*Thermochimica Acta*, 110 (1987) 165–169
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands


# OUTLINE OF SOME NEW CALORIMETRIC TECHNIQUES AND INSTRUMENTATION

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## ABSTRACT

Some new calorimetric instruments and techniques with special regard to solution calorimetric methods and thermometric analysis are reviewed.

## INTRODUCTION

One of the indispensable methods of chemical thermodynamics is calorimetry, which very often usefully complements thermal analysis methods.

Conventional methods of thermal analysis involve primarily, though not exclusively, the characterization of solid samples. An increase in temperature causes a change in the state or composition of the sample, which is registered and evaluated. In calorimetry, a reaction is used to bring about a temperature change, which is then measured. The notable feature of calorimetric methods is their universal applicability, because the change in heat content is the most general property of chemical reactions.

## INSTRUMENTS AND METHODS

In the last decade, a great number of different calorimetric techniques and instruments have been designed and used with success. Every year some papers are devoted to new designs of calorimeters for different purposes. Some of them are based on known principles, but new measuring techniques, increased accuracy, the use of computers and automation make them applicable to both academic research and industry [1–3].

Very often, different types of calorimeters are designed for special purposes and are not produced for sale, because they can hardly compete with the instruments produced in large numbers by companies with a long

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

0040-6031/87/$03.50 

tradition, equipped with up-to-date research laboratories and workshops. Recently, significant progress was made in the instrumentation used for combustion calorimetry, which also influences other types of calorimetry. New instruments from Leco Co. (U.S.A.), Parr (U.S.A.), etc., allow more than 50 analyses per 8-h day. A new concept with an air envelope was employed in a new automatic anisothermal combustion IKA-Calorimeter, type C-700 T (double dry). Several types of automated calorimeters are produced by Tronac Co. (U.S.A.). The French company Setaram supplies calorimeters based on the Tian–Calvet heat-flow principle. Their main advantage is their applicability to reactions or physical phenomena at different temperatures. Very promising are the liquid-flow calorimeters from Setaram, LKB (Sweden), Microscal (England), etc. The last is especially suitable for the study of adsorption/desorption phenomena and surface-area determination. The ARC thermal kinetic calorimeter (Columbia Scientific Ind., Texas) is designed for hazardous evaluations of exothermic reactions [4]. A computerized instrument, SEDEX (Sensitive Detector of Exothermic Processes), was designed for similar purposes [5]. This calorimeter, formerly developed for sensitive detection of the initial temperature of exothermic processes, has become a flexible system for the investigation of the thermal behaviour of substances and reaction mixtures under production plant conditions.

Isothermal calorimeters, where the exothermic effect of a reaction in a metal crucible is compensated by Peltier cooling (Tronac Co. design), are rather complicated in construction, but enable an easy evaluation of results [6]. Horák and Šilhánek [7] replaced the electrical Peltier cooling by a teflon cooling coil immersed in a reaction vessel. The reaction heat is removed by stepwise addition of a coolant (usually water) to the coil, which is controlled and registered. The usefulness and accuracy of this thermokinetic method was demonstrated with the oxidation of ethanol by hydrogen peroxide catalyzed by ferric ions.

Another heat-exchange calorimeter for measurement of the instantaneous caloric effect was designed by Fujieda and Nakanishi [8]. Heat evolved in a vessel, placed in water-bath is exchanged with the ambient water. The thermal phenomena are expressed by a simple differential equation. The total heat evolved or the rate of heat evolution is estimated on-line by means of thermistors in the reaction and reference vessels and calculated by a microcomputer. These authors are well known in the calorimetric literature; their paper [9] describes an amplifier for the compensation of environmental heat exchange used in instruments for thermochemical analysis [10].

Other Japanese workers from Sinku Riko Co. [11] designed a very clever calorimeter for measuring the thermal diffusivity of thin films of steel, nickel, aluminum, silicon, etc. The sample is irradiated by a halogen lamp, which results in an increase in the temperature of the sample by up to hundreds of degrees Celcius. The plots of the thermal diffusivity against

temperature show breaks indicating phase changes, e.g., for nickel–silicon–boron alloy at 459.5°C.

An interesting paper by Kocherzhinsky and Turkevich [12] deals with the theory of diathermal calorimetry. They describe three types of diathermal calorimeters and their advantages and disadvantages. Recommendations for the embodiment of the respective designs are made.

Recently many papers have been devoted to the determination of the specific heats of solids and liquids, which are very complex in nature. Martín developed a procedure [13] allowing a simple analysis of the temperature dependence of the specific heat, with corrections including those for anharmonic effects.

A very promising field of calorimetry is thermochemical (enthalpimetric) analysis (TCHA) in solutions, which is used in three modes, titration, flow and direct injection enthalpimetry, DIE [2,10,14–16]. In the DIE method a reagent solution is injected in excess into a fixed volume of the solution to be analyzed, bringing about a temperature change which is usually measured by means of a thermistor. The same procedure can be used for the analysis or quality tests of solid samples, which are usually dosed as a powdered form into the reagent solution. The instrument displays the result of the analysis digitally, e.g., directly in per cent. The method has broad application in all branches of chemistry [14,17,18]. For example, it enables the determination of one component in two phases (amorphous and crystalline $SiO_2$), of one component in two or three oxidation states, simultaneous measurement of the reaction heats and kinetics, etc. A promising use of TCHA is in biology and biochemistry [19–21].

Sajó introduced the DIE method into industrial analysis on a large scale in the fifties. He developed different instruments, the most recent of which, automatic model Dithermanal OD 506/25, controls the individual steps of the analysis and evaluates the results. Similar instruments designed at the Technical University of Brno having the name Enthalpiograph use a water-bath and can be applied to solid–liquid reactions [15]. This enlarges the scope of DIE and enables, e.g., the determination of the heat of hydration of cement, of the pozzolanic activity of fly ashes or silicates, of the available lime in quicklime, testing of the quality or fineness of different finely powdered samples and industrial wastes [15,16,22,23]. Recently, many papers have been devoted to determination of the heats of adsorption [24–26], immersion and specific areas, the activity of catalysts, the kinetics of corrosion, etc.

Owing to Sajó, DIE is widely used in Hungary. Marik-Korda elaborated several methods of determination of water in different materials by use of the Karl Fischer reagent [27], oxidimetric determination of urea in agriculture [28], etc. The main novelty of Marik-Korda's technique consists in the use of a considerable excess of reagent solution in a reaction beaker, to which the liquid or solid sample can be added several times, because the

thermal capacity of the contents of the reaction beaker is practically unchanged after each measurement.

An automatic titrator was designed for the analysis of raw products from the aluminum industry [29], where TCHA methods are very promising [30,31].

The above represents only a brief survey of problems which can be solved by calorimetric techniques. Last year, a bibliography containing more than 600 references on thermochemical analysis and calorimetry was produced [32]. A second volume under the title "Calorimetry and Thermochemistry in Solutions" is in the press.

The recent trend in DIE is to construct smaller automatic table instruments for use in smaller plants for routine analyses. The importance of thermochemical methods can be seen in the increasing number of papers published every year.

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