Journal of Advances and Scholarly Researches in Allied Education
Vol. 16, Issue No. 6.1, May-2019 (Special Issue), ISSN 2230-7540

Study on Spectrophotometric Determination of Tin (II) In Cetylpyridinium Chloride

M. Arockiyadass[1]* J. Senthilkumaran[2]

[1] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

[2] Assistant Professor, Dhanalakshmi Srinivasan College of Arts and Science for Women, Perambalur, Tamil Nadu, India

ABSTRACT

A straightforward, particular and touchy spectrophotometric technique has been produced for the assurance of tin(II) utilizing a recently blended reagent diacetylmonoxime p-hydroxybenzoylhydrazone in cationic micellar medium. The molar absorptivity and Sandell's affectability of the shaded species are 3.20×104 L mol-1 cm-1 and 3.6 ng cm-2 separately. Lager's law is complied between 0.25-2.76 µg mL-1 of Sn(II)) at 430 nm. The stoichiometry of the complex was discovered to be 1:2 (metal: ligand). An exceptionally specific first request subsidiary spectrophotometric technique for the assurance of tin is additionally announced. The created strategy has been effectively applied for the assurance of tin in different amalgam tests and manufactured combinations of some low liquefying compounds.

Key Words – *Tin, Diacetylmonoxime, Micellar, Spectrophotometry*

INTRODUCTION

Tin is broadly utilized as a covering component for prepares and as an alloying specialist in a wide assortment of metal sytheses. The chief utilization of tin in hardware is in the welds for the joining of electronic parts. It very well might be brought into the human climate either as inorganic tin or as natural tin compounds; through they utilized as fungicides in crops, in food bundling, in some veterinary details, in wood protection, as stabilizer for polyvinylchloride and as electrochemical catalysts.1 It has been accounted for that canned food varieties or plastic pressing materials can prompt expanded tin levels in human tissues. Intense tin harming is portrayed by eye and skin disturbances, migraine, stomach throb and serious sweating.2 Therefore it is vital to build up an exceptionally precise and delicate strategy for the assurance of tin at microgram levels in different example materials. The most generally utilized strategies incorporate spectrophotometry,3-5 nuclear ingestion spectrometry with hydride generation,6 and electrochemical analysis7,8 dependent on polarography or stripping voltammetry. Of these, spectrophotometric techniques possess an uncommon situation because of their straightforwardness, more affordable instrumentation and high affectability. Countless spectrophotometric reagents, for example, pyrocatechol violet,9,10 phenylfluorone,11,12

Article submitted at :
National Conference on Advances in Multidisciplinary Research (NCAMR-2019)
Organized by : Kurukshetra Institute of Professional Studies, Kurukshetra, Haryana

bromopyrogyallol red,13 pyrimidine azo compounds,14 potassium ethyl xanthate,15 ferron,16 N,N-diphenylbenzamidine,17 isoamyl xanthate,18 calcein19 and trimethoxy phenylfluorone20 have been accounted for the assurance of tin(II, IV) content. Among these strategies pyrocatechol violet and phenylfluorone have been generally utilized for the assurance of tin in composites, minerals and canned foods.21 They are non-specific chromogenic reagents which structure hued chelates with numerous other metal particles. Regularly the greater part of these strategies are not straightforward and require broad and relentless strides for the division of tin from the networks utilizing techniques, for example, particle exchange,10 extraction,15-18 co-precipitation of tin22 or the expansion of appropriate veiling agents.4,9 In the proposed strategy the utilization of micellar framework empowers the estimation in a fluid medium, accordingly keeping away from the extraction steps while the derivatisation of the otherworldly profiles upgrades the selectivity of the strategy as firmly covered assimilation groups of the meddling particles become resolved.23-26 In the current examination we report a basic, delicate and non extractive subordinate spectrophotometric assurance of Sn(II) utilizing a recently incorporated reagent diacetylmonoxime p-hydroxybenzoylhydrazone (DMPHBH) within the sight of cetylpyridinium chloride (CPC), a cationic surfactant. The particular benefit of the proposed strategy is that the ordinarily related metal particles particularly Fe, Cu, Al, Pb, Cd, Zn and Bi don't meddle in the assurance of Sn(II) dissimilar to the detailed methods.15-18 Tin and Indium are the fundamental constituents of number of fusible or low liquefying composites. Tin doped indium oxide is a straightforward leading material, which is utilized to make electronic gadgets, for example, fluid gem shows (LCDs). Accordingly it is of extraordinary interest to decide tin within the sight of indium. A technique for particular assurance of Sn(II) within the sight of In(III) with no pre-partition is additionally detailed. Effects of shifting boundaries like impact of acids, convergence of surfactant and reagents on the absorbance and the steadiness of the complex have been considered. The created strategy has been effectively applied for the assurance of tin in different composite examples and manufactured combinations of some low dissolving amalgams.

EXPERIMENTAL

Apparatus

A Shimadzu 1601 UV/VIS. Spectrophotometer furnished with 1.0 cm quartz cells was utilized for all unearthly estimations. The instrumental boundaries were improved and the best outcomes were gotten with an output speed 145 nm/min., cut width of 1 nm and $\Delta\lambda$ = 2 n m for the main request subordinate mode in the frequency range 350–650 nm. A Systronics µ pH framework 362 was utilized for pH estimations.

Reagents

All synthetics utilized were of insightful evaluation . A stock arrangement o f tin (I) (1000 µg mL-1) was set up by dissolving precisely gauged $SnCl_2 \cdot 2H_2O$ (S.D. Fine-Chem. Ltd. India) in 1mL of concentrated hydrochloric corrosive and made sufficient in a 100 mL volumetric cup. This stock arrangement was standardised27 and working arrangements were set up by weakening the stock answer for a proper volume. Arrangements of the examined meddling particles of appropriate fixations were readied utilizing A.R. grade reagents. Fluid arrangements of 1% cetylpyridinium chloride (CDH Pvt.Ltd. India) and 10% ascorbic corrosive (SRL Pvt.Ltd., India) were set up in refined water. A 0.1% arrangement of DMPHBH was set up in ethanol. A 0.2 M HCl was additionally arranged.

Synthesis and Characterization of DMPHBH

Diacetylmonoxime p-hydroxybenzoylhydrazone was incorporated by refluxing equimolar measures of diacetylmonoxime and p-hydroxybenzoylhydrazide in ethanolic mode for 2 hours. The subsequent hydrazone was recrystalised from ethanol (yield, 73%; mp 306 °C). IR (KBr) ν, 3300-3320 (OH&NH), 1647 (C=O), 1608, 1580 (C=N), 972 (N-O). 1 H-NMR (300 MHz, DMSOd6) δ 11.34 (s, 1H, oxime OH), 10.48 (s, 1H, phenolic OH), 10.08 (s, 1H, NH), 2.27 (s, 6H, 2xCH_3), 6.84 (d, J 8.4 Hz, 2H, ArH), 7.76 (d, J 8.4 Hz, 2H, ArH). MS m/z, 236 (M+H, 8), 97 (100). Butt-centric. Calcd. for $C_{11}H_{13}N_3O_3$: C 56.17, H 5.53, N 17.87, Found: C 56.48, H 5.32, N 17.80. The primary recipe of DMPHBH is given in Figure 1.

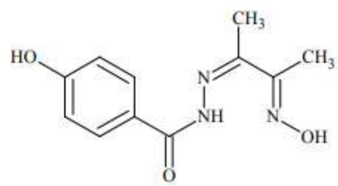

Figure 1. Structural formula of DMPHBH.

General Procedure

In every one of a bunch of 10 mL standard jars, shifting measures of Sn(II), 2 mL of 10% ascorbic corrosive, 2 mL of 0.2 M HCl, 0.5 mL of 0.1 % DMPHBH and 1.5 mL of 1% cetylpyridinium chloride were added and weakened to the imprint with refined water. The absorbances were estimated at 430 nm against the reagent clear. The adjustment chart was developed by plotting the absorbance against the centralization of Sn(II) particles.

First Derivative Spectrophotometer

For the above set of arrangements first request subsidiary spectra were recorded regarding the reagent clear in the frequency range 350-650 nm. In the subsidiary range top tallness (PH) at 400 nm or box profundity (TD) at 480 nm was estimated from the zero line of the range to decide its reliance on the metal particle focus. Alignment diagrams were developed by plotting the subordinate plentifulness against the grouping of Sn(II) particles. For the assurance of Sn(II) in presence of In(III) particles by utilizing first-request subsidiary spectrophotometry, alignment diagram was set up by estimating subordinate amplitudes at 405 nm (zero-intersection point of In(III)- DMPHBH complex).

RESULTS AND DISCUSSION

Absorption Spectra

The ingestion spectra of DMPHBH and its Sn(II) complex under the ideal conditions are appeared in Figure 2. The Sn(II)- DMPHBH complex shows greatest absorbance at 430 nm where the reagent clear doesn't retain apparently.

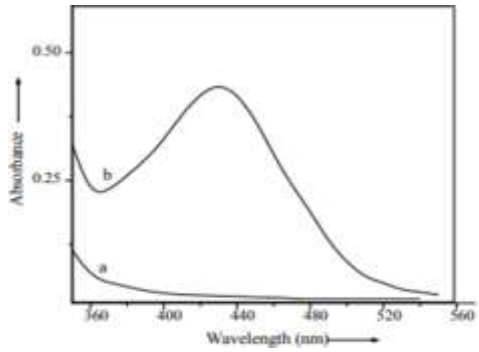

Figure 2. Absorption (zero order) spectra: (a) Reagent blank, (b) Sn(II) - DMPHBH system of 1.2 µg mL-1 of Sn(II); each containing 2 mL of 10% ascorbic acid, 2 mL of 0.2 M HCl, 0.5 mL of 0.1% DMPHBH and 1.5 mL of 1% CPC in a total volume of 10 mL.

Effect of Experimental Variables

Primer examinations have shown that DMPHBH responds with Sn(II) in watery acidic medium within the sight of cetylpyridinium chloride at room temperature to frame yellow hued species. A lethargic reduction in absorbance was noticed for the shaded species following 15 minutes. As tin(II) is oxidized to tin(IV) in air, a decreasing specialist ought to be added to forestall oxidation. Impact of different decreasing specialists, for example, ascorbic corrosive, thioglycollic corrosive and hydroxylamine hydrochloride has been examined to acquire most extreme security and power. Ascorbic corrosive (2 mL of 10 %) was discovered to be most for appropriate for this insightful work. The absorbance esteem stayed consistent in any event for 5 hours. The impact of various acids on the absorbance of Sn(II)- DMPHBH species has been researched utilizing HCl, HNO3, H2SO4 and CH3COOH. These shaded species are insecure in nitric corrosive and in sulphuric corrosive and don't give most extreme shading power in acidic corrosive medium. HCl medium (0.03 M-0.06 M) was discovered to be ideal for this scientific work in view of higher affectability and longer solidness of the shaded species. Consequently 2 mL of 0.2 M HCl in a complete volume of 10 mL was liked for additional insightful examinations. A 10-crease molar overabundance of DMPHBH is discovered to be essential for most extreme and steady shading improvement. Overabundance of reagent had no impact on the affectability and soundness of the complex. The impact of different surfactants, for example, Triton X-100 (impartial surfactant), sodium lauryl sulfate, SLS (anionic surfactant), cetylpyridinium chloride, CPC and cetyltrimethylammonium bromide, CTAB (cationic surfactants) on the ingestion profiles of the framework has been researched. Within the sight of CPC, the chelate displayed most extreme molar absorptivity (Table 1). Thus CPC has been chosen to improve the affectability and strength of the shaded species and 1.5 mL of 1 % CPC was discovered to be ideal for this insightful work.

Table 1. Influence of different surfactants on the absorbance of Sn(II)-DMPHBH complex.

Surfactant (0.15%)	Type	Sn(II)-DMPHBH	
		λ (nm)	Absorbance
None	-	428	0.279
Triton X-100	Neutral	428	0.276
CPC	Cationic	430	0.314
CTAB	Cationic	430	0.301
SLS	Anionic	426	0.263

Condition: [Sn(II)]= 1.20 µg mL-1; 2.0 mL of 10% ascorbic acid; 2 mL of 0.2 M HCl; 0.5 mL of 0.1% DMPHBH in a total volume of 10 mL.

Calibration Graphs and Analytical Parameters

The molar absorptivity and Sandell's affectability upsides of Sn(II)- DMPHBH species determined from Beer's law information are 3.2x104 L mol-1 cm-1 and 3.6 ng cm-2 individually. Lager's law is complied in the focus range 0.25-2.76 µg mL-1. The straight relapse examination of absorbance, [A] at λmax of the complex versus metal particle focuses (µg mL-1), shows a decent direct fit (Table 2).First request subsidiary spectra of Sn(II)- DMPHBH complex shows a top at 400 nm, a box at 480 nm and a get over point at 430 nm, relating to the λmax of the unpredictable (Figure 3).

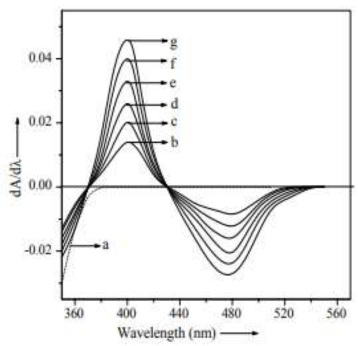

Figure 3. First order derivative spectra of Sn(II)-DMPHBH system: (a) Reagent blank, (b-g) contain increasing amounts of Sn(II) in the concentration range 0.18-3.20 µg mL-1 and all other conditions as in figure 2.

The subsidiary amplitudes estimated at 400 nm and 480 nm were discovered to be relative to the centralization of Sn(II). The qualities of adjustment diagrams are given in Table 2. The high worth of connection coefficient and closeness of the block to zero show that alignment charts are straight and comply with Beer's law. Direct plots are acquired in the fixation range 0.18-3.2 µg mL-1 and 0.22-3.2 µg mL-1 of Sn(II) at 400 and 480 nm separately.

Table 2. Photometric parameters and calibration data for the determination of Sn(II)

Parameter	Normal (430 nm)	First derivative	
		400 nm	480 nm
Detection Limit C_L(k=3) (µg mL^{-1})	$7.27x10^{-2}$	$3.48x10^{-2}$	$6.18x10^{-2}$
Quantitation Limit C_Q(k=10) (µg mL^{-1})	$2.42x10^{-1}$	$1.16x10^{-1}$	$2.06x10^{-1}$
Regression equation y^a			
Slope, b	$2.475x10^{-1}$	$1.72x10^{-2}$	$1.01x10^{-2}$
Intercept, a	$9x10^{-3}$	$5.7x10^{-4}$	$8.0x10^{-4}$
Correlation coefficient, r	0.9998	0.9999	0.9995
RSD %	1.14	0.56	0.83

A y= a + bx where y, absorbance/peak height/trough depth; b, slope; a, intercept; x, analyte concentration.

Breaking point of recognition CL (k=3) and cutoff of measurement CQ (k=10) in typical and subordinate modes are accounted for in Table 2. The accuracy of the strategy in various modes, detailed as relative standard deviations, RSD controlled by estimating absorbance or subsidiary sufficiency of five duplicate examples containing 1.2 μg mL-1 of Sn(II). In light of the better affectability and reproducibility, estimation of subsidiary amplitudes at 400 nm is suggested for the assurance of tin composite examples.

Stoichiometry and Stability Constant

The stoichiometry of the complex was examined by Job's consistent variety strategy and mole proportion technique and was discovered to be 1:2 (metal: ligand). The idea of the species was examined by passing an aliquot of the arrangement through a cation (Amberlite IR 120) and an anion (Amberlite IRA 400) trade gum. Just cation trade tar held the hued species, demonstrating the cationic idea of the species. A cautious examination of the IR range of the Sn(II)- DMPHBH complex with that of DMPHBH showed that DMPHBH goes about as a bidentate ligand. The chelate development through N iotas is affirmed by the change in νC=N to bring down frequencies (15-20 cm-1) when contrasted with ligand (νC=N = 1580 cm-1 and 1608 cm-1). νC=O and νOH&NH groups stayed unaltered in the metal buildings exhibiting noninvolvement of these gatherings in coordination. The νN-O band movements to a higher recurrence and showed up at 1043 cm-1. This proposes the N-coordination of the oxime bunch. The most plausible design of the chelate is given in Figure 4.

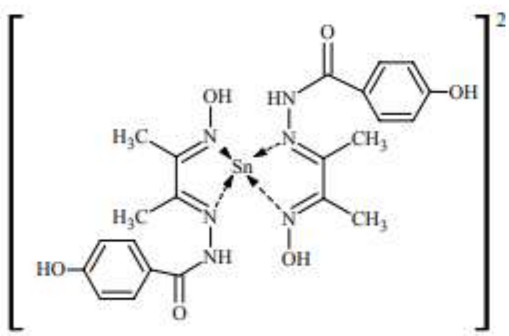

Figure 4. Proposed structure of Sn(II)-DMPHBH complex.

The stability constant of complex was determined by limiting logarithmic method28 and was found to be 2.6×108.

Effect of Diverse Ions

To survey the handiness of the proposed technique the impact of assorted particles on the follow level assurance of tin (1.2 μg mL-1) has been examined in typical and subsidiary modes. As far as possible was taken to be the sum that caused a ±3% change in absorbance. The resistance furthest reaches of the unfamiliar particles tried are given in Table 3. Cations of metals like Fe, Cu, Al, Pb, Cd, Zn and Bi, which are normally connected with tin containing tests didn't meddle in the assurance of Sn(II) in both zero request and subsidiary modes. Hg(II) could be endured when present in hundred-crease overabundance. The most genuine obstruction was from In(III) particles. The impedance because of the presence of In(III) particles in the assurance of tin could be overwhelmed by utilizing the subsidiary mode.

ANALYTICAL APPLICATIONS OF THE METHOD

Determination of Tin in Standard Alloy Samples

About 0.5 g of composite example was weighed precisely, treated with least measure of water regia until the example broke down totally and afterward warmed to exhaust of oxides of nitrogen. After it was cooled, 10 mL concentrated H2SO4 was added and vanished nearly to dryness. We rehashed the vanishing and H2SO4 treatment multiple times to eliminate all the HNO3. The buildup left over was treated with 20 mL of refined water and sifted through Whatman channel paper No.40. The filtrate was gathered in a 250 mL volumetric cup and made sufficient with refined water. The example arrangement was suitably weakened to acquire the fixation in the necessary reach. Reasonable aliquots were taken and broke down for tin utilizing the proposed methodology. The outcomes got are in acceptable concurrence with the affirmed esteems (Table 4).

Table 4. Determination of tin in standard alloy samples

Sample.	Composition (%)	Tin ($\mu g\ mL^{-1}$)		RSD %
		Certified value	Found[a]	
BCS 364	Cu, 80; Sn, 9.35; Pb, 9.25; Ni, 0.28; Sb, 0.18; Zn, 0.13; As, 0.065; P, 0.056; Al, 0.002; Si, 0.003.	1.12 1.87	1.140 1.880	1.05 0.79
Gun metal	Zn, 1.37; Sn, 9.22; Cu, 87.95; Pb, 1.13; Fe, 0.01; P, 0.07; Ni, 0.24.	1.10 2.02	1.120 2.015	0.71 0.49
SRM 127b Solder	Ag, 0.01; Cu, 0.011; Ni, 0.012; As, 0.01; Sn, 39.3; Sb, 0.43; Bi, 0.06; Pb, 60.16.	1.57 2.35	1.580 2.340	1.13 0.85
SRM 54d Tin-base alloy	Ag, 0.0032; Pb, 0.62; Sn, 88.57; Sb, 7.04; Bi, 0.044; Cu, 3.62; Fe, 0.027; Ni, 0.0027.	1.06 1.77	1.070 1.785	0.75 0.67

[a] mean value of five determinations

Table 5. Determination of tin in synthetic mixtures of tin-and lead- base alloy samples and low melting alloys

Sample.	Composition (%)	Tin ($\mu g\ mL^{-1}$)		RSD %
		Certified value	Found[a] (Recovery %)	
Tin alloy (ANSI/ASTM B32; Grade 96TS)	Sn, 96.0; Pb, 0.2; As, 0.05; Cu, 0.08; Ag,0.36; Fe, 0.02 Al, 0.005; Zn, 0.005.	1.44 2.40	1.460 (101.3) 2.380 (99.2)	1.02 0.92
Tin alloy (ANSI/ASTM B32; Grade 63A)	Sn, 63.0; Pb, 37.0; As, 0.03; Cu, 0.08; Fe, 0.02; Al, 0.005; Zn, 0.005	1.26 1.89	1.280 (101.5) 1.870 (98.9)	1.17 0.75
Lead alloy (ANSI/ASTM B32; Grade 20B)	Pb, 85.0; As, .02; Sn, 15.0; Cu, 0.08; Fe,0.02; Al, 0.005; Zn, 0.005.	1.35 1.80	1.330 (98.5) 1.815 (100.8)	1.12 0.66
Lead alloy (ANSI/ASTM B32; Grade 35C)	Pb, 65.2; As,0.02; Sn,35.0; Cu,0.08; Fe,0.02; Al, 0.005; Zn, 0.005.	1.05 1.75	1.060 (100.9) 1.770(101.1)	0.85 1.14
Ostalloy No. 117[b]	In, 19.1; Sn, 8.30; Bi, 44.7; Pb, 22.60; Cd,5.3.	1.00 1.66	1.010 (101.0) 1.650 (99.3)	0.89 0.96
Ostalloy No. 136[b]	In, 21.0; Sn, 12.0; Bi, 49.0; Pb, 18.0.	1.20 2.40	1.190 (99.2) 2.420 (100.8)	0.75 0.82
Ostalloy No. 178[b]	In, 29.6; Sn, 16.30; Bi, 54.1.	1.63 2.44	1.640 (100.6) 2.460 (100.8)	0.79 0.81
Ostalloy No. 200[b]	In, 44.0; Sn, 42.0; Cd,14.0.	1.26 2.10	1.245 (98.8) 2.120 (100.9)	1.10 0.47

[a] mean value of five determinations.
[b] measurement in the first derivative mode at 405 nm.

Determination of tin in synthetic alloy samples

The proposed strategy has been effectively applied for the assurance of tin in some manufactured examples that had pieces as indicated by lead-and tin-base alloys29 and some fusible or low softening amalgams. The outcomes are given in Table 5. The great arrangement between these outcomes and the realized qualities show the fruitful pertinence of the proposed technique for the assurance of tin in presence of indium in different fusible combinations and in complex examples.

CONCLUSION

The proposed strategy offers the benefits of high affectability, selectivity and effortlessness for the assurance of Sn(II) without the requirement for natural dissolvable extraction, pre-focus or pre-detachment. The proposed strategy can be utilized as an elective technique for the assurance of follow measures of tin in different amalgams as the related metal particles in these materials don't meddle with the assurance.

REFERENCES

[1] S. B. Adeloju, F. Pablo, Anal. Chim. Acta 1992, 270, pp. 143–152.

[2] G. Weber, Fresenius Z. Anal. Chem. 1985, 321, pp. 217–224.

[3] B. Chen, Q. Zhang, H. Minami, M. uto, S. Inoue, Anal. Lett. 2000, 33, pp. 2951–2961.

[4] Singh, R. Saini, Ann. Chim. 1995, 85, pp. 193–198.

[5] R. Saran, N. K. Baishya, S. Roy, Chem. Anal. (Warsaw) 2002, 47, pp. 131–138.

[6] J. Aznarez, J. M..Rabadan, A. Ferrer, P. Cipres, Talanta 1986, 33, pp. 458–460.

[7] G. Somer, A. Arslantas, Analyst 1994, 119, pp. 1257–1260.

[8] G. Ekmekci, R. Inam, G. Somer, Anal. Sci. 2000, 16, pp. 1151–1155.

[9] C. Spinola Costa, L. S. G. Teixeira, S. L. C. Ferreira, Talanta 1995, 42, pp. 1973–1978.

[10] L. F. Capitan-Valley, M. C. Valencia, G. Miron, Anal. Chim. Acta 1994, 289, pp. 365–370.

[11] D. Wang, Z. Xie, Q. Wu, Y. Song, S. Jin, Analyst 1991, 116, pp. 1189–1193.

[12] H. Kurihara, H. Kuwabara, Bunseki Kagaku 1984, 33, pp. 199–202.