Arkangelskaya, 1958). The most serious objection to this method is the necessity for the construction of an apparatus incorporating a number of different heating rates, each of which must, of course, be reproducible and, if possible, linear.

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Increased Sensitivity. Refinement of recording equipment overcomes the difficulties associated with variation in sample weight and heating rate. It also permits the use of the sample-dilution technique which greatly reduces base-line drift and the adverse side effects of fusion of the sample; the latter is frequently encountered with soil clays derived from igneous parent materials. Mackenzie and Mitchell (1957) discussed various means of recording the differential thermal curve, and indicated that a mirror-type galvanometer was probably the most suitable way of achieving high sensitivity of recording commensurate with cost. Recently, a pen-and-ink microvolt recorder has been incorporated in the apparatus in use at the Macaulay Institute (Mitchell and Mackenzie, 1959) and since the development of the curve can now be followed continuously, suitable alterations to the sensitivity of recording can be instantly carried out in order to accommodate heat energy changes of markedly different magnitudes.

Increased sensitivity is not, however, without attendant difficulties. Deviations of the differential thermal curve from the base line attributable to several factors can still occur and may be confused with energy changes in the sample under investigation. The elimination of these spurious effects calls for care and precision in the design and construction of the apparatus. In this respect particular consideration has had to be paid to the thermocouple circuits, the block, the furnace, and the linearity of the heating rate.

Thus, base-line drift can occur if the thermocouples are not centrally placed in the wells of the specimen holder. However, interference from stray e.m.f.s. in the external circuit is just as important and it was found necessary, in the Macaulay Institute apparatus, to use screened conductors from the thermocouples to the recording instruments.

The block must be placed symmetrically in the furnace tube to ensure uniformity of heating. If particular considerations demand that a ceramic block be used, then the material from which it is fabricated must possess a high degree of homogeneity and be accurately machined. Preferably, however, the block should be of metal (for example, nickel or inconel) and earthed, in order to minimize the effect of electrical surges in the furnace winding.

Most of the spurious deviations of the differential thermal curve are attributable to e.m.f.s. arising from the furnace winding. To overcome this Pask (1953) inserted a cylinder of earthed nickel foil

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between the inside of the furnace tube and the block and also earthed both limbs of the differential thermocouple through large capacitance condensers. Using a conventionally-wound furnace, Mitchell and Mackenzie (1959) incorporated a 0·01 inch thick nickel sheath within the furnace tube. Since, however, this sheath is prone to corrosion in the furnace atmosphere and has a short effective life, it has been found desirable to replace it by a cylinder of inconel with a wall thickness of 0·05 inch. This is as efficient as the nickel for screening purposes and has a much longer life.

Departures from linearity of heating rate tend also to give peaks on the differential thermal curve which may be mistakenly identified as heat changes associated with the sample. The use of the inconel cylinder with its large heat capacity serves to nullify any minor inequalities in heating rate not covered by the carefully-calibrated control equipment.

Experience has shown that careful consideration of the factors enumerated above enables a very high degree of sensitivity together with high accuracy to be achieved in differential thermal studies.

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