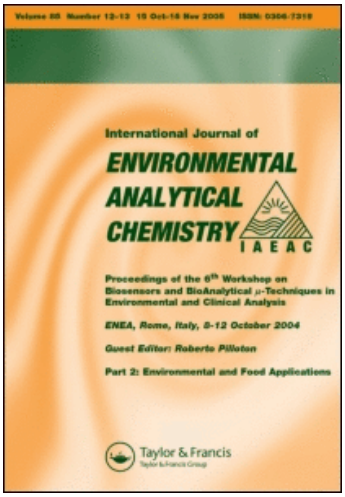

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Kinetic Determination of Sulphide in Water and Air Samples

C. Sánchez-Pedreño[a]; M. S. García[a]; M. I. Albero[a]; L. Tobal[a]
[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Murcia, Spain

To cite this Article Sánchez-Pedreño, C. , García, M. S. , Albero, M. I. and Tobal, L.(1996) 'Kinetic Determination of Sulphide in Water and Air Samples', International Journal of Environmental Analytical Chemistry, 62: 4, 273 — 279
To link to this Article: DOI: 10.1080/03067319608026247
URL: http://dx.doi.org/10.1080/03067319608026247

Intern. J. Environ. Anal. Chem., Vol. 62, pp. 273–279
Reprints available directly from the publisher
Photocopying permitted by license only

KINETIC DETERMINATION OF SULPHIDE IN WATER AND AIR SAMPLES

C.SÁNCHEZ-PEDREÑO*, M. S. GARCÍA, M. I. ALBERO and L. TOBAL

Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, 30071 Murcia, Spain

(Received, 10 January 1995; in final form, 27 July 1995)

A kinetic method for the determination of sulphide based on its inhibition of the Pd(II) catalysed reaction between pyronine G and the hypophosphite ion is described. The reaction was followed spectrophotometrically by measuring the decrease in the absorbance at 548 nm. The influence of reaction variables and the interfering effect of other substances were studied. Under the selected experimental conditions of 5.0×10^{-5} M pyronine G; pH 3.2; 0.7 μg ml^{-1} Pd(II); 0.4 M $H_2PO_2^-$ and 25 ± 0.2°C, sulphide was determined in the range 10–200 ng ml^{-1}. The method was applied to the determination of sulphide in water and air samples.

KEY WORDS: Kinetic determination, sulphide, air and water samples.

INTRODUCTION

Sulphide has a wide variety of effects even at low concentrations[1], including the corrosion of metal surfaces and, when oxidized to sulphate, the degradation of concrete. Sulphide is also of environmental concern because of its obnoxious odour and toxicity (as hydrogen sulphide). Sulphide is often present in waste waters and groundwater, especially in hot springs and atmospheric air (as H_2S). Analytical methods are therefore needed to determine sulphide in the environmental context.

Various methods are available for its determination[2]. The gravimetric and iodometric methods are still widely used, but interference by other anionic sulphur species is often a problem. The spectrophotometric method recommended as standard[3] for trace amounts of sulphide requires strict control of conditions for reproducible results to be obtained. There are a number of kinetic methods for the determination of sulphide. Most catalytic methods are based on the iodine-azide reaction catalysed by sulphide[4–11]. Other reactions catalysed[12–16] or inhibited[17,18] by sulphide have also been described.

In an earlier paper[19], the catalytic effect of Pd(II) on the reduction of pyronine G by the hypophosphite ion was studied. It was also found that some ions exert a strong inhibitory effect on this catalysed reaction[20,21].

This paper reports a new kinetic method for the determination of sulphide based on its inhibitory effect on the Pd(II)-catalysed reaction between the pyronine G and hypophosphite anion. The procedure is successfully applied to the determination of sulphide in samples of water of different origin and atmospheric air.

EXPERIMENTAL

Apparatus

Absorbance-time (A–t) curves were recorded on a Perkin-Elmer (Beaconsfield, Buckinghamshire, UK) Model 550SE dual-beam spectrophotometer equipped with 1–cm path length cells, kept at a constant temperature by means of a Colora Minicryostat MCIII apparatus (Messtechnik, Lorch, FRG). A Radiometer (Copenhagen, Denmark) PHM 63 pH-meter was used for pH measurements.

Reagents

Pyronine G 5×10^{-4} *M.* Prepared by dissolving 0.0378 g of 3,6-bis(dimethylamino) xanthylium chloride (C.I. 45005) (Merck, Darmstadt, FRG) in 250 ml of distilled water.

Palladium dichloride (Merck), 5×10^{-3} *M.* Prepared in 0.2 M HCl.

Sodium hypophosphite (Probus, Barcelona, Spain) 3M. Prepared weekly and stored in a dark bottle.

Standard sulphide solution 100 μg ml^{-1} *(*3×10^{-3} *M).* The solution was prepared fresh whenever required by dissolving 0.0751 g of $Na_2S.9\ H_2O$ (Merck) in 100 ml of distilled water. The crystal surfaces were initially rinsed with ethanol. The sulphide content was determined iodometrically[22].

Britton-Robinson buffer, pH 3.

All chemicals were of analytical grade. Doubly distilled water was used throughout.Working solutions of lower concentrations were prepared by appropriate dilution prior to use.

Analytical procedure

A 0.3 ml volume of 5×10^{-4} M Pyronine G, 1.0 ml of Britton-Robinson buffer of pH 3.2 and 0.2 ml of 11 μg ml^{-1} Pd(II) were placed in the spectrophotometric cell and appropriate volumes of standard solution of 1 μg ml^{-1} S^{2-} were added to give a final sulphide concentration between 10–200 ng ml^{-1}. The solutions were diluted to 2.6 ml with distilled water and the cells were kept at a constant temperature of 25 ± 0.2°C. A 0.4 ml volume of 3 M sodium hypophosphite was then added and the A-t curves recorded at 548 nm.

The cells were cleaned after use by immersion in 1 + 1 HNO_3, in order to remove any traces of Pd(0) adsorbed into the walls.

Procedure for analysis of water samples

A 250 ml volume of the water sample was placed in a distillation flask, 20 ml of concentrated H_3PO_4 are added and the liberated hydrogen sulphide was swept out with argon. The gas was retained in 100 ml of 0.1 M NaOH. Sulphide was determined in 1.5 ml aliquots according to the Analytical Procedure, with the buffer solution replaced by 0.5 ml of 0.2 M phosphoric, boric and acetic acid solution. A calibration graph was constructed in the same way.

Hot springs water samples: 1 ml of 1 M zinc acetate solution was added to 250 ml of water at the sampling moment, to precipitate ZnS. The precipitate was filtered off, washed with a 0.1 M zinc acetate solution and introduced into a distillation flask containing 150 ml of distilled water; after vigorous shaking the mixture was acidified with 20 ml of concentrated H_3PO_4 and the liberated H_2S was retained in 100 ml of 0.1 M NaOH. Aliquots of between 0.1 and 1.5 ml were taken and the procedure previously described was followed.

Procedure for the determination of hydrogen sulphide in air

Air samples were bubbled at a flow rate of 1 l min^{-1} for between 30 min and 2 h through two impinger vessels, connected in series containing 250 ml of 0.1 M NaOH. After sampling, both solutions were mixed, 10.0 ml of this solution was diluted to 100 ml with distilled water and aliquots of 1.5 ml were analysed by the Analytical procedure.

RESULTS AND DISCUSSION

A previous work[19] demonstrated that over a wide pH range hypophosphite does not reduce pyronine G, but that Pd(II) is a sensitive catalyst of this process. We have found that sulphide has no effect on the pyronine-$H_2PO_2^-$ system. On the other hand, it has a strong inhibitory effect on the Pd(II) catalysed reaction, whose rate for a fixed amount of Pd(II) in the medium is proportional to the concentration of sulphide.

The inhibitory effect of the sulphide can be explained by the fact that it acts as a precipitating agent for Pd(II), thus decreasing the amount of catalyst available for the pyronine G-hypophosphite anion.

The reaction was monitored spectrophotometrically by measuring the time required for the absorbance of the pyronine G to decrease by 0.1 (measured at the absorption maximum of 548 nm).

Influence of experimental variables

The studies were carried out by altering each variable in turn while keeping the others constant. All concentrations described here are the initial concentrations in the reaction mixtures at time zero after mixing. Each kinetic result is the average of three determinations.

The selected reaction conditions chosen were those which yielded a maximum and constant inhibition percentage and which resulted in a reaction order of zero or near to zero in the variables concerned. The inhibition percentage was calculated from

$$\% \text{ inhibition} = 100\,(V_{cat}-V_{inh})/V_{cat}$$

The effect of pH on the inhibited reaction was studied over the pH range 2.0–4.5 by using samples containing 5.0×10^{-5} M pyronine G, 0.7 μg ml^{-1} Pd(II), 0.4 M $H_2PO_2^-$, both in the absence and presence of 100 ng ml^{-1} of sulphide. Figure 1(a) shows the inhibition percentage versus pH; the inhibitory effect of the sulphide is maximum and constant over the range 3.0–3.7. The partial inhibition reaction order in the hydrogen ion is zero in the pH range 3.0–3.5. All subsequent investigations were performed at pH 3.2.

The influence of the concentration of pyronine was studied in the range 10^{-5}–7.5×10^{-5} M. The experiments were carried out at pH 3.2, 0.4 M $H_2PO_2^-$, 0.7 μg ml^{-1} of Pd(II) and no inhibitor or 100 ng ml^{-1} of sulphide. The rate of both the catalysed and the inhibited reaction increased as the concentration of pyronine increased. Figure 1(b) shows the inhibition percentage of sulphide versus pyronine concentration. A concentration of 5.0×10^{-5} M pyronine, which produced the maximum constant inhibitory effect of sulphide, was selected.

The influence of the concentration of hypophosphite was studied over the range 0.1–0.6 M. The rates of the catalysed and inhibited processes increased with increasing hypophosphite concentrations . As can be seen in Figure 1(c), the inhibitory effect of

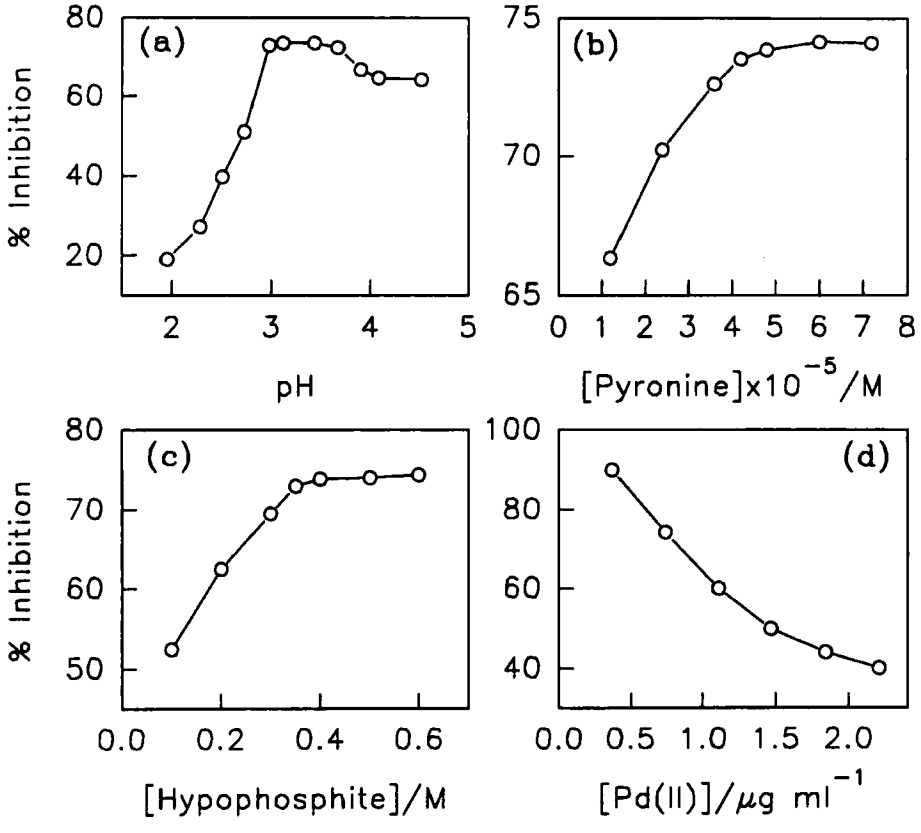

Figure 1 Influence of reaction variables on the inhibitory effect of sulphide: (a) pH; (b) Pyronine-G concentration; (c) $H_2PO_2^-$ concentration and (d) Pd(II) concentration.

sulphide is maximum and constant in the concentration range 0.4–0.6 M of $H_2PO_2^-$; a concentration of 0.4 M was chosen for further experiments.

An important variable to be taken into account is the concentration of palladium. It was observed that when the concentration of sulphide was constant the rate of the process increased considerably with the concentration of Pd(II), showing a kinetic order of + 1 over the range 0.2–2.0 μg ml^{-1} of Pd(II). The inhibitory effect of sulphide decreased when the Pd(II) concentration increased, as can be seen in Figure 1(d), which shows the results obtained in the presence of 100 ng ml^{-1} sulphide and increasing amounts of Pd(II). In addition, the range of sulphide concentration which could be determined and the slopes of the calibration graphs obtained in the selected experimental conditions depended on the concentration of the catalyst. A concentration of 0.7 μg ml^{-1} Pd(II) was selected as being the most suitable, as the linear range for the determination of sulphide is wide and the method presents good sensitivity.

The influence of temperature, under the experimental conditions described, was studied in the range 20.0–40.0°C. A temperature of 25 ± 0.2°C was chosen because the inhibition percentage was higher than at the other temperatures studied.

Features of the analytical method

Under the selected experimental conditions of pH 3.2; 5.0×10^{-5} M Pyronine G; 0.4 M $H_2PO_2^-$; 0.7 μg ml^{-1} of Pd(II) and 25 ± 0.2°C a calibration graph, linear between 10 and 200 ng ml^{-1} of sulphide was obtained. The regression equation found was $\ln t = 1.5 \times 10^{-4} \times [S^{2-}] + 2.80$, where t is the time required for the absorbance of the pyronine G to decrease by 0.1 and the concentrations of sulphide is expressed in ng ml^{-1}, with a correlation coefficient of 0.9997. The precision of the method was tested by analysing 10 replicate samples containing 100 ng ml^{-1} of sulphide. The relative standard deviation obtained was ± 1.4% and the limit of detection was 4 ng ml^{-1}.

The selectivity of the method was determined by adding different amounts of potentially interfering species to samples containing 100 ng ml^{-1} of sulphide. The tolerance limit was taken as the concentration causing an error of no more than ± 5% in the determination of sulphide. The results obtained are summarized in Table 1.

Table 1 Interferences in the determination of 100 ng ml^{-1} of sulphide.

Species assayed	*Limiting molar ratio [Species]/[S^{2-}]*
NO_3^-, SO_4^{2-}	10000
Mg^{2+}, Ca^{2+}	2500
Ni^{2+}, Co^{2+}, Al^{3+}	300
Cl^-, F^-, HPO_4^{2-}	100
Zn^{2+}	50
Mo (VI), W(VI)	5
Bi^{3+}, Br^-	1
Cr(VI), Mn^{2+}, Hg^{2+}	0.5
I^-, IO_3^-, Ag^+, As^{3+}, Cd^{2+}, SO_3^{2-}, Pb^{2+}, V(V), Cu^{2+}, Fe^{3+}, NO_2^-	< 0.5

Applications

In order to demonstrate the applicability of the proposed method to the determination of sulphide, the method was applied to the analysis of sulphide in various environmental samples: mineral, ground and hot spring waters; and as hydrogen sulphide in atmospheric air and in the air of the workroom of one of our laboratories. The results are summarized in Tables 2 and 3. All the samples were analysed by applying the proposed and the reference Methylene Blue methods[3-23]. The results obtained by both methods in water and air samples were compared by applying the F and t tests at 95% confidence level. The calculated F and t values did not exceed the theoretical values ($F_{4,4} = 6.38$; $t_7 = 2.36$) indicating that there were no significant differences between the precision and the mean content of sulphide or hydrogen sulphide obtained by the proposed and the respective reference methods.

Table 2 Determination of sulphide in water samples.

	$S^{2-}/\mu g\ ml^{-1}$		
Water sample	*Added*	*Found*	
		*Reference method**	*Proposed method**
Mineral			
1	0.050	0.050 ± 0.003	0.049 ± 0.004
2	0.100	0.098 ± 0.003	0.100 ± 0.003
3	0.200	0.199 ± 0.008	0.199 ± 0.003
Ground			
1	0.050	0.049 ± 0.002	0.051 ± 0.001
2	0.085	0.085 ± 0.002	0.082 ± 0.002
Hot springs			
1	–	0.351 ± 0.008	0.357 ± 0.006
2	–	1.016 ± 0.019	1.004 ± 0.008
3	–	5.283 ± 0.117	5.481 ± 0.040

*Mean of five determinations ± SD

Table 3 Determination of hydrogen sulphide in air samples.

Sample	H_2S *content/mg* m^{-3}	
	*Reference method**	*Proposed method**
1	1.33 ± 0.03	1.34 ± 0.02
2	22.4 ± 0.2	22.9 ± 0.1

*Mean of five determinations ± SD

CONCLUSIONS

The kinetic method proposed is very sensitive, and permits the determination of very low sulphide concentrations (10 ng ml^{-1}) . Its sensitivity is similar to that obtained by other kinetic methods. The method is widely applicable to the determination of sulphide in different water samples and of hydrogen sulphide in air samples.

Acknowledgment

We gratefully acknowledge the CGICYT (Project PB93–1139) for financial support.

References

1. R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology* (Wiley, New York, 1981) Vol. 17, 3rd ed., p. 395.
2. W. J. Williams, *Handbook of Anions Determination*, (Butterworths, London, 1979) p. 568.
3. *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, American Water Works Association and Water Pollution Control Federation, 1985) 16th ed., p. 475.
4. A. K. Babko and L.V. Markova, *Zavod. Lab.*, **25,** 1283–1285 (1959).
5. L. P. Atkinson and J. G. Natoli, *Anal. Chem.*, **46**, 1316–1319 (1974).
6. H. Weisz, W. Meiners and G. Fritz, *Anal. Chim. Acta*, **107**, 301–307 (1979).
7. J. Kurzawa and Z. Kurzawa, *Chem. Anal.*, **31**, 99–103 (1986).
8. A. Sakuragawa, T. Harada, T. Okutani and S. Utsumi, *Bunseki Kagaku*, **29**, 264–266 (1980).
9. N. Kiba, M. Mishijima and F. Furusawa, *Talanta*, **27**, 1090–1092 (1980).
10. J. Kurzawa, *Anal. Chim. Acta*, **173**, 343–348 (1985).
11. G. Ramis, R. Villanueva, R. M. Gonzalvez and J. García, *Termochim. Acta*, **112**, 171–177 (1987).
12. L. Tamarchenko, *Zh. Anal. Khim.*, **33**, 824–827 (1978).
13. V. González, B. Moreno, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, **65**, 1897–1902 (1993).
14. D. Mealor, and A. Towsend, *Talanta*, **15**, 1477–1481 (1968).
15. J. Teckentrup and D. Klockow, *Talanta*, **28**, 663–666 (1981).
16. S. Kawarkubo, M. Iwatsuki and T. Fukasawa, *Anal. Chim. Acta*, **282**, 389–395 (1993).
17. H. Ludwing, H. Weisz and T. Lenz, *Anal. Chim. Acta*, **70**, 359–361 (1974).
18. M. Cejas, A. Gómez-Hens and M. Valcarcel, *Bunseki Kagaku*, **33**, 151–153 (1984).
19. C. Sánchez-Pedreño, M. I. Albero and M. S. García, *Quím. An.*, **4**, 168–176 (1985).
20. C. Sánchez-Pedreño, M. I. Albero, M. S. García and A. Saez, *Analyst*, **115**, 1257–1260 (1990).
21. C. Sánchez-Pedreño, M. I. Albero, M. S. García and A. Saez, *Talanta*, **38**, 677–681 (1991).
22. W. J.Williams, *Handbook of Anions Determination*, (Butterworths, London, 1979) p. 570.
23. P. O. Warner, *Analysis of Air Pollutans* (spanish edition, Paraninfo, Madrid, 1981) p. 140.