PRESENT STATE AND FUTURE DEVELOPMENT OF INSTRUMENTAL TECHNIQUES FOR SOLUTION THERMOCHEMICAL (THERMOMETRIC) ANALYSIS*

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A review of instruments for thermochemical (thermometric) solution analysis is given, including new types of isoperibol reaction of bomb calorimeters, the design of which can influence the future development of thermochemical measuring techniques.

The new type of Dithermanal (Vaskut-EMG, Hungary, and Herrmann–Morris, France) controls the individual steps of the thermochemical analysis, adding memory and computing capabilities. Similar programming units with microprocessors for bomb and/or reaction calorimetry have been developed by Parr Comp. and Leco Comp. (USA). The latest modification of the Technicon flow analyzer permits on-line analysis of solid samples. For thermochemical titrations, the Sanda titrator (USA) and Vaskut automatic titrator (Hungary) are available. In the USA, the Tronac isothermal or isoperibol calorimeters are widely used. At the Technical University of Brno, ČSSR, smaller table instruments with a water-bath are applied for different modes of solution thermochemical analysis, and also for the reactions of solid samples in liquids. For the measurement of very small temperature differences, PTC thermistors are used.

The possibilities of the future development of measuring techniques are outlined.

In the past decade, measuring techniques in all branches of physico-chemical analysis have markedly improved. This has made possible the renaissance of some methods the principles of which have been known for a long time, and the increase of their applications and accuracy. Due to the new precise measuring instruments, the methods of solution thermochemical (thermometric) analysis have become widely used in this period. Considerable progress in the use of direct injection enthalpimetry in routine analytical chemistry has been achieved, especially in Hungary [1–4].

In the development of solution thermochemical analysis, different methods and different instruments are employed [5–7]. Automatic titrators accelerated the development of thermochemical titrations and titration calorimetry. Instruments for direct injection enthalpimetry differ considerably from commercially available reaction calorimeters in their reaction and measuring parts. Many recent laboratory instruments, including those used in calorimetry and solution thermochemical analysis, are equipped with microprocessors controlling the program of individual steps and evaluating the results of analysis or measurement.

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As the basis of instruments for thermochemical analysis, classical reaction and solution calorimeters have been used [8–10]. Because the thermodynamic values found via different calorimetric measurements and calculations are of fundamental significance for solution thermochemical analysis too, it is necessary to follow the new results of reaction or solution calorimetry at room temperature, and not only from an instrumental point of view.

The latest publications dealing with the design of new reaction or solution calorimeters are nowadays of less importance, because these instruments can hardly compete with the apparatus produced in large series by companies with long traditions, equipped with up-to-date research laboratories. First of all, a review of commercially available reaction or solution calorimeters will be presented, all of which have been markedly improved in the last few years.

The French company Setaram supplies calorimeters based on the Tian-Calvet heat flow principle [11]. Their main advantage is their use for studying reactions or physical phenomena at different temperatures (−206 to 1750°), even with a low reaction rate and with a minute amount of sample. The Calvet microcalorimeter, most useful for measuring heats of reaction, hydration, solution, dilution, adsorption, chemical kinetics, etc., has two models: 15 ml and 100 ml. The similar CRMT calorimeter is used instead of the Calvet microcalorimeter, from ambient temperature to 200°, if great experimental flexibility and facility of adaptation are sought. The newest heat flow calorimeter, the C 80, operates isothermally or with scanning at 0.1 to 2°/min from ambient temperature to 300°. The dynamic liquid continuous flow Picker microcalorimeter, designed primarily for the measurement of heats of mixing, is also applicable for thermometric titrations of samples or continuous titration in "on-line" analysis. The new Setaram differential scanning calorimeter is a quantitative differential thermal analyzer, also suitable for the measurement of specific heats. It can be very useful in the study of conditions for the use of solution calorimetry for analytical purposes, as can the Perkin–Elmer DSC calorimeter, e.g. in analyzing salts with crystal or adsorbed water, etc.

The Swedish company LKB produces a series of calorimeters for different purposes. A well-tried precision calorimetry system includes a reaction calorimeter [12] suitable for thermochemical (thermometric) titrations and direct injection enthalpimetry. The volume of the glass reaction vessel is 100 ml, and that of the platinum vessel 25 ml. These instruments use a thermistor as a temperature sensor. A new type of reaction calorimeter is now under construction. Most commercially-available LKB calorimeters are designed especially for their use in microbiology. All of them use the heat flow principle and thermopiles in twin arrangement with measuring and reference cells. Batch and/or flow microcalorimeters can also be used for determination of the heat of reaction, and the latter for thermometric titrations too. A sorption and ampoule model finds different applications in inorganic and physical chemistry.

The Ika company, Janke and Kunkel, West Germany, supplies the reliable C 400 adiabatic calorimeter, which is widely used in Europe. Their latest improve-

ment is the DKT 400 digital thermometer with a platinum wire sensor, covering a temperature span of 20–30°. A new programming and calculating unit is being produced.

The Knauer universal temperature measuring instrument Type 31.00 (West Berlin) covers the range −250° to 1800° by means of different resistance sensors. For accurate measurement or monitoring in calorimetry or solution thermochemical analysis, single or differential measurement by thermistors allows a resolution of 10^{-4}°.

Excellent progress in the calorimetric technique was achieved by the American Parr company. Its traditional instruments are oxygen bomb calorimeters (plain, semimicro or adiabatic) and a solution calorimeter. This multi-purpose solution calorimeter utilizes a unique rotating cell for solid or liquid samples and a sensitive thermistor thermometer for measuring heats of reaction, mixing, solution, dilution and wetting at room temperature and atmospheric pressure, covering energies from 10 to 4000 Joules. Temperature changes are plotted on a strip chart for easy interpretation and analysis. A most interesting new development is the "Master control" for automatic operation of calorimetric tests [13]. This new instrument replaces the separate digital thermometer, programmer and printer previously offered with Parr calorimeters, adding additional monitoring, memory and computing capabilities. All steps in the operation of the calorimeter are controlled by an intelligent program of checks and commands stored in the microprocessor. At each step in the test the system responds or proceeds to the next operation only after the microprocessor determines that all requirements for the previous operation have been met. The microprocessor also contributes to the excellent resolution obtained with the thermistor thermometer, converting the voltage signal from the probe to a frequency signal which can then be processed with minimum interference from voltage fluctuations and extraneous electronic noise. The working range covers the ten-degree span from 20 to 30°, and readings are resolved to better than 0.0001°. Immediately after finishing a run, this instrument will print a preliminary report listing all essential data taken during the test and showing the result. For large volume users, Parr offers a dual-channel Master control, which handles two calorimeters at the same time and permits up to 12 tests per hour. After certain modifications, this Master control seems to be extraordinarily suitable for thermochemical analysis automation.

The American LECO Instruments company have improved their AC-100 bomb calorimeter with microprocessor dual-channel accessories allowing 50 analyses per 8-hour day.

The ARC thermal-kinetic calorimeter (Columbia Scientific Industries, Texas), equipped with a microprocessor control system, is designed for hazardous evaluations of exothermic reactive chemicals.

The cement calorimeter from Seebeck Envelope Calorimeters (Thermonetics Corporation, San Diego, USA), using a heat flux transducer principle, is of interest; this measures the heat release/time functions in samples of cement after water addition. These measurements give quantitative information that classifies

and rates the cement batches for the cement manufacturer. Other Seebeck envelope calorimeters of different types and sizes are assigned for biomedical applications.

The Microscal (England) flow microcalorimeter is especially suited to the study of adsorption/desorption phenomena, and a further important application is surface area determination. A special mixing attachment makes possible the study of liquid/liquid interactions, i.e. thermometric titrations too.

Wheatstone DC or AC bridges are designed and produced for the precise measurement of temperature sensor resistance. For example, AC bridges by Automatic Systems Laboratories (England) are used especially in high-accuracy resistance thermometry, for absolute or differential measurement. These bridges are used not only in resistance thermometry and automatic calorimetry, where data are recorded and processed automatically, but especially for thermometric calibration, e.g. for the checking of the linearity of thermistor thermometers, which is of principal importance for precise solution thermochemical analysis.

The Tronac (Orem, Utah, USA) calorimeters, developed by Hansen, Eatough, Christensen *et al.*, are relatively unknown in Europe but are used in the United States for thermometric analysis, in both calorimetric titrations and direct injection enthalpimetry. The isoperibol mode calorimeter uses Dewar reaction vessels of different volumes, even 2 ml. As the volume of the Dewar decreases, the relative importance of corrections such as heat inputs from stirring or solvent evaporation increases. More complicated in construction, but easier in result calculation is the Tronac isothermal calorimeter, using Peltier cooling of the reaction vessel. Both types of calorimeters are used mostly in environmental chemistry and biochemical applications.

For routine industrial analysis involving determinations of medium and higher concentrations of different components in solution, an automatic thermometric analyzer based on the design of Hagedorn and Peuschel [14] is produced by the Technicon company (Tarrytown, USA). Samples for analysis, placed in 40 cups in a sampler, are aspirated by a peristaltic pump into a mixing cell placed in a water-bath at constant temperature. Simultaneously an excess amount of the reagent solution is pumped through a separate tube into the cell with a special mixing rotor. The reaction takes place and the products of the reaction then flow to waste. The 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. The latest modification of this instrument by Hagedorn permits on-line analysis of solid samples [15].

Only a few instruments are in production and commercially available that are exclusively designed for solution thermochemical analysis.

The first Titra-thermo-mat (Aminco, USA) instrument, designed by Jordan *et al.*, was markedly improved in 1972; the new Enthalpimeter was used primarily for thermometric titration.

For thermometric titration, the Sanda titrator (USA) is available and is supplied together with application leaflets on request.

For the same pupose, Sajó, Ujvári *et al.* (Vasipari Kutató Intézet, Hungary) designed a universal instrument available for thermometric and/or electrometric titrations [16].

For the direct injection enthalpimetry mode, special instruments have been produced in Hungary since 1963, all of these based on Sajó's design or conception. The first commercially available instrument was the Directhermom (MOM, Budapest), which suffered from various teething problems and was soon replaced by the Spectrothermom, and subsequently by the smaller Silicotherm and Directhermom D. These instruments are no longer produced.

In the second generation of these instruments, a new era in direct injection enthalpimetry [2] began with Sajó's Ditermanal (Vaskut-EMG). The Ditermanal is a twin direct reading reaction calorimeter; two thermistors measure the temperature difference between the solutions in the measuring and reference plastic beakers, respectively. Special immersion pipettes allow the determination of even three components successively in one solution. The latest, third generation of this instrument includes a small computer and a programming device, the "Thermorobot", or permits the coupling with a small table computer, programming unite and crystal quartz timer, so that all the operations programmed proceed automatically. In the near future, the French company Herrmann–Morris will supply the computer technique for the Ditermanal instruments for other European countries. The precision of measuring is excellent, so that it is also possible to use these instruments for arbitrary analyses.

Several instruments have been designed at the Technical University of Brno. These instruments are the result of the development of a number of techniques, some of which are new in themselves, and which together provide accurate and flexible instruments for different modes of solution thermochemical analysis. The standard bench-top twin instrument for routine analyses the Enthalpiograph [17, 18], contains two disposable styrofoam reaction beakers in Dewar vessels immersed in a water-bath. Styrofoam beakers of minimum weight and heat capacity improve the accuracy of measurements. Reagent solutions are added from plastic immersion pipettes, which are filled and emptied electromechanically. Volumetric flasks with sample solutions and reagent stock solution bottles are placed in the same water-bath. By reduction of the sample solution volume to 100 ml, a considerable saving of chemicals is achieved. For the measurement of the reactions of solids in liquids, an adapted plastic syringe sampler is used [19]. This simple device has considerably enlarged the use of the instrument for thermochemical analysis.

A simpler type of Enthalpiograph with one cell without a water-bath, with styrofoam insulation of the Dewar flask with a reaction beaker, is used to measure reactions accompanied by a larger temperature change (1–3°), e.g. many reactions between solids and liquids [20]. This instrument is applied in different industrial routine analyses, e.g. in the production of lime [21], cement [22], etc. As a measuring instrument, a digital voltmeter together with a recorder is employed. The combination with a calculator and printer [23, 24] is very useful. A DC Wheatstone bridge with adjustable voltage is used.

Another bridge with digital display is in fact a thermistor thermometer for measuring the temperatures of three solutions at the same time, or temperature differences [25].

For measurement of minimal temperature differences, a positive temperature coefficient thermistor bridge has been used [26]. This sensor is 5 to 10 times more sensitive than the commonly used NTC thermistors. A special instrument has been constructed for the determination of the cement content in a fresh concrete mixture [27].

Calibration of the measuring device for the calculation of reaction heats: The values of reaction heats in the literatures often differ substantially from one another or are not to be found at all. Calibration by comparison with a chemical reaction (usually neutralization) gives good results only in the case of very dilute solutions, where the difference in the heat capacities is negligible. Electric calibration is therefore preferred. The device for calibration consists of a timer (preferably a quartz crystal), a source of stabilized current and a resistance heater [28]. The latest stabilizers of current, voltage and power with a digital display are very precise. Resistance heaters are of different constructions; manganine wire in an appropriate envelope to prevent corrosion is generally used. Resistance heating by higher power input, which is a permanent problem, is preferably substituted by a discharge condensator effect. In calibration, following the temperature jump of the reaction studied as closely as possible eliminates the differences in the heat leaks of the two compared experiments.

Further development of the instrumental technique for thermochemical analysis will take into account all experience and techniques used in the most recent instruments mentioned above. Smaller bench-top, not too complicated instruments will be preferred, with separate measuring and reaction parts. To increase the precision and repeatability of individual measurements, the same constant temperature of all analyzed solutions must be ensured, for a difference of 1° in sulphate determination, for instance causes an error of 0.3% [29]. The concept involving a water-bath seems to be the most advantageous. As temperature sensors, precise and stable NTC or PTC thermistors will be used. Disposable styrofoam reaction beakers of different volumes are much better than Dewars. Stirring with a rod or electromagnetic stirrer has nearly the same effect; the rotation of the reaction vessel is complicated, because the construction must allow the quick exchange of samples. A simple device for analyzing solid samples is necessary. The free volume above the liquid level should be as small as possible. Because of the use of microprocessors, the twin arrangement will possibly be abandoned.

The measuring part will be similar to the Parr Master control device or the Vaskut–Herrmann-Morris design. Only the use of microprocessors permits control of the steps and correction and evaluation of the results by means of a simple and cheap technique; expensive computers are not necessary. The corrections of the thermochemical measurements should include [23, 30]:

1. The heat capacity of the empty calorimeter (parts coming into contact with the solution in the measuring beaker) plus heat capacities of the solutions.

2. Heat exchange with the surroundings in the pre-reaction and reaction periods.
3. Heat contribution by stirring.
4. Joule heat contribution by the thermistor.
5. Bridge linearizing factor.
6. Heat of dilution on mixing two reaction solutions (blank).
7. Conversion factor of corrected entry to corresponding result value in joules, calories, per cent, mol/litre or g/litre concentration, etc.

The combination of the device for its use in flow mode, for on-line analysis, seems to be superfluous. For rapid industrial quality tests of different products and materials by a thermochemical method, a very simple instrument is required; unfortunately, this is not taken into account by the manufacturers.

For the propagation and enhancement of the use of solution thermochemical analysis, it is also necessary to elaborate many new methods in other branches of science and industry where thermochemical methods are very promising. Only a few analytical determinations use the heat of solution of the samples [15]. Prof. Bark has outlined many new simple methods and possibilities in thermochemical organic analysis [31, 32]. Good results can be obtained by measuring resolvation heats in organic, inorganic and mixed solvents. Very promising new fields are thermoporometry [33] and specific surface area determination by thermochemical method [34]. In full agreement with the opinion of Prof. Barthel [35, 36], many theoretical problems must be studied in support of the development of new methods and instruments for solution thermochemical analysis, such as solvation effects, heats of dilution, the influence of ionic strength, heat capacities of individual ions [37] and other theoretically important phenomena. The data bank of thermodynamic values important for thermochemical analysis is very poor.

Last but not least, it is necessary to stress the importance of international cooperation in new, progressive branches of instrumental analytical chemistry such as solution thermochemistry, with its rapidly developing instrumental techniques and methods of determination. Laboratory teams are usually too small, publications are delayed 1 – 2 years and only a smaller proportion of the research results are published, while negative results are unfortunately not published at all. Monothematic conferences and seminars are therefore very necessary, and in the periods between the conferences, private contacts and meetings are of very great value.

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RÉSUMÉ — On passe en revue les instruments utilisés pour l'analyse thermochimique (thermométrie), y compris les types récents de calorimètres à réactions et à combustion, dispositifs qui peuvent avoir une influence sur le développement futur de la technique des mesures thermochimiques.

Un "Dithermanal" nouveau (Vaskut-EMG, Hongrie et Herrmann—Morris, France) programme les étapes individuelles de l'analyse thermochimique et calcule les résultats. Les calorimètres à combustion de Parr et Leco (Etats-Unis) possèdent également un contrôle de programme similaire avec des microprocesseurs pour le traitement des données. La dernière modification du "Thermoanalyzer" de Technicon rend possible les analyses "on-line" d'échantillons solides.

Pour les titrages thermométriques, les appareils "Sande Titrator" (Etats-Unis) et le modèle automatique Vaskut (Hongrie) sont en vente. Aux Etats-Unis, le calorimètre à réactions "Tronac isothermal et isoperibol" est répandu.

A l'Ecole Supérieure Technique de Brno (ČSSR), on utilise de petits instruments de table avec bain-marie, pour divers buts de l'analyse thermique, ainsi que pour la mesure des chaleurs de réaction d'échantillons solides en solutions. Pour la mesure de très petites différences de température, on utilise des thermistors PTC.

On indique les possibilités du développement futur de la technique de mesure.

ZUSAMMENFASSUNG — Es wurde eine Übersicht der Instrumente für die thermochemische (thermometrische) Analyse in Lösungen gegeben, inklusive neuerer Typen von Reaktions- und Verbrennungskalorimeter, welche Konstruktionen die zukünftige Entwicklung der thermochemischen Meßtechnik beeinflussen können.

Ein neuer Dithermanal (Vaskut-EMG, Ungarn, und Herrmann—Morris, Frankreich) programmiert die einzelnen Schritte der thermochemischen Analyse und berechnet die Resultate. Eine ähnliche Programmsteuerung mit Mikroprozessoren für die Datenbearbeitung besitzen auch Verbrennungskalorimeter von Parr und Leco (USA). Die letzte Variante des Technicon Thermoanalyzers ermöglicht die on-line Analysen von festen Proben.

Für die thermometrischen Titrationen sind der Sanda Titrator (USA) und der Vaskut automatische Titrator (Ungarn) erhältlich. In der USA ist der "Tronac isothermal und isoperibol" Reaktionskalorimeter verbreitet.

An der Technischen Hochschule in Brno (ČSSR) werden kleinere Tischinstrumente mit Wasserbad für verschiedene Zwecke der thermometrischen Analyse benutzt, desgleichen für die Messung der Reaktionswärme von festen Proben in Lösungen. Für die Messung kleinster Temperaturdifferenzen werden PTC Thermistoren angewendet.

Die Möglichkeiten der zukünftigen Entwicklung der Meßtechnik sind angegeben.

Резюме — Представлен обзор приборов для термохимического (термометрического) анализа растворов, включая новые типы реакций, протекающих в калориметрах закрытого типа, и конструирование которых может оказать влияние на будущее развитие термохимического метода измерений. Новый тип прибора Дитерманал (Вашкут-ЕМГ, Венгрия) с дополнительной памятью и вычислительными средствами и Херманн-Моррис (Франция) позволяют контролировать отдельные стадии термохимического анализа. Подобные микропроцессорные программные устройства для калориметрии с закрытым сосудом и открытым реактором были разработаны фирмами Пэрр и Леко (США). Последняя модель проточного анализатора Текникон позволяет проводить анализ твердых образцов в режиме на линии. Для термохимических титрований доступными являются титратор фирмы Санда (США) и автоматический титратор Вашкут (Венгрия). В США широко используются изотермические калориметры фирмы Тронак. В Техническом университете г. Брно (ЧССР) для различных видов термохимического анализа в растворе, а также для исследования реакций твердых образцов в жидкости, используются малого размера настольные приборы с водяной баней. Для измерений очень малых изменений температуры используют ПТЦ термисторы. В общих чертах представлены возможности будущего развития методов измерений.