SIMULTANEOUS DETERMINATION OF CYANIDE AND SULFIDE BY REVERSED FLOW INJECTION ANALYSIS

Ma Huichang* Liu Jingfu

Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing, 100085

Feng Jianzhang Gao Yue

Department of Chemistry, Peking University, Beijing, 100871

SUMMARY

A method for simultaneous determination of cyanide and sulfide by reversed flow-injection technique is described. Cyanide, which diffused through the PTFE membrane from the acidified stream (donor stream) to the accepter stream, was determined by the pyridine-barbituric acid method. While sulfide, remained in the donor stream, was determined by iron(Ⅲ) in the presence of 1,10-phenatroline at pH4.6. The detection limits of cyanide and sulfide are 0.2mg dm^{-3} and 0.4mg dm^{-3}, respectively. The relative stardand deviation (r.s.d.) of the determination at the level of 3.0mg dm^{-3} cyanide and 10.0mg dm^{-3} sulfide are 0.5% and 0.7% (n=11), respectively. Carbonate, nitrate, formaldechyde, iodide, thiocyanate, and bromide did not interfere with the determination.

* To whem correspondence should be addressed.

Introduction

The determination of cyanide and sulfide is very important in environmental mornitoring. Rios et al[1] reported a method for simultaneous determination of cyanide and sulfide by reversed flow injection analysis (rFIA) technique. In their method, N–(1–Naphthyl)–ethylenediamine and pyridine–barbituric acid were injected as chromogenic reagents of sulfide and cyanide, respectively. Unfortunately, the method suffered from low sampling rate and interference of some coexisting species.

In this paper, a rapid method for simultaneous determination of cyanide and sulfide by rFIA technique was described. Cyanide and sulfide were separated by a PTFE micropore membrane in a gas–diffusion unit. The separated cyanide was determined by detecting an intermediate of the pyridine–barbituric acid reaction[2], While sulfide was determined using its chromogenic reaction with iron(Ⅲ)/ 1,10–phenatroline reagent. As a gas–diffusion system was introduced, the interference of most coexisting species was eliminated.

EXPERIMENTAL

Reagents

All reagents were of analytical grade and deionized water was used throughout.

The stock solution and working standard solution of cyanide, pyridine–barbituric acid reagent and phesphate buffer solution were prepared as described elsewhere[2].

Chloramine–T / buffer solution: Dissolve 0.5g of chloramine–T in 100ml of the above prepared phosphate buffer solution.

EDTA / hydrochloric acid solution: Dissolve 0.4g of ethylenediamine–tetraacetic acid disodium salt in 500ml of water, add 250ml of concentrated hydrochioric acid and dilute to 1000ml with water. This solution

contains 0.001 mol dm^{-3} of EDTA and 3 mol dm^{-3} of hydrochloric acid.

Sodium hydroxide solution: Disslve 2.0g of sodium hydroxide in 100ml of water, pipette 5ml of this solution and dilute to 500ml with water.

Sodium sulfide stock solution: Dissolve 6.0g of sodium sulfide in 250ml of boiled and cooled water, keep it in refrigerator. The stock must be standardized everyday and working solutions should be prepared freshly by diluting this stock just before use.

Sodium acetate solution: Dissolve 82.0g of anhydrous sodium acctate in 500ml of water.

Iron(Ⅲ) stock solution (0.05 mol dm^{-3}): Dissolve 6.0g of $NH_4Fe(SO_4)_2$ $12H_2O$ in water, add 5ml of concetrated sulfuric acid and dilute to 250ml with water.

1,10–phenathroline stock solution (1.0%); Add 2.50g of 1,10–phenathroline in 2ml of (1+1) hydrochloric acid, add appropriate water to dissolve it, dilute to 250ml with water.

Iron(Ⅲ) / 1,10–phenathroline solution: Mix 30ml of the Iron(Ⅲ) stock solution with 40ml of the 1,10–phenathroline stock solution, dilute to 100ml with water.

Apparatus

A 5020 Flow Injection Analyzer (Tecator, Sweden), a FIA–91 Flow Injection Analyzer(Shanghai No.3 Analytical Instrument Factory. China) and a compact pH meter (Horiba, Japan) were Used. A Chemifold V (Tecator), a 5101 thermostat (Tecator) and a diversion Valve were used to construct the manifold. The PTFE micropore membrane was provided by Tecator.

Procedure

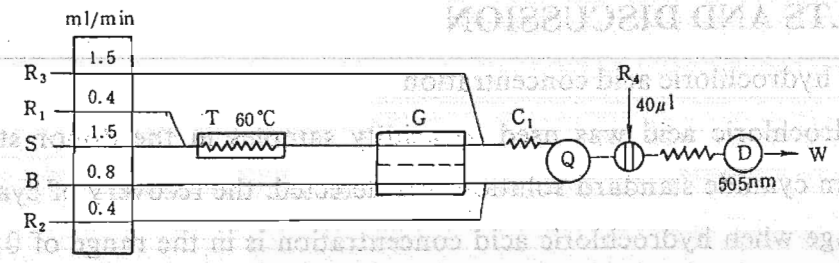

Fig.1 Manifold used for the simultaneous determination of cyanide and sulfide. T, 5101 thermostat, temperature set at 90℃ ; G, Chemifold V which contains the gas–diffusion module; Q, Diversion valve; D, Detecter; C1, Reaction coil (30cm long, 0.7mm i.d.); C2, Reaction coil (60cm long, 0.7mm i.d.); B, 0.005 mol dm^{-3} NaOH; R1, EDTA / hydrochloric acid solution; R2, Chloramine–T / buffer solution; R3, 2 mol dm^{-3} NaAc; R4, Pyridine–barbituric acid or iron(Ⅲ) / 1,10–phenathroline reagent. S, Sample; W, Waste.

Fig.1 shows the optimized manifold used for simultaneous determination of cyanide and sulfide. Samples were mixed with a stream of EDTA / hydrochloric acid solution to form the donor stream. The donor stream was heated to 60℃ while passing through the 100cm long PTFE coil(0.7mm i.d.) in the 5101 thermostat. The liberated hydrogen cyanide diffused through the PTFE membrane and was absorbed by a acceptor solution of 0.005 mol dm^{-3} NaOH. Then, the acceptor was mixed with chloramine–T / buffer solution and pyridine–barbituric acid reagent was injected to produce a colour species with peak absorbance at 494nm wavelength. On the other hand, the donor stream was then adjusted to pH4.7 by mixing with a sodium acctate solution, a iron(Ⅲ) / 1,10–phenathroline chromogenic reagent was injected, and another colour species with a peak absorbance at 510nm was produced by the reaction of sulfide with the iron(Ⅲ) / 1,10–phenathroline reagent. Using a diversion valve only one spectrophotometer setting at 505nm, the composite absorbance wavelength of the above two colour species, was needed as detector.

RESULTS AND DISCUSSION

Effect of hydrochloric acid concentration

Hydrochloric acid was used to acidify samples in the donor stream. If potassium cyanide standard solution was detected, the recovery of cyanide did not change when hydrochloric acid concentration is in the range of 0.2–3 mol dm^{-3}. However, the cyanide recovery increased with the increase of hydrochloric acid concentration if metal interferences such as nickel and copper were existed. Furthermore, higher hydrochloric acid concentration is helpful for the separation of cyanide from sulfide. Table 1 indicates that 50 times of sulfide did not interfere the determination of cyanide when a 3 mol dm^{-3} of hydrochloric acid solution was used. EDTA was added into the hydrochloric acid solution to assist the dissociation of some stable metal cyanide complexes.

Table 1. Effect of hydrochloric acid concentration on the separation of cyanide and sulfide. Total cyanide concentration 2 mg dm^{-3}.

Hydrochloric acid concentration(mol dm^{-3})	1	1	1	3	3	3
Ratio of amount of sulfide to cyanide	30	50	100	30	50	100
Cyanide recovery(%)	106	128	177	101	106	138

Effect of iron(Ⅲ) / 1,10–phenathroline concentration

The concentration of iron(Ⅲ) and 1,10–phenathroline were optimized respectively. Results shown in Fig.2 and Fig.3 indicate that the optimum concentration of iron(Ⅲ) and 1, 10–phenathroline were 0.015 mol dm^{-3} and 0.4%, respectively.

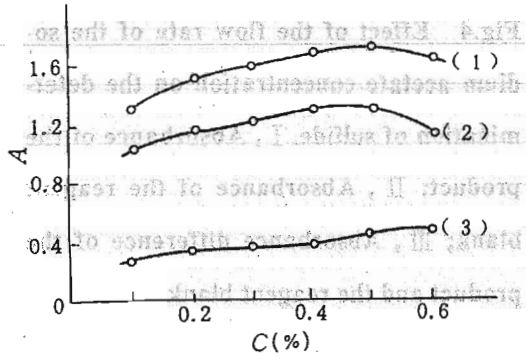

Fig.2 Effect of iron(Ⅲ) concentration on the determination of sulfide. Ⅰ, Absorbance of the product; Ⅱ, Absorbance of the reagent blank; Ⅲ, Absorbance difference of the product and the reagent blank.

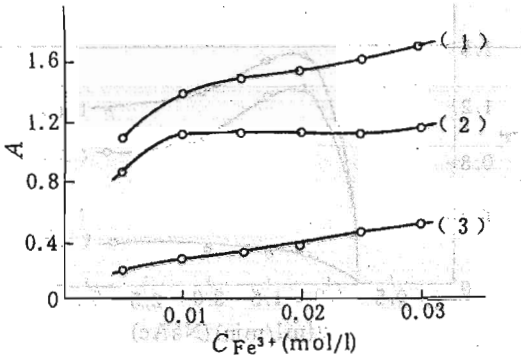

Fig.3 Effect of 1,10–phenathroline concentration on the determination of sulfide. Ⅰ, Absorbance of the product; Ⅱ, Absorbance of the reagent blank; Ⅲ, Absorbance difference of the product and the reagent blank.

Effect of pH

The pH for the determination of cyanide was optimized in our previous study[2]. The purpose of this study is to optimized the pH for the determination of sulfide. A stream of 2 mol dm^{-3} sodium acetate solution was introduced into the donor stream to adjust and control its pH value. Because the introduced sodium acetate can cooperate with the hydrochloric acid to form a buffer, a series of pH value of the donor stream was obtained by varying the flow rate of the sodium acetate solution. Results shown in Fig.4 indicates that the highest sensitivity of the chromogenic reaction was obtained when the flow rate of the sodium acetate solution was 1.5 ml / min. Under this flow rate, the pH value in the donor stream and in the injected iron(Ⅲ) / 1,10–phenathroline reagent zone were 4.7 and 4.6, respectively.

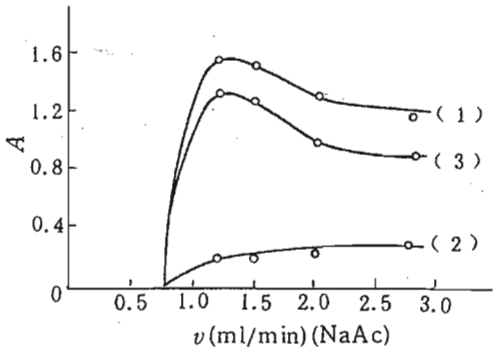

Fig.4 Effect of the flow rate of the sodium acetate concentration on the determination of sulfide. Ⅰ, Absorbance of the product; Ⅱ, Absorbance of the reagent blank; Ⅲ, Absorbance difference of the product and the reagent blank.

Effect of temperature

Previous study[2] shows that temperature has significant influence on the sensitivity of the cyanide chromogenic reaction. In this study, the effect of temperature on the sulfide chromogenic reaction was investigated. The reaction coil C2 (in Fig.1) was replaced by a 5101 thermostat and temperature was varied from 30 ℃ to 90℃. Though results shown in Fig.5 indicates that higher temperature is helpful for the chromgenic reaction, room temperature was adopted for convenience.

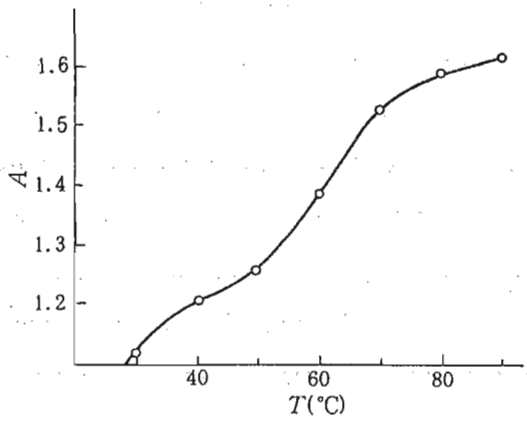

Fig.5 Effect of temperature on the determination of sulfide.

Characteristics of the method

Although two rinds of chromogenic reagents must be injected respectively for determining cyanide and sulfide, a sampling rate of $30h^{-1}$ was obtained. Some other characteristics of the method were listed in Table 2.

Table 2. Some characteristics of the method

	Cyanide	sulfide
Regression equation	$A=0.0699[CN^-]+0.372$	$A=0.0597[S^{2-}]+0.612$
Regression coefficient	0.9997	0.999
Linear range / mg dm^{-3}	0–6.0	0–20.0
r.s.d. / (n = 11)	0.5%	0.7%
Concn.for r.s.d / mg dm^{-3}	3.0	10.0
Detection limit / mg dm^{-3}	0.2	0.4

Interference study

The effect of coexisting species on the determination of cyanide and sulfide were studied respectively. Results show that only Co^{2+} and formaldehyde interfere the determination of cyanide. Other common interferents such as SCN^-, Br^-, I^-, S^{2-}, Ni^{2+}, Cu^{2+}, Ag^+ and Hg^{2+} did not interfere the determination.

Table 3 shows the effect of some coexisting species on the determination of sulfide. From Table 3, it is seen that only NO_2^-, F^-, oxalic acid and tartaric acid interfered the determination significantly. Fortunately, their interference could be decreased by appropriately treating the samples. If appropriate amount of Al^{3+} was added, up to 20 times of F^- and oxalic acid did not interfere the determination of sulfide. The interference of NO_2^- could be decreased by adding a small amount of amidosulfonic acid in acidic medium. Table 3 also shows that up to 20 times of $S_2O_3^{2-}$ and 30 times of SO_3^{2-} did not interfere the determination, this is becacuse that they changed into SO_2 and diffused through the PTFE membrane to acceptor stream from the donor stream.

Table 3. Effect of coexisting species on the determination of 5.0mg dm^{-3} sulfide

Species	Tolerance ratio	Recovery(%)
F^-*	5	79
oxalic acid*	2	105
tartaric acid	2	103
CO_3^{2-}	100	98
NO_3^-	50	103
$S_2O_3^{2-}$	20	103
NO_2^-*	10	134
SO_3^{2-}	30	104
PO_4^{3-}	20	99
I^-	100	105
formaldehyde	100	94
SCN^-	50	103
Br^-	50	99

* Species whose interference can be reduced by appropriately treating the samples.

Stimultaneous determination of cyanide and sulfide in water

Five synthetic water samples and two electroplating wastewater samples were analysed by the proposed method. Results were shown in Table.4 which indicates that the proposed method is suitable for the simultaneous determination of cyanide and sulfide in water.

Table 4. Simultaneous determination of cyanide and sulfide in water samples.

Sample	Concentrations added ($mg\ dm^{-3}$)		Concentrations found ($mg\ dm^{-3}$)		Recovery (%)	
	cyanide	sulfide	cyanide	sulfide	cyanide	sulfide
1	0.0	4.9	0.3	5.1	—	104
2	1.0	6.0	1.0	6.2	100	103
3	1.6	12.0	1.5	12.0	94	100
4	5.0	5.3	5.2	5.5	104	104
5	5.6	10.2	5.8	10.7	104	104
6*	—	—	1.4	5.0	—	—
	2.0	10.0	3.3	15.0	95	100
	3.0	15.0	4.2	19.5	93	97
7*	—	—	3.7	11.0	—	—
	1.0	5.0	4.71	15.7	100	94
	2.0	7.5	5.8	25.3	105	95

* Electroplating wastewater.

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Reference

1. Rios, A., Luque de Castro, M.D. and Valcarcel, M., Analyst, 1984, 09, 1487.
2. Ma, H., and Liu, J., Anal. Chim. Acta, 1992, 261, 247.

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