# Sequential Titrimetric and Spectrophotometric Determinations of Trace Amounts of Tin(II) and Tin(IV) by Amplification Reactions

**Mohammed S. El-Shahawi,* and Ali Z. Abu Zuhri†**

Department of Chemistry, Faculty of Science at Damiatta, Mansoura University, Damiatta, Egypt

†Department of Chemistry, Faculty of Science, Al-Najah National University, Nabulus, West Bank, Jordan

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Two simple and accurate titrimetric and spectrophotmetric methods have been developed for the determination of tin. The methods were based upon the oxidation of tin to tetravalent tin with sodium periodate at pH 2.2—3.5; excess periodate ions were then masked with 5% sodium molybdate at the same pH. The released iodate ions were determined spectrophotometry (at 350 nm) as triiodide after the addition of KI. This proposed procedure offered a six-fold amplification for each tin(II) ion. Alternatively, the released iodine was extracted with chloroform and shaken with an aqueous solution of 1% (w/v) sodium sulfite. The iodide ions produced in the aqueous phase were then oxidized with sodium periodate after removing the unreacted sodium sulfite by boiling with $H_2SO_4$ (2 M). The released iodate was finally determined by iodometry or spectrophotometry. This procedure offered 144-fold amplification per tin(II) ion. The determination of tin(IV) after prior reduction to tin(II) with sulfur dioxide was also found to be suitable. Analyses of the binary mixtures of tin(II)–tin(IV) in an aqueous solution, tin in organotin compounds and tin(II) and tin(IV) in artificial sea-waters were successfully carried out.

Interest in the determination of tin compounds has risen dramatically over recent years as a result of increased awareness of their toxicity in the environment. The increased worldwide production and consumption of tin are primarily due to the wide range of industrial applications discovered for organotin chemicals.[1)]

Organotin compounds are known to be potent toxins, and are widely used in different industries, specifically as poly(vinyl chloride) stabilizers, pesticides, and fungicides as well as industrial and agricultural biocides.[2,3)] Large trialkyl or triaryltin compounds are directly introduced in the environment as agricultural pesticides, or result from the degradation of such metals as poly(vinyl chloride).[4)] The introduction of such compounds into the environment could cause serious problems, mainly due to their high toxicity and tendency to bioaccumulation.[5)]

The determination of tin compounds in the environment is becoming increasingly more important.[6)] Several techniques have already been employed to determine tin and/or its organic derivatives, including gas chromatography,[4,7)] flow- injection using solid- phase spectrophotometry,[8)] voltammetry,[9)] and atomic spectrometry.[10,11)]

Tin ion in inorganic compounds is probably best determined titrimetrically with iodate after reduction to tin(II) with aluminum metal under a protective atmosphere.[12)] This oxidimetric method took time, and was thus not tried on the micro scale. The obvious interferences are all those ions which undergo similar redox reactions.

Iodometric chemical amplification procedures with their simplicity and sensitivity are still of special interest.[13—15)] Thus, the present study reports on an evaluation of several digestion methods with the aim to obtain simple, rapid, and accurate iodometric and spectrophotometric amplification procedures for the determination of tin(II) and (IV) and organotin compounds.

## Experimental

**Apparatus:** A Pye Unicam double-beam UV-visible spectrophotometer (model SP 8-400) with 10 mm quartz cells was used for adsorbance measurements. A Philips digital pH meter (model 9418) with glass and saturated calomel electrodes was also used for pH measurements.

**Reagents and Materials:** Unless otherwise specified, all of the chemicals used were of analytical reagent grade. The reagents sodium molybdate (5% w/v), sodium periodate solution (0.35% w/v), sodium thiosulfate ($5\times10^{-3}$ M, 1 M = 1 mol $dm^{-3}$), aqueous solution of starch (1% w/v) and solution of sodium sulfite (2 M) were freshly prepared in distilled water and 8-hydroxyquinoline (Merk) in isobutylmethyl-ketone (IBMK) (0.5% w/v). Buffer solutions of pH 2.2—4.7 were prepared by mixing 150 $cm^3$ of glacial acetic acid with an appropriate amount of saturated sodium acetate and diluting with water whenever is required. All glassware was kept in 10% nitric acid for at least 20 h, and subsequently washed three times with ultrapture water before use.

Standard solutions of tin ($Sn^{2+}$ and $Sn^{4+}$) were prepared by dissolving $SnCl_2\cdot2H_2O$ (supplied by Prolabo) and $SnCl_4$ (supplied by GVL Apioda) in 100 $cm^3$ of double-distilled water in the presence of 10 $cm^3$ of concentrated hydrochloric acid in order to prevent the hydrolysis of tin(IV).[17)] The tin(II) solution was kept under nitrogen and in the presence of metallic Al in order to prevent aerial oxidation and stabilizing the tin(II) species.[18,19)] Butyltin(II) chloride and dibutyltin(IV) dichloride (95—96.5% purity) were obtained from

Alfa product. Standard butyltin solutions (50 μg $cm^3$ as Sn) were prepared separately by dissolving appropriate amount of each butyltin compound in water. These solutions were then stored at 4 °C, and dilute ones were prepared daily.

Synthetic marine water[20] with a salinity of about 36 g $kg^{-1}$ was prepared from demineralized water and salts in the following molar concentration: NaCl, 0.41, $MgCl_2$, 0.029, $MgSO_4$, 0.028, and KCl, 0.009 M.

**Determination of Tin(II):** Aliquot portions (1—5 $cm^3$) of tin(II) solutions containing 1—50 μg of the element were transferred into a 100 $cm^3$ conical flask. Then 10 $cm^3$ of acetate buffer of pH 2.5—3.4 and 5 $cm^3$ of periodate solution were added. The reaction mixture was heated on a boiling water bath under $N_2$ for 30 min. to attain complete oxidation. The reaction mixture was cooled to room temperature and 5 $cm^3$ of 5% sodium molybdate solution added. Then crystalline KI (20—40 mg) was added and the solution was treated by one of the following methods: (i) 6-fold amplification. The released iodine spectrophotometry was determined as triiodide at 350 nm after the addition of KI (0.1 g). A blank determination was run and the necessary correction applied, (ii) 144-fold amplification. Alternatively, the released iodine was extracted with 10 $cm^3$ (2×5) portions of chloroform, and the extracts collected in a separating funnel and then shaken with two 5 $cm^3$ portions of sodium sulfite to reduce the released iodine to iodide. After the aqueous (upper) layer was transferred to a 100 ml Erlenmeyer flask, 5 $cm^3$ of 2 M $H_2SO_4$ was added and heated until dryness to remove $SO_2$. To the produced solid residue of iodide, 20 $cm^3$ of water was added and the pH of the solution adjusted to pH 3 with acetate buffer; finally, 5 ml of $NaIO_4$ was added. The flask was stoppered and the reaction mixture allowed to stand for 10 min at room temperature; it was then placed in a boiling water bath for 20 min. After the solution was cooled 5 $cm^3$ of sodium molybdate, 10 $cm^3$ of acetate buffer (pH≃3), and 20—40 mg of KI were added and the released iodine determined by iodometry or spectrophotometry. A blank was run to correct the reagent error and any error caused by the possible aerial oxidation of tin(II).

**Determination of Tin(IV):** A known volume (1—5 $cm^3$) of a tin(IV) solution containing various amounts of the tetravalent element (1—50 μg) was transferred into 100 $cm^3$ Erlenmeyer flasks, and 2—5 $cm^3$ of a saturated sodium sulfite solution added to each flask followed by 5 $cm^3$ of 2 M $H_2SO_4$. The reaction was left to stand for 3 min and then gently evaporated on a hot plate until excess $SO_2$ had been completely removed. Then, ca. 5 $cm^3$ of water was added, and the pH of the water solution adjusted to pH 3; then 10 $cm^3$ of acetate buffer of pH 3 was added and the released tin(II) determined using the recommended procedure. A blank was run to correct the reagent error.

**Analysis of Binary Mixtures of Tin(II) and Tin(IV):** Different aliquot portions of the mixture were transferred to a 100 $cm^3$ conical flask containing various amounts of tin(II) and (IV). The tin(II) in the aliquot was determined titrimetrically or spectrophotometrically as in the procedure employing 144-fold amplification. The tetravalent element was reduced to the divalent state with sodium sulfite in an acid solution, and the total content of the element determined following the procedure of tin(IV) determination. The difference between the two values of the thiosulfate solutions or the absorbance of $I_3^-$ ions was equivalent to tin(IV).

**Determination of Tin(II) or (IV) in Marine Water:** Marine water samples (100 $cm^3$) acidified to pH 2 with hydrochloric acid (0.1 M) were filtered through a 0.45 μm Millipore filter followed by adding 10 $cm^3$ of tartaric acid (1 M) and 10 $cm^3$ of sodium salt of EDTA ($1\times10^{-3}$ M). Various amounts (5—25 μg) of the tin(II) or tin(IV) were added to aliquots of water samples, followed by adding ca. 10 $cm^3$ of bromine water and 10 $cm^3$ of 1 M sodium fluoride. After the reaction mixture was allowed to stand for 10 min. and excess bromine boiled off, 5 $cm^3$ oxine (0.5%) in IBMK was added and shaken for 1 min. The extraction was then repeated three times and the extracts were combined and evaporated to dryness. The residue was then redissolved in 10 $cm^3$ of water–HCl (4 : 1 v/v); finally, the total tin content was determined following the above recommended procedure of tin(IV) determination after adjusting the pH to 3. A blank was then run to correct the reagent error.

**Analysis of Tin in Organotin Compounds:** An accurate weight of organotin compounds was digested in a 250 $cm^3$ combustion flask with 10 $cm^3$ of concentrated $H_2SO_4$ and 5 $cm^3$ of 30% $H_2O_2$, as reported by Marr.[21] The tin content according to the recommended procedure of tin(IV) were then determined.

## Results and Discussion

Sodium or potassium periodate in acid medium was found to oxidize tin(II) to tin(IV) as follows:

$$Sn^{2+} + IO_4^- + 2H^+ \rightarrow IO_3^- + Sn^{4+} + H_2O. \quad (1)$$

The released iodate and tin(IV) ions react with KI in acid media according to the following equations:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O, \quad (2)$$

$$Sn^{4+} + 4I^- \rightarrow SnI_4. \quad (3)$$

It was reported[22] that reaction (2) take place rapidly and quantitatively in an acidic medium at pH≤3.5. Reaction (3) takes place and proceeds forward in a strong acidic medium (4 M $H_2SO_4$). This statement is criticized here since preliminary experiments showed that the tin(IV)-iodide reaction is a function of the solution pH, and that the reaction is difficult to take place and is quite negligible in a moderate acidic medium (pH≥3).

The oxidation of tin(II) with potassium periodate was found to depend on the pH, the reaction time and the temperature. Thus, fixed amounts (100 μg) of tin(II) adjusted to pH 2.5—6.5 were allowed to react with sodium periodate (5 $cm^3$) for different time intervals (5—30 min) and different temperatures (ambient or 100 °C) on a boiling water bath. The solutions were then adjusted to pH≃3 with 5 $cm^3$ of the acetate buffer; the unreacted periodate ions were then masked with sodium molybdate, forming heteropoly acid $H_5[I(MoO_4)_6]$.[23,24] The released iodate was then allowed to react with KI. The complete oxidation of tin(II) with periodate was found in the pH range 2.2—3.2 after heating the reaction mixture on a boiling water bath for 20 min. Fortunately, the pH values suitable for the quantitative oxidation of tin(II) element with periodate are quite appropriate for masking the excess periodate with molybdate.[25,26] Thus, the acetate buffer solution (pH=3) was added at the beginning of the experiment and before the addition of KI.

At pH > 3.6 reactions (1—3) were very slow, while at pH < 2.2 the reactions proceeded rapidly with 6-fold amplification of tin(II). The molybdate did not mask the unreacted periodate quantitatively at pH < 2.2, since the molybdate-periodate was partially decomposed,[23] and aerial oxidation

of iodide can also occurred under these conditions in the absence of bubbling $N_2$. Therefore, at pH 3 each original tin(II) element liberated six equivalents of iodine, i.e. the proposed method afforded a six-fold amplification for each tin(II) ion. The released iodine (Eq. 2) was then determined spectrophotometry as $I_3^-$ at 350 nm. The developed procedures were employed for the determination of varying amounts (10—50 μg) of tin(II). Satisfactory results were obtained with recovery percentage of determination being 96.40—102.5% and with the standard deviation in the range 0.15—0.26 (Table 1). The lowest measurable concentration ($3\sigma$) under the prementioned conditions was found to be 0.20 ppm tin(II) or tin(IV).

Tin(IV) was determined by a prior reduction to tin(II) followed by a determination of the produced tin(II) element by the proposed procedure. Sodium sulfite in an acidic media was found to be the most suitable reducing agent, where the unreacted sulfite ion could be easily removed by boiling off the formed sulfur dioxide. The spectrophotometric determination of various levels (10—50 μg) of tin(IV) in aqueous media by the proposed 6-fold amplification is given in Table 2 with the standard deviation in the range 0.15—0.26.

Alternatively, the proposed 6-fold amplification procedure of tin(II) determination was further improved where after masking the unreacted periodate the released iodine from Eq. 2 at pH 3 was extracted quantitatively on shaking with two 10 $cm^3$ portions of $CHCl_3$. The extracted iodine was then shaken with sodium sulfite solution in order to reduce the iodine to iodide according to the equation[25]

$$I_2 + 2SO_3^{2-} + 2H_2O \rightarrow SO_4^{2-} + 2I^- + 4H^+. \quad (4)$$

The released iodide in the aqueous (upper) layer was then allowed to react with sodium periodate to produce iodate according to the following equation:[21]

$$3IO_4^- + I^- \rightarrow 4IO_3^-. \quad (5)$$

The released iodate produced from Eq. 5 was determined iodometrically, and also by spectrophotometry (at 350 nm) after the addition of potassium iodide, as described. Thus, according to Eq. 5, the overall amplification employing oxidation of iodide by sodium periodate would be a 144-fold amplification of the iodine per each tin(II) element originally present. The proposed 144-fold amplification procedure was successfully employed for the analysis of tin(II). The results of the analysis of tin(II) iodometry and spectrophotometry are summarized in Table 3 with standard deviation and error percentage in the range 0.12—0.32 and 0.52—2.2%, respectively. Moreover, a spectrophotometric procedure employing 144-fold amplification can be extended to lower concentrations of tin(II) by the extraction of the released iodine in $CHCl_3$ containing alcoholic KI, and measuring the absorbance of the triiodide ion formed at 360 nm.[26] If a reasonably large amount of tin(II) ion > 1 ppm is present it is preferable to dilute the solutoin of the released iodate produced from the 144-fold method to 100 $cm^3$, and to measure the concentration of the released iodine by either iodometry or spectrophotometry. The detection limit (3× noise) and the correlation coefficient were found to be 0.2 ppm and 0.99, respectively.

The absorbance–concentration relationship was found to be linear over the concentration range 0.05—10 μg $cm^{-3}$ employing 144-fold amplification for a tin(II) determination. The optimum concentration range for the effective spectrophotometric determination, evaluated by Ringbom's method,[27] was found in the range 0.15—5 ppm for 144 amplification. The standard deviation calculated for five measurements at 3 ppm of tin(II) was 0.6. The detection limit (3× noise) and the correlation coefficient were found to be 0.01 ppm and 0.992, respectively.

An analysis of a binary mixture of tin(II) and (IV) ions in aqueous media was employed by the proposed procedure. An aliquot mixture was first allowed to react with sodium periodate employing the procedure described for a tin(II) determination. Another aliquot mixture was then reduced to tin(II), as described in the above recommended procedure. On the basis of these procedures the volume ($V_1$ $cm^3$) of sodium thiosulfate or the absorbance ($A_1$) of the released iodine of the first aliquot would be equivalent to tin(II). The volume ($V_2$ $cm^3$) of sodium thiosulfate or the absorbance ($A_2$) of the released iodine for the aliquot would be equivalent to the sum of Sn(II) and Sn(IV). Thus, the volume ($V_2 - V_1$ $cm^3$) or the absorbance ($A_2 - A_1$) is equivalent to tin(IV).

Table 1. Spectrophotometric Determination of Various Amounts of Sn(II) in Aqueous Media

| Sn(II) ion present (μg) | Sn(II) found (μg)[a] | % Error[b] |
|---|---|---|
| 50 | 48.30±0.22 | −2.60 |
| 20 | 20.40±0.26 | 02.00 |
| 10 | 10.25±0.15 | 02.50 |

a) Average of 5 determinations±standard deviation.

b) % Error=$\frac{\text{Average of tin found} \times 100}{\text{tin added}}$.

Table 2. Spectrophotometric Determination of Various Amounts of Sn(IV) in Aqueous Media

| Sn(IV) ion present (μg) | Sn(IV) found (μg)[a] | % Error |
|---|---|---|
| 50 | 50.40±0.26 | 0.80 |
| 20 | 20.20±0.15 | 1.00 |
| 10 | 10.20±0.22 | 2.00 |

a) Average of 5 determinations±standard deviation.

Table 3. Determination of Various Amounts of Tin(II), Iodometry (a) and Spectrophotometry (b) Using 144-fold Amplification Procedure[a]

| Tin(II) taken (μg) | Tin(II) found (μg) | | Error (%) | |
|---|---|---|---|---|
| | a | b | a | b |
| 10 | 10.20±0.21 | 10.1±0.12 | 2.00 | 1.00 |
| 20 | 20.30±0.20 | 20.1±0.20 | 1.50 | 0.50 |
| 50 | 51.10±0.32 | 50.5±0.26 | 2.20 | 1.00 |

a) Average of 5 determination±standard deviation.

Satisfactory results were obtained with standard deviations in the range 0.40—0.52 and 0.26—0.36 for the iodometry and spectrophotometry of the released iodine, respectively. The volume of sodium thiosulfate (0.005 M) equivalent to the blank taken through the whole procedure using freshly prepared $NaIO_4$ was in the range 0.2—0.25 $cm^3$.

**Effect of Diverse Ions:** The interference of various ions $Tl^+$, $Zn^{2+}$, $Pt^{2+}$, $Mn^{2+}$, $Cr^{3+}$, $Cr^{6+}$, $Ni^{2+}$, $Ru^{3+}$, $Al^{3+}$, $Li^+$, $Co^{2+}$, $Fe^{3+}$, $Pd^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Ba^{2+}$, and $La^{3+}$ at a concentration (10 μg) approximately exceeding those normally found in sea water was investigated employing a 6-fold amplification procedure. The selectivity of the proposed method was tested by the determination of a fixed concentration (5 μg) of tin(II). Satisfactory results were obtained with a percentage recovery of 97.2—103.5. $Mn^{2+}$, $Tl^+$, $Cr^{6+}$, $Pt^{2+}$, $Fe^{3+}$, and $Ru^{3+}$ seriously interfered. The interference of $Fe^{3+}$ was masked by the addition of 2 $cm^3$ of NaF (1 M). The selectivity of the 6-fold procedure was examined by the relatively high excess (0.1 mg) of the following ions: $WO_4^{2-}$, $HCO_3^-$, $Br^-$, $PO_3^{3-}$, $SO_3^{2-}$, $SbO_3^{2-}$, and $CO_3^{2-}$. The percentage recovery of tin(II) was 100±5%.

**Application of the Proposed Method:** The applicability of the proposed procedures for the analysis of tin(II) and tin(IV) in 0.1 $dm^3$ artificial sea and marine water were carried out employing the standard addition method. In separate experiments aliquot samples spiked with various amounts (5—25 μg) of tin(II) were added to the water samples, and were analyzed spectrophotometry employing the 144-fold amplification procedure as described. A blank was run for a correction. Satisfactory results (Table 4) were obtained for the spiked samples with the help of a concurrently standard curve prepared under the same instrumental setting. A percentage error of 2—4.8% ($n$=5) and a correlation coefficient of 0.988 were obtained. The total tin in the unspiked water samples (blank) employing the recommended procedure of the extraction with oxine in IBMK were found in the range 5—7±1.2 ppm, in agreement with the results obtained by a method reported by Bermejo-Barrera.[10] The values are quite high, possibly due to the characteristics of the places where the samples were collected. In estuaries the water is more static than that in open seas; also, in small harbors (sport and fishing) antifouling paints containing butyltin compounds are used more than in bigger harbors. The analysis is of a low concentration of tin (<0.1 ppm) in water is also possible by the proposed procedure after preconcentration and elution of tin employing a polyurethane foam column,[28,29] followed by the determination of the tin(II) according to the above described procedure.

Table 4. Analysis of Various Amounts of Tin(II) Spiked to Marine Water Iodometry (a) and Spectrophotometry (b) Employing 144-fold Amplification Procedure[a]

| Tin(II) taken (μg)[a] | Tin(II) found (μg)[b] | | Error (%) | |
|---|---|---|---|---|
| | a | b | a | b |
| 05 | 05.20±0.32 | 05.10±0.26 | 4.00 | 2.00 |
| 20 | 20.50±0.41 | 20.40±0.23 | 2.50 | 2.00 |
| 25 | 26.20±0.31 | 25.41±0.29 | 4.80 | 2.20 |

a) Total volume of aqueous sea water was 0.1 $dm^3$. b) Average of 5 determinations±standard deviation.

Table 5. Determination of Tin in Organic Compounds Using 144-fold Amplification Reaction Procedure

| Compound | % Tin calcd | % Tin found[a] | % Error |
|---|---|---|---|
| Monobutyltin(II) chloride | 56.20 | 57.70±0.21 | +2.27 |
| Tributyltin chloride | 36.50 | 37.44±0.31 | +2.57 |
| Dibutyltin chloride | 39.08 | 40.30±0.38 | +3.12 |

a) Average of 5 determination±standard deviation.

The proposed 144-fold amplification titrimetric procedure was successfully employed for the analysis of tin in organotin compounds. A survey of the literature indicates that an acid mixture of $H_2SO_4$–$H_2O_2$ digestion and Oxygen flask techniques is the most favorite digestion system for the decomposition of tested organotin compounds. Therefore, an accurate weight of the organotin compound was digested with 10 $cm^3$ of concentrated sulfuric acid and 5 $cm^3$ of hydrogen peroxide (30%). After digestion, tin was usually present in the di- and tetravalent states, and was determined according to the described procedure for tin(IV). The results concerning the analysis of different organotin compounds are summarized in Table 5 along with the average error percentage in the range 2.27—3.12%.

## Conclusion

The present article demonstrates the applicability of amplification the reactions involving periodate in the analysis of organotin compounds. Although the 6-fold amplification procedure for tin(II) determination is faster, 144-fold amplification procedures are more sensitive for lower concentrations. The two methods provide a simple, inexpensive, reliable and precise approach in the routine analysis of tin. The spectrophotometric method provides an attractive alternative to atomic absorption for the determination of tin. A clear advantage of the method is that it is applicable for tin(II) or (IV) speciation in their mixture.

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