

Special Reviews

DIRECT READING THERMOMETRIC ANALYSIS

A RAPID METHOD FOR SERIAL ANALYSIS IN INDUSTRY

I. SAJÓ

Research Institute for Iron Industries, Budapest, Hungary

(Received February 25, 1969)

According to the direct reading thermometric method the concentration of the component to be determined is established from the temperature variation of the sample solution obtained on adding to it an excess of a reagent which reacts selectively with the respective component. Under suitably chosen experimental conditions the concentration of the respective component is determined from a single measured value. Since the established measurement technique requires little manual work and the respective components may be determined from the sample solution directly without any separations, the method in its present form is chiefly suitable for rapid serial analyses.

Direct-reading thermometric analysis is a recent method of quantitative analysis which is expanding increasingly. The method utilizes for analytical purposes the most common phenomenon accompanying chemical transformations, i.e., the heat of reaction. It is a well-known fact that the amount of heat evolved or consumed during a chemical reaction is a measure of the quantity of reagents which have taken part in the reaction. Thus an analytical method of general applicability can be based on the measurement of the reaction heat, which is equally useful for inorganic or organic quantitative analysis. The measurement of the heat of reaction is rather difficult, however, compared with the analytical methods generally employed and so calorimetry has so far been applied only for solving some special analytical tasks. Theoretically, it can be proved that it is not only the amount of heat evolved or consumed during the reaction, being rather difficult to measure, which is proportional to the amount of the reacting components; in analyses carried out in solutions this is also the case for the temperature variation of the sample solution if the values of certain parameters (the heat capacity of the equipment, of the sample solution, and of the reagent solution, and the molal reaction heat) are all kept constant. In this case the technique of measurement becomes very simple: the concentration of the component in question is obtained from a single measured value, namely from the temperature variation of the sample solution during the reaction. Since the concentration of the component is determined directly by temperature measurement, the method is called direct thermometric analysis [1–3].

In order to illustrate the simplicity of the procedure of direct thermometric analysis, the various steps of the general working procedure are described below [4-6].

1) The sample solution is prepared for analysis according to the given instructions. The instruction for solution preparation is generally different for each type of material. By preparing the solution according to instructions identical values for the specific heat, specific gravity, volume and heat capacity of the sample solution are guaranteed for each determination.

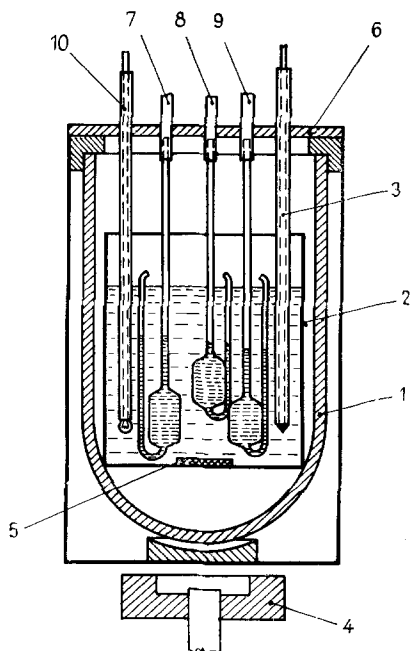


Fig. 1. Sketch of the direct reading thermometric analysing apparatus. 1 - Dewar vessel; 2 - plastic beaker; 3 - thermistor; 4, 5 - magnetic agitators; 6 - cover plate; 7, 8, 9 - dip pipettes; 10 - calorifer

2) The temperature of the sample solution prepared according to instructions is adjusted to the temperature of the measuring cell and the sample solution is placed in the measuring cell (Fig. 1).

3) The thermistor used for temperature measurement, the agitator and the reagent or reagents are dipped into the solution.

The reagent is contained in a dip pipette which prevents the sample solution and the reagent solution from mixing before the introduction of the latter into the sample solution and also guarantees a rapid equalization of the temperature differences of the sample and reagent solutions. The temperature and concentration of the reagent used for analysis should always be adjusted exactly according to the instructions in order to ensure that the heat ca-

capacity of the reagent is constant. For the determinations we use reagents which — as far as possible — react selectively with the component to be determined. The volume of the reagent is chosen to furnish a certain excess of reagent even when the respective component is present in the sample solution in its highest possible concentration. Since out of the reagent present in excess it is always only that part equivalent to the component to be determined which can enter into reaction, the amount of reaction products and the amount of heat evolved during the reaction are determined by the component to be measured. Therefore the heat of reaction evolved is proportional to the concentration of the component to be determined.

4) After waiting for some minutes for the equalization of the temperature differences within the system, the reagent is introduced into the sample solution and the temperature variation of the sample solution during the reaction is observed.

5) The concentration of the required component is evaluated on the basis of the observed temperature difference from calibration graphs established in similar circumstances with model solutions of known composition. However, when a direct reading thermometric device is used for analysis, the results can be read on the detector directly in practical units of concentration (e.g. as a percentage or in g/l) as the analysis channel has been calibrated for direct evaluation with a standard sample of known concentration.

As can be seen from the above, the results of the direct thermometric method are obtained from calibration graphs established with solutions or standards of known concentration or from a similarly calibrated analysing device supplying direct concentration data.

That is to say, the direct thermometric method is a relative method. Such relative methods are useful in the first place for carrying out series analyses. Thus the direct thermometric method in its present form may be proposed chiefly for performing series analyses in plants.

According to the literary data, Howard [1] at the beginning of this century really used this method for the same purpose: he determined the free SO_3 content of fuming sulphuric acid in series from the temperature variation of the sample solution obtained by reacting SO_3 under suitable experimental conditions with H_2O . This was the starting point of direct thermometry. The method itself was used until the middle of the fifties only sporadically and for similar purposes, i.e. for the determination of acid anhydride with water or, conversely, for the determination of water with acid anhydride [7]. There are two reasons for the fact that this very simple method did not find more extended application in laboratories earlier and that its development has only been begun in the last decade by several research groups working independently:

a) The technique of temperature measurement was rather cumbersome before the invention of thermistors and their application to analytical purposes by Linde, Rogers and Hume [8].

b) The methods of thermometric analysis had an insufficient chemical basis. The selective reactions for determining the various components thermometrically had not been developed and the various interfering subsidiary reactions had not been studied. These reactions produced temperature variations in the sample solu-

tion partly in proportion to the concentration of the respective component and partly independently of it. In the types of material occurring in practical analysis – e.g. in the analysis of silicates, metals or plating baths – the relative concentrations of the various components may vary by several orders of magnitude which means that they may mutually disturb the determination of one another. Therefore, it is understandable that the first thermometric determinations were used to solve analytical tasks with large temperature variations accompanying the reaction, which were easy to measure and did not involve the interfering effect of components present in various and varying concentrations.

Thus the development of the direct thermometric method had had to move along in two directions:

1) One of these consisted in a refining of the measuring technique to permit the extension of the method to the determination of components present in low concentrations or for which the molar heat of reaction was small. We have furnished detailed reports on our relevant investigations in some earlier papers [4, 5, 9,10].

2) Direct thermometric methods required a chemical basis with regard to the demands of analysts. Methods had to be developed for determining frequently occurring cations and anions. We had to find out how to take into account or how to compensate for the effects of various interfering subsidiary reactions. We had to study the structure of solutions from the point of view of thermochemistry, since all variations occurring in the structure of solutions – e.g. dissociation, hydration, solvation, etc. – are combined with heat effects, and, since two solutions are always mixed during analysis, the structure of the sample solution changes and we must know the nature and size of the interfering effect to be expected from this source. Finally much work had to be expended on the selection of selective reactions suitable for the direct thermometric determination of various components [11–13].

Methods which are suitable for series analysis in plant control are required to be rapid. It is usually characteristic of rapid methods that the determination of the respective component is carried out without separation since any form of this considerably increases the time of analysis. This is why the thermometric method is able to compete successfully with well-proved and widely used methods of analysis, since in most cases it permits a determination of the component in question without any separation so that the determinations may be performed rapidly and with little manual work. The analysis may be accelerated further by the possibility of determining in most cases several components consecutively in the same sample solution without any separation.

It was indeed this possibility of consecutive determinations which led us to the intensive study of the direct thermometric method, since we were able in the middle of the fifties to perform a relatively complex task in the field of the rapid analysis of silicates, namely the determination of the basicity, the SiO_2 and FeO content of open hearth slags, within 10 minutes by the thermometric method with all three components determined consecutively from the same solution according to the first developed variant of the method [2]. Since very little work had

been expended on the development of this method as compared with the solution of other comparable tasks, we started to develop this promising method to a procedure for general application under plant conditions. On the basis of the experience gained in this work we should like to show in a following paper some possibilities of the application of the method to the determination of one component in a solution containing several other components, and to that of several components in one solution, without separation.

References

1. H. HOWARD: Chem. Zentralblatt, I (1910) 1452.
2. I. SAJÓ: Kohászati Lapok, 7 (1957) 287.
3. J. C. WASILEWSKI, P. T. S. PEY, I. JORDAN: Anal. Chem., 36 (1964) 2131.
4. I. SAJÓ, J. ÚJVÁRY: Z. anal. Chem., 202 (1964) 177.
5. I. SAJÓ, B. SIPOS: Z. anal. Chem., 222 (1966) 23.
6. I. SAJÓ, B. SIPOS: Talanta, 14 (1967) 203.
7. L. H. GREATHOUSE, H. J. JANSSEN, C. M. HAYDEL: Anal. Chem., 28 (1956) 257.
8. H. W. LINDE, L. B. ROGERS, D. M. HUME: Anal. Chem., 25 (1953) 404.
9. I. SAJÓ, B. SIPOS: Mikrochim. Acta, (1967) 2, 248.
10. I. SAJÓ: Hungarian Scientific Instruments, 12 (1967) 1.
11. I. SAJÓ: Communications of the Research Institute of Ferrous Metallurgy, 2 (1965) 684.
12. I. SAJÓ: Dissertation (1965).
13. I. SAJÓ: Magy. Tud. Akad. Kém. Közlemény. 26 (1966) 119.

RÉSUMÉ. — Selon la méthode thermométrique à lecture directe, on détermine la concentration du constituant cherché d'après la variation de température de la solution échantillon que l'on additionne d'un excès de réactif sélectif de celui-ci. Dans les conditions expérimentales appropriées, une seule mesure suffit pour déterminer la concentration du constituant cherché. Comme la technique de mesure qui a été mise au point demande peu de travail et comme on peut doser sans aucune séparation les constituants étudiés, la méthode dans sa forme actuelle se prête en premier lieu aux dosages en séries industriels.

ZUSAMMENFASSUNG — Bei der thermometrischen Methode mit Direktablesung wird die Konzentration der gesuchten Komponente aus der Temperaturänderung der Probelösung bestimmt, die nach Zugabe eines Überschusses von einem selektiv reagierenden Reagens wahrnehmbar ist. Unter geeigneten Versuchsbedingungen kann man die Konzentration der gesuchten Komponente aus einem einzigen Meßwert, nämlich der Temperaturänderung der Probelösung bestimmen. Da die ausgearbeitete Meßtechnologie wenig Arbeit erfordert und die gesuchten Komponenten ohne jede Trennung direkt bestimmt werden können, ist die Methode in ihrer jetzigen Ausführungsart hauptsächlich zu betriebsmäßigen Serien-Schnellanalysen geeignet.

Резюме. — По термометрическому методу визуального отсчета можно определить концентрацию компонента измерением изменения температуры пробного раствора, полученного добавлением к нему избытка реагента, реагирующего избирательно с исследуемым компонентом. При соответствующих условиях эксперимента концентрация компонента определяется однократным измерением. Измерение описанным методом требует мало ручных операций. Можно определить исследуемый компонент непосредственно, не выделяя его из пробного раствора. В описанном виде метод можно применять в лабораториях при проведении серийных анализов.