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# NEW INSTRUMENTS AND METHODS FOR ENTHALPIMETRIC ANALYSIS AND CALIBRATION

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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]. If the proper conditions are selected, the digital display shows the energy in joules. Certain difficulties arise in calibrating higher reaction heats; for this purpose, special heating elements are in preparation. In heating, following the temperature jump of the reaction studied as closely as possible is necessary to eliminate the heat leak during the experiment.

New or improved instruments have led to the elaboration of new methods or to the improvement of the precision of many determinations, so that they can be used even in arbitrary analyses [13].

The precision Tronac calorimeters enable one to use 3 ml Dewar reaction flasks for calorimetric titrations [14]. The previously-mentioned new flow thermometric method [3, 4] is very promising, especially for medium and higher concentration ranges in industrial routine analysis. The use of a new double injection method intending to apply solutions without temperation [15] appears to be very limited [16]. Correction calculus proposed to improve the accuracy of the double injection method [17] seems rather complicated.

New methods elaborated in the past two years cover all branches of chemistry and related sciences. Many analytical methods are summarized in [18–20]. Calorimetric titrations [14] and their analytical applications appear very important and useful in solving theoretical problems. Direct injection enthalpimetry permits rapid routine complete analyses of silicates, ores, alloys and many organic compounds, the determination of the water contents of solids or liquids [21, 22], the analysis of cement and lime [7, 8, 23, 24], etc.

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RÉSUMÉ — On passe en revue les instruments récemment mis au point et utilisés en analyse thermométrique ainsi que les nouvelles méthodes d'enthalpimétrie par injection directe.

Dans les deux dernières années, divers types de calorimètres ont été mis au point: TRONAC (Orem, Utah) et SETARAM (Lyon, France). La réalisation d'une nouvelle cellule de mélange a permis de mettre au point un appareil à flux pour les analyses thermométriques automatiques (TECHNICON, Tarrytown, N. Y.). Un nouveau type d'instrument hongrois, DITERMANAL (ORION, Budapest) permet d'effectuer des analyses arbitrales.

A l'université technique de Brno de petites tables instruments jumeaux isopériboliques permettant aussi d'effectuer des analyses directes des corps solides ont été réalisés. L'application de thermistors PTC et un dispositif pour l'étalonnage augmentent l'exactitude des mesures.

Des méthodes nouvelles nombreuses pour l'analyse des silicates, des pierres calcaires, de l'eau, etc., ont fait l'objet d'études.

ZUSAMMENFASSUNG — Eine Übersicht über die zur thermometrischen Analyse eingesetzten, entwickelten Instrumente und neuen Methoden der Direkt-Injektion Enthalpimetrie wird gegeben.

In den zwei vergangenen Jahren wurden verschiedene Kalorimetertypen TRONAC (Orem, Utah) und SETARAM (Lyon, France) entwickelt. Eine neue Mischzellenkonstruktion ermöglichte es ein Durchflussinstrument für automatische thermometrische Analysen (TECHNICON, Tarrytown, N. Y.) zu entwickeln. Ein neuer ungarischer Instrumententyp, DITERMANAL (ORION, Budapest), ermöglicht die Durchführung von Schiedsanalysen.

An der Technischen Universität Brno wurden kleinen Zwillings-Isoperibol-Tisch Instrumente entwickelt, welche auch die direkten Analysen fester Proben ermöglichen. Der Einsatz von PTC-Thermistoren und einer Eichvorrichtung erhöhte die Messgenauigkeit.

Viele neue Methoden der Silikat- und Kalkanalyse, Wasserbestimmungen usw. wurden erarbeitet.

Резюме — Приведено обозрение недавно разработанных приборов, используемых в термометрическом анализе и новых методов прямой инжекционной энтальпиметрии. За прошедшие два года были разработаны несколько типов калориметров ТРОНАК (Орем, Юта) и СЕТРАМ (Лион, Франция). Новая конструкция смесительной ячейки позволила разработать прибор для автоматического термометрического анализа (ТЕХНИКОН, Территаун, Нью-Йорк). Новый тип венгерского прибора Дитерманал (ОРИОН, Будапешт) дает возможность судебного анализа. В Техническом Университете в Брно были разработаны небольшие приборы, дающие возможность прямого анализа твердых образцов. Использование термисторов и калибрационных устройств улучшает точность измерения. Были разработаны новые методы анализа силикатов, извести, определение воды и др.