



Liquid-liquid Extraction of Selenium(IV) and Tellurium(IV) by N-n-octylcyclohexylamine followed by their Spectrophotometric Determination

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Abstract

A simple and selective solvent extraction method has been derived for selenium (IV) and tellurium (IV) by sequential mode from each other as well as from other accompanying elements. N-n-octylcyclohexylamine (N- n -OCA) has been used for quantitative extraction of selenium (IV) and tellurium (IV) in dichloromethane (DCM) – xylene solvent mixture. The quantitative extraction of selenium (IV) was observed in the acidic range of 0.4 – 0.8 M hydrochloric acid (HCl) with 0.05 M N- n – OCA in DCM – xylene. Whereas that of tellurium(IV) was observed in the acidic range of 6.8 to 7.5 M HCl. Selenium(IV) and tellurium(IV) from the organic phase were stripped with 1:1 NH₃ and determined spectrophotometrically with 1-(4'-Bromophenyl)- 4,4,6-trimethyl-1,4- dihydropyridine-2-thiol (4'-bromo PTPT) at 350 nm and 440 nm, respectively. The optimum extraction conditions were evaluated by a critical study of acidity, extractant concentration, period of equilibrium and effect of diluents. Sequential separation of selenium(IV) and tellurium(IV) has been achieved taking the advantage of difference in acidity for the extraction flow sheet – I. The separation of these metal ions from one another in varying ratio of selenium(IV) : tellurium(IV) and multi components mixture of commonly associated metals was found to be possible by this method. It was successfully applied for analysis of selenium(IV) and tellurium(IV) in real sample such as alloys, pharmaceutical samples and thin film.

Keywords: Liquid-liquid extraction, spectrophotometry, N-n-octylcyclohexylamine, selenium(IV), tellurium(IV), sequential separation.

Introduction

Selenium has found in the different technological applications, such as electronics for the production of semiconductors, photocell and rectifiers; glass industry for staining of glass; chemical industry for catalyst; rubber industry for accelerating vulcanization; and pharmaceuticals in treatment of disease due to selenium deficiency. In agriculture organo selenium compounds are used as bactericides, fungicides and herbicides¹⁻⁴. Selenium is essential micronutrients for human health. It was regarded as a toxic element before 1973⁵. Evidence indicates that there is a gap between toxic and essential levels of selenium in human beings⁶. Diet with less than 0.1 µg Se g⁻¹ results in deficiency, while regular consumption of food containing more than 1 µg Se g⁻¹ results in toxicity⁷.

Tellurium is a useful metalloid in the metallurgical and electric industries and is found in the environment. It is most commonly alloyed with steel, but may also be combined with copper and lead to improve their workability and to make them more resistant to vibration and friction. Small amount of tellurium are used in the rubber and textile industry, as catalyst. High purity grade tellurium 6 N is used in the development of strategic semiconductor compounds that are increasingly employed in a wide variety of electric and optical devices like CdTe, Cd_{1-x} Zn_x

for nuclear detection photo refractivity and IR optoelectronics. The emission of inorganic tellurium compounds leads to acute and chronic toxicity. Furthermore, tellurium's toxicity, bioavailability and environmental transport mechanism highly depends on its chemical nature is 10 times more toxic than telluride⁸.

A solid phase extraction - multisyringe flow injection system for the spectrophotometric determination of selenium with 2, 3 - diamionaphthalene has been described⁹. However the method involves the number of steps and was time consuming. A new spectrophotometric method was developed for determination of selenium in cosmetic and pharmaceutical preparations after preconcentration with cloud point extraction¹⁰.

Catalytic spectrophotometric determination of tellurium using Lauth's violet¹¹ with sodium sulphide and cationic red violet¹² and Astrasone Red 3G (AR3G) basic have been investigated. These reactions are pH sensitive. Spectrophotometric determination of selenium with organic reagents and basic dyes was studied¹³. Determination of tellurium(IV) with agents containing nitrogen and sulfur as well as with basic dyes was studied¹⁴. 4-Bromophenyl-hydrazine, N-(1-naphthyl) ethylenediamine dihydrochloride and 3- methyl 2- benzo thiozoline hydrazone hydrochloride were used as a sensitive spectrophotometric reagent for determination of tellurium(IV) in biological samples¹⁵. The method based on 2, 3-

dimethoxystrychindin – 10 – one requires oxidation of reagents with tellurium(IV). Synergetic extraction and spectrophotometric determination of trace level tellurium(IV) by *p*-[4-(3,5-dimethylisoxazolyl) azophenylazo] calyx(4) arene¹⁶ have been developed and positive synergistic effects were investigated. Comparative spectrophotometric study of the tellurium(IV) complexation and extraction with extraction with various ligands (chloride, bromide, iodide), and cyanine dye N,N' – di(acetoxyethyl) indocarbocyanine (DAIC) was realized¹⁷.

High molecular weight amines have emerged as a powerful extractant for many elements; some others have reviewed earlier work and describe the separation methods. High molecular weight amines such as Aliquat 336, trioctylamine¹⁸, quaternary ammonium cation¹⁹ and tri - iso - octyl amine²⁰ have been effectively used for solvent extraction separation of tellurium (IV) as an ion- association complexes. Solvent extraction studies have been made on some metals in the same periodic group from HCl solution by dialkyl and aryl sulphoxides²¹. This method requires lithium chloride as salting out agent. Extraction studies on tellurium(IV) from its acidic solution using di- (2 ethyl hexyl) phosphoric acid in kerosene as carrier was presented, method suffers from requirement of higher concentration of reagent and more equilibration time²² for quantitative extraction.

A critical review for determination of selenium(IV) and tellurium(IV) in environmental sample was given by Alessandro D' Ulivo²³. In the separation of selenium(IV) and tellurium(IV) from HCl media by tributyl phosphate has been carried out, method requires high extractant concentration²⁴. S. M. Khopkar et al. carried out the separation of selenium(IV) and tellurium(IV) by using reversed phase extraction chromatography using salting out agent(LiCl) and stripping requires higher hydrochloric acid concentration²⁵. Liquid-liquid extraction of selenium(IV) and tellurium(IV) with cyanex 925²⁶ in toluene from aqueous HCl media was studied, method requires high reagent concentration with the use of salting out agent. Separation of selenium(IV) and tellurium(IV) was carried out by solvent extraction with the use of N- *n*- octylaniline^{27,28}, however the reagent is less sensitive towards the metal ions. The literature showed that there are very few methods which are devoted for the sequential separation of selenium(IV) and tellurium(IV) from their mixtures.

However there is no work reported on sequential separation of selenium(IV) and tellurium(IV) with N-*n*-octylcyclohexylamine (N-*n*-OCA) as an extractant. In view of all the above, sequential separation and determination of selenium(IV) and tellurium(IV) have been receiving considerable attention by the researchers.

Material and Methods

Apparatus: Absorbance measurements were made on an Electronics, India digital Spectrophotometer (Model No - 301) with 1cm quartz cell. pH measurement were carried out using Elico digital pH meter model LT – 120 and Tapson's Analytical balance was used.

Stock solution of selenium(IV) and tellurium(IV): A bulk solution of 1 mg/mL was prepared by dissolving 1.404 g of selenium dioxide (Fluka) in concentrated HCl and diluted to 1000 mL with distilled water. From this, a working solution of 400 µg/mL was prepared by suitable dilution with water. A stock solution of tellurium(IV) (1 mg/mL) was prepared by dissolving 1 g of tellurium powder (BDH Chemicals Ltd., Poole, England) in 50 mL of concentrated HCl followed by addition of small portions of concentrated nitric acid. The solution was heated until the tellurium is dissolved. Further, water was added and solution was boiled for five min to expel oxides of nitrogen. The moist dry residue was leached with 20 mL of concentrated HCl and solution was diluted with water to 1 L. The stock solution was diluted to obtain the working solution of lower concentration with water (50 µg/mL).

All chemicals were of analytical grade and their solutions were prepared in water. Doubly distilled water was used throughout the experiment. 4' - Bromo PTPT was prepared by the method of Mathes²⁹ from 4-bromoaniline and used as 10 mL of a 0.02 M solution in chloroform for the determination of selenium(IV)³⁰ and tellurium(IV)³¹. A 0.05 M solution of N- *n* - OCA³² in dichloromethane (DCM) - xylene (1:4) was used as an extractant.

Experimental procedure: Aliquot containing selenium(IV) (400 µg) and tellurium(IV) (50 µg) were taken and their acidities were adjusted to appropriate values with HCl and total volume were made up to 25 mL and transferred to a separatory funnels. Then 10 mL of 0.05 M N- *n* - OCA in DCM: xylene (1:4) was added for both selenium(IV) and tellurium(IV) and shaken for 5 min, two phases were allowed to separate. Selenium(IV) and tellurium(IV) from the organic phase were stripped with (1:1) NH₃. The selenium(IV) and tellurium(IV) from aqueous solution were determined spectrophotometrically by 4' - bromo PTPT^{30,31} at 350 nm for selenium(IV) and at 440 nm for tellurium(IV). All the experiments were repeated on average of three times and accuracy of the metal concentration in the loaded phase determined by mass balance, checked by complete stripping loaded organic phase and analyzing the stripped solution.

Dissolution of real samples: A solution of sample of alloys (0.1 g) were prepared and to this 10 mL of 1 mg/mL of selenium(IV) or 5 mL of 1 mg/mL of tellurium(IV) solution was added and the solution was diluted to 100 mL with water. An aliquot of 4 mL filtrate containing approximately 400 µg of selenium(IV) or 1mL of filtrate containing approximately 50 µg of tellurium(IV) was taken for extraction and determination by proposed method.

Pharmaceutical samples (3 - 4 tablets) were heated with the minimum amount of concentrated HCl followed by the addition of 1 mL of concentrated nitric acid. The organic matter was destroyed by treatment with 5 mL concentrated perchloric acid. The solution was slowly evaporated to moist dryness. The residue was dissolved in hot dilute HCl and made up to required

volume with distilled water, selenium(IV) was determined by the recommended procedure.

Shampoo (1 mL) was taken in 100 mL beaker. To this mixture of 1:1 perchloric acid and nitric acid were added, evaporated to moist dryness. The residue was treated in dil HCl and finally in distilled water. A 100 mL stock solution was prepared, a definite aliquot of the above solution was subjected to the recommended procedure.

The semiconductor film, with support was placed in a 50 mL beaker; 5 mL nitric acid was added and the film was dissolved with moderate heating. When the dissolution of the film was complete, the support was removed and rinsed with water. The mass of the film was obtained from the difference in weight of the support before and after dissolution, quartz glass, insoluble in nitric acid, was used as the support. The obtained solution was treated with 3 mL sulfuric acid and evaporated to the appearance of white fumes. The residue was dissolved in 0.1 M sulfuric acid, transferred to 25 mL volumetric flask and brought to the mark with water. An appropriate aliquot part of solution is transferred to 25 mL volumetric flask and the analysis continued as in the determination of selenium(IV) and tellurium(IV) in recommended procedure.

Results and Discussion

Various parameters were analyzed which affect the extraction of selenium(IV) and tellurium(IV). By optimizing parameters same method was applied for real samples. Method is valid in presence of large amount of foreign ions. Detection limit for selenium(IV) is 100 µg and for tellurium(IV) is 20 µg by 4' - bromo PTPT method.

Extraction as a function of acidity: Selenium(IV) was extracted in the acidic range of 0.1 - 1.0 M HCl and tellurium(IV) with 1.0 - 10.0 M HCl. Quantitative extraction of selenium(IV) was observed in the acidic range of 0.4 to 0.8 M

HCl. Where as that of tellurium(IV) was found in the acidic range 6.8 to 7.5 M HCl, hence for all further experimental studies 0.6 M HCl and 7.0 M HCl were used for selenium(IV) and tellurium(IV), respectively (figure-1). There was incomplete extraction in sulphuric acid, nitric acid, perchloric acid and acetic acid.

Extraction as a function of N-n-octylcyclohexylamine: In order to optimize the conditions for extraction and separation of selenium(IV) and tellurium(IV), a solution of N-n-octylcyclohexylamine in DCM : xylene (1:4) with varying molar concentration 0.001 to 0.2 were employed. It was found that 10 mL of 0.05 M was sufficient for quantitative extraction of selenium(IV) and tellurium(IV). A decrease in concentration of N- n - OCA results in lower distribution ratio (D) values for both selenium(IV) and tellurium(IV).

Extraction with various diluents: Selenium(IV) and tellurium(IV) were extracted with 10 mL of 0.05 M N- n - OCA in various solvents (table 1). The reagent was partially soluble in majority of solvents and completely soluble in DCM. There was no complete extraction of ion-pair complexes of selenium(IV) and tellurium(IV) in DCM. Hence we were prepared a series of mixtures of DCM and xylene. The reagent was dissolved in minimum quantity of DCM and diluted with xylene with different ratio. It was found that there was quantitative extraction in the solvent ratio of DCM : xylene from 1:4 to 1:2.3 hence DCM : xylene ratio 1:4 was preferred as a suitable diluents mixture for both the metals as it provides better phase separation (figure- 2).

Effect of time of equilibrium: The organic and aqueous phases were shaken for varying period ranging from 0.5 to 30 min. The extraction was quantitative over after 3 min. So equilibrium time 5 min was used throughout for both metals to ensure the complete extraction. There was no adverse effect on extraction of both selenium(IV) and tellurium(IV).

Table- 1
Study of extraction as a function of diluents for selenium(IV) and tellurium(IV)

Diluent	Dielectric Constant	Te(IV)		Se(IV)	
		Percentage Extraction, %E	Distribution Ratio, D	Percentage Extraction, % E	Distribution Ratio, D
Xylene*	2.30	100.0	∞	100.0	∞
Toluene	2.38	96.1	61.6	90.8	24.6
Methyl isobutyl ketone	13.1	88.6	19.5	72.4	6.5
n-Butanol	17.8	40.9	1.7	19.7	0.6
Amyl acetate	4.8	86.8	16.4	47.3	2.2
Amyl alcohol	13.9	52.3	7.5	25.8	0.9
Chloroform	4.8	20.7	0.7	47.3	2.2
Carbon tetrachloride	2.2	40.9	1.7	48.7	2.4
1,2- Dichloroethane	10.3	63.6	2.4	63.6	2.4
Dichloromethane	9.1	86.4	15.8	90.8	24.6

* Recommended for general extraction procedure

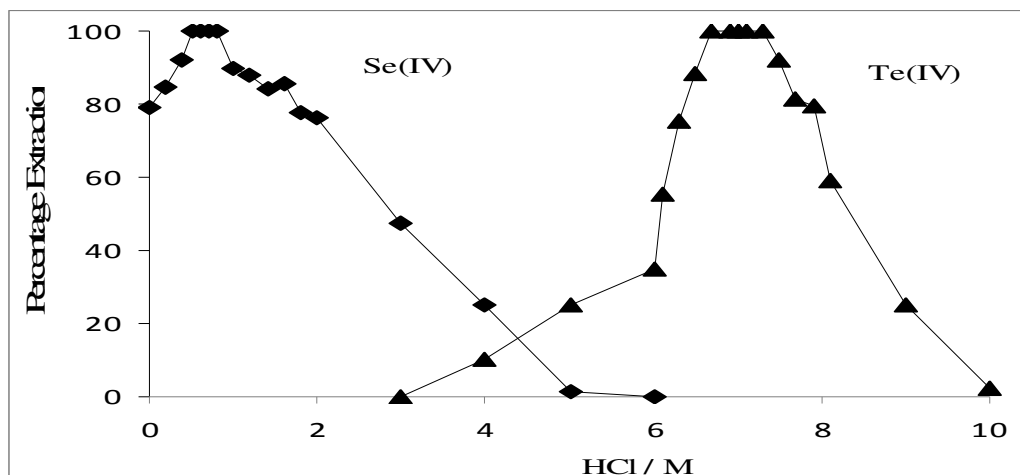


Figure-1
Extraction of selenium(IV) and tellurium(IV) as a function of hydrochloric acid concentration

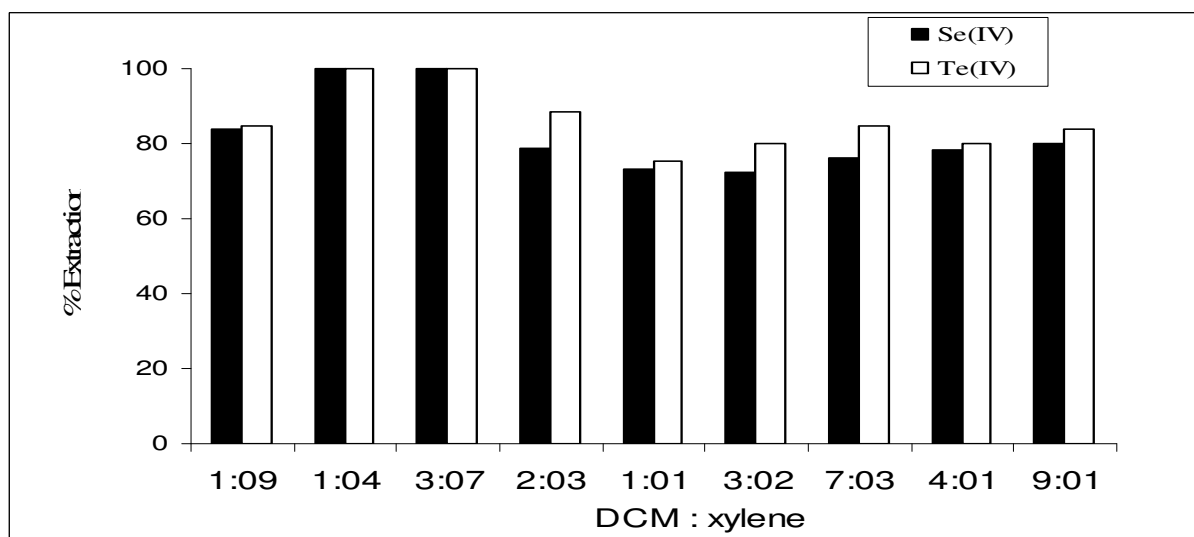


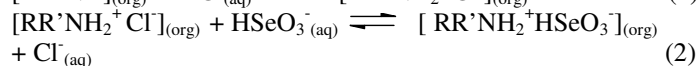
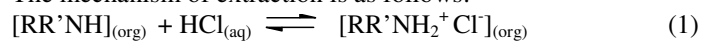
Figure-2
Extraction of selenium(IV) and tellurium(IV) as a function of DCM : xylene ratio

The effect of stripping agents: Selenium(IV) and tellurium(IV) were stripped with different strengths of mineral acids, weak acids and bases after their extraction such as HCl, HNO₃, H₂SO₄, HClO₄, CH₃COOH and bases NaOH, KOH and NH₃. The stripping of selenium(IV) was quantitative with 3 to 9.0 M HCl as well as to 5 to 10 M NH₃ whereas that of tellurium(IV) was quantitative with 5 to 9 M NH₃. Ammonia solution was preferred to HCl because it was easier to remove from the aqueous phase by evaporation prior to determining tellurium(IV) and selenium(IV)³³.

Nature of extracted species for selenium(IV) and tellurium(IV): Stoichiometry of the extracted species was investigated by analyzing the experimental data with conventional slope analysis method. The log D_[M] vs log M_[N-n-OCA] plots for the extraction of selenium(IV) and tellurium(IV) were taken. The results showed the expected species was

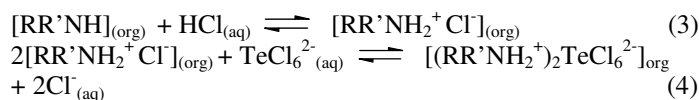
ascertained from the slope of the plots of log D_[Se] versus log M_[N-n-OCA] for different concentrations of HCl. The slope at 2.5 M HCl and 2.0 M HCl were 0.95 and 0.93, respectively (figure 3) indicating that the metal to amine ratio in the extracted species is 1:1, hence probable extracted species is [RR'NH₂⁺HSeO₃⁻]³⁴.

The mechanism of extraction is as follows:



where, R = -C₆H₁₁ R' = -CH₂(CH₂)₆CH₃

For that of tellurium graph was plotted at 6.5 M and 6.0 M of HCl (figure 4) indicating metal to amine ratio in the extracted species 1:2 and the probable extracted species is [(RR'NH₂⁺)₂TeCl₆²⁻]_{org}³⁵.



where, R = -C₆H₁₁ R' = -CH₂(CH₂)₆CH₃

From reaction we can write following equation for extraction equilibrium, K_{ex} for tellurium(IV) as follow

$$K_{ex} = \frac{[(RR'NH_2^+)_2 TeCl_6^{2-}]_{(org)} \cdot [Cl^-]_{(aq)}^2}{[TeCl_6^{2-}]_{(aq)} \cdot [RR'NH_2^+ Cl^-]_{(org)}^2} \quad (5)$$

$$\text{Distribution Constant, } K_D = \frac{[(RR'NH_2^+)_2 TeCl_6^{2-}]_{(org)}}{[TeCl_6^{2-}]_{(aq)}} \quad (6)$$

Distribution constant is useful as they allow the calculation of the concentration of remaining analyte in the solution, even after a number of solvent extractions have occurred. They also provide guidance in choosing the most efficient way to conduct an extractive separation.

Now, from equation (5) and (6)

$$K_{ex} = [K_D Cl^-]_{(aq)}^2 / [RR'NH_2^+ Cl^-]_{(org)}^2 \quad (7)$$

similarly, equation for extraction equilibrium K_{ex} for selenium(IV) as follows,

$$K_{ex} = \frac{[RR'NH_2^+ HSeO_3^-]_{(org)} \cdot [Cl^-]_{(aq)}}{[HSeO_3^-]_{(aq)} \cdot [RR'NH_2^+ Cl^-]_{(org)}} \quad (8)$$

$$\text{Distribution Constant } K_D = \frac{[RR'NH_2^+ HSeO_3^-]_{(org)}}{[SeCl_6^{2-}]_{(aq)}} \quad (9)$$

Now combining equation (8) and (9)

$$K_{ex} = K_D [Cl^-]_{(aq)} / [RR'NH_2^+ Cl^-]_{(org)} \quad (10)$$

Where K_{ex} = Extraction equilibrium and K_D = Distribution Constant

Loading capacity of the extractant: The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of the same concentration for a 10 mL 0.05 M solution in DCM-xylene at 7.0 M and 0.6 M of HCl for tellurium(IV) and selenium(IV), respectively. The maximum loading capacity of tellurium(IV) was found to be 4.0 mg and for selenium(IV) 3.0 mg at room temperature.

Effect of temperature on extraction of selenium(IV) and tellurium(IV): The extraction of selenium(IV) and

tellurium(IV) from HCl media adjusted to 6.0 M and 2.5 M, respectively using 0.05 M N- n - OCA at varying temperature from 298 to 310 K gives results shown in (Table 3 and 4). It was found that in the extraction of selenium(IV) and tellurium(IV) in DCM - xylene, the distribution coefficient increase with rise in temperature. The change in the extraction equilibrium constants (K_{ex}) with temperature is expressed by van't Hoff equation $d(\log K_{ex}) / d(1/T) = -\Delta H / 2.303 R$ (11)

The plot of log K_{ex} versus 1000 / T is linear with a slope value for selenium(IV) - 2.6 and that of tellurium(IV) -3.4 (figure 5) and the enthalpy change of the extraction carried out at constant molar of HCl were evaluated as $\Delta H = 51.58 \text{ kJ mol}^{-1}$ for selenium(IV) and that of tellurium(IV) value was $\Delta H = 65.78 \text{ kJ mol}^{-1}$. It means that it is an endothermic process.

The free energy ΔG and entropy ΔS were calculated from equations 12 and 13

$$\Delta G = -2.303 RT \log K_{ex} \quad (12)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (13)$$

Where ΔG = Gibbs free energy; ΔS = Entropy; ΔH = Enthalpy

The negative values of free energies imply that reaction is spontaneous. The positive enthalpy value indicates that the extraction of selenium(IV) and tellurium(IV) with N- n - OCA was favorable with rise in temperature.

Effect of diverse ions: The effect of diverse ions on extraction of selenium(IV) and tellurium(IV) was studied. The tolerance limit was set as an error of $\pm 2\%$ in absorbance measurement. In extraction of selenium(IV) and tellurium(IV) many anions and cations do not interfere (table - 3).

Applications: Validity of the method: To study the applicability of the proposed method for real samples, the method was employed for analysis of selenium(IV) and tellurium(IV). Since standard alloy samples containing selenium(IV) or tellurium(IV) were not available at the working place, we analyzed BCS- 387, BCS- 320, Alloy 33b, Brass, Solder alloy, Bronze, Gun Metal to which a known amount of selenium(IV) or tellurium(IV) has been added. Selenium(IV) or tellurium(IV) was recovered from HCl media by the proposed method (table 4).

Table- 2
Effect of temperature on the extraction of Se(IV) at 2.5 M HCl and Te(IV) at 6.0 M HCl

Temperature (K)	Log K _{ex}		$\Delta G \text{ kJ mol}^{-1}$		$\Delta S \text{ J K mol}^{-1}$		$\Delta H \text{ kJ mol}^{-1}$	
	Se(IV)	Te(IV)	Se(IV)	Te(IV)	Se(IV)	Te(IV)	Se(IV)	Te(IV)
298	0.26	0.27	-1.48	-1.54	0.18	0.22	51.58	65.78
301	0.34	0.36	-1.98	-2.07	0.18	0.22		
304	0.44	0.48	-2.56	-2.79	0.18	0.22		
307	0.53	0.61	-3.11	-3.58	0.18	0.22		
310	0.61	0.73	-3.62	-4.33	0.18	0.22		

Table- 3
Study of diverse ion for selenium(IV) and tellurium(IV)

Foreign ion	Added as	Tolerance limit, for Te(IV) (mg)	Tolerance limit for Se(IV) (mg)	Foreign ion	Added as	Tolerance limit, for Te(IV) (mg)	Tolerance limit for Se(IV) (mg)
I ⁻	KI	25	50	Se(IV)	SeO ₂	05	-----
F ⁻	NaF	25	35	Co(II)	CoCl ₂ .6H ₂ O	05	5.0
Br ⁻	KBr	50	25	Th(IV)	Th(NO ₃) ₄	03	5.0
NO ₃ ⁻	KNO ₃	50	50	Al(III)	AlCl ₃ .6H ₂ O	03	5.0
SO ₄ ²⁻	Na ₂ SO ₄	50	100	In(III)	InCl ₃ .4H ₂ O	03	5.0
NO ₂ ⁻	NaNO ₂	50	25	Sb(III)	Sb ₂ O ₃	01	0.5
PO ₄ ⁻²	Na ₂ PO ₄	50	100	Bi(III)	Bi(NO ₃) ₃ .5H ₂ O	01	3.0
SCN ⁻	KSCN	50	50	Sn(II)	SnCl ₂ .2H ₂ O	01	3.0
S ₂ O ₃ ²⁻	Na ₂ S ₂ O ₃ .5H ₂ O	50	100	Pb(II)	Pb(NO ₃) ₂	01	5.0
Tartarate	Tartaric Acid	100	70	Cr(III)	CrCl ₃	0.5	3.0
Ascorbate	Ascorbic Acid	90	75	Ag(I)	AgNO ₃	0.1	0.4
Acetate	Acetic Acid	100	100	Au(III)	HAuCl ₄ .4H ₂ O	0.3	0.2
Citrate	Citric Acid	100	25	Pd(II)	PdCl ₂	0.1	0.5
Succinate	Succinic Acid	80	70	V(V)	NH ₄ VO ₃ .H ₂ O	0.1	0.2
Salicylate	Salicylic Acid	100	80	Ge(IV)	Germanium powder	0.05	0.2
Thiourea	Thiourea	50	40	Te(IV)	Tellurium powder	--	6.0
Oxalate	Oxalic Acid	50	35				
EDTA	Na ₂ EDTA	25	25				
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ . 2H ₂ O	25	5.0				
Zn(II)	ZnSO ₄ .7H ₂ O	25	5.0				
Ni(II)	NiCl ₂ .H ₂ O	25	10.0				
Cu(II)	CuSO ₄ .5H ₂ O	25	10.0				

Table-4
Analysis of alloy for selenium(IV) and tellurium(IV)

Alloy sample	Composition %	Metal Taken in µg		Recovery * %		R. S. D. %	
		Se (IV)	Te (IV)	Se (IV)	Te(IV)	Se(IV)	Te(IV)
BCS-387 Nickel-Base Alloy (Nimonic- 901)	Cr-12.46; Co-0.21; Ti-2.9; Al-0.24; C-0.03; Mn-0.08; Si-0.28; Fe-36; Ni-41.9; Cu-0.032; S-0.003; P-0.007; Mo-5.83; B-0.016.	400	50	99.72	99.52	0.28	0.48
Cast- Iron alloy 33b	Cr-0.5; Mo-0.5; Cu-1.5; P-0.03; Ni-2.5; Si-1.5; S-0.03.	400	50	99.58	99.68	0.42	0.32
BCS-320 Carbon steel (mild- steel)	C-0.25; Mo-0.1; Si-0.37; V-0.008; S-0.009; W-0.25; P-0.02; Ti-0.018; Mn-0.29; As-0.058; Ni-0.172; Sn-0.024; Cr-0.22; Sb-0.004.	400	50	99.72	99.52	0.28	0.48
Cast Iron alloy 33d	Tc-2.0; Si-2.0; S-0.05; P-0.1; Mn-0.5; Ni-2.0; Mo-0.5; Cr-0.5.	400	50	99.86	99.76	0.14	0.24
Brass	Cu-61; Zn-29.	400	50	99.62	99.22	0.38	0.88
Solder alloy	Sn-60; Pb-40.	400	50	99.74	99.54	0.26	0.46
Bronze	Cu-78.30; Sn-3.15; Pb-13.22; Zn-4.5.	400	50	99.86	99.66	0.14	0.34
Gun Metal	Pb-80; Sn-17; Sb-0.31; Pb-2.31.	400	50	99.84	99.34	0.16	0.66

*Average of five déterminations

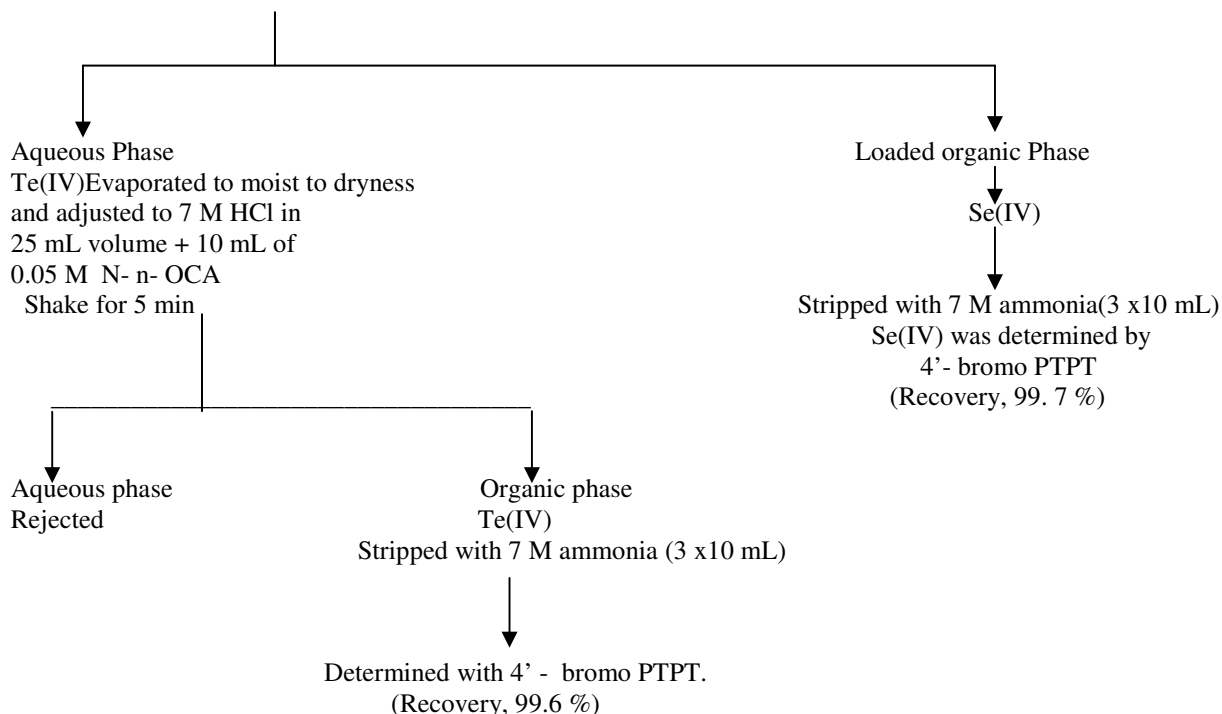
Sequential separation scheme for selenium(IV) and tellurium(IV): The proposed extractive separation procedure was applied for sequential separation of selenium(IV) and tellurium(IV). These two metals are present in the same group, having similar chemical and physical properties and hence it is difficult to separate. However, we have developed the separation procedure based on the difference in acidity (HCl) (flow sheet 1).

Separation of selenium(IV) and tellurium(IV)

Aqueous phase: 400 μg Se(IV) + 50 μg Te(IV) + 0.6 M HCl + water up to 25 mL.

Organic phase: 10 ml solution of 0.05 M N- n - OCA in DCM: xylene (1:4)

Equilibrium Time : 5 min



Determination of selenium in pharmaceutical samples: The proposed method was used for determination of selenium(IV) from pharmaceutical samples such as supravative complete, Vitared – plus, Menopace Iso and Antioxide tablet. Selenium(IV) in mediated shampoo such as selsum was also determined. The results obtained were precise and accurate with standard data. (table 5).

Determination of selenium(IV) and tellurium(IV) in semiconductor film: Semiconductor material for selenium(IV) like Sb_2Se_4 and for tellurium(IV) like $\text{Mo}_1\text{Bi}_2\text{Te}_5$ were analyzed by recommended procedure and results were good agreement with standard data (table- 6).

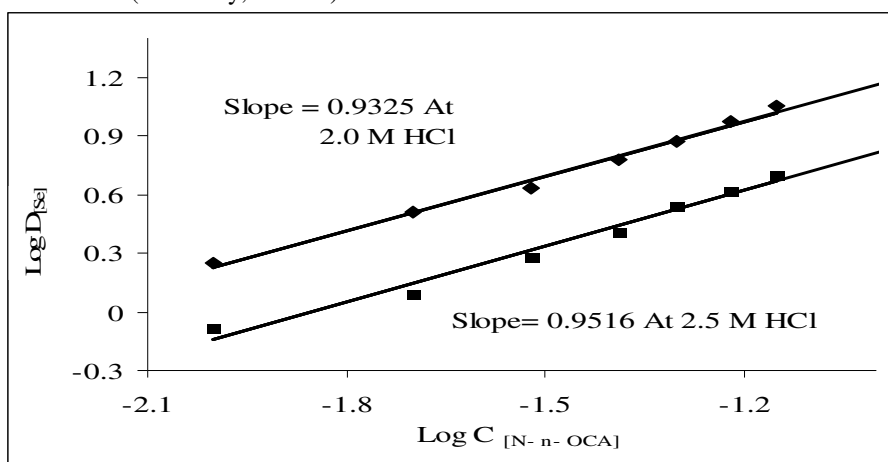


Figure-3

Log- log plot of distribution ratio Log D_[Se] as a function of Log C_(N- n- OCA) concentration

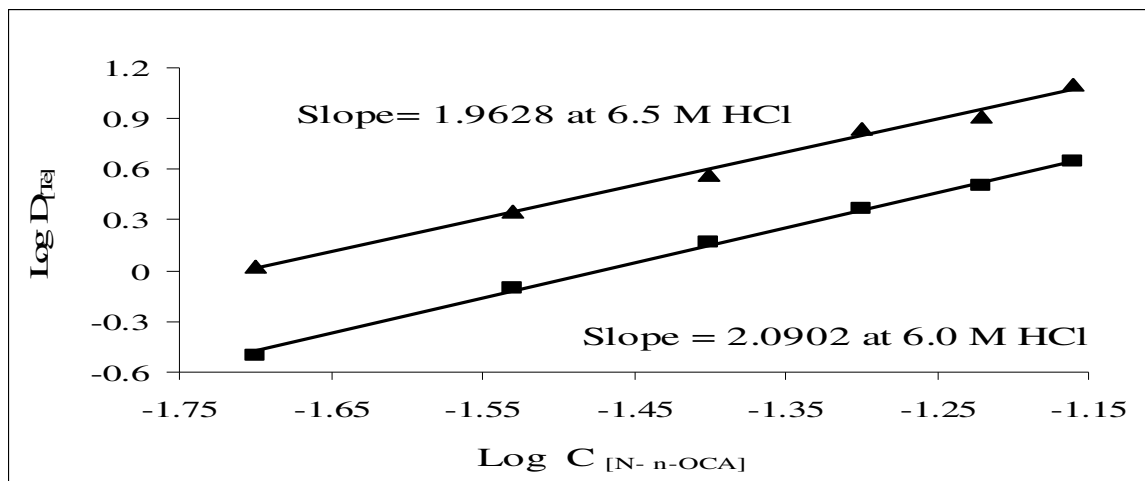


Figure-4
Log- log plot of distribution ratio $\text{Log } D_{\text{TeI}}$ as a function of $\text{Log } C_{\text{[N-n-OCA]}}$ concentration

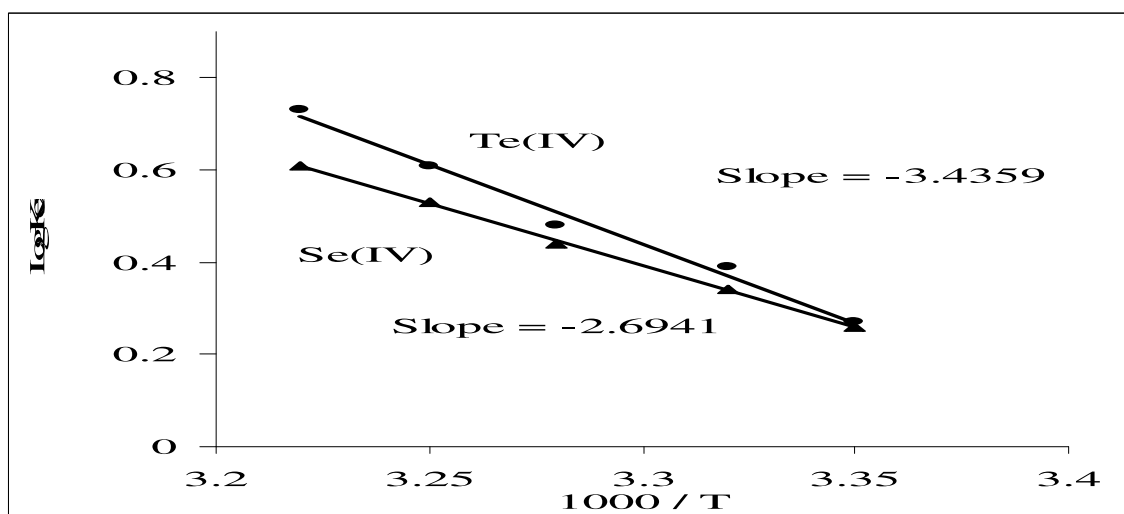


Figure-5
Extraction of selenium(IV) and tellurium(IV) as a function of temperature

Table- 5
Pharmaceutical Sample analysis for selenium(IV)

Sample	Composition	Certified value of selenium(IV) In μg	Amount of selenium(IV) * Found in μg	R.S.D. %
Supraactive Tablet	Vit- c 1mg Vit- E 500 μg Potassium 1mg Iron- 500 μg Calcium- 1mg Vit- b12 – 12 μg Selenium - 500 μg	500	499.1	0.18
Vitared Plus	Ascorbic acid- 50 mg Riboflavin-5mg Folic acid- 1mg Chromic Chloride - 65 μg Vit E- 25 mg Selenium-60 μg	240	239.5	0.21
Menopace ISO	Vit- C- 75mg Vit- E – 20mg Nicotinamide- 10mg Iron – 5 mg Iodine- 225 μg Selenium – 100 μg	400	399.6	0.1
Antioxide Tablet	Beta carotene- 5mg Sulphate monohydrate- 2 μg Selenium – 70 μg	280	279.23	0.27
Selsum	Selenium 2.5%w/v	500	498.23	0.15

*Average of five détermenations

Table- 6
Analysis of semiconductor film for selenium(IV) and tellurium(IV)

Sample	Manufacturer	Composition	Amount of Se(IV) / Te(IV) Certified %	Amount found by proposed method* %	R.S.D. %
Semi conducting material	Material Research lab. Department of Chemistry, Shivaji University, Kolhapur.	Mo ₁ Bi ₂ Te ₅	62.50	62.25	0.40
Semi conducting material	Nanomaterials Research lab. Department of Physics, Shivaji University, Kolhapur.	Sb ₂ Se ₄	60.00	59.79	0.35

*Average of five determinations

Conclusion

The important features of the method here are i. from the results it is observed that selenium(IV) and tellurium(IV) are extracted with N- n – OCA in DCM – xylene mixture by an ion – pair formation mechanism, ii. it permit selective separation of selenium(IV) and tellurium(IV) from other large metal ions, specifically separates selenium(IV) and tellurium(IV) from each other sequentially, iii. low reagent concentration is required for quantitative recovery of both selenium(IV) and tellurium(IV), iv. The thermodynamic functions enthalpy(ΔH), entropy(ΔS) and free energy changes (ΔG) in the extraction of selenium(IV) and tellurium(IV) with N- n – OCA were evaluated. The extraction reaction are an endothermic process with the extraction percentage increases with increasing temperature, v. N- n- OCA extracts selenium(IV) and tellurium(IV) in DCM - xylene from HCl media by anion exchange mechanism in which a complex of stoichiometric formula $[RR'NH_2^+HSeO_3^-]$ and $[(RR'NH_2^+)_2TeCl_6^{2-}]$ are formed, vi. Method is free from interference of a large number of foreign ions which are associated with selenium(IV) and tellurium(IV) in it's natural occurrence, vii) It applicable to the analysis of selenium(IV) and tellurium(IV) in alloys, pharmaceutical samples, viii) Another important feature of the proposed method is that extraction of selenium(IV) and tellurium(IV) using 10 mL 0.05 M N- n- OCA in DCM – xylene from aqueous solution results in 99. 74 % recovery within 5 min. ix) The developed method is very simple, selective reproducible and rapid; requires less time for separation and determination.

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References

- Combs G.F. and Combs S.B., The role of Selenium in Nutrition, New York: Academic Press Inc, (1986)
- Pinho J., Canario J., Cesario R. and Vale C.A., rapid acid digestion method with ICP-MS detection for the determination of selenium in dry sediments, *Anal. Chim. Acta.*, **551**, 207 (2005)
- Rosenfeld J. and Beath O.A., Selenium- Geobotany, Biochemistry, Toxicity and Nutrition, New York: Academic Press (1964)
- Schamberger R.J., In E. Frieden (Ed.), Biochemistry of the essential ultra trace elements, Plenum Press, New York, 201 (1994)
- Dubois F. and Belleville F., Selenium: physiologic role and value in human pathology, *Pathol. Biol.*, **36**(8), 1017 (1988)
- Suhajda A., Hegoczki J., Janzso B., Pais I. and Vereczkey G.J., Preparation of selenium yeasts I, preparation of selenium-enriched *Saccharomyces cerevisiae*, *Trace Elem. Med Biol.*, **14**, 43 (2000)
- Whanger P.D., Selenocompounds in Plants and Animals and their Biological Significance, *J. Am. Coll. Nutr.*, **21**, 212 (2002)
- Karlson U., Franken Berger W.T. and Marcel D., Metal Ions in Biological Systems, New York, 185 (1993)
- Serra A.M., Estela J.M., Coulomb B., Boudenne J.L. and Cerda V., Solid phase extraction Multisyringe flow injection system for the spectrophotometric determination of selenium with 2,3-diaminonaphthalene, *Talanta*, **81**, 572 (2010)
- Soruraddin M.H., Heydari R., Puladvand M. and Zahedi M.M., A new spectrophotometric method for determination of selenium in cosmetic and pharmaceutical preparations after preconcentration with cloud point extraction int, *J. Anal chem.*, **2011**, 1 (2011)
- Tabatabaee M. and Esmailzadeh M., Catalytic determination of traces of tellurium (iv) using the reduction of lauth's violet with sodium sulfide, *j. phys. Theor. Chem. IAU Iran*, **4**, 223 (2008)
- Andruch V. and Balogh I.S., Investigation of the extraction of tellurium complexes with basic dye reagents, *Chem. Pap.*, **57**, 332 (2003)
- Balogh J., Spectrometric and extraction– spectrometric for selenium determination, *Chem. Letters*, **92**, 729 – 734 (1998)
- Andruch V. and Matherny N., Spectrophotometric method determining teluria, *Chem. Letters*, **92**, 521-529, (1998)

15. Suvardhan K., Krishna P.M., Puttaiah E.T. and Chiranjeevi P., Spectrophotometric determination of tellurium (IV) in environmental and telluride film samples, *J. Anal. Chem.*, **62**, 1032 (2007)
16. Kumar A. Sharma P. Chandel L. K. and Kalal B. L., Synthesis and metal extraction behavior of pyridine and 1,2,4-triazole substituted calix[4]arenes, *J. Incl. Phenom. Macrocycl. Chem.*, **61**, 335.(2008)
17. Balogh I.S. and Andruch V., Comparative spectrophotometric study of the complexation and extraction of tellurium with various halide ions and N,N' - di(acetoxyethyl)indocarbocyanine, *Analytica Chim. Acta.*, **386**, 161- 167, (1999)
18. El- Sweify F.H. and Metwally E., Comparative study of the extraction of Te(IV) from various aqueous solutions using different organic diluents and solvents, *Radiochemistry*, **49**, 403, (2007)
19. Yamamoto K. and Adachi K., Liquid-liquid distribution of ion associates of hexabromotellurate (IV) with quaternary ammonium counter ions, *Talanta*, **47**, 1065, (1998)
20. Mandal D. K. Bhattacharya B. And Das R. D., Recovery of tellurium from chloride media using tri-iso-octylamine, *Sep. Purif. Technol.*, **40**, 177, (2004)
21. Reddy A. S. and Reddy B. R., Solvent extraction separation of Cr(VI)-Mo(VI)- W(VI), Zr(IV)-Hf(IV), and Se(IV)-Te(IV) with sulphoxides, *Can. J. Chem.*, **60**(1), 40-43, (1982)
22. Chakraborty R. and Datta S., Extraction of Te(IV) by liquid surfactant membrane, *Hydrometallurgy*, **43**, 169, (1996)
23. D' Ulivo A. Determination of selenium and tellurium in environmental samples, *Analyst*, **122**, 117, (1997)
24. Hon Y.C. Chang C.C. Cheng W.L. and Shaw I., The separation of selenium from tellurium in hydrochloric acid media by solvent extraction with tri-butyl phosphate, *Hydrometallurgy*, **9**, 381, (1983)
25. Haddur R.B. and Khopakar S.M., Separation of selenium(IV) and tellurium(IV) from mixtures by extraction chromatography with trioctylphosphine oxide, *Talanta*, **35**, 594, (1988)
26. Mhaske A.A. and Dhadke P. M., Separation of Te(IV) and Se(IV) by Extraction with Cyanex 925, *Separ. Sci. Technol.*, **38**, 3575 (2003)
27. Sargar B.M. Mahamuni S.V. and Anuse M.A., Sequential separation of selenium(IV) from tellurium(IV) by solvent extraction with N-n-octylaniline: Analysis of real samples, *J. Saudi Chem Soc.*, **15**, 177 (2011)
28. Sargar B.M. and Anuse M.A., Liquid-liquid extraction study of tellurium(IV) with N- n-octylaniline in halide medium and its separation from real sample. *Talanta*, **55**, 469, (2001)
29. Mathes R.A. 2-Pyrimidinethiols, *J. Am. Chem. Soc.*, **75**, 1747, (1953)
30. Kolekar G.B. and Anuse M.A., Extractive spectrophotometric determination of Se(IV) using 1-(4'-bromophenyl)-4,4,6- trimethyl-(1H,4H) pyrimidine- 2- thiol from alloys and pharmaceutical samples Research, *J. Chem. Environ.*, **2**, 9 (1998)
31. Kolekar G.B. and Anuse M.A., Extraction, separation and spectrophotometric determination of tellurium(IV) with 1-(4'-bromophenyl) -4,4,6-trimethyl-1,4- dihydropyrimidine- 2- thiol, *Bull. Chem. Soc. Jpn.*, **71**, 859 (1998)
32. Moore J.L., Taylor S.M. and Soloshonok V.A., An efficient and operationally convenient general synthesis of tertiary amines by direct alkylation of secondary amines with alkyl halides in the presence of Huenig's base, *ARKIVOC*, **6**, 287 (2005)
33. Rajmane M.M. Mahamuni S.V. and Anuse M.A., Selective solvent extraction of tungsten(VI) with N-n-octylaniline in xylene. *Bull. Chem. Technol. Macedonia.*, **24**, 1 (2005)
34. Cotton F.A. and Wilkinson G., Advanced Inorganic chemistry, A Comprehensive Text book, third ed., New Delhi, 449, (1985)
35. Othmer K., Encyclopedia of Chemical Technology, John Willey and Sons, Inc. 76, (1969)