



Effect of Nonionic Surfactant (Triton X–114) on the Spectrophotometric Determination of Selenium (IV) With Isonitriso p-Isopropyl Acetophenone Phenyl Hydrazone

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ABSTRACT

The effect of nonionic surfactant (Triton X–114) on the sensitive, simple and inexpensive, spectrophotometric method was developed for the determination of Selenium(IV) with Isonitriso p-Isopropyl Acetophenone Phenyl Hydrazone (HIPAPH). Selenium was complexed with Isonitriso p-Isopropyl Acetophenone Phenyl Hydrazone (HIPAPH) in presence of surfactant (Triton X–114). Absorption spectrum of Se-HIPAPH complex in the presence of surfactant medium shows a peak at 513 nm. Beer's law is valid over the concentration range 0.25-10.0 ppm of selenium (IV). Sandell's sensitivity of the reaction is found to be $3.462 \times 10^{-3} \text{ mg.cm}^{-2}$ and the molar absorptivity of the complex was $9.32 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 513 nm. The composition of the complex (metal: ligand) was 1:2. The method was employed for the determination of selenium in Buck Wheat and Rajgira Seeds samples.

Keywords: Triton X–114, spectrophotometric method, Selenium, Isonitriso p-Isopropyl Acetophenone Phenyl Hydrazone.

INTRODUCTION

Selenium is found in sulfide ores such as pyrite, where it partially replaces the sulfur. Minerals that are selenide or selenate compounds are also known, but are rare. The chief commercial uses

for selenium today are in glassmaking and in pigments. Uses in electronics, once important, have been supplanted by silicon semiconductor devices. It is a semiconductor with the unusual property of conducting electricity better in the light than in the dark, and is used in photocells. Selenium is a trace mineral that is essential to good health but required only in small amounts. Selenium is incorporated into proteins to make selenoproteins, which are important antioxidant enzymes. The antioxidant properties of selenoproteins help prevent cellular damage from free radicals. Free radicals are natural by-products of oxygen metabolism that may contribute to the development of chronic diseases such as cancer and heart disease. Other selenoproteins help regulate thyroid function and play a role in the immune system.

Selenium is one of the trace elements which plays an active role in many biological systems[1] as it has toxicological and physiological effects [2,3]. It has been reported on a large scale in specific geographical locations such as the People's Republic of China[4]. It is an essential nutrient at trace level but toxic in excess[5]. When selenium is present in animal feeds at a concentration less than 0.1 mg l^{-1} , deficiency symptoms develop, but when present at a higher concentration, exceeding 5 mg l^{-1} , chronic selenosis occurs. Selenium tends to weaken the toxic action of some heavy metals in animal and human organisms[6,7]. A number of methods have been suggested for the spectrophotometric determination of selenium[8-21]. Most of these methods suffer from limitations.

MATERIALS AND METHODS

Schimadzu, PR1 UV-visible – recording spectrophotometer, UV-240 and Elico digital pH meter LI-120 were used in the present investigation. Isonitroso p-isopropyl Acetophenone Phenyl Hydrazone was prepared by standard method [22]. All the reagents and neutral surfactants Triton X-114 (Fig-1) are of analytical grade and all the solutions are prepared in double distilled water. 2.207g of selenium chloride was dissolved in deionized double distilled water and the solution was made up to 1000mL. Buffer of different pH values were prepared by standard procedures. Hydrochloric acid – potassium chloride buffer (pH 2.0 – 4.0), acetic acid – sodium acetate buffer (pH 4.0 – 7.0) and ammonium chloride and ammonium hydroxide buffer (pH 8.0 – 12.0) were prepared. 0.6639 g of Isonitroso p-isopropyl Acetophenone Phenyl Hydrazone is dissolved in 1000mL of double distilled water ($3 \times 10^{-3} \text{ M}$ solution).

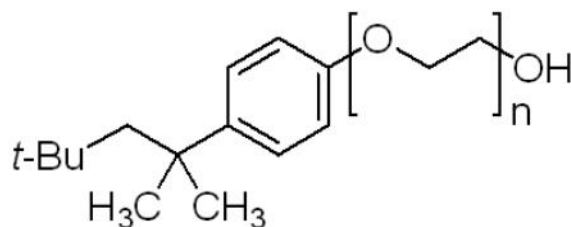


Fig-1 Structure of Triton X-114

General Procedure : An aliquot of the solution containing 10 – 200 μg of selenium(IV) was taken. To this 3.0mL of acetic acid – sodium acetate buffer and 2.0mL of Isonitroso p-isopropyl Acetophenone Phenyl Hydrazone solution (HIPAPH) are added and the total volume was diluted to 10mL by deionized double distilled water and the mixture was transferred into a 50ml separatory funnel. The red coloured selenium p-isopropyl Acetophenone Phenyl Hydrazone complex Se- HIPAPH formed was extracted into 10mL of MIBK, after shaking vigorously for

2.5 minutes, the absorbance of Se(IV)-HIPAPH complex was measured at 513nm against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectrum of Se-(HIPAPH)₂ complex in the presence of surfactant shows a peak at 513nm against water blank. It was shown in Fig-2. In absence of Triton X-114, Se-(HIPAPH)₂ has a maximum absorbance at 460nm in MIBK, Since complex was extracted into MIBK. In the absence of Triton X-114, the stability of complex is very low hence it was extracted into MIBK, where in the presence of Triton X-114 the complex was solubilized completely and the extraction step is avoided. Hence further studies were carried out at 513nm in the presence of Triton X-114. (No change was observed when the mixture was shaken from 1.5 to 3.0 minutes. Hence 2.5 minutes of shaking time was enough for the complete formation of complex).

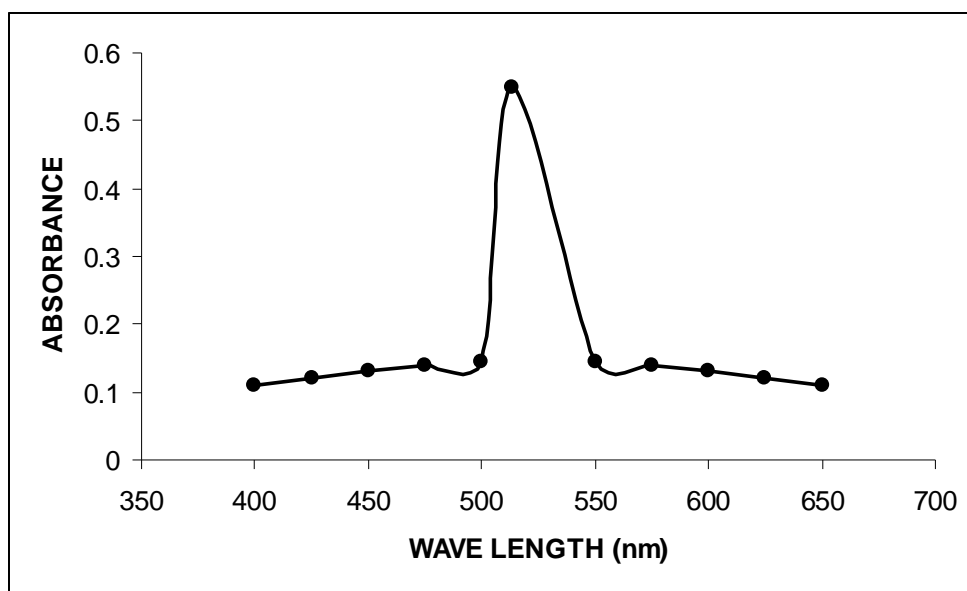


Fig: 2 Absorption Spectra of Cs(Hipaph)₂ Complex in Presence of Triton X-114

The behavior of Se-(HIPAPH)₂ complex was studied in the presence of Triton X-114 over a wide range of pH values. The pH studies were carried out varying the pH from 4.0 to 10.0 with 8.0 µg/mL of selenium(IV). It was observed that the Hg-(HIPAPH)₂ complex formation increases from pH 4.0 and reaches a maximum intensity at pH 6.0 and decrease beyond 6.0. Hence, all further studies were carried out at 6.0 pH. The effect of reagent concentration was studied by measuring the absorbance of solutions containing 8.0 µg/mL metal ion and it was observed that a twenty five fold excess of reagent was sufficient to produce maximum intensity of colour. This is equal to 2.0mL of 0.5% HIPAPH solution. The effect of different Triton X-114 concentrations was studied by measuring absorbance of solutions containing 8.0 µg/mL of metal ion of pH 6.0. The results indicate that 2.0mL of 0.001N Triton X-114 gave a maximum absorbance which was selected and used for further studies.

With the optimum conditions developed the calibration curve was constructed. It was observed that Beer's law was obeyed in the concentration range of 0.25 µg to 10.0 µg of

selenium (IV) (Fig-3). It was observed that in the presence of Triton X-114 the sensitivity of the complex is increasing tremendously. Sandell's sensitivity of the reaction obtained from Beer's law was $3.462 \times 10^{-3} \text{ mg.cm}^{-2}$ and the molar absorptivity of the complex is calculated as $9.32 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Aliquots containing $8.0 \text{ }\mu\text{g/mL}$ of selenium (IV) gave a standard deviation of 0.3246×10^{-3} and coefficient of variation was 0.1245 percent.

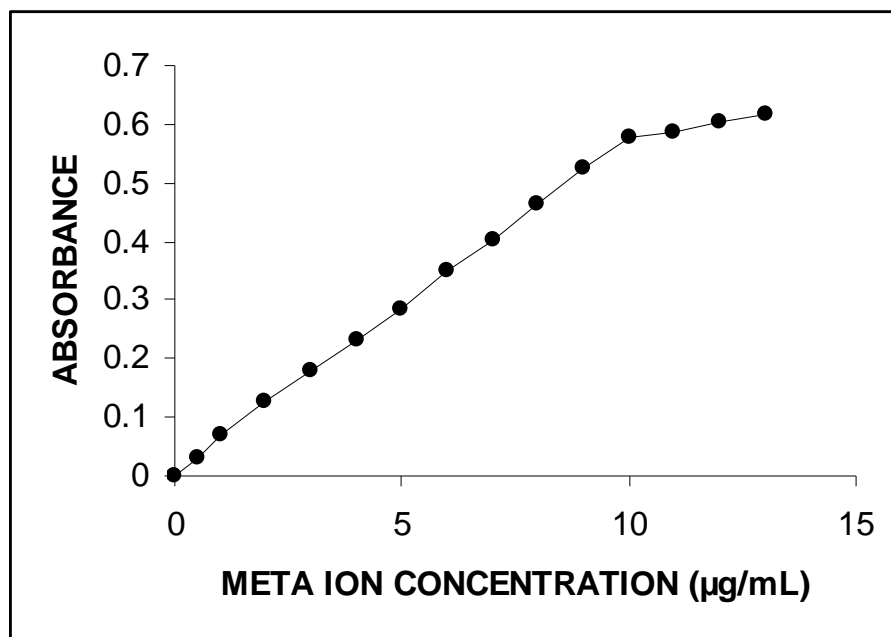


FIG: 3 PLOT OF $[\text{Se}^{+4}]$ Vs ABSORBANCE

The composition of selenium (IV) complex was found to be 1:2 according to Job's method, molar ratio method and Asma's method. The instability constant of the complex was found to be 2.216×10^{-8} by Edmond's and Birnbaum's method.

In order to assess the possible analytic applications of this method, the effect of diverse ions on spectrophotometric determination of selenium (IV) were studied in the presence of Triton X-114. A known amount of the ion in question was added to a solution containing $15 \text{ }\mu\text{g/mL}$ of selenium(IV). The tolerance limit was set at the amount required, so as not to cause beyond ± 2 percent error in mercury recovery. The results were presented in Table-1.

Table – 1 Effect of Foreign Ions on the Extraction of Se–(HIPAPH)₂ Complex

Foreign ion	Sources of the ion	Tolerance Limit (µg)
Ba (II)	BaCl ₂ .2H ₂ O	5500
Sr (II)	Sr (NO ₃) ₂	5500
Cd (II)	(CH ₃ COO) ₂ Cd.H ₂ O	2000
Zn (II)	ZnSO ₄ .7H ₂ O	2500
Sn (II)	SnCl ₂	4000
Mg (II)	MgSO ₄ .6H ₂ O	5500
Mn(II)	MnSO ₄ .H ₂ O	3000
Fe (III)*	FeCl ₃	-
Cu (II)*	CuCl ₂	-
Co (II)*	CoCl ₂ .6H ₂ O	-
Fluoride	NaF	5000
Chloride	KCl	5000
Acetate	CH ₃ COONH ₄	3500
Tartrate	COOK. CHOH. CHOH. COONa.4H ₂ O	3500
Sulphate	Na ₂ SO ₄	2000
Thiocyanate	NH ₄ SCN	1000

* Masked by using 1.0mL of 0.4% citrate solution, [Triton X-114] ÷ 2.0mL of 0.001N, [Se⁺⁴]- 8.0 µg/mL, [HIPAPH]- 2.0mL of 0.5%, pH – 6.0, λ_{max} – 513nm

The results revealed that, cations like Ba (II), Sr (II) and Mg (II) do not have any effect when present up to 5500µg in the extraction of Se- (HIPAPH)₂ complex. Zn (II), Sn (II) and Cd (II) can be tolerated up to 2500 µg 4000 µg and 2000 µg respectively. Mn (II) ions did not interfere even when present up to 3000µg. Fe (III), Cu (II) and Co (II) interfere severely with the determination of Se (IV). The interference due to Fe (III), Cu (II) and Co (II) can be suppressed by using 1.0 mL of 0.4per cent citrate solution.

Anions like fluoride and Chloride up to 5000µg, acetate and tartrate up to 3500 µg, sulphates up to 2000 µg and thiocyanate up to 1000 µg do not interfere in the determination of Se(IV).

Determination of Selenium(IV) in Buck Wheat and Rajgira Seeds : Determination of selenium(IV) content in Buck Wheat and Rajgira Seeds samples were carried out using present method. 5.0 g of dried sample was weighed and brought to the solution by dry ash method [23]. The results tabulated in Table – 2 shows that the selenium content obtained by the present method was in good agreement with the standard atomic absorption spectrophotometry method.

The results indicate that selenium content in Rajgira Seeds (0.743mg) is more when compared to the Buck Wheat (0.876mg)

Table-2 Determination of Selenium (IV) in Buck Wheat and Rajgira Seeds Samples (5g Sample)

S.No.	Name of the Sample	Selenium found*		Recovery (%)
		By AAS method (mg)	By present method* (mg)	
1	Buck Wheat	0.75	0.743	99.0
2	Rajgira Seeds	8.7	8.7	100

* Average value of three determinations,
Concentration of the reagent (KIBX) -3.0 ml of 0.5%, pH- 6.0, λ_{Max} -378 nm

APPLICATIONS

The procedure developed is applicable for the determination of selenium(IV) in Buck Wheat and Rajgira Seeds samples.

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