



On-site determination of tin in geological and water samples using novel organic reagent with iodide

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ARTICLE INFO

Article history:

Received 10 May 2008

Received in revised form 4 July 2008

Accepted 26 July 2008

Available online 3 August 2008

Keywords:

Tin
Iodide
N-Octylacetamide
Spectrophotometry
Water
Geological

ABSTRACT

A new, simple and sensitive method for spectrophotometric determination of tin (IV) with iodide and amide is described. The Sn(IV)–I[−] complex is extracted with chloroform solution of amide (*N*-phenylacetamide, *N*-alkylacetamide, alkyl = butyl, phenyl, hexyl and octyl group) in the strong sulphuric acid solution. Among five amides studied, *N*-octylacetamide (OAA) has been selected as it yielded best sensitivity. The apparent (at twofold preconcentration) molar absorptivity with respect to tin is $(2.40) \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at λ_{max} , 410 nm. The detection limit of the method is $4 \mu\text{g L}^{-1}$ Sn. The method is free from interferences of common ions that are normally associated with Sn. The method is highly sensitive and found to be applicable for the rapid determination of tin in water samples at micro-gram levels.

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1. Introduction

Tin is present in the earth's crust at a concentration of about 2.2 mg kg^{-1} (milligram per kilogram) and its concentration in seawater is about $0.01 \mu\text{g L}^{-1}$ (micro-grams per liter). Tin poses external as well as internal health hazards. The main causes of internal exposure are ingestion of food and water containing tin isotopes. Tin is a volatile element and is widely used as stabilizer in plastic industries and as pesticides in agriculture [1]. Though tin is an essential metal it is toxic when present in organic forms [2–3]. Organotin compounds with alkyl or aryl groups are among the most toxic compounds. The contamination of tin is due to natural as well as anthropogenic causes. Coal burning, smelting of pyrite minerals are the major anthropogenic sources. On the other hand, organotin compounds are used for many years as antifouling paint agents, fungicides and wood preservatives [4].

Several organic reagents such as 2,6,7-trihydroxyphenyl-fluorone, catechol violet, bromopyrogallol red + nonyl phenoxy polyethoxyethanol + cetyltrimethylammonium bromide, diacetylmonoxime *p*-hydroxybenzoylhydrazine in cationic micellar

medium, 1-(2-pyridylazo)-2-naphthol (PAN) + Triton X-100 and bis(2-ethylhexyl) sulfosuccinate, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, etc. were reported for spectrophotometric determination of tin [5–11]. However, these methods are not suitable for routine monitoring as the procedures are complicated, report poor sensitivity and susceptible to pH changes and interferences. In the present work, new, simple and selective method for the sensitive extraction and spectrophotometric determination of tin with *N*-octylacetamide (OAA) in the presence of iodide ions is described. The proposed method is more sensitive and selective than the most of the methods reported for the spectrophotometric determination of Sn. The method is applicable for the rapid determination of tin in the water samples at micro-gram levels.

2. Experimental

2.1. Apparatus

A Systronics VIS-spectrophotometer type-106 matched with 1-cm quartz cell was used for the absorbance measurement. A GBC AAS-932 equipped with HG-3000 was used for the data validation.

2.2. Reagents and solution preparations

All the chemicals used were analytical reagent grade. Tin metal, potassium iodide, ascorbic acid were purchased from E. Merck

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(Darmstadt, Germany). Acetic anhydride and alkyl amine for the synthesis of alkyacetamide was obtained from Sigma (St. Louis, MO, USA). A fresh standard solution of tin ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving weighed amount (0.25 g) of tin metal in minimum quantity of H_2SO_4 , evaporating to dryness and dissolving the residue in 0.07 mol L^{-1} ammonium oxalate in 250 mL of de-ionised doubly distilled water. The working standard solutions were prepared by an appropriate dilution of the stock solution. Freshly prepared solution of 3 mol L^{-1} KI (50%, w/v) containing 0.56 mol L^{-1} (10%, w/v) ascorbic acid was used to prepare iodo complex of tin. The amides were synthesized as prescribed in the literature [12]. A 0.15 mol L^{-1} (2.5%, v/v) *N*-octylacetamide (OAA) solution in chloroform was used for the extraction of the iodo-stannate complex. All solutions used were presaturated with chloroform.

2.3. Procedure

An aliquot of the sample solution containing 250–5000 μg of tin (IV) was transferred into a 100 mL-separatory funnel followed by the addition of 2.5 mol L^{-1} H_2SO_4 . To this, 2.5 mL KI solution was added and shaken with 5.0 mL chloroform solution of OAA for 1 min. The organic extract was dried using anhydrous sodium sulfate ($\approx 2.0 \text{ g}$) in a 10-mL volumetric flask. The absorbance of the extract was measured at 410 nm against the reagent blank.

3. Results and discussion

3.1. Absorption spectra

Tin (IV) reacts with iodide ions to give a yellow-colored complex. It is extractable into non-polar solvent such as chloroform in the presence of a base (phenylacetamide, butylacetamide, pentylacetamide, hexylacetamide, and octylacetamide), possibly due to the formation of an ion-associate species. Hence, the iodo complex of tin was extracted using phenylacetamide, butylacetamide, pentylacetamide, hexylacetamide, and octylacetamide in chloroform. Among the bases tested, the highest value of molar absorptivity of the complex was observed with *N*-octylacetamide (OAA). Hence, it was selected for further detailed studies. The absorption spectra of $\text{Sn(IV)}-\text{I}^-$ complex and the reagent blank are summarized in Fig. 1. The complex in chloroform exhibited a sharp λ_{max} around 410 nm.

3.2. Effect of acidity

The effect of HCl and H_2SO_4 on the determination of Sn in the presence of I^- ions and OAA was examined. The extraction of the metal was suppressed in presence of HCl, may be due to formation non-extractable chloro complex. However, near quantitative extraction of the metal (>99.0%) was achieved in H_2SO_4 medium. The optimum acidity was ranged between 2.0 and 3.5 mol L^{-1} H_2SO_4 . An acidity value of 2.5 mol L^{-1} H_2SO_4 was selected for further experimental work.

3.3. Effect of iodide and ascorbic acid

Iodide ions act as primary ligand in the formation of the ternary complex. A consistent and maximum extraction of the metal (>99%) was achieved when the concentration of I^- ions was $>0.54 \text{ mol L}^{-1}$, and further addition up to 0.66 mol L^{-1} KI caused no adverse effect. In the present work, a 0.6 mol L^{-1} KI was used for further studies. Ascorbic acid was added in order to prevent the liberation of iodine by any oxidizing species formed in situ. A 0.01 mol L^{-1} ascorbic acid was sufficient to prevent the liberation of iodine from iodide and its further addition up to 0.2 mol L^{-1} had no

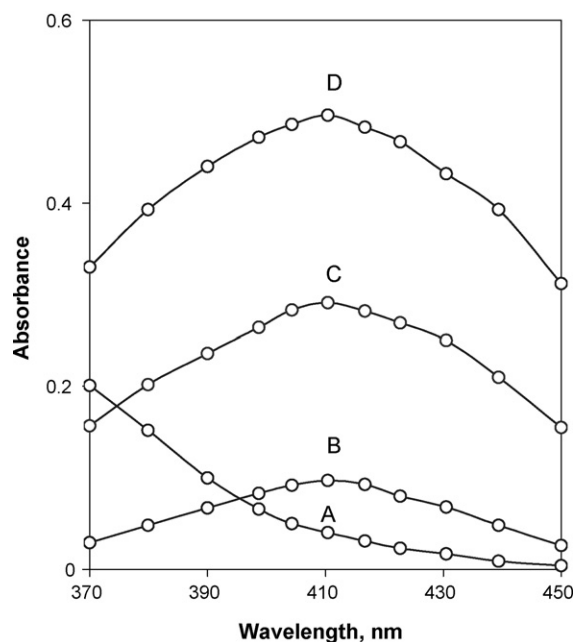


Fig. 1. Absorption spectra of the $\text{Sn(IV)}-\text{I}^-$ -OAA complex and reagent blank against the relevant reference. (A) Reagent blank in chloroform; (B) $[\text{Sn}] = 4.0 \times 10^{-7} \text{ mol L}^{-1}$; (C) $[\text{Sn}] = 1.2 \times 10^{-6} \text{ mol L}^{-1}$; (D) $[\text{Sn}] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$.

adverse effect. For the present work, 0.11 mol L^{-1} ascorbic acid was used.

3.4. Effect of amide

Amide is expected to act as cationic surfactant in acidic medium to neutralize the iodo-stannic anion to be extracted as neutral complex [13,14]. Amides (*N*-phenylacetamide, butylacetamide, pentylacetamide, hexylacetamide, and octylacetamide) are capable to extract the iodo-complexes, may be due to higher basicity. Among them, the highest value of molar absorptivity of the complex was observed with *N*-octylacetamide (OAA), possibly due to higher distribution coefficient in chloroform. At least, 0.12 mol L^{-1} OAA in chloroform was found to be needed for the complete extraction of the metal. Its further addition up to 0.2 mol L^{-1} had no adverse effect but thereafter, the extract become viscous. A 0.15 mol L^{-1} OAA solution in chloroform was used for the detailed extraction work.

3.5. Effect of other variables

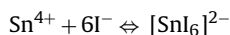
The sequence of addition of reagents was not found to be critical. The absorptivity of the extract was stable for at least 2 h over temperature range between 10 and 28°C . Beyond 28°C , the complex was found to be unstable. The detailed experimental work was carried out at room temperature ($22 \pm 2^\circ\text{C}$). Addition of 0.5 mol L^{-1} of Na_2SO_4 to the aqueous solution had no adverse effect on the absorptivity of complex. No change in the absorptivity of the extract was observed when the volume ratio of the aqueous to the organic phase was varied from 1:2 to 3:1.

3.6. Composition of complex

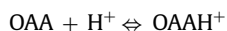
The mole ratio of Sn(IV) to I^- ions and OAA in the extracted complex was determined by the curve-fitting method, plotting log distribution ratio (D) versus $\log [\text{I}^-]$ or $[\text{OAA}]$ at equilibrium. The value of slope obtained for the curve, $\log D$ versus $\log [\text{I}^-]$ and $\log D$ versus $\log [\text{OAA}]$ was found to be 5.8 and 2.1 (close to integer 6

and 2), respectively. The molar ratio of Sn:I⁻:OAA is expected to be 1:6:2 in the extracted complex. The probable reaction mechanism for the extraction of the complex is expressed:

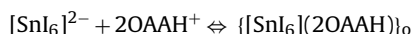
(i) Formation of iodo complex



(ii) Protonation of amide in the acidic solution



(iii) Extractable ion-associate complex with OAA



whereas the subscript 'o' denotes to the organic phase and the sensitivity of the complex is expected due to dehydration of the complex with *N*-octylacetamide micelle.

3.7. Optimum concentration range, sensitivity and precision

The calibration curve prepared by plotting absorbance versus concentration of Sn was found to be linear over the range of 25.0–500 $\mu\text{g L}^{-1}$ Sn with slope, intercept and correlation coefficient of 1.9627, -6.0×10^{-4} and +0.99, respectively. The R.S.D. of the method for four replicate measurements ($n=4$) at level of 100 $\mu\text{g L}^{-1}$ Sn was found to be $\pm 1.5\%$. The apparent value (at twofold enrichment) of molar absorptivity of the complex with respect to tin was $(2.40) \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at λ_{max} , 410 nm. The detection limit of the method was found to be 4.0 $\mu\text{g L}^{-1}$ Sn.

3.8. Effect of diverse ions

The effect of diverse ions in the determination of 100 $\mu\text{g L}^{-1}$ Sn was examined. None of the tested ions were found to interfere in the determination of tin. Their tolerance limits in the determination of tin are summarized in Table 1.

3.9. Accuracy of the method

The accuracy of present method was tested by analyzing the Sn content in the SRM (USGS) standard reference materials. Accurately weighed reference material was digested with aqua regia (25 mL), and excess of nitric acid was removed by heating with concentrated HCl (5 mL). The residue was dissolved in 2.5 mol L⁻¹ H₂SO₄ and diluted to 50-mL with the same acid. The solution was filtered and the tin content was determined by the present method as recom-

Table 1
Tolerance limit of diverse ions in the determination tin (100 $\mu\text{g L}^{-1}$)

| Ion added | Tolerance limit ^a ($\mu\text{g mL}^{-1}$) | Ion added | Tolerance limit ^a ($\mu\text{g mL}^{-1}$) |
|-------------------|---|----------------------------------|---|
| Mn(II), Ni(II) | 3400 | Citrate, tartrate | 600 |
| Mn(VII) | 3000 | Zn(II) | 500 |
| Cr(III) | 2100 | Ir(III), Ca(II) | 400 |
| W(VI) | 1800 | Pt(IV), Hg(II), SCN ⁻ | 300 |
| Mg(II), Al(III) | 1500 | Mo(VI), Se(IV) | 250 |
| Fe(II), Co(II) | 1000 | PO ₄ ³⁻ | 150 |
| Thiourea, Fe(III) | 900 | Pb(II), As(V) | 100 |
| Zr(IV), Ti(IV) | 720 | Sb(V), Bi(III) | 75 |
| EDTA, Cu(II) | 650 | | |

^a Causing error $\leq \pm 2\%$.

Table 2
Determination of tin in the reference material

| Reference material | Certified value (mg kg^{-1}) | Present method (mg kg^{-1}) | R.S.D. ($n=4$), $\pm\%$ |
|--------------------|--|---|---------------------------|
| SRM-1 | 4.5 | 4.37 | 1.4 |
| SRM-2 | 2.6 | 2.54 | 1.5 |

Table 3
Determination of tin in the contaminated water

| Sample | Present method | | HG-AAS method | |
|--------|----------------------|---------------------------|----------------------|---------------------------|
| | $\mu\text{g L}^{-1}$ | R.S.D. ($n=4$), $\pm\%$ | $\mu\text{g L}^{-1}$ | R.S.D. ($n=4$), $\pm\%$ |
| SW-1 | 265 | 1.1 | 276 | 2.9 |
| SW-2 | 827 | 1.2 | 811 | 3.5 |
| SW-3 | 391 | 1.3 | 403 | 3.0 |
| SW-4 | 434 | 1.1 | 428 | 3.3 |
| SW-5 | 496 | 1.0 | 490 | 3.2 |
| SW-6 | 210 | 1.3 | 202 | 2.9 |

SW = surface water samples obtained from Bacheli and Dantewara.

mended in the procedure. A good agreement was found with the reported values, Table 2.

3.10. Application of the method

The application of the method for the determination of Sn in surface water collected from a tin deposit area, Nerly (Bacheli) and Katekalyan (Dantewara), Baster, Chhattisgarh, India was tested. The water sample (500 mL) was collected in polyethylene container in February 2006. After, the sample was treated with few drops of ultra-pure nitric acid. The solution was filtered with Whatman filter paper no. 42 and acidity was adjusted to 2.0 mol L⁻¹ with H₂SO₄ (15 mol L⁻¹). The tin content was determined by the present method as described in the procedure. The data was validated by analyzing tin in samples with the AAS-HG method as prescribed in the literature [14]. The precision obtained by both methods was found to be comparable, Table 3.

4. Conclusions

The proposed method is simple, selective and sensitive for the detection of tin at micro-gram levels. The high sensitivity of the method is assumed due to micelle role of *N*-octylacetamide as surfactant. The sensitivity of the present method is comparable with the reported method with enhanced selectivity [5–11].

References

- [1] Sources of Common Contaminants and Their Health Effects, EPA, <http://www.epa.gov/oerrpage/superfund/programs/er/hazsubs/sources.htm>.
- [2] World Health Organization, Tributyl Compounds, Environment, Health Criteria, vol. 116, Geneva, 1990.
- [3] P.T.S. Wong, Y.K. Chau, M.D. Brown, M. Whittle, Butyltin compounds in Severn Sound, Lake Huron, Canada, Appl. Organometall. Chem. 8 (1994) 385–391.
- [4] W.M.R. Dirks, R. Lobinski, F.C. Adams, Speciation analysis of organotin in water and sediments by gas chromatography with optical spectrometric detection after extraction separation, Anal. Chim. Acta 286 (1994) 309–318.
- [5] D. Wang, Z. Xie, Q. Wu, Y. Song, S. Jin, Study of hypersensitive color reactions of tin(IV) with 2,6,7-trihydroxyphenylfluorone derivatives in the presence of nitrilotriacetic acid and mixed surfactants, Analyst 116 (1991) 1189–1193.
- [6] M.J. Hernandez, C.B. Moreno, M.R. Carabias, D.L. Gutierrez, Spectrophotometric determination of tin (IV) with catechol violet sensitized with polyvinylpyrrolidone, Microchem. J. (35) (1997) 288–292.
- [7] X. Huang, W. Zhang, S. Han, X. Wang, Determination of tin in canned foods by UV/visible spectrophotometric technique using mixed surfactants, Talanta 44 (1997) 817–822.
- [8] A. Varghese, A.M.A. Khadar, Highly selective derivative spectrophotometric determination of tin (II) in alloy samples in the presence of cetylpyridinium chloride, Acta Chim. Slov. 53 (2006) 374–380.

- [9] J.L. Manzoori, M. Amjadi, D. Abolhasani, Spectrofluorimetric determination of tin in canned foods, *J. Hazard. Mater.* 137 (2006) 1631–1635.
- [10] S.V. Bandekar, P.M. Dhadke, Solvent extraction separation of tin (IV) with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), *Talanta* 46 (1998) 1181–1186.
- [11] A.C.S. Costa, L.S.G. Teixeira, S.L.C. Ferreira, Spectrophotometric determination of tin in copper-based alloys using pyrocatechol violet, *Talanta* 42 (1995) 1973–1978.
- [12] A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd ed., Longman, Green, London, 1962.
- [13] J.M. Richard, *Cationic Surfactants: Organic Chemistry, Fatty Acid Amide Surfactants*, CRC Press, New York, USA, 1990, pp. 1–29.
- [14] R. Danby, S. Shaw, *GBC Automatic Hydride Generator, Operation Manual* Dan-denong, Australia, 1990.