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Spectrophotometric Determination of Nanogram Amounts of Tin after Extraction from Iodide Media

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A spectrophotometric method for the determination of trace amounts of tin is described. Tin was selectively extracted as SnI_4 into benzene and stripped into water. The stripping was treated with bromine water and the resulting iodate was treated with iodide to liberate iodine. The iodine was extracted into benzene and equilibrated with iodate in the presence of excess chloride and acid to produce ICl_2^- which was reextracted into benzene as ionpair with rhodamine 6G. Measurement of the benzene extract at 535 nm permitted the determination of tin when present in the concentration range 4—200 ng. The molar absorption coefficient was found to be 1.54×10^6 dm^3 mol^{-1} cm^{-1} and the color system is stable for 1 h. The relative standard deviation for ten determinations of 100 ng of tin was found to be 2.1%. The efficiency of the reaction sequence was found to be 96.2%. The method was found useful for the precise determination of tin in steel and alloy samples.

Ion associates of anionic complexes of metals with basic dyes have been found useful for the determination of many elements with high degree of sensitivity. Recently methods have been described for the determination of tin based on the formation of ionpair between tris(3nitroalizarinato)stannate(IV)–brilliant green,[1] hexathiocyanatostannate(IV)–rhodamine S/rhodamine 6Zh,[2] and tetrachlorostannate(II)–rhodamine 6G.[3] Though these color systems are sensitive they are not sufficiently selective and hence necessiate the preliminary separation of tin from accompanying elements.

Our attempts to develop a reliable alternative method for direct application to practical samples revealed that the interaction between ICl_2^- and rhodamine 6G cation can be exploited for the indirect determination of tin in the concentration range 4—200 ng. Tin was extracted as SnI_4 into benzene from 0.1 M (1 M=1 mol dm^{-3}) iodide solution acidified to 4 M with respect to H_2SO_4. After stripping the SnI_4 into 0.05 M H_2SO_4, oxidation of associated iodide to iodate using bromine water and treatment with excess iodide released 24 iodine atoms for each atom of tin initially present. The iodine produced, after extraction into benzene and equilibration with acidified solution of iodate in the presence of chloride and rhodamine 6G facilitated the formation of 30 ICl_2^- species equivalent to 30 dye molecules for each Sn(IV). The formed ionpair was extracted into benzene for spectrophotometric measurement at 535 nm. The method proposed is simple, rapid and works satisfactorily for the determination of tin in various alloys and steel samples.

Experimental

Apparatus. Absorbance were measured with Carl Zeiss PMQ(II) spectrophotometer with 10 mm quartz cells.

Reagents. Standard tin(IV) solution (1000 μg cm^{-3}): Prepared by dissolving 0.1 g of metal in 30 cm^3 of hot concentrated sulfuric acid. The solution was cooled and made upto 100 cm^3 with distilled water. Suitable volume of this solution was diluted to obtain working standards. *p*-Toluidine solution (2%): Prepared by dissolving 2 g of *p*-toluidine in 100 cm^3 of benzene.

The following solutions were prepared by dissolving appropriate amounts of reagents in distilled water.

Potassium iodate	0.01%
Rhodamine 6G	0.02%
Sodium chloride	15%
Potassium iodide	0.25 M and 1 M [In 1 M KI a few crystals of thiosulfate has incorporated]
Sulfuric acid	0.05 M, 4.5 M, 10 M
Sulfosalicylic acid	0.5%
Bromine water	5%

Thiophene free benzene was used for extraction.

Procedure. **Separation of Tin:** Transfer the sample solution (<75 cm^3) containing not more than 200 ng of Sn(IV) into a separatory funnel. Add enough sulfuric acid and KI to make their concentration 4 M and 0.1 M respectively. Shake the solution for one min with 5 cm^3 of benzene. Separate the organic phase and treat with 2 cm^3 of 2% *p*-toluidine in benzene. Shake the organic phase with 5 cm^3 of 4.5 M H_2SO_4 for 1 min. Discard the aqueous layer. Equilibrate the benzene layer with 10 cm^3 of 0.05 M H_2SO_4 for 1 min. Retain the aqueous layer and discard the organic layer.

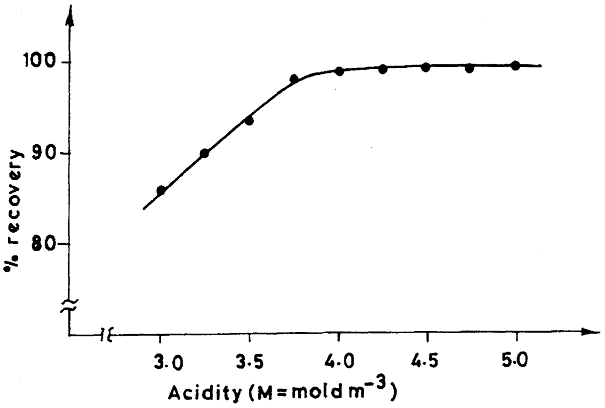
Determination: Treat the aqueous stripping with sufficient bromine water until a slight excess is present (pale yellow). Add with mixing 1 cm^3 of 0.5% sulfosalicylic acid followed by 1 cm^3 of 0.25 M KI. Equilibrate the solution with 5 cm^3 of benzene for 1 min and allow the layers to separate. Wash the organic phase twice with water using 5 cm^3 each time. Discard the washings. Treat the organic layer with 2 cm^3 each of 0.01% KIO_3, 2.5 M H_2SO_4, and 0.02% rhodamine 6G, followed by 4 cm^3 of 15% NaCl. Dilute the solution to 25 cm^3 with distilled water and equilibrate for 1 min. Transfer the organic layer into a dry test-tube and add about 1 g of anhydrous sodium sulfate. Measure the absorbance of the extract at 535 nm in 10 mm cells against the reagent blank run through the entire procedure. Establish the concentration of tin with reference to the calibration graph prepared with 4—200 ng of tin(IV) and following the procedure described above.

Results and Discussion

Extraction Studies: The first step was to determine the conditions most suitable for the selective separation of tin as SnI_4. Although several extraction solvents like diethyl ether,[4,5] carbon tetrachloride,[6] carbon disulfide,[6] and benzene[7] have been found useful, the use of benzene was chosen because very few ions would be coextracted into this solvent.

Figure 1 shows the extraction of tin(IV) as a function of H_2SO_4 concentration. The extent of extraction was established by determining the amount of tin remaining in the aqueous layer spectrophotometrically using pyrocatechol violet method.[8] As much as 100 µg of Sn(IV) could be quantitatively extracted from 4 M H_2SO_4 by single equilibration for 30 s. with 5 cm^3 of benzene, when the iodide concentration was in excess of 0.1 M. Under these conditions the extraction remained unaffected upto an aqueous phase volume of 75 cm^3.

Under conditions optimal for Sn(IV) extraction of Sn(II) was quite incomplete and the results were not reproducible possibly due to varying amounts of Sn(IV) formed in the solution by aerial oxidation. Attempts to oxidise Sn(II) to Sn(IV) revealed that bromine water was effective and excess bromine could be destroyed by the addition of sulfosalicylic acid. The presence of excess sulfosalicylic acid in the medium did not affect the recovery of tin.



Acidity H_2SO_4 x M, Sn(IV) = 20µg,
KI 0.1 M, Total volume - 10 ml,
Benzene - 5 ml for extraction purposes

Fig. 1. Effect of acidity on the extraction of Sn(IV) from iodide media.

No interference was caused by the presence of milligram amounts of oxalate, tartrate, citrate, thiosulfate, and EDTA which were known to form complex with Sn(IV). Metal ions which oxidised iodide to iodine [Sb(V), Cu(II), Fe(III), As(V)] and which formed insoluble precipitates [Ag(I), Tl(I), Pb(II)] were not found to affect the recovery of tin or coextract with tin. Only As(III), Bi(III), and Sb(III) which formed neutral iodides similar to Sn(IV) were found to coextract to an extent of ca. 75% under conditions optimal for Sn(IV).

Experiments to strip SnI_4 quantitatively from the benzene layer showed that it can be quantitatively returned to the aqueous layer by shaking it for 1 min with 10 cm^3 0.1 M NaOH, 0.1 M HCl or 0.05 M H_2SO_4. With H_2SO_4, it was found that stripping was incomplete above 2.5 M and practically negligible when the acidity was greater than 4.5 M. However, As(III), Sb(III), and Bi(III) iodides were found to strip quantitatively into 4.5 M H_2SO_4. This finding was put to advantage to selectively separate SnI_4. Initial equilibration with 4.5 M H_2SO_4 quantitatively stripped the coextracted iodides and subsequent equilibration with 0.05 M H_2SO_4 caused SnI_4 remaining in the benzene layer to return to aqueous phase.

Development of the Method: In earlier work,[9] it was reported that the ICl_2^-–rhodamine 6G ionpair was formed by the reaction of iodide with a solution containing 2 cm^3 each of 2.5 M H_2SO_4, 0.02% KIO_3, 0.02% rhodamine 6G and 4 cm^3 of 15% NaCl in a total volume of 25 cm^3 before extraction into benzene for spectrophotometric measurement at 535 nm. After stripping SnI_4 from the benzene layer into 0.05 M H_2SO_4 the possibility of determining the iodide remaining associated with Sn(IV) after oxidation to ICl_2^- and extraction as ionpair with rhodamine 6G was investigated.

Difficulties were encountered because of high blank due to coextraction of HI along with SnI_4. As washing the benzene layer with 4.5 M H_2SO_4, which did not strip SnI_4, was found to be ineffective, experiments were done to determine whether HI could be selectively stripped by forming an amine salt. The addition of 1 cm^3 of 2% solution of both *p*-toluidine and *o*-nitroaniline in benzene to the organic layer before equilibrating with 4.5 M H_2SO_4 was examined. This approach was found to be highly effective as the blank values were found to be comparable to the normal blank. Systematic examination revealed that equilibration for 1 min with 4.5 M H_2SO_4 was adequate for the selective stripping of amine salt.

Attempts were then made to combine the method of determination after oxidation of iodide present as SnI_4

Table 1. Analysis of Synthetic Solutions

Composition of the solution	Absorbance
Sn^{4+} (100 ng)	0.255
Fe^{3+} (0.1 mg) + Cu^{2+} (0.1 mg) + Sn^{4+} (100 ng)	0.250
Fe^{3+} (0.1 mg) + Sb^{3+} (0.1 mg) + Sn^{4+} (100 ng)	0.245
Cu^{2+} (0.1 mg) + Al^{3+} (0.1 mg) + Sn^{4+} (100 ng)	0.250
Bi^{3+} (0.1 mg) + As^{3+} (0.1 mg) + Sn^{4+} (100 ng)	0.260
As^{3+} (0.1 mg) + Bi^{3+} (0.1 mg) + Sn^{4+} (100 ng)	0.260
Sb^{3+} (0.1 mg) + Cu^{2+} (0.1 mg) + Sn^{4+} (100 ng)	0.250

Table 2. Determination of Tin in Alloy and Steel Samples

Sample (Wt/Vol)	Tin present	Tin added	Tin found[a)]		Recovery
	µg	µg	µg	%	%
BCS No. 216/2	0.056%	—	13.50	0.054	—
Duralumin alloy		5	18.45	—	99.0
(Cu 4.56%, Mg 0.75%, Si 0.71%)		10	23.60	—	101.0
0.025 g/100 cm^3					
FEW 2/167	0.035%	—	17.00	0.034	—
Tungsten steel		5	21.80	—	96.0
(W 79.57%, C 0.48%)		10	26.85	—	98.5
0.05 g/100 cm^3					
Euronium-CRM 087-1	0.017%	—	17.50	0.0175	—
0.15% carbon steel		5	22.55	—	101.0
(Mn 0.67%, C 0.140%, Si 0.263%, As 0.024%)		10	27.39	—	98.9
0.1 g/100 cm^3					

a) Average of 3 determinations.

in the stripping to iodate. A method that seemed worth investigating was to add a slight excess of bromine water to the acidic stripping followed by sufficient sulfosalicylic acid to destroy the excess bromine. It was confirmed by experiments that the oxidation was quantitative when the acidity of the stripping was greater than 0.04 M with respect to H_2SO_4. Addition of 1 cm^3 of 0.5% sulfosalicylic acid or 5% formic acid was sufficient to destroy the excess bromine and it was found that 0.01 M KI was sufficient to liberate iodine from iodate.

The overall efficiency of the conversion of Sn(IV) to measurable iodine by the procedure evolved was established by comparing the absorbance of Sn(IV) carried through the procedure developed with iodine solution in benzene and completing the determination as described for Sn(IV).

$$SnI_4 + 12Br_2 + 12H_2O \longrightarrow 4IO_3^- + 24HBr + Sn^{4+} \quad (1)$$

$$4IO_3^- + 20I^- + 24H^+ \longrightarrow 12I_2 + 12H_2O \quad (2)$$

$$12I_2 + 6IO_3^- + 60Cl^- + 36H^+ \longrightarrow 30ICl_2^- + 18H_2O \quad (3)$$

As each microgram of Sn(IV) would yield 25.7 µg of I_2 (Eqs. 1 and 2), experiments were performed using 100 ng of Sn(IV) and 2.5 µg of I_2 in benzene. The absorbance were found to be 0.25±0.02 and 0.26±0.02 respectively. This indicated that the reaction sequence proceeds with 96.2% efficiency.

A calibration graph prepared as described under 'Experimental' was a straight line for 4—200 ng of Sn(IV) and passed through the origin. The apparent molar absorption coefficient was calculated to be 1.54×10^6 $dm^3\ mol^{-1}\ cm^{-1}$.

The precision of the method proposed was checked by establishing the concentration of ten samples containing 100 ng of Sn(IV). The mean recovery was found to be 98 ng with a relative standard deviation of 2.1%.

Effect of Foreign Ions: The interference of 0.1 mg each of the following ions on the determination of 100 ng of tin(IV) were studied. A deviation of the absorbance value of 0.015 from the value of tin(IV) in the absence of any other interfering species was taken as the sign of interference.

Sb(V), Cu(II), Fe(III), AsO_4^{3-} which were found to oxidise iodide to iodine did not interfere since the iodine formed did not strip into 0.05 M H_2SO_4. Ag(I), Tl(I), Pb(II) which were precipitated as insoluble iodides were not extracted into benzene and hence did not interfere.

As(III), Bi(III), Sb(III) which formed neutral iodides similar to Sn(IV), though extracted into benzene, were found to strip quantitatively into 4.5 M H_2SO_4 along with HI. Hence, the method needs no special precaution from the species that react with iodide as the extraction and stripping procedure evolved is highly specific for Sn(IV).

Determination of Sn(IV) in Synthetic and Practical Samples. The method thus developed was used to analyse the synthetic solution containing 100 ng of Sn(IV) and varying amounts of extraneous ions. The results, shown in Table 1 were satisfactory.

The results of analysis of alloys and steel samples are shown in Table 2.

Carbon steel was brought into solution by heating with 100 cm^3 of 1 : 1 H_2SO_4 and 10 cm^3 of 1 : 1 HNO_3.$^{10)}$ The solution was cooled and made upto a known volume.

Aluminium alloy samples were treated with a solution containing 10 cm^3 of concentrated HCl and 1 cm^3 of 30% hydrogen peroxide. Slowly concentrated NaOH was added until a precipitate was formed. The precipitate was redissolved with 5 cm^3 of 1 : 1 H_2SO_4,$^{11)}$ heated to destroy excess peroxide and made upto a known volume.

Tungsten alloy sample was heated with 5 cm^3 of concentrated HNO_3 in a platinum crucible till the volume was reduced to 2 cm^3. After cooling, a few drops of HF was added, heated till it became clear$^{12)}$ and made upto a known volume.

Suitable aliquots were taken and analysed by the procedure given under 'Experimental'.

Conclusion

The method described involving oxidation and stabilization of 24 atoms of iodine released for each atom of tin(IV) as ICl_2^- species and its measurement as ionpair with rhodamine 6G allows the precise determination of tin at nanogram levels. The molar absorption coefficient of the ion pair is 1.54×10^6 dm^3 mol^{-1} cm^{-1} which is superior to the widely used phenylfluorone ($\epsilon=7.7\times10^4$ dm^3 mol^{-1} cm^{-1}) and pyrocatechol violet ($\epsilon=9.6\times10^4$ dm^3 mol^{-1} cm^{-1}) method. It is virtually specific because of high selectivity of extraction and stripping of SnI_4 prior to spectrophotometric measurement. In view of high selectivity and sensitivity, the method can find use for the determination of tin at nanogram levels in various practical samples.

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