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Studies on Methods Development for Voltammetric Trace level Determination of Anionic Forms of Sulfur in Industrial Waste

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Abstract

In view of biochemical importance of sulfur species, herein, efforts were made to determine thiosulfate and sulfite simultaneously. The studies on electrochemical behavior of sulfur species has enabled the development of a voltammetric method for the trace level determination $_4$in industrial waste based on the electrochemical reduction at mercury electrode. 0.1 M CH_3COONa in presence of 0.1 M HCl was found most adequate supporting electrolyte where $S_2O_3^{2-}$ and SO_3^{2-} showed distinct polarographic waves at –0.60V, and –0.20V, respectively. The possible interference of commonly present metal ions was examined and ruled out. A linearity between $S_2O_3^{2-}$ and SO_3^{2-} concentration and peak current was obtained with a coefficient of correlation 0.993 for both the ions. A limit of determination of 0.6 µg/ml and 1.0 µg/ml were achieved using differential pulse polarography for $S_2O_3^{2-}$ and SO_3^{2-} respectively.

Keywords: Thiosulphate, Sulphite, Voltammetry, DPP, Real samples.

Introduction

Sulfur and its compounds are widely used in industries of paper, pulp, tanneries and textile. These subsequently produce a large number of anionic forms of sulfur such as sulfide, sulfite, sulfate, thiosulfate and tetrathionate [1].

In completely reducing environment which is devoid of oxygen, sulfurexists predominantly in the form of sulfide. Under oxidising conditions, the stable sulfur species is sulfate, while in partially reducing atmosphere, there might be present a range of sulfur species such as sulfite, thiosulfate and tetrathionate [2].

Sulfide is a frequent water pollutant that may originate from sewage of industrial waste waters [3]. Salts of sulfite are widely used as additives in food beverages to prevent bacterial and enzymatic growth during production and storage. These species are stable in anionic environment like ponds and lakes, and subsequently

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toxic to most organisms and linked to water pollution [4].

The first study of SO_3^{2-} ion in acid solutions was reported by Gosman [5]. It was followed by Kolthoff and Miller [6], who recommended 0.1 N to 1 N solution of acid as supporting electrolyte for measurement of sulfite.Stankovicet. al. [7] and Katagiri et al. [8] have shown electro-oxidation of sulfide. Yilmaz and Somer [9] have described trace determination of sulfite by differential pulse polarography. Simultaneous determination of sulfite and thiosulfate at sub-ppm level by differential pulse polarography (DPP) at a dropping mercury electrode has also been given by Kalal and co-workers [10].There are some recent reports on electrochemical detection of sulfite ion on modified electrodes [11-13].

Amperometric [14-16], pulse polarographic [17,18], and many other direct and indirect electrochemical methods for trace determination of sulfite are also reported elsewhere [19-23].

Thiosulfate forms a fairly stable complex with mercuric ion and produced anodic wave.Forzis [24] has shown a new type of conductivity cell for the conductometric determination of thiosulfate. Marathe [25] has investigated sulfur species including thiosulfate on a glassy carbon electrode. Krista et al. [26] have determined thiosulfate at low concentration by cathodic stripping voltammetry. Broderson et al. [27] have described indirect determination of traces of thiosulfate by pulse polarography. Ensafi et al. [28] have reported determination of S^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ based on the electrocatalytic interaction with homogenous mediator tris (2,2'-bipyridyl) Ru(II).Umiker et al. [29] have also shown determination of thiosulfate and other sulfur species using differential pulse polarography.The adsorption of thiosulfate on silver electrode for its trace determination has been reported by Srinivasan [30]. Raoof and co-workers [31] have described electrocatalytic determination of thiosulfate at micro levels.

Efforts have been made in present work to develop optimum electroanalytical conditions for simultaneous determination of thiosulfate and sulfate at sub-micro gram level in real samples based upon the fact that most sulfur species apart from sulfate are electroactive, and therefore enable to measurements.

The methods offer considerable selectivity and an opportunity of direct determination of sulfur species without any chemical separation.

Materials and Methods

Technique

Voltammetric methods are considered more suitable to the conventional methods for the estimation thiosulfate and sulfite simultaneously because the measurement of chemical form of the concerned ion is possible due to certain selectivity of the redox potential. Differential pulse polarography (DPP) has proved useful in such determinations. Therefore, the suitability of DPP is envisaged in present studies [32].

The polarographic determination of thiosulfate and sulfite could only be accomplished by increasing the rate of electroreduction, by adding a catalyst and a strong supporting electrolyte which would give rise to a polarographic wave. The results obtained by suggested procedure have also been compared by UV-vis. spectrophotometric method.

Instrumentation

Voltammetric Set-up: A microprocessor based pulse polarographic analyzer (Model CL–362) in combination with a drop–timer assembly, all from Elico Limited, Hyderabad, India, was used for voltammetric measurements. Current voltage curves were recorded by an Epson printer (Epson–LX–300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode; pulse amplitude, 25 mV; drop time, 0.5 s; scan rate, 12mV/sec and charging current compensation, 20%. The saturated calomel electrode (SCE) and platinum wire worked as reference and auxiliary electrodes, respectively.

PH meter: The pH measurements were made by a digital pH meter (Model- 5000) of India.

UV-Vis spectrophotometer: Sample analysis was also carried out by a UV-Vis spectrophotometer (Model SL-160) of Elico. It has a wavelength range of 190-1100 nm. The tungsten-halogen deuterium lamp and wide range photomultiplier were also used as the light source and detector, respectively. The spectral band width of resolution was 0.5 nm.

Sample Preparation

Waste water samples were collected in clean polyethylene containers. These were filtered in order to separate any suspended particulate matter and were acidified with hydrochloric acid to pH 2.0 for storage. A 100 ml aliquot of the sample was treated with 1 ml of oxidizing mixture of nitric acid and sulfuric acid to destroy the biological and organic matters [33].

Chemicals

Chemicals used were of analytical grade purity. Solutions were prepared in milli-Q-water (Millipore). The measurements were made in air conditioned laboratory at 25 ± 1^{0}C. The test solutions were deaerated by bubbling purified nitrogen for 20 mins prior to voltammetric recordings. Nitrogen was purified by passing it through a vanadous chloride scrubbing solution [34].

2. Results and Discussion

Electrochemical characteristics and choice of medium

The electrochemical behavior of thiosulfate and sulfite ions were investigated simultaneously in different supporting electrolytes. Among them 0.1 M CH_3COONa in presence of 0.1 M HCl was found most adequate supporting electrolyte where $S_2O_3^{2-}$ and SO_3^{2-} showed distinct polarographic waves at –0.60V, and –0.20 V, respectively as shown in following figure:

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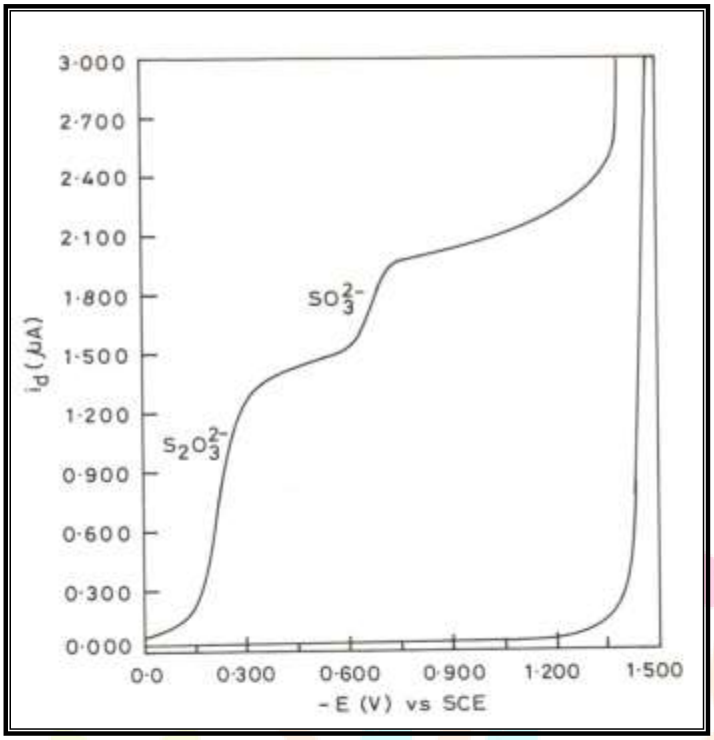
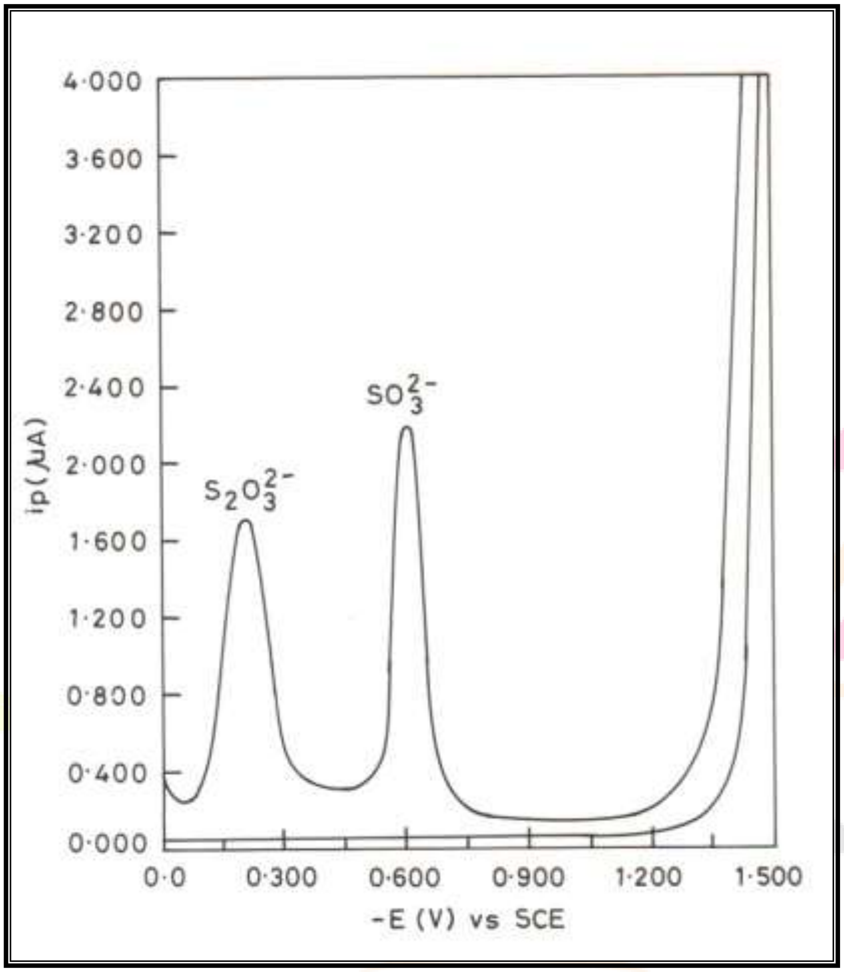


(a) DC polarogram of blank solution of 0.1 M CH_3COONa in 0.1M HCl

(b) DC polarogram of 1 x 10^{-4} M$S_2O_3^{2-}$ and SO_3^{2-}in 0.1 M CH_3COONa in 0.1M HCl

Method Development

Thiosulfate and sulfite also gave distinct DP peaks at -0.20 V and -0.60 V, respectively as shown in figure.



(a) DP polarogram of blank solution of 0.1 M CH_3COONa in 0.1 M HCl

(b) DP polarogram of 8.0 ppm$S_2O_3^{2-}$ and 13.0 ppm SO_3^{2-} in 0.1 M CH_3COONa in 0.1 M HCl

It was noticed that the peak currents were increased in proportional to the varied concentration of $S_2O_3^{2-}$ and SO_3^{2-}. The DP polarograms at different concentrations are shown in following figure:

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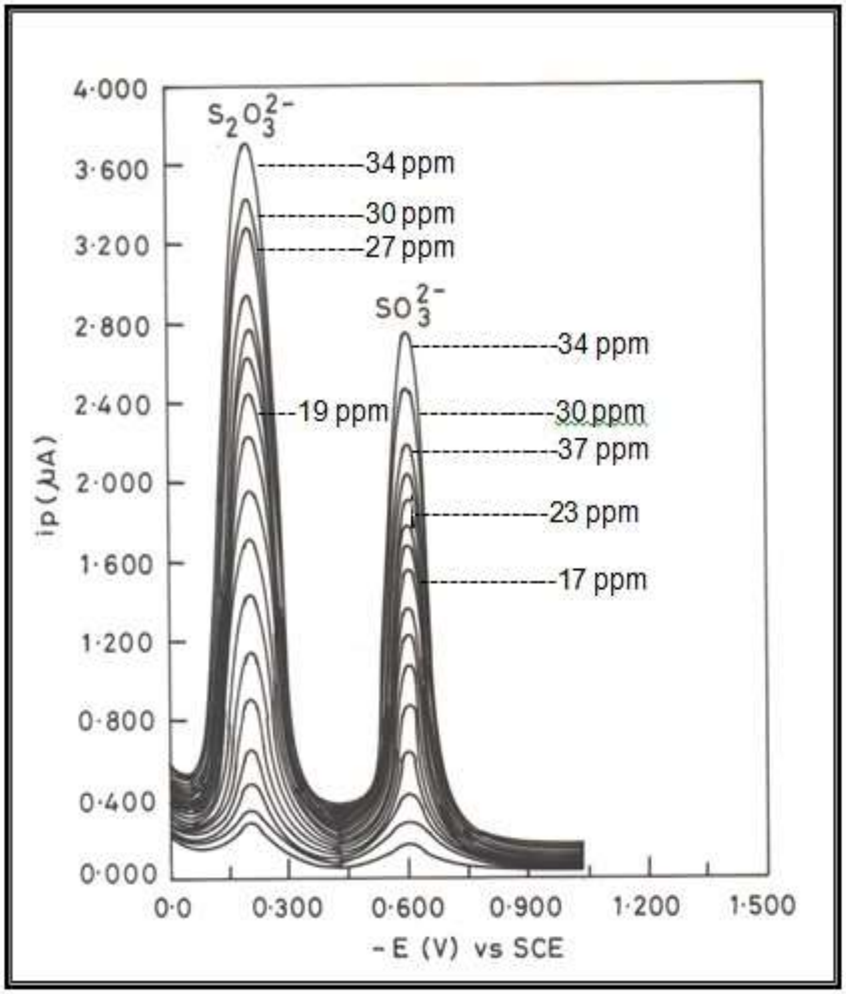

The calibration curves of thiosulfate and sulfite between peak current and concentration have been drawn in following figure and the characteristics of the calibration curve are given in Table. The linearity between the peak current and perchlorate concentration was observed from 0.4 ppm and 35 ppm. For simultaneous determination of $S_2O_3^{2-}$ and SO_3^{2-} by DPP, the limits of determination were found to be 0.6μg/ml and 1.0 μg/ml, respectively.

Table – Calibration Curve Characteristics

S. No.	Parameters	$S_2O_3^{2-}$	SO_3^{2-}
1.	Slope	0.099	0.071
2.	Coefficient of correlation	0.993	0.993
3.	Intercept	0.007	0.004
4.	Standard Deviation	0.023	0.007

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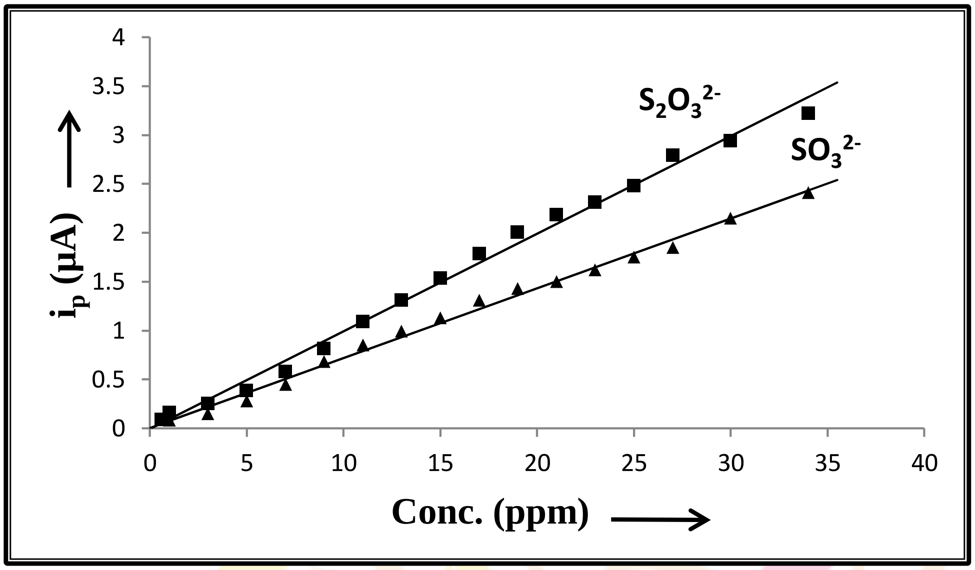
THE CALIBRATION CURVES (CONCENTRATION vs PEAK CURRENT) OF THIOSULFATE AND SULFITE



Precision and Accuracy

The reproducibility of DPP determinations was evaluated by making individual measurements of a solution containing known concentration of both the ions. The DPP measurements in terms of determination of thiosulfate and sulfite were evaluated for precision and accuracy. Relevant data are given in table inferring that method is precise and accurate.

PRECISION AND ACCURACY OF THIOSULFATE AND SULFITE DETERMINATION

S.E. = 0.1 M CH_3COONa in 0.1 M HCl

Species	Conc.(μg/ml)		S.D. (±)	R.S.D. (%)	Relative Error (%)
	Present	Determined*			
$S_2O_3^{2-}$	2.5	2.47	0.014	0.56	1.20
SO_3^{2-}	2.5	2.46	0.019	0.77	1.60

* Average of three determinations

Interference Study

The peak potential of lead and zinc in presence of 0.1 M CH_3COONa in 0.1 M HCl were found to be -0.41 V and -1.01 V, respectively. They were well separated from that of thiosulfate and sulfite [Eps: $S_2O_3^{2-}$, -0.20 V;

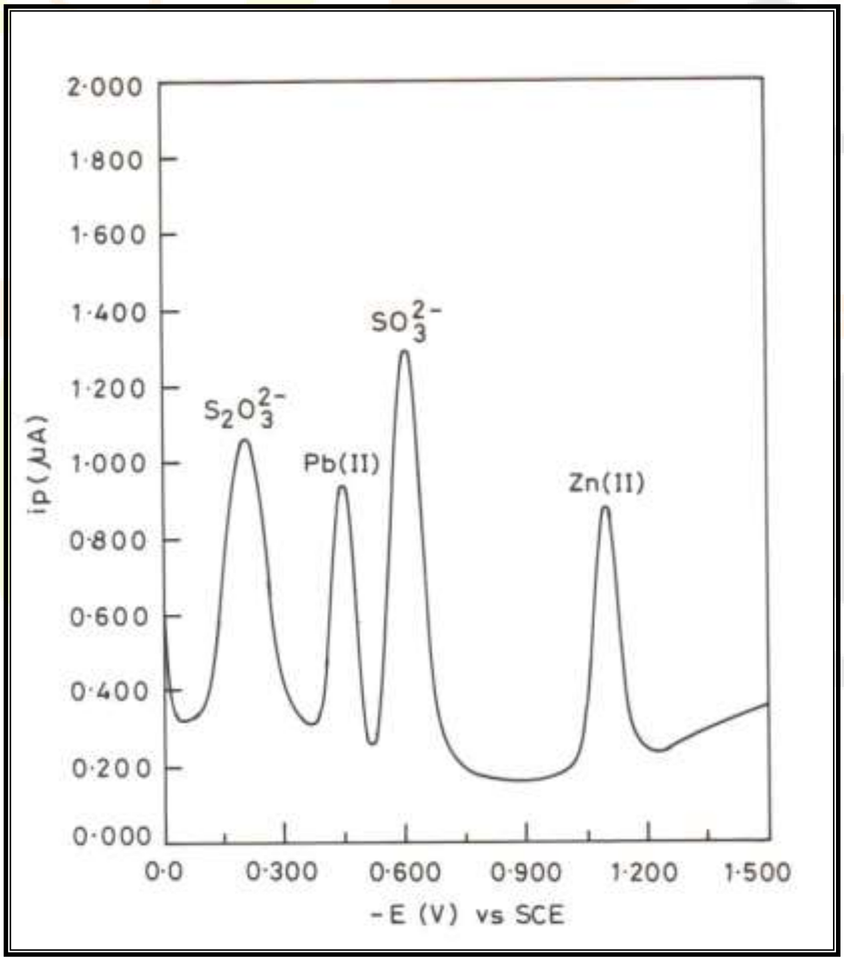
SO_3^{2-}, -0.60 V]. Thus such metal ions did not interfered in DPP determination of sulfur species. It has been clarified in figure. Peak potentials of metal ions in 0.1 M CH_3COONa in 0.1 M HCl are listed in following figure:

PEAK POTENTIAL OF METAL IONS

S.E. = 0.1 M CH_3COONa in 0.1 M HCl

S.No.	Interfering ions	–Ep (V) vs SCE
1.	$S_2O_3^{2-}$	0.20
2.	Pb (II)	0.41
3.	SO_3^{2-}	0.60
4.	Zn (II)	1.01

DP POLAROGRAM OF THIOSULFATE AND SULFITE IN PRESENCE OF METAL IONS



$S_2O_3^{2-}$, 8.0 ppm;Pb (II), 5.0 ppm; SO_3^{2-}, 13 ppm;

and Zn (II), 2.0 ppm

3. Analytical Applications

Voltammetric measurements

The prepared sample was taken into the polarographic medium of 0.1 M CH_3COONa in 0.1 M HCl supporting electrolyte. DP polarograms were recorded from -0.0 V to -0.8 V. Peak Currents were measured at -0.20 V and -0.60 V for thiosulfate and sulfite, respectively. The concentrations in all observations were determined by the standard addition method [35]. The results of determination of sulfite and thiosulfate in this manner are summarised in following tables:

DPP DETERMINATION OF THIOSULFATE IN DIFFERENT SAMPLES

S. No.	Sample	$S_2O_3^{2-}$ Conc.(μg/ml)*			S.D. (±)	C.V. (%)
		Min.	Max.	Ave.		
1.	Paint Industry	1.29	1.34	1.31	0.021	1.64
2.	Suncity Alloys	1.44	1.48	1.46	0.016	1.11
3.	Common Nala	2.00	2.08	2.03	0.001	0.06

* Average of three determinations

DPP DETERMINATION OF SULFITE IN DIFFERENT SAMPLES

S. No.	Sample	SO_3^{2-} Conc.(μg/ml)*			S.D. (±)	C.V. (%)
		Min.	Max.	Ave.		
1.	Paint Industry	1.28	1.30	1.29	0.008	0.63
2.	Textile Industry	2.65	2.68	2.67	0.014	0.52
3.	Common Nala	1.83	1.88	1.85	0.021	1.16

* Average of three determinations

Comparison

The UV-vis spectrophotometric method was used to compare the results obtained by DPP. The comparative data for thiosulfate and sulfite are included in following tables:

COMPARISION OF RESULTS OF $S_2O_3^{2-}$ DETERMINATION BY DPP AND UV–VIS SPECTROHOTOMETRY

S. No.	Sample	$S_2O_3^{2-}$ Conc.(μg/ml)*	
		DPP	UV –vis.
1.	Paint Industries	1.31	1.29
2.	Suncity Alloys	1.46	1.36
3.	Common Nala	2.03	2.01

*Average of three determinations

COMPARISION OF RESULTS OF SO_3^{2-} DETERMINATION BY DPP AND UV–VIS SPECTROHOTOMETRY

S. No.	Sample	SO_3^{2-} Conc.(μg/ml)*	
		DPP	UV –vis.
1.	Paint Industries	1.29	1.26
2.	Textile Industries	2.67	2.64
3.	Common Nala	1.85	1.83

*Average of three determinations

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4. Conclusion

The suggested method has enabled the determination of thiosulfate and sulphite individually as well as in presence of each other i.e. simultaneously. In addition lead and zinc did not interfered. Thus, method seems to be quite satisfactory for trace level determination of sulfur species.

REFERENCES

1. "*Trace Elements in the Environment*", Advances in Chemistry Series No. 106, American Chemical Society, Washington DC, 1971.
2. W. Davison, J. Buffle and R. Devitre, Pure Appl. Chem., **60**, 1535 (1998).
3. J. Buffle, R. Devitre, D. Perret and G.G. Leppard in "*Metal speciation : Theory, Analysis and Applications*", (J.R. Kramer and H.E. Allen, Eds.), Lewis, Chelsea, 1988.
4. J. Buffle, O. Zali, Zumstein and R. Devitre, Sci. Total Environ.,**64**, 41 (1987).
5. B. Gosman, Collection Czechoslov Chem. Communs., **2**, 185 (1930).

6. I.M. Kolthoff and C.S. Miller, J. Am. Chem. Soc., **63**, 2818 (1944).
7. V.D. Stankovic, Z.D. Stankovic and M. Rajcic – Vujasinovic, Proc. 46th Annual Meeting Extended Abstr., Xiamen, China, Aug. 27–Sep. 1,1995.
8. A. Katagiri, H. Arai and Z. Takehara, J. Electrochemical Soc., **142**, 2899 (1995).
9. U. T. Yilmaz and G. Somer, Anal. Chim. Acta., **603**, 30 (2007).
10. H.S. Kalal, M. Ghadiri, B. A. A. MiranBeigi and S. A. S. Seyed, Anal.Chim. Acta., **502**, 133 (2004).
11. A.S. Adekunle, O.A. Arotiba and B.B. Mamba, Int. J. Electrochem. Sci., **7**, 8503 (2012).
12. A. Salimi, M. Roushani, R. Hallaj, Electrochim. Acta.,**51**, 1952 (2006).
13. T.R.L. Dadamos, M.F.S. Teixeira, Electrochim. Acta.,**54**, 4552 (2009).
14. I.G. Casella and R.M. Archese, Anal. Chim. Acta.,**311**, 1990 (1995).
15. L.S.T. Alamo,T. Tangkuaram and S.Satienperakul, Talanta, **81**, 1793 (2010).
16. M. Amatatongchai, W. Sroysee, S.Chairam and D. Nacapricha, Talanta, **133**, 134 (2015).
17. W. Holakand B. Patel, J. Assoc. off. Anal. Chem., **70**, 572 (1987).
18. W. Holak and J. Specchio., J. Assoc. off. Anal. Chem., **72**, 476 (1989).
19. P. Linares, M.D. Luque de Castra and M. Valcareel, Anal. Chim. Acta., **225**, 443 (1985).
20. G.B. Marshall and D. Midgley, Analyst, **108**, 701 (1983).
21. M. Granados, S. Marpoch and M. Blanco, Anal. Chim. Acta.,**179**, 445 (1986).
22. T.J. Cardwell, R.W. Cattrall, G.N. Chen, G.R. Scollary and I.C. Hamition, Analyst, **116**, 253 (1991).
23. N.T.K. Thanh, L.G. Deenop –Weevern and W. Th. Kok, Fresenius J. Anal. Chem., **349**, 469 (1994).
24. E. Forizs, Talanta, **43**, 1639 (1996).
25. S.G. Marathe, Proc. 7th Nat. Conf. Electrochemists, Souvenir &Abstrs, Kohlapur, Nov. 18-20, 1996.
26. J. Krista, M. Kopanica, and L. Novotny, Anal. Chim. Acta.,**386**, 21 (1999).
27. K. Broderson, U. Werner, Y.A. Gawagious, and S. Huang, Talanta, **38**, 785 (1991).
28. A.A. Ensafi, H.A. Soleymani and E. Mirmomtaz, Microchem. J.,**89**,108 (2008).
29. K.J. Umiker, M.J. Morra, I. F. Cheng, Microchem. J., **73**, 287 (2002).
30. R. Srinivasan, J. Appl. Electrochem.,**28**, 993 (1998).
31. J.B. Raoof, R. Ojani and H.K. Maleh, Chinese Chemical letters, **21**, 1462 (2010).
32. W. Davison and E. Rigg, Analyst, **101**, 634 (1976).
33. W. Davison and J. J. Morgan, *Aquatic Chemistry*, Wiley, New York (1970).
34. W. Davison, J. A. Harrison and J. Thompson, Farady Discuss. Chem. Soc., **56**, 171 (1973).
35. Willard H, Merit L and Dean J. 1974. Instrumental methods of analysis. Edn. 5, D. Van Nostrand, New York.

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