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ON THE LESS-COMMON THERMAL ANALYSIS TECHNIQUES

L. STOCH
Academy of Mining and Metallurgy, 30-059 Kraków (Poland)

E. KAISERSBERGER
Netzsch-Gerätebau GmbH, P.O. Box 1460, D-8672 Selb (F.R.G.)

ABSTRACT

The International Conference for Thermal Analysis is also regularly a forum for contributions describing less used TA methods. The methods described here are those methods which in the opinion of the authors, despite being defined and included in the ICTA standard definitions, have not found widespread or general application. Due to the multiplicity of techniques, and sometimes only slight differences, only a selected few can be reported and it is in no way the intention of the authors to evaluate or judge the methods. As well as thermo-optic, -acoustic, and -electrometry, special methods of EGD and EGA will be discussed.

INTRODUCTION

Analytical techniques have played an important and often decisive role in the development of many modern scientific fields. Every introduction of a new technique or instrument, through the opening up of new research possibilities, is often the breakthrough into a new scientific field.

During the early development of thermal analysis all instruments were home-made and used for specific studies. They were as a rule simple, non-automatic apparatuses. Construction of this equipment was the first vital step on the road for many thermo-scientists. Smothers and Chiang's book on "Differential Thermal Analysis" [1] was largely a compendium of these individually developed equipments.

Nevertheless, thanks to simple DTA units great progress was made in many fields, e.g., in mineralogy. DTA was one of the first modern methods for identification, especially for clay minerals. Mackenzie's book on "The Differential Thermal Investigation of Clays" [2] was in fact the first manual of thermal analysis.

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Along with the widening range of applications there was a strong emphasis on the methods and techniques. Thus at the ICTA Conferences and in the literature methodological problems were of great importance. It was also the beginning of the commercialization of instrumentation.

Instrument manufacturers now offer a large variety of equipment for a widening range of specific applications. However, standard commercial equipment used to solve new scientific problems, which appear continuously, must be modified and improved. Sometimes it is necessary to make the equipment easier to use. It is a field of activity for experienced scientists. They discover new possibilities and new fields of application for thermal analysis. This activity should be carefully followed. At the 8th ICTA Conference many new and novel methods were presented.

METHODS

Thermoluminescence is a specific and less known phenomenon. It can be observed, for example, as an emission (glowing) when some oxide or hydroxide gels are heated. The thermoluminescence of quartz is used in petrology and archeology as an ageing method.

Kaplan et al. [3] propose the use of radio-thermoluminescence for the study of phase transitions and special crystallization of glasses at low temperatures. Glassy hydrocarbon mixtures and aqueous NaOH solutions are the subject of their investigations. The samples are previously gamma-irradiated at 77 K. A simple technique of registration of the phase transitions based on the measurement of relative intensity of radiation of chemiluminescent additives J_0 during heating and cooling of samples is suggested. Phase transition appears as a gap in the J_0 vs. temperature curve.

The knowledge of the gaseous products of decomposition and of the quantity of the evolving compounds plays an important role in the investigations of thermal dissociation processes.

Today a great variety of detectors and analysis systems are in use for EGD and EGA. The introduction of mass spectroscopy in practical thermal analysis was almost a revolution; the knowledge of the mechanism of many reactions has been considerably enlarged by this almost optimal EGA method. In combination with simultaneous thermogravimetry the difficulty of quantitative calibration in mass spectrometry can be frequently avoided.

However, mass spectrometer identification of more complex molecules is not always explicit and the search for complementary methods of evolved gas analysis has been paralelly undertaken.

Pavlath et al. in their experiments connected thermogravimetry, gas chromatography (GC) and mass spectrometry [4]. Gas flow from a TG analyser could be introduced either directly to the mass spectrometer or first to the column of the GC to adsorb organic molecules (only water passes through).

The gas chromatograph was programmed to separate the adsorbed materials while continuously monitoring the effluent gases with a mass spectrometer. The mass spectrometric data compared with the GC spectrum allowed better identification of components.

A paper dealing with the technique in which optical atomic absorption spectrometry is used to detect volatile decomposition products has been prepared by T. Kantor [5]. A flame atomic absorption spectrometer has been coupled with a modified thermoanalytical quartz furnace for element detection of the evolved species. This method offers complementary information to that available by the known thermal analysis techniques. It has been used to investigate the reactions in the heterogeneous system: ZnO–polyvinylchloride (PVC) and some other organohalides. During this reaction the evolution of zinc halide and zinc vapour has been observed.

A new system for temperature-dependent measurements of vapour pressures of substances in the range $1–10^{-5}$ Pa was presented by Emmerich and Pfaffenberger [6]. The authors use a modern vapour pressure balance for their measurements. They inform us that the method is simple and versatile. A combination of this measuring principle with automatic data processing gives scientists an instrument that yields the substance data quickly and reliably.

In recent years the determination of the smallest pressures in the above-mentioned range has become increasingly important for structural research in the field of organic chemistry, for high vacuum physics and also for environmental applications.

A further special form of EGD, emanation thermal analysis (ETA) appears, from the number of works presented, to be becoming more widespread. Also theoretical works obviously contribute to this, e.g., Kříž et al. [7] and Habersberger and Balek [8]. ETA offers versatile application possibilities to show structural changes in amorphous systems, e.g., glasses (see Bordas et al. [9]), surface activities (Habersberger and Balek [8]) and mechano-chemical effects of powders (Ishii [10]) and development of micropore structures in the pyrolysis of coal (De Koranyi and Balek [11]). Different methods for radioactive labelling of samples are described in the papers cited; a special nomenclature for the detection of radioactive krypton has been used here: Dekryptonation TA (see Lukáč [12] and Tölgyessy et al. [13]). In the work of Hrdlička [14] a method is shown which detects all reactions which are connected with a change in the bound-hydrogen content: neutron radiographic TA.

Thermosonometry, closely connected with the name of Lønvik (Trondheim, Norway), is applied to a technically important process: Lach and Slavik [15] describe the results obtained from thermosonometry for the development of microstructure during a ceramic firing process.

Thermoelectrometry methods were introduced by Šolc et al. [16] for the estimation of the reactivity of powders by measurement of the conductivity, impedance and special parameters for dielectric materials. Compared to DTA, in thermoelectrometry the reactions for the selected powders become apparent up to 120°C earlier. To establish phase diagram Thiel et al. [17] describe exact EMF measurements with the use of galvanic cells consisting of solid-state electrolytes. Electrochemical cells as specific EGD detectors for some kinds of gases such as CO_2, SO_2 and SO_3 are described by Saito et al. [18] and Maruyama [19].

An interesting field is offered by the use of microwaves in thermoanalytical methods. The former works of Karmazsin are expanded in ref. 20 where the polymerization "curing" of epoxy resin by continuous or pulsed microwaves is shown. There, a higher Young's modulus is achieved in a shorter time by heating the microwaves.

Known individual methods of TA can be described as "less common" when temperatures are extended into extreme ranges as shown in the contribution by Gmelin [21] about low temperature calorimetry. The same applies for the high temperature ranges, 2000°C and above.

CONCLUSION

A study of the 8th ICTA Conference Proceedings in addition to the endeavour to obtain optimum information from the participation in the conference for a comprehensive report about less common TA methods at the same time shows how difficult an undertaking this is: e.g., the defining of what constitute common methods. The authors have presented an individual selection which does not claim to be comprehensive. It is, however, essential that the less common methods in practical thermal analysis are not neglected as they have earned their place through the scientific and technical information they provide.

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