PART - II

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TRACE ELEMENTS

CHAPTER IV

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM

RESUME

Solvent extraction spectrophotometric and atomic absorption spectrophotometric methods for the determination of selenium(IV) in microgram quantities are described. The selenium(IV) forms yellow coloured complex with N-phenylbenzohydroxamic acid (PBHA) extractable into chloroform from 7 M $HClO_4$. Se-PBHA complex has maximum absorbance at 345 nm with a molar absorptivity 1.5×10^5 l $mol^{-1}cm^{-1}$ and Sandell's sensitivity 0.000526 µg/cm^2. Effect of molarity, reagent concentration, diverse ions on the extraction of selenium complex were studied. The selenium is determined in presence of tellurium.

INTRODUCTION

Selenium and its compounds have been used commercially in the production of rectifiers, photocells and pigments. Selenium has long been regarded as a toxic metal, because of the wellknown selenium poisoning of cattle (1) ("alkali disease and blind staggers") caused by consumption of selenium bearing plants. Selenium and its compounds are toxic and affect various organs. Very small amounts of selenium and selenium derivatives irritate the respiratory tract and cause colds and headache.

Considerable attention has been devoted to trace analysis of selenium in environmental (2), geological (3) and biological (4) samples by various techniques (5-16). These techniques are time consuming and suffering from interference of various ions or require sophisticated instrumentation.

Diaminobenzidine (5), 4-dimethylamino-1, 2-phenelene diamine and 4-methylthio-1, 2-phenelene diamine (6) reagents were used for the determination of Se(IV) in the absence of oxidizing ions.

Hydroxamic acids have received a great deal of attention as gravimetric, titrimetric and colorimetric reagents for several metal ions (17-19). In the present investigation a new, rapid solvent extraction, and spectrophotometric method for microgram determination of selenium in presence of tellurium is described.

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used in this study were of AnalaR and GR grades of B.D.H. or E. Merck, respectively, unless otherwise specified.

The N-phenylbenzohydroxamic acid (PBHA) was freshly synthesised as described elsewhere (20). Purity was checked by melting point, thin layer chromatography, infrared and ultra violet spectra; and its 0.1% solution was prepared in chloroform.

Metallic selenium (99.99% pure) was dissolved in nitric acid and the solution evaporated to dryness on a waterbath. Perchloric acid was added and the mixture heated on a waterbath, filtered, and diluted to 100 ml with doubley distilled water. The selenium concentration was determined colorimetrically (5).

APPARATUS

The spectrophotometric measurements were made on a Bausch and Lomb, spectronic 20 spectrophotometer, and a GBC 901 atomic absorption spectrophotometer equipped with GBC HG 900 vapor generation accessary. The selenium line at 196 nm with argon gas was used.

EXTRACTION PROCEDURE

2.0 ml of selenium solution (3.73 µg) was transferred into 60-ml separatory funnel followed by 15 ml $HClO_4$ (11.6 M) and 8 ml water (to keep final molarity of $HClO_4$ at 7.0 M). Then 10 ml of chloroform solution of the reagent was added, and the contents were shaken for 5 min. The yellow coloured chloroform extract was separated, dried over anhydrous sodium sulfate, and collected into a 25-ml volumetric flask. The extraction was repeated with 2 ml of reagent solution to check the complete extraction of selenium. The anhydrous sodium sulfate was washed with chloroform, and the washings were collected. The extracted layer was diluted by adding chloroform upto the mark, and the absorbance was measured at 345 nm vs the blank which was prepared in the absence of selenium.

Atomic absorption measurements

For the AAS measurements the selenium was back extracted with 0.1 M HCl from the chloroform extract and estimated using a GBC HG 900 vapor generation accessary.

RESULTS AND DISCUSSION

Absorption spectra

The yellow coloured Se-PBHA complex has a maximum absorbance at 345 nm. The blank has an insignificant absorbance at 345 nm.

Effect of acidity

The extraction of selenium was carried out in the 3-9 M $HClO_4$ range and results shown in Table 1. An optimum (100%) extraction was obtained at 7.0 M $HClO_4$ with higher or lower acidity tending to decrease the % extraction.

Effect of solvents

The selenium was extracted with various solvents including chloroform, toluene, and benzene. Chloroform was found the most suitable solvent for extraction of selenium (Table 2).

Effect of reagent concentration

Selenium was extracted at 7 M $HClO_4$ while varying the reagent concentrations and results shown in Table 3. The results showed that 10 ml of 0.1% N-phenylbenzohydroxamic acid (PBHA) was adequate for the quantitative extraction of selenium. Lower concentration gave incomplete extraction.

TABLE 1

Effect of acidity on the extraction of selenium(IV)

Se(IV)	: 0.149 ppm	Solvent	: $CHCl_3$
PBHA	: 0.1%, 10 ml in $CHCl_3$	λmax	: 345 nm
		Colour of complex	: Yellow

Molarity of $HClO_4$	Molar absorptivity $l\ mol^{-1}cm^{-1}$	% E
3.0	0	0
4.0	0	0
5.0	0	0
6.0	4.7×10^4	31
7.0	1.5×10^5	100
8.0	8.0×10^4	54
9.0	7.3×10^4	48

TABLE 2

Effect of solvents on the extraction of selenium(IV)

Se(IV) : 0.149 ppm

PBHA : 0.1%, 10 ml in $CHCl_3$

Molarity : 7.0 M $HClO_4$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex : Yellow

Solvents	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
Chloroform	1.5×10^5	100
Toluene	1.0×10^5	66.6
Benzene	NE	NE

NE = Not extracted

TABLE 3

Effect of reagent concentration

Se(IV) : 0.149 ppm

PBHA : 10 ml in $CHCl_3$

Molarity : 7.0 M $HClO_4$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex: Yellow

PBHA (0.1%) ml	Absorbance	Molar absorptivity $l\ mol^{-1}cm^{-1}$	% E
2.5	0.16	8.0×10^4	55.2
5.0	0.23	1.2×10^5	79.3
7.5	0.29	1.5×10^5	100
10.0	0.29	1.5×10^5	100
15.0	0.29	1.5×10^5	100

Hence all the extractions were done with 10 ml of 0.1% reagent.

Effect of shaking time and stability of the colour

It was confirmed that manual shaking time of 5-10 min was adequate for the complete extraction of selenium. However, a longer shaking time had no effect on the equilibrium system. The complex was stable under optimum conditions and the absorbance remained unchanged for several hours.

Beer's law

Beer's law was obeyed in the range of 0.015-0.6 ppm of selenium. The molar absorptivity was 1.5×10^5 l $mol^{-1}cm^{-1}$ at 345 nm. The Sandell's sensitivity is 0.000526 $\mu g/cm^2$.

Effect of diverse ions

Different amounts of diverse ions were added to a fixed amount of selenium and extracted according to the procedure. Most of the metal ions associated with selenium do not interfere. The interference of the large amount of Te^{4+} can be tolerated by masking with thioglycolic acid. The data are shown in Table 4.

TABLE 4

Effect of diverse ions on the extraction of selenium(IV)

Selenium(IV) : 0.149 ppm

PBHA : 0.1%, 10 ml in $CHCl_3$

Molarity : 7 M $HClO_4$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex: Yellow

Ions	Added as	Amount added (mg)	Absorbance
Al^{3+}	$Al(NO_3)_2$	(60)	0.29
As^{3+}	AsF_3	(60)	0.28
Ba^{2+}	$BaCl_2$	(60)	0.29
Be^{2+}	$BeSO_4$	(80)	0.29
Bi^{3+}	$BiONO_3$	(60)	0.28
Ca^{2+}	$Ca(NO_3)_2$	(80)	0.30
Cd^{2+}	$CdSO_4$	(60)	0.29
Co^{2+}	$Co(C_2H_3O_2)_2.4H_2O$	(60)	0.28
Cr^{3+}	CrO_3	(40)	0.29
Cu^{2+}	$CuSO_4$	(60)	0.30
Ga^{3+}	GaI_3	(40)	0.30
Mg^{2+}	$Mg(NO_3)_2$	(60)	0.29
Mn^{2+}	$Mn(C_2H_3O_2)_2.4H_2O$	(60)	0.29
Nb^{5+}	Nb_2O_5	(60)	0.30
Ni^{2+}	$NiCl_2$	(60)	0.29
Pb^{2+}	$Pb(C_2H_3O_2)_2.4H_2O$	(40)	0.29
Sb^{3+}	$SbCl_3$	(60)	0.29
Sn^{2+}	$SnCl_2$	(60)	0.29
Ta^{5+}	Ta_2O_5	(60)	0.30
Te^{4+a}	$Te(ClO_4)_4$	(40)	0.29
Th^{4+}	$Th(NO_3)_4$	(60)	0.29
Ti^{4+}	$TiCl_4$	(60)	0.28
V^{5+b}	NH_4VO_3	(40)	0.28
Zn^{2+}	$ZnCl_2$	(40)	0.28
Zr^{4+}	$Zr(NO_3)_4.5H_2O$	(40)	0.28

a = masked with thioglycolic acid;

b = masked with ascorbic acid

Determination of selenium in the presence of tellurium

Selenium and tellurium have similar analytical and chemical properties and usually occur together. Hence, separation of selenium from tellurium presents some importance, particularly as tellurium causes an interference in the measurement of selenium.

Tellurium forms a reddish-yellow complex with PBHA extractable into $CHCl_3$ from highly acidic media together with selenium. However, tellurium can be selectively masked with thioglycolic acid, the resulting Te-thioglycolic acid complex was soluble in water and selenium can be extracted as Se-PBHA complex. The results are shown in Table 5.

Composition of the complex

The stoichiometry of the Se-PBHA complex was determined by taking a fixed amount of metal and gradually increasing the amount of reagent. The slope of the plot of log D_M (the logarithm of the distribution coefficient of the metal). against the log C (the logarithm of the ligand concentration) was found to be 2.0, confirms that the selenium to PBHA ratio is 1:2.

TABLE 5

Determination of selenium in presence of tellurium

Selenium taken (ppm)	Tellurium added (mg)	Selenium found (ppm)**		Relative % error
		Present* method	AAS	
0.20	40	0.20	0.19	0.0
0.50	40	0.49	0.50	2.0
1.00	60	1.01	1.00	1.0
1.50	60	1.50	1.51	0.0
2.00	60	2.00	2.00	0.0
2.50	70	2.49	2.49	0.4

* Six determinations

** The regression equation for the two methods is
$S = 0.996\ A + 0.005$; $r = 0.999$
Where S = Selenium + Spectrophotometric, A = Selenium by atomic absorption spectrophotometry and
r = Correlation coefficient

The probable reaction based on the above results is as follows :

$$Se(ClO_4)_4 + 2\ HA \rightleftharpoons Se(A)_2\ (ClO_4)_2 + 2HClO_4$$

where HA = PBHA.

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