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APPARATUS FOR DSC ANALYSIS OF MILLIGRAM SAMPLES

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Abstract

A novel DSC apparatus is based on resistance thermometers comprising two legs of a modified resistance bridge (Halas-Kamiński bridge) in which one resistor can be energized from an external source. Two metal spirals installed in a regulated oven are used as thermometers and sample holders. Two scans for 20 mg of NH_4NO_3 demonstrate the high sensitivity of this method.

Keywords: DSC apparatus, Halas-Kamiński bridge, resistance thermometers

Introduction

Differential scanning calorimeters (DSC) have been widely used for about 30 years in studies of the thermal properties of solids and liquids. The commercial instruments, however, are expensive due to their complexity. This paper presents a novel construction of a DSC which has reduced complexity, but which retains the essential properties of a commercially available instrument.

This DSC relies on a method rarely used in differential thermal analysis in which two resistance thermometers are replaced by thermocouples, e.g. [1]. In our apparatus, two metal ribbons or wires are wound into spirals, which are supported by thicker endpieces made of the same metal. These spirals are placed inside a regulated oven. In one of them, the investigated sample is loaded. If the sample is a weak conductor, then no insulating pan is required. A thermal effect can be detected in consequence of the temperature difference of the two spirals. In DTA apparatus with resistance thermometers, it was sufficient to arrange a resistance bridge [1, 2]. In DSC, however, we always have to equalize the temperatures of the two spirals, and hence we have to apply an external source to energize the spiral which is becoming cooler during the temperature scan in the oven. In our laboratory, we have developed several ways of energizing one leg of a resistance bridge from an external AC or DC source [3–5]. For DSC apparatus, we have invented a very useful configuration of electronic components [6], which is described below.

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Fundamental concept

It is well known that differential thermal analysis may be performed by using resistance thermometers instead of thermocouples. In our apparatus, the block diagram of which is shown in Fig. 1, two metal spirals R_1 and R_2, installed in a regulated oven, P, are used in a triple role: (1) as sample and reference holders, (2) as resistance thermometers, (3) and as two legs of a Halas-Kamiński resistance bridge [3]. The sample interacts thermally with one of the spirals, while the temperature of the spirals rises continuously. If an electronic circuit (denoted as *UP* in Fig. 1) forces the resistances of the spirals to be the same, then the whole system may be regarded as a differential scanning calorimeter.

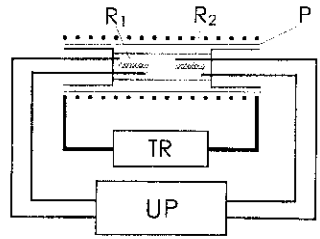

Fig. 1 Block diagram of DSC apparatus. *P* is a regulated oven, *TR* is a temperature controller. R_1 and R_2 are delicate metallic spirals and *UP* is an electronic circuit

When an endothermic reaction proceeds at a certain temperature, then some power has to be supplied from an external source to the sample spiral in order to equalize the temperature of the spirals. In the case of an exothermic effect, the analysed sample has to be loaded into the opposite spiral, since it is easier to add power from the external source to keep the spirals at the same temperature, than to remove it. The electronic circuit is arranged as shown schematically in Fig. 2.

In this schematic diagram, the resistance of the metal spirals, R_1 and R_2, the diodes D_1 and D_2, and two resistances R' and R'', form the Halas-Kamiński bridge, which is excited by the source U_1. To minimize the power consumption

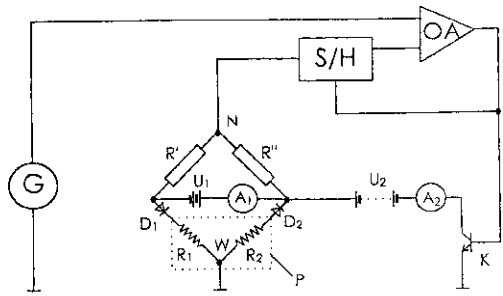

Fig. 2 Electronic circuit of DSC apparatus. *G* is a triangular wave generator, *S/H* is a noninverting sample-and-hold amplifier, *OA* is a comparator, R_1 and R_2 are the low-value resistance of the spirals, while R' and R'' are high-value resistances, A_1 is a meter for the temperature record, while A_2 is one for the DSC signal

from the excitation source, U_1, the resistances R' and R'' are significantly higher than R_1 and R_2. When the bridge is excited by U_1, then amperometer A_1 can be used as a meter of the temperature in the oven P. The output signal at point N is amplified and held the output of the sample-and-hold amplifier, *S/H*. The resistance R_2 can be energized from the source U_2. The voltage of U_2 is essentially higher than that of U_1. Hence, each time the transistor K conducts, the bridge is not excited from U_1 due to the presence of the diode D_2 (D_1 is added for bridge symmetry). By means of a triangular wave generator, G, and an operational amplifier, *OA*, the resistance R_2 is periodically energized during a fraction of the whole period, which depends on the bridge imbalance signal at point N.

The generator G with the *S/H* circuit and operational amplifier (which compares their voltages) comprises a pulse width modulator. The resulting positive pulses at the output of *OA* are used to switch the mode of the *S/H* and K units.

Results

Our system is very sensitive and stable. Hence, reproducible results are obtained on milligram samples. So far, we have recorded scans for gypsum, polyhalite, their mixtures and ammonium nitrate.

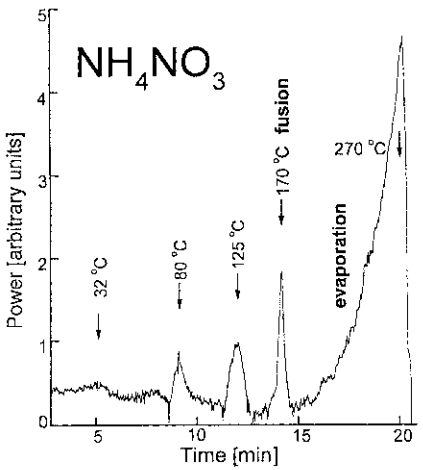

Fig. 3 DSC scan for 20 mg of ammonium nitrate, recorded at atmospheric pressure with platinum spirals. The rate of temperature rise was about 15°C min^{-1}. The peaks at 125 and 170°C have enthalpies of 12.4 and 19.0 cal g^{-1}, respectively [7]

A typical example of ammonium nitrate analysis is shown in Figs 3 and 4, where four distinct peaks are recorded. Two narrow peaks below the melting point represent structural transitions of the crystal lattice [7], while the broad peak extending from the melting to the boiling point (170 to 270°C) represents heat loss due to evaporation. From the preliminary results, it may be estimated that the sensitivity of the new apparatus is of order of 10 mcal mg^{-1}.

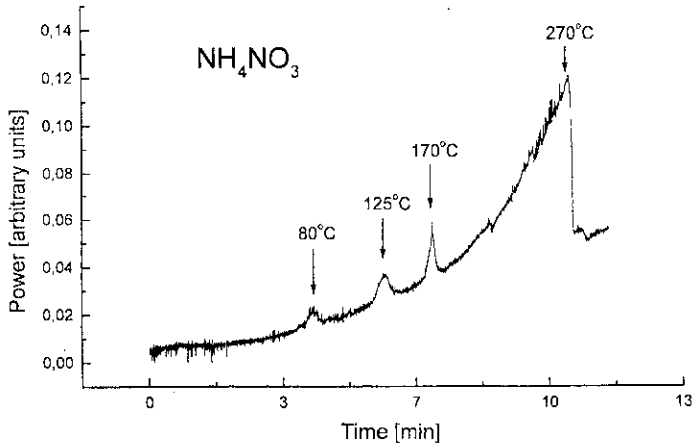

Fig. 4 The same record as in Fig. 3, but obtained using molybdenum spirals and molybdenum leads

It is seen from Figs 3 and 4 that the baseline is more stable in the case of platinum spirals and platinum leads. The trend observed in the case of molybdenum may be due to metal oxidation at higher temperatures.

Conclusions

The apparatus in its early development stage seems to be promising for numerous applications in which small thermal effects can be recorded on small-size samples in a reasonably short time. The apparatus has a potential for operation within a wide range of temperature (from subambient to approaching the melting point of Pt) and pressure, including vacuum conditions.

* * *

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