

## Spectrophotometric Determination of Tellurium(IV) with 2-Mercaptoethanol

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The reaction of Te(IV) with 2-mercaptoethanol (L) can form a complex with the formula  $Te:L_4$  in present Britton-Robinson buffer of pH 2. The complex is soluble in water and shows maximum absorption at 241 nm and this was used as the basis for the spectrophotometric determination of Te(IV). Beer's law is obeyed over the concentration range 1.0-200.0  $\mu$ M of Te(IV). The molar absorptivity of the complex is  $6918 \text{ L mol}^{-1} \text{ cm}^{-1}$ , formation time is 20 min and the working temperature is 50 °C. The relative standard deviation (RSD %) did not exceed  $\pm 4.1$  %.

**Key Words:** Tellurium, 2-Mercaptoethanol, Complex, Spectrophotometric determination.

### INTRODUCTION

Spectrophotometric determination of tellurium(IV) by means of extraction with 100 % tributylphosphate (TBP) of pH 1 was studied. Tellurium forms yellow complex with thiourea in a dilute hydrochloric acid solution and the complex is extracted into TBP whenever potassium thiocyanate is present in excess in the solution. For the determination of tellurium, the absorbance of the TBP phase was measured spectrophotometrically at 400 nm<sup>1</sup>. An ultraviolet spectrophotometric method for the determination of tellurium is proposed which is based on the formation of *tetrakis*-1-pyrrolidinecarbodithioate tellurium(IV) which is extractable with chloroform. The molar absorptivity at 257 nm is  $8.12 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Conformity to Beer's law was observed<sup>2</sup>. A method for determining 0.0001-0.1000 % of tellurium in copper, nickel, molybdenum, lead and zinc concentrates is described. After sample decomposition, tellurium is separated from most of the matrix elements by co-precipitation with hydrated ferric oxide from an ammoniacal medium. The yellow ion-association complex formed between tellurium(IV) hexabromide and diantipyrylmethane is extracted into chloroform from a 2 M sulphuric acid 0.6 M potassium bromide medium. The molar absorptivity of the complex is  $1.82 \times 10^3 \text{ L mol}^{-1} \text{ mm}^{-1}$  at 336 nm<sup>3</sup>. Potassium morpholine-4-carbodithioate has been examined as a reagent for the spectrophotometric determination of tellurium after extraction into molten naphthalene. Beer's law holds in the concentration range: 5.7-125.0  $\mu$ g of Te/10 mL of the final solution. The molar absorptivity is calculated to be  $1.075 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 415 nm. Aliquots containing

25.5  $\mu$ g of tellurium gave a mean absorbance of 0.215 with a relative standard deviation<sup>4</sup> of 0.0013. A new reliable method for the spectrophotometric determination of tellurium(IV) after extraction of its 1-pyrrolidinecarbodithioate into molten naphthalene is developed. Tellurium reacts with 1-pyrrolidinecarbodithioate to form a water-insoluble, thermally stable coloured complex which can be quantitatively extracted into molten naphthalene in the pH range of 0.5-2.5. The extracted naphthalene crystals are dissolved in dimethylformamide<sup>5</sup>. A rapid spectrophotometric method has been developed for microdetermination of Te(IV) after co-precipitation of its morpholine-4-carbodithioate complex in chloroform. The molar absorptivity at 415 nm is  $9.18 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Beer's law is obeyed over the range 5-75  $\mu$ g of Te(IV) in 10 mL. The method has been tested for determination of tellurium in some alloys and synthetic mixtures<sup>6</sup>. A spectrophotometric method for the determination of trace amounts of tellurium(IV) in dilute hydrochloric acid is described. Concentrations between 0.2 and 7.0  $\mu$ g mL<sup>-1</sup> of tellurium(IV) in the final solution can be determined by measuring the absorbance at 382 nm of the complex formed by the reaction of tellurium(IV) with tetramethylthiourea ( $\epsilon = 2.14 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>7</sup>. A highly sensitive spectrophotometric method have been developed for the determination of tellurium(IV), based on its colour reactions with tungstate and basic dyes (BD) in aqueous solution in the presence of poly(vinyl alcohol). Tellurium(IV) reacts with tungstate and basic dyes to form ion-association complexes. The methods have been successfully applied to the spectrophotometric determination of trace amounts of tellurium(IV)<sup>8</sup>. A method is proposed for the extraction, separation and spectrophoto-

ometric determination of trace levels of tellurium(IV) from hydrochloric acid media with 1-(4-bromophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol (4-bromoPTPT) in chloroform. The yellow-coloured complex absorbs at 440 nm and the system obeys Beer's law in the 1-15 ppm concentration range. The molar absorptivity is  $8.1 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The probable composition of the extracted species is  $\text{TeL}_2$ <sup>9</sup>. A simple and sensitive kinetic spectrophotometric method for the determination of ultra trace amounts of tellurium(IV) has been proposed. It is based on the catalytic effect of Te(IV) on the reduction of galloyanine by sodium sulphide. The method allows the determination of tellurium concentration at 618 nm in the range 2.0-200.0 ng/mL, with the detection limit of 1 ng/mL. The relative standard deviation for 10 replicate determinations of 20 and 50 ng/mL Te(IV) is 1.7 and 1.1 %, respectively<sup>10</sup>. A simple and highly sensitive method is proposed for the determination of Te(IV) by its catalytic effect on the reduction of thionine by sodium sulfide in the presence of cetyl trimethyl ammonium bromide as a micelle media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of thionine at 600 nm. Tellurium can be measured in the concentration range of 0.6-500.0 ng/mL. The relative standard deviation for 10 replicate measurements of 0.020 and 50.000 ng/mL Te(IV) was 2.1 and 1.9 %, respectively<sup>11</sup>. Three simple, rapid and sensitive spectrophotometric methods for the determination of traces and ultratraces of tellurium(IV) were studied. These methods were based on either the oxidation of 4-bromophenylhydrazine (4-BPH) by tellurium in a basic medium and coupling with N-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) to give a purple-coloured product, the oxidation of 3-methyl-2-benzothiazoline hydrazone hydrochloride (MBTH) by tellurium in a basic medium and coupling with chromotropic acid (CA) to yield a red-coloured species or the oxidation of 2,3-dimethoxystrychnidin-10-one (2,3-DMSO) by tellurium in an acidic medium to yield an orange-coloured derivative. Beer's law was obeyed in the range 1-25  $\mu\text{g/mL}$  (purple-coloured product), 0.7-20.0  $\mu\text{g/mL}$  (red-coloured species) and 0.3-15  $\mu\text{g/mL}$  (orange-coloured derivative)<sup>12</sup>. A rapid, simple and sensitive spectrophotometer method for the determination of traces and ultra traces of tellurium(IV) were studied. These method were based on either the oxidation of leuco methylene green (LMG) to its blue form of methylene green by tellurium in acidic medium, the formed dye shows an absorption maximum at 650 nm in acetate buffer medium (pH 3-5). Beer's law were obeyed in the concentration range 0.4-2.5  $\mu\text{g mL}^{-1}$ , having molar absorptivity of  $4.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  ( $\lambda_{\text{max}} = 650 \text{ nm}$ )<sup>13</sup>. A spectrophotometric method for the determination of palladium, iron and tellurium from nitric acid media after extraction of their *p*-[4-(3,5-dimethylisoxazolyl)azophenylazo] calix(4)arene [DMIAPAC] complexes has been developed and possible synergistic effects have been investigated. Chloroform, carbon tetrachloride, cyclohexane, 1,2-dichloroethane, toluene and xylene were used as the diluents. Beer's law obeyed in the concentration range of 10-140  $\mu\text{g}/10 \text{ mL}$  of the final solution of tellurium<sup>14</sup>.

In the present study, the reaction of Te(IV) with 2-mercaptoethanol ( $\text{HSCH}_2\text{CH}_2\text{OH}$ ) in presence of Britton-Robinson buffer of pH 2 and formation of a  $\text{Te:L}_4$  complex and this is used as the basis for determination of Te(IV) were applied.

## EXPERIMENTAL

Spectrophotometric measurements was made in a Biotech E.M. UV-Visible spectrophotometer with 1 cm quartz cells. The pH measurement was performed with EUTECH COPERSCAN-500. A ultrasonic processor model POWERSONIC 405 was used to sonicate the sample solutions.

All chemicals were obtained from Merck. The solutions are prepared with distilled water from analytical-reagent grade chemicals as the following:

**Standard tellurium solution,  $1 \times 10^{-3} \text{ M}$ :** Dissolve 1.596 g of tellurium dioxide by heating gently with 15 mL of concentrated HCl, cool and dilute to 500 mL with distilled water. Dilute 10 mL of this stock solution to 200 mL with distilled water ( $1 \times 10^{-3} \text{ M}$ ). Prepare fresh as needed (the tellurium dioxide used was found to be pure, by titration with potassium permanganate).

**2-Mercaptoethanol solution  $5 \times 10^{-3} \text{ M}$ :** Dissolve 1.750 mL of 2-mercaptoethanol (L) with 20 mL distilled water (containing 0.2 M  $\text{NaNO}_3$ ) and dilute to 50 mL. Dilute 1 mL of this solution to 100 mL with distilled water ( $5 \times 10^{-3} \text{ M}$ ).

**Britton-Robinson buffer of pH 2:** Dissolve 2.472 g of boric acid with 50 mL distilled water, add 2.30 mL of glacial acetic acid and 2.70 mL orthophosphoric acid 85 % in 100 mL volumetric flask then diluted to the mark with distilled water.

**General procedures:** Aliquots of standard tellurium solution, 5 mL of Britton-Robinson buffer of pH 2 and 2 mL of 2-mercaptoethanol solution  $5 \times 10^{-3} \text{ M}$  were transferred into a series of 10 mL calibrated volumetric flasks and diluted to the mark with distilled water, then kept aside for 20 min at 50 °C. The absorbance was measured at 241 nm for  $\text{Te:L}_4$  against a similar reagent blank (without Te). The amount of Te(IV) was computed from its Beer's law plot prepared with standard tellurium solutions under identical conditions.

## RESULTS AND DISCUSSION

**Effect of the ligand to Te molar ratio:** Provided that the ligand to Te molar ratio was maintained above a certain value, the variations in the ligand (L) concentration did not affect the absorption of the complex. For a constant Te concentration of  $1 \times 10^{-4} \text{ M}$ , formation time of 20 min, temperature 50 °C and using Britton-Robinson buffer pH of 2, the ligand (2-mercaptoethanol) to metal molar ratio,  $Y = \text{L}:\text{Te}$ , was varied between 1 and 15. The solution with  $Y = 1$  to 4 the absorbance of the complex increases linearly with increasing concentration of ligand and when the concentration of ligand is 5 times the absorbance increase was slightly (less than 1 %). Finally when the ligand concentration increased from 6 to 15 times the absorbance remains almost constant (Fig. 1). For the absorbance values at 241 nm, a value for Y of 4 proved to be critical. Above this value there was no change in the absorbance. The complex showed no change in absorption at 241 nm after 2 h.

**Effect of pH, time and temperature:** The effect of pH values in the range 0.2-4.0 on the absorbance (A) of  $\text{Te:L}_4$  complex was examined. It was found that the optimum value of pH is 2 for highest absorbance. The effect of time and temperature on the absorbance of the  $\text{Te:L}_4$  complex solution was studied. It was found that, the optimum time was 20 min and the optimum temperature was 50 °C.

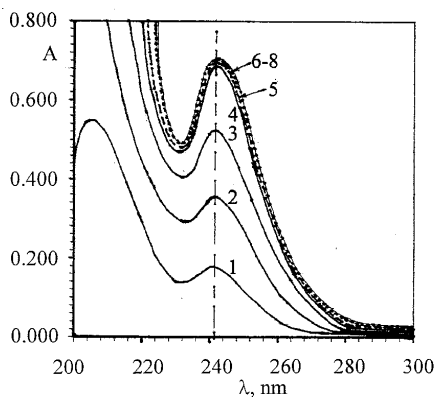


Fig. 1. Variations in the absorption spectra for different ligand (L) concentrations to Te (molar ratios) and formation L:Te complex: (1)  $1 \times 10^{-4}$ , (2)  $2 \times 10^{-4}$ , (3)  $3 \times 10^{-4}$ , (4)  $4 \times 10^{-4}$ , (5)  $5 \times 10^{-4}$ , (6)  $6 \times 10^{-4}$ , (7)  $10 \times 10^{-4}$  and (8)  $15 \times 10^{-4}$  M ( $C_{\text{Te(IV)}} = 1 \times 10^{-4}$  M, by using Britton-Robinson buffer of pH 2 as blank,  $\ell = 1$  cm, L is 2-mercaptoethanol)

**Composition of Te:L complex:** The composition of Te:L complex was determined by Job's method of continuous variation and mole-ratio method<sup>15</sup> as follows:

**Molar ratio method:** The stoichiometry of Te:L complex by molar ratio method,  $A_{\text{max}} = f\left(\frac{[\text{L}]}{[\text{Te(IV)}]}\right)$ , confirms that the ratio of complex Te:L is equal to 1:4. Where the concentration of Te(IV) is constant ( $1 \times 10^{-4}$  M) and the concentrations of 2-mercaptoethanol (L) is change from 0-1 to  $10^{-3}$  M (Fig. 2).

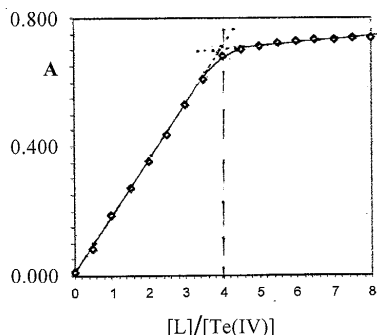


Fig. 2. Molar ratio method to calculate coupling ratio for complex Te:L, Te(IV) concentration is constant  $1 \times 10^{-4}$  M (by using Britton-Robinson buffer of pH = 2 as blank,  $\lambda_{\text{max}} = 241$  nm,  $\ell = 1$  cm, L is 2-mercaptoethanol)

**Continuous variation method:** The ratios of Te:L complex

by continuous variation method,  $A_{\text{max}} = f\left(\frac{[\text{Te(IV)}]}{[\text{Te(IV)}] + [\text{L}]}\right)$ ,

in which  $C_{\text{Te}^{4+}} + C_{\text{L}} = 5 \times 10^{-4}$  M (constant) were studied. The stoichiometry of Te:L complex are equal to 1:4 (Fig. 3).

**Spectrophotometric results:** UV spectra by using Britton-Robinson buffer of pH 2 as blank were studied. The Te(IV) solutions do not absorb in range 200-300 nm, while the ligand L solutions has good absorption at 212 nm. When the concentration of Te(IV) increases to  $C_{\text{Te(IV)}} \leq \frac{1}{4} C_{\text{L}}$ , a new peak for Te:L complex at  $\lambda_{\text{max}} = 241$  nm sharply increases. After that, when  $C_{\text{Te(IV)}} > \frac{1}{4} C_{\text{L}}$ , the peak for Te:L complex

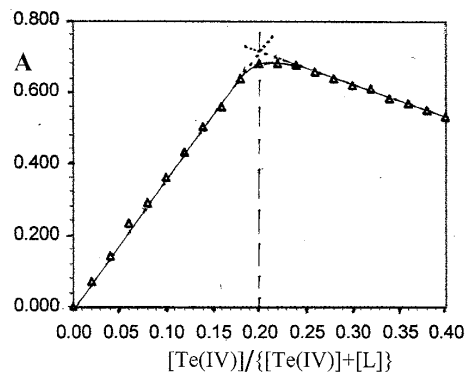


Fig. 3. Continuous variation method to calculate coupling ratio for Te:L complex (by using Britton-Robinson buffer of pH = 2 as blank,  $\lambda_{\text{max}} = 241$  nm,  $\ell = 1$  cm, L is 2-mercaptoethanol)

slowly increases [Fig. 4(a)]. UV spectra of Te:L<sub>4</sub> complex solutions against a similar reagent blank (without Te) show that, only the absorbance peak of Te:L<sub>4</sub> complex was shown at 241 nm [Fig. 4(b-c)].

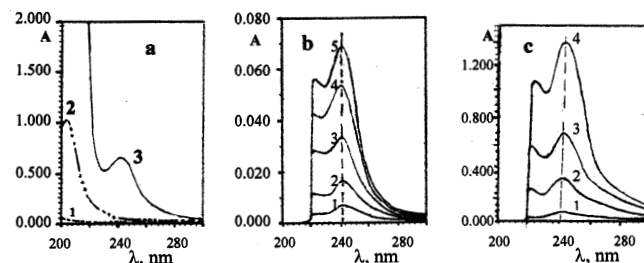


Fig. 4. (a) UV spectra of Te(IV)  $1 \times 10^{-4}$  M (1), ligand L  $2 \times 10^{-4}$  M (2) and Te:L<sub>4</sub> complex  $C_{\text{Te(IV)}}: 1 \times 10^{-4}$  M and  $C_{\text{L}}: 1 \times 10^{-3}$  M (3) against a Britton-Robinson buffer. (b) UV spectra of Te:L<sub>4</sub> complex ( $C_{\text{Te(IV)}}: (1) 1 \times 10^{-6}, (2) 2.5 \times 10^{-6}, (3) 5 \times 10^{-6}, (4) 8 \times 10^{-6}, (5) 1 \times 10^{-5}$  M against a similar reagent blank (without Te). (c) UV spectra of Te:L<sub>4</sub> complex ( $C_{\text{Te(IV)}}: (1) 1 \times 10^{-5}, (2) 5 \times 10^{-5}, (3) 1 \times 10^{-4}$  and (4)  $2 \times 10^{-4}$  M against a similar reagent blank (without Te)

**Calibration curve:** The calibration curves for Te:L<sub>4</sub> showed excellent linearity over concentration ranges of 1-200  $\mu\text{M}$ . The spectra characteristics of the Te:L<sub>4</sub> solutions as  $\epsilon$ ,  $\lambda_{\text{max}}$ , Beer's law, the equation ( $A = mC + b$ ; A = absorbance, C = concentration of Te(IV) in M, b = intercept and m = slope) and the correlation coefficient ( $R^2$ ) are summarized in Table-1.

TABLE-1  
ANALYTICAL CHARACTERISTICS OF COMPLEX Te:L<sub>4</sub> IN BRITTON-ROBINSON BUFFER

Factors	Parameters
Working temperature	50 °C
pH	2.0
Linearity	1.0-200 $\mu\text{M}$
Detection limit	0.15 $\mu\text{M}$
Molar absorptivity ( $\epsilon$ ) ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$6.918 \times 10^3$
$\lambda_{\text{max}}$ (nm)	241
Formation time (min)	20
Stoichiometric relationship, Te:L complex	1:4
Regression equation <sup>a</sup> :	
Slop (m)	6918
Intercept (b)	0.0182
Correlation coefficient ( $R^2$ )	0.9984
RSD (%)	4.1

<sup>a</sup>A = mC + b, where C = concentration in M and A = absorbance.

The precision and accuracy of method were tested by determining the Te(IV) concentration, ranged within the Beer's law, for 5 replicates time for each concentration ( $n = 5$ ) are given in Table-2.

TABLE-2  
DETERMINATION OF TELLURIUM(IV) BY FORMATION Te:L<sub>4</sub>  
COMPLEX IN BRITTON-ROBENSON BUFFER OF pH 2 USING  
SPECTROPHOTOMETRIC ANALYSIS  
(L is 2-mercaptoethanol  $1 \times 10^{-3}$  (M),  $\lambda_{\max} = 241$  nm)

$C_{\text{Te(IV) taken}} (\mu\text{M})$	$C_{\text{Te(IV) found}} (\mu\text{M})$ $\bar{X} \pm \text{SD}$	RSD (%)	Analytical standard error $\frac{\text{SD}}{\sqrt{n}}$ ( $\mu\text{M}$ )	Confidence limit $\left( \bar{X} \pm \frac{\text{SD}}{\sqrt{n}} \times t \right)$ ( $\mu\text{M}$ )	Recovery (%)
1.0	1.02 ± 0.042	4.1	0.0188	1.02 ± 0.052	102.0
2.5	2.50 ± 0.097	3.9	0.0434	2.50 ± 0.120	100.0
5.0	5.01 ± 0.185	3.7	0.0827	5.01 ± 0.229	100.2
8.0	7.98 ± 0.271	3.4	0.1210	7.98 ± 0.336	99.7
10.0	10.0 ± 0.30	3.0	0.1340	10.0 ± 0.372	100.0
20.0	20.4 ± 0.57	2.8	0.2550	20.4 ± 0.708	102.0
30.0	30.1 ± 0.75	2.5	0.3350	30.1 ± 0.930	100.3
40.0	39.5 ± 0.91	2.3	0.4070	39.5 ± 1.13	98.7
50.0	50.2 ± 1.05	2.1	0.4690	50.2 ± 1.30	100.4
75.0	75.6 ± 1.51	2.0	0.6750	75.6 ± 1.87	100.8
100.0	100.1 ± 1.8	1.8	0.8050	100.1 ± 2.23	100.1
125.0	125.0 ± 2.12	1.7	0.9480	125.0 ± 2.63	100.0
150.0	149.5 ± 2.24	1.5	1.0000	149.5 ± 2.78	99.7
175.0	174.3 ± 2.26	1.3	1.0100	174.3 ± 2.80	99.6
200.0	198.6 ± 2.38	1.2	1.0600	198.6 ± 2.94	99.3

$n = 5, t = 2.776.$

## Conclusion

Spectrophotometric determination of tellurium(IV) with 2-mercaptoethanol (L) and formation Te:L<sub>4</sub> complex in present

Britton-Robinson buffer of pH 2 were studied. The complex is soluble in water and shows maximum absorption at 241 nm and this was used as the basis for determination of Te(IV). Beer's law is obeyed over the concentration range 1-200  $\mu\text{M}$  of Te(IV). The molar absorptivity of the complex is  $6918 \text{ L mol}^{-1} \text{ cm}^{-1}$ , formation time is 20 min and the working temperature is 50 °C. The per cent relative standard deviation (RSD %) did not exceed 4.1 %.

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