Evaluation of Environmental Sulphide by Stabilisation of the Initial Product of the Pentacyanonitrosylferrate(II)-sulphide Reaction

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Abstract

Determination of environmental sulphide requires non-interference from other anions. Cyanide stabilisation of the transient red-violet product of the pentacyanonitrosylferrate(II)-sulphide reaction enables effective quantification of a 0.3 - 5 working range and a 0.2 µg ml^{-1} limit of detection. Sulphide in standard 2.0 µg ml^{-1} solutions was detected to within 2.4% standard deviation. The technique has been applied to hot-spring water, marshland water and boiled eggs. The mean sulphide levels were 1.7 ± 0.2, 9.9 ± 0.2 and 21.7 ± 0.2, which compared favourably with 1.9 ± 0.3, 10.9 ± 0.3 and 22.6 ± 0.3 µg ml^{-1}, respectively, by iodimetry.

Keywords: Environmental sulphide, determination, pentacyanonitrosylferrate(II)-sulphide reaction, cyanide stabilisation

Introduction

Sulphide is toxic and needs careful quantification in the environment. Existing methods are either too expensive or are fraught with interference. There is therefore a need to continue searching for more suitable and environmentally friendly techniques. In this study, we test the new technique on several environmental situations and find it to be effective, affordable, and free of interference.

The sulphide anion is an important environmental derivative of sulphur and is responsible for the unpleasant odour and toxicity of hydrogen sulphide gas that usually ensues from sulphide-containing aqueous systems[1, 2]. One of the major sulphide toxic effects is associated with deactivation of enzymes by coordination of S^{2-} to metal co-factors such as Fe^{2+}, Mg^{2+} or Cu^{2+}. The human body normally detoxifies hydrogen sulphide by oxidation into sulphate or thiosulphate via haemoglobin-bound oxygen in the blood or by liver enzymes[3]. Lethal toxicity occurs when the gas swamps the body's detoxification capacity. Ironically, the curative effect of hot-spring water is usually associated with its hydrogen sulphide content. Therefore determination of sulphide is of importance in the monitoring and control of both toxic and therapeutic hydrogen sulphide[4, 5] emissions arising from wastewaters and natural waters in the environment.

A number of expensive techniques have been developed to quantify total sulphide[2,6]. These include spectrophotometric methods with methylene blue[1], ethylene blue[7], nitroprusside[8], copper quin-8-olate[9] and by direct measurement[2]. A variety of other methods using spectrofluorimetry, flow injection analysis, gas chromatography and polarography have been used to quantify S^{2-} as well[10]. A less expensive, however, but effective spectrophotometric method, based on the formation of a transient red-violet product (I) from the pentacyanonitrosylferrate(II)-sulphide reaction[8], has been known as a sensitive (Gmelin) test for the presence of the S^{2-} anion. The product is unstable and fades within seconds to form clear solutions.

This study describes the observed stabilising effect of the cyanide ion on the pentacyanonitrosylferrate (II)-sulphide reaction, which has made possible the determination of sulphide in the environment using manual spectrophotometry, and could provide an alternative and effective analytical procedure that is within the means of most laboratories.

Materials and Methods

All chemicals were of reagent grade quality and distilled-deionised water was used throughout. All aqueous sodium pentacyanonitrosylferrate(II) (sodium nitroprusside) solutions were freshly prepared and kept in the dark. Fresh stock sulphide solutions were prepared by bubbling purified hydrogen sulphide gas through a 10% sodium hydroxide solution. The concentration of dissolved sulphide was then determined iodometrically[11].

Intermediate standard sulphide solutions (50 μg ml^{-1}) were prepared by dilution of the stock solutions with 0.025 M sodium hydroxide. Working sulphide solutions (0.3 - 5 μg ml^{-1}) were prepared by dilution of the intermediate standard solutions with phosphate buffer to pH 11.4 immediately before use. To the buffered test sulphide solution was added 1 ml potassium cyanide (0.1 M) and 0.1 ml sodium nitroprusside (0.02 M), with all due precautions accorded to handling the cyanide and the resultant mixture made up to the mark in a 5ml volumetric flask. Potentiometric measurements were made using a Corning Pinnacle 555 pH meter. All UV-VIS spectra were measured in quartz-tandem cells of 1-cm path length on a Shimadzu UV-1700 CE spectrophotometer. The absorbance of the coloured mixture was measured immediately after mixing at λ_{max}= 534 nm.

Determination of the sulphide anion in selected environmental systems: The nitroprusside-S^{2-} technique based on the conditions in the present work was applied to the determination of sulphide in water from several environmental systems in Uganda. In one instance water samples were collected from Kitagata hot springs (latitude 00° 40' 00.24" S, longitude 30° 09' 00.24" E) in Bushenyi district in the south-western part of the country. The determination of the sulphide content was carried out as described above. In a separate development, boiled eggs were collected from a local canteen, the shells removed and each egg crashed and placed in a 250 ml conical flask containing sulphuric acid (0.01 M, 100 ml). The mixture was heated to 40°C for 30 minutes and the distillate, collected in an aqueous solution of sodium hydroxide (25 ml, 0.025 M), subsequently analysed for its S^{2-} anion content.

Sample preparation: The slightly turbid aqueous samples were first filtered to remove any solid suspended matter that could be present. The pH of these samples was usually in the range 6.2-6.9 at room temperature (25°C). They were then made alkaline by adding sodium hydroxide pellets (0.2 g per 1000 ml of sample) and immediately tightly Stoppard in order to minimise the loss of S^{2-} as H_2S which tends to occur under acidic conditions. The pH of the samples (100 ml each) was maintained at pH 11.5 using a phosphate buffer by the addition of Na_2HPO_4 (1.42 g) and NaOH (0.2 g). A known amount of stabiliser, normally an alkali metal cation, was at the same time added to the filtrate, which was then ready for analysis.

Results and Discussion

When cyanide was added to the presumed $[Fe(CN)_5NOS]^{4-}$ (I) reaction solution there was an enhanced increase in optical absorbance as well as increased stability of the product. The concentration of the cyanide ion needed to maximise stability was found to be in the range 0.02-0.04 M, fig. 1. Within this concentration range, the absorbance at λ_{max} = 534 nm remained stable for periods up to 30 minutes. Fig. 2 shows the time dependence of the absorbance, with an isosbestic point at λ = 465 nm that was contrary to when cyanide was absent[8]. This phenomenon was attributed to the decomposition of the initial product. The rate of decomposition was observed to follow first order kinetics in I with an observed rate constant k_{obs} = (3.3 ± 0.1) x 10^{-3} at 298 K. This was contrary to the values of (6.0 ± 0.1) x 10^{-3} (this work) and (8.5 x 10^{-3}) s^{-1} in the absence of cyanide[12]. However, whereas the peak at λ_{max} = 534 nm was still evident even after 30 minutes no such peak could be traced after this period in the absence

of cyanide. The observed persistence of the peak to periods longer than 30 min lends support for increased stability of the complex as a result of the addition of cyanide. Worthy of note is the raised time dependent shoulder at λ_{max} between 350 and 400 nm (fig. 2). This is probably due to the nature of the nitroprusside-S^{2-} complex. The use of CN^- as a lone stabiliser was discounted as upon the addition of excess aqueous nitroprusside to aqueous S^{2-} containing CN^-, the solution gradually became purple as opposed to when CN^- was absent. This phenomenon was not observed in the presence of alkali metal cations.

A number of workers have studied various kinetic aspects of nitric oxide transition M-complexes[13-15]. It was proposed[8] that the observed increase in rate and absorbance with pH could be attributed to further attack of S^{2-} ions on the nitroprusside. In view of the present work, it is highly probable that λ_{max}=534 nm arises owing to the prolonged existence of the $[Fe(CN)_5(NOS)]^{4-}$ species. It has been suggested[16] that I can lose either CN^- or $[NOS]^-$. Since solutions of I when left to stand gradually become more alkaline, it is reasonable to assume a proton-assisted elimination of one of the cyanide ligands, equations (2) and (3). This predicts that at constant pH the presence of added excess cyanide should cause I to preponderate, as observed in fig.1.

$$[Fe(CN)_5NO]^{2-}_{(aq)} + S^{2-}_{(aq)} \rightleftharpoons [Fe(CN)_5NOS]^{4-}_{(aq)}\ \mathbf{I} \quad (1)$$

$$[Fe(CN)_5NOS]^{4-}_{(aq)} + H_2O \rightleftharpoons [Fe(CN)_4(H_2O)NOS]^{3-}_{(aq)} + CN^-_{(aq)} \quad (2)$$

$$CN^-_{(aq)} + H_2O \rightleftharpoons HCN_{(aq)} + OH^- \quad (3)$$

This technique was employed to determine the sulphide content in various environmental systems and the results were compared to those obtained using standard iodimetric titration. Analysis of tightly corked bottled water from Kitagata hot-springs (latitude 00° 40' 00.24" S, longitude 30° 09' 00.24" E) in the south-western part of Uganda was carried out 12 hours after sampling. This time lag served a double purpose: travel from the site to the analytical laboratory and allowing the samples, some of which were initially hot, to equilibrate to room temperature. The sample bottles had to be airtight not to allow any hydrogen sulphide to escape. The mean sulphide levels in 78 samples (table 1a, with *n* representing the number of samples at each location) were found to be 1.7 ± 0.2, which compared favourably with a value of 1.9 ± 0.3 μg ml^{-1} found by iodimetry on the same samples. These results together demonstrate that sulphide was present to a level of 1.9 ± 0.3 μg ml^{-1} in the hot spring water, where it probably arises as a result of geochemical processes in the underground water. The hot spring water owes its characteristic rotten egg smell to this content. Results from similar treatment of samples of marshland water (*n* = 70) from Katonga swamp in central Uganda (table 1b) gave values of 9.9 ± 0.2 and 10. 9 ± 0.3 μg mL^{-1} for the nitroprusside and iodimetric techniques, respectively, which were in good agreement of each other. Free sulphide in marshland water comes mainly from the bacterial decomposition of dead plant and animal matter in the swamp environment. The variation in the sources of sulphide and the differences on site in temperature of the samples, may be taken into account for the divergent sulphide levels in hot spring and marshland natural waters.

The freshness of boiled eggs, like that of most cooked protein foods, tends to deteriorate rather rapidly. Analyses performed on such boiled egg distillate using both techniques agreed to within 0.9 ± 0.5 μg mL^{-1} of each other and indicated that the sulphide level increased considerably with time (table 1c). The mean sulphide level in freshly boiled eggs was obtained as 7.6 ± 0.3 using both techniques, rising to 22.2 ± 0.3 μg ml^{-1} distillate in three days of overstay. It is thought that consumption of boiled eggs that have overstayed may be injurious to one's health owing in part to the toxic effect associated with the ingestion of such significant amounts of free sulphide. The values so obtained can however at best be regarded as only a rough estimate, as during the distillation process some hydrogen sulphide gas tends to escape. Also the sulphide content depends on the type of diet offered to the poultry. This could also possibly account for

the observed more noticeable difference in total sulphide levels in samples E5, E8 and E11 (table 1c) obtained using the two methods, as compared to the remaining samples.

The results obtained for the determination of sulphide in a number of environmental samples show that the improved nitroprusside-cyanide technique compares favourably with the conventional iodimetric method and is reliable for the analysis of water samples in the environment. Owing to the interference with iodimetry of several well-known sulphur-related ions such as sulphite and thiosulphate, this study indicates that the nitroprusside technique is free of such interference (table 2) and is a satisfactory method in handling environmental sulphide toxicity and therapeutic[4,5] analytical issues, and should be considered in situations where there seems to be no better method of choice.

During the course of this work it has been observed that the ratio of excess nitroprusside to S^{2-} tends to affect the stability of the initial product. Excessively large nitroprusside enhances the instability of the product. We would therefore recommend that a not >10-fold excess is good enough for analysis. The pH at which the analysis is done should be maintained at the same level for all analyses. A pH not <11 is advisable if satisfactory results are to be achieved. The limit of detection for the improved method was found to be 0.2 µg ml^{-1} (Blank + 3 s.d.). Consequently, the method is considered to have a reliable detection limit of 3 µg ml^{-1}. This detection limit is indicative of a significant improvement and the method could subsequently be applied in the effective detection and quantification of S^{2-} concentrations ≥0.3 µg ml^{-1}.

The effect of several cations and anions on the technique was given due attention. Various amounts of different ionic species were added to the S^{2-} solution. The greatest anionic interference to this method was expected to come from SO_3^{2-} that reacts with nitroprusside in a similar manner to produce a red coloured product $[Fe(CN)_5(NOSO_3)]^{4-}$ with λ_{max} = 437 nm. In this work it was found that S^{2-} could be determined without such interference in the presence of a SO_3^{2-} anion concentration of ≤1000 µg mL^{-1}. Cationic interference normally stems from species such as Cu^{2+} and Zn^{2+} that tend to form sparingly insoluble sulphides. This possibility could be minimised by the use of strong complexing agents, in particular EDTA, that mask these species and as a result eliminate interference.

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Table-1: Total sulphide levels in various environmental situations*

Concentration (µg/mL)								
(a) **Hot spring water, Kitagata**			**(b) Marshland water, Katonga**			(c) **3-day overstayed boiled eggs**		
Site No	**Nitroprusside technique**	**Iodometric titration**	**Site No**	**Nitroprusside technique**	**Iodometric titration**	**Sample No.**	**Nitroprusside technique**	**Iodometric titration**
W1 (n = 6)	2.3 ± 0.2	2.3 ± 0.3	X1 (n = 5)	12.0 ± 0.2	14.1 ± 0.3	E1	25.7 ± 0.2	24.1 ± 0.3
W2 (n = 5)	2.2 ± 0.2	2.1 ± 0.3	X2 (n = 4)	10.7 ± 0.2	13.4 ± 0.3	E2	20.1 ± 0.2	27.0 ± 0.3
W3 (n = 4)	2.3 ± 0.2	2.4 ± 0.3	X3 (n = 6)	8.9 ± 0.2	12.5 ± 0.3	E3	22.9 ± 0.2	25.3 ± 0.3
W4 (n = 5)	1.9 ± 0.2	2.2 ± 0.3	X4 (n = 3)	7.7 ± 0.2	11.9 ± 0.3	E4	31.4 ± 0.2	29.1 ± 0.3
W5 (n = 6)	2.3 ± 0.2	2.0 ± 0.3	X5 (n = 6)	11.6 ± 0.2	9.8 ± 0.3	E5	23.6 ± 0.2	19.7 ± 0.3
W6 (n = 5)	2.0 ± 0.2	2.4 ± 0.3	X6 (n = 4)	7.9 ± 0.2	9.6 ± 0.3	E6	19.7 ± 0.2	26.0 ± 0.3
W7 (n = 7)	1.4 ± 0.2	1.6 ± 0.3	X7 (n = 7)	9.8 ± 0.2	12.1 ± 0.3	E7	22.8 ± 0.2	25.4 ± 0.3
W8 (n = 6)	1.3 ± 0.2	1.6 ± 0.3	X8 (n = 8)	10.8 ± 0.2	13.2 ± 0.3	E8	15.7 ± 0.2	19.7 ± 0.3
W9 (n = 5)	1.4 ± 0.2	1.6 ± 0.3	X9 (n = 4)	11.5 ± 0.2	9.5 ± 0.3	E9	23.9 ± 0.2	20.6 ± 0.3
W10 (n = 8)	1.6 ± 0.2	1.7 ± 0.3	X10 (n = 5)	6.9 ± 0.2	7.1 ± 0.3	E10	19.8 ± 0.2	21.3 ± 0.3
W11 (n = 6)	1.1 ± 0.2	1.3 ± 0.3	X11 (n = 6)	11.6 ± 0.2	9.7 ± 0.3	E11	20.1 ± 0.2	24.0 ± 0.3
W12 (n = 7)	1.1 ± 0.2	1.4 ± 0.3	X12 (n = 5)	9.8 ± 0.2	7.9 ± 0.3	E12	17.9 ± 0.2	14.7 ± 0.3
W13 (n = 8)	1.6 ± 0.2	1.8 ± 0.3	X13 (n = 7)	10.0 ± 0.2	10.5 ± 0.3	E13	18.1 ± 0.2	17.0 ± 0.5
Average	1.7 ± 0.2	1.9 ± 0.3	Average	9.9 ± 0.2	10.9 ± 0.3	Average	21.7 ± 0.2	22.6 ± 0.3

*The tolerances are mean errors

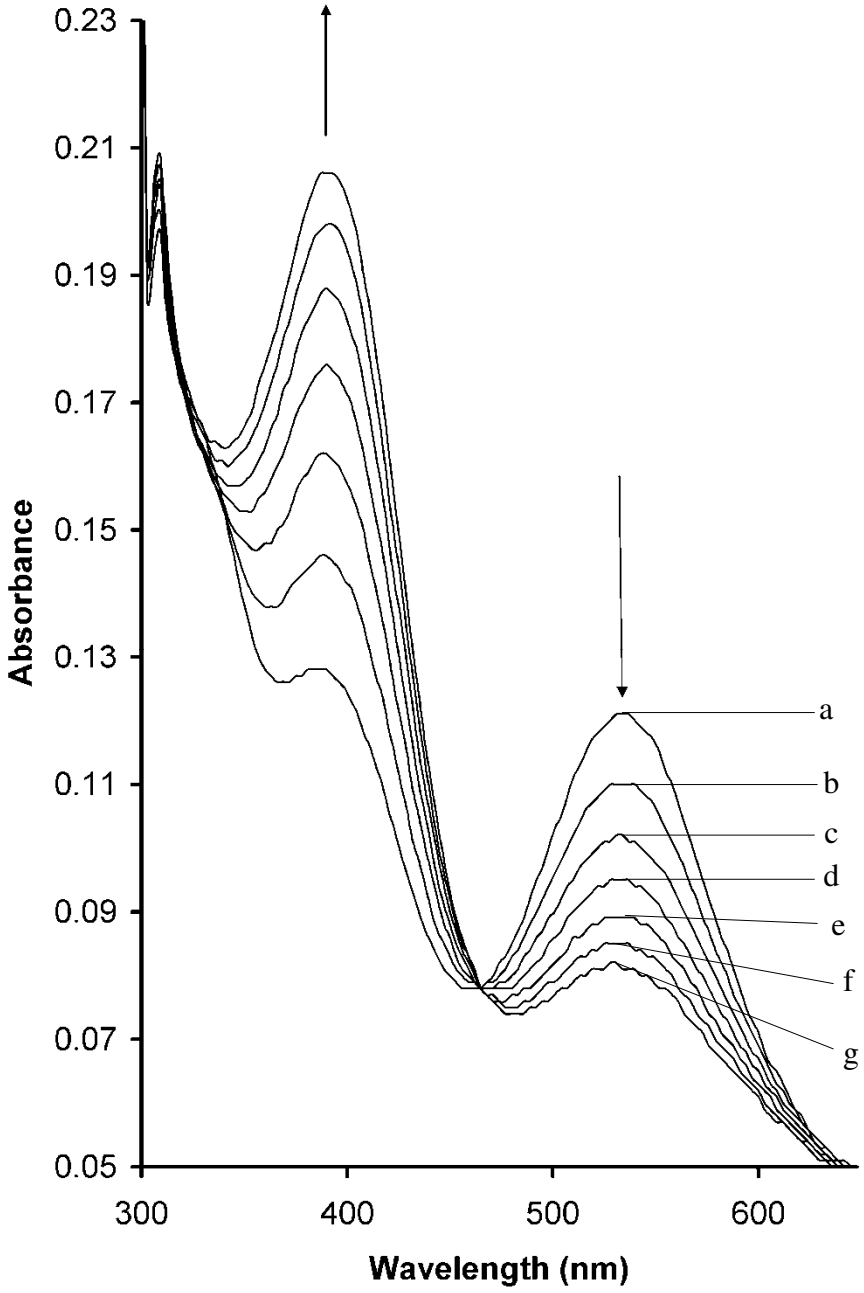

Figure-2: Absorption of the pentacyanonitrosylferrate(II)-sulphide reaction mixture at 25 s intervals (a) – (g) in presence of 1 M KCl and 0.02 M cyanide at 2 x 10^{-5} M sulphide, 1 x 10^{-5} M pentacyanonitrosylferrate(II) and at pH 11.0.

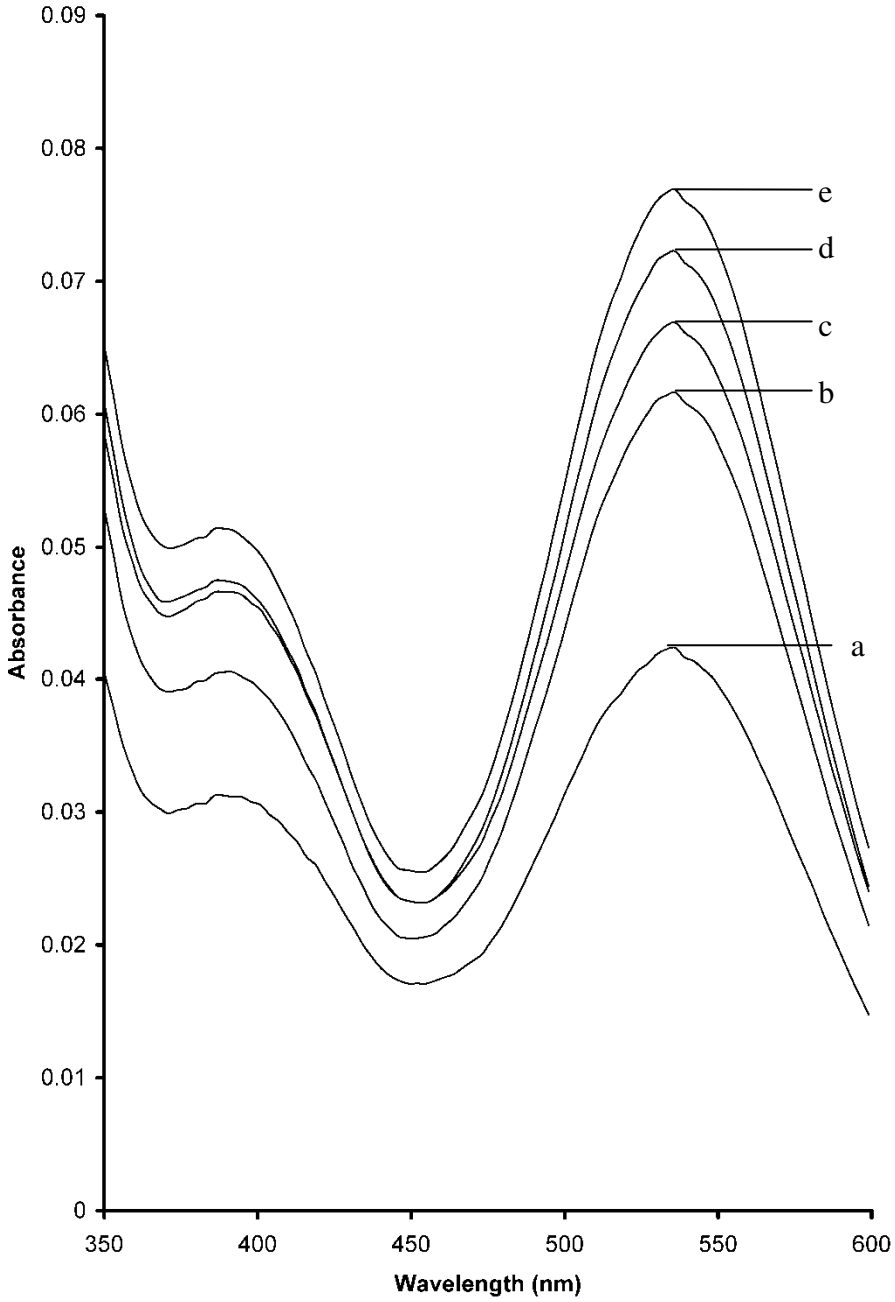

Figure-1: Visible absorption spectra of the initial product of the pentacyanonitrosylferrate(II)-sulphide reaction at cyanide concentrations of (a) 0.02 (b) 0.04 (c) 0.06 (d) 0.08 (e) 0.10 M after 30 s at 4 x 10^{-5} M sulphide, 1 x 10^{-3} M pentacyanonitrosylferrate(II) and at pH 11.5.