# The Separation of Tin from Water and Sea-water by Flotation and the Determination of Tin by Atomic Absorption Spectrophotometry Following Stannane Generation

Susumu NAKASHIMA

*Institute for Agricultural and Biological Sciences, Okayama University, Kurashiki-shi, Okayama 710*

(Received November 30, 1978)

A method is described for the separation and determination of sub-microgram levels of tin in water. A sub-microgram amount of tin(II, IV) in a 1000-ml sample of water is coprecipitated with iron(III) hydroxide at pH $4.0\pm0.2$. The precipitate is floated with the aid of sodium dodecyl sulfate and small air bubbles, and then separated and dissolved in 2 ml of 6 M hydrochloric acid and diluted to 10 ml with water. Finally, the tin content is determined by the generation of stannane, using sodium borohydride as a reductant, followed by atomic absorption spectrophotometry with a long absorption cell ($60\times1.2$ cm i.d.). This separation technique has also been successfully applied to the determination of sub-microgram amounts of tin in natural sea-water. The time required for the pre-concentration of tin from a 1000-ml volume of solution is about 15 min per sample after 15 min of stirring.

It is important to establish a rapid, sensitive, and accurate method to determine tin in natural waters from the viewpoints of environmental chemistry, geochemistry, marine biology, and limnology. Tin has so far received little attention as an environmental pollutant in natural waters. Furthermore, almost nothing is known about the tin content in natural waters. Tin probably exists at concentrations below 1 $\mu g\ l^{-1}$ in natural water samples. At such low concentrations, a precise, direct determination is impractical, even by the atomic absorption spectrophotometry of stannane, which has a high sensitivity.[1-3] In addition, nickel(II) causes serious negative interference in the determination of tin by the above hydride-generation method. Hence, it is necessary to pre-concentrate tin from water and separate it from nickel(II) prior to determination.

Coprecipitation with iron(III) hydroxide[4-6] or zirconium hydroxide[7,8] is used as a pre-concentration technique for the determination of tin in aqueous systems. These bulky amorphous precipitates, however, are difficult to filter, and centrifugation is cumbersome for larger volumes.

Mizuike and Hiraide[9] reported a flotation technique carried out with the aid of a hot ethanolic paraffin solution and small nitrogen bubbles for the separation of the tin(IV) coprecipitated with iron(III) hydroxide. This separation technique was successfully applied to the spectrophotometric determination of tin at the ppb level in high-purity zinc metal.

In a previous paper,[10] a flotation technique[9,11,12] in which the precipitate of iron(III) hydroxide is floated with the aid of sodium oleate and small air bubbles was used for the pre-concentration of arsenic in natural non-saline waters.

This communication will describe the application of this separation technique, with suitable modifications, to the pre-concentration of sub-microgram amounts of tin(II, IV) in water. The precipitate is readily separated from the mother liquor and then dissolved in dilute hydrochloric acid for the atomic absorption spectrophotometry by the generation of stannane, using sodium borohydride as a reductant. The various parameters that affect the flotation and determination of tin were investigated. This method is simple and rapid, and it is applicable to the extraction of tin at low ppb levels from large volumes of water and sea-water.

## Experimental

*Apparatus.* A Nippon Jarrell-Ash, Model AA-1 Mark II, atomic absorption spectrophotometer equipped with a Jarrell-Ash tin hollow-cathode lamp and a custom-made silica absorption cell ($60\times1.2$ cm i.d.) was used, along with a Beckman burner supplied with nitrogen and hydrogen.

The apparatus used for the stannane generation was a modified Nippon Jarrell-Ash, Model ASD-1A, hydride-measurement unit coupled to a custom-made hydride-generating cell. The schematic diagram of the analytical system is similar to that described previously.[10]

All the pH measurements were carried out with a Hitachi-Horiba, Model M-5, pH meter, together with a combined glass electrode.

The flotation and separation apparatus was similar to that described by Mizuike and his coworkers.[11,12] The flotation cell was a glass cylinder, $40\times6.5$ cm i.d., which was fitted with a sintered-glass filter (No. 4) to generate small bubbles. A side arm was added near the bottom of the cell in order to drain out the mother liquor rapidly after the flotation, as is shown in Fig. 1.

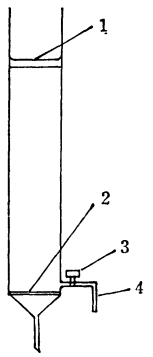


Fig. 1. Flotation cell for pre-concentration of tin.
1: Foam layer containing iron(III) hydroxide and tin, 2: sintered-glass disk (porosity 4), 3: cock, 4: drain pipe.

*Reagents.* All the reagents were of an analytical-reagent grade except for sodium dodecyl sulfate and sodium oleate. The aqueous reagents were prepared in de-ionized, distilled water. The tin standard solutions were freshly prepared by diluting stock solutions before use.

*Tin(IV) Stock Solution (1 mg ml$^{-1}$)*: Some (500 mg) high-purity tin metal was dissolved in 40 ml of concentrated sulfuric acid by heating. After cooling, the solution was made up to 500 ml with 2 M hydrochloric acid.

*Tin(II) Stock Solution (1 mg ml$^{-1}$)*: Some (950 mg) stannous chloride dihydrate was freshly dissolved in 50 ml of concentrated hydrochloric acid, and then the solution was made up to 500 ml in 2 M hydrochloric acid.

*Iron(III) Solution (5 mg ml$^{-1}$)*: Some (43.17 g) ammonium iron sulfate was dissolved in water, after which the solution was diluted to 1000 ml in 1 M hydrochloric acid.

*Sodium Dodecyl Sulfate Solution (1 mg ml$^{-1}$)*: Sodium dodecyl sulfate (powder, extra-pure reagent, Wako Pure Chemical Industries, Ltd.) was dissolved in 99.5 v/v % ethanol.

*Sodium Oleate Solution (1 mg ml$^{-1}$)*: Sodium oleate (powder, extra-pure reagent, Wako Pure Chemical Industries, Ltd.) was dissolved in 99.5 v/v % ethanol with stirring.

*Sodium Borohydride Solution (5 w/v %)*: This solution was used in a 0.1 M sodium hydroxide solution.

*Procedure for the Flotation Step.* One thousand ml of acidified water is placed in a 1000-ml beaker, and 2 ml of an iron(III) solution is added. The pH of the solution is adjusted to 4.0±0.2 with an aqueous ammonia solution, while being stirred magnetically, in order to precipitate iron(III) hydroxide, and the mixture is stirred for 15 min. After adding 2 ml of a sodium dodecyl sulfate solution to the beaker, the contents of the beaker are transferred to a flotation cell and the residue in the beaker is washed into the cell by using three small portions of water. Air is passed through at a flow rate of 50 ml min$^{-1}$ from the lower end of the cell for about 2 min in order to obtain a complete mixing and flotation of the precipitate. Most of the mother liquor is drained from the side arm by opening the cock of the drain pipe. After closing the cock, the residual mother liquor is sucked off through the sintered-glass disk, and the precipitate is washed with 30 ml of water. Two ml of 6 M hydrochloric acid is added to the cell to dissolve the precipitate, the filtrate is collected by suction in a 10-ml calibrated flask, the sintered-glass disk is washed with water, the washings are added to the flask, and the mixture is diluted to 10 ml with water.

*Procedure for the Determination of Tin.* One ml of a freshly prepared 5 w/v % sodium borohydride solution is transferred into a stannane-generating cell and the cell is attached to the apparatus. A plastic syringe containing 1 ml of the sample solution is inserted into the side-arm seal of the cell. The four-way stopcock of the apparatus is turned to the sweep position in order to introduce nitrogen into the system, and the sample is injected into the cell. The stannane thus generated is swept into the long absorption cell with nitrogen and then atomized in the nitrogen-hydrogen flame, and the absorption signal is recorded on a recorder. The stopcock is returned to the by-pass position. The cell is carefully rinsed with distilled water.

A calibration curve is constructed using 1.2 M hydrochloric acid solutions containing 1.0 mg ml$^{-1}$ of iron(III) and 0—0.10 μg ml$^{-1}$ of tin(IV); this curve is linear within the above range of tin. The detection limit of tin was found to be 0.5 ng ml$^{-1}$. No appreciable difference in sensitivity was observed between tin(II) and tin(IV). The coefficients of variations were 1.5 and 1.4 % in 10 replicate runs of 0.04 and 0.08 μg ml$^{-1}$ of tin(IV) respectively.

The atomic absorption apparatus was operated under the following conditions: wavelength, 286.3 nm; lamp current, 8 mA; gas-flow rates: nitrogen, 1.5; hydrogen, 1.5, and auxiliary nitrogen, 6 liter min$^{-1}$; slit (spectral band width), 1 nm.

## Results and Discussion

*The Optimum Conditions for the Determination of Tin.* The effect of the sodium-borohydride concentration on the evolution of stannane was investigated. As is shown in Fig. 2, it was found that more than 3 w/v % of the reductant concentration (1 ml volume) can quantitatively reduce up to 0.10 μg of tin to stannane. In this work, 1 ml of 5 w/v % of the solution was used.

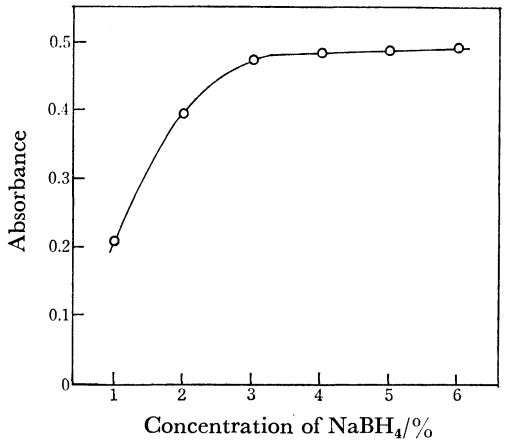


Fig. 2. Effect of sodium borohydride concentration on the evolution of stannane.
Solution containing 0.10 μg of Sn(IV), sample volume: 1 ml.

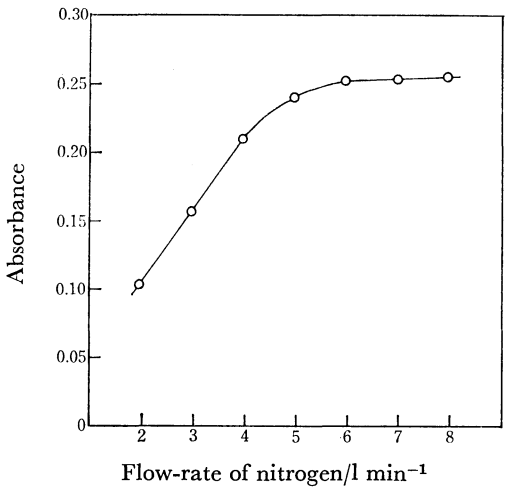


Fig. 3. Effect of nitrogen flow-rate on the evolution of stannane.
Solution containing 0.05 μg of Sn(IV), sample volume: 1 ml.

The optimum conditions for the sensitivity of tin were dependent on the flow rate of auxiliary nitrogen, as is shown in Fig. 3. The tin absorbance increased with an increase in the flow rate of auxiliary nitrogen up to 6 l min$^{-1}$ when the flow rates of both nitrogen and hydrogen were 1.5 l min$^{-1}$. The optimum sensitivity was obtained with a flow rate of auxiliary nitrogen

between 6 and 8 l $min^{-1}$; a flow rate of auxiliary nitrogen of 6.0 l $min^{-1}$ was, therefore, adopted throughout.

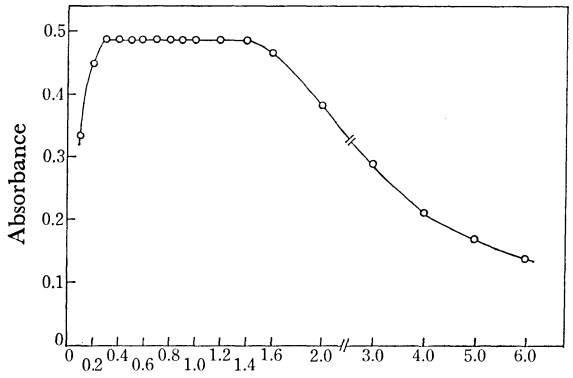


Fig. 4. Effect of hydrochloric acid concentration on the evolution of stannane.
Solution containing 0.10 μg of Sn(IV), sample volume: 1 ml.

Figure 4 shows the effect of the hydrochloric-acid concentration on the generation of stannane. The optimal concentration of hydrochloric acid is between 0.3—1.4 M and is critical because of the pronounced decrease in sensitivity with an increase in the acid concentration. Therefore, it is necessary to adjust the acid concentration of the sample solution carefully for reliable results. The use of a tin(II) solution gave similar results. Thus, the final acidity of hydrochloric acid was maintained at 1.2 M in further work.

The effect of iron(III) added as a collector on the generation of stannane was also studied. A slighter larger suppression (about 6%) of the tin absorbance was observed in the presence of 0.25—2.5 mg $ml^{-1}$ of iron(III) in comparison with that in the absence of iron(III). Therefore, a calibration curve for tin was constructed using tin(IV) solutions containing 1.0 mg $ml^{-1}$ of iron(III).

*The Optimum Conditions for the Flotation of Tin.*

*Effect of* pH: The effect of the pH of a 1000-ml solution containing 0.8 μg of tin(II, IV), 10 mg of iron(III) and 2.0 mg of surfactant on the coprecipitation of tin was studied. Hydrochloric acid and an aqueous ammonia solution was used to adjust the pH to values within the range of 3.4—10.0. The results are shown in Fig. 5. Quantitative recoveries of both the divalent and the tetravalent states of tin were obtained over this range, as well as in the case of arsenic(III, V).[10] The most stable layer of surface foam supporting the precipitate of iron(III) hydroxide when sodium dodecyl sulfate was

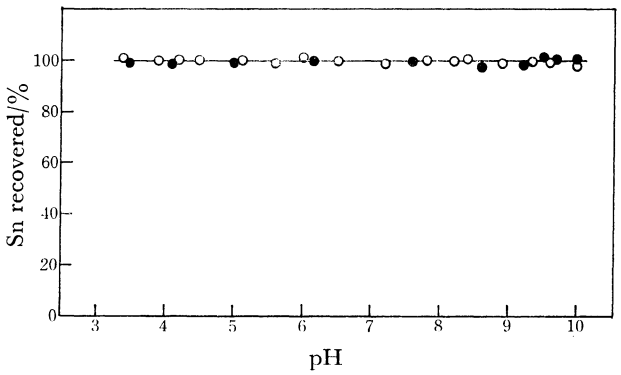


Fig. 5. Coprecipitation of tin with iron(III) hydroxide as a function of pH.
Solution containing 0.8 μg of Sn and 10 mg of Fe(III), sample volume: 1000 ml, ●: Sn(II), ○: Sn(IV).

used was found within the pH range of 3.4—7.0; the pH of 4.0±0.2 was, therefore, used throughout the work. At a pH above 7, a stable surface-foam layer was obtained by using sodium oleate as a surfactant.

*Amounts of Iron(III) and Surfactant*: The recovery of tin as a function of the amount of iron(III) added to the solution is given in Table 1. Quantitative recoveries of tin were obtained above 5.0 mg of iron(III). In this work, therefore, 10 mg of iron(III) was added to 1000 ml of a solution. The amount of sodium dodecyl sulfate required for the complete flotation of the precipitate was also studied. Quantitative recoveries of tin were obtained between 0.5—8.0 mg of sodium dodecyl sulfate, and so 2.0 mg of it in a 1000 ml solution was added in further work.

*Stirring Time*: The relation between the stirring time and the recovery of tin was investigated. The results are shown in Table 2. Coprecipitation was quantitative over the range of 5—40 min; stirring for 15 min was found best.

Table 2. Relation between stirring time and recovery of tin[a)]

| Stirring time (min) | 5 | 10 | 15 | 20 | 25 | 30 | 40 |
|---|---|---|---|---|---|---|---|
| Sn recovered (%) | 95 | 99 | 100 | 98 | 99 | 102 | 100 |

a) Solution containing 0.8 μg of Sn(IV) and 10 mg of Fe(III); pH, 4.0±0.2; sample volume, 1000 ml.

*Effect of Foreign Ions*: By following the proposed procedure, the effects of various ions on the separation and determination of tin(IV) were investigated. Table 3 compares the permissible amounts of foreign ions for the determination of tin(IV) with and without coprecipitation. As can be seen, when coprecipitation at

Table 1. Relation between amount of iron(III) added and recovery of tin[a)]

| Fe(III) added (mg) | 2.5 | 5.0 | 7.5 | 10.0 | 15.0 | 20.0 | 25.0 |
|---|---|---|---|---|---|---|---|
| Sn recovered (%) | 91 | 99 | 100 | 99 | 99 | 100 | 101 |

a) Solution containing 0.8 μg of Sn(IV) and 2 mg of sodium dodecyl sulfate; pH, 4.0±0.2; sample volume, 1000 ml.

Table 3. Comparison of permissible amounts of foreign ions for determination of tin with and without coprecipitation

| Ion | Limit, [Ion]/[Sn] | | Ion | Limit, [Ion]/[Sn] | |
|---|---|---|---|---|---|
| | Direct[a] | With copptn[b] | | Direct[a] | With copptn[b] |
| $Mo^{6+}$ | 600 | 1000 | $Sb^{3+}$ | 100 | 100 |
| $Hg^{2+}$ | 400 | 1000 | $Cu^{2+}$ | 60 | 800 |
| $Te^{4+}$ | 400 | 400 | $As^{3+}$ | 50 | 50 |
| $Se^{6+}$ | 200 | 1000 | $As^{5+}$ | 50 | 50 |
| $Bi^{3+}$ | 100 | 100 | $Se^{4+}$ | 40 | 40 |
| $Co^{2+}$ | 100 | 1000 | $Ni^{2+}$ | 2 | 800 |

The following are tolerable: $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$, $NO_3^-$, $SiO_3^{2-}$ (excess, $\times 10000$), $Sr^{2+}$, $Ba^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Cr^{6+}$, $Pb^{2+}$, $V^{5+}$, $PO_4^{3-}$ (excess, $\times 1000$). a) Solution containing 0.10 μg of Sn(IV); sample volume, 1 ml. b) Solution containing 1.0 μg of Sn(IV) and 10 mg of Fe(III); sample volume, 1000 ml.

pH 4.0±0.2 is used, most foreign ions normally present in natural waters hardly interfere at all with the determination of tin(IV), and suppressive effects by diverse ions, especially, those by nickel(II), copper(II), cobalt(II), selenium(VI) and mercury(II), were found to be largely eliminated in comparison with those which occur when tin is directly determined without coprecipitation. The values of the permissible amounts (Ion/Sn in weight) of these ions in the proposed method increased from 2, 60, 100, 200, and 400 to 800, 800, 1000, 1000, and 1000 for nickel(II), copper(II), cobalt(II), selenium(VI), and mercury(II) respectively, compared with the values permissible in the direct determination. However, hydride-forming elements, such as selenium(IV), antimony(III), arsenic(III, V) and bismuth(III), are coprecipitated with iron(III) hydroxide in the same way as tin and had a relatively great effect on the generation of stannane.

*Recovery of Tin*: The solutions (1000 ml) at pH 4.0±0.2 containing 10 mg of iron(III), 2.0 mg of sodium dodecyl sulfate, and 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 15.0, and 20.0 μg of tin(IV) were analyzed by the procedure described above. The recoveries of the tin that had been added were greater than 95% in all instances. No blank value was detected throughout the whole analytical process. The proposed conditions, therefore, appear to be optimal for 1000-ml volumes of a solution containing up to 20 μg of tin(IV).

The relative standard deviations of ten-times-repeated analyses of the solutions containing 0.4 and 0.8 μg of tin(IV) per 1000 ml were 2.4 and 2.3% respectively.

*Applications to Natural Sea-water*: In order to investigate the applicability of this method to sea-water, the recoveries of known amounts of tin(IV) added to natural sea-water samples taken up at two different locations were examined by the above procedure. The analyses were carried out 1000-ml aliquots of clear, uncontaminated sea-water, filtered through 0.45 μm Millipore filters after the addition of hydrochloric acid immediately after sampling. Table 4 presents the

Table 4. Recovery of tin added to natural sea-water samples[a]

| Tin added (μg) | Tin[b] found (μg) | Tin recovered (μg) | Mean recovery (%) | Tin in sample (μg $l^{-1}$) | |
|---|---|---|---|---|---|
| None | 0.139±0.004 | | | 0.14 | c) |
| 0.200 | 0.338±0.008 | 0.199 | 100 | | |
| None | 0.068±0.003 | | | 0.07 | d) |
| 0.400 | 0.459±0.009 | 0.391 | 98 | | |

a) Volume of sample, 1000 ml. b) The mean value of four measurements. c) This sample was taken at Shibukawa, Okayama Prefecture. d) This sample was taken at Ajino, Okayama Prefecture.

recovery data of the tin. These results indicate that the analytical process had a satisfactory recovery of tin from sea-water at pH 4.0±0.2. The average tin concentrations for both sea-water samples were low, 0.07 and 0.14 μg $l^{-1}$.

Hamaguchi *et al.*[5,6] reported an average of 0.81 μg $l^{-1}$ in the range of 0.30—1.22 μg $l^{-1}$ of the tin concentrations in four sea-water samples collected from the Pacific Ocean. Moreover, Kodama and Tsubota[13] reported that the tin concentrations in six water samples from the North Pacific ranged from 0.63 to 1.93 μg $l^{-1}$, showing an average of 1.15 μg $l^{-1}$. The reason for the discrepancy between the values reported in this work and those in the literature is not clear. A possible explanation may be that the former sea-water samples were collected near the seashore, and the latter ones, in the ocean.

## Conclusions

The flotation of sub-microgram amounts of tin(II, IV) coprecipitated with iron(III) hydroxide is useful as a pre-concentration technique for the extraction of tin(II, IV) from a large volume of water, and subsequent atomic-absorption measurement in a long absorption cell of the stannane from the tin(II, IV) is an accurate method for the determination of tin. In addition, the satisfactory isolation of tin from such interfering ions as nickel(II) and copper(II) present in water is the advantage of the proposed method.

The author wishes to thank Professor Atsushi Mizuike and Dr. Masataka Hiraide of Nagoya University for their helpful advice on the flotation technique, and Assistant Professor Fuji Morii of Okayama University for her useful discussions.

## References

1) K. C. Thompson and D. R. Thomerson, *Analyst (London)*, **99**, 595 (1974).
2) P. N. Vijan and C. Y. Chan, *Anal. Chem.*, **48**, 1788 (1976).
3) H. D. Fleming and R. G. Ide, *Anal. Chim. Acta*, **83**, 67 (1976).
4) K. Shimizu and N. Ogata, *Bunseki Kagaku*, **12**, 526 (1963).

5) H. Hamaguchi, K. Kawaguchi, N. Onuma, and R. Kuroda, *Anal. Chim. Acta*, **30**, 335 (1964).
6) H. Hamaguchi, R. Kuroda, N. Onuma, K. Kawaguchi, T. Mitsubayashi, and H. Hosohara, *Geochim. Cosmochim. Acta*, **28**, 1039 (1964).
7) W. Yoshimura, *Bunseki Kagaku*, **24**, 714 (1975).
8) E. Amakawa, K. Onishi, N. Taguchi, and H. Seki, *Bunseki Kagaku*, **27**, 81 (1978).
9) A. Mizuike and M. Hiraide, *Anal. Chim. Acta*, **69**, 231 (1974).
10) S. Nakashima, *Analyst(London)*, **103**, 1031 (1978).
11) M. Hiraide, Y. Yoshida, and A. Mizuike, *Anal. Chim. Acta*, **81**, 185 (1976).
12) M. Hiraide and A. Mizuike, *Bunseki Kagaku*, **26**, 47 (1977).
13) Y. Kodama and H. Tsubota, *Bunseki Kagaku*, **20**, 1554 (1971).