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RECENT DEVELOPMENT IN THERMOCHEMICAL SOLUTION ANALYSIS

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ABSTRACT

A review of techniques used in thermochemical analysis (TCHA) is given with regard to the available instruments. A survey of versatile applications of this mode of calorimetry in solutions (measuring of heats of liquid-liquid or solid-liquid reactions) in analytical, physical, organic etc. chemistry is outlined.

INTRODUCTION

Conventional methods of thermal analysis involve primarily (though not exclusively) the characterisation of solid samples.The increasing temperature causes a change in the state or composition of the sample, which is registered and evaluated.

Thermochemical solution analysis, on the other hand, belongs to the calorimetric methods : a reaction in solution is used to bring about a temperature change, which is measured for analytical purposes. Liquid-liquid and solid-liquid reactions are preferably utilized. The notable feature of thermochemical methods is their universal applicability, because the change in heat content is the most general property of chemical reactions.

Three techniques are used in thermochemical analysis (TCHA) - titration, flow and direct injection enthalpimetry (DIE). This paper presents the most promissing applications of DIE, preferably in chemical analysis.

APPARATUS AND METHODS

The DIE method is based on the injection of an excess of a reagent solution into a fixed volume (usually 50-200 ml) of the analyzed solution or on dosing a weighed solid sample into a reagent solution. The temperature change of the solution is measured usually by means of a thermistor in a Wheatstone bridge circuit with a digital millivoltmeter and is registered by a recorder or printer. Most recent instruments (Dithermanal or Actimet, Budapest) control the individual steps of the measurement and evaluate the results [1]. Calorimeters produced by Tronac Comp. (Orem, Utah)

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are applicable for all kinds of thermometric analysis. At the Technical University of Brno, small table instruments (Enthalpiograph) of isoperibolic type were designed for different modes of routine analyses [2,3]. The review of available calorimetric instruments used is given in [4].

The broad application of DIE methods in various branches of industry and research is given in [1,5-8]. In following paragraphs, the most promissing applications are outlined including some new methods, not yet published.

The rapid thermochemical analysis often permits the determinations or quality tests not realizable by other methods, e.g. subsequent determination of three components in one solution, determination of one component in two or even three oxidation states (Fe in slags), the possibility to differentiate one compound in the crystalline and amorphous state (SiO_2), measuring of reaction heats and the kinetics at the same time etc.

Many papers were devoted to the total thermochemical routine analysis of slags, cement, glass and other silicates, alloys [1-3,5,6,8]. Rapid determination of SiO_2 can be performed using the complex SiF_6^{2-} forming reaction or by the precipitation reaction giving rise to insoluble K_2SiF_6.

Standard time-consuming gravimetric determination of sulfates can be replaced by rapid thermochemical method measuring the exothermic effect of the same precipitation reaction [9].

In the determination of aluminum, $Sr_3(AlF_6)_2$ is precipitated, which makes it possible to determine milligram amounts of Al [10]. Subsequent determination of Al_2O_3 and SiO_2 in one solution [11] is used in routine analysis of silicates.

The reaction of powdered lime with dilute hydrochloric acid enables to determine the content of the available lime in quicklime [12] even in the mixture with fly ash [13]. Measuring of dissolution heat of cement, hydrated or unhydrated [14,15], makes it possible to determine the effect of different admixtures.

Thermochemical methods enable to distinguish between crystalline and amorphous silicon dioxide; the latter reacts rapidly with the mixture of hydrofluoric and nitric or hydrochlorid acids. Therefore this reaction is especially suitable for the determination of pozzolanic activity of different silicate materials, like fly ashes [16]. This test characterizes not only the chemical composition of the solid material, but also its physical state (fineness).

At present, this assay is used for testing the quality of solid wastes [17] , which is in close connection with the environment protection. Many papers devoted to the analysis of smelter plumes in environmental studies were published by Eatough et al. [18] .

By the measuring of the kinetics of the reactions of glass, ceramics, fibres etc. in acids or alkaline solutions, the resistance to the corrosion of the materials can be studied.

In the determination of water, constitutional or mechanical moisture, the Karl Fischer reagent is used [19] . Thermometric mode is faster than electrochemical titration and makes possible many subsequent determinations in one solution.

Very promissing is thermometric determination of heat of wetting and surface areas, mostly of fine powdered samples [8] . In physical chemistry, thermochemical measurements enable to determine thermodynamic parameters [20,21] . Many papers are devoted to the problems of kinetics of inorganic or organic reactions [22] .

The use of thermochemical analysis in organic chemistry was reviewed by Bark [23] , Jordan [7] and others [6,8] . The increasing number of publications devoted to the thermochemical studies in pharmaceutical chemistry, biochemistry, medicine and other sciences is compiled in the bibliography [8] . The routine rapid determination of ammonia in plants [24] improve the control in agriculture. The disintegration of tablets in water or reagent solutions and the subsequent determination of a component of interest can be performed in one experiment [25] . Only a few analytical determinations are based on a measuring of the heat of resolvation in organic and/or mixed solvents, which is studied by Krestov [26] and others [8] . At present, much attention is paid to the thermochemical research in biochemistry and biology by Wadsö and others [27, 8].

The wide possibilities of TCHA were outlined by the 3rd Seminar on Thermochemical Analysis in 1983 in Mariánské Lázně [28] . Next seminar will be held in 1986 in Hungary.

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