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Research Article

SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC, LEAD IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES USING 2, 5-THIOPHENE DICARBOXALDEHYDE, THIOSEMICARBAZONE

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ABSTRACT

Analytical application of 2,5-thiophene dicarboxaldehyde, thiosemicarbazone(TDATSC) is described for the direct non-extractive spectrophotometric determination of As^{III}, and Pb^{II} in aqueous environmental and biological samples .The reagents react with arsenic, in acidic medium (pH 6.0., sodium acetate-acetic acid buffer) to form light yellow colored, 2:1 (M: L) complexes. The reagents react with lead in basic medium (pH 9.0. buffer) to form light blue colored, 2:1 (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 TDATSC methods are found to be 1.45 X 10^4 L mol^{-1} cm^{-1} and 0.0014 µg cm^{-2} of As^{III}, of. 1.89 X 10^4 L mol^{-1} cm^{-1} and 0.0019 µg cm^{-2} of Pb^{II} respectively. The systems obey Beer's law in the range of 0.123-2.537 µg/ml of As^{III}, 2.0– 2.4 µg/ml of Pb^{II} .Since TDATSC method is more sensitive it was applied for the determination of Arsenic, lead in environmental and biological samples

Key words: Spectrophotometry, Arsenic, Lead, 2, 5-thiophene dicarboxaldehyde, thiosemicarbazone in environmental and biological sample

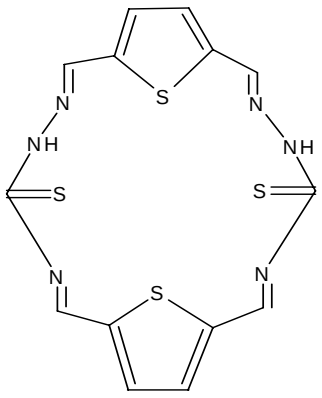
INTRODUCTION

Thiosemicarcarbazones are important reagent widely used for the spectrophotometric determination of metal ions[2a,10,17]. 2, 5-thiophene dicarboxaldehyde, thiosemicarbazone is new important reagent used for the spectrophotometric determination of metal ions arsenic, lead. Arsenic compound widely used and have long been recognized as toxicants[5,15,22].Trace concentration of arsenic can also affect the physical and mechanical properties of metal and alloys[23]. In environmental arsenic is widely distributed in the nature. It occurs as inorganic and organic compounds in many environmental matrices such as natural water and soil as trivalent and tetravalent[19,20,21].Animals vary in their arsenic accumulation depending upon the type of food they consume (John & Jeanne, 1994)[8].Acute arsenic exposure can give symptoms with rapid onset of headache, nausea and severe gastrointestinal irritation (Allan *et al.,* 1995)[1]. Similarly, increased levels of copper cause liver, kidney and brain damage, which may follow hemolytic crisis (Judith, 1994)[9]. with increasing industrialization, more and more industrial waste get accumulated in various regions and make their passage through soil into animal body, especially, in their liver, kidney and lean meat[12].

Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol (Renner, R. 1995)[18] Presence of even traces of Pb(II) in environmental samples leads to environmental pollution and many fatal diseases including dysfunction of renal blood and neurological systems. Pb(II) easily deposits in blood, kidney, reproductive system, nervous system and brain, and acute lead poisoning can result in colic shock, severe anaemia and irreversible brain damage. Lead compounds as ant knocking agents in automobile fuels cause air pollution

The determination of trace amounts of lead is very important in the context of environmental monitoring however a large number of spectrometric methods for determination of lead are reported to face interference due to the presence of several metal ions, (Du, B. et. al 2002[3], Fargussion, J.1990[5,] Ferreira, S. L. C. et.al 1991[6], Dutta, S. & Das,A. K. 2007[4], Kiehei, U. et. al 2000[11], Mondal[14,] B. C., Das, A. K. 2002[4], Dutta, S. & Das, A. K. 2007[19 .] The present study was planned to determine the prevalence of selected Trace elements in lean and organ pig kidney and liver ,and in water samples.

This paper describes synthesis, characterization and analytical properties of new reagents 2,5-thiophenedicarboxaldehyde thiosemicarbazon TDATSC. The spectrophotometric determination of arsenic, lead using TDATSC is included in this paper. Since the latter reagent is more sensitive, it was used for the determination of lead, Arsenic in various biological and water samples.



TDATSC

Experimental

Preparation of TDATSC

The reaction mixture containing 2,5-thiophene dicarboxaldehyde (1g, 0.00708 mol in 20ml of methanol) thiosemicarbazone (0.64g, 0.00708 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 1.4. g; m .p . 86°C.

Characterisation of TDATSC

The reagents have been characterized by IR and ^{1}H NMR spectral data. Infrared spectrum of TDATSC shows bands at [3340(s); 3251(m, br)]; 3178(m), 3140(m);1609(m); 1552(s),1435(s); 1362(s); 1248(m) 1174(m), 1297(m); 842(δ), 733(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, (TDATSC) 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 3.4,(1H,s); 7.24-7.5 7.81-7.88, (4H,m); 8.18 (2H,s) due to C-H,10.5(1H s)due to N-H C_4H_2S(Thiophene), C=Nand =N-NH(hydrazine) proton groups of thiosemicarbazone.

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 TDATSC were 6.91 (pK_1); 8.94(pK_2).

The reagent (TDATSC) 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 12 Hydrochloric acid (1 M)-sodium acetate (1 M) (pH 0.5-3.5); 0.2 M NaOAc-0.2 M AcOH (pH 4-6) and 2 M NH4cl-2 NH_4OH (pH 7-10) solutions were used. A stock solution (1 mg L^{-1}) was prepared by dissolving 312.01 mg of $Na_2HAsO_4.7H_2O$ (E.Merck preanalysis) in 1000-ml de-ionized water. . Dilute standard solutions were prepared from this stock solutions as and when required.

1000 ppm stock solution of Lead was prepared by

dissolving 1.83 g of lead acetate 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 0.24-2.36 mg/ml(or ppm) of Arsenic(III) ,10 ml of NaOAc-AcOH buffer solution (pH 6.0) and 1.0 ml of 0.01 M TDATSC 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 280 nm against respective reagent blank. The measured absorbance is used to compute the amount of Arsenic 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.

Dried pig liver and kidney samples (2-5 g) were taken in a 250 ml beaker. A 6 ml of concentrated nitric acid was added and gently heated for half an hour. After the disappearance of the froth, 6 ml of 1:1 nitric acid and perchloric acid were added [13,22,2]. The contents were digested for one hour and repeatedly treated with 6 ml portions of nitric acid and perchloric acid mixture until the solution becomes colourless. The acidic solution was evaporated to dryness and the resulting white residue was dissolved in minimum volume of 1 M nitric acid and made up to the volume in a 50 ml volumetric flask. Aliquots of this solution were taken for analysis following the recommended procedure.

Determination of arsenic, lead in natural and polluted water

Water samples from a river receiving in polyethalene bottles and filtered through whatman 41 filter paper. Pb(II),As(V) if any is reduced to As(III) by the process described. Arsenic and Lead content was determined directly according to the recommend method and also by the reported method[16].

RESULTS AND DISCUSSION

The reagents TDATSC may be easily prepared. The reagent solutions (0.01M) are found to be stable for 24 h. The absorption band from 270 to 295 nm indicates that in solution on increasing the pH, the colour reactions of some important metal ions with TDATSC are summarized in Table1. In basic medium (above pH 9.0) coordinates the tetravalent metal ion as mono anion to give neutral complexes[13].

Arsenic (III), Lead(II) reacts with TDATSC in acidic, basic pHs to give water soluble complexes. The colour reactions are instantaneous at room temperature. The change in the order of addition of metal ion, reagent (TDATSC), 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 = 2:1) was determined by job's continuous variation and molar ratio methods. Sodium acetate (0.2M)-acetic acid (0.2M) buffer solution (pH 6.0, pH 9.0, and T=300 K) and equimolar (1.45 X 10^4 M),(1.89X 10^4 M) solutions of As (III), Pb (II) and TDATSC were used in the calculation of stability constants of the complexes.

The effect of various cations and anions which are generally associated with the metal ion in the determination Arsenic (III), Pb(II) was studied by measuring the absorbance of Arsenic the a complexes containing 1.4µg/ml of Arsenic (III), 1.2µg/ml Pb(II) 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 (TL) values in ppm for various anions and cations in TDATSC methods respectively are as follows: citrate (1152,1152); tarrate (888,888); ascorbate (752,752); iodate (761,761); iodide(612,761), thiocyanate (507,507); phosphate(465,465); urea (384,384); bromide (317,317); sulphate (252,384); thiosulphate (246,246), nitrate (212,244); oxalate (281,281); fluoride (75,75); Ba^{2+} (675,800); Mn^{2+} (275, 325); Mg^{2+} (125,150); Sr^{2+} (1 00,125); W^{6+} (110,110); Sn^{2+} (47,47); Cd^{2+} (23,26); Mo^{6+} (19,23); Tl^{3+} (14,14); Fe^{2+} (12,10); Cr^{6+} (10,12); Zn (10,10), Pt^{4+} (8,8); Fe^{3+}(5,4); Au (4,4); Ag^{+} (2,5); Ni^{2+} (1,1.2); Cu^{2+}(1,1) . Higher amounts of Fe^{3+} (13,17) do not interfere in the presence of 70ppm of fluoride. Larger amounts of Hg^{2+} (40,48) do not interfere in the presence of 500 ppm of iodide.

The present method (TDATSC) was applied for the determination of Arsenic when present alone and present in biological samples (Table 2).

The present ligands containing heterocyclic ring are found to be potential and cost effective for the determination of Arsenic (III),lead(II) 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 Arsenic (III) ,lead(II) in aqueous medium.

Performance of the proposed method and statistical comparison with reported methods

The proposed method was applied for the determination of Arsenic, Lead by spiked environmental and biological samples with known quantity of As(III),Pb(II) and carrying out recovery studies. The results obtained by the proposed method were confirmed by measurements of arsenic, lead 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 4, that there is no significant difference between the spiked.

Table 1: Physico-chemical and analytical properties of As^{III} , Pb^{II} complexes with TDATSC

S.No.	Characteristics	As-TDATSC	Pb- TDATSC
1	λmax (nm)	280	442
2	pH range (optimum)	6.0	9.0
3	Mole of reagent required per mole of metal ion for full colour development	10-fold	10-fold
4	Time stability of the complex (in hours)	24	24
5	Beer's law validity range (µg/ml)	0.236-2.357	2.0-2.4
6	Molar absorptivity (L $mol^{-1}cm^{-1}$)	1.4 X 10^4	1.89X 10^4
7	Specific absorptivity (ml g^{-1} cm^{-1})	0.25	0.86
8	Sandell's sensitivity (µg of As^{III} cm^{-1})	0.0014	0.0019
9	Composition of the complex as obtained in Job's and molar ration methods (M:L)	1:2	2:1
10	Stability constant of the complex	4.40 X 10^{10}	8.40 X 10^{10}
11	Standard deviation	0.0049	0.0042
12	Relative standard deviation (RSD)	0.46%	0.36%

Table 2: Determination of Arsenic, lead in liver & kidney

Sample	Arsenic (µg/g)[a]		Recovery	Sample	Lead (µg/g)[a]		Recovery
	ADDED	FOUND	±S.D.%		ADDED	FOUND	±S.D.%
Pig liver	0	0.517		Pig liver	0	0.317	
	100	100.52	98.9 ± 0.53		100	103.02	95.9 ± 0.43
	500	501.02	100.6 ± 0.48		500	505.10	100.6 ±0.48
Pig kidney	0	0.28		Pig kidney	0	0.243	
	100	100.30	100.0 ± 0.2		100	102.02	98.1 ± 0.22
	500	503.10	100.3±0.19		500	505.10	100.4 ± 0.01

[a] Average of five determinations

Table 3: Determination of arsenic in water sample

Sample	proposed µg/ml^{-1}±S.	Referenc [25] µg/ml^{-1}±S.D[a]	t-test[b] method	F-test[c] Method
Polluted water sample [(d)] ground water	1.02 ± 0.02	1.01 ± 0.03	0.62	2.25
	2.02 ± 0.05	1.99 ± 0.07	0.52	1.62
	1.19 ± 0.05	17 ± 0.05	0.7	1.56
Polluted water sample [(e)] tap water	1.30 ± 0.02	1.34 ± 0.03	1.62	2.25
	1.52 ± 0.05	1.59 ± 0.06	0.57	1.62
	1.40 ± 0.04	1.37 ± 0.03	0.45	1.76
Polluted water sample [(d)]	0. 49 ± 1.44	0.501 ± 1.60	2.35	2.25
	1.49 ± 0.37	1.50 ± 0.67	2.63	2.78
	2.49 ± 0.20	3.02 ± 0.39	2.73	2.26

[a.] Mean ± Relative Standard Deviation (n = 5)

[b.] Tabulated t-value for eight degrees of freedom at P (0.95) is 2.306.

[c.] Tabulated F-value for (4,4) degrees of freedom at P (0.95) is 6.39.

[d.]. Palamanaru ground water-Chittour,A.P.india.

[e]Palamanaru tap water-Chittour,A.P.india

Table 4: determination of lead in water sample

Sample	proposed µg/ml^{-1}±S.	Referenc [25] µg/ml^{-1}±S.D[a]	t-test[b] method	F-test[c] Method
Polluted water sample [(d)]	0.49 ± 1.44	0.501 ± 1.60	2.35	2.25
	1.49 ± 0.37	1.50 ± 0.07	2.63	2.78
	2.49 ± 0.20	3.02 ± 0.39	2.73	2.26

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