# Special Review

## NOVEL MULTIPLE METHODS AND RESULTS IN THERMAL ANALYSIS

J. SIMON

*Department of General and Analytical Chemistry, Technical University, Budapest*

(Received January 16, 1976)

The development of the multiple thermal methods and the results obtained with them during the past three years are discussed.

More than 900 papers dealing with thermal analysis have been published in the past three years (1973–1975). This corresponds to a 150% increase as compared to the preceding three years. The literature sources on which this review is based, as well as numerical data are listed in Table 1. In view of the great number of papers, the author could not undertake to survey the complete material. The object of the present review is the discussion of instruments for multiple thermal techniques and of the results obtained with these techniques.

### Development of instruments

The Hungarian representative of instruments for multiple techniques is the derivatograph manufactured by MOM, Budapest. F. Paulik and J. Paulik have lately further developed the method towards quasi-isothermal and quasi-isobaric measuring techniques [1]. Thereby the investigation of decomposition processes close to the equilibrium temperature and pressure (in the physicochemical sense) became feasible. Thermal results obtained with the novel procedure have been reported by the inventors in several papers [2–4].

Further development consists in combining the quasi method and gas titrimetry. In this manner, quasi-thermogravimetric curves (QTG) and quasi-thermogastitrimetric curves (QTGT) are simultaneously obtained [5].

Polish researchers [6] made use of the derivatograph supplied with a 1500° furnace for determining the Curie point of ferromagnetic substances. The magnetic field produced by the heating current establishes a magnetic relation with the ferromagnetic substance. At the Curie point, where the substance turns paramagnetic, a sharp apparent weight decrease is measured.

The efforts to combine the light microscope and the DTA method appear of interest. The DLI (depolarized light intensity) technique simultaneously records the DTA curve and measures changes in light intensity under dynamic conditions [7]. The authors claim particular importance of the method in the plastics

industry for studies of crystallization, rates of crystallization and melting points of polymers.

American researchers report about combinations of high-pressure TG and magnetic susceptibility measurements in the 1–68 atm pressure range. The method has been successfully applied in investigations of coordination compounds where a change occurs in the number of the odd electrons of the central metal atom [8].

There is an increasing demand for the analysis of volatiles evolved during thermal analysis. This task is solved in an up-to-date manner by combining thermal analysis and mass spectrometry. Various such combinations are known. American researchers report results obtained by combining TG-DTA-MS-computer equipment, particularly for geochemical applications [9].

DTA-MS-magnetic tape data storage [10] has been used in studies of inorganic compounds, coordination compounds, organic metal compounds.

The combination TG-DTG-DTA-MS [11] has been used to study the dehydratation of $MgCl_2.6H_2O$.

The decomposition of $UO_4.2NH_3.2HF$ has been investigated with the combination TG-DTA-MS to clarify the reaction mechanism [12].

Simultaneous DTA-EC (electrical conductivity) measurement has been reported [13].

DTA-EC-EGA (evolved gas analysis) has been used by Soviet authors for the analysis of 21 sulphide-containing compounds [14].

The essence of DTA-TG-ETA (emanation analysis) is that some radioactive isotope, e.g. krypton, is previously built into the crystal lattice of the substance to be studied. The radioactive isotope evolved from the surface under the effect of heat is measured with a GM tube and yields information regarding crystal structure, crystal rearrangement etc. [15].

A combination of X-ray-TG-MS [16] is known. The sample is placed into a heatable X-ray cell and the diffraction pattern is taken in the usual manner. The evolved decomposition products are then transferred through a special vacuum-proof valve to the thermobalance which is under high vacuum. The so-called "molecular beam" formed of the decomposition products strikes against the balance pans and displaces the balance. The displacement is proportional to the rate of decomposition, consequently its integral yields the TG curve. MS-curves can be obtained simultaneously.

Belgian researchers [17] studied the decomposition of Ca, $Mg(HCO_3)_2$ using the combination DTA-EGA. Others [18] used a similar combination for investigations of the decomposition of sodium and calcium dithionate-hydrates.

## Theoretical research

In this field, numerous papers deal with the kinetic interpretation of solid-phase reactions, since apparent kinetic parameters, namely activation energy, order of reaction, activation enthropy and frequency factor can be calculated from