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Extraction, Separation, and Spectrophotometric Determination of Tellurium(IV) with 1-(4-Bromophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol

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A method is proposed for the extraction, separation and spectrophotometric 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-colored complex absorbs at 440 nm and the system obeys Beer's law in the 1—15 ppm concentration range. The molar absorptivity and Sandell's sensitivity are 8.1×10^3 dm^3 mol^{-1} cm^{-1} and 16 ng cm^{-2}, respectively. The probable composition of the extracted species is TeL_2. The interference of various ions was studied. Various parameters, such as the effects of the acidity, reagent concentration, equilibration time etc., have been established for the extractive spectrophotometric determination of tellurium(IV). The method has been applied for the determination of tellurium(IV) in various synthetic samples corresponding to alloys, and provides for the binary separation of tellurium(IV) from lead, bismuth, copper, gold, and antimony. It is also applicable for the simultaneous determination of selenium(IV) and tellurium(IV). The method is accurate, simple, rapid, and selective, and the overall process of extraction and determination takes about 15 to 20 min.

Tellurium is widely distributed in small amounts in the earth's crust with the average concentrations in crystal rocks of tellurium being reported as 0.002 ppm. In general, it appears that tellurium is less toxic than selenium. Tellurium is a powerful chilling agent in iron castings. Tellurium copper containing 0.5% tellurium has been employed for welding and soldering tips, requiring an alloy having good machinability and high electrical and thermal conductivity. Copper–tellurium, lead–tellurium, and tin-base alloys have been developed as bearing alloys for automotive use. Tellurium has its catalytic activity, particularly in processes where a catalyst of moderate activity, but high selectivity, is required. The most promising applications of semiconducting tellurium compounds lie in the area of thermoelectricity for either power generation, as with lead telluride, or refrigeration, as with bismuth telluride. Tellurium has also been used in the ceramics industry for manufacturing glasses and porcelains of various colors. In view of this, the separation of tellurium from associated elements is desired.

Some spectrophotometric methods of tellurium(IV) are available in the literature. These are Malachite Green,[1)] *p*-nitrophenylfluorone,[2)] potassium iodide-Rhodamine,[3)] *N*,*N*′-di(acetoxyethyl) indocarbocyanine,[4)] halide ion-cationic red-violet,[5)] Bismuthiol II,[6)] Sodium 2,3-dimercapto-1-propane sulfonate (Unithiol),[7)] 1-methylpiperazine-4-carbodithioate,[8)] tetramethylthiourea,[9)] potassium *o*-2,2,2-trifluoroethyl dithiocarbonate,[10)] 2-mercaptobenzimidazole,[11)] iodide-cetyltrimethylammonium ion,[12)] potassium morpholine-4-carbodithioate,[13)] 2-furanthiocarbothiohydrazide,[14)] 4-quinolinedithiocarboxylate,[15)] and dithiopyrulmethane.[16)]

A novel chromogenic reagent, pyrimidine-2-thiols, also known as cyclic thioureas, constitutes a versatile class of analytical reagents. The use of such compounds as extractants for the platinum group and coinage metals was investigated in our laboratory.[17—22)] An extension of this work has shown that 1-(4-bromophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol (4-bromoPTPT) could also be used for the extraction separation and spectrophotometric determination of tellurium(IV) from hydrochloric acid media. The method is applicable for the determination of tellurium(IV) in a synthetic mixture and alloys.

Experimental

Reagents and Apparatus: Absorbance measurements were made on an Elico digital spectrophotometer (model CL-27) with 1 cm quartz cells used for the absorbance measurement. Then, pH measurements were carried out using an Elico digital pH meter (model LI-120).

Standard Tellurium(IV) Solution: Dissolve 1.785 g of sodium trioxotellurate ($Na_2TeO_3\cdot3H_2O$) in distilled water, dilute to 500 ml and standardize[23)] gravimetrically by reducing with hydrazine sulfate and dilute the stock solution to obtain a working solution of lower concentration with distilled water.

4-bromoPTPT: Prepared by the method of Mathes[24)] from 4-bromoaniline. The compound is a colorless crystalline solid with a sharp mp at 188 °C, and is used as 10 ml of a 0.02 M solution (1 M = 1 mol dm^{-3}) in chloroform. This solution is colorless and stable.

Other standard solutions of different metals used to study the effect of foreign ions are prepared by dissolving weighed quantities of their salts in distilled water or dilute hydrochloric acid. Solutions of anions are prepared by dissolving the respective alkali metal salts in distilled water. All of the chemicals used are of AR grade. Distilled water is used throughout.

Methods Used for Purification of Organic Solvents.[25,26] **1) Benzene:** Benzene may contain thiophene (C_4H_4S) with a bp of 84 °C, which cannot be separated by distillation or by fractional crystallisation. By shaking with concentrated H_2SO_4, thiophene is more readily sulfonated than benzene. Benzene is shaken repeatedly with about 15% of its volume of concentrated sulfuric acid in a stoppered separatory funnel until the acid layer is colorless or until the thiophene test is negative. After each shaking lasting a few minutes, the mixture is allowed to settle and the lower layer of acid is drawn off. The benzene is then shaken twice with water in order to remove most of the acid, once with a 16% sodium carbonate solution, again with water, and finally dried with anhydrous calcium chloride. After filtration, the benzene is distilled through an efficient column and the fraction (bp 80—81 °C) is collected.

2) Toluene: Toluene may contain methyl thiophenes (bp 112—113 °C), which cannot be removed by distillation. The simplest procedure involves mechanically stirring one litre of toluene with 100 ml of concentrated sulfuric acid for about 30 min; the temperature is not allowed to rise above 30 °C by occasional cooling. The lower layer is removed, and the process is repeated twice. The subsequent working up is carried out as described under benzene. Pure toluene has a bp of 110.5 °C/760 mmHg (1 mmHg = 133.322 Pa).

3) Chloroform: Chloroform contains up to 1% of ethyl alcohol, which is added as a stabiliser. The chloroform is shaken five or six times with about half its volume of water, then dried over anhydrous calcium chloride for at least 24 h and distilled. Pure chloroform has a bp of 61 °C/760 mmHg. The solvent, when free from alcohol, should be kept in the dark in order to avoid any photochemical formation of phosgene.

4) *n*-Butyl Acetate: The ester (50 ml) contains some acid; wash it with about 100 ml of water repeatedly, followed by about 25 ml of saturated sodium bicarbonate solution and 50 ml of water. The ester must, of course, be separated between each washing. Dry the ester with 5—6 g of anhydrous sodium or magnesium sulphate, filter through a small funnel containing fluted filter paper into a dry 100 ml distillating flask and distill. Collect the pure *n*-butyl acetate at a bp of 124—125 °C.

5) Carbon Tetrachloride: Carbon tetrachloride may contain up to 4% of carbon disulphide; this may be removed by the following method. One litre of carbon tetrachloride is treated with potassium hydroxide dissolved in an equal weight of water and 100 ml of rectified spirit; and the mixture is vigorously shaken for 30 min at 50—60 °C. After washing with water, the process is repeated with half the quantity of potassium hydroxide. The alcohol is then removed by shaking several times with 500 ml of water, followed by shaking with small portions of concentrated sulfuric acid until there is no further coloration. The carbon tetrachloride is then washed with water, dried over anhydrous calcium chloride and distilled. The pure compound boils at 76.5 °C/760 mmHg.

6) Pentyl Acetate: Pentyl acetate was successively washed with a solution saturated with sodium bicarbonate and sodium chloride until the effervesence ceased, and then dried and distilled. The pure compounds boil at 105—107 °C and 765 mmHg.

7) Xylene: For solvent purposes various grades of xylenes (the mixture of isomers and ethyl benzene) are available; the purification and drying procedures are similar to those used for benzene and toluene. The bp range is 138—144 °C/760 mmHg.

8) 4-Methyl-2-pentanol: It may be purified by drying with anhydrous potassium carbonate or with anhydrous calcium sulphate, and is fractionated after filtration from a desiccant. If the perfectly anhydrous alcohol is required, the redistilled alcohol may be treated with the appropriate alkyl phthalate or succinate.

9) 4-Methyl-2-pentanone (MIBK): A preliminary purification is effected by drying the 4-methyl-2-pentanone (MIBK) with anhydrous potassium carbonate or anhydrous calcium sulphate, filtering from the desiccant, and fractionating through an efficient column. This may be further purified with sodium iodide; the ketone is saturated with sodium iodide by boiling under reflux; the solution is filtered through a hot water funnel and cooled in a freezing mixture; white crystals are filtered off and then fractionally distilled through a column. Pure 4-methyl-2-pentanone (MIBK) has a bp of 117 °C/760 mmHg.

General Procedure: An aliquot of the sample solution containing 1—15 ppm of tellurium(IV) was taken and acidity was adjusted to 6—8 M with hydrochloric acid in 25 ml volume. The solution was transferred into a 125 ml separatory funnel and thoroughly mixed with 10 ml of a 0.02 M reagent solution for 4 min. The two phases were allowed to separate and dried over anhydrous sodium sulfate; the absorbance of the organic phase was measured against chloroform at 440 nm. The tellurium(IV) content was computed from a calibration graph.

Results and Discussion

Absorption Spectra: The absorption spectrum of the tellurium(IV)–4-bromo-PTPT complex in chloroform was studied over the wavelength range of 350—500 nm. The yellow-colored complex strongly absorbs at 440 nm where the reagent solution in chloroform is colorless and, hence, does not absorb in the visible region. Thus, in every instance the absorption was measured at 440 nm against a chloroform blank.

Effect of Acidity: In order to study the effect of the acidity on the absorbance values of the yellow-colored tellurium(IV) complex, the color reaction was carried out at different values of the hydrochloric acid concentration. While other conditions in the procedure remained constant, an optimum acidity range of 6—8 M HCl (Fig. 1) was observed. Since there was no complexation in H_2SO_4, HNO_3, and $HClO_4$ media, all of the extractions were carried out at 7 M HCl.

Effect of the Reagent Concentration: Various amounts of 0.02 M 4-bromo-PTPT were equilibrated to a solution containing 100 μg of tellurium(IV) at 7 M HCl. The procedure described above was followed. The absorbance remained constant when 6 ml of 0.02 M reagent solution was used. Therefore, 10 ml of a 0.02 M reagent was preferred throughout the experiment.

Effect of Equilibration Time: The equilibration time for complexation was varied between 5 s to 15 min. It was observed that the absorbance remained constant when the shaking period was 3 min or more. There was no adverse effect of the equilibration time for up to 15 min. Therefore, an equilibration time of 4 min was chosen in order to ensure complete complexation. The complex is stable for more than 48 h.

Choice of Organic Solvent: Various organic solvents were examined for the extraction of such complexes as bu-

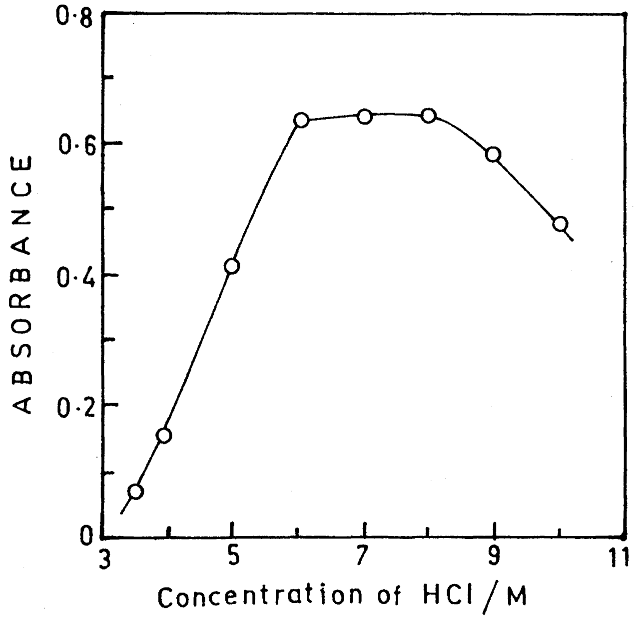

Fig. 1. Effect of acidity on absorbance of the Te^{IV}–4-bromo-PTPT complex. $Te^{IV} = 10$ ppm.

tyl acetate, carbon tetrachloride, 4-methyl-2-pentanol, pentyl acetate, 4-methyl-2-pentanone (MIBK), toluene, xylene, benzene, and chloroform. It was observed that complex extraction was incomplete in all of the solvents, except for chloroform (Table 1). In chloroform, complex is readily extracted because the complex has high distribution ratio in it.

Composition of the Complex: The composition of tellurium(IV)–4-bromo-PTPT was established by Job's method. A sharp peak at a 0.30 molar fraction suggested that TeL_2 was extracted into chloroform under these conditions, probably due to the reduction of tellurium(IV) to tellurium(II) by pyrimidine-2-thiol in hydrochloric acid media. Further, the composition was also ascertained by the mole-ratio method. Therefore, both methods conclusively confirm the composition of the complex as being 1 : 2 ($Te : L_2$).

Beer's Law and Sensitivity: The calibration graph was plotted under the optimum conditions described above. The graph obeys Beer's law over the concentration range of 1—15 ppm of tellurium(IV). Ten replicate determinations on samples containing 100 μg of tellurium(IV) gave a mean absorbance of 0.640 when measured in a 1 cm cell with a standard deviation of 0.005 and a coefficient of variation of 0.83%. The molar absorptivity was calculated to be 8.1×10^3 $dm^3\ mol^{-1}\ cm^{-1}$ at 440 nm, and Sandell's sensitivity was 16 $ng\ cm^{-2}$ of tellurium(IV) for an absorbance of 0.001.

Table 1. Effect of Organic Solvent on Tellurium Extraction Tellurium(IV) = 100 μg

Solvent	Dielectric constant	% $E^{a)}$	$D^{b)}$
Chloroform	4.8	99.90	2497.5
Butyl acetate	5.0	59.53	3.67
4-Methyl-2-pentanone	13.1	31.87	1.1694
4-Methyl-2-pentanol	—	28.12	0.9780
Pentyl acetate	4.8	17.50	0.5303
Carbon tetrachloride	2.2	12.50	0.3571
Toluene	2.4	12.50	0.3571
Xylene	2.6	9.37	0.2594
Benzene	2.3	3.12	0.0805

a) Extractability of Tellurium (%). b) Distribution ratio of Tellurium.

Effect of Diverse Ions: The effect of diverse ions commonly associated with the tellurium(IV) was studied by the recommended procedure. The criterion for interference was an error greater than 2% in the absorbence. The tolerance limits for the tested ions are given in Table 2. Thiourea and thiocyanate interfere in the determination of tellurium(IV). Of the cations examined, only Cu^{II}, Bi^{III}, Cd^{II}, Co^{II}, and Cr^{VI} interfered. The interference of Cu^{II}, Bi^{III}, Co^{II}, and Cr^{VI} was eliminated by masking with 2 ml of 10% tartaric acid and that of Cd^{II} with 2 ml of 10% citric acid.

Comparison with Other Methods: A comparison of the proposed method with some of the reported ones is given in Table 3. The present method for the extractive spectrophotometric determination of tellurium(IV) using 4-bromoPTPT involves a simple technique. Since the method is highly selective it is applicable for separation and determination of tellurium(IV) from associated metal ions. The complex is stable for a long time (> 48 h). The effect of the reagent concentration and shaking time do not have any effect on the absorbance. Most of the associated metals do not interfere. The sensitivity of the present method is promising, as indicated by the molar-absorptivity values.

Applications

Binary Separation of Tellurium(IV) from Pb^{II}, Bi^{III}, Cu^{II}, Au^{III}, and Sb^{III}. This method permits the separation and determination of tellurium(IV) from a binary mixture containing either Pb^{II}, Bi^{III}, Cu^{II}, Au^{III}, or Sb^{III} (Table 4).

Tellurium(IV) is separated from lead and antimony by its extraction with 10 ml of 0.02 M 4-bromoPTPT in chloroform from 7 M of hydrochloric acid. Under this condition both lead and antimony remain quantitatively in the aqueous phase where they are determined spectrophotometrically with 4-(2-pyridylazo)resorcinol (PAR)[29)] and potassium iodide,[30)] respectively. A yellow-colored complex of Tellurium–4-bromoPTPT from the organic phase was measured at 440 nm.

Tellurium(IV) and bismuth(III) is separated by its extraction with 10 ml of 0.02 M 4-bromoPTPT in chloroform from 7 M hydrochloric acid in the presence of 2 ml of 10% tartaric acid as a masking agent for bismuth(III) (Table 1). Under this condition bismuth(III) remains quantitatively in the aqueous phase where it is determined spectrophotometrically with thiourea[30)] by demasking with cond nitric acid. Tellurium(IV)–4-bromoPTPT complex from the organic phase is determined by following general procedure.

Tellurium(IV) and copper(II) are separated by extracting copper at pH 5.0 with 5 ml of each of 0.01 M 4-chloro-PTPT[20)] and 0.5 M pyridine in chloroform. Tellurium(IV)

Table 2. Effect of Diverse Ions on the Extractive Determination of Tellurium(IV) Tellurium(IV) = 0.100 mg Aqueousphase = 7 M HCl

Aqueous phase = 7 M HCl

Concomitant substance	Added as	Amount tolerate d mg	Absorbance at 440 nm Without masking agent	With masking agent	Remarks
None	—	—	0.640	0.640	
$\mathrm{Mn^{II}}$	$\mathrm{MnCl_2{\cdot}6H_2O}$	15	0.640		
$\mathrm{Cr^{III}}$	$\mathrm{CrCl_3}$	15	0.640		
$\mathrm{Cu^{II}}$	$\mathrm{CuSO_4{\cdot}5H_2O}$	10	0.440	0.645	After masking with 2 ml
		5	0.510	0.650	10% tartaric acid
		2	0.640	0.640	
$\mathrm{Hg^{II}}$	$\mathrm{HgCl_2}$	20	0.640		
$\mathrm{Ca^{II}}$	$\mathrm{CaCl_2}$	20	0.640		
$\mathrm{Bi^{III}}$	$\mathrm{Bi(NO_3)_3{\cdot}5H_2O}$	10	0.520	0.650	After masking with 2 ml
		5	0.608	0.645	10% tartaric acid
		2	0.638	0.640	
$\mathrm{Mg^{II}}$	$\mathrm{MgCl_2{\cdot}6H_2O}$	20	0.640		
$\mathrm{Sn^{II}}$	$\mathrm{SnCl_2{\cdot}2H_2O}$	20	0.638		
$\mathrm{Cd^{II}}$	$\mathrm{CdCl_2{\cdot}2\ 1/2H_2O}$	15	0.457	0.637	After masking with 2 ml
		10	0.630	0.640	10% citric acid
$\mathrm{Ni^{II}}$	$\mathrm{NiCl_2{\cdot}6H_2O}$	20	0.640		
$\mathrm{Pb^{II}}$	$\mathrm{Pb(NO_3)_2}$	10	0.640		
$\mathrm{V^{V}}$	$\mathrm{NH_4VO_3{\cdot}H_2O}$	10	0.641		
$\mathrm{Co^{II}}$	$\mathrm{CoCl_2{\cdot}6H_2O}$	5	0.485	0.635	After masking with 2 ml
		2	0.630	0.640	10% tartaric acid
$\mathrm{Zn^{II}}$	$\mathrm{ZnSO_4{\cdot}7H_2O}$	10	0.640		
$\mathrm{Cr^{VI}}$	$\mathrm{K_2Cr_2O_7}$	5	0.485	0.638	After masking with 2 ml
		2	0.578	0.637	10% tartaric acid
		1	0.635	0.640	
$\mathrm{Rh^{III}}$	$\mathrm{RhCl_3{\cdot}3H_2O}$	2	0.640		
$\mathrm{Mo^{VI}}$	$\mathrm{(NH_4)_6Mo_7O_{24}{\cdot}2H_2O}$	5	0.640		
$\mathrm{Sb^{III}}$	$\mathrm{Sb_2O_3}$	5	0.640		
$\mathrm{Tl^{III}}$	$\mathrm{Tl(NO_3)}$	10	0.640		
$\mathrm{Ir^{III}}$	$\mathrm{IrCl_3{\cdot}}x\mathrm{H_2O}$	2	0.640		
Citrate	Citric acid	500	0.640		
Tartarate	$\mathrm{C_4H_2O_6}$	500	0.640		
Acetate	$\mathrm{CH_3COONa}$	200	0.640		
Glycine	Glycine	200	0.638		
Iodide	KI	200	0.640		
Fluoride	NaF	50	0.640		
Borax	Borax	500	0.638		
Phosphate	$\mathrm{Na_3PO_4}$	500	0.640		
Oxalate	$\mathrm{(COOH)_2{\cdot}2H_2O}$	100	0.640		
Malonate	Malonic acid	200	0.639		
EDTA	EDTA (Disodium salt)	200	0.640		

remains in the aqueous phase quantitatively (Fig. 1); the extracted copper(II)–4-chloroPTPT–pyridine adduct is measured spectrophotometrically at 400 nm while tellurium(IV) in the aqueous phase is determined spectrophotometrically by reducting the aqueous phase with 4-bromoPTPT.

Similarly, gold(III) and tellurium(IV) are separated by extracting gold(III) from a 1 M hydrochloric acid solution with 10 ml of 0.01 M 4-chloroPTPT[18)] as an extractant in chloroform. Tellurium(IV) remains in the aqueous phase quantitatively (Fig. 1). The extracted gold(III)–4-chloroPTPT complex was destroyed with perchloric acid and determined spectrophotometrically with the tin(II) chloride method.[30)]

The recovery of tellurium and that of the added ions was $\geqslant$99.7%. The results are given in Table 4.

Analysis of Synthetic Mixtures: The proposed method was applied to the extraction and spectrophotometric determination of tellurium(IV) from hydrochloric acid media in various synthetic mixtures. The results are given in Table 5.

Analysis of Alloys: Since standard alloy samples containing tellurium(IV) were not available, we analyzed BCS-320, BCS-387, and a tin-base white metal alloy (The Bureau of Analysed Samples Ltd., UK) to which a known amount of tellurium(IV) had been added. The tellurium(IV) was recovered from hydrochloric acid media by the proposed method.

Table 3. Comparison of the Proposed Method to Some of the Reported Methods

Reagent used	Medium, pH/acidity	λ_{max} nm	Beer's range	Molar absorptivity l mol^{-1} cm^{-1}	Remarks
Potassium iodide-Rhodamine B[3]	—	560	20—70 ng ml^{-1}	2.8×10^6	—
Bismuthiol II[6]	pH 4.0 ± 0.1	330	1—40 μg Te$^{\text{IV}}$ ml^{-1}	3.64×10^4	Use of masking agent for Se$^{\text{IV}}$
Sodium 2,3-dimercapto-1-propane sulfonate (unithiol)[7]	2 equiv H_2SO_4-pH 5	248	0.02—0.04 mg ml^{-1} of Te$^{\text{IV}}$	6880	Absorbance was measured within 5—10 min
Tetramethylthiourea[9]	dil. HCl	382	0.2—7 μg ml^{-1} of Te$^{\text{IV}}$	2.14×10^4	Bi$^{\text{III}}$, Se$^{\text{IV}}$, Fe$^{\text{III}}$, and Cu$^{\text{II}}$ interfered
Potassium 0-2,2,2-trifluoroethyl dithiocarbonate[10]	pH 0.5—2.5	—	1.5—20 ppm	6.698×10^3	—
Iodide-Cetyltrimethyl ammonium ions (CTA)[12]	0.3 M H_2SO_4 extraction in $CHCl_3$	366	< 2.5 μg Te$^{\text{IV}}$ ml^{-1}	5.9×10^4	Se$^{\text{IV}}$, Au$^{\text{III}}$, Bi$^{\text{III}}$, Cd$^{\text{II}}$, Cu$^{\text{II}}$, Sb$^{\text{III}}$, Sn$^{\text{II}}$, Ti$^{\text{IV}}$, and platinum group metals interfered
Potassium morpholine-4-carbodithioate[13]	Extraction in molten naphthalene	415	5.7—125.0 μg Te$^{\text{IV}}$ 10 ml^{-1}	1.075×10^4	—
2-Furancarbothio hydrazide[14]	1.3—2.0 M HBr	380	0.5—8 μg Te$^{\text{IV}}$ ml^{-1}	1.116×10^4	2 min shaking time. Lower tolerance limit for foreign ions.
	extraction in CCl_4	490	1—8 μg Te$^{\text{IV}}$ ml^{-1}	4.467×10^3	
4-quinoline dithiocarboxylic acid[15]	pH 0.6—5.0 extraction in $CHCl_3$	270	0.06 μg Te$^{\text{IV}}$ ml^{-1}	9×10^4	Cu$^{\text{II}}$, Au$^{\text{III}}$, and Sb$^{\text{III}}$ interfered.
Dithiodiantipyryl methane[16]	0.001—0.3 M HCl	360	—	5.2×10^4	Cu$^{\text{II}}$ and Bi$^{\text{III}}$ interfered.
HCl–CH_3COOH[27]	4 : 1 HOAC–4.0 M HCl	288	< 2500 μg Te$^{\text{IV}}$ 50 ml^{-1}	4.660×10^3	Se$^{\text{IV}}$ interfered
Thiocyanate-ethyl violet[28]	Strong acidity	560	0—5 μg Te$^{\text{IV}}$ 25 ml^{-1}	1.55×10^6	—
4-bromoPTPT (the present method)	6—8 M HCl Extraction in $CHCl_3$	440	1—15 ppm	8.1×10^3	—

Table 4. Binary Separation of Tellurium(IV) from Pb$^{\text{II}}$, Bi$^{\text{III}}$, Cu$^{\text{II}}$, Au$^{\text{III}}$, and Sb$^{\text{III}}$

Composition of metal ion/μg	Recovery[a)] %	Relative standard deviation/%
Te$^{\text{IV}}$, 100;	99.73	0.46
Pb$^{\text{II}}$, 100	99.77	0.95
Te$^{\text{IV}}$, 100;	99.99	0.32
Bi$^{\text{III}}$, 100.	99.66	0.23
Te$^{\text{IV}}$, 100	99.84	0.16
Cu$^{\text{II}}$, 100.	99.85	0.26
Te$^{\text{IV}}$, 100	99.58	0.48
Au$^{\text{III}}$, 100	99.58	0.18
Te$^{\text{IV}}$, 100	99.89	0.09
Sb$^{\text{III}}$, 100	99.56	0.40

a) Average of six determinations.

The procedure is given below.

A known weight (1 g) of alloy was dissolved in a mixture of 9 ml of concentrated sulfuric acid and 50 ml of water. After the initial reaction was over the solution was heated with a 5 ml portion of nitric acid until white fumes were observed, boiled to dissolve the soluble matter and filtered to remove silica or metastannic acid; to the filtrate solution, 5 mg of tellurium was added and the solution was diluted to 100 ml with distilled water. An aliquot of 2 ml of filtrate containing 100 μg of tellurium(IV) was taken for extraction and determination by the proposed method. The results of the analysis are given in Table 6.

The method is selective and permits the rapid separation and determination of micro amounts of tellurium(IV). The average recovery of tellurium was 99.74%. Each determination took 15—20 min.

Simultaneous Determination of Tellurium(IV) and Selenium(IV): Extraction and Selectivity of Selenium-

Table 5. Analysis of Synthetic Mixtures

Amount of metal ion present/μg	Amount present μg	Amount found[a)] μg	Recovery %	Relative standard deviation/%
Al, 500; Bi,[c)] 500; Cr, 500; Cu, 500; Fe, 500; Sn, 1000.	50	49.86	99.68	0.26
Al, 500; Bi,[c)] 500; Cr, 500; Cu, 500; Fe, 500; Sn, 1000.	30	29.90	99.66	0.26
Se, 500; Pt, 500; Os,[d)] 500; Rh, 500	40	39.84	99.60	0.35
Au, 500; Ag,[b)] 500; Bi,[c)] 500	100	99.61	99.61	0.28
Bi,[c)] 1000; Cu, 1000 Fe, 1000; Pb, 1000.	100	99.52	99.52	0.35

a) Average of six determinations. b) Centrifuged out. c) Masked with tartaric acid. d) Prior extraction with 4-chloroPTPT.[18)]

Table 6. Analysis of Alloys

Alloy sample	Composition %	Tellurium (IV) taken μg	Recovery %	Relative standard deviation %
BCS-320 Carbon steel (Mild steel)	C, 0.22; Si, 0.02; S, 0.009; P, 0.019; Mn, 0.19; Ni, 0.022; Cr, 0.131; Mo, 0.22; V, 0.004; W, 0.17; Ti, 0.021; As, 0.031; Sn, 0.085; Al, 0.013; Sb, 0.003	100	99.68	0.17
BCS-387 Nickel-base alloy Nimonic-'901'	Cr, 12.46; Co, 0.21; Ti, 2.9; Al, 0.24; C, 0.030; Mn, 0.08; Si, 0.28; Fe, 36.0; Ni, 41.9; Cu, 0.032; S, 0.003; P, 0.007; Mo, 5.83; B, 0.016	100	99.71	0.23
434/1 Tin-base white metal	Sn, 82.2; Sb, 9.45; Cu, 4.58; Pb, 3.18; As, 1.15; Bi,[a)] 0.10; Cd, 0.14; Fe, 0.024; Ni, 0.17; Zn, 0.4	100	99.84	0.20

a) Masked with tartaric acid.

(IV): The yellow-colored selenium (IV)–4-bromoPTPT complex was extracted in chloroform and exhibited an absorption maximum at 350 nm, where the reagent showed negligible absorption. The maximum absorbance in the acid concentration range was 5—6 M HCl. It was observed that the absorbance remained constant when the shaking period was 3 min or more. For full color development, 8 ml of a 0.02 M reagent in chloroform was used. It was found that the absorbance of the complex was maximum in chloroform. Under the optimum experimental conditions, Beer's law was obeyed over the concentration range of 50—700 μg of selenium(IV) per 10 ml of the organic phase. The molar absorptivity was calculated to be 1.1×10^3 dm^3 mol^{-1} cm^{-1} at 350 nm and Sandell's sensitivity was 68 ng cm^{-2} of selenium(IV) for an absorbance of 0.001. The complex was stable for more than 48 h.

In a diverse-ions study, most of the cations do not interfere in the determination of selenium(IV), except for Cu$^{\mathrm{II}}$, Cr$^{\mathrm{III}}$, and Bi$^{\mathrm{III}}$. The interference of Cu$^{\mathrm{II}}$ and Cr$^{\mathrm{III}}$ was overcome by masking with 2.5 ml of 10% tartaric acid, whereas Bi$^{\mathrm{III}}$

interference was overcome by using 3 ml of 10% citric acid as a masking agent. However, tellurium(IV) interfers in the determination of the selenium(IV) extraction procedure. The optimum conditions for the extraction of selenium(IV) and tellurium(IV) are similar. Under similar optimal conditions both selenium(IV) and tellurium(IV) are extracted with 4-bromoPTPT. Hence in order to determine tellurium(IV) in the presence of selenium(IV), we have developed a simultaneous determination of these metal ions while taking advantage of the difference in the wavelength of the maximum absorbance and additivity of the absorbances. This method can be applied for the determination of traces of tellurium(IV) and selenium(IV) in diethylzinc[31)] and such catalysts as 6-tungsto-6-selenotelluric acid.[32)]

There is a difference of 90 nm in the wavelength of the absorption maximum of the selenium(IV) and tellurium(IV) complexes (Fig. 2). It is possible to set up the following two equations:

$$A_{350} = \varepsilon^{\mathrm{Se}}_{350}[\mathrm{Se}] + \varepsilon^{\mathrm{Te}}_{350}[\mathrm{Te}],$$
$$A_{440} = \varepsilon^{\mathrm{Se}}_{440}[\mathrm{Se}] + \varepsilon^{\mathrm{Te}}_{440}[\mathrm{Te}].$$

Combining these gives

$$[\mathrm{Se}] = \frac{A_{350}\varepsilon^{\mathrm{Te}}_{440} - A_{440}\varepsilon^{\mathrm{Te}}_{350}}{\varepsilon^{\mathrm{Te}}_{440}\varepsilon^{\mathrm{Se}}_{350} - \varepsilon^{\mathrm{Te}}_{350}\varepsilon^{\mathrm{Se}}_{440}},$$
$$[\mathrm{Te}] = \frac{A_{440}\varepsilon^{\mathrm{Se}}_{350} - A_{350}\varepsilon^{\mathrm{Se}}_{440}}{\varepsilon^{\mathrm{Te}}_{440}\varepsilon^{\mathrm{Se}}_{350} - \varepsilon^{\mathrm{Te}}_{350}\varepsilon^{\mathrm{Se}}_{440}}.$$

Here, A and ε indicate the total absorbance and molar absorptivities. The molar absorptivities of selenium(IV)–4-bromoPTPT complex are 1.1×10^3 dm^3 mol^{-1} cm^{-1} at 350 nm and 53 dm^3 mol^{-1} cm^{-1} at 440 nm. The molar absorptivities of the tellurium(IV)–4-bromoPTPT complex are 6.3×10^3 dm^3 mol^{-1} cm^{-1} at 350 nm and 8.1×10^3 dm^3 mol^{-1} cm^{-1} at 440 nm.

Procedure for the Simultaneous Determination of Selenium(IV) and Tellurium(IV): A mixture containing selenium(IV) and tellurium(IV), each at a concentration with its optimum range [30—40 ppm of selenium(IV) and 2.5—4.0 ppm of tellurium(IV)] is adjusted to about 25 ml so that its

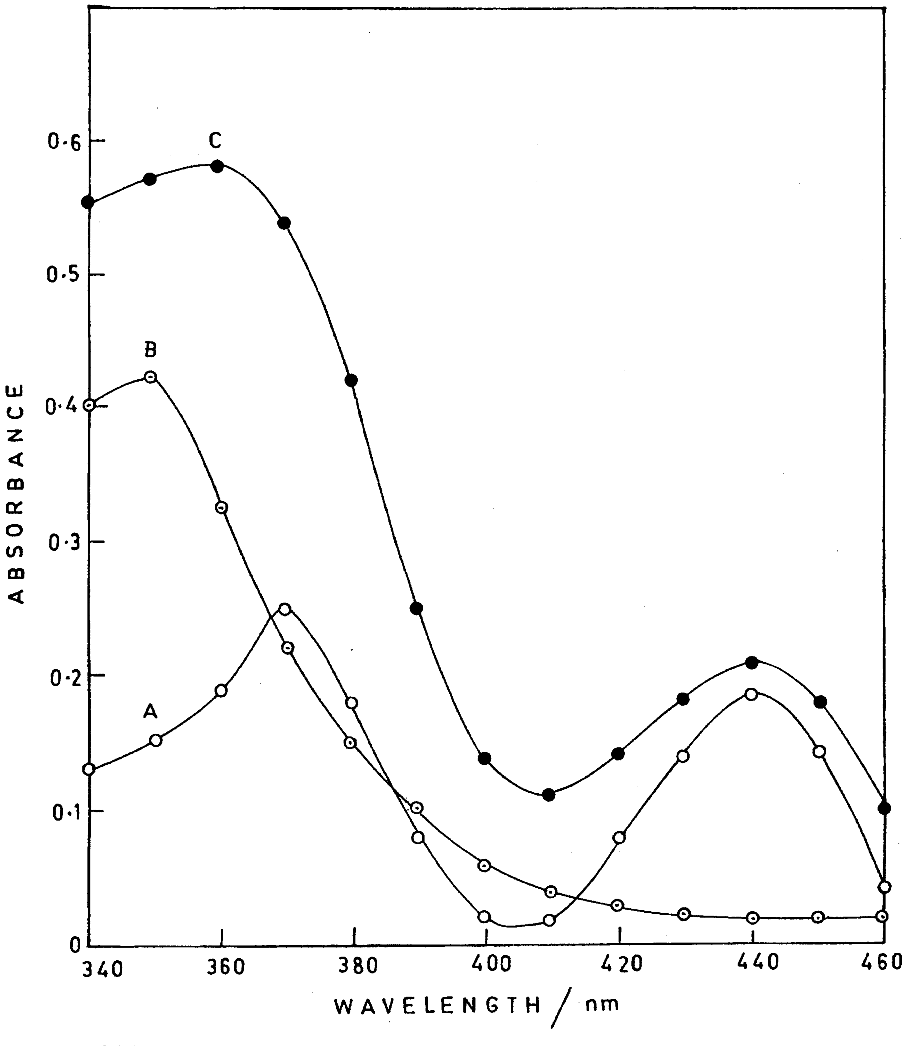

Fig. 2. Absorbance curves of 4-bromoPTPT complexes of: A: Tellurium(IV), 3 ppm; B: Selenium(IV), 30 ppm; C: Tellurium(IV), 3 ppm plus Selenium(IV), 30 ppm.

Table 7. Simultaneous Determination of Tellurium(IV) and Selenium(IV) from Synthetic Mixture

Tellurium(IV)			Selenium(IV)			Relative standard deviation/%	
Taken	Found[a)]	Recovery	Taken	Found[a)]	Recovery		
μg	μg	%	μg	μg	%	Te^{IV}	Se^{IV}
25	24.93	99.73	350	349.04	99.72	0.24	0.02
30	29.90	99.66	300	298.50	99.50	0.33	0.17
35	34.96	99.88	400	399.37	99.84	0.17	0.05
40	39.99	99.97	300	299.83	99.94	0.03	0.10

a) Average of six determinations.

hydrochloric acid concentration is 6 M. It is then shaken for 4 min with 10 ml of 0.02 M 4-bromoPTPT in chloroform. The organic layer is separated and the absorbance measured at 350 and 440 nm against a reagent blank. Real samples were not available at the working place, which forced us to use synthetic mixtures. The results of some synthetic mixtures are summarized in Table 7. The relative standard deviations for selenium(IV) and tellurium(IV) were found to be in the range of 0.02—0.17% and 0.03—0.33%, respectively.

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