ENTHALPIMETRIC DETERMINATIONS WITH SODIUM HYPOBROMIT

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The applicability of sodium hypobromite as a reagent in enthalpimetric determinations of various organic and inorganic compounds is reviewed. Using this method it is possible to determine various oxidizable nitrogen and sulphur compounds, e.g. ammonium salts, urea, α-amino acids, sulphides, sulphites, thiosulphates, organic compounds with sulphidic sulphur, aromatic amines, mono- and polyphenols, and other compounds. Determinations are sufficiently precise and sensitive. The enthalpy changes of these reactions are approximately 10^2 to 10^3 kJ mole^{-1}. Suggested determinations are advantageous due to their simplicity, quickness and possible automatization of measurements.

Solutions of alkali metal hypobromites, which may be easily prepared by the action of bromine upon aqueous solutions of alkali metal hydroxides, are frequently applied as oxidants in quantitative analysis. During these oxidation-reduction reactions hypobromites change into bromides according to Eq. (1) [1–5]:

$$BrO^- + H_2O + 2e \rightarrow Br^- + OH^-; \quad E^0 = +0.76\,V \tag{1}$$

At first individual papers were published referring to the application of hypobromites in titrimetric determinations [6–9]. Later, Jellinek and Kresteff [10] suggested hypochlorites as a general agent for oxidimetric titrations. However, great problems arose when solutions of hypochlorites and hypobromites were used for titrations, because of their instability. Another problem in these titrations was the selection of a suitable method for the indication of the equivalence point. Many authors studied the application of hypochlorites and hypobromites for titrimetric analyses. Kolthoff and Stenger [11] suggested application of a more stable solution of calcium hypochlorite instead of unstable alkali metal hypochlorites, and addition of potassium bromide to the titrated solution so that hypobromite formed during the titration exhibited oxidative action. In most titrations it is recommended to add excessive amount of titrant (= reagent) to the titrate (= analyzed substance) and to re-estimate the excess of titrant by means of direct or indirect titration. Many authors studied various methods of application of hypochlorites and hypobromites in titrimetric analysis and developed various methods of assays with these reagents (see surveys of literature dealing with oxidation-reduction titrations [2, 3]).

Tomiček et al. [12, 13] tested possibilities of application of hypochlorites and hypobromites in direct potentiometric titrations and studied the course of oxidation-reduction reactions during the titration. They also pointed out that a certain amount of bromate (giving different oxidation-reduction reactions than hypobromite) may be formed in solutions of hypobromite, and that this may be the source of errors in stoichiometric calculations of the titrate concentration.

Hypochlorite or hypobromite solutions were also used as titrants in amperometric titrations [14–17].

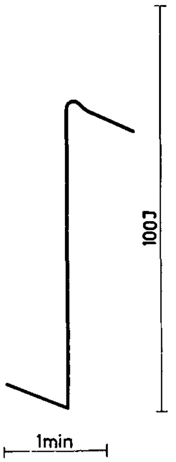

Fig. 1. Enthalpogram obtained during the reaction of ammonium sulphate with sodium hypobromite in 0.5 *M* sodium hydroxide solution. Approximately 3 ml of sodium hypobromite solution was added to 100 ml of ca 0.5 *M* sodium hydroxide containing 0.1 millimole of ammonium sulphate (i. e. 2.8 mg of nitrogen). Voltage on the Wheatstone bridge: 200 mV. Scale range of the recorder: 0–1 mV

The oxidative action of hypobromite was utilized in coulometric titrations [18–20]. In these assays hypobromite is formed directly in solution during the coulometric titration through the anodic oxidation of bromide in alkaline solution.

The present paper deals with possible use of hypobromite in enthalpimetric (thermometric) experiments.

For measurements, direct injection enthalpimetry (DIE) [21–28] was used, called by Vaughan [29] enthalpimetric titration; this method represents a more modern application of the well-known thermometric titrations [29–36]. When this method is used, titrant in excess is injected to the titrate, and the change of temperature resulting from the heat developed during the chemical reaction is recorded (Fig. 1). If the rate of reaction is greater than that of titrant application, a sudden change in the temperature of the titrate occurs. If a constant thermal capacity of the system is ensured by means of application of constant volumes of uniformly prepared titrates, addition of small constant volumes of the same concentrated titrant solution, use of identical starting temperatures of titrates, titrants and equipment, then this temperature change ΔT is directly proportional to the concentration of substance (c) in titrate:

$$c = k\Delta T \qquad (2)$$

In Eq. (2) c is the molar concentration of the estimated substance in the titrate, and k the corresponding constant of proportionality.

The concentration of the estimated substance may also be expressed in other concentration units (e.g. mass percentage, grams per litre, etc.); in this case Eq. (2) is also valid, but with other values of the constant of proportionality.

The use of alkali metal hypobromite as a reagent is suitable, especially due to the fact that direct injection enthalpimetry may also be carried out with unstable reagents. When this method is used, a great excess of reagent is injected into the analyzed solution and the reaction heat produced is measured; the decomposition of a small amount of reagent may not affect the accuracy of measurements.

Experimental

Enthalpimetric titrations were carried out by means of the enthalpimeter developed by Brandstetr et al. [37–38].

Each sample (0.5 to 5.0 ml) was made up to a constant volume (100 ml in a volumetric flask) with a solution of sodium hydroxide (mostly 0.5 *M* NaOH).

As reagent the solution of sodium hypobromite (20 ml of bromine in 1000 ml of 1 *M* sodium hydroxide solution) proved to be very suitable.

Approximately 3 ml of sodium hypobromite was added to the sample solution by means of an immersible pipette after the equalization of the temperatures. In the case of samples of some aromatic compounds, in which not only oxidative but also halogenative reactions might take place, 5 ml of reagent was added, instead of 3 ml, to ensure a sufficient excess of reagent during the reaction.

A thermistor (11 NR, PRAMET, Šumperk, ČSSR) was used to measure the temperature of the analyzed sample during the reaction. A corresponding change in the voltage on a Wheatstone bridge was recorded on an electronic line compensative recorder EZ 7 (Laboratorní přístroje, Prague).

In our experiments the voltage of the Wheatstone bridge, the measurement range of the recorder, and the rate of chart drive were 200 mV, 0–1 mV, and 40 mm per min, respectively.

The concentration of analyzed substances in the sample was estimated by means of calibration curves expressing the dependence of measured deviations upon the concentration of the unknown substance; these curves were constructed on the basis of measurements with standard solutions.

A detailed description of the apparatus and the method may be found in [37–40].

Results and discussion

The titrimetric determination of ammonium salts with hypobromites is a relatively well-known method [1–3]. In reactions of ammonium salts with hypobromites in alkaline solution ammonia is oxidated to nitrogen according to Eq. (3):

$$2NH_3 + 3BrO^- \rightarrow N_2 + 3Br^- + 3H_2O \qquad (3)$$

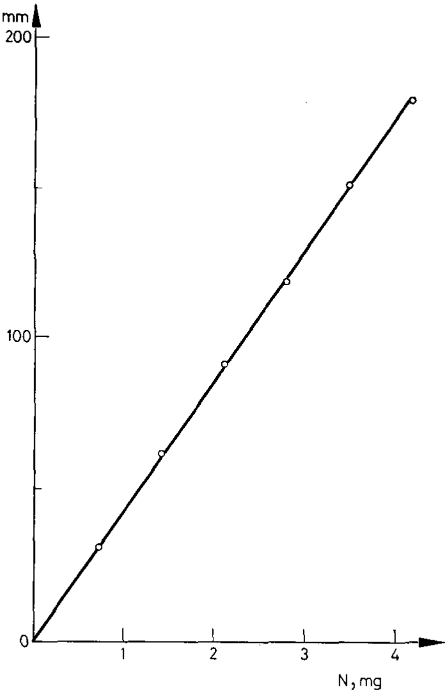

Fig. 2. Dependence of the recorder deviation on the concentration of ammonium sulphate (quoted in mg of N in 100 ml of analyzed solution). Approximately 3 ml of sodium hypobromite solution was added to 100 ml of ca 0.5 *M* sodium hydroxide containing 0.025 to 0.150 millimole of ammonium sulphate (i. e. 0.7 to 4.2 mg of nitrogen). Voltage on the Wheatstone bridge: 200 mV. Scale range of the recorder: 0—1 mV

When measuring this reaction by direct injection enthalpimetry, we found that the reaction is very suitable for this purpose because it was very quick and developed considerable amounts of heat which were directly proportional to the concentration of ammonium salts in the solution (Figs 1 and 2).

In the first enthalpimetric assays the oxidation of ammonium salts with hypobromite was carried out in the presence of sodium tetraborate recommended for titrimetric determinations of ammonium salts [1–3]. Later, however, it was found that in enthalpimetric assays it was more convenient to oxidize ammonium salts with hypobromite in sodium hydroxide solution. In contrast to enthalpimetric determinations in the presence of sodium tetraborate, the value for a blank experiment carried out in solution containing sodium hydroxide was zero, i.e. no heat was developed after the addition of alkali metal hypobromite solution into that of sodium hydroxide without ammonium salts. In enthalpimetric assays the zero value for blank experiments is very convenient because it is not necessary to add the titrant so accurately.

Experimentally, it was also tested whether changes in the concentration of sodium hydroxide and the time of standing of ammonium salts in the presence of sodium hydroxide affected the results obtained. Many measurements showed that changes in the alkalinity of the solution (from 0.05 to 0.5 *M* sodium hydroxide) did not affect the heat produced during the reaction. Further, it was demonstrated that solutions of ammonium salts were sufficiently stable in both 0.05 and 0.5 *M* sodium hydroxide and that they did not decompose to produce ammonia, because identical values were obtained in enthalpimetric assays carried out as late as after three hours of standing of these solutions.

By means of high-sensitivity measurements it was possible to analyze solutions of ammonium salts containing only 0.07 to 0.35 mg of nitrogen in 100 ml.

The accuracy of enthalpimetric determinations of ammonium salts with sodium hypobromite is indicated by the standard deviations of the measurements, calculated according to Dean and Dixon [41, 42] (Table 1).

Table 1

Accuracy of enthalpimetric determinations of ammonium salts with sodium hypobromite

Approximately 3 ml of sodium hypobromite solution was added to 100 ml of sodium hydroxide solution containing 0.1 millimole of ammonium sulphate

Solution	Deviations of the recorder in individual measurements, mm	Arithmetic mean	Standard deviation
0.05 *M* NaOH	122.0; 120.0; 120.0; 120.0; 120.0	120.4	1.05
0.5 *M* NaOH	120.0; 120.0; 120.0; 122.0; 118.0; 120.0	120.0	1.26

Voltage on the Wheatstone bridge: 200 mV.
Scale range of the recorder: 0 – 1 mV.

Comparison of this reaction (i.e. of ammonium sulphate with sodium hypobromite) with the neutralization of hydrochloric acid with sodium hydroxide (producing a known amount of neutralization heat) revealed that the approximate value of the enthalpy change (ΔH) under the conditions mentioned above was approximately -741 kJ per mole of ammonium sulphate.

A detailed description of enthalpimetric determinations of ammonium salts with sodium hypobromite may be found in one of our earlier papers [43].

Enthalpimetric determinations of ammonium salts with hypobromite were also used for the determination of nitrogen according to Kjeldahl [44]. The solution obtained after the mineralization of the sample by heating with concentrated sulphuric acid in the presence of catalysts was neutralized and then subjected to enthalpimetric analysis. The advantage of this method consists in the fact that there is no need to distil the ammonia and that the duration of analysis is considerably reduced. Of the common catalysts, e.g. cupric sulphate, selenium or mercury, only the latter shows disturbing effects.

If the analyzed solution contains a higher concentration of sodium sulphate (more than 0.5 M Na_2SO_4) formed by the neutralization of the excess of sulphuric acid in the mineralized sample before the enthalpimetric measurements with sodium hydroxide, it is necessary to construct a calibration curve using standard solutions of ammonium salts in the presence of corresponding concentrations of sodium sulphate [44].

Enthalpimetric determinations with hypobromite may also be used for the determination of urea and its derivatives, e.g. guanidine, semicarbazide and thiourea, and for the determination of hydrazine [45]. Values of ΔH for the reactions of urea, guanidine, semicarbazide and hydrazine with hypobromite in 0.5 M sodium hydroxide solution ranged from -611 to -770 kJ mole^{-1}. The highest ΔH (955 kJ mole^{-1}) occurred during the reaction of thiourea with hypobromite. It was experimentally demonstrated [45] that during this reaction not only amino groups but also sulphur was oxidized.

The suitability of enthalpimetric determination of ammonium salts and urea with sodium hypobromite was also demonstrated in experiments on the determination of these compounds in fertilizers [46].

Hypobromite oxidizes various oxidizable inorganic sulphur compounds to sulphates [2, 3]. Enthalpimetry with hypobromite enables one to determine various inorganic compounds, e.g. sulphides, sulphites, disulphites and thiosulphates [47]. With hypobromite it is also possible to determine enthalpimetrically cyanides [47] and thiocyanates [47], which oxidize to cyanates [2] and sulphates [2], respectively. Changes in enthalpy during these reactions in 0.1 M sodium hydroxide varied, depending on the number of oxidizable groups, within the range -314 to -1047 kJ mole^{-1}.

The possibility of enthalpimetric determinations of organic compounds containing differently situated amino groups or sulphidic sulphur was tested in experiments with several derivatives of acetic acid, e.g. acetamide, glycine, thioglycolic acid and thioacetamide [48]. It was found that all these compounds could be determined enthalpimetrically with hypobromite. Assays were carried out in 0.5 M sodium hydroxide solution. It resulted from these experiments that a considerable amount of heat was produced in nearly all reactions. Values of ΔH ranged from -687 to 959 kJ mole^{-1}; the only exception was the reaction of acetamide with hypobromite, which showed a considerably lower ΔH: -67 kJ mole^{-1}. However, amide may be changed into ammonium salt by means of hydrolysis with dilute acids; this ammonium salt, which produces a considerably higher amount of heat during the oxidation, may then be easily determined using enthalpimetry with hypobromite, as was demonstrated in our experiments [48].

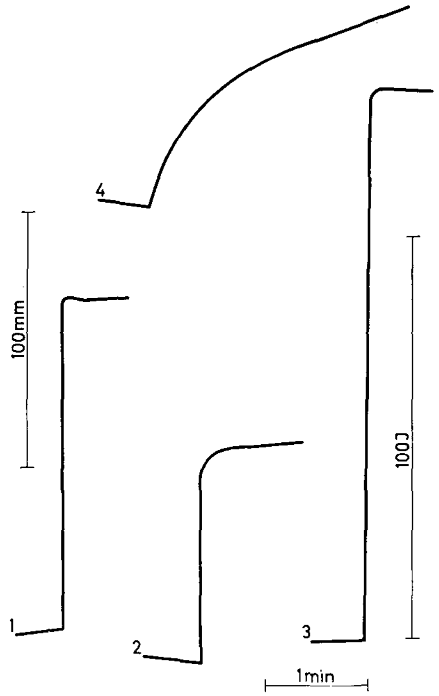

Fig. 3. Examples of enthalpograms obtained during reactions of some amino acids with sodium hypobromite in 0.5 *M* sodium hydroxide solution. Approximately 3 ml of sodium hypobromite solution was added to 100 ml of ca 0.5 *M* sodium hydroxide containing 0.1 millimole of amino acid (in the case of cystine only 0.05 millimole). 1. glycine, 2 leucine, 3 cystine, 4. proline. Voltage on the Wheatstone bridge: 200 mV. Scale range of the recorder: 0 — 1 mV

As it was found that considerable amounts of heat were produced during the reaction of glycine (i.e. aminoacetic acid) with hypobromite [48], the possibility was tested of enthalpimetric determinations of a number of amino acids known as products of protein hydrolysis [49], reactions of altogether 22 amino acids were measured. Reactions of amino acids with hypobromite were carried out in 0.5 *M* sodium hydroxide solution.

The experimental results showed that all amino acids reacted with hypobromite very quickly, producing considerable amounts of heat which were directly proportional to the concentration of amino acid in the solution; for this reason these reactions were very suitable for enthalpimetric determinations of amino acids. Less distinctive deviations, and thus less accurate results, were observed only in proline assays; this might be explained by the fact that proline has no free reactive amino group in the α-position. Experiments on the reaction of β-alanine with hypobromite showed that the amino group in the α-position was the active group in reactions of amino acids with hypobromite. The afore-mentioned reaction produced heat only very slowly. Enthalpograms obtained during reactions of several amino acids with hypobromite are presented in Fig. 3.

Oxidation and neutralization reactions of amino acids with sodium hypobromite and sodium hydroxide, respectively, were compared with the neutralization of hydrochloric acid with sodium hydroxide, which produced a known amount of neutralization heat; approximate values of ΔH were calculated on the basis of these measurements (Table 2). Reactions of amino acids with hypobromite can be seen to be associated with relatively high values of ΔH, ranging from -486 to -1260 kJ mole^{-1}. With cystine, however, an even higher ΔH was found, viz. -2634 kJ mole^{-1}. It is obvious that high changes in enthalpy occurred in reactions of hypobromite with those amino acids which contained more amino groups or also sulphidic sulphur or other reactive groups. Table 2 shows that the ΔH of oxidation reactions of amino acids with hypobromite was fifty to nearly hundred

Table 2

Values of ΔH during the neutralization of amino acids with sodium hydroxide and during the oxidation of amino acids with sodium hypobromite in 0.5 *M* sodium hydroxide solution

Amino acid	Enthalpy change, kJ mole^{-1}	
	during neutralization with NaOH	during oxidation with NaBrO
Glycine	−11.7	−808
D-α-Alanine	−11.7	−532
D,L-α-Amino-n-butyric acid	−11.7	−515
D,L-Norvaline	−11.7	−515
D,L-Valine	−11.7	−486
D,L-Leucine	−11.7	−498
L-Aspartic acid	−64.8	−678
L-Glutamic acid	−64.8	−515
D,L-Ornithine hydrochloride	−15.1	−992
D,L-Lysine hydrochloride	−11.7	−955
L-Asparagine	−18.8	−984
L-Arginine hydrochloride	−11.7	−1130
L-Serine	−15.1	−913
D,L-Threonine	−13.0	−938
D,L-Methionine	−15.1	−997
L-Cysteine hydrochloride	−91.7	−1260
L-Cystine	—	−2634
D,L-β-Phenyl-α-alanine	−18.8	−532
L-Tyrosine	—	−775
L-Histidine hydrochloride	−39.8	−938
D,L-Tryptophan	−11.7	−1097
L-Proline	−15.9	(−264)

times higher than for neutralization reactions with sodium hydroxide, earlier suggested for thermometric determination of amino acids [50]. Enthalpimetric determination of amino acids with hypobromite was therefore very sensitive.

The accuracy of the determination of amino acids with hypobromite corresponds with the needs of quantitative analysis; this is indicated by the values of standard deviations calculated from results with glycine and cystine (Table 3).

Table 3

Accuracy of enthalpimetric determinations of amino acids with sodium hypobromite (examples of measurements with glycine and cystine)

Approximately 3 ml of sodium hypobromite solution was added to 100 ml of solution of ca 0.5 *M* sodium hydroxide containing 0.1 or 0.05 millimole of glycine or cystine, respectively

100 ml of 0.5 *M* NaOH containing	Deviations of the recorder during individual measurements, mm	Arithmetic mean	Standard deviation
Glycine	132.5; 132.0; 131.5; 133.0; 132.0; 133.0; 133.0; 133.0; 133.0; 132.0	132.5	0.57
Cystine	214.0; 214.0; 214.0; 214.0; 215.0	214.2	0.43

Voltage on the Wheatstone bridge: 200 mV.
Scale range of the recorder: 0 – 1 mV.

Reactions of a number of phenols and aromatic amines with hypobromite in alkaline solution were tested, as well as their suitability for enthalpimetric determinations [51].

Enthalpimetric measurements were carried out with solutions containing 0.025 to 0.200 millimoles of analyzed substance in 100 ml. Five ml of reagent was used in cases where it was necessary to ensure a linear dependence of the height of the recorded deviation upon the concentration of the analyzed compound in the measured range of concentration. In all cases reactions with hypobromite were carried out in 0.5 *M* sodium hydroxide solution to allow a comparison of their behaviours in the course of reaction.

Experiments showed that reactions of most of these aromatic compounds showed that reactions with hypobromite were quick and reproducible. This was observed with mono- and polyphenols (phenol, *m*- and *p*-cresol, thymol, β-naphthol, catechol, resorcinol, hydroquinone, phloroglucinol), quinones (*p*-benzoquinone, alizarin), aromatic hydroxyacids of a phenolic nature (salicylic acid, acetylsalicylic acid, sulphosalicylic acid), aromatic amines and their derivatives (aniline, *o*- and *m*-aminophenol, *o*- and *p*-aminobenzoic acid, sulphanylic acid), and some hydroxy derivatives of heterocyclic compounds (e.g. oxine, i.e. 8-hydroxyquinoline).

Although the reactions of these aromatic compounds with hypobromite are very complicated (hypobromite may induce both oxidative and halogenative reactions and they may be influenced by the different alkalinities of the solution), sufficiently reproducible results were obtained under the conditions described above. It may be concluded that these reactions are also suitable for quantitative analysis. As shown in our experiments, the course of reaction depends on the nature of the groups on the aromatic ring of the analyzed compounds and on their position. For example, reactions of *m*- and *p*-cresol or *β*-naphthol are sufficiently quick and reproducible, but those of *o*-cresol and α-naphthol are so slow that it is not possible to read the height of the deviation and the measurements are therefore imprecise (Fig. 4). Reactions of pyrogallol, gallic acid and *p*-aminophenol with hypobromite are rapid and give distinctive deviations during enthalpimetric measurements; however, the results are not sufficiently reproducible, probably due to the considerable instability of alkaline solutions of these compounds in the air. However, it may be possible to ensure, e.g. by means of changed solution alkalinity or other methodological changes, reaction conditions which would enable one to obtain satisfactory results even with these compounds. Details about these measurements and their evaluation are presented in one of our earlier papers [51]. Several enthalpograms obtained in these measurements are presented in Fig. 4.

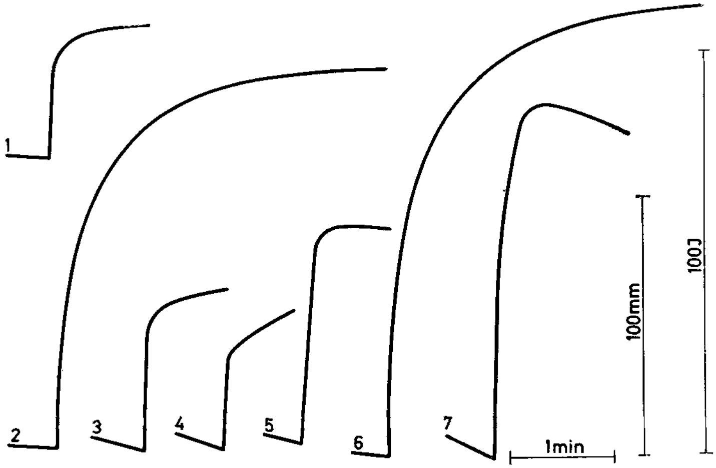

Fig. 4. Examples of enthalpograms obtained during reactions of various monophenols with sodium hypobromite in 0.5 *M* sodium hydroxide solution. Approximately 3 ml (with thymol approx. 5 ml) of sodium hypobromite solution was added to 100 ml of ca 0.5 *M* sodium hydroxide containing 0.1 millimole of phenol. 1. Phenol, 2. *o*-cresol, 3. *m*-cresol, 4. *p*-cresol, 5. thymol, 6. α-naphthol, 7. *β*-naphthol. Voltage on the Wheatstone bridge: 200 mV. Scale range of the recorder: 0 — 1 mV

Measurements are very sensitive because values of ΔH recorded in reactions of aromatic compounds with hypobromite are rather high (usually ranging between -209 and -837 kJ mole^{-1}; the ΔH of quinhydrone is as high as -1507 kJ mole^{-1}) so that it is possible to analyze up to 10^{-4} *M* solutions of these aromatic compounds. During our experiments, however, the maximum sensitivity of the apparatus was not fully utilized. If the maximum sensitivity were used, the sensitivity of measurement could be increased approximately ten times.

It is obvious that after a considerable dilution enabling a complete dispersity of the substances analyzed, and in the presence of excessive amounts of reagent, reactions of many aromatic compounds with hypobromite are sufficiently quick and reproducible. Under these conditions, however, the course of reaction may differ considerably from that observed in more concentrated solutions, i.e. in various preparative reactions. For this reason enthalpimetric measurements may provide a new insight into the chemism of these reactions. Direct injection enthalpimetry is very suitable for this purpose because the rate of the reaction can be followed in the enthalpograms.

A number of reactions between organic or inorganic compounds and sodium hypobromite demonstrated the suitability of the latter as an enthalpimetric reagent. Enthalpimetric measurements may be used not only for quantitative analyses of various compounds (because of the promptness, rapidity, and easy automatibility), but also for studies on individual reactions, e.g. when determining different factors influencing the process of reaction, because the course and kinetics of each reaction may easily be followed in the enthalpograms.

References

1. A. Jilek, Odměrná analysa, díl II, Oxydimetrie, reduktometrie (Volumetric Analysis, Vol. II, Oxidimetry, Reductometry), Technicko-vědecké vydavatelství, Praha 1951, p. 230.
2. I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyama, Volumetric Analysis, Vol. III, Titration Methods, Oxidation-Reduction Reactions, New York 1957. (Russian translation) Gos. nauč.-techn. izdat. chim. lit., Moskva 1961, p. 689.
3. A. Berka, J. Vulterin and J. Zýka, Vybrané oxydačně redukční odměrné metody (Selected Oxidation-Reduction Titrimetric Methods), Stát. nakl. techn. lit., Praha 1961, p. 30.
4. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, J. Wiley & Sons, Inc., 1966. (Czech translation) Academia, Praha 1973, p. 553.
5. J. Gažo, J. Kohout, M. Serátor, T. Šramko and M. Zikmund, Všeobacná a anorganická chémia (General and Inorganic Chemistry), Alfa, Bratislava 1974, p. 288.
6. F. Plehn, Ber., 8 (1975) 582.
7. E. Quinquaud, Monit. sci. (3), 11, 641; Z. Anal. Chem., 21 (1882) 605.
8. Krocker, E. Dietrich, Z. Anal. Chem., 3 (1864) 64.
9. H. H. Willard and E. W. Cake, J. Am. Chem. Soc., 42 (1920) 2646.
10. K. Jellinek and W. Kresteff, Z. Anorg. Chem., 137 (1924) 333.
11. I. M. Kolthoff and V. A. Stenger, Ind. Eng. Chem., Anal. Ed., 7 (1935) 79.
12. O. Tomíček and M. Jašek, Collection Czech. Chem. Commun., 10 (1938) 353.
13. O. Tomíček and P. Filipovič, Collection Czech. Chem. Commun., 10 (1938) 340, 415.
14. I. M. Kolthoff, W. Stricks and L. Morren, Analyst, 78 (1953) 405.
15. H. A. Laitinen and D. E. Woerner, Anal. Chem., 27 (1955) 215.
16. G. S. Desmukh, M. G. Bapat, E. Balkrishnan and M. C. Eshwar, Naturwiss., 45 (1958) 129.

17. V. Simon, I. Sekerka and J. Doležal, Chem. Listy, 46 (1952) 617.
18. G. M. Arcand and E. H. Swift, Anal. Chem., 28 (1956) 440.
19. A. K. Krivis, G. R. Supp and E. S. Gazda, Anal. Chem., 35 (1963) 2216.
20. G. D. Christian, E. C. Knobloch and W. C. Purgy, Anal. Chem., 35 (1963) 2217.
21. I. Sajó, Kohász. Lapok, 7 (1957) 287.
22. I. Sajó and J. Ujvári, Z. Anal. Chem., 202 (1964) 177.
23. J. C. Wasilewski, P. T.– S. Pei and J. Jordan, Anal. Chem., 36 (1964) 2131.
24. I. Sajó, Kémiai Közlemény., 26 (1966) 119.
25. I. Sajó and B. Sipos, Z. Anal. Chem., 222 (1966) 23.
26. I. Sajó and B. Sipos, Talanta, 14 (1967) 203.
27. I. Sajó, J. Thermal, Anal., 1 (1969) 221.
28. I. Sajó, Termometria, Műszaki Könyvkiadó, Budapest 1971.
29. G. A. Vaughan, Thermometric and Enthalpimetric Titrimetry, Van Nostrand Reinhold Company Ltd., London 1973.
30. J. M. Bell and C. F. Cowell, J. Am. Chem. Soc., 35 (1913) 49.
31. P. Dutoit and E. Grobet, J. Chim. Phys., 19 (1922) 324.
32. H W. Linde, I. B. Rogers and D. N. Hume, Anal. Chem., 25 (1953) 404.
33. L. S. Bark and S. M. Bark, Thermometric Titrimetry, Pergamon Press, Oxford – London— Edinburgh – New York 1969. Russian translation, "Metallurgija", Moszkva 1973.
34. J. Jordan, Thermometric Enthalpy Titrations, I. M. Kolthoff and P. Elving (Eds), Treatise on Analytical Chemistry, Part I, Vol. 8, Interscience Publishers, New York, 1968, p. 5175.
35. W. W. Wendlandt, Thermal Methods of Analysis, P. J. Elving and I. M. Kolthoff (Eds), Chemical Analysis, Vol. 19, Interscience Publishers, New York – London – Sydney 1964, p. 271.
36. J. V. Tyrrell and A. E. Beezer, Thermometric Titrimetry, Chapman and Hall Ltd., London 1968.
37. J. Brandštetr, M. Malinger and J. Kupec, Chem. Listy, 66 (1972) 88.
38. J. Brandštetr, M. Malinger and J. Kupec, Sbor. Vys. učení techn. v Brně (1973), No. 1 – 4, 35.
39. N. Malingerová, Acta univ. agric. (Brno), Fac. argon., 17 (1969) 15.
40. N. Malingerová, Výzkum method stanovení dusíku, jeho sloučenin a dalších biogenních prvků (Methods of Determination of Nitrogen, its Compounds, and Other Biogenous Elements), Final report of the research task, University of Agriculture, Brno 1975.
41. R. B. Dean and W. J. Dixon, Anal. Chem., 23 (1951) 636.
42. K. Eckschlager, Chyby chemických rozborů (Errors of Chemical Analyses), Stát. nakl. techn. lit., Praha, 1971, p. 111.
43. N. Malingerová, Acta univ. agric. (Brno), Fac. agroecon., 8 (1972) 343.
44. N. Malingerová and M. Malinger, Acta univ. agric. (Brno), Fac. agroecon., 9 (1973) 111.
45. N. Malingerová and M. Malinger, Acta univ. agric. (Brno), Fac. agroecon., 8 (1972) 355.
46. A Halász, R. Szórád and M. Ifcsics, Hung. Sci. Instruments (1973), No. 28, 41.
47. M. Malinger and N. Malingerová, Sbor. Vys. učení techn. v Brně, (1973), No. 1—4, 44.
48. N. Malingerová and M. Malinger, Acta univ. agric. (Brno), Fac. agroecon., 9 (1973) 103.
49. N. Malingerová, Acta univ. agric. (Brno), Fac. agroecon., 9 (1973) 221.
50. K. K. Chatterjee and A. K. Ghosh, J. Indian Chem. Soc., 34 (1957) 407.
51. N. Malingerová and M. Malinger, Acta univ. agric (Brno), Fac. agroecon., 10 (1974) 249.

RÉSUMÉ — Les auteurs examinent l'emploi de l'hypobromite de sodium comme réactif pour le dosage enthalpimétrique de divers composés organiques et inorganiques. Par cette méthode il est possible de doser différents composés azotés et sulfurés, par ex. les sels d'ammonium, l'urée, les α-amino-acides, les sulfures, les sulfites, les thiosulfates, les composés organiques sulfurés, les amines aromatiques, les phénols mono et polyvalents et d'autres composés. Les dosages sont suffisamment précis et sensibles. Les variations d'enthalpie de ces réactions sont de l'ordre de 10^2—10^3 kJ · mol^{-1}. Les dosages proposés ont l'avantage d'être simples, rapides et susceptibles d'être automatisés

ZUSAMMENFASSUNG — Die Autoren geben einen Überblick zur Anwendung von Natriumhypobromit als Reagenz bei den enthalpimetrischen Bestimmungen verschiedener organischer und anorganischer Verbindungen. Der Einsatz dieser Methode ermöglicht die Bestimmung verschiedener oxidierbarer Stickstoff- und Schwefelverbindungen, wie z.B. Ammoniumsalze, Karbamid, α-Aminosäuren, Sulfide, Sulfite, Thiosulfate, organische Verbindungen mit Sulfidschwefel, aromatische Amine, ein- und mehrwertige Phenole und andere Verbindungen. Die Bestimmungen sind genügend genau und empfindlich. Die Enthalpie-Änderungen dieser Reaktionen liegen in der Größenordnung von 10^2 is 10^3 kJ Mol^{-1}. Die vorgeschlagenen Bestimmungen sind wegen ihrer Einfachheit, Schnelligkeit und der Möglichkeit der Automatisierung der Messungen vorteilhaft.

Резюме — Авторы обсудили применение гипобромита натрия, как реагента, при энтальпиметрических определениях раЗличных органических и неорганических соединений. Использование этого метода позволяет определять различные окисляемые азот- и серосодержащие соединения, как например: аммониевые соли, мочевину, α-аминокислоты, сульфиды, сульфиты, тиосульфаты, органические соединения с сульфидной серой, ароматические амины, одноатомные и многоатомные фенолы и другие соединения. Определения являются достаточно точными и чувствительными. Изменения энтальпии этих реакций составляют приблизительно 10^2 до 10^3 кдж/моль. Преимуществом предложенных определений является их простота, быстрота и возможность их автоматизации.