Thermochimica Acta, 112 (1987) 171–177
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPIMETRIC DETERMINATION OF SULPHIDE AND THIOSULPHATE BY THE CATALYSIS OF THE IODINE–AZIDE REACTION

G. RAMIS RAMOS, R.M. VILLANUEVA CAMAÑAS, J.C. GOZÁLVEZ RODRÍGUEZ
and M.C. GARCÍA ALVAREZ-COQUE

Departamento de Química Analítica, Facultad de Química, Universidad de Valencia, Burjassot, Valencia (Spain)

(Received 1 July 1986)

ABSTRACT

The enthalpimetric determination of sulphide and thiosulphate, in the presence and absence of Zn^{2+} and Cd^{2+}, making use of the catalysis of the iodine–azide reaction is studied. An excess of the cations avoids losses of sulphide as H_2S and, when cadmium is used, a 30% enhancement of the sensitivity is observed in the determination of sulphide. On the other hand, both cations depress the analytical response produced by thiosulphate, but iodide can be used as an enhancement agent. Limits of detection of 0.1 and 0.3 ppm are obtained for sulphide and thiosulphate, respectively, and linear dynamic ranges comprise about two orders of magnitude.

INTRODUCTION

The reaction between iodine and azide is very useful for the determination of elemental sulphur and reduced sulphur compounds which catalyze the reaction selectively, as has been shown in a recent review [1]. These compounds are irreversibly oxidized by iodine to inactive species, producing a decrease in the rate of the catalyzed reaction, until it eventually ceases. Under adequate experimental conditions, the extent of the reaction is proportional to the initial concentration of the catalyst.

The iodine–azide reaction is highly exothermic and, therefore, the extent of the reaction can be advantageously established by direct injection enthalpimetry. The determination of thiosulphate and other catalysts by an enthalpimetric–turbidimetric procedure in a 75% glycerol medium was described by Weisz et al. [2] and the enthalpimetric determination of sulphide was studied by Kiba et al. [3]. In this work, the enthalpimetric determination of sulphide and thiosulphate, in the presence and absence of Zn^{2+} and Cd^{2+}, is studied. Zinc depresses the analytical response produced by sulphide, whereas an unexpected enhancement is obtained in the presence of cadmium. These effects are of analytical interest.

In the procedure proposed by Kiba et al. [3], the final step must be the injection of the sample into the cell, in order to avoid losses of sulphide as H_2S. However, in most calorimeters, because of the temperature mismatching between injected and cell solutions, small volumes of the former must be used, which limits sensitivity and reproducibility when the injected solution contains the analyte. The use of an excess of Cd^{2+} avoids losses of sulphide, making it possible to invert the order of addition of the reagents. In this work, larger volumes of the sample are introduced into the cell and the reaction is started by injection of an iodine solution. Furthermore, in the analysis of sulphide, a previous distillation is usually performed, and the evolved H_2S is retained in a Zn^{2+} or Cd^{2+} solution. The proposed enthalpimetric procedure permits the direct determination of sulphide in the resulting cadmium sulphide suspension.

EXPERIMENTAL

Reagents

Sulphide and thiosulphate solutions 0.01 M and 0.1 M, respectively, were prepared in freshly boiled distilled water and iodometrically standardized [4]. Sulphide solutions were renewed every 4 h. Analytical grade sodium sulphide was stored in a vacuum desiccator containing silica gel. Sodium azide solutions were prepared daily. An iodine (0.2 M)–potassium iodide (1 M) solution was used for injection. Zinc and cadmium solutions (0.15 M) were prepared from their nitrate salts.

Apparatus

A constant DC power supply and a Wheatstone bridge were built according to the method of Lumbiarres et al. [5]. The temperature-sensing element was a thermistor of 5 KΩ nominal resistance at 25°C. At the sensitivity setting used, a response of 15.27 mV $°C^{-1}$, corresponding to 305.4 and 152.7 mV $°C^{-1}$ pen deflections on the recorder, was obtained.

Triplicate experiments were performed in a thermostatted room at 25.0 ± 0.1°C. The reaction vessel was a 30 ml polyethylene cell in an isothermic air bath [6]. The iodine solution was injected into the cell by means of a Metrohm Multidosimat E-415 apparatus. The solution in the cell was mechanically stirred.

Procedure

In the absence of Zn^{2+} or Cd^{2+}, the reagents were pipetted into the cell in the following order: buffer (5 ml), azide solution (5 ml) and enough water to make a final total volume of 20 ml before injection. The sample was added and the reaction started by injection of 2 ml of the iodine–iodide solution.

In other experiments, 2 ml of the cation solution were also used. For thiosulphate determination, the same order was followed as above, the cation solution being pipetted before injection; for sulphide, the cation solution was mixed with the sample in the cell before the introduction of the buffer.

In some experiments, an additional amount of iodide was added before the buffer solution, and the mixture was allowed to stand for 10 min to reach thermal equilibrium with its surroundings. In this way, errors arising from the dilution heat of the concentrated iodide solution were minimized.

In all cases, the blank temperature jump was obtained from experiments carried out in the absence of the catalyst and subtracted. Blank response mainly corresponds to the dilution heat of the iodine–iodide solution.

RESULTS AND DISCUSSION

As shown in Fig. 1, the reaction catalyzed by sulphide in the absence of the cations and by thiosulphate is very rapid and stops suddenly, which is very convenient for the precise measurement of the temperature jump.

In the presence of an excess of Zn^{2+} or Cd^{2+}, sulphide also provides a quick advance, which is followed by a progressive detention, that can take a few minutes. However, reproducible values of the height of the temperature jump are obtained if a tangent is drawn to the curve, with a constant and arbitrary slope (Fig. 1). A slope corresponding to a tangent point located 30–40 s after injection is adequate.

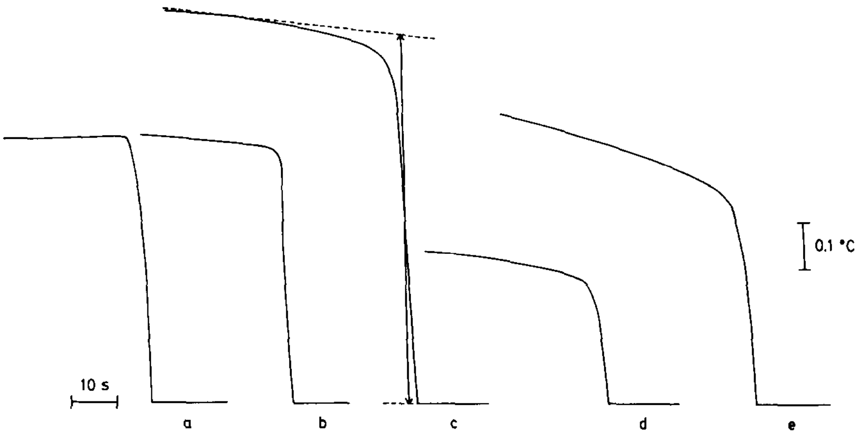

Fig. 1. Enthalpograms obtained in a 0.6 M azide solution: (a) 6.25×10^{-5} M thiosulphate; (b) 1.25×10^{-4} M sulphide; (c) sulphide in 0.015 M Cd^{2+}; (d) sulphide in 0.015 M Zn^{2+}; (e) sulphide in 0.015 M Zn^{2+} and 1.2 M iodide.

It is interesting to note that zinc depresses the analytical response caused by sulphide, whereas cadmium produces an enhancement. These effects amount to more than -60 and $+30\%$ for Zn^{2+} and Cd^{2+}, respectively. Otherwise, the presence of these cations gives a 10 and 15% diminution of the analytical response when thiosulphate is the catalyst.

Over minimum practical values, stirring and injection speeds have no influence on the shape and height of the temperature jump.

The influence of acidity has been studied using 0.2 M KH_2PO_4–NaOH buffer solutions (pH 6–10.5) and measuring the resultant pH after injection with a glass electrode. Ethylenediammine cannot be used as the buffer reagent since it inhibits the iodine–azide reaction.

In the determination of sulphide as a free ion, or in the presence of Zn^{2+} or Cd^{2+}, sensitivity is maximum and independent of acidity in the pH range 6.5–8. In order to avoid losses of sulphide by volatilization, a pH value close to 8 was chosen for the determination in the absence of the cations. Using a pH 8.1 0.2 M KH_2PO_4 NaOH buffer solution, the pH after injection took a value of 7.9. Under these conditions and injecting the iodine solution within 3 min after the addition of the sample, no losses of sulphide are observed.

Experiments performed in the presence of an excess of Cd^{2+} or Zn^{2+} were carried out by adding a pH 10.5 0.2 M KH_2PO_4–NaOH buffer solution, which provided a final pH value of 7.5 after injection. And additional amount of NaOH in the buffer was necessary to neutralize the protons liberated during the precipitation of the cation excess with phosphate. In the presence of a phosphate excess, the metallic suphide, much more insoluble than the corresponding phosphate, did not redissolve. Similar results were achieved when thiosulphate was used as the catalyst, the same buffers being adequate.

When the iodine solution was injected in at least 30% excess, with respect to the consumed iodine, the volume of the injected iodine had no influence on the sensitivity. On the other hand, an increase in azide concentration always gave rise to a greater sensitivity, as shown in Fig. 2. The dependence of the catalytic activity of thiosulphate on azide concentration, in the presence of Zn^{2+} or Cd^{2+}, was similar to that shown in their absence. It is, however, more convenient to use a moderate azide concentration which allows both a good sensitivity and a cheaper procedure to be achieved. A 0.6 M azide solution (before injection) was chosen for further experiments.

As shown in Fig. 3, approximately linear increases of sensitivity were obtained in absence of Zn^{2+} and Cd^{2+}, when additional amounts of iodide were added into the cell before the injection of the iodine solution. Sensitivity enhancement amounted to 100% and 70% per mol l^{-1} of added iodide, for sulphide and thiosulphate, respectively. In the presence of Zn^{2+}, the effect produced on the catalytic activity of sulphide by the added iodide was much less pronounced, whereas in the presence of Cd^{2+} a strong inhibition was observed and the response reached zero for iodide concentrations larger

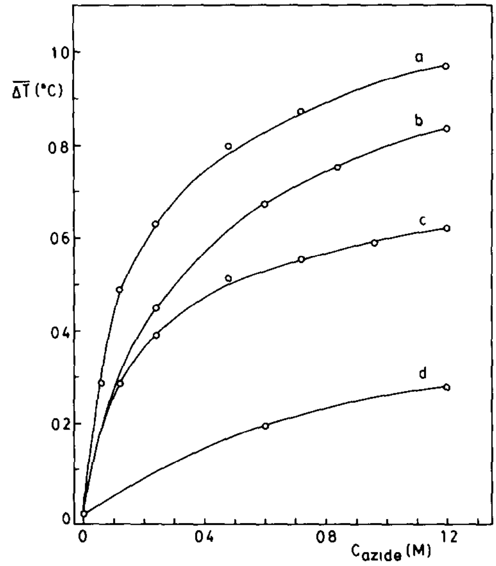

Fig. 2. Influence of azide concentration: (a) 1.25×10^{-4} M thiosulphate, (b) 1.25×10^{-4} M sulphide in 0.015 M Cd^{2+}; (c) sulphide; (d) sulphide in 0.015 M Zn^{2+}.

than 1.2 M. Besides, the enthalpograms obtained at large iodide concentrations showed a rounded upper zone, being inadvisable to use a iodide concentration larger than 1 M. Similar but much less pronounced effects were observed for thiosulphate.

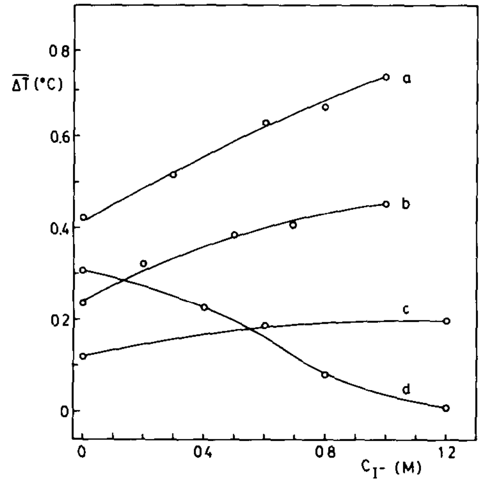

Fig. 3. Influence of an additional amount of iodide in the cell: (a) 6.25×10^{-5} M thiosulphate; (b) 6.25×10^{-5} M sulphide; (c) sulphide in 0.015 M Zn^{2+}; (d) sulphide in 0.015 M Cd^{2+}; 0.6 M azide in all cases.

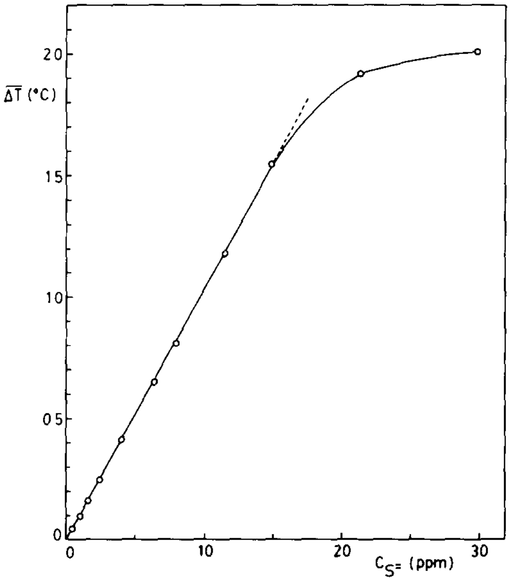

Fig. 4. Calibration curve for sulphide in a 0.6 M azide solution.

The height of the blank jumps increased with the injected iodine–iodide solution volume and, in a smaller proportion, with azide concentration. A change in iodide concentration did not produce any effect on the blank height. The height values of the blanks ranged between 0.05 and 0.15 °C.

A calibration curve for sulphide, obtained in a 0.6 M azide medium, is given in Fig. 4. The curve departed from linearity when more than 70% of the injected iodine was consumed. The use of a greater iodine concentration allows the upper limit of the linear range to be increased. The coefficients of

TABLE 1

Determination of sulphide and thiosulphate in different experimental conditions

Ion	Conc. before injection [a] (M)		Slope (°C ppm^{-1})	Detection limit (ppm)
	Iodide	Cation		
S^{2-}	0	[Cd(II)] 0	0.104	0.15
	0.6	[Cd(II)] 0	0.176	0.10
	0	[Cd(II)] 0.015	0.135	0.12
	0.6	[Zn(II)] 0.015	0.0488	0.32
$S_2O_3^{2-}$	0	[Cd(II)] 0	0.0326	0.48
	0.6	[Cd(II)] 0	0.0480	0.32
	0	[Cd(II)] 0.015	0.0289	0.55
	0.6	[Zn(II)] 0.015	0.0460	0.34

[a] Azide concentration is 0.6 M in all cases.

variation associated with the measurements (6 experiments) were within 3%. The detection limit was 0.15 ppm, according to the 3s criterion, and taking into account that the standard deviation of the blank was ±0.006°C (10 experiments). Table 1 shows the values of the slopes and detection limits for different experimental conditions. Dynamic linear ranges comprise approximately two orders of magnitude.

The most sensitive determinations of sulphide and thiosulphate were achieved in the presence of iodide and the absence of zinc and cadmium. However, it is preferable to perform the determination of sulphide in the presence of cadmium and absence of iodide, in order to avoid losses by volatilization. Moreover, this procedure is the most useful from a practical point of view, since sulphide is frequently retained in a solution containing an excess of cadmium, and the analysis can be carried out on the metallic sulphide suspension.

REFERENCES

1 G. Ramis Ramos, M.C. García Alvarez-Coque and R.M. Villanueva Camañas, Analyst (London), 111 (1986) 1001.

2 H. Weisz, W. Meiners and G. Fritz, Anal. Chim. Acta, 107 (1979) 301.

3 N. Kiba, M. Nishijima and M. Furusawa, Talanta, 27 (1980) 1090.

4 I.M. Kolthoff and R. Belcher, Volumetric Analysis, Vol. 3, Interscience, New York, 1957.

5 J. Lumbiarres, C. Mongay and V. Cerdá, Analusis, 8 (1980) 62.

6 G. Ramis Ramos, R. Ibáñez Tomás, M.C. García Alvarez-Coque and C. Mongay Fernández, Thermochim. Acta, 98 (1986) 213.