Thermochimica Acta, 110 (1987) 51–56
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TRENDS IN THERMAL ANALYSIS INSTRUMENTATION

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ABSTRACT

This paper deals with the current status of and trends in instrumentation for thermal analysis (TA) from a philosophical point of view and exemplifies the ideas by some contributions to the 8th International Conference on Thermal Analysis.

INTRODUCTION

The current situation in the field of thermal analysis (TA) instrumentation may be characterized by the following facts.

(1) The methodological principles are well known. The thermal analysis nomenclature according to ICTA provides a nearly exhaustive list of definitions as a framework. It appears hardly possible to imagine further methods.
(2) Many methodological ideas have found principally different technological realizations. One can recall the various possibilities of achieving an increase in temperature by Ohm's resistance heating, infrared radiation and high-frequency heating. In the case of DTA, sensors for ΔT include thermocouples, thermopiles, metallic and semiconductor resistance thermometers and pyrometers. Similar variations are obvious in other TA techniques with regard to sensors and to other equipment.
(3) The instrument manufacturing industry offers a wide range of commercial equipment, at least for the more familiar techniques. The exhibition at the 8th ICTA Conference contained a representative section of what is available world-wide, and this can readily be supplemented from advertisements in relevant scientific journals and magazines.

Consequently, one may assume that most tasks presented to thermoanalysts can be solved by using commercially available equipment. So, *why do we need new instrumentation*?

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

0040-6031/87/$03.50

ECONOMIC ASPECTS

The most forcing demands arise from economic aspects. On the one hand we have highly sophisticated, expensive equipment and scientists with high qualifications. Of course, the productivity of both thermal analyzers and thermoanalysts has to be increased. This can be achieved by automation of (i) equipment that allows 24 h per day working with minimal supervision and (ii) the evaluation of results, which relieves the thermoanalyst from routine work.

The control of four [1] or two [2] independent synchronous or successive TA experiments by one master controller is one possibility of multiplying the data output rate. Using two or more detection modules of the same type, one can run experiments simultaneously under different conditions (e.g., sample mass, atmosphere). On-line data processing and graphical recording of results is now standard. Another impressive example of automation is the change of samples (more than 90) after each run by a robot [3] now commercially available.

Thanks to the recent enormous progress in microelectronics, in the last 10 years we have witnessed a rapid development of controlling and recording systems for TA equipment. This development, started in a few laboratories, is now being pushed forward mainly by commercial instrument makers (e.g., refs. 4 and 5). The control of experimental conditions and the evaluation/output of results are achieved either by two independent microcomputers [6] or via the same data processing unit. As a prospective development one can easily believe that measurement results will soon be evaluated directly in order to control immediately the running of an experiment by a special feedback.

As a result of the digital storage and evaluation of data, the sensitivity, reliability and reproducibility of results have been improved. Consequently, the repetition of experiments in order to find the optimal recording conditions is becoming unnecessary, providing another economic advantage.

Certainly such developments have a price. The reverse of the economic aspect is limited budgets, which prohibit many laboratories from buying highly sophisticated instrumentation. They are confined to laboratory-made equipment with more or less commercial components, designed for specific applications. A newcomer among TA instrument manufacturers, realizing this tendency, has developed a new, inexpensive, robust and sufficiently sensitive DSC unit that matches the demands of routine work in laboratories and industry [7] and can be coupled to a personal computer with a video display. For the future one can assume that well established TA manufacturers will follow this example and offer modern, less expensive equipment for routine and education purposes in addition to their highly advanced and costly apparatus for universal scientific work.

TECHNOLOGICAL ASPECTS

It is a general trend to advance the limits of available equipment by modifying one or more components but with maintenance of the basic principles. Usually the aim is to allow for new applications. In spite of, or possibly as a consequence of, the progress made in the control and evaluation of TA experiments as a result of computerization, TA instrument manufacturers have paid little attention to developing the heart of their equipment, viz., the specimen holder assembly, including the sensors. Thus, certain tasks made it necessary to design modifications to the usual or commercial instruments.

The idea of "gradientless" DTA to improve the sensitivity and calorimetric evaluation of solid-state reactions was approximated [8] by the use of small, light-weight metallic specimen holders and restriction of the heat flux to that along the thin thermocouple wires and through the gaseous medium around them. However, Shishkin [8] does not discuss the problem that the time constant would become high. Consequently, the temperature programme of the sample is ill-defined and the resolution of close-lying effects is only moderate, rendering this DTA system disadvantageous in other respects.

Microautoclaves have been proposed for DTA [9] and heat-flux DSC [10,11] under a self-generated atmosphere at elevated pressure. In both instances the pressurized volume is restricted to the sample alone and not, as is more familiar, to the overall specimen holder assembly. The former [9] is directed to the study of chemical reactions under hydrothermal conditions. One can imagine that DTA will also find use in investigating hydrothermal equilibria, solubilities, etc. The reversibility of decompositions can be easily tested by cooling and reheating the same sample.

Further, refs. 10 and 11 are remarkable for another idea. To determine specific heats by DSC, the heat flux represented by the temperature differences between an empty sample holder and either the sample or a reference standard are recorded simultaneously by a triple thermocouple system [12]. A highly symmetric construction of the measuring head is essential. Then, compared with the usual procedure of successively recording of ΔT curves for (i) an empty crucible, (ii) the crucible with c_p standard and (iii) the crucible with the sample, much time is saved and the influence of incidental operating variations between the runs is suppressed. Applications of this instrument have been demonstrated [13–15]. Another heat flux DSC system with a triple measuring head is offered commercially [16].

If no standard is necessary, a triple thermocouple system can be used to duplicate the throughput of a DTA machine. Again, it is possible to investigate under strictly identical conditions different but similar samples in order to find out minor differences among them [17].

The maximum temperature limit of DTA equipment has been shifted

above 2600°C by using metal thermocouple sensors [18] or photocells [19]. A high-temperature DTA instrument using pyrometric sensors for ΔT measurement is not yet available commercially. Possibly such an instrument will find a market in the near future.

METHODOLOGICAL ASPECTS

The methodological aspects may be illustrated by the invention of a new working principle or a new sensor for TA or by the combination of such a new sensor with an established instrument, e.g., to extend the TA investigation by a new dimension.

For the specific analysis of evolved gases, many new detectors have been developed. Potentiometric solid-state cells can be used to measure the concentration of oxygen [20], carbon dioxide [21,22] and SO_2/SO_3 [23]. Infrared absorption is applied to the determination of carbon monoxide [24]. Commercial TA instrument manufacturers should take up the challenge to provide such inexpensive specific detectors for simultaneous EGA studies with TG and DTA instruments.

Volatile metallic compounds can be fed to an atomic absorption spectrometer for quantitative evaluation [25].

In evolved gas analysis, mass spectrometry is the most versatile (and most expensive) sensing principle. Combination with mass spectrometers is available with many commercial TG and DTA instruments. The long-felt demand to improve the EGA capabilities of the famous derivatograph has now been fulfilled [26] by coupling to a quadrupole mass spectrometer via a capillary.

A rather exotic TA technique is the determination of the neutron transmittance of a sample subjected to a temperature programme [27]. This method provides information about the content of hydrogen-containing compounds such as water or OH groups and their distribution over the sample.

In all classical TA techniques, the temperature of the sample or its environment is varied according to a predetermined programme and a parameter of the sample is monitored by a specific sensor as a function of temperature or time. An inverted principle of thermal analysis in general was outlined by Rouquerol [28], in which the output of the sensor is used to control the temperature programme. Thus the programme is modified in such a way that the deviations from thermodynamic equilibrium (due to the dynamic nature of classical TA) are reduced. This is the philosophy of quasi-isothermal quasi-isobaric TG introduced by Paulik and Paulik [29]. Adiabatic scanning calorimetry (in the sense defined by Hemminger and Höhne [30]) may be grouped under this heading. A simpler device for "inverted" TA was proposed [31] for temperatures up to 2000°C. Here the temperature difference between the sample and the heater is kept constant

by a feedback circuit, and a temperature versus time curve is recorded. Compared with classical heating curves, the effects of phase transformations are greatly improved. One can think of other variations of inverted TA where the approximation to thermodynamic equilibrium is advantageous.

CONCLUSION

The separation of technological and methodological aspects of equipment developments may appear arbitrarily. Surely the success of both will provide economic benefits for the user.

Concerning the future of instrumentation, it is my belief that new sensors will enrich the methodological arsenal of thermoanalysts, and that new combinations of sensors will widen the range of simultaneous TA techniques. Interesting developments may be predicted for the variants of thermoelectrometry and thermoptometry.

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