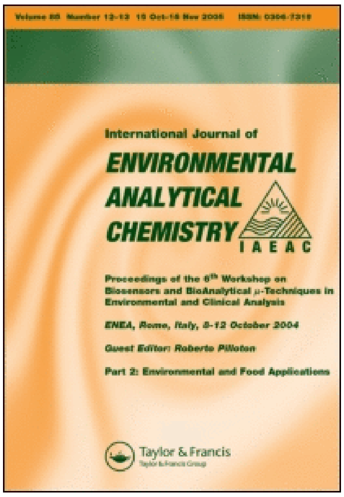

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF TIN IN ENVIRONMENTAL SAMPLES

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A highly selective and sensitive method for the spectrophotometric determination of tin(IV) in industrial waste waters is described. It is based on the selective extraction of tin(IV) with bromide into a chloroform solution of N,N'-diphenylbenzamidine(DPBA), and subsequent treatment with iodide. The molar absorptivity of the iodostannate complex formed is $(1.50) \times 10^4$ l mole^{-1} cm^{-1} at $\lambda_{max} = 385$ nm. The detection limit of the method is 0.1 ppm. The method is highly selective as none of the common metals and anions tested interfere.

KEY WORDS: Tin(IV) determination, extraction, Spectrophotometry, N,N'-diphenylbenzamidine, environmental sample analysis.

INTRODUCTION

Spectrophotometric methods for the determination of tin by extraction of tin(IV) with iodide into benzene, carbon tetrachloride or cyclohexane have been reported but they suffer from low sensitivity and selectivity[1–4]. Many organic reagents and dyes, such as dithiol[1], phenylfluorone[5], 9-hydroxyquinoline[6], bis-(2-ethylhexyl) hydrogen phosphate[7], 5,7-dichloroquinolin-8-ol[8], pyrocatechol violet[9], 1-(2-pyridylazo)-2-naphthol[10] and 5-ethyl-amino-2-(2-pyridylazo)-p-cresol[11], cinnamylfluorone and hexadecyltrimethylammonium bromide[12], catechol violet and hexadecylpryridinium bromide[13], poly(vinylpyrrolidinone)[14], thiocyanate and triphenylmethane dyes[15], disulphophenylfluorone[16], 4-nitrophenylfluorone[17], N-p-chlorophenyl-2-furo-hydroxamic acid[18] and 2,4-dichlorophenylfluorone and cetyltrimethylammonium bromide[19] have also been employed for the spectrophotometric determination of tin(IV). However, almost all the above methods lack selectivity and some of them sensitivity. In the present investigation tin(IV) is selectively extracted with N,N'-diphenylbenzamidine into chloroform as a bromostannate complex, and then the extract is equilibrated with iodide for sensitive spectrophotometric determination of the metal. The method has been applied for the determination of tin in environmental samples.

EXPERIMENTAL

An ECIL UV-VIS spectrophotometer GS-865 with matched quartz cells (1 cm) was used for absorbance measurements.

A standard solution of Sn(IV) was prepared by dissolving a weighed amount of tin metal in concentrated sulphuric acid, evaporating to dryness, and dissolving the residue in 0.07 M ammonium oxalate. Fresh solutions of potassium bromide (40%, w/v), potassium iodide (80%, w/v) and ascorbic acid (8%, w/v) were used. 10 M HCl and 10 M H_2SO_4 solutions were employed for extraction. DPBA was synthesized as reported in the literature[20]; a 0.1% w/v solution in chloroform was used. All chemicals used were of A. R. grade (E. Merck).

Extraction of Sn(IV) with iodide and DPBA

An aliquot of solution containing up to 200 μg Sn(IV) and 3 ml sulphuric acid is taken in a 100-ml separatory funnel and dipped in a thermostat having a temperature of 15 ± 2°C. The analyte is treated with 1 ml KI solution and 2 ml ascorbic acid solution, diluted to 10 ml with deionized water and shaken for 2 min. The chloroform layer is separated off and the aqueous layer is washed with 3 × 2 ml of chloroform. The total extract is dried over anhydrous sodium sulphate (2 g) in a 25-ml beaker, transferred to a 25-ml volumetric flask and chloroform is added up to the mark. The absorbance of the extract is measured at λ_{max} of the complex against the reagent blank.

Extraction of Sn(IV) with bromide and iodide with DPBA

A sample solution containing Sn(IV), 1 ml HCl and 2 ml KBr solution is taken in a 100-ml separatory funnel and diluted to 10 ml with deionized water. The aqueous solution is shaken with 10 ml chloroform solution of DPBA for 2 min and the chloroform extract is subsequently reacted with KI in another separatory funnel as in the above procedure.

RESULTS AND DISCUSSION

Extraction of Sn(IV) with bromide and DPBA

Tin is quantitatively extracted with bromide into a chloroform solution of DPBA using 0.3–3.0 M HCl; 0.17–3.4 M KBr is adequate for maximum extraction of the metal. At least 0.00054 M DPBA in chloroform is needed for the quantitative extraction of the metal. The absorption spectra of the bromostannate complex thus formed show nearly negligible absorption for wavelengths of 350–850 nm. The complex in the organic solution is stable for at least 10 h at room temperature (20 ± 2°C).

Extraction of Sn(IV) with iodide and DPBA

The absorption spectrum of the tin(IV) iodide complex in chloroform shows maximum absorption at 385 nm against a reagent blank. The molar absorptivity of the complex at λ_{max} is (1.50) × 10^4 l mole^{-1} cm^{-1}. Of various acids tested like HCl, H_2SO_4, HNO_3, only H_2SO_4 is adequate for quantitative extraction of the metal. The optimum acidity range is 2.5–4.0 M H_2SO_4. At least 0.45 M KI and 0.00036 M DPBA in chloroform are necessary for maximum extraction. Ascorbic acid is used to remove iodine liberated by any oxidizing species present in the solution. It must be added after complexation of the metal with iodide; up to 1.8 M its addition has no adverse effect. The extraction of the metal is not affected when the temperature of the aqueous phase is varied from 5 to 25°C. The extract is stable for at least 5 h at 20 ± 2°C.

Varying the volume ratio from 2:1 to 2:5 (V_{org}:V_{aq}) has no adverse effect on the absorbance of the extract. Various organic solvents like 1-pentanol, isobuylmethylketone, ethyl acetate, toluene, benzene, carbon tetrachloride and chloroform were tested for the extraction of the metal. Of these, chloroform was selected because of the high colour intensity and the stability of the tin-iodide complex formed. The stoichiometry of the complex was determined by plotting log D (distribution ratio of the metal) versus log molar concentration of KI and DPBA (in chloroform). The data obtained show the involvement of 5 I^- and 2 DPBA for each Sn(IV) to give the chloroform-extractable ion pair complex $[SnI_5]^- \cdot H^+ (DPBA)_2$. Of the common metal ions tested, only Fe^{3+}, Cu^{2+}, As^{3+}, Sb^{3+} and Ge^{4+} interfere seriously: if present at the same concentration level as Sn, they cause positive interferences due to co-extraction of their yellow coloured complexes under the experimental conditions mentioned above.

Extraction of Sn(IV) with bromide and iodide and DPBA

Tin(IV) is first extracted with bromide into a chloroform solution of DPBA, and the extract is allowed to react with iodide as discussed in the Experimental section. The absorption spectrum of the complex thus formed in chloroform has maximum absorption at 385–390 nm. The molar absorptivity of the complex at λ_{max} is (1.50) × 10^4 l mole^{-1} cm^{-1}. The system obeys Beer's law up to 8 ppm of Sn(IV). The detection limit of the method is 0.1 ppm. Ten replicate measurements at a level of 4 ppm Sn(IV) in the organic solution gave a relative standard deviation of ±1.5%.

Effects of diverse ions

The effect of diverse ions on the determination of 100 μg Sn(IV) was studied using the procedure outlined above. The ions seriously interfering in the Sn(IV)-I^--DPBA method do not interfere in the determination of the metal by the Sn(IV)-Br^--DPBA-I^- procedure as the co-extraction of their bromo complexes is practically negligible up to a 25-fold excess. The tolerance limits of various ions (in mg) causing an error of less than 2% are given in parentheses: Ag^+ (1), Pd^{2+}, Be^{2+}, La^{3+}, Sb^{3+} (2.5), Bi^{3+}, V^{5+}, NO_3^- (3), Se^{4+}, Mo^{6+}, Re^{7+}, Hg^{2+}, Nb^{5+} (1.0), Ir^{3+}, Pt^{4+}, U^{6+} (5),

Table 1 Determination of tin in industrial waste waters ($n = 5$)

*Sample**	*Sn added (ppm)*	*Total Sn found (ppm)*	*Actual Sn present (ppm)*	*RSD %*
a	2	3.75	1.75	1.3
b	2	3.05	1.05	1.5
c	2	2.80	0.80	1.2
d	3	3.50	0.50	1.4
e	3	3.10	0.10	1.1

* a, b, c d and e are waste waters from B.S.P., Bhilai; Singhania Steels; Advani Oerlikon; Kesari Metals and Swastik Wires, Raipur, respectively.

Ti^{4+}, Ru^{3+}, W^{6+} (6), Pb^{2+}, Zr^{4+}, $C_2O_4^{2-}$, EDTA (7.5), Co^{2+}, Fe^{3+} (9), Al^{3+} (12), Cu^{2+}, Cr^{3+}, Cd^{2+} (20), Ni^{2+}, Mn^{2+}, Zn^{2+} (35).

Application

The present method has been applied for the determination of tin in industrial waste water (Table 1). A known volume of the sample (400 ml) is taken and evaporated to about 10 ml and made up to 25 ml in a volumetric flask. 2–3 ml of this solution are taken and the tin content is determined with standard addition of the metal by the proposed Sn(IV)-Br^--DPBA-I^- procedure.

CONCLUSION

A novel, sensitive and highly selective spectrophotometric method for the determination of tin is proposed. It is based on the separation of the metal as bromo complex with DPBA prior to conversion into the iodo complex; this remarkably increases the selectivity of the conventional iodide method. Owing to its high selectivity, the method can be successfully used for accurate and precise determination of the metal in water samples.

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