Effect of some Interfering Ions on the Polarographic and Spectrophotometric Determination of Cyanide and Sulfide Ions in Water.

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Abstract

Spectrophotometric and polarographic techniques were used for cyanide and sulfide ions determination. Chloramine-T and barbituric acid were used as reagents for complex formation and 0.5M H_3BO_3+ 0.1M KOH and 0.02 M ascorbic acid + 0.018 M disodium EDTA + 100 mL of 1M NaOH supporting electrolytes for polarography. The Interference effect of the interfering ions Cl^-, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Cu^{2+} was studied. For eliminating the effect of interference , distillation method was used for distillation of cyanide solutions. The concentration of cyanide ion in several samples of drinking water, natural water and waste water were determined by both techniques. The linearity of cyanide determination by spectrophotometric was ranged from (0.05 - 0.5 ppm) at a wavelength (578 nm). The linearity for cyanide ion determination by polarography was ranged from (0.02 - 0.2 ppm).

Key Words: Cyanide and sulfide determination, polarography and spectrophotometry, effect of interference.

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تأثير تداخل بعض الايونات على قياس ايونات السيانيد والكبريتيد في الماء باستخدام الطرق الطيفية والبولاغرافية

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** دائرة بحوث الصناعات البتروكيمياوية – وزارة العلوم والتكنولوجيا – الجادرية – بغداد العراق

الخلاصة

تم تعيين تركيزي ايوني السيانيد و الكبريتيد باستخدام الطرق الطيفية والبولاروكرافية و قد تم تثبيت مدى التحسس بالطريقة الطيفية التي تتراوح في المدى (0.05 - 0.5 ppm) بتكوين معقد مع Chloramine – T و Barbituric acid عند طول موجي(578 nm) . كانت درجة التحسس بالطريقة البولاروكرافية تتراوح من (0.02 – 0.2 ppm) . وكما درست التداخلات الحاصلة نتيجة تواجد الايونات التالية (Cl^- , Fe^{2+} , Mg^{2+} , Ca^{2+} , S^{2-} , Cu^{2+}) قبل و بعد عملية التقطير لمحلول السيانيد و قد وجد ان الايونات الموجبة لها تاثير مباشر على تعيين السيانيد اما ايون الكبريتيد فله تداخل عالي جدا لا يمكن ازالته بعد التقطير و يمكن ازالة تاثيره باضافة كاربونات الكادميوم او تحويل السيانيد الى حامض الفورميك .تم تعيين السيانيد في نماذج من ماء الحنفية و المياه الطبيعية ومياه الفضلات.

مفاتيح البحث : السيانيد ، الكبريتيد ، البولاروكرافي ، التداخلات.

Introduction

Cyanide is used in many chemical and refining processes, found in the effluent from electroplating and metal cleaning operations, coke ovens, steel manufacturing facilities and gas scrubbers also Cyanide is one of the most lethal poisons known [1,2] Polarographic method (DPP) for the quantitative analysis of enalapril maleate has been developed by Fikriye Elmali et al.[3-6] .A peak was obtained at -1.4 V in methanol and the concentration range ranged from 20 to 100 µg / mL. Deqian Huang et al.[10] developed a simple and sensitive method for sulfide in water and waste water samples by anodic stripping voltammetry using mercury-film electrode based on cadmium reaction with sulfide. The detection limit is 1.3 x 10^{-8} Mole / L calculated under the optimum conditions. Shayessteh et al.[11] use indirect determination of cyanide in water and industrial waste water by flow injection–atomic absorption spectrophotometry. Barzegar et al.[12] determine sulfide ions based up on the reaction of sulfide with methyl green using UV-visible spectrophotometer. Amitabh et al.[13] used cyanide – selective electrode for cyanide determination and study the effect of pH on the response of the cyanide electrode also the effect of metal ion on the response due to the formation of metal – cyanide complexes.

An extractive spectrophotometric method for the determination of cyanide in waste water is developed by Anjum et al.[14]. The complex formed by reaction of cyanide with bromine and pyridine and extract with n-butanol in acidic medium, absorbs at 520 nm with concentration range of 0.03 – 0.20 µg / mL . The method has been successfully applied for determination of cyanide in waste water and biological fluid.

A spectrophotometric method was developed for the determination of cyanide ions in aqueous media by Al-Saidi [15]. The method based on the nucleophilic addition of cyanide ion to the reagent 4 – hydroxyl-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-6(3H)-one

abbreviated as (HOTT). A red complex showed a sharp peak at 466 nm and used for cyanide determination in tap and drinking water and the results were compared with ion selective electrodes.

In this work spectrophotometric and polarographic techniques were used for cyanide and sulfide determination at low concentration, in presence of the ions Cl^- , Cu^{2+}, Ca^{2+}, Fe^{3+}, Mg^{2+} as interfering ions. Distillation method was used for free cyanide and sulfide determination in order to eliminate the interference species.

Experimental part

Equipments

1. UV-VIS spectrophotometer type Shimadzu 1650 PC from JAPAN.
2. Polarograph type Metrohm consists of E-506 polarecord with E-505 polarograph stand.
3. Cyanide distillation apparatus was constructed according to the procedure given in reference[7,8].

Reagents

Chloramines –T (N-Chloro-4-toluenesulfonamide sodium salt**)** from Sigma - Aldrich

Potassium cyanide (KCN) from Sigma - Aldrich

barbituric acid: 2,4,6-trioxypyrimidine from BDH

Pyridine from BDH

Sodium di-hydrogen phosphate ($NaH_2PO_4.H_2O$) from BDH

All other chemicals are ANALAR from BDH

1. Chloramines – T solution: Dissolve 1gm white water soluble powder in 100 mL water. Prepare weakly and store in refrigerator.
2. Sodium hydroxide solution 0.25 N: Dissolve 10 gm of NaOH in 1 liter distilled water.
3. Stock cyanide solution (1000µg/mL CN^-): Dissolve approximately 2gm KOH and 2.5gm KCN in one liter distilled water.
4. Standard cyanide solution (10 µg / mL): Dilute 10 mL of the stock KCN to one liter with 0.25 N NaOH M. A second 10 mL of standard cyanide diluted to 100 mL with 0.25 NaOH was prepared.
5. Pyridine–barbituric acid reagent: place 15gm barbituric acid in a 250 mL volumetric flask. Add 75 mL pyridine and 15 mL concentration HCl mix, and cool to room temperature. Dilute to with water.
6. Sodium di-hydrogen phosphate 1M: Dissolve 138 gm $NaH_2PO_4.H_2O$ in 1 liter distilled water.
7. Standard solution 100ppm S^{-2} : dissolve 0.8125 g $Na_2S.XH_2O$ in 100 mL distilled water.
8. Prepare a mixture of 0.5M H_3BO_3+ 0.1M KOH solution at PH = 9.75 as supporting electrolyt.
9. Mixture of 0.02 M ascorbic acid + 0.018 M disodium EDTA + 100 mL of 1M NaOH in 500 mL volumetric flask dilute with distilled water.
10. Prepare 100,000 µg / mL standard solution of Ca^{2+}, Fe^{3+}, Cu^{2+},Mg^{2+}, Cl^- ions.

Results and discussion

Cyanide ion determined by polarographic method according to the procedure given in Bulletin[9] using Dp mode and electrolyte solution of 0.3M H_3BO_3 + 0.1 M KOH. Scanning voltage range from 0.0 V to -0.4 V and the polar shows $E_{1/2}$ at -0.3 V. The linearity for the cyanide concentration was ranged from 0.02 to 4 µg / mL. Figure 1 shows the calibration curve of cyanide ion ranged from 0.02 to 0.2 µg / mL using two support electrolytes 0.5M H_3BO_3 + 0.1M KOH and 0.02 M ascorbic acid + 0.018 M disodium EDTA + 100 mL of 1M NaOH . Relative standard deviation for cyanide determination at concentrations 0.02, 0.05 and 0.1 µg / mL are 5.39 %, 1.68 % and 1.39 %, respectively. Best calibration was obtained by using 0.5M H_3BO_3 + 0.1M KOH as a supporting electrolyte.

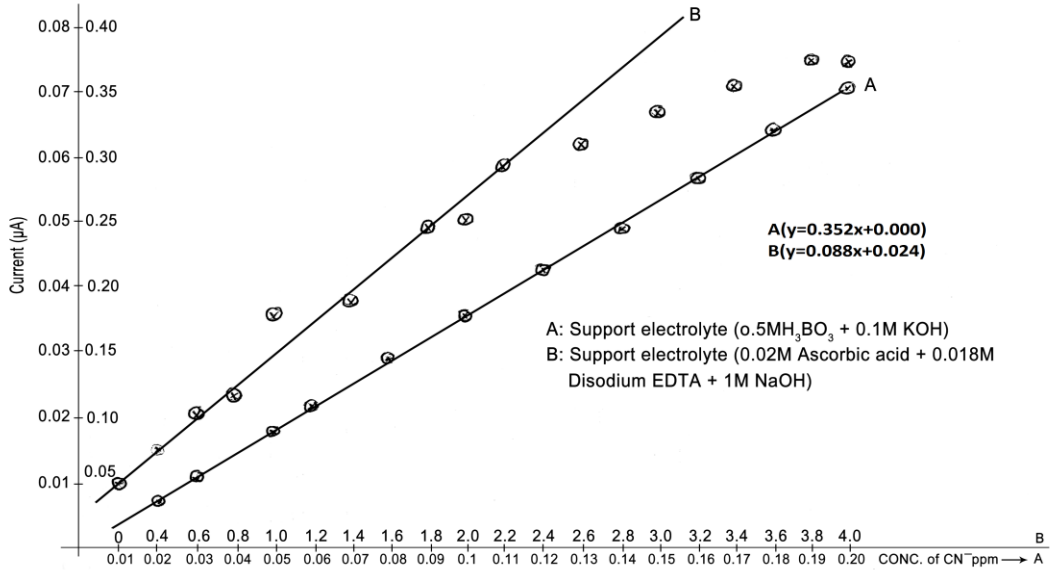

Figure 1 Calibration curve of cyanide ion by polarographic method using two supporting electrolytes.

Sulfide ion concentration determined by polarographic technique using Dp mode and the support electrolytes used are 0.02 M ascorbic acid + 0.018M EDTA + 1M NaOH and 0.02 M ascorbic acid + 0.018 M disodium EDTA + 100 mL of 1M NaOH . The voltage was ranged from – 0.56 V to – 1.2 V and the polarogram shows $E_{1/2}$ at – 0.76 V. Detection limit of sulfide ion obtained was 0.04 µg / mL. Relative standard deviation for three concentration of S^{-2} ion at 0.1, 0.5, 1.0 µg / mL were calculated 6.2, 5.07 and 3.11%, respectively. Figure 2 shows the calibration curve for S^{-2} ion ranged from 0.02 µg / mL to 1.00 µg / mL.

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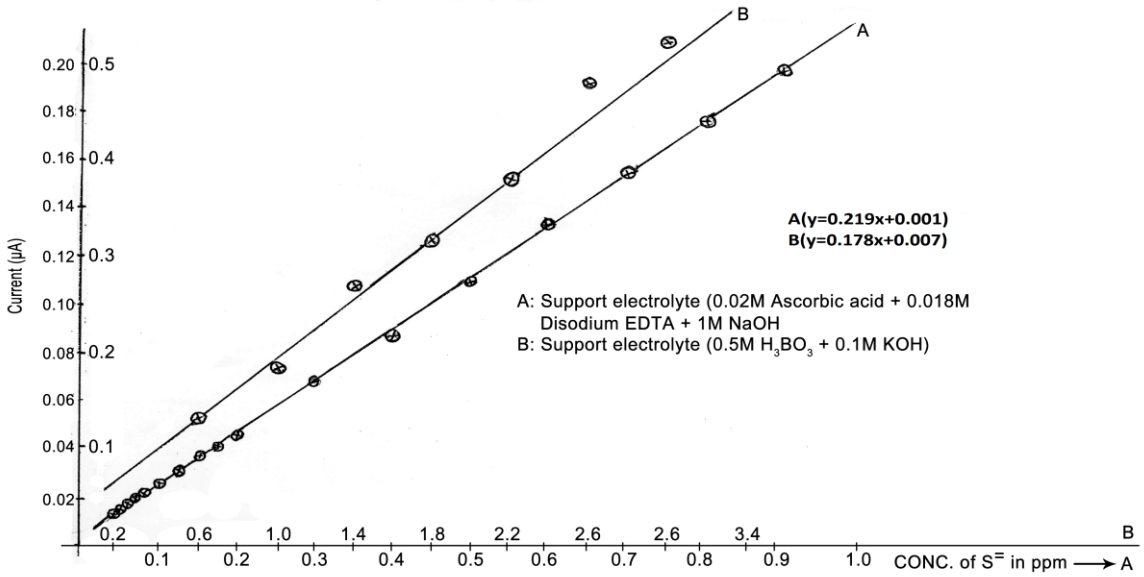

Figure 2 Calibration curve of sulfide ion by polarographic method using two supporting electrolytes.

A polarogram of sulfide and cyanide mixture was determined by polarography using boric acid + KOH as a supporting electrolyte , several experiments were done for fixing the experimental conditions and a typical polarogram is shown in Figure 3. $E_{1/2}$ for cyanide and sulfide obtained from the polarogram are -0.224 V and -0.58 V, respectively. Overlap of the peaks of cyanide and sulfide was obtained by using ascorbic acid + EDTA + NaOH as a supporting electrolyte. Therefore, the best supporting electrolyte for a mixture cyanide and sulfide is boric acid with potassium hydroxide.

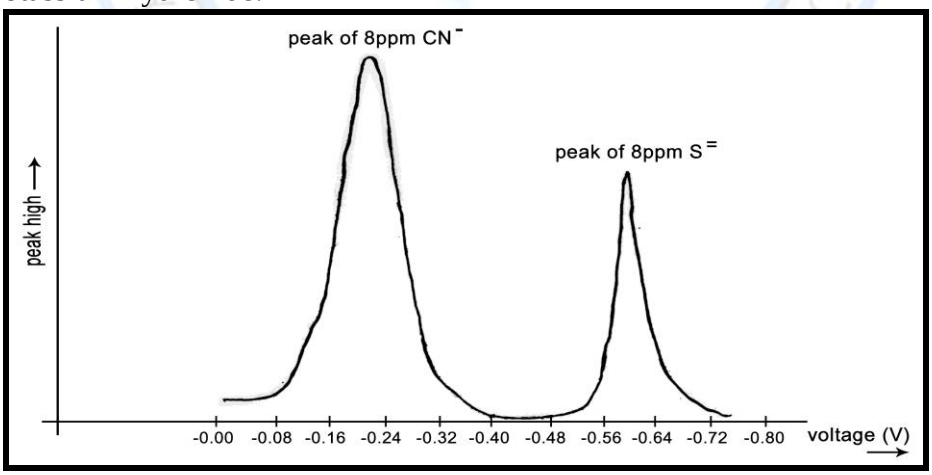

Figure 3 polarogram of cyanide and sulfide ions in support (boric acide + KOH) using Dp mode using differential puls polarography.

Interfering ions Cl^- , Ca^{2+}, Mg^{2+}, Fe^{3+} and Cu^{2+} on Cyanide and sulfide determination by polarography was studied.

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Cyanide determination by polarography was effected in the presence of the interfering ions Cl^-, Ca^{2+}, Mg^{2+}, Fe^{3+} and Cu^{2+}. Also these ions interfere with sulfide ion during the determination of sulfide by polarography. Figures 4 and 5 show the effect of the ions Cl^-, Ca^{2+}, Mg^{2+}, Fe^{3+} and Cu^{2+} on cyanide and sulfide determination by Dp mode using the supporting electrolyte consist of boric acid and KOH.

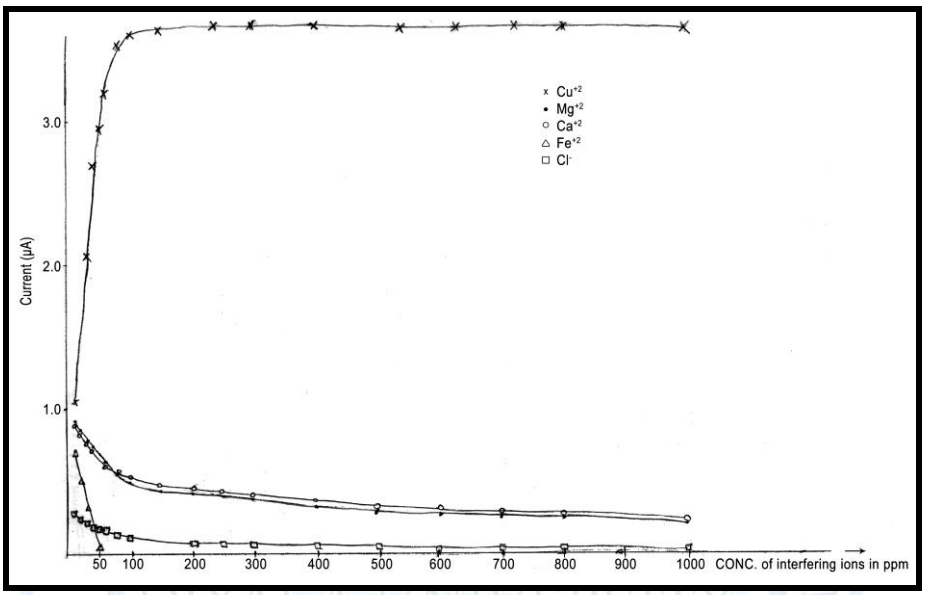

Figure 4: Effect of the interfering ions on cyanide ion determination using polarographic method.

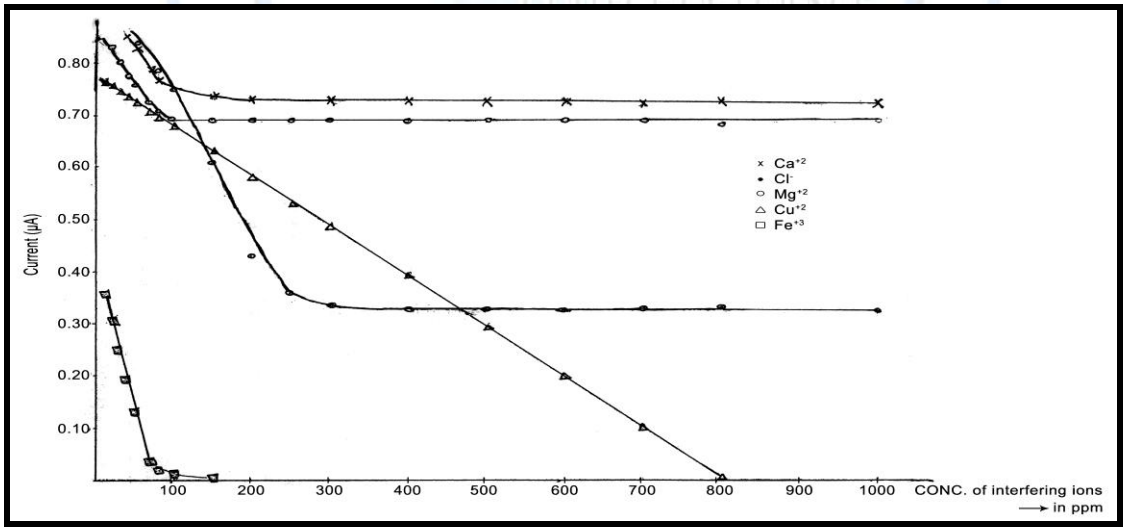

Figure 5 Effect of the interfering ions on sulfide ion determination using the polarographic method.

A complex of cyanide with chloramines-T was measured at 578 nm and the calibration curves were constructed from 0.05 µg / mL to 0.5 µg / mL using two stock solutions of KCN and NaCN. Determination of cyanide in the presence of different concentrations of chloride, copper, iron, calcium and sulfide were recorded. Two concentrations of cyanide 0.05 µg / mL

and 0.4 µg / mL were used for interference study while the concentrations of the interferences were ranged from 20 µg / mL to 1000 µg / mL. No interference of chloride ion on cyanide determination was noticed. High interference was obtained with the other cations. The high interference of magnesium ion with cyanide determination is due to a white precipitate formation during addition to cyanide solution. The results of percentage recovery of cyanide ion at two concentrations 0.05 µg / mL and 0.4 µg / mL mixed with magnesium ion are listed in Table 1.

The recovery of cyanide determination at concentration 0.05 µg / mL was decreased to 35% at magnesium concentration of 1000 µg / mL and 68% for 0.4 µg / mL cyanide concentration. This behavior indicates that the magnesium ion react with the reagent of chloramine-T and barbituric acid instead of cyanide ion and white precipitate formation. In order to check this behavior of reaction of magnesium ion with the reagent, the absorption of a solution containing 20 mL NaOH + 15 mL phosphate buffer + 2 mL chloramines-T and 5 mL barbituric acid without cyanide ion was recorded at 578 nm and the maximum absorption was 0.113.

This value of absorption was decreased to 0.102 when 50 µg / mL magnesium ion was added to the solution and a further decrease to 0.082 by adding 100 µg / mL magnesium ion. Interference of copper ion is due to precipitation of cupric oxide at pH above 11. A severe interference was noticed during cyanide determination in the presence of iron and calcium and sulfide ions. By adding iron to cyanide solution a gelatinous precipitate was formed due to hydrolysis of iron. To eliminate these interfering species, a distillation of cyanide was used.

Table 1 Interference of Magnesium ions on cyanide ions determination by a spectrophotometric method.

Samples	Absorption	Measured CN conc.	E%
0.4 µg / mL CN^-	0.134	0.395	1.25
0.4 µg / mL + 20 Mg^{2+} µg / mL	0.173	0.620	55
0.4 µg / mL + 50 Mg^{2+} µg / mL	0.173	0.620	55
0.4 µg / mL + 100 Mg^{2+} µg / mL	0.169	0.600	50
0.4 µg / mL + 500 Mg^{2+} µg / mL	0.101	0.200	50.0
0.4 µg / mL + 1000 Mg^{2+} µg / mL	0.090	0.140	65
0.05 µg / mL CN^-	0.074	0.046	8
0.05 µg / mL + 20 Mg^{2+} µg / mL	0.074	0.046	8
0.05 µg / mL + 50 Mg^{2+} µg / mL	0.074	0.064	28
0.05 µg / mL + 100 Mg^{2+} µg / mL	0.074	0.064	28
0.05 µg / mL + 500 Mg^{2+} µg / mL	0.072	0.034	32
0.05 µg / mL + 1000 Mg^{2+} µg / mL	0.072	0.034	32

The percentage recovery of cyanide ion from the solution containing interfering ions after distillation was around 99.8%. A severe interference was noticed in the presence of sulfide ion even after distillation of cyanide solution. The results of cyanide recovery in the presence of sulfide ion are listed in Table 2. Abnormal results were obtained is due to complex formation of sulfide with the chloramines-T and barbituric acid absorbed at a wavelength 578 nm which is the same wavelength of cyanide complex.

Table 2:- Interference of sulfide ions on cyanide ions determination by a spectrophotometric method.

Samples	Absorption	Measured CN^- conc.	E%
0.4 µg / mL CN^-	0.135	0.401	0.25
0.4 µg / mL + 20 S^{-2} µg / mL	0.323	1.500	275
0.4 µg / mL + 50 S^{-2} µg / mL	0.640	3.350	737
0.4 µg / mL + 100 S^{-2} µg / mL	0.645	3.380	745
0.4 µg / mL + 500 S^{-2} µg / mL	0,693	3.660	815
0.4 µg / mL + 1000 S^{-2} µg / mL	0.710	3.760	840
0.05 µg / mL CN^-	0.075	0.052	4.0
0.05 µg / mL + 20 S^{-2} µg / mL	0.223	0.913	1726
0.05 µg / mL + 50 S^{-2} µg / mL	0.462	2.310	4520
0.05 µg / mL + 100 S^{-2} µg / mL	0.503	2.550	5000
0.05 µg / mL + 500 S^{-2} µg / mL	0.587	3.036	5972
0.05 µg / mL + 1000 S^{-2} µg / mL	0.596	3.090	6080

Sulfide ion cannot eliminate after distillation of cyanide solution therefore, an experiment was done by adding cadmium carbonate to cyanide solution in order to precipitate of CdS (Table 3). The results given in Table 3 shows incomplete remove of sulfide ion from 0.4 µg / mL cyanide solution by adding 200 µg / mL $CdCO_3$.

The recovery was reduced from 845 to around 65% and percentage of error from 745% to 34.2% even the concentration of $CdCO_3$ increased to 500 µg / mL $Cd^{+2.}$

Table3:- Recovery and percentage of error of cyanide in solution containing sulfide ion with various Concentrations of $CdCO_3$

Solutions	% Recovery of cyanide	% E
0.4 µg / mL CN^-	101.3	1.3
0.4 µg / mL CN^- + 100 µg / mL S^{-2}	845 (Table 2)	745 (Table 2)
0.4 µg / mL CN^- + 100 µg / mL S^{-2} + 200 µg / mL $CdCO_3$	65.7	34.25
0.4 µg / mL CN^- + 100 µg / mL S^{-2} + 400 µg / mL $CdCO_3$	66.7	33.25
0.4 µg / mL CN^- + 100 µg / mL S^{-2} + 500 µg / mL $CdCO_3$	57.4	42.5

Free cyanide and sulfide concentrations were determined in samples taken from different area in Baghdad (Ashtar village, Zuapharania, Dyala River and Tigirs River). The samples were distillated before measuring by polarography and spectrophotometry, the results are listed in Table 4.

Table 4 Concentration of cyanide and sulfide in water samples using polarographic and spectrophotometric methods

Water samples	CN^- concentration (µg / mL)		S^{-2} concentration (µg / mL)	
	Spectro.	Polarography	Spectro.	Polarography
Ashtar village (tap water)	< 0.05	< 0.02	< 0.02	< 0.02
Zuapharania (tap water)	< 0.05	< 0.02	< 0.02	< 0.02
Dyala River	< 0.05	< 0.02	< 0.02	< 0.02
Tigirs River	< 0.05	< 0.02	< 0.02	< 0.02

References

1. Ng BW, Lenigk R, Wong YL, Wu XZ, Yu NT, Renneberg R.," Poisoning influence of cyanide on the catalytical oxygen reduction by cobalt (III) tetra (3-methoxy-4-hydroxylphenyl) porphyrin modified electrode", J Electrochem Soc; 147(6):2350-4, 2000.

2.Rao VK, Suresh SR, Rao NBSN, Rajaram P.," An electrochemical Sensor for detection of hydrogen cyanide gas", Bull Electrochem , 13(7):327-9, 1997.

3. Fikriye, E.; G¨uzin, A.; Sule, A.; Sidika, S., "Differential Pulse Polarographic Determination of Enalapril Maleate", Turk J. Chem., 27, 65 – 69, **2003**.

4. Sreedhar N. Y., Reddy P. P., Sankara M. N., D., Differential Pulse Polarographic for determination of Cd(II) and Pb(II) in Milk Samples after Solid-phase Extraction Using Amberlite XAD-2 Resin Modified with 2,2_-DPED3P. Journal of the Chinese Chemical Society, *56*,Pp 1139-1146, 2009.

5. Atle H., Øyvind M. and Knut H, Analysis of nicotine in antismoking pharmaceutical products by differential pulse Polarography and Voltammetry, Collect. Czech. Chem. Commun., Vol. 72, No. 9, pp. 1207–1213, 2007**.**

6- Neelam Y. S , Thommandru R. B. , Kethamreddy S. , Devarapalli S. , Thenepalli T., Differential Pulse Polarographic Determination of Procymidone in Formulations and Wine , Journal of AOAC INTERNATIONAL , vol. 85.Issue: 3,Pp 731-735, 2002.

7. Standard Methods for the Examination of Water and Wastewater, 20th ed.; American Public Health Association, American Water Works Association and Water Environment Federation: Washington DC, 1998; pp 4-32-4-53.

8. RAND, M.C., et al.," Standard method for examination of water and waste water", 14th ed.; American Public Health Association, American Water Works Association and Water Environment Federation: Washington DC, **1975.**

9- The polarographic determination of inorganic anions, Application Bulletin,Metrohm, NO.111, 1977.

10- Deqian, H., Bolei, X.; Jie, T., Jian, L., Luhong, C., Lili, Y., Zhengbiao, Y., Shuping, B.; "Indirect determination of sulfide ions in water samples at trace level by anodic stripping voltammetry using mercury film electrod ", Analytical Methods Vol.2, 154-158, 2010.

11 - Shayessteh D., Ali M. H. S., Fatema T., Maryam R., "Indirect determination of free cyanide in water and industrial waste water by flow injection-atomic absorption spectrometry", Micro Chemical Acta, 158, 159 -163, 2007.

12. Barzega, M. M., Jabbar, A., Esmaell, M.," Kinetic Spectrophotometric Determination of Trace Amounts of Sulfide" , Bull Korean Chem. Soc., Vol.24, No.9, 1261- 1264,**2003**.

13. Amitabh, G., Ernest, F. J., Richard, H. S," Effect of metal ions on the response of a cyanide-selective electrode," Anal. Chimica Acta, Vol.171, 351-355, **1985**.

14. Angum, A.; Sulbha, A., Gupta, V.K.," trace level extraction and spectrophotometric determination of cyanide in waste water and biological fluid", Indian Journal of Chemical Technology, Vol. 15**,** 301-305 , **2008.**
15. Al-Saidi, H. M.; Al-arique, Q. N. M. H.," Determination of Cyanide Ion in Water Based on the Nucleophilic Addition of Cyanide to the new reagent of 4-hydroxy -3-(2-Oxoindolin-3-Ylideneamino)-2-Thioxo-2H-1,3-Thiazin-6(3H)-one", International Journal of Chemical Engineering Research, ISSN 0975-6442 Vol. 2, No.1, 73-84, **2010**.