



## Development of surfactant assisted spectrophotometric method for determination of selenium in waste water samples

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### ABSTRACT

A new, simple and highly selective method for spectrophotometric determination of selenium in waste water samples is described. Selenium(IV) oxidizes  $I^-$  ions into  $I_2$  which subsequently reacts with excess of  $I^-$  ion in the acidic media to give tri-iodide ions ( $I_3^-$ ), and it further reacts with cetylpyridinium cation ( $CP^+$ ) to give a violet colored species. The value of molar absorptivity of the ion-associate species in terms of selenium is  $1.80 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  510 nm. The detection limit of the method is  $10 \text{ ng mL}^{-1}$  Se. The calibration curve is linear over 50–1000  $\text{ng mL}^{-1}$  Se with slope, intercept and co-relation coefficient of 0.23,  $-4.0 \times 10^{-4}$  and +0.99, respectively. None of the tested diverse ions interfered in the present method. The method has been tested for the determination of selenium in waste water samples.

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### 1. Introduction

Selenium is an essential element for humans at trace level, but it is toxic at higher concentration. A maximum acceptable concentration of selenium in drinking water is  $10 \text{ ng mL}^{-1}$  [1]. Food is the main source for intake of selenium for individuals who are not occupationally exposed; thus, toxic effects have most often been associated with food intake. A safe and adequate range of selenium intake of 50–200  $\mu\text{g}$  per person per day has been recommended for adults, with correspondingly lower ranges for infants and children. Selenium occurs in natural waters in trace amounts as a result of geochemical processes, such as weathering of rocks and erosion of soils, and is usually present in water as selenate or selenite. Excess of selenium causes toxic effects in living organism, and toxicity depends on many factors such as chemical form, pH, presence of other ions, etc. [2]. It is known that Se in inorganic forms i.e. selenate ( $\text{SeO}_4^{2-}$ ), selenite, ( $\text{SeO}_3^{2-}$ ), and selenide ( $\text{Se}^{2-}$ ) causes mutagenic effects [3,4]. In the environment, elemental selenium is generally associated with sulfur. It is released in the environment as a result of anthropogenic activity i.e. fossil fuel combustion, high thermal industrial processes, industrial and municipal waste. The large area of environment is contaminated with toxicants like, As, Se, Hg, Pb,

etc. due to exploitation of the natural resourced materials i.e. minerals, coal, etc. [5–7]. The separation and preconcentration steps are needed in order to remove interferences of complex matrices and enhance the sensitivity of the method. There are several approaches that have been proposed for the separation and preconcentration of selenium from various matrix samples [8–12]. These sample pre-treatments are tedious, time consuming and require multi-steps procedures for the preconcentration of analytes. Thus, simple and sensitive method is required to undertake the preventive measures from contamination of selenium in different compartments of the environment.

Several reagents i.e. J acid, hexamethyleneiminecarbodi-thiote, methylene blue, 2,3-diamino-1-4-dibromonaphthalene, 2, 3-diaminonaphthalene, thionin, maxilon blue-SG, iodide-rhodamine, 5,5-dimethyl-1,3-cyclohexanedione, methdilazine hydrochloride, 4-aminoantipyrine+ *N*-(naphthalen-1-yl)ethane-1,2-diamine dihydrochloride, etc. are reported for the spectrophotometric determination of selenium [13–24]. Most of them either suffer with interference of some ions commonly associated with Se in environmental samples, or/and require a prolonged standing time to develop a maximum and constant absorptivity of the species at the elevated temperature. So, it is desirable to develop simple and sensitive method for the determination of selenium(IV) in various samples.

In the present study, novel reaction mechanism of ion associate species ( $I_3^-CP$ ) is used for the determination of selenium from complex matrices samples. The factors, which affect the

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formation of ion-associate species, are optimized. The present method is applied for the determination of selenium in waste water samples. The proposed method is also compared with other existing spectrophotometric methods.

## 2. Experimental

### 2.1. Apparatus

A Systronics VIS-spectrophotometer type-106 matched with 1 cm quartz cell was used for absorbance measurement. Checkmate analyzer was used for measurement of pH values. A GBC-932AA atomic absorption spectrophotometer (AAS) equipped with HG-3000 hydride generator and selenium hollow cathode lamp (wavelength = 223.1 nm, lamp current = 10.0 mA, band pass = 0.2 nm) was employed for the data validation [25].

### 2.2. Reagents

All chemicals used were of analytical grade reagents obtained from E. Merck (Darmstadt, Germany). A standard solution of selenium ( $1000 \text{ mg L}^{-1}$ ) was prepared in deionized water. The working standard solutions were prepared by an appropriate dilution of the stock solution. A  $1.5 \text{ mol L}^{-1}$  HCl solution was used for oxidation of  $\text{I}^-$  ions. The fresh solution of  $0.12 \text{ mol L}^{-1}$  KI (2.0%, w/v),  $3.2 \times 10^{-6} \text{ mol L}^{-1}$  ( $5.6 \times 10^{-5}\%$ , w/v) ascorbic acid was used.  $1.4 \times 10^{-4} \text{ mol L}^{-1}$  ( $5.0 \times 10^{-3}\%$ , w/v) cetylpyridinium chloride (CPC) solution was used to intensify the absorptivity of the complex. Sodium acetate trihydrate solution  $2.0 \text{ mol L}^{-1}$  (27.2%, w/v) was used to maintain pH.

### 2.3. Procedure for spectrophotometric determination of selenium

An aliquot of solution containing 0.5–10.0  $\mu\text{g}$  Se (IV) was transferred into a 10 mL volumetric flask, and 1.0 mL, each of ascorbic acid, HCl and KI solutions were added. The mixed solution was shaken well until yellow color due to liberation of iodine was appeared. Into it, 1.0 mL CPC solution was added by maintaining pH value to  $\approx 2.5$  with acetate buffer. Subsequently, it was diluted to 10 mL with the distilled water. After 1 min, the absorbance of the ion-associate species was measured at 510 nm against the reagent blank.

### 2.4. Procedure for determination of selenium in water

The water sample (500 mL) was collected in polyethylene bottle in February 2006 using the established methodology from different source sites. The sample was treated with few drops of ultra pure nitric acid to avoid the co-precipitation of the metal. The water samples were filtered with Whatmann-42 filter paper in the laboratory.

## 3. Results and discussion

### 3.1. Absorption spectra

Selenium (IV) selectively oxidizes  $\text{I}^-$  ions into  $\text{I}_2$  species which subsequently react with  $\text{I}^-$  to give tri-iodide ion,  $\text{I}_3^-$  in the hydrochloric acid medium. It forms an ion-associate species with bulky cationic group i.e. cetylpyridinium chloride (CPC). It is a violet colored species, exhibits a sharp absorption maximum,  $\lambda_{\text{max}}$  around 510 nm, Fig. 1. At this wavelength, the reagent blank had some absorbance ( $\approx 0.035$ ). Hence, it was used as reference for all measurements.

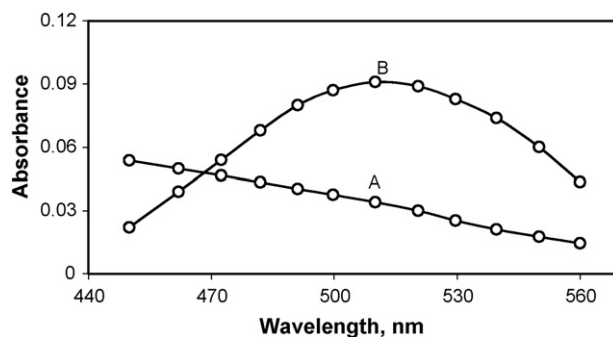


Fig. 1. Absorption spectra of the  $\text{CP}^+\text{I}_3^-$  ion-associate species against the reagent blank. A = the reagent blank, B =  $\text{Se(IV)} = 5.0 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[\text{HCl}] = 0.75 \text{ mol L}^{-1}$ ,  $[\text{KI}] = 0.040 \text{ mol L}^{-1}$ , ascorbic acid =  $8.0 \times 10^{-7} \text{ mol L}^{-1}$ ,  $[\text{CPC}] = 1.4 \times 10^{-5} \text{ mol L}^{-1}$ .

### 3.2. Optimization of analytical variables

#### 3.2.1. Effect of acid

The effect of acids like HCl,  $\text{H}_2\text{SO}_4$  were examined in the oxidation of  $\text{I}^-$  ions with Se(IV). In the  $\text{H}_2\text{SO}_4$ , the absorptivity of the ion-associate species was suppressed due to slow reaction kinetics. In HCl, the oxidation of  $\text{I}^-$  ions was fast, and a constant and maximum absorptivity of the ion-associate species was attained within 1 min. The optimum acidity range was found to be  $0.5\text{--}1.25 \text{ mol L}^{-1}$  HCl. In the present work, the oxidation of  $\text{I}^-$  ions with Se(IV) was carried out at acidity value of  $\approx 0.7 \text{ mol L}^{-1}$  HCl.

#### 3.2.2. Effect of pH on formation of ion-associate species

The effect of pH in the formation of ion-associate species ( $\text{CP-I}_3$ ) was examined. In the acidic solution ( $\text{pH} < 2.0$ ), the reaction kinetics was slow, and a prolonged standing time ( $\approx 5$  min) was needed to attain the maximum and constant absorptivity of the  $\text{CP-I}_3$  species. Above pH value of 2.0, the reaction kinetics was fast, and the maximum and constant absorptivity of the  $\text{CP-I}_3$  species was attained within 1 min. In the present work, the formation of  $\text{CP-I}_3$  species was carried out at pH value of  $\approx 3.0$ .

#### 3.2.3. Effect of iodide ions in reduction of Se(IV)

Fig. 2 shows the effect of potassium iodide concentration in the reduction of Se(IV). At least  $0.04 \text{ mol L}^{-1}$  KI for the reduction of  $10 \mu\text{g}$  Se(IV) was needed, and its further addition up to  $0.05 \text{ mol L}^{-1}$  KI had no adverse effect. Thereafter ( $> 0.05 \text{ mol L}^{-1}$  KI), the reaction kinetics for formation of  $\text{CP-I}_3$  species was decreased. A  $0.040 \text{ mol L}^{-1}$  KI was employed for further detailed work.

#### 3.2.4. Effect of ascorbic acid

In present work, ascorbic acid was used to prevent the oxidation of  $\text{I}^-$  ions by the third species present in the situ. Addition of ascorbic acid in the range of  $1.2 \times 10^{-6}$  to  $5.0 \times 10^{-6} \text{ mol L}^{-1}$  had no

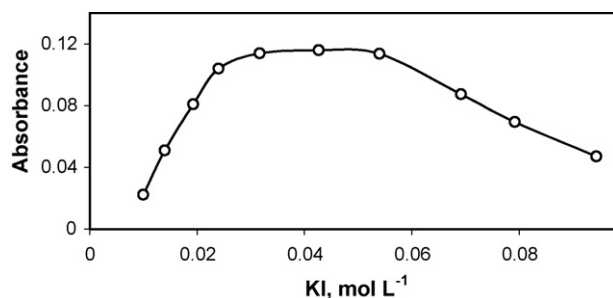


Fig. 2. Effect of the concentration of potassium iodide solution on absorptivity of the  $\text{CP-I}_3$  ion associate species.

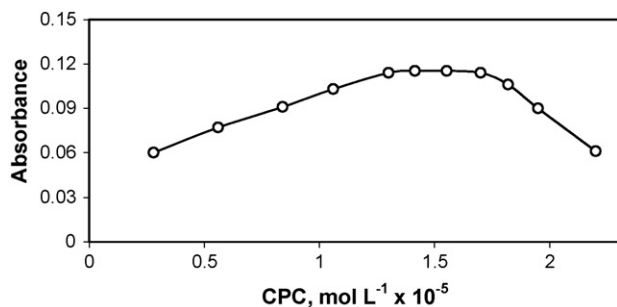


Fig. 3. Effect of the concentration of CPC solution on absorptivity of CP-I<sub>3</sub> ion-associate species.

adverse effect in the oxidation of I<sup>-</sup> ions with Se(IV) in the acidic solution. Further addition of KI, suppressed the reaction kinetics, and a prolonged standing time was required in order to attain a maximum and constant absorptivity of the ion-associate species. In the present work, the oxidation of I<sup>-</sup> ions with Se(IV) was carried out in the presence of  $8.0 \times 10^{-7}$  mol L<sup>-1</sup> ascorbic acid solution in order to make the method more selective.

### 3.2.5. Effect of surfactants

Various anionic, cationic and neutral surfactants (i.e. sodium laurylsulfate, titron-100, cetylpyridinium chloride, cetyltrimethylammonium bromide, tetradecyltri-methylammonium bromide, dodecyltrimethylammonium bromide, etc.) were tested towards reaction of I<sub>3</sub><sup>-</sup>. Among them, only cationic surfactant i.e. cetylpyridinium chloride (CPC) forms a stable violet colored ion-associate species with I<sub>3</sub><sup>-</sup>. The optimum concentration range of CPC was found to be  $(1.3\text{--}1.7) \times 10^{-5}$  mol L<sup>-1</sup>. Beyond  $1.7 \times 10^{-5}$  mol L<sup>-1</sup> CPC, the absorptivity of the ion associate species was found decreased, may be due to their co-precipitation shown in Fig. 3. A  $1.4 \times 10^{-5}$  mol L<sup>-1</sup> CPC concentration in the final dilution was employed for the detailed experimental work.

### 3.2.6. Effect of temperature

The effect of temperature in the oxidation of I<sup>-</sup> ions as well as in the formation of CP-I<sub>3</sub> species was examined. The temperature of the aqueous should be between 10 and 40 °C for the liberation of iodine. Beyond 40 °C, some fraction of I<sub>2</sub> was lost due to evaporation. The temperature of the aqueous solution should be in the range of 15–30 °C. Beyond 30 °C, the absorptivity of the ion-associate species was decreased due to their thermal instability. The absorptivity of the ion-associate species was stable for 2 h at room temperature ( $23 \pm 2$  °C).

### 3.3. Optimum concentration range, sensitivity and precision of the method

The calibration curve prepared by plotting absorbance versus concentration of Se(IV) was found to be linear over the range

Table 1

Optical characteristics, precision and accuracy of the spectrophotometric determination of selenium

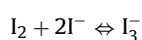
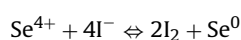
Parameters	Optimum condition
$\lambda_{\text{max}}$ (nm)	510
Beer's law range (ng mL <sup>-1</sup> )	50–1000
Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )	$1.8 \times 10^4$
Slope	0.23
Intercept	$-4.0 \times 10^{-4}$
Correlation coefficient	0.99
Relative standard deviation (%)	1.5
Limit of detection (ng mL <sup>-1</sup> )	10
Recovery (%)	98.0–99.0

of 50–1000 ng mL<sup>-1</sup> Se(IV) with slope, intercept and correlation coefficient of 0.23,  $-4.0 \times 10^{-4}$  and +0.99, respectively. The value of molar absorptivity in the term of Se(IV) was found to be  $1.80 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> at  $\lambda_{\text{max}}$ , 510 nm. The detection limit (causing more absorbance than thrice of standard deviation) of the method was found to be 10 ng mL<sup>-1</sup> Se(IV). The accuracy of the present method was assessed by adding known different amount of Se in the coal mine waste water sample. The average recovery for Se in the industrial waste water sample solution was found to be 98–99%. The relative standard deviation (RSD) of the method for six replicate measurements ( $n=6$ ) was determined, and found to be  $\pm 1.3\%$  at level of 300 ng mL<sup>-1</sup> Se(IV). The beer's law range, absorptivity, precision, recovery and other parameters are summarized in Table 1.

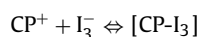
### 3.4. Composition of ion-associate species

The mole ratio of I<sub>3</sub><sup>-</sup> to CP<sup>+</sup> in the colored species was determined by the curve-fitting method [26], by plotting  $\log[A_{\text{eq}}/A_{\text{max}} - A_{\text{eq}}]$  versus  $\log[\text{CPC}]$ . The value of slope of the curve was found to be 1.1 close to integer 1. The involvement of I<sub>3</sub><sup>-</sup> and CP<sup>+</sup> in the colored species was expected to be in 1:1 mole ratio. The reaction mechanism can be expressed as follows.

Oxidation of I<sup>-</sup> ions into iodine with Se(IV) and subsequent formation of I<sub>3</sub><sup>-</sup>



Formation of ion-associate species with CP<sup>+</sup>



The scripts, CP<sup>+</sup>, CPC,  $A_{\text{eq}}$  and  $A_{\text{max}}$  denote the cetylpyridinium cation, cetylpyridinium chloride, absorbance of the CP-I<sub>3</sub> when CPC was in the equilibrium and absorbance of the CP-I<sub>3</sub> when CPC was in the large excess.

Table 2

Effect of diverse ions in the determination of 100 ng mL<sup>-1</sup> of selenium

Ions	Tolerance limit <sup>a</sup> ( $\mu\text{g mL}^{-1}$ )	Ions	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
Na(I), K(I), Ca(II)	25000	F <sup>-</sup> , V(V), Mg(II), NO <sub>3</sub> <sup>-</sup>	200
Oxalate	1500	Cr(III), SCN <sup>-</sup>	150
Citrate, tartrate	1000	As(V), Co(II)	100
Urea, thiourea, Sn(II)	700	Mn(II), PO <sub>4</sub> <sup>3-</sup>	75
Zn(II), Sn(IV), SO <sub>4</sub> <sup>2-</sup>	500	Fe(II)	60
Al(III)	400	Hg(II)	50
Ni(II), Zr(IV)	250	Cu(II), Bi(III), Fe(III)	30

<sup>a</sup> Causing error  $\leq \pm 2\%$ .

**Table 3**  
Determination of selenium in waste water samples

Sample	Site	Found by the present method (ng mL <sup>-1</sup> )	RSD (n = 6) (±%)	found by the HG-AAS method (ng mL <sup>-1</sup> )	RSD (n = 6) (±%)
IWW-1	Korba	525	1.3	536	1.8
IWW-2	Karba	442	1.1	456	2.2
IWW-3	Bhilai	340	1.5	349	2.6
IWW-4	Bhilai	267	1.3	265	2.4

IWW = industrial waste water.

**Table 4**  
Comparison of the present method with other spectrophotometric methods of selenium determination

Reagents	$\lambda_{\max}$ (nm)	Detection limit (ng mL <sup>-1</sup> )	Remarks	Ref.
2,3-Diaminonaphthalene	378.5	12	Less sensitive, most oxidants and reductants interfere	[17]
Variamine blue	546	30	CrO <sub>4</sub> <sup>2-</sup> , Fe(III), Ce(IV), IO <sub>3</sub> <sup>2-</sup> interfere	[22]
KI+ oleic acid	435	2500	SCN <sup>-</sup> , CN <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup> interfere	[27]
p-Nitroaniline +NEDA	515	17	Less sensitive	[28]
Methyl orange + BrO <sub>3</sub> <sup>-</sup>	525	12	Hg(II),Te(IV), V(V), Sb(III) interfere	[29]
Methylene blue + CTAB	660	3	Fe(III) interfere and masked by EDTA	[15]
KI + CPC	510	10	Simple, sensitive and selective	Present method

### 3.5. Effect of diverse ions

The effect of various diverse ions in the determination of 100 ng mL<sup>-1</sup> Se was examined. The oxidizing, reducing and sequestering agents i.e. V(V), Cr(VI), Mn(VII), Fe(III), ascorbic acid, hydrazine sulfate, oxalic acid, tin(II), fluoride, EDTA, tartaric acid, thiocyanate did not interfere in the determination of Se(IV). The metal ions, i.e. Cr(VI), Mn(VII), Fe(III), Sn(IV), etc. were reduced into their lower non-reactive oxidation states with ascorbic acid prior to the determination of Se(IV). The tolerance limits of various diverse ions ( $\mu\text{g mL}^{-1}$ ) in determination of 100 ng mL<sup>-1</sup> Se are summarized in Table 2.

### 3.6. Application of the method

The proposed method has been successfully applied for the determination of selenium in waste water samples. For this, an aliquot of the water samples (5.0–6.0 mL) was taken in a 10-mL volumetric flask and treated with 1.0 mL, each of HCl and KI and ascorbic acid solution. After complete liberation of I<sub>2</sub>, 1.0 mL CPC solution was added for formation of a violet colored ion-associate species, CP-I<sub>3</sub>. The pH value of solution was maintained to  $\approx 2.5$ , and diluted to the mark with de-ionized double distilled water. The absorbance of the solution was measured at 510 nm, against the reagent blank. The concentration of selenium in water was calculated from calibration curve. The results obtained are given in Table 3.

### 3.7. Comparison of the proposed method with other methods

The proposed method was compared with other existing spectrophotometric methods reported for determination of selenium in various samples. Table 4 indicates that the proposed method is more rapid and simple than the existing methods and provides a sensitive determination of selenium from complex matrices samples.

## 4. Conclusions

The proposed method is new, simple, selective and useful for detection of Se at sample source in water containing Se > 10 ng mL<sup>-1</sup>. It overcomes most of the drawbacks (i.e. interferences of oxidizing and reducing agents, requirement of a prolonged time to develop

full absorbance, etc.) of most of the established methods reported for the spectrophotometric determination of Se.

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