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POSSIBILITIES OF SELECTIVE THERMOMETRIC DETERMINATIONS IN MULTI-COMPONENT SYSTEMS

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The methods elaborated for the thermometric determination of the component to be analyzed in samples containing several interfering components are described. The following possibilities have so far been found for performing the determinations: The application of selective or partially selective reactions. Increasing the selectivity of the reactions by masking the interfering components. Increasing the selectivity of the reactions by utilizing the differences in behaviour of the various components towards the reagent, as for instance, differences in solubility, in stability constants, in the variation of the stability constants with pH, in the reaction rate. The use of indirect methods. Finally the correction of the interfering effect of certain components by calculation in the case of binary and multicomponent systems.

The direct-reading thermometric method is a relative method, since the results are evaluated by means of a calibration graph established with model solutions [1—4] of known composition or, when using special equipment, with known standards [5, 6]. Methods of this type are suitable mainly for serial analyses; the time expended on standardization and calibration is recovered only in the analysis of several samples. Many components may be determined quickly by the direct-reading thermometric method which in its present form is a rapid method for industrial serial analysis [7, 8]. Samples analysed in plant laboratories usually contain several components. Since rapidity is the chief advantage of the methods, the analyses should be carried out so as to permit the determination of various components as far as possible without separation. Below we give a detailed description of the possibilities of thermometric determinations without separation.

The basic principle of thermometric determinations carried out in the presence of other components is very simple. We have to use reagents which react selectively with the component to be determined. The determination of various elements has to be accomplished as otherwise the method is incapable of general application. Below we shall give a detailed description of various methods to be used in a given case.

Almost all types of reaction may be used successfully as the measured reaction in thermometry, as for instance the formation of a precipitate, reduction-oxidation reactions, complex formation, addition, double decomposition etc. [9—13, 30, 31]. The chosen reactions must usually be modified, however, according to the requirements of thermometric analysis. Below we present some examples as a practical illustration.

Determinations based on the formation of precipitates

The determination of barium may be achieved via the formation of a precipitate, of barium sulphate [5]; this is accompanied by the evolution of a significant heat of reaction which permits the thermometric determination of barium; using this reaction it is possible to determine barium in almost all types of material.

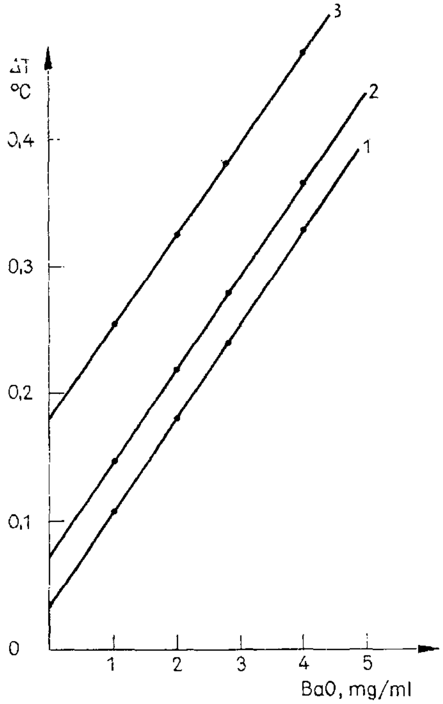

Fig. 1. Calibration graphs for the evaluation of the BaO content. 1) 1 ml, 2) 2 ml, 3) 5 ml sulphuric acid (specific gravity 1.3)

The precipitation of barium sulphate does not proceed instantaneously (this is also the case in other precipitation reactions) especially when the concentration of barium ions in the solution is low. Therefore a barium sulphate suspension is added to the solution before the determination to provide crystal nuclei which strongly accelerate the process. In the case of a prolonged reaction the effects of the environment must be taken into account since it is impossible to insulate the system from its environment for a long period with regard to heat transfer. Hence one must endeavour to increase the rate of reactions.

The chosen example is also suitable for illustrating the interfering effects of subsidiary reactions and the methods of their elimination.

When sulphuric acid is used as precipitant the heat of hydration of sulphuric acid has to be taken into consideration in addition to the heat of precipitation of barium sulphate. It is easy to see that the heat of hydration, which is independent of the barium concentration of the solution, will always be constant if the same volume of sulphuric acid of the same concentration is used for each determination. In this case the calibration curve established for the evaluation of the barium content will not pass through the origin of coordinates. The results may be evaluated from the calibration graph only as long as the same volume of sulphuric acid of the same concentration is used for analysis as has been used to establish the calibration curve. Any variation of the concentration or volume of sulphuric acid will cause a parallel shift of the calibration curve (Fig. 1).

When the volume and the concentration of the reagent are held constant and the results are evaluated from the calibration graph, this type of subsidiary reaction will cause an error only if the temperature variation of the sample solution caused by subsidiary reactions is excessively high (e.g. if it amounts to more than 10–20% of the scale of the reading instrument). In this case the addition of one drop more or less of the reagent will produce a temperature variation which may surpass that caused by the main reaction in the sample solution. Therefore it is best in thermometric analysis to use a reagent for which no heat of dilution can be observed, or perhaps with a decreased amount of heat of dilution. The heats of dilution may be compensated by chemical methods or by means of a suitable measuring technique. If the heats of dilution of the reagents are too high, they may be compensated most expediently by chemical means.

The compensation of the heat of dilution by chemical means [5, 6]

Reagents for which no heat of dilution can be observed are generally binary systems, e.g. sulphuric acid and ammonium sulphate. It is easy to see that there must exist a certain sulphuric acid to ammonium sulphate ratio in which the heat of hydration of sulphuric acid and the heat of dissociation of ammonium sulphate exactly balance when the solution is mixed with a medium of a given composition.

Smaller amounts of heats of dilution may be compensated by means of a suitable measuring technique [14, 15]. One of these uses the method of thermometric difference measurement. This consists in preparing a blank solution which contains all the reagents occurring in the sample solution except the component to be determined. During analysis the same volume of reagent of the same concentration is added to both the sample and the blank solution. This addition produces in the sample solution both the main reaction and the subsidiary reactions, but in the blank solution only the latter. The temperature variations of the solutions are measured by separate thermistors which are interconnected so that the temperature differences caused by the subsidiary reactions compensate each other. The result of the measurement is the temperature difference of the main reaction. This method is often better than the one mentioned above (use of reagents for which no heat of reaction can be observed) since the exact compensation of the heats of dilution requires a relatively long time; this latter method, however, requires only reagents with reduced heats of dilution which are easy to prepare;

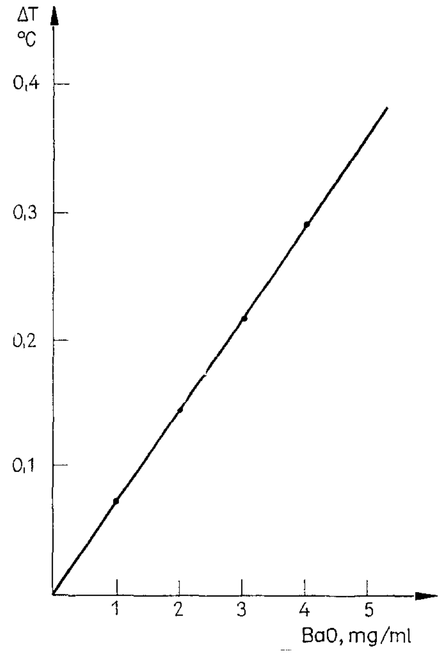

Fig. 2. Calibration curve for the evaluation of the BaO content (heat of dilution of sulphuric acid compensated for)

the residual heats of dilution are compensated by the technique of measurement. This compensation may be carried out in other ways also, e.g. by shifting the scale of the sensing instrument, as has been described in detail in a previous publication [13]. After the compensation of the heats of reaction the calibration curves pass through the origin of coordinates (Fig. 2).

The method described above has often been applied successfully in thermometric analysis. The application of many selective reagents (especially organic ones) has been hindered, however, by the fact that we have been unable so far to compensate their heats of solvation or hydration, or to reduce them to an acceptably low level.

The application of oxidation-reduction reactions

The possibilities of applying oxidation-reduction reactions will be illustrated by the example of the determination of iron and manganese.

For the determination of iron a suitably modified form of the Zimmermann–Reinhardt method may be used [5, 16]. Hydrofluoric acid is usually added to the sample solution to transform iron(II) to a fluoro complex which prevents its oxidation by atmospheric oxygen. The solution prepared in this way is placed in the measuring cell and iron(II) is oxidized to iron(III) by a suitable selective oxidant; the temperature variation of the sample solution is observed. We have found ammonium persulphate to be the most suitable selective oxidant, but in some cases hydrogen peroxide may be used equally well. Potassium permanganate solution cannot be used, since the reagent must always be used in excess in thermometric analysis and any excess of potassium permanganate will react with hydrochloric acid in the solution at a measurable rate, thus rendering the end point of the reaction rather indefinite. The above method permits the determination of a 50% iron content in iron ores with an absolute error of ±0.2%.

In the analysis of iron a selective oxidant was needed to oxidize iron(II); conversely in the determination of manganese according to Procter–Smith, formalin solution was found to be a selective reductant [17]. Manganese(VII) ions are reduced selectively by formalin solution in the presence of chromium(VI) and vanadium(V) ions and the thermometric manganese determination developed on this basis may be used just as extensively as the original Procter–Smith method.

The application of complexing agents

Our investigations have shown that most of the problems in direct thermometry may be solved with complexing agents. Inorganic ligands are especially significant in this respect and among them the most important is the fluoride ion. Our tests have shown that fluoro complexes will play a similarly important role in analysis (by way of the thermometric methods) as do iminoacetic acids among organic complexants in volumetric analysis.

As an example of the application of inorganic complexing agents silicic acid may be determined thermometrically in almost all types of material in the form of the complex K_2SiF_6, just as copper may be determined at pH 6–7 with the organic complexant thiourea in the presence of almost all cations [12, 18].

Partially selective reactions

The methods described above are so selective that their application permits the determination of the component in question in the most varied types of material by the same working method. However, it is not possible to find such a selective method for every component. In such cases different reactions are used for determining the same component in different types of material, and the reaction is selected to exclude any interference by at least those components which may be counted upon to be present in this type of material. E.g. the determination of boric acid in plating baths may be carried out with hydrofluoric acid [6], since the bath does not contain any component which reacts with hydrofluoric acid; the determination of boric acid in glasses may be carried out with mannitol [19], since the presence of SiO_2 and Al_2O_3 in the glass hinders the determination of boric acid with hydrofluoric acid.

Increasing the selectivity of reactions by masking the interfering component

If no suitable selective reaction can be found for determining some component without any side effects from the components present in the solution, the reaction may be rendered selective by masking the interfering components. E.g. molybdenum may be determined very easily thermometrically with hydrogen peroxide. Various alloys, however, very often contain significant amounts of titanium in addition to molybdenum and this also reacts with hydrogen peroxide. Titanium(IV) ions in an acidic medium form a stable complex with hydrofluoric acid; thus they may be masked with respect to hydrogen peroxide and molybdenum may be determined thermometrically with hydrogen peroxide in the presence of titanium and hydrofluoric acid [20].

In certain cases there are several components in the solution which hinder the reaction chosen for determining the respective component and these cannot be masked by a single reagent. For instance potassium cyanide has been found to be the most suitable reagent for the determination of zinc in manganese–zinc ferrites. Potassium cyanide, however, also reacts with iron(III) and manganese(II) ions and so these have to be masked. Zinc determination may be carried out with potassium cyanide if iron is masked with tartaric acid and manganese with EDTA [21].

The application of complexants also increases the selectivity of many oxidation-reduction reactions. For instance it is possible to determine thallium(III) in the presence of almost all cations thermometrically and selectively, if the cations present besides thallium(III) [e.g. iron(III)] are transformed into complex compounds with EDTA at pH 4–5; after the formation of the metal chelates sodium sulphite solution is added as reagent to the sample solution to reduce thallium(III) selectively to thallium(I) with the evolution of a significant amount of heat of reaction [12, 22].

The sufficient precondition of selectivity in the case of binary systems [23]

Masking of the interfering ions is not always possible, but it is not always necessary. This is often the case in the analysis of binary systems, i.e. those types of material in which the sum of the concentrations of the two main components approaches 100% and other possible components occur only as contaminants. Such materials are, for instance brass, which consists of copper and zinc; and calcined limestone, which may be regarded as a mixture of calcium oxide and calcium carbonate according to the degree of calcination.

In binary systems (as will be shown below) the concentrations of both components may be determined thermometrically from a single measured value if both components react with the applied reagent and the temperature variations produced by the same concentrations are different for the two components.

For instance, brass is dissolved and the sample solution suitably prepared. Potassium cyanide is added to react with both copper and zinc. The relationship between the temperature variation measured and the copper and zinc content of the sample can be expressed by the following equation:

$$\frac{a}{100}\Delta T_1 + \frac{(100-a)}{100}\Delta T_2 = \Delta T \qquad (1)$$

where a is the percentage copper content of the sample,
$(100 - a)$ is the percentage zinc content of the sample,
ΔT_1 is the temperature variation which would be obtained on analyzing a sample containing 100% copper,
ΔT_2 is the temperature variation which would be obtained if the sample contained 100% zinc,
ΔT is the temperature variation obtained in the analysis of the sample containing a % copper and $(100 - a)$ % zinc.

From Eq. (1) the percentage copper content of the sample is given by the following expression:

$$a = 100\frac{\Delta T - \Delta T_2}{\Delta T_1 - \Delta T_2} \qquad (2)$$

The analysis of Eq. (2) shows that the value of a can be calculated from the measured data when

$$\Delta T_1 \neq \Delta T_2$$

Thermometric analysis may be carried out the more accurately the larger the difference between ΔT_1 and ΔT_2.

The efficiency of limestone calcination is just as easy to control on the basis of the temperature variation obtained in consequence of the evolution of the heat of neutralization during the dissolution of the limestone sample in hydrochloric acid.

Possibilities of evaluating the results when non-selective reagents are used

The masking of the interfering components, however, does not always yield the necessary results. For instance, if silicic acid is determined with hydrofluoric acid in the presence of aluminium and titanium, all three components will react with hydrofluoric acid and produce a significant amount of heat of reaction. In this case it is impossible to mask titanium and aluminium, since there is no known complexing agent which produces more stable complexes with these ions than does fluoride. However, thermometric analysis can be carried out in this case too. There are two possibilities:

1) the use of corrections,

2) the separation of the interfering components.

ad 1) The method of applying corrections is useful when the heat effect produced by the interfering components is significantly less than the heat effect due to the component to be determined. If it is larger than, or equal to, the main heat effect, the correction usually introduces a rather large error in the analysis which surpasses the error permitted in the determination. The cases where correction is permitted may be classified into two groups:

A) *The disturbing components and the components to be determined are present in varying concentrations.* The determination of the SiO_2 content of blast furnace slags may serve as an example [5]. Blast furnace slags contain generally 30–45% SiO_2, 5–15% Al_2O_3 and 0–2% TiO_2. When hydrofluoric acid is used as reagent for determining the SiO_2 content, all three components will react with it and the sum of the temperature variations produced is measured during analysis. A correction may be introduced, however, for the temperature variation due to the interfering components and thus it is possible to calculate the temperature variation produced by the main component. We must know

a) the concentration of the perturbing component, or, if we determine it by some independent reaction (e.g. with H_2O_2 for TiO_2),

b) the percentage of the component to be determined corresponding to the temperature variation produced by 1 per cent of the disturbing components. In the present case for instance:

the temperature variation produced by 1% Al_2O_3 corresponds to 0.22% SiO_2, and the temperature variation produced by 1% TiO_2 corresponds to 0.29% SiO_2.

Hence it is possible to determine the SiO_2 content of blast furnace slags with hydrofluoric acid.

B) *The concentration of the interfering component is constant.* This case is more simple than that described in A) since the temperature variation produced by the interfering component present in a constant concentration may be regarded as constant; when the calibration graph is established with the aid of standard samples of the same type it will already include the correction.

The determination of the Si content of cast iron is presented as a relevant example [15]. The iron content of cast iron may be regarded as constant to within

1 to 2 per cent. When hydrofluoric acid is used as reagent to determine the silicon content, both the silicon and the iron contained in cast iron will react with it. The temperature variation produced by a 1% iron content, however, corresponds only to a temperature variation produced by 0.08% Si. Thus a variation of the iron content of 1 to 2 per cent only produces a fluctuation of the silicon content of 0.01 – 0.02 per cent. It is not necessary to apply a separate correction for this; if the calibration curve is established with cast iron samples of known Si content, it will include the necessary corrections. Many similar cases may be encountered in direct thermometry.

ad 2) The determination of the Al_2O_3 content of cements [24] is given as an example of the separation of the interfering components.

Cements usually contain 4 – 5 per cent Al_2O_3 besides about 20 per cent SiO_2. Our tests yielded the result that the thermometric determination of both aluminium and silicic acid is accomplished most easily with hydrofluoric acid. The heat effect due to 20% silicic acid is, however, much larger than that produced by 5 per cent Al_2O_3. Therefore we have found that Al_2O_3 may be determined reliably only when it is separated from silicic acid. The latter is dehydrated with sulphuric acid and filtered off; Al_2O_3 may be determined accurately in the filtrate.

Various possibilities for increasing the selectivity of the reaction used

The possibilities are the following: differences in solubility, in stability, in the behaviour as a function of pH, and in the rate of formation. These may be illustrated by some practical examples.

a) *The use of differences in solubility* [25]

The fluoro complexes of various metals give salts of various solubilities with alkali and alkaline earth metals. The least soluble of these is potassium hexafluorosilicate. This observation may be applied to the selective determination of SiO_2. In practice the sample is dissolved in hydrofluoric acid with the transformation of SiO_2 to H_2SiF_6, while the disturbing components (e.g. Al_2O_3 and TiO_2) yield the fluoro complexes H_3AlF_6 and H_2TiF_6. A solution of potassium chloride is added to precipitate K_2SiF_6 from the mixture of fluoro complexes with the evolution of a significant amount of heat of reaction. This method is suitable for determining the SiO_2 content in the presence of Al_2O_3 and TiO_2 directly, without any separation or correction.

b) *Utilizing the dependence of the stability of complexes on the pH*

As a practical example we give the thermometric determination of Al_2O_3 in the presence of silicic acid and TiO_2 without any separation [26].

The reaction of neutral aluminium hydroxide with potassium or sodium fluoride produces free sodium hydroxide. This reaction shows that the fluoro complex of aluminium is stable even in a relatively strongly basic medium. The fluoro complexes of other metals are hydrolyzed under similar conditions. This reaction is therefore applicable not only to the selective qualitative detection of aluminium but also to its selective quantitative thermometric analysis. In practice the Al_2O_3 precipitate is deposited from solution at pH 7 and a mixture of sodium carbonate and bicarbonate is added to the solution as a buffer. When a solution of potassium fluoride is added to the prepared sample solution it reacts with aluminium hydroxide with the formation of free potassium hydroxide; this immediately reacts with bicarbonate with the evolution of a significant heat of reaction. Since silicic acid and titanium do not yield this reaction, aluminium may be determined in their presence.

c) *Utilization of the differences in reaction rate*

Jordan and Billingham [27] were the first to employ this possibility when they developed the thermometric titration of calcium with ammonium oxalate in the presence of magnesium ions as a result of their observation that oxalate ions react more rapidly with calcium than with magnesium ions. They very aptly named this method of separation kinetic masking. They used the more rapidly proceeding reaction for analytical purposes; below we present an example for the application of the slower reaction [29].

The determination of Al_2O_3 in cements and blast furnace slags without separation is a suitable example. We have found that aluminium ions form a readily acid-soluble calcium fluoroaluminate complex with hydrofluoric acid in the presence of a large excess of calcium ions. On the addition of potassium ions the compound $CaKAlF_6$ is precipitated. The precipitation, however, does not take place instantaneously. The rate of precipitation may be controlled by the amount of potassium chloride added. The reaction starts at a measurable rate within 3 to 4 minutes after the addition of potassium salt. If SiF_6^{2-} ions, which react instantaneously with potassium ions, are also present in the solution, two heat steps, definitely separated in time, are obtained; the first step corresponds to the formaation of K_2SiF_6 and the second to the formation of $CaKAlF_6$; in this way Al_2O_3 may be determined in cement and blast furnace slag on the basis of the difference of precipitation rates without any further separation.

The methods described above are direct methods of analysis for several components present in the same solution. However, in thermometric analysis we often employ indirect methods.

Molybdate ions form a complex with peroxide, in a medium containing nitric acid, with the evolution of a significant heat of reaction. Molybdate bound in the ammonium phosphomolybdate complex does not produce this reaction. If varying amounts of phosphate are precipitated with a fixed excess amount of molybdate solution of the same concentration, then the addition of hydrogen peroxide to the solution without any preliminary filtration of the precipitate yields a temperature variation which is the smaller the higher the original phosphate content of the solution since less free molybdate ions remain in solution. On measuring the temperature variation of the solutions after the addition of hydrogen peroxide the phosphate content of the sample may be determined indirectly with the aid of a calibration curve established under similar circumstances [9].

The ammonia content of ammonium salts is also easy to determine by an indirect method [28]. In practice the weighed sample is dissolved and neutralized and a constant excess of sodium hydroxide is added to the neutral solution. This liberates the ammonia which may be eliminated by boiling for 4 to 5 minutes. When no traces of ammonia can be found in the fumes with an indicator paper, the solution is cooled, placed in the measuring cell and neutralized by the addition of excess nitric acid or perchloric acid. The heat of neutralization obtained in this reaction is smaller the more the ammonia is eliminated from the solution by boiling. This permits the determination of the ammonia content by an indirect method.

Thermometric methods may also be utilized in organic analysis [11, 12]. For instance formalin reacts in a basic medium with potassium cyanide, permitting its rapid and simple determination; similarly phenol can be determined by its reaction with bromine water, and urea by its reaction with nitrite in acidic solutions.

In inorganic analysis this method is of general usefulness already, since it permits very complicated analyses such as those of metals, ores, rocks or silicates. Each component is analyzed thermometrically without filtration or other separation. Thus the results require very little manual work, the methods may be accelerated further and will require even less work, when several components are determined consecutively in the same sample solution by a combination of the methods described above. These possibilities will be discussed in detail in the near future.

References

1. H. HOWARD, Chem. Zentr., I (1910) 1452.
2. L. H. GREATHOUSE, H. J. JANSSEN and C. M. HAYDEL, Anal. Chem., 28 (1956) 257.
3. I. SAJÓ, Kohász. Lapok, 7 (1957) 287.
4. J. C. WASILEWSKI, P. T. S. PEY and J. JORDAN, Anal. Chem., 36 (1964) 2131.
5. I. SAJÓ and B. SIPOS, Z. Anal. Chem., 222 (1966) 23.
6. I. SAJÓ and B. SIPOS, Talanta, 14 (1967) 203.
7. I. SAJÓ and J. UJVÁRY, Z. Anal. Chem., 202 (1964) 177.
8. I. SAJÓ, Hung. Sci. Instr., 1 (1967) 1.
9. I. SAJÓ and B. SIPOS, Mikrochim Acta, 2 (1967) 248.
10. J. JORDAN, Chimia (Aarau), 17 (1963) 101.
11. I. SAJÓ, Vasipari Kutató Intézet Évkönyve, 2 (1965) 684.
12. I. SAJÓ, Dissertation 1965.
13. I. SAJÓ, Magy. Tud. Akad. Kém. Oszt. Közlemény., 26 (1966) 119.
14. H. J. KEILLY and D. M. HUME, Anal. Chem., 36 (1964) 543.
15. I. SAJÓ, Z. anal. Chem., 242 (1968) 165.

16. I. SAJÓ and B. SIPOS, Bányász. Lapok, (in the press).
17. I. SAJÓ and B. SIPOS, Radex Rundschau, 3 (1968) 178.
18. I. SAJÓ and B. SIPOS, Ind. Ceram. (in the press).
19. I. SAJÓ, Hung. Sci. Instr., 14 (1968) 21.
20. I. SAJÓ, W. FÖRSTER and H. RUDIGER, Neue Huette, 12 (1967) 500.
21. B. SIPOS and I. SAJÓ, Proceedings of the Analytical Chemical Conference (1966) 455.
22. I. SAJÓ, Acta Chim. Acad. Sci. Hung., 28 (1961) 253.
23. I. SAJÓ and B. SIPOS, Kohász. Lapok, 101 (1968) 484.
24. I. SAJÓ and B. SIPOS, Zement-Kalk-Gips, 32 (1968).
25. I. SAJÓ and B. SIPOS, Tonind. Ztg. Keram. Rundschau, 92 (1968) 88.
26. I. SAJÓ, Analytical Chemical Conference, Balatonszéplak (1965) 101.
27. J. JORDAN and E. J. BILLINGHAM, Anal. Chem., 33 (1961) 120.
28. I. SAJÓ, Magy. Kém. Lapja (in the press).
29. I. SAJÓ, Metallurgie (Paris), 101 (1969) 95.
30. L. S. BARK and E. BARK, Thermometric titrations. Elsevier, 1968.
31. J. TYRREL, Thermometric titrations. London, 1968.

RÉSUMÉ. — On a appuyé par des exemples les possibilités de dosage thermométrique d'un constituant dans une solution contenant plusieurs ions gênants. Le dosage peut s'effectuer à l'aide de réactions sélectives ou partiellement sélectives. On peut améliorer la sélectivité en masquant les constituants gênants. Un autre moyen d'améliorer la sélectivité consiste à mettre à profit des différences individuelles dans le comportement des différents constituants vis-à-vis d'un réactif. Telles sont les différences dans les valeurs des constantes de stabilité et dans la variation de ces valeurs en fonction du pH. Finalement, dans certains cas, on peut éliminer par le calcul les effets gênants des systèmes contenant deux ou plusieurs constituants.

ZUSAMMENFASSUNG. — An Beispielen wurden die Möglichkeiten der thermometrischen Bestimmung einer Komponente in mehrere störende Komponenten enthaltender Lösung gezeigt. Hierbei kann man selektive oder teilweise selektive Verfahren anwenden. Die Selektivität kann durch Maskierung der störenden Komponenten erhöht werden. Es läßt sich eine verbesserte Selektivität erzielen, indem man die individuellen Differenzen der verschiedenen Komponenten gegenüber einem Reagens ausnützt, wie z. B. Differenzen in Löslichkeit, in den Stabilitätskonstanten und deren Änderung im pH-Wert. Die störenden Einwirkungen können in gewissen Fällen bei aus zwei oder mehr Komponenten bestehenden Systemen auch rechnerisch korrigiert werden.

Резюме. — Описаны методы определения термометрическим способом компонента, находящегося в анализируемых образцах, в присутствии некоторых мешающих компонентов. До сих пор для выполнения работ такого характера имелись следующие возможности: Применение избирательных и частично избирательных реакций. Повышение избирательности реакций маскировкой мешающих компонентов. Повышение избирательности реакций использованием различий в поведении компонентов по отношению к реагенту, например разница по растворимости, по постоянным стабильности, по изменению постоянных стабильности в зависимости от pH, по скорости реакции. Использование косвенных методов и наконец, расчетные поправки на мешающие эффекты, обусловленные некоторыми компонентами, в случае бинарных и многокомпонентных систем.