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Research Article

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM IN WATER, SOIL SAMPLES USING 2-ACETYL-5-CHLORO THIOPHENE, PHENYLENEDIAMINE

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Abstract: Analytical application of 2-acetyl-5-chlorothiophene, phenylenediamine (ACTPDA) is described for the direct non-extractive spectrophotometric determination of Selenium. The synthesized and characterized using IR and NMR spectral data .The reagents react with Selenium, in acidic medium (pH 6.0., sodium acetate-acetic acid buffer) to form yellow colored1:2 (M: L) complexes. The colour reactions are instantaneous and absorbance values remain constant for over 24 h. The molar absorptivity and Sandell's sensitivity of ACTPDA methods are found to be 1.002 X 10 ^{4} L mol^{-1} cm^{-1} 8.66 X10^{-4} µg cm^{-2} ,0.075 µgmL^{-1} and0.025 µgmL^{-1} of Se^{IV} respectively. The systems obey Beer's law in the range of 2.5 -10 µg/ml of Se^{IV}. Since ACTPDA method is more sensitive it was applied for the determination of selenium in water and soil samples.

Key words: Spectrophotometry, Selenium, 2-Acetyl-5-chlorothiophene, phenylenediamine, Water and soil, Samples.

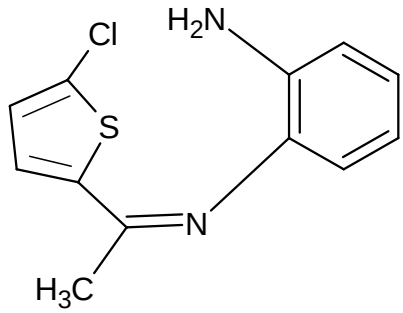
INTRODUCTION

Selenium is one of the trace metal which plays an active role in many biological systems[1] as it has toxicological and physiological effects[2,3] .It is an essential nutrient at trace level but toxic in excess[4]. Selenium is both highly toxic a an essential trace element for all living beings[5,6] becase selenium act as a cofactor i n cell membrance glutathione peroxidise and is important in cellular detoxification of peroxidise[7] .it is widely distributed innature in relatively small concentrations in rocks,plants,coal and other fossil fuels.in china selenium deficiency in soil is associated with Kaschin Beck disease,[8,9].

When selenium is present in animal feeds at a concentration less than 0.1mgL^{-1}, deficiency synmptoms develop,but present higher concentration ,exceeding 5gL^{-1},chronic selenouse occers.selenium compo und are widely used in paints, dyes, glass electrical, rubber, insecticides, and many other industries. Some indusrial and agreicultural processes release selenium as aby-product and selenium form such sources has caused environmental disaster[10].

The threshold limit[11] value for selenium compounds in air is 0.1-0.2mg dm-3;in water it is 4.0ppm.the toxicity, availability and environmental mobility of selenium are very much dependent on its chemical form[12] .selenium can occur in different oxidation state in organic and inoraganic compounds.in many environmental matrixes, e.g.natural water and soils, the predominant oxidation state of selenium are Se(IV)andSe(VI).Precise knowledge of the amount of selenium and its compounds present in a system is therefour, required for accurate assessment of the environmental and biological impact of selenium. This has resulted in an increasing need for analytical methods suitable for the determination of selenium at trace levels .Selenium enter into natural water through seepage from seleniferrous soil and industeral waste.water drained from such soilcause severe environmental pollution and wide life toxicity. selenium is also reported to be present in cigarette paper,tobacco[13] ,and various cosmetic sample [14]. Because of its significance ,several analytical techniques has been reported concerning the determination of selenium[15-18]. Many spectrophotometric methods for determination of selenium have been reported have been reported with som chromogenic reagents ,such as 3,3-diaminobenzidine[19] ,1,1-dianthrimide[20,21] ,2,2-dianthrimide[22], 4-methyl-o-phenyl-enediamine[23] diaminochrysazine[24] ,,N-methyl-0-phenylene-diamine[25] , 1,10-phenanthroline(witheosin)[26] ,dithiozone[27] , 4,5,-diamino -2,6-dimercaptophyrimidine[28] , 8-hydroquinoline[29] , 4,5,6-triaminopyrimidine [30] ,chromotropic acid [31] ,1-naphthylamine-7-sulphonic acid[32] , leuco crystal violet [33] ,variamin blue [34], thioinne [35] ,maxilon blue SG [36],rhodamineB-thiocyanate-gelatine-OP system[37], and potassium iodide and starch [38].of these reagents some have been reported to be less selective and sensitive.

In the present investigation a rapid sensitive and selective method has been reported for the determination of selenium with 2-Acetyl-5-chlorothiophene, phenylenediamine as a reagent employed for the determination of selenium in water and soil samples,



ACTPDA

EXPERIMENTAL

Preparation of ACTPDA

The reaction mixture containing 2-acetyl-5-chlorothiophene, (2g, 0.01229 mol in 20ml of methanol) phenylenediamine (1.32g, 0.01229 mol in 20ml of methanol dissolved in hot condition) was taken in 250-ml round bottom flask and refluxed for 8h. On cooling the reaction mixture, dark yellow coloured product was formed. It was collected by filtration and washed with hot water and 50 percent cold methanol. This compound was recrystallised from ethanol and dried in vacuo, yield 2.8. g ; m .p . 37°C.

Characterisation of ACTPDA

The reagents have been characterized by IR and ^{1}H NMR spectral data. Infrared spectrum of ACTPDA shows bands at [3432(s) 3386(S), 3286(m),3176(m),2979(m);1630(m); 1591(s),1435(s); 1362(s); 1248(m) 1174(m), 1297(m); 871(δ), 730(δ); cm^{-1} respectively corresponding to υNH-symmetric, υNH-asymmetric, υ (C-H) aromatic stretch, υ (C=S) stretching, υC=N symmetric, υ (C-C) aromatic ring, δ(C-H) of Thiophene ring, (ACTPDA) and δ (C-H)-oop bend (aromatic) and δ (C-C)-oop bend aromatic ring vibrations. ^{1}H NMR spectra of TDATSC ($CDCl_3$ + DMSO-d6) showed signals at 2.54

(3H,S)due to -CH_3 ,3.4,(2H,s); 6.6(2H),7.7 (4H,m);due to aromatic ring, 7.4 (2H,s) due to NH_2, C_4H_2S (Thiophene).

pK_a values of reagents

The pK_a values were determined by recording the UV-Visible spectra of 4 X 10^{-5} M solutions of the reagent at various pH values and by taking the arithmetic mean of the values obtained from the measurements at different wave lengths determined spectrophotometrically using Phillips and Merrit method. The values of deprotonation of ACTPDA were 6.0 (pK_1)

The reagent (ACTPDA) solution (0.01 M) was prepared by dissolving 50 mg of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 24 h. Hydrochloric acid (1 M)-sodium acetate (1 M) (pH 0.5-3.5); 0.2 M NaOAc-0.2 M AcOH (pH 4-6) solutions were used .A stock solution (1 mg L^{-1}) was prepared by dissolving 0.00945(0,001m) mg of Na_2SeO_4. (E.Merck preanalysis) in 50 ml de-ionized water. . Dilute standard solutions were prepared from this stock solutions as and when required.

1000 ppm stock solution of Selenium was prepared by:

dissolving 0.189m g of Sodium Selenate in one litre of distilled water. (E.Merck preanalysis) in 1000-ml de-ionized water. Dilute standard solutions were prepared from this stock solutions as and when required.

Recommended procedure:

An aliquot of the solutions containing 0.023-0.070 -µgmL $^{-1}$ of Selenium(IV) ,10 ml of NaOAc-AcOH buffer solution (pH 6.0) and 1.0 ml of 0.01 M ACTPDA were mixed in a 25-ml volumetric flask and resulting solution was diluted to the mark with distilled water. The absorbance of this solution was measured at 295 nm against respective reagent blank. The measured absorbance is used to compute the amount of selenium present in the samples using predetermined calibration plot. Schimadzu 160A UV-Visible spectrophotometer equipped with 10. cm quartz cell and an ELICO model LI-610pH meter were used in the present study.

Determinatin of selenium in natural and polluted water

Each filterd environmental water samples (100 ml) was analysed for selenium .They all tested negative .to these sample a knowen amount of the selenium was added and analysed for selenium by proposed and referenc method [34] . result are presented in table-2 .

Determinatin of selenium in polluted soil sample

A knowen amount of a soil sludge (2g) sample having known amount of selenium was placed in a 50ml beaker and extracted with concentration HCl (4-5). The extract was boiled for 10 min to convert any Se oxidation ,cooled and diluted to 25 ml with distill water .aliquots of the solution wear analysed by the proposed and reference method[34].

RESULTS AND DISCUSSION

The reagents ACTPDA may be easily prepared. The reagent solutions (0.01M) are found to be stable for 24 h. The absorption band from to 295 nm indicates that in solution on increasing the pH, the colour reactions of some important metal ions with ACTPDA are summarized in Table1. In basic medium (above pH 6.0) coordinates the trivalent metal ion as mono anion to give neutral complexes[13].

Selenium (IV), reacts with ACTPDA in acidic to give water soluble complexes. The colour reactions are instantaneous at room temperature. The change in the order of addition of metal ion, reagent (ACTPDA), and buffer has no effect on the absorbance of complexes. Analytical characteristics of the complexes are summarized in Table 1. The stiochiometry of the complexes (M:L = 1:1) was determined by job's continuous variation and molar ratio methods. Sodium acetate (0.2M)-acetic acid (0.2M) buffer solution (pH 6.0, T=300 K) and equimolar (1.002 X 10 ^{4}) solutions of Se (IV) AC TPDA were used in the calculation of stability constants of the complexes.

The effect of various cations and anions in 10 µgmL $^{-1}$ of selenium . which are generally associated with the metal ion in the determination selenium (IV) was studied by measuring the absorbance of Selenium the a complexes containing 0,070 µgmL $^{-1}$ of selenium (IV) in solution. The colour reaction is developed as described in the standard procedure. An error of ±2% in the absorbance reading was considered tolerable. The tolerance limit (µgmL^{-1}) values in µgmL $^{-1}$ for various anions and cations in ACTPDA methods respectively are as follows: Acetate (150),Sulphate(100)$^{-1}$ phosphate(200); bromide (200); nitrate (100); Borate(100) Chromate(150), Chloride(150), Ba^{2+} (100); Mg^{2+} (100); W^{6+} (50); Cd^{2+} (75); Mo^{6+} (50); Tl^{4+} (50); Fe^{3+} (100); Zn^{+2} (75), Pt^{4+} (10); Fe^{3+}(100); Al^{3+} (50); V^{4+} (100); Ni^{2+} (50); Cu^{2+}(25) . Hg^{2+} (75),Co^{2+}(50),In^{3+} (25),Ti^{4+} (50),W^{6+}(50),U^{6+} (50).

Table 1: Physico-chemical and analytical properties of Se^{IV} complexe with ATCPDA

S. No.	Characteristics	Se-ACTPDA
1	λmax (nm)	475
2	pH range (optimum)	6.0
3	Mole of reagent required per mole of metal ion for full colour development	10-fold
4	Time stability of the complex (in hours	24
5	Beer's law validity range (µg/ml)	2.5-10
6	Molar absorptivity (L $mol^{-1}cm^{-1}$)	1.002 X 10 ^{4}
7	Specific absorptivity (ml g^{-1} cm^{-1})	0.075
8	Sandell's sensitivity (µg of Se^{IV} mL^{-1})	0.025
9	Composition of the complex as obtained in Job's and molar ration methods (M:L)	1 : 1
10	Stability constant of the complex	4.40 X 10^{10}
11	Standard deviation	0.65
12	Relative standard deviation (RSD)	0.46%

The present method (ACTPDA) was applied for the determination of selenium when present alone and present in water and soil sample (Table 2).

The present ligands containing heterocyclic ring are found to be potential and cost effective for the determination of selenium(IV) without the need for extraction using the toxic solvents. Further, the reagents are easy to synthesize using commercially available precursors. Moreover, the present method is simple, rapid and very sensitive for non-extractive spectrophotometric determination of selenium(IV) in aqueous medium.

Performance of the proposed method and statistical comparison with reported methods

The proposed method was applied for the determination of selenium(IV) by spiked environmental and biological samples with known quantity of selenium(IV) and carrying out recovery studies. The results obtained by the proposed method were confirmed by measurements of selenium (IV) contents using the reported methods [**22**]. The results were analyzed statistically by Student's *t*-test and the variance ratio *F*-test at 95% confidence level. The calculated t and *F*-values did not exceed those theoretical values. It is evident from Table 2 that there is no significant difference between the spiked

Table 2: Determination of selenium in water sample

Se(IV) Added	Proposed µg/ml^{-1}± S.D[a]	Referenc [34] µg/ml^{-1}± S.D[a]	t-test[b] method	F-test[c] method
Polluted water sample [(d)] ground water				
5.0	5.02 ± 0.03	99.6 ± 0.08	1.78	1.77
10.0	9.98 ± 0.05	99.2 ± 0.30	1.52	2.77
Polluted water sample [(e)] tap water				
5.0	1.30 ± 0.02	1.34 ± 0.03	1.62	2.25
10.0	1.52 ± 0.05	1.59 ± 0.06	0.57	1.62
Polluted soil sample [(f)]				
5.0	4.98 ± 0.02	1.34 ± 0.03	98.8	0.75
10.0	9.02 ± 0.05	1.59 ± 0.06	99.5	0.87

[a] Mean ± Relative Standard Deviation (n = 5)
[b] Tabulated t-value for eight degrees of freedom at P (0.95) is 2.308.
[c] Tabulated F-value for (4,4) degrees of freedom at P (0.95) is 6.39.
[d,e,f]. Palamanaru ground water-Chittour,A.P.india.

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