Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2693-2697

Development of New Reagent for The Facile and Sensitive Spectrophotometric Determination of Selenium in Water Samples

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Spectrophotometric method was developed which is simple, sensitive and highly selective for the determination of selenium (IV) in various environmental samples using 4-dimethylaminobenzaldehyde thiosemicarbazone (4-DMABTS). Selenium forms a red coloured complex with (4-DMABTS) in acetate buffer medium (pH 4) which increases the sensitivity. Under optimum conditions the maximum absorption of colour complex was measured at 481 nm. The Beer's law was obeyed in the range of 0.05-11.0 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity of the complex were as 2.3512×10^4 L mol^{-1} cm^{-1} and 0.00276 μg cm^{-2}, respectively. The detection limit was found to be 0.020 mg mL^{-1}. Interference of the foreign ions was studied. The proposed method was successfully applied for the determination of selenium in various environmental samples. The performance of the present method was successfully analyzed by Student's F and t-tests.

Key Words: Selenium(IV), 4-Dimethylamino benzaldehyde thiosemicarbazone (4-DMABTS), Spectrophotometry, Water samples.

INTRODUCTION

Selenium is an essential and important element from the point of view of its clinical and environmental effects. The valence state of selenium is important information in the determination of selenium. The speciation of selenium compounds has been reviewed somewhere else[1,2]. Due to its enzymatic actions, this element has been recognized as an essential nutrient for all organisms. In addition selenium acts as significant role in anticarcinogenic activity and prevention of heavy metal toxic effects[3,4].

Several authors[5-9] reported about speciation and biological activities of selenium in different matrices, such as biological and environmental samples which gave the importance of the subject. Because of its significance, few spectrophotometric methods have been reported with chromogenic reagents, such as starch and iodine[10], 8-hydroxyquinoline[11], J-acid[12], *o*-phenylendiamine[13] and leuco crystal violet[14]. But, these methods suffer from poor sensitivity, selectivity, stability of colour derivative and few are developed colour at particular pH. Thus, in such circumstances a need to develop new, facile and reliable method for the determination of trace amounts of selenium in environmental samples.

The present work provided facile, sensitive and rapid spectrophotometric method for the determination of trace amounts of selenium in environmental samples of significance importance. Here, authors successfully synthesized new analytical reagent 4-dimethylamino benzaldehyde thiosemicarbazone (4-DMABTS) for the determination of selenium in environmental samples.

EXPERIMENTAL

All the reagents were used as received from Merck Chemicals. Stock selenium solution was prepared by dissolving weighed quantity of SeO_2, with double distilled water along with concentrated HNO_3 sufficient to get final concentrations of 1 mol L^{-1} in a 100 mL flask.

Hitachi U 2001 spectrophotometer with a 1.0 cm matched quartz cells used for all absorbance measurements. An Elico Li-129 model pH meter with combined glass electrode was used for pH measurements.

4-Dimethylaminobenzaldehyde thiosemicarbazone (4-DMABTS) was synthesized as described in literature[15]. Its m.p. is 212-215ºC. The confirmation of the synthesised reagent was analysed with the help of NMR and Mass spectrophotometry was shown in below ES1-MS: m/z 223(M+H^-, methanol). ^{1}H NMR (DMSO-d_6.TMS.500MHz); δ (ppm) 11.179 (HN, 5).7, 999(CH.S), 7.932-7.571(C_6H_4.4H, m), 6.707(NH_6, S). 2.957 (Me_6N, 6H, S).

Procedure: To an aliquot of working standard solution containing 0.05-100 µg mL^{-1} was taken 50 mL standard flask. 5 mL of acetate buffer (pH 4), 2 mL of reagent solution and salting out agent 0.1 M magnesium sulphate were added to this solution. The mixture was allowed to stand for few minutes to form red colour complex and diluted up to the mark. The absorbance of the coloured complex was measured at 481 nm against the corresponding reagent blank and the calibration graph was constructed.

Determination of selenium in water sample: The distillation procedure for the determination of selenium in waste water as follows. To an aliquot (100 mL) of known sample taken in a distillation flask, 1 g of KBr and 10 mL of concentrated H_2SO_4 treated with 0.5 mL of saturated bromine water were added. The solution was distilled under vacuum till copious white fumes of SO_3 vapours were evolved and this process converts all other forms of selenium into selenium(IV). The distilled was collected in 10 mL of hydroxyl ammonium chloride solution (5 %), then made up to a fixed volume and analyzed by the described earlier.

RESULTS AND DISCUSSION

Analytical parameters: Selenium(IV) reacts with 4-DMABTS to form 1:1 red coloured complex in acetate buffer at pH 4. Under optimum conditions the maximum absorption of red coloured complex was measured at 481 nm against the reagent blank. The complex is stable for more than 12 h. Various factors such as pH, reagent concentration, choice of solvent and salting out agent, influence of diverse ions were studied in the present investigation in order to enhance the sensitive method for the determination of selenium(IV) in µg level. Beer's law was obeyed in the concentration range of 0.05-11.0 µg mL^{-1}. The molar absorptivity of complex is 2.35 × 10^4 L mol^{-1} cm^{-1} and Sandell's sensitivity of the method was found to be 0.00276 µg cm^{-2}. The correlation coefficient (r) for the experimental data is 0.9996 and other parameters were presented in Table-1 and absorption spectra was shown in Fig. 1.

TABLE-1
OPTICAL CHARACTERISTICS AND PRECISION DATA

Parameters/Characteristics		
Colour		Red
λ_{max} (nm)		481
Beer's law range (µg mL^{-1})		0.05-11.0
Molar absorptivity (L mol^{-1} cm^{-1})		2.3512×10^4
Sandell's sensitivity (µg cm^{-2})		0.00276
Detection limit (µg mL^{-1})		0.020
Regression equation (Y)*	Slope (a)	0.17734
	Intercept (b)	0.0142
Correlation coefficient (r)		0.9996
Relative standard deviation (%)$^+$		0.8957
Range of error (95 % confidence level)		±1.2425
% error		0.1427

*Y=ax+b, where x is the concentration of selenium in µg mL^{-1}, $^+$ n=5.

Effect of the reagent concentration: To a series of 50 mL standard flasks, each containing 1 mL of Se (IV) solution, 5 mL of buffer solution (pH 4.0) were added in different volume of the reagent solution to obtain the maximum colour formation. From the experimental observation it was found that beyond a 6 fold excess of the reagent the absorbance remained almost constant. Hence, 2 mL of the reagent was recommended for complete colour development.

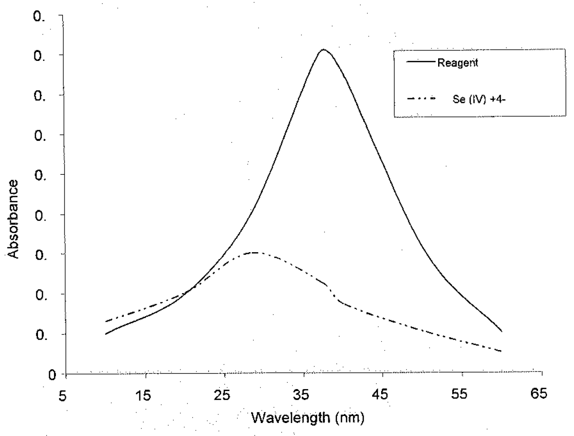

Fig. 1. Absorption spectra of the selenium with 4-DMABTS

Effect of foreign species: Several anions and cations were studied in detail. Table-2 summarizes the tolerance limits of interfering ions in the determination of 50 μg mL^{-1} Se (IV). The tolerance limit was taken as the amount causing an error of ± 2% at the peak height. The results are shown in Table-2.

TABLE-2
TOLERANCE LIMITS OF FOREIGN IONS ON THE DETERMINATION OF 50 μg mL^{-1} SELENIUM

Tolerance limit (μg mL^{-1})	Foreign ions
50,000	K^+, Na^+, Ca^{2+},Mg^{2+},Cl^-,Br^-
10,000[a]	PO_3^{3-}, CO_3^{3-},SO_4^{2-}, Al^{3+},Cr^{3+}.
5000[b]	NO_3^-, Zn^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}
800[c]	Fe^{2+}, Fe^{3+}, Mn^{2+} , Co^{2+}, Ni^{2+}

[a] Can be masked up to 10,000 μg mL^{-1} by the addition of 2 mL of EDTA, thiosulfate, cyanide.

[b] Can be masked up to 5000 μg mL^{-1} by the addition of 2 mL of 2 % citrate solution.

[c] Can be masked up to 800 μg mL^{-1} by the addition of 1% thiocyanate.

Comparison of the present method with reported method: The proposed method for the determination of selenium (IV) has been employed for various environmental samples were presented in Tables-3. The results were compared with reported method in terms of sensitivity and selectivity. The analytical data summarized in Table-3 suggests that the percentage recovery of selenium (IV) from various environmental samples range from 91.20 to 97.20 % which is more reliable and sensitive than the other method reported in the literature.

TABLE-3
DETERMINATION OF SELENIUM (IV) IN WATER SAMPLES

Sample	Selenium added (µg mL^{-1})	Proposed method		Reported method[4]	
		Found[a] (µg mL^{-1})	Recovery (%)[a]	Found[a] (µg mL^{-1})	Recovery (%)[a]
Spiked water	0.4	0.37	92.5 ± 0.10	0.39	97.5 ± 0.09
	1.0	0.93	93.0 ± 0.03	0.90	95.0 ± 0.10
	1.6	1.52	95.0 ± 0.10	1.55	96.8 ± 0.03
Dam water[a]	-	0.36	-	0.38	-
	0.8	1.16	92.0 ± 0.09	1.18	98.3 ± 0.06
	1.2	2.36	93.3 ± 0.14	2.38	97.5 ± 0.09
River water[b]	-	0.36	-	0.38	-
	0.8	1.16	91.2 ± 0.03	1.18	95.0 ± 0.10
	1.2	2.56	90.9 ± 0.49	2.38	99.1 ± 0.08
Spring water	-	0.18	-	0.19	-
	0.4	0.37	92.5 ± 0.04	0.39	97.5 ± 0.05
	0.6	0.56	93.0 ± 0.05	0.59	98.3 ± 0.03
Polluted water[c]	-	0.55	-	0.56	-
	0.9	1.45	96.6 ± 0.08	1.46	97.3 ± 0.27
	1.2	1.75	97.2 ± 0.18	1.76	97.7 ± 0.16

[a] n=5, [a] Collected from Kalyani Dam, Chandragiri, Chittoor District, A.P., India. [b] Collected from Swarnamuki River, Tirupati, Chittoor District, A.P., India.

[c] Collected from Industrial Estate, Gajulamanyam, Chittoor District, A.P., India.

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(*Received*: 18 February 2006; *Accepted*: 27 December 2006) AJC-5309