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### Selective Determination of Tin (II) Ion in Water by Solvent Extraction with Salicylidenamino-2-thiophenol Followed by Reversed-Phase High-Performance Liquid Chromatography with Photometric Detection

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**Selective Determination of Tin (II) Ion  
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**ABSTRACT**

A selective determination method for tin (II) ion by reversed-phase high-performance liquid chromatography (HPLC) has been developed. Tin (Sn) ion was extracted into 4-methyl-2-pentanone at pH 4.5 as salicylideneamino-2-thiophenol (SATP) chelate. Sn–SATP chelate in the organic layer was then separated on a phenyl column with an eluent of methanol/water mixture containing 1 mmol/L NaCl and detected at 430 nm. The correlation coefficients of the calibration curves obtained with 5 mL Sn standards were

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more than 0.999 over the range of 10 ng/mL (ppb) to 1 µg/mL (ppm). The detection limit of Sn ion in 5 mL solution was 1.4 ppb, which corresponded to 3 times the standard deviation of the blank peak area. The detection limit was better than that of inductively coupled plasma-atomic emission spectroscopy (ICP-AES, 2 ppm). Reproducibility for 50 ppb Sn standard was 2.3% as relative standard deviation ( $N = 7$ ). Recovery tests were carried out by the presented HPLC method and ICP-AES with a spiked river water sample. The recoveries obtained by the HPLC method were 100.6% (500 ppb) and 96.3% (50 ppb). Since ICP-AES could not detect Sn ion at the ppb level, a recovery test was carried out for 5 ppm Sn with 99.8% recovery. Effects of foreign ions on the method were investigated with 55 metal ions. Almost none of the ions interfered except for Hg(II) and Zr(IV).

*Key Words:* Salicylideneamino-2-thiophenol; HPLC; Solvent extraction; Tin; Sn.

## INTRODUCTION

Though atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) are routinely used for metal analysis, ICP-AES and ICP-MS require expensive apparatuses, and the detection sensitivity of AAS and ICP-AES differs considerably according to the metal. On the other hand, the application of high-performance liquid chromatography (HPLC) in the separation and determination of metal ions has increased in recent years.<sup>[1-5]</sup> The authors reported determination of metal ions by RP-HPLC with photometric detection using dithiocarbamate<sup>[6,7]</sup> and  $\beta$ -diketones<sup>[8,9]</sup> as pre-column chelating reagents. In the case of photometric detection of a metal chelate, detection sensitivity is influenced by the molar absorptivity and retention time of the chelate. A more sensitive quantitative analysis is possible by combining pre-column derivatization HPLC with a simple solvent extraction.

Recently, some alkyl tin (Sn) compounds, such as tributyltin, were noted as endocrine disrupters (environmental hormone). Though organotin compounds have been determined by HPLC,<sup>[5]</sup> no determination method of Sn ion by HPLC was found in the literature cited.<sup>[1-5]</sup> Salicylideneamino-2-thiophenol has been used for determination of Ni,<sup>[10]</sup> Cu,<sup>[11]</sup> and Sn<sup>[12]</sup> by solvent extraction followed by molar absorption spectroscopy. We found that Sn reacted with SATP and was extracted into 4-methyl-2-pentanone [methyl isobutyl ketone (MIBK)] as Sn-SATP chelate.

In general, metal chelates sometimes dissociate in reversed-phase eluents and give no peak. However, the Sn-SATP chelate was found to be stable at certain HPLC conditions.



In this paper, analytical conditions such as extraction pH, shaking time, and eluent composition were studied for selective and sensitive determination of Sn(II) ion. The presented method does not use chlorinated solvents for extraction or HPLC separation. The detection limits, working range of calibration curves, reproducibility, and recovery were compared with the results obtained by ICP-AES.

## EXPERIMENTAL

### Instrumentation

The HPLC system consisted of a Jasco PU-1580i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), Rheodyne 9125i injector (Cotati, CA), Jasco UVIDEK-100-VI photometric detector, Cosmosil 5 Ph stainless steel column (250 × 4.6 mm ID, Nacalai Tesque, Kyoto, Japan), Shimadzu Chromatopac C-R8A data processor (Shimadzu Co., Kyoto, Japan), and thermostat water bath. A microsyringe with Ni-Ti alloy plunger was used for sample injection. A Yamato SA-31 auto-shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction. A Plasma-Spec I ICP-AES (Leeman Labs Inc., MA) was also used for Sn analysis. A micropipette was used for 1 mL or less volume of solution.

### Reagents

All reagents used were of analytical-reagent grade unless otherwise stated. Milli-Q water was used for aqueous solution preparation. The chelating reagent SATP (CAS No. 3449-05-6) was obtained from Dojindo Laboratories (Kumamoto, Japan) for use as a MIBK solution. Tin standard solution of 1000 µg/mL (ppm) for AAS was obtained from Wako Pure Chemical Industries (Osaka, Japan). The solution was prepared with SnCl<sub>2</sub> and 6 mol/L HCl. The other Sn solutions were obtained by dilution of the above solution (1000 ppm) with 0.6 mol/L HCl. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 µm). Acetic acid-sodium acetate buffer solution (pH 4.5) was prepared with 2 mol/L acetic acid and 2 mol/L sodium acetate solutions. River water was collected from the Kakehashi River (Komatsu, Japan). Concentrated hydrochloric acid was added to the river water immediately to adjust the pH to 1. The solution was then filtered through a membrane filter (0.45 µm pore size) and used as the river water sample for HPLC and ICP-AES analysis.



### Chelate Composition of Sn–SATP Chelate

To a centrifuge tube,  $(5 - x)$  mL of Milli-Q water,  $x$  mL of 1000-ppm ( $8.424 \times 10^{-3}$  mol/L) Sn standard solution, 2 mL of acetate buffer solution (pH 4.5),  $(1 - y)$  mL of MIBK, and  $y$  mL of 10 mmol/L SATP MIBK solution were added. After shaking for 20 min, the organic layer was chromatographed and the peak area of Sn–SATP was measured. Where  $(x, y)$  were (0.3, 0.7), (0.4, 0.6), (0.5, 0.5), (0.6, 0.4), (0.7, 0.3), the mole ratios of  $[\text{Sn}]/([\text{Sn}] + [\text{SATP}])$  were 0.27, 0.36, 0.46, 0.56, 0.66, respectively. The concentration of  $[\text{Sn}] + [\text{SATP}]$  was about  $1.2 \times 10^{-3}$  mol/L in the centrifuge tube.

### Recommended Extraction Procedure and HPLC Conditions

Transfer a sample solution or an Sn standard solution (5.0 mL) into a 10-mL centrifuge tube with a stopper. Adjust the pH of the solution to 4 or 5 if necessary. Add 2 mL of acetate buffer (pH 4.5) and 500  $\mu\text{L}$  of 0.1-mol/L SATP MIBK solutions. Shake the contents for 10 min. After standing for 5 min, determine the Sn–SATP chelate under the recommended HPLC conditions.

Column: Cosmosil 5 Ph (250  $\times$  4.6 mm ID, particle size 5  $\mu\text{m}$ ), column temperature: 40°C; eluent: methanol/water/0.1 mol/L NaCl (75 : 24 : 1, v/v); flow rate: 1.0 mL/min; injection volume: 10  $\mu\text{L}$  (organic layer), detection wavelength: 430 nm.

### Recovery Tests with a River Water Sample

River water samples (pH 1) of 4.5 mL and 500  $\mu\text{L}$  of Milli-Q water were taken into a centrifuge tube. To another centrifuge tube, 4.5 mL of a river water sample and 500  $\mu\text{L}$  of Sn standard were added. Sn concentrations in these solutions were determined according to the recommended procedure, and the recovery percentage was calculated by the results. A similar experiment was carried out by ICP-AES (Ar plasma, 40 MHz) with 224.60 nm for detection of Sn.

## RESULTS AND DISCUSSION

### Chelate Composition of Sn–SATP Chelate

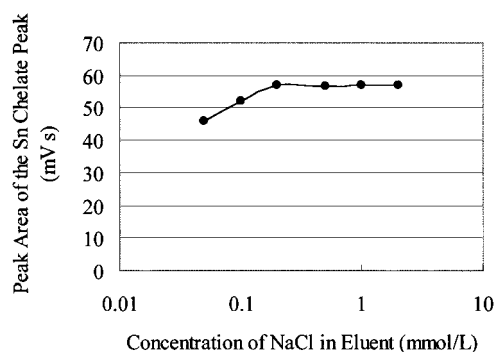
Ishii and Einaga reported that the mole ratio of Ni/SATP<sup>[10]</sup> and Cu/SATP<sup>[11]</sup> in both chelates were 1 : 1. The chelate composition of Sn–SATP was



examined by HPLC in a manner similar to the method mentioned above and the maximum peak area was obtained at a mole ratio of 0.46. Although the mole ratio of 0.500 (1 : 1 chelate) or 0.333 (1 : 2 chelate) was not measured, it seemed that the mole ratio of Sn–SATP chelate was 1 : 1 by considering our results and those of Ni–SATP and Cu–SATP. Since SATP appeared to ionize to  $\text{SATP}^-$  and  $\text{H}^+$ , another anion ( $X^-$ ) was probably required to form the neutral chelate  $[\text{Sn–SATP}]^+ X^-$ .

### HPLC Conditions

As an analytical column, Cosmosil 5C<sub>18</sub>-MS and Cosmosil 5 Ph columns were examined and the later was selected for rapid analysis because retention time of a blank peak appeared after the Sn chelate was shorter than that obtained by a Cosmosil 5C<sub>18</sub>-MS column. The Sn–SATP chelate seemed slightly unstable in a methanol–water eluent because the correlation coefficient of the calibration curve for Sn was not so good ( $r = 0.995$ ). At first, SATP was added to the methanol–water eluent for quantitative elution of the Sn–SATP chelate. However, a constant peak area was not obtained at a SATP concentration range of 0.1–1.0 mmol/L. When Sn was extracted into MIBK, there were significant amounts of chloride (Sn standard) and acetate anion (buffer solution) in the aqueous layer. We thought that the third component of Sn–SATP chelate was a chloride anion. Thus, the effect of NaCl on the peak area of Sn–SATP chelate was examined at a concentration range of 0.05–2.0 mmol/L and the result is shown in Fig. 1. Because constant and maximum peak areas were obtained at NaCl concentrations of 0.2–2.0 mmol/L, 1.0 mmol/L was employed. The detection wavelength (430 nm) was set for maximum



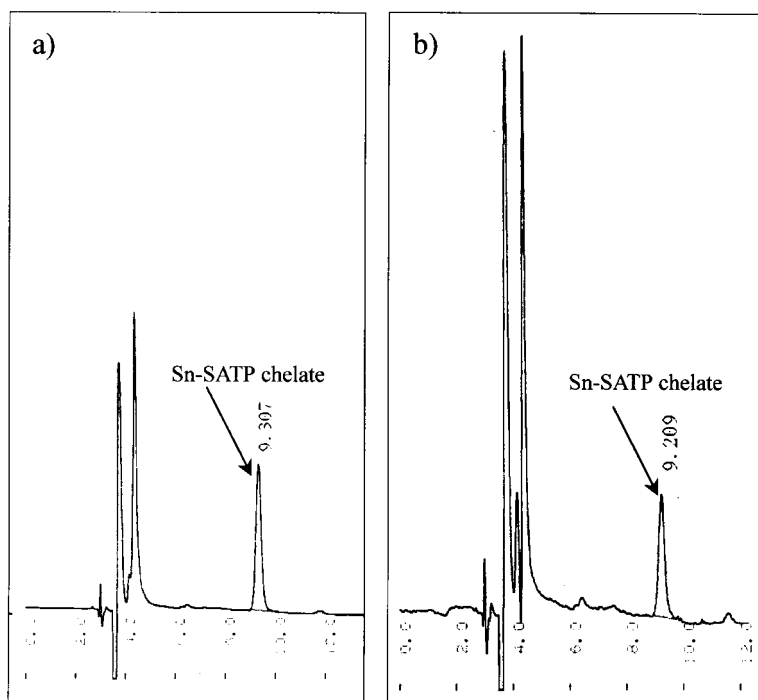
**Figure 1.** Effect of NaCl concentration in eluent on peak area of Sn–SATP chelate.



absorption of Sn-SATP.<sup>[12]</sup> The column temperature was set at 40°C considering the separation time (column pressure). Typical chromatograms of Sn-SATP chelates are shown in Fig. 2.

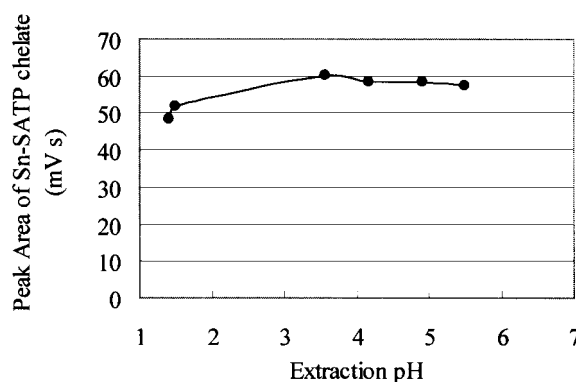
### Extraction Conditions

In order to extract Sn ion quantitatively into MIBK as SATP chelate, extraction conditions must be optimized. Thus, the extraction pH and shaking time were investigated according to the recommended procedure. The effect of pH on the extraction of Sn-SATP chelate is summarized in Fig. 3. Since constant and maximum peak areas were obtained over the pH range of 3.0–6.0, pH 4.5 was employed. This pH is easily controlled by an acetate buffer solution (acetic acid/sodium acetate).



**Figure 2.** Typical chromatogram of Sn-SATP chelate. Column: Cosmosil 5 Ph (250 × 4.6 mm ID); eluent: methanol–water–0.1 mol/L NaCl (75:24:1, v/v); flow rate: 1.0 mL/min, detection: 430 nm, concentration of Sn ion in 5 mL solution: (a) 0.4 ppm and (b) 0.04 ppm. Extraction conditions are in the text.





**Figure 3.** Effect of pH on extraction of Sn-SATP chelate. Extraction conditions are the same as the recommended procedure, except for pH.

Because the Sn ion was quantitatively extracted into MIBK by shaking for 5–30 min, 10 min was selected.

Stability of the Sn-SATP chelate in MIBK (organic layer) was also examined. Extraction was carried out according to the recommended procedure and the organic layer was put into a micro test tube with a stopper. After standing, the organic layer of 10  $\mu$ L was chromatographed and the peak areas of the Sn chelate peak were plotted against the standing time. The result indicated that Sn-SATP chelate is stable for at least 6 hr.

### Calibration Curves, Detection Limit, and Reproducibility

Calibration curves for Sn ion were prepared with Sn standard of varying concentrations by the recommended procedure. Correlation coefficients of the

**Table 1.** Calibration curves for Sn ion.

Concentration range (ppm)	Equation of line	Correlation coefficient	Measuring points (ppm)
2–10	$y = 3.9879x + 72.938$	0.9806	2, 4, 6, 8, 10
0.1–1	$y = 126.7x + 0.0114$	0.9995	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1	$y = 137.3x + 1.1938$	0.9996	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10

*Note:*  $y$ : peak area (mV s);  $x$ : concentration of Sn (ppm).





**Table 2.** Effects of foreign metal ions on determination of 0.1 ppm Sn ion.

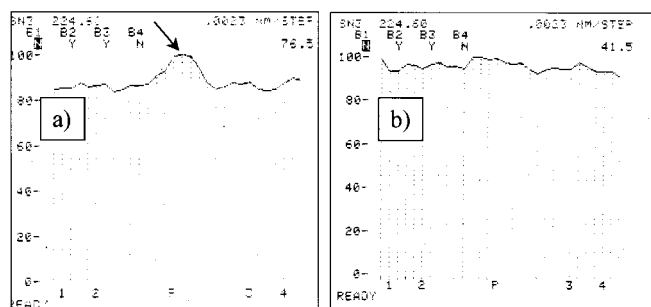
Tolerance limit (ppm)	Metal ion
100	As(III), Ba(II), Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cs(I), Dy(III), Eu(III), Er(III), Fe(III), Ga(III), Gd(III), Ge(IV), Ho(III), K(I), La(III), Lu(III), Mg(II), Mn(II), Mo(VI), Na(I), Nd(III), Pb(II), Pd(II), Pr(III), Pt(IV), Sb(III), Se(IV), Si(IV), Sm(III), Sr(II), Tb(III), Tl(I), Tm(III), Yb(III), Y(III), Zn(II)
40	Ag(I), Au(III), In(III), Sc(III), V(V)
20	Cu(II)
10	Cr(VI), Ni(II)
4	Al(III), Te(IV), W(VI)
1	Rh(III), Ti(IV)
0.4	Zr(IV)
0.1	Hg(II)

*Note:* The tolerance limit value of the foreign ion concentration was taken as the value that caused an error of less than 10% in the recovery of Sn ion.

calibration curves were more than 0.999 over the concentration range of 10 ppb to 1 ppm, as shown in Table 1.

The detection limit of Sn ion in 5 mL solution was 1.4 ppb, which corresponded to 3 times the standard deviation of the blank peak area.

Reproducibility of Sn chelate peak areas obtained with 50 ppb Sn standard was 2.3% as relative standard deviation ( $N=7$ ).



**Figure 4.** Profiles (spectra) of Sn peaks (see the arrow) by ICP-AES. Concentration of Sn ion: (a) 5 ppm and (b) 1 ppm.



Effects of Foreign Ions

The effects of 55 foreign ions on the determination of 0.1 ppm Sn ion (5 mL) were investigated. Alkali and alkaline earth metal ions did not interfere with the determination of Sn ion at a thousand times the concentration of Sn

Table 3. Recovery tests for Sn ion with a river water sample.

No. of run	Sample (ppm)	Added (ppm)	Found (ppm)	Recovery	Equation of calibration curve	Correlation coefficient
HPLC						
1	0.00	0.500	0.485	97.0	$y = 123.74x - 1.4601$	0.9999
2	0.00	0.500	0.507	101.5		
3	0.00	0.500	0.495	99.0		
4	0.00	0.500	0.509	101.7		
5	0.00	0.500	0.518	103.6		
Average				100.6		
SD				2.6		
RSD				2.6		
1	0.00	0.050	0.0483	96.5	$y = 277.42x + 1.8044$	0.9992
2	0.00	0.050	0.0488	97.5		
3	0.00	0.050	0.0473	94.5		
4	0.00	0.050	0.0504	100.7		
5	0.00	0.050	0.0461	92.1		
Average				96.3		
SD				3.2		
RSD				3.4		
ICP-AES						
1	0.00	5.00	4.33	86.6	$y = 323.12x - 487.39$	0.9985
2	0.00	5.00	4.93	98.6		
3	0.00	5.00	5.60	112.0		
4	0.00	5.00	4.92	98.4		
5	0.00	5.00	5.17	103.4		
Average				99.8		
SD				9.2		
RSD				9.2		

Note: Detector response of HPLC was 0.04 AUFS (0.5 ppm) and 0.02 AUFS (0.05 ppm). Recoveries obtained by HPLC on other days were  $98.4\% \pm 1.6\%$  for 0.5 ppm Sn and  $98.6\% \pm 2.1\%$  for 0.05 ppm Sn ( $N = 5$ ).

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ion. Hg ion of 0.2 ppm and 1 ppm Zr interfered with the determination of 0.1 ppm Sn ion. The other metal ions could coexist at 10 times or more the concentration of Sn ion as shown in Table 2.

### Recovery Tests with a River Water Sample by HPLC and ICP-AES

The concentration of Sn ion in a collected river water sample was less than the determination limits (10 ppb) of the HPLC method. Thus, a recovery test was carried out with the sample. The Sn standard was added to the river water sample. Then the solution was analyzed by the proposed HPLC method and ICP-AES. The recoveries obtained by HPLC for 0.05 and 0.5 ppm Sn were 96.3% and 100.6%, respectively. A similar experiment by ICP-AES fell through because the detection limit of Sn was about 2 ppm. The detection limit of Sn ion by ICP-AES was determined by the 5 and 1 ppm profiles (spectra) shown in Fig. 4. Thus, a recovery test for 5 ppm Sn was carried out and 99.8% recovery was obtained. Similar recovery tests were repeated by the HPLC method and almost equal results were obtained. More details are shown in Table 3.

### CONCLUSION

The presented method for tin analysis does not use chlorinated solvents for extraction or HPLC separation. This method requires a conventional HPLC apparatus equipped with a photometric detector. The extraction procedure is simple and requires no skill. Though this method is simple and easy, reproducibility and linearity of calibration curves were better than those of ICP-AES. Furthermore, the detection limit (1.4 ppb) and lower determination limits (10 ppb) of Sn ion were superior to those of ICP-AES (2 ppm and 2 ppm, respectively).

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