CHAPTER V

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM

RESUME

Solvent extraction, spectrophotometric and atomic absorption spectrophotometric determination of tellurium(IV) in nanogram levels are described. The tellurium(IV) forms yellow coloured complex with N-phenylbenzohydroxamic acid (PBHA) which is extractable into chloroform from 7 M $HClO_4$. Te-PBHA complex has a maximum absorbance at 345 nm with the molar absorptivity 3.5×10^4 l $mol^{-1}cm^{-1}$ and Sandell's sensitivity 0.00365 $\mu g/cm^2$. The tellurium(IV) is also determined in the range of 0.01-0.08 ppm by flameless atomic absorption spectrophotometry using GBC HG 900 vapor generation accessary. Effect of molarity, reagent concentrations, diverse ions on the extraction of tellurium complex were studied. The tellurium was determined in presence of selenium and also in standard sample.

INTRODUCTION

In recent years tellurium steels have been widely used in automation, radioengineering and semiconductor technology. This has increased the interest in tellurium, and led to large scale studies on the inorganic and analytical chemistry of tellurium.

Numerous methods have been proposed for the spectrophotometric determination of traces of tellurium. Several reagents like bromopyrogallol (1), rhodamine 6G (2), malachite green(3), bismuthol II (4), thiourea (5), sodium diethyl dithiocarbomate (6,7) were used for the determinations of tellurium(IV).

In recent years more sophisticated techniques such as neutron activation (8), isotope dilution mass spectrophotometry (9) and atomic absorption spectrophotometry (AAS) have been employed to analyse tellurium. The major difficulty in the determination of tellurium by atomic absorption spectrophotometry is that the limits are high and the major elements constituting the silicate matrix must be separated before estimation.

Hydroxamic acids have received a great deal of attention as spectrophotometric gravimetric, titrimetric and colorimetric reagents for several metal ions (10-13). In the present investigation a new rapid solvent extraction, and spectrophotometric method for nanogram levels of tellurium in presence of selenium is described. A sensitive flameless atomic absorption spectrophotometric method is also 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 (14). Its purity was checked by mp, TLC, infrared and ultraviolet spectra, and its 0.2% solution was prepared in chloroform.

0.5 gm of tellurium metal (99.99) was dissolved in 20 ml of conc. HCl and HNO_3 (1:3) and diluted to 500 ml with doubly distilled water. This solution contains 1000 ppm of tellurium.

APPARATUS

The spectrophotometric measurements were made on a Bausch and Lomb, Spectronic 20, spectrophotometer, GBC 901 atomic absorption spectrophotometer (AAS) with GBC HG 900 vapor generation accessary is used for AAS determination of tellurium. The tellurium line at 214.3 nm with lamp current 7 mA and argon gas was used.

EXTRACTION PROCEDURE

2.0 ml of tellurium solution (20 ppm) 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 $HClO_4$ to 7.0 M). Then 10 ml of chloroform solution of the reagent (PBHA) was added, and the contents were shaken for 10 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 2.0 ml of reagent solution to check the complete extraction of tellurium. The anhydrous sodium sulfate was washed with chloroform, and the washings were collected. The extracted layer was diluted with chloroform upto the mark, and the absorbance was measured at 345 nm against the blank which was prepared in the similar manner in absence of tellurium.

Atomic absorption measurements

For the AAS measurements the tellurium 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 Te-PBHA complex has a maximum absorbance at 345 nm. The blank does not absorb at this wavelength. The molar absorptivity is 3.5×10^4 l $mol^{-1}cm^{-1}$. The data obtained by the present method are in good agreement with those obtained by AAS and the correlation coefficient is 0.998.

Effect of acidity

The extraction of tellurium was carried out in the range of 6-8 M $HClO_4$. The results given in Table 1 indicate that the 50% extraction is obtained at 6.5 M $HClO_4$ and maximum (100%) extraction is at 7.0 M $HClO_4$. Above 7.0 M the extraction decreases and hence all the extractions were carried out at 7.0 M $HClO_4$.

Effect of solvent

The tellurium was extracted with various solvents including chloroform, toluene, isoamyl alcohol and methyl isobutyl ketone. Chloroform was found the most suitable solvent for extraction of tellurium (Table 2).

TABLE 1

Effect of acidity on the extraction of tellurium

Te(IV) : 0.80 ppm

PBHA : 0.2%, 10 ml in $CHCl_3$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex : Yellow

Molarity of $HClO_4$ (M)	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
5.0	0	0
5.5	0	0
6.0	6.3×10^3	18
6.5	1.6×10^4	46
7.0	3.5×10^4	100
7.5	2.4×10^4	69
8.0	2.0×10^4	58

TABLE 2

Effect of solvents on the extraction of tellurium with N-phenylbenzohydroxamic acid

Te(IV) : 0.80 ppm

PBHA : 0.2%, 10 ml in $CHCl_3$

Molarity : 7 M $HClO_4$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex: Yellow

Solvents	Molar absorptivity $l\ mol^{-1}cm^{-1}$	% E
Chloroform	3.5×10^4	100
Toluene	1.9×10^4	54
Isoamyl alcohol	NE	NE
Methylisobutyl ketone	NE	NE

NE = Not extracted

Effect of reagent concentration

Tellurium was extracted at 7 M $HClO_4$ with varying the reagent concentrations. The results given in Table 3 show that 10 ml of 0.2% N-phenylbenzohydroxamic acid (PBHA) is adequate for the quantitative extraction of tellurium. Lower PBHA concentration gave incomplete extraction. Hence all the extractions were carried out with 10 ml of 0.2% PBHA. Higher PBHA concentration has no adverse effect on the extraction of tellurium.

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 tellurium. However, a longer shaking time had no adverse effect on the equilibrium system. The complex is stable under optimum conditions and the absorbance remained unchanged for several hours.

Beer's law

Beer's law is obeyed in the range of 0.10 to 5.0 ppm of tellurium. The Sandell's sensitivity is 0.00365 $\mu g/cm^2$. The Beer's law limit for the flameless atomic absorption spectrophotometric determination of tellurium is 0.01 - 0.08 ppm.

TABLE 3

Effect of reagent concentration

Te(IV) : 0.80 ppm

Molarity : 7 M $HClO_4$

Solvent : $CHCl_3$

λmax : 345 nm

Colour of complex: Yellow

PBHA (0.2%) ml	Absorbance	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$	% E
2.5	0.12	1.9×10^4	54.5
5.0	0.16	2.5×10^4	72.7
7.5	0.22	3.5×10^4	100
10.0	0.22	3.5×10^4	100
15.0	0.22	3.5×10^4	100

Effect of diverse ions

Different amounts of diverse ions were added to a fixed amount of tellurium and extracted according to the procedure. Most of the metal ions associated with tellurium do not interfere. The interference of large amount of Se(IV) can be tolerated by masking it with the mixture of citric acid, sodium tartarate and EDTA. The data are shown in Table 4.

Determination of tellurium in the presence of selenium

Tellurium and selenium have similar analytical and chemical properties and usually occur together. Hence, separation of tellurium from selenium is very difficult.

Selenium forms reddish yellow complex with PBHA extractable into chloroform from highly acidic media together with tellurium. However, selenium can be selectively masked with the mixture of citric acid, sodium tartarate and EDTA, the resulting complex was soluble in water and tellurium can be extracted as Te-PBHA complex. The results are shown in Table 5.

Stoichiometry of the Te:PBHA complex

The stoichiometry of the Te-PBHA complex was determined by taking a fixed amount of metal and gradually increasing the amount of reagent. The slope of the plot of

TABLE 4

Effect of diverse ions on the extraction of tellurium

Te(IV) : 0.80 ppm

PBHA : 0.2%, 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
Ag^+	$AgNO_3$	(40)	0.22
As^{3+}	AsF_3	(40)	0.22
Ba^{2+}	$BaCl_2$	(40)	0.21
Be^{2+}	$BeSO_4$	(50)	0.22
Ca^{2+}	$Ca(NO_3)_2$	(40)	0.22
Cd^{2+}	$CdSO_4$	(50)	0.21
Co^{2+}	$Co(C_2H_3O_2)_2.4H_2O$	(40)	0.22
Cu^{2+}	$CuSO_4$	(40)	0.22
Ga^{3+}	GaI_3	(40)	0.22
In^{3+}	$InCl_3$	(40)	0.22
La^{3+}	$La(NO_3)_3.6H_2O$	(40)	0.21
Mg^{2+}	$Mg(NO_3)_2$	(50)	0.22
Nd^{3+}	$Nd(NO_3)_3$	(40)	0.22
Ni^{2+}	$NiCl_2$	(40)	0.22
Sn^{2+}	$SnCl_2$	(40)	0.22
Se^{4+}	$Se(ClO_4)_4$	(40)[a]	0.22
Ti^{4+}	$TiCl_4$	(50)	0.22
Th^{4+}	$Th(NO_3)_4$	(40)	0.21
V^{5+}	NH_4VO_3	(40)[b]	0.22
Zn^{2+}	$ZnCl_2$	(40)	0.22

a = masked with mixture of citric acid + Na-tartrate + EDTA

b = masked with ascorbic acid

TABLE 5

Determination of tellurium in presence of selenium

Tellurium taken (ppm)	Selenium added (mg)	Tellurium found (ppm)**		Coefficient variation
		Present* method	AAS	%
1.0	50	1.00	0.99	1.00
3.0	50	3.01	3.00	0.66
5.0	60	5.01	3.00	0.20
7.0	60	6.99	7.00	0.28
9.0	70	9.00	9.00	0.22
11.0	70	10.99	10.99	0.27

* Seven determinations

** The regression equation for the two methods is

$T = 0.998\,A + 0.0137$, $r = 1.000$

where T = Tellurium by spectrophotometry,
A = Tellurium by AAS and
r = Correlation coefficient

TABLE 6

Determination of tellurium in NBS cartridge brasses

Sample	Certified Te %	Te found %	Coefficient of variation %
NBS - 1100	0.0035	0.0034	5.88
NBS - 1101	0.0015	0.0013	7.69
NBS - 1102	0.0003	0.0003	16.66

D_M (the logarithm of the distribution coefficient of the metal) against the log C (the logarithm of the ligand concentration) (15), was found to be 2.2 confirms that the tellurium to PBHA ratio is 1:2.

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

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

where HA = PBHA.

Determination of tellurium in NBS cartridge brasses

The method was also applied to three standard reference cartridge brass samples. The results of these analyses are shown in Table 6.

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