NEW INSTRUMENTS AND METHODS
FOR ENTHALPIOMETRIC ANALYSIS AND CALIBRATION

J. BRANDŠTĚTR

Department of Chemistry, Technical University, Brno, ČSSR

(Received October 31, 1977)

A review is given of recently developed instruments used in thermometric analysis and new methods of direct injection enthalpimetry.

In the past two years, several types of Tronac (Orem, Utah) and Setaram (Lyon, France) calorimeters have been developed. A new mixing cell construction led to development of a flow instrument for automated thermometric analyses (Technicon, Tarrytown N.Y.). A new type of Hungarian instrument, Ditermanal (Orion, Budapest) permits arbitrary analyses.

At the Technical University in Brno, small table twin isoperibol instruments allowing the direct analyses of solid samples have been developed. The use of PTC thermistors and a calibration device improved the accuracy of measurements.

Many new methods of silicate and lime analysis, water determination, etc. have been elaborated.

In the past three years, measuring techniques in thermometric (enthalpimetric) analysis have markedly improved.

Several companies have developed new instruments or improved their calorimeters. The Tronac Company (USA) produces two types of calorimeters (isoperibol and isothermal), developed by Hansen, Eatough, Christensen et al. [1, 2]. These calorimeters are used for titration calorimetry, thermometric titrations and/or direct injection enthalpimetry. The LKB Company (Sweden) has developed a new sorption microcalorimeter with flow and sorption reaction cells to its precision flow and batch calorimeters. The Setaram Company (France) produces a new dynamic Picker continuous flow microcalorimeter, applicable in analytical chemistry (on-line), biochemistry, chemical thermodynamics, etc.

For routine analyses a new automated thermometric analyser (Technicon, USA) has been developed. Samples for analysis are poured into 40 plastic cups in a sampler. A peristaltic pump aspirates a precise quantity of sample into a mixing cell [3, 4] placed in a water-bath held at constant temperature. Simultaneously an excess amount of the reagent solution is pumped through a separate tube into the cell, where it is rapidly mixed by a special rotor. The reaction takes place and the products of reaction then flow to waste. Temperature difference is measured by a thermistor placed in the stainless steel surface of the measuring cell. The results are shown graphically as a series of peaks on a recorder, each peak being proportional to the concentration of the measured component.

For direct injection enthalpimetry, two Hungarian instruments for routine analyses are commercially available. The Directhermom D (MOM, Budapest) is a newer type of the older Silicotherm. One reaction plactic beaker is placed in a Dewar flask; a digital millivoltmeter enables one to read the concentration of the
analysed component in percent. Another instrument, the Dithermanal (Research Inst. for Iron Ind., – Orion, Budapest), designed by Sajó, is a twin reaction calorimeter with digital display. The environmental heat exchange is compensated by a special increasing voltage source. A new generation of this instrument, equipped with a small computer, has just been completed.

At the Technical University of Brno, several instruments have been developed for different modes of thermometric analysis. The standard table twin instrument for routine analyses contains two styrofoam disposable reaction beakers in Dewar flasks immersed in a water-bath.

Styrofoam beakers of minimum heat capacity markedly improve the accuracy of measurements. Reagent solutions are added from plastic dipping pipettes [5, 6], which are filled and emptied electromechanically. A newer type of the instrument permits addition of the thermostated reagent solution from an external stock bottle by a dispenser.

A simpler type of enthalpimeter with one reaction beaker without water-bath is used for measuring reactions accompanied by a larger temperature change (1–3°), e.g. in many reactions between solids and liquids. For addition of solid samples, an adapted plastic syringe is used [7, 8].

As a measuring instrument, recorders or digital millivoltmeters are used; an interface and a printer may be appended. Two thermistors are connected in a simple DC Wheatstone bridge with adjustable voltage. More complicated bridges are equipped with a digital display and a device for compensation of environmental heat exchange.

This is especially necessary when positive temperature coefficient thermistors are used, because this sensor is 4–20 times more sensitive than the commonly used NTC thermistors and allows measurement of extremely small temperature differences. With choice of the proper thermistor voltage, millivoltmeter shunt or amount of sample, the digital display shows the content of the determined compound in percent.

Another bridge is in fact a digital thermistor thermometer in the temperature range 20–26°. Three sensors enable one to measure the temperatures of the sample solution, reagent solution and water-bath. These measurements permit omission of the use of dipping pipettes, and the data found are corrected by a simple calculation. A semi-automated device equipped with microprocessors is under construction.

Another semi-automated device has its single plastic reaction beaker fully immersed in the water-bath, so that no heat exchange with the environment occurs and the temperature of the sample solution in the pre-reaction period is constant. Individual steps of the assay (filling and emptying of the reaction beaker and reagent pipette, etc.) are controlled electromechanically by push-buttons [9].

A special instrument has been constructed for the determination of the cement content in a concrete mixture [10].

For calibration of reaction heats, a joulemeter consisting of quartz crystal timer, source of stabilized current and resistance heater is used [11, 12].