Scientific Paper

Highly Selective Derivative Spectrophotometric Determination of Tin (II) in Alloy Samples in the Presence of Cetylpyridinium Chloride

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Abstract

A simple, selective and sensitive spectrophotometric method has been developed for the determination of tin(II) using a newly synthesised reagent diacetylmonoxime *p*-hydroxybenzoylhydrazone in cationic micellar medium. The molar absorptivity and Sandell's sensitivity of the coloured species are 3.20×10^{4} L mol^{-1} cm^{-1} and 3.6 ng cm^{-2} respectively. Beer's law is obeyed between 0.25-2.76 μg mL^{-1} of Sn(II)) at 430 nm. The stoichiometry of the complex was found to be 1:2 (metal: ligand). A highly selective first order derivative spectrophotometric method for the determination of tin is also reported. The developed procedure has been successfully applied for the determination of tin in various alloy samples and synthetic mixtures of some low melting alloys.

Key words: tin, diacetylmonoxime *p*-hydroxybenzoylhydrazone, micellar medium, derivative spectrophotometry

1. Introduction

Tin is extensively used as a coating element for steels and as an alloying agent in a wide variety of metal compositions. The principal use of tin in electronics is in the solders for the joining of electronic components. It may be introduced into the human environment either as inorganic tin or as organic tin compounds; through they used as fungicides in crops, in food packaging, in some veterinary formulations, in wood preservation, as stabilizer for polyvinylchloride and as electrochemical catalysts.[1] It has been reported that canned foods or plastic packing materials can lead to increased tin levels in human tissues. Acute tin poisoning is characterized by eye and skin irritations, headache, stomach ache and severe sweating.[2] Therefore it is of great importance to establish a highly accurate and sensitive method for the determination of tin at microgram levels in various sample materials. The most commonly used methods include spectrophotometry,[3-5] atomic absorption spectrometry with hydride generation,[6] and electrochemical analysis[7,8] based on polarography or stripping voltammetry. Of these, spectrophotometric methods occupy a special position due to their simplicity, less expensive instrumentation and high sensitivity. A large number of spectrophotometric reagents such as pyrocatechol violet,[9,10] phenylfluorone,[11,12] bromopyrogyallol red,[13] pyrimidine azo compounds,[14] potassium ethyl xanthate,[15] ferron,[16] *N,N*-diphenylbenzamidine,[17] isoamyl xanthate,[18] calcein[19] and trimethoxy phenylfluorone[20] have been reported for the determination of tin(II, IV) content. Among these methods pyrocatechol violet and phenylfluorone have been widely used for the determination of tin in alloys, minerals and canned foods.[21] They are non-selective chromogenic reagents which form coloured chelates with many other metal ions. Normally most of these methods are not simple and require extensive and laborious steps for the separation of tin from the matrices using procedures such as ion exchange,[10] extraction,[15-18] co-precipitation of tin[22] or the addition of suitable masking agents.[4,9] In the proposed method the use of micellar system enables the measurement in an aqueous medium, thereby avoiding the extraction steps while the derivatisation of the spectral profiles enhances the selectivity of the method as closely overlapped absorption bands of the interfering ions become resolved.[23-26]

In the present investigation we report a simple, sensitive and non extractive derivative spectrophotometric determination of Sn(II) using a newly synthesised reagent diacetylmonoxime *p*-hydroxybenzoylhydrazone (DMPHBH) in the presence of cetylpyridinium chloride (CPC), a cationic surfactant. The distinct advantage of the proposed method is that the commonly associated metal ions especially Fe, Cu, Al, Pb, Cd, Zn and Bi do not interfere in the determination of Sn(II) unlike the reported methods.[15-18] Tin and Indium are the main constituents of number of fusible or low melting alloys. Tin doped indium oxide is a transparent conducting material, which is used to make electronic devices such as liquid crystal displays (LCDs). Therefore it is of great interest to determine tin in the presence of indium. A method of selective determination of Sn(II) in the presence of In(III) without any pre-separation is also reported. Impacts of varying parameters such as effect of acids, concentration of surfactant and reagents on the absorbance and the stability of the complex have been studied. The developed procedure has been successfully applied for the determination of tin in various alloy samples and synthetic mixtures of some low melting alloys.

2. Experimental

2.1. Apparatus

A Shimadzu 1601 UV/VIS. Spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimised and the best results were obtained with a scan speed 145 nm/min., slit width of 1 nm and $\Delta\lambda = 2$ nm for the first order derivative mode in the wavelength range 350–650 nm. A Systronics μ pH system 362 was used for pH measurements.

2.2. Reagents

All chemicals used were of analytical grade. A stock solution of tin(II) (1000 μg mL^{-1}) was prepared by dissolving accurately weighed $SnCl_2$. $2H_2O$ (S.D. Fine-Chem. Ltd. India) in 1mL of concentrated hydrochloric acid and made up to the mark in a 100 mL volumetric flask. This stock solution was standardised[27] and working solutions were prepared by diluting the stock solution to an appropriate volume. Solutions of the studied interfering ions of suitable concentrations were prepared using A.R. grade reagents. Aqueous solutions of 1% cetylpyridinium chloride (CDH Pvt.Ltd. India) and 10% ascorbic acid (SRL Pvt.Ltd., India) were prepared in distilled water. A 0.1% solution of DMPHBH was prepared in ethanol. A 0.2 M HCl was also prepared.

2.3. Synthesis and Characterization of DMPHBH

Diacetylmonoxime *p*-hydroxybenzoylhydrazone was synthesised by refluxing equimolar amounts of diacetylmonoxime and *p*-hydroxybenzoylhydrazide in ethanolic medium for 2 hours. The resulting 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, DMSO-d_6) 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). Anal. 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 structural formula of DMPHBH is given in Figure 1.

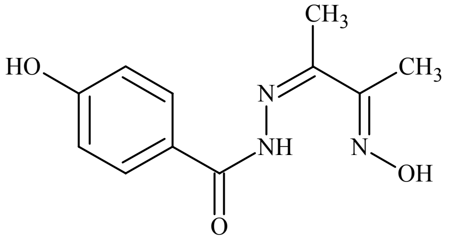

Figure 1. Structural formula of DMPHBH.

2.4. General Procedure

In each of a set of 10 mL standard flasks, varying amounts of Sn(II), 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% cetylpyridinium chloride were added and diluted to the mark with distilled water. The absorbances were measured at 430 nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of Sn(II) ions.

2.5. First Derivative Spectrophotometry

For the above set of solutions first order derivative spectra were recorded with reference to the reagent blank in the wavelength range 350-650 nm. In the derivative spectrum peak height (PH) at 400 nm or trough depth (TD) at 480 nm was measured from the zero line of the spectrum to determine its dependence on the metal ion concentration. Calibration graphs were constructed by plotting the derivative amplitude against the concentration of Sn(II) ions. For the determination of Sn(II) in presence of In(III) ions by using first order derivative spectrophotometry, calibration graph was prepared by measuring derivative amplitudes at 405 nm (zero-crossing point of In(III)-DMPHBH complex).

3. Results and Discussion

3.1. Absorption Spectra

The absorption spectra of DMPHBH and its Sn(II) complex under the optimum conditions are shown in Figure 2. The Sn(II)-DMPHBH complex shows maximum absorbance at 430 nm where the reagent blank does not absorb appreciably.

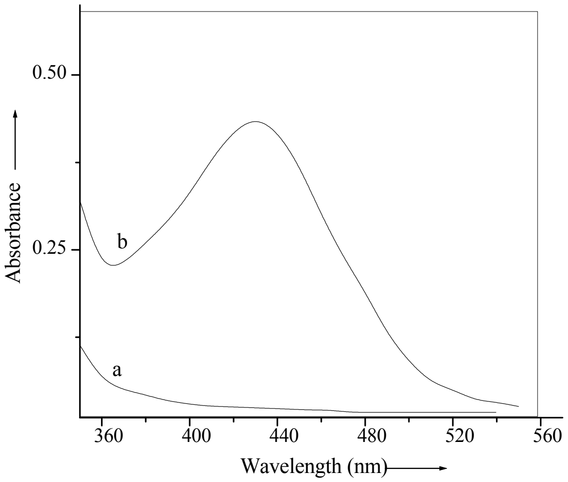

Figure 2. Absorption (zero order) spectra: (a) Reagent blank, (b) Sn(II) - DMPHBH system of 1.2 μg mL^{-1} of Sn(II); each containing 2 mL of 10% ascorbic acid, 2 mL of 0.2 M HCl, 0.5 mL of 0.1% DMPHBH and 1.5 mL of 1% CPC in a total volume of 10 mL.

3.2. Effect of Experimental Variables

Preliminary investigations have shown that DMPHBH reacts with Sn(II) in aqueous acidic medium in the presence of cetylpyridinium chloride at room temperature to form yellow coloured species. A slow decrease in absorbance was observed for the coloured species after 15 minutes. As tin(II) is oxidised to tin(IV) in air, a reducing agent should be added to prevent oxidation. Effect of various reducing agents such as ascorbic acid, thioglycollic acid and hydroxylamine hydrochloride has been investigated to obtain maximum stability and intensity. Ascorbic acid (2 mL of 10 %) was found to be most for suitable for this analytical work. The absorbance value remained constant at least for 5 hours.

The effect of different acids on the absorbance of Sn(II)-DMPHBH species has been investigated using HCl, HNO_3, H_2SO_4 and CH_3COOH. These coloured species are unstable in nitric acid and in sulphuric acid and do not give maximum colour intensity in acetic acid medium. HCl medium (0.03 M-0.06 M) was found to be optimum for this analytical work because of higher sensitivity and longer stability of the coloured species. Hence 2 mL of 0.2 M HCl in a total volume of 10 mL was preferred for further analytical studies.

A 10-fold molar excess of DMPHBH is found to be necessary for maximum and constant colour development. Excess of reagent had no effect on the sensitivity and stability of the complex. The effect of various surfactants such as Triton X-100 (neutral surfactant), sodium lauryl sulphate, SLS (anionic surfactant), cetylpyridinium chloride, CPC and cetyltrimethylammonium bromide, CTAB (cationic surfactants) on the absorption profiles of the system has been investigated. In the presence of CPC, the chelate exhibited maximum molar absorptivity (Table 1). Hence CPC has been selected to improve the sensitivity and stability of the coloured species and 1.5 mL of 1 % CPC was found to be optimum for this analytical 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.

3.3. Calibration Graphs and Analytical Parameters

The molar absorptivity and Sandell's sensitivity values of Sn(II)-DMPHBH species calculated from Beer's law data are 3.2×10^4 L mol^{-1} cm^{-1} and 3.6 ng cm^{-2} respectively. Beer's law is obeyed in the concentration range 0.25-2.76 μg mL^{-1}. The linear regression analysis of absorbance, [A] at λ_{max} of the complex versus metal ion concentrations (μg mL^{-1}), shows a good linear fit (Table 2).First order derivative spectra of Sn(II)-DMPHBH complex shows a peak at 400 nm, a trough at 480 nm and a cross over point at 430 nm, corresponding to the λ_{max} of the complex (Figure 3).

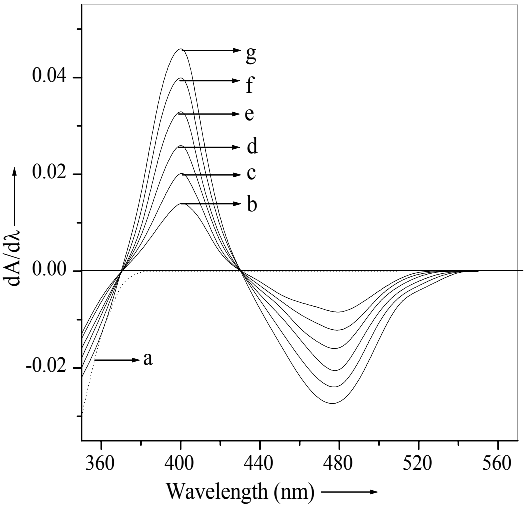

Figure 3. First order derivative spectra of Sn(II)-DMPHBH system: (a) Reagent blank, (b-g) contain increasing amounts of Sn(II) in the concentration range 0.18-3.20 μg mL^{-1} and all other conditions as in figure 2.

The derivative amplitudes measured at 400 nm and 480 nm were found to be proportional to the concentration of Sn(II). The characteristics of calibration graphs are given in Table 2. The high value of correlation coefficient and closeness of the intercept to zero show that calibration graphs are linear and obey Beer's law. Linear plots are obtained in the concentration range 0.18-3.2 μg mL^{-1} and 0.22-3.2 μg mL^{-1} of Sn(II) at 400 and 480 nm respectively.

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.

Limit of detection C_L (k=3) and limit of quantification C_Q (k=10) in normal and derivative modes are reported in Table 2. The precision of the method in different modes, reported as relative standard deviations, RSD determined by measuring absorbance or derivative amplitude of five replicate samples containing 1.2 μg mL^{-1} of Sn(II). Based on the better sensitivity and reproducibility, measurement of derivative amplitudes at 400 nm is recommended for the determination of tin alloy samples.

3.4. Stoichiometry and Stability Constant

The stoichiometry of the complex was investigated by Job's continuous variation method and mole ratio method and was found to be 1:2 (metal: ligand). The nature of the species was investigated by passing an aliquot of the solution through a cation (Amberlite IR 120) and an anion (Amberlite IRA 400) exchange resin. Only cation exchange resin retained the coloured species, indicating the cationic nature of the species.

A careful comparison of the IR spectrum of the Sn(II)-DMPHBH complex with that of DMPHBH showed that DMPHBH acts as a bidentate ligand. The chelate formation through N atoms are confirmed by the shift in $\nu_{C=N}$ to lower frequencies (15-20 cm^{-1}) as compared to ligand ($\nu_{C=N}$ = 1580 cm^{-1} and 1608 cm^{-1}). $\nu_{C=O}$ and $\nu_{OH\&NH}$ bands remained unchanged in the metal complexes demonstrating non involvement of these groups in coordination. The $\nu_{N\text{-}O}$ band shifts to higher frequency and appeared at 1043 cm^{-1}. This suggests the N-coordination of the oxime group.

The most probable structure of the chelate is given in Figure 4.

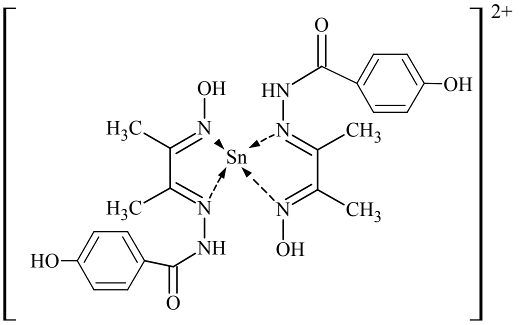

Figure 4. Proposed structure of Sn(II)-DMPHBH complex.

The stability constant of complex was determined by limiting logarithmic method[28] and was found to be 2.6×10^8.

3.5. Effect of Diverse Ions

To assess the usefulness of the proposed method the effect of diverse ions on the trace level determination of tin (1.2 μg mL^{-1}) has been investigated in normal and derivative modes. The tolerance limit was taken to be the amount that caused a ±3% change in absorbance. The tolerance limits of the foreign ions tested are given in Table 3. Cations of metals like Fe, Cu, Al, Pb, Cd, Zn and Bi, which are usually associated with tin containing samples did not interfere in the determination of Sn(II) in both zero order and derivative modes. Hg(II) could be tolerated when present in hundred-fold excess. The most serious interference was from In(III) ions. The interference due to the presence of In(III) ions in the determination of tin could be overcome by using the derivative mode.

Table 3. Tolerance limit of diverse ions in the determination of 1.2 μg mL^{-1} of tin(II).

Ions	Tolerance limit (μg mL^{-1})
Chloride, bromide, nitrate, phosphate, sulphate, fluoride, oxalate, acetate	< 4500
Na(I), K(I), Mg(II), Ba(II), Ca(II), Sr(II), Al(III), W(VI), Cr(III), Zr(IV), Mo(VI)	≤ 900
Co(II), Ni(II), Mn(II), Zn(II), Cd(II), Pb(II), Bi(III), Fe(III)	≤600
Cu(II), V(V)	≤ 500
Hg(II)	120
Ti	25 (150)^a

[a] in presence of 1 mg mL^{-1} of fluoride.

Determination of Sn(II) in presence of In(III) using first derivative spectrophotometry

In(III) forms coloured species on interaction with DMPHBH having maximum absorbance at 405 nm. The determination of Sn(II) in presence of In(III) by conventional spectrophotometry was difficult since the spectral profiles of these species in zero order modes overlap with each other significantly. The selectivity of the method is considerably enhanced by recording spectra in the derivative mode in which closely overlapped absorption profiles in the normal mode of the analyte (Sn(II)) and the interfering ions (In(III)) get resolved into separate peaks, troughs and cross-over points as shown in Figure 5.

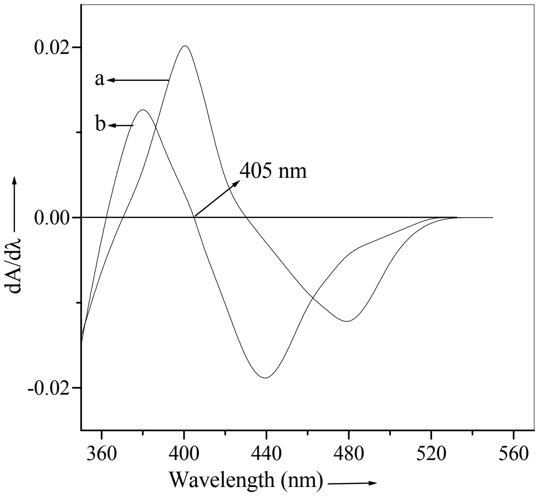

Figure 5. First order derivative spectra of Sn(II)-DMPHBH and In-DMPHBH complexes.
(a).1.2 µg mL^{-1} of Sn(II), (b) 0.9 µg mL^{-1} of In(III) and all other conditions as in figure 2.

The calibration graph for the determination of Sn(II) in presence of In(III) ions was constructed by measuring the derivative amplitudes (peak height) at 405 nm (zero crossing point of In(III)-DMPHBH complex). The derivative amplitudes measured at 405 nm were found to be independent of concentration of In(III). This was confirmed by the construction of calibration graphs for the standards containing Sn(II) alone and in the presence of In(III) ions. The linear regression analysis of the change in derivative amplitudes versus the analyte concentration gives the following equations. Correlation coefficient values are given in parenthesis.

$$[\mathrm{PH}]_{405\ \mathrm{nm}} = 1.52\mathrm{x}10^{-2}\ [\mathrm{Sn(II)}] + 4.5\mathrm{x}10^{-4}\ (0.9997) \qquad (1)$$

$$[\mathrm{PH}]_{405\ \mathrm{nm}} = 1.53\mathrm{x}10^{-2}\ [\mathrm{Sn(II)}] + 5.2\mathrm{x}10^{-4}\ (0.9995) \qquad (2)$$

Equation (2) represents linear regression analysis of calibration graph in presence of 0.90 µg mL^{-1} indium. Thus by measuring the derivative amplitudes at 405 nm the interference due to indium can be eliminated up to 10-fold excess without any pre-separation or addition of masking agents.

4. Analytical applications of the method

4.1. Determination of Tin in Standard Alloy Samples

About 0.5 g of alloy sample was weighed accurately, treated with minimum amount of aqua regia until the sample dissolved completely and then heated to fumes of oxides of nitrogen. After it was cooled, 10 mL concentrated H_2SO_4 was added and evaporated almost to dryness. We repeated the evaporation and H_2SO_4 treatment three times to remove all the HNO_3. The residue left over was treated with 20 mL of distilled water and filtered through Whatman filter paper No.40. The filtrate was collected in a 250 mL volumetric flask and made up to the mark with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range. Suitable aliquots were taken and analysed for tin using the proposed procedure. The results obtained are in good agreement with the certified values (Table 4).

Table 4. Determination of tin in standard alloy samples

Sample.	Composition (%)	Tin (µg 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 (µg 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	1.460 (101.3)	1.02
		2.40	2.380 (99.2)	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	1.280 (101.5)	1.17
		1.89	1.870 (98.9)	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	1.330 (98.5)	1.12
		1.80	1.815 (100.8)	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	1.060 (100.9)	0.85
		1.75	1.770(101.1)	1.14
Ostalloy No. 117[b]	In, 19.1; Sn, 8.30; Bi, 44.7; Pb, 22.60; Cd,5.3.	1.00	1.010 (101.0)	0.89
		1.66	1.650 (99.3)	0.96
Ostalloy No. 136[b]	In, 21.0; Sn, 12.0; Bi, 49.0; Pb, 18.0.	1.20	1.190 (99.2)	0.75
		2.40	2.420 (100.8)	0.82
Ostalloy No. 178[b]	In, 29.6; Sn, 16.30; Bi, 54.1.	1.63	1.640 (100.6)	0.79
		2.44	2.460 (100.8)	0.81
Ostalloy No. 200[b]	In, 44.0; Sn, 42.0; Cd,14.0.	1.26	1.245 (98.8)	1.10
		2.10	2.120 (100.9)	0.47

[a] mean value of five determinations.

[b] measurement in the first derivative mode at 405 nm.

4.2. Determination of tin in synthetic alloy samples

The proposed method has been successfully applied for the determination of tin in some synthetic samples that had compositions according to lead- and tin- base alloys[29] and some fusible or low melting alloys. The results are given in Table 5. The good agreement between these results and the known values indicate the successful applicability of the proposed method for the determination of tin in presence of indium in various fusible alloys and in complex samples.

5. Conclusion

The proposed method offers the advantages of high sensitivity, selectivity and simplicity for the determination of Sn(II) without the need for organic solvent extraction, pre-concentration or pre-separation. The proposed method can be used as an alternative method for the determination of trace amounts of tin in various alloys as the associated metal ions in these materials do not interfere with the determination.

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7. References

1. S. B. Adeloju, F. Pablo, *Anal. Chim. Acta* **1992**, *270*, 143–152.
2. G. Weber, *Fresenius Z. Anal. Chem*. **1985**, *321*, 217–224.
3. B. Chen, Q. Zhang, H. Minami, M. uto, S. Inoue, *Anal. Lett.* **2000**, *33*, 2951–2961.
4. I. Singh, R. Saini, *Ann. Chim.* **1995**, *85*, 193–198.
5. R. Saran, N. K. Baishya, S. Roy, *Chem. Anal. (Warsaw)* **2002**, *47*, 131–138.
6. J. Aznarez, J. M..Rabadan, A. Ferrer, P. Cipres, *Talanta* **1986**, *33*, 458–460.
7. G. Somer, A. Arslantas, *Analyst* 1994, *119*, 1257–1260.
8. G. Ekmekci, R. Inam, G. Somer, *Anal. Sci.* **2000**, *16*, 1151–1155.
9. A. C. Spinola Costa, L. S. G. Teixeira, S. L. C. Ferreira, *Talanta* **1995**, *42*, 1973–1978.
10. L. F. Capitan-Valley, M. C. Valencia, G. Miron, *Anal. Chim. Acta* **1994**, *289*, 365–370.
11. D. Wang, Z. Xie, Q. Wu, Y. Song, S. Jin, *Analyst* **1991,** *116*, 1189–1193.
12. H. Kurihara, H. Kuwabara, *Bunseki Kagaku* **1984**, *33*, 199–202.
13. X. Huang, W. Zhang, S. Han, X. Wang, *Talanta* **1997**, *44*, 817–822.
14. A. S. Amin, *Ann. Chim.* **2002**, *92*, 729–739.
15. S. P. Arya, A. Bansal, *Mikrochim. Acta* **1994,** *116*, 63–67.

16. S. P. Arya, S. C. Bhatia, A. Bansal, *Fresenius' J. Anal. Chem*. **1993**, *345*, 679–682.
17. A. R. Chakraborty, K. S. Patel, R. K. Mishra, *Int. J. Environ. Anal. Chem.* **1991**, *45*, 229–233.
18. S. P. Arya, S. C. Bhatia, A. Bansal, M..Mahajan, *J. Indian Chem. Soc*. **2002**, *79*, 359–360.
19. D. G. Li, Z. M. lou, C. Yang, H. Y. Liang, *Fenxi Kexue Xuebao* **2004**, *20*, 72–74.
20. W. Cao, J. H. Yang, X. E. Wang, C. Liu, G. L. Yin, *Fenxi Shiyanshi*, **2004**, *23*, 39–41.
21. Z. Marczenko *Separation and spectrophotometric determination of elements,* John Wiley and sons 1973, chapter 55.
22. S. Ambujavally, N. Premavathi, *Anal. Chem.* **1976,** *48,* 2152–2154.
23. T. C. O' Haver, G. L. Green, *Anal. Chem*. **1976,** *48,* 312–318.
24. N. K. Agnihotri, V. K. Singh, R. Ratnani, S. K. Sukla, G. K. Parashar, *Anal. Lett*. **2004**, *37*, 2515–2529.
25. C. B. Ojeda, F. S. Rojas, J. M. C. Pavon, *Talanta* **1995**, *42*, 1195–1214.
26. V. P. Gordana, B. P. Lidija, M. S. Violeta, *J. Serb. Chem. Soc*. **2000**, *65*, 457–472.
27. G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denney, *Vogel'sText Book of Quantitative chemical analysis*. 5th ed: Addison Wesley Longman Ltd. 1996, pp–329.
28. R. L. Moore, R. C. Anderson, *J. Am. Chem. Soc.* **1945**, *67*, 108–110.
29. Worldwide Guide to Equivalent Nonferrous Metals and Alloys, **1980**, American Society for Metals (ASM), USA.

Povzetek

Razvili smo enostavno, selektivno in občutljivo spektrofotometrično metodo za določevanje kositra(II) z uporabo novega sintetiziranega reagenta diacetilmonoksim *p*-hidroksibenzoil hidrazona v raztopini s kationskimi površinsko aktivnimi snovmi. Molarni ekstinkcijski koeficient pri valovni dolžini 430 nm in Sandellova občutljivost obarvanega kompleksa sta 3.20×10^4 L mol^{-1} cm^{-1} in 3.6 ng cm^{-2}. Beerov zakon velja za koncentracijsko območje 0.25-2.76 µg mL^{-1} Sn(II). Ugotovljeno je bilo stehiometrično razmerje kovina-ligand 1:2. Opisana je tudi derivativna spektrofotometrična metoda prvega reda z visoko selektivnostjo. Razvite postopke smo uspešno uporabili za določevanje kositra v različnih zlitinah in pripravljenih zmeseh zlitin z nizkim tališčem.