

*Original Paper*

## Speciation Analysis of Inorganic Tin (Sn(II)/Sn(IV)) by Graphite Furnace Atomic Absorption Spectrometry Following Ion-Exchange Separation

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**Abstract.** A new method based on anion exchange resin separation and graphite furnace atomic absorption spectrometry (GFAAS) detection is proposed for the determination of inorganic tin species. The result showed that Sn(IV) was quantitatively retained on the resin when  $[HCl] = 9.0 \text{ mol} \cdot \text{L}^{-1}$ , but Sn(II) could not be adsorbed on the resin under the same condition. Thus, a separation of Sn(II) and Sn(IV) has been realized. When the concentration of NaOH solution was between  $2.0\text{--}7.0 \text{ mol} \cdot \text{L}^{-1}$ , Sn(IV) that adsorbed on the resin could be eluted from the resin completely. Meanwhile, under the atmosphere and the nitrogen states, the translation between Sn(II) and Sn(IV) was investigated. Under the optimal conditions, the detection limit of Sn(IV) is  $0.40 \mu\text{g} \cdot \text{L}^{-1}$  with RSD of 2.3% ( $n = 5$ ,  $c = 2.0 \mu\text{g} \cdot \text{L}^{-1}$ ). The proposed method was applied to the speciation analysis of tin in different water samples and the recovery of total Sn was in the range of 98.7–101.7%. In order to verify the accuracy of the method, a certified reference water sample was analyzed and the results obtained were in good agreement with the certified value.

**Key words:** Speciation of inorganic tin; ion exchange resin; graphite furnace atomic absorption spectrometry.

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Tin is a toxic metal that could gather in human's body and tissue of animals [1]. Tin in the atmosphere mainly comes from metal smelt and combustion of coal. Under many situations, tin, especially meals that have high concentration of tin brought serious interference to metabolize of Zinc [2]. As well known, there are mainly two chemical species of inorganic tin (Sn(II)/Sn(IV)) in environmental samples. The toxicity of  $\text{SnCl}_2$  to living organisms has been demonstrated [2]. Differential toxicities of the different forms of an element have dictated an increasing development and use of analytical determination for the chemical species. The behavior of inorganic tin species as a moderately corrosion-resistant metal is of considerable interest due to its important applications in food and electronic industries [3]. Therefore, the analysis and monitoring of inorganic tin species in environmental samples are extremely important.

In order to determine trace or ultra-trace inorganic tin species in environmental sample, a chemical separation and preconcentration step is often necessary prior to analysis. For the speciation of inorganic tin, the separation methods reported in literature are usually based on solvent extraction [4], liquid chromatography [5], gas chromatography [6], solid extraction [7]. However, most methods above-mentioned are often complicated and time-consuming. Thus, a new

simple separation technique for tin species is essential. The ion exchange procedure with the advantages of relative simplicity in the operation and high pre-concentration factors [8, 9], was widely employed in chemical separation procedures. Several techniques have been employed for the determination of inorganic tin in various sample materials. These include spectrophotometry, which has some disadvantages, mainly poor detection limit of about  $1.0 \text{ mg} \cdot \text{L}^{-1}$  [10, 11]; ICP-AES [12]; the hydride generation (HG) technique, which has high sensitivity and selectivity but always been strongly interfered by the acidity of the matrixes in sample [13]. GFAAS was a favorable method for the determination of tin at very low concentration, which has high sensitivity, selectivity and much less interference [2]. Many researches showed that the effective means of speciation analysis are combining convenient and reliable separation and pre-concentration with sensitive detection methods. Most of above analytical methods cannot distinguish Sn(II) and Sn(IV). Literature [14, 15] developed alternative, sensitive and selective polarographic methods for the determination of inorganic tin species, other methods for the determination of inorganic tin species seems to be lacking. In this paper, an original system for researching the adsorption behavior of Sn(II) and Sn(IV) on 717<sup>#</sup> anion exchange resin has been devised. Under the optimal conditions, Sn(IV) could quantitatively retain on the resin and be separated from Sn(II). Following preconcentration, the analyte in eluted solution was detected by GFAAS with ascorbic acid (VC) as the matrix modifier [11]. Under the atmosphere and the nitrogen states, the translation between Sn(II) and Sn(IV) were investigated. The proposed method was applied to the determination of inorganic tin species in water samples with satisfactory results.

## Experimental

### Apparatus and Reagents

Unless other stated, all the reagents used were of analytical grade.

- (1) 717<sup>#</sup> anion exchange resin, Cl<sup>-</sup> type, (80–100 mesh) (Shanghai Chemical Reagent Corporation, Shanghai, China).
- (2) Stock solution of  $1.000 \text{ mg} \cdot \text{mL}^{-1}$  Sn(II) was prepared by dissolving of 0.0905 g of SnSO<sub>4</sub> (Shanghai Chemical Reagent Corporation, Shanghai, China) in  $3.0 \text{ mol} \cdot \text{L}^{-1}$  H<sub>2</sub>SO<sub>4</sub>. The solution was prepared daily. Stock solution of  $1.000 \text{ mg} \cdot \text{mL}^{-1}$  Sn(IV) was prepared by dissolving of 0.1000 g of tin (99.99%) in 5.0 mL H<sub>2</sub>SO<sub>4</sub>, used  $0.5 \text{ mol} \cdot \text{L}^{-1}$  H<sub>2</sub>SO<sub>4</sub> diluted to scale. 5.0% (W/V) ascorbic acid (VC) (Shanghai Chemical

**Table 1.** Operating condition for GFAAS

Parameters	
Element	Sn
Wavelength/nm	286.3
Slit/nm	1.3
HCL Current/mA	5
Graphite furnace	
Dry temp. (°C)	100 (Ramp 15 s, Hold 15 s)
Ashing temp. (°C)	800 (Ramp 10 s, Hold 10 s)
Atomization temp. (°C)	2500 (Ramp 0 s, Hold 6 s)
Cleaning temp. (°C)	2700 (Ramp 2 s, Hold 3 s)
Flow rate (Ar)	$200 \text{ mL} \cdot \text{min}^{-1}$

Reagent Corporation, Shanghai, China) solution: 0.5000 g VC was prepared by dissolving in 10 mL of deioned water. The solution was prepared daily.  $1.0\text{--}10.0 \text{ mol} \cdot \text{L}^{-1}$  HCl solution.  $1.0\text{--}8.0 \text{ mol} \cdot \text{L}^{-1}$  NaOH solution. All other reagents used in this work were of the highest available purity free from tin traces and dissolved in the deioned water.

A WFX-100 graphite furnace atomic absorption spectrometer (Beijing RuiLi Instrument Company, China). The hollow cathode lamp for Sn (Beijing RuiLi Instrument Company, China) was used. The operating condition for GFAAS was given in Table 1. A pH-25 pH-meter (Shanghai jingkeleici, China), A timing multifunctional oscillator (Guohua Limited Company, China) were used.

### Recommended Procedure

Pretreatment of 717<sup>#</sup> anion exchange resin (Cl<sup>-</sup>-type).

The resin was steeped in the saturated NaCl solution and then, rinsed by the deioned water. Washed the resin by  $1.5 \text{ mol} \cdot \text{L}^{-1}$  HCl solution, deioned water,  $1.5 \text{ mol} \cdot \text{L}^{-1}$  NaOH solution and deioned water in sequence, the volume of the saturated NaCl, HCl and NaOH solution and deioned water were all two times of the volume of the resin, stirred in each case during 15 min. At last, the resin was put over again in the saturated NaCl solution. After that step, the resin was finally rinsed with deioned water and air-dried [16].

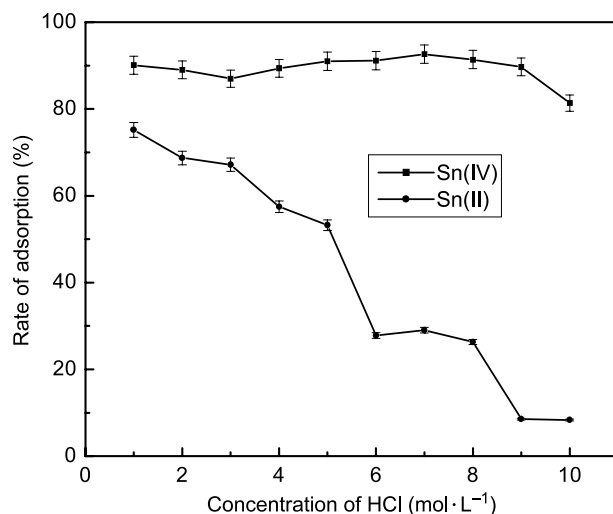
### Adsorption and Desorption of Sn(II)/Sn(IV)

10.0 mL analytical solution containing Sn(II) [and/or Sn(IV)] and 0.3000 g 717<sup>#</sup> anion exchange resin was adjusted the acidity to be required and kept the nitrogen atmosphere. The mixture was shaken on the timing multifunctional oscillator for 3 h and then, was eluted by NaOH solution. Sn(IV) in effluent solution was detected by GFAAS. Sn(II) was calculated by total Sn and Sn(IV).

## Results and Discussion

### Effect of the HCl Concentration on Adsorption of Sn(II)/Sn(IV)

The acidity of the solution is one of the important factors affecting the adsorption of Sn(II)/Sn(IV). The influence of acidity on the adsorption efficiency of Sn(II) and Sn(IV) on the 717<sup>#</sup> anion exchange resin was researched (Fig. 1).



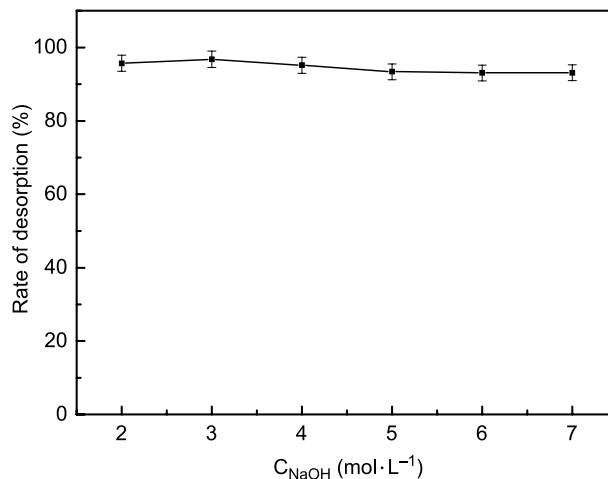
**Fig. 1.** Effect of the HCl concentration on adsorption of Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ ) and Sn(II) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ )

It could be seen from Fig. 1, the maximum adsorption of Sn(IV) is at about  $4.0\text{--}9.0 \text{ mol} \cdot \text{L}^{-1}$  HCl and the adsorption of Sn(II) decreases gradually with the concentration of HCl increasing. As a result, Sn(II)/Sn(IV) could be separated at  $[\text{HCl}] = 9.0 \text{ mol} \cdot \text{L}^{-1}$ . As we known, the ion exchange resin could exchange metal ions based on their size, charge density etc [17].

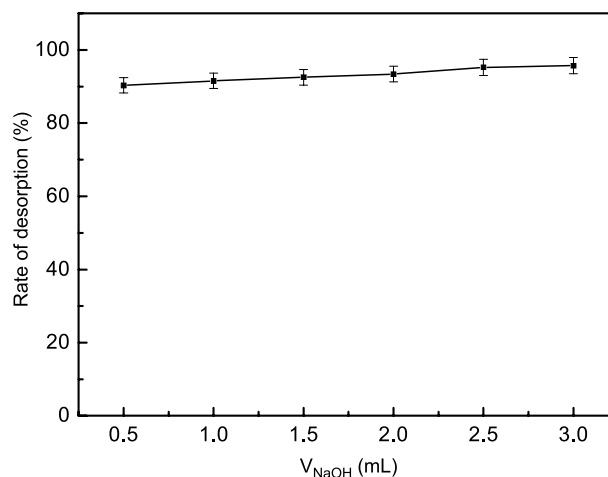
In high concentration of HCl solution, not only the inorganic tin exists as Sn(II) and Sn(IV) but also organo-tin has the tendency to cleavage the C–Sn band and form Sn(II) and Sn(IV) [18]. Sn(II) exists as  $\text{SnCl}_4^{2-}$  which has a regular tetrahedron configuration, however, Sn(IV) exists as  $\text{SnCl}_6^{2-}$  and has an octahedron configuration. Through the calculational methods of B3LYP/Lan12DZ [19–21], the band length of  $\text{SnCl}_4^{2-}$  was 2.82,  $\text{SnCl}_6^{2-}$  was only 2.54. The band length of  $\text{SnCl}_4^{2-}$  was longer than  $\text{SnCl}_6^{2-}$  and the results were in agreement with those obtained by reference [22]. Consequently,  $\text{SnCl}_6^{2-}$  has smaller size and higher charge density, and the adsorption on the resin was easier. So, the separation of Sn(II) and Sn(IV) was achieved. In the later work,  $[\text{HCl}] = 9.0 \text{ mol} \cdot \text{L}^{-1}$  was chosen.

#### Effect of the NaOH on Desorption of Sn(IV)

With NaOH as the eluant, the eluted behavior of Sn(IV) was studied. Sn(IV) could be eluted from the resin completely when the concentration of NaOH was between  $2.0\text{--}7.0 \text{ mol} \cdot \text{L}^{-1}$  (Fig. 2). So, the eluted



**Fig. 2.** Effect of the NaOH concentration on desorption of Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ )



**Fig. 3.** Effect of the volume of NaOH on desorption of Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ )

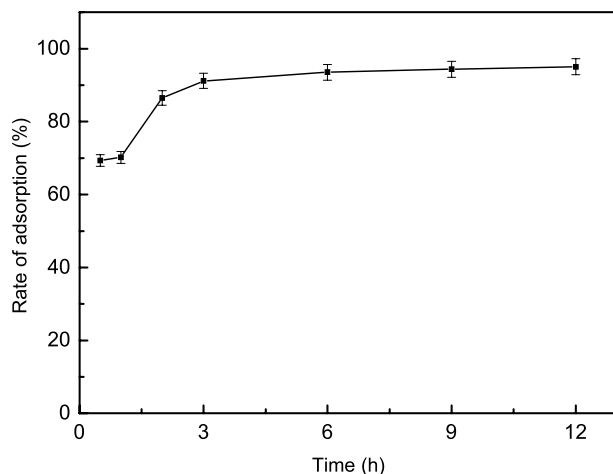
concentration of NaOH equaled to  $3.0 \text{ mol} \cdot \text{L}^{-1}$  was selected.

Amount of  $3.0 \text{ mol} \cdot \text{L}^{-1}$  NaOH solution were added variously to investigate the effects on the rate of desorption of Sn(IV), the result was shown in Fig. 3. The rate of desorption of Sn(IV) was increased with the volume of NaOH, So optimum volume of NaOH solution chosen for this work was 3.0 mL.

#### Effect of Time on Adsorption of Sn(IV)

The effect of time on the rate of adsorption was investigated and the results were illustrated in Fig. 4.

It could be seen that the adsorption of Sn(IV) after 0.5 h was close to the adsorption of 1 h, but after 2 h, it

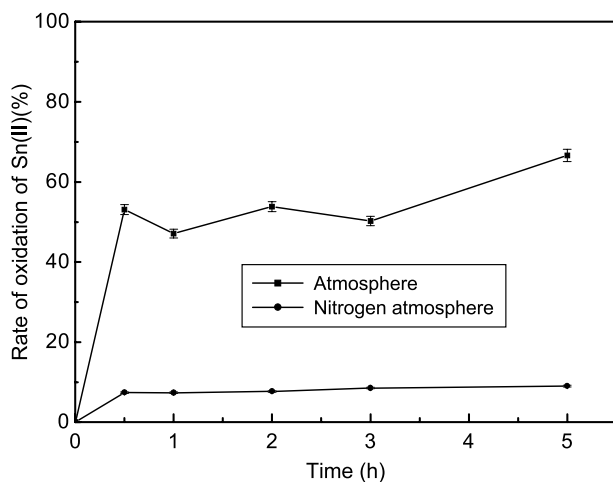


**Fig. 4.** Effect of time on adsorption of Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ )

raised quickly and reached the optimal adsorption after 3 h. Lengthened time, the rate adsorption of Sn(IV) no longer increased. Thus, the adsorption time was 3 h.

#### Transformation Between Sn(II) and Sn(IV)

Species stability in the samples is an important issue, since natural environment samples are not usually analyzed immediately after sampling and long-term storage can produce a significant alteration of the chemical. As the early depiction, Sn(II) and Sn(IV) could translate reciprocally. Therefore, it is very important to consider the influence of the factor on the translation between Sn(II) and Sn(IV). In the atmosphere and the nitrogen atmosphere states, the translation



**Fig. 5.** Effect of time of the transformation between Sn(II) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ ) and Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ )

between Sn(II) and Sn(IV) was studied. The results were shown in Fig. 5.

In the atmosphere, Sn(II) was oxidized to Sn(IV) after 0.5 h and the oxidation gradually increased along with the time. But in the nitrogen, there was less than 10% of Sn(II) was oxidized. Resulting in a gradual decrease in Sn(II) concentration the oxidation of Sn(II) by atmospheric oxygen was an unwanted process for most of the practical. In this work, Sn(II) was not oxidized to Sn(IV) due to nitrogen.

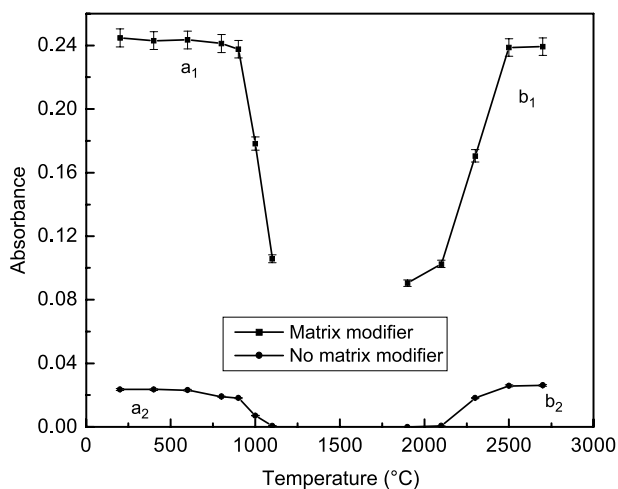
#### Matrix Modifier

In GFAAS, the tendency of tin to form volatile compounds during the ashing and drying steps and its interaction with the carbon of the graphite tube wall causes erratic results easily [23]. The modifiers stabilize the analyte of interest to a higher temperature so that the interfering matrix can be removed during the drying stage [24]. In this paper, VC was employed as the matrix modifier in this work. Ashing curve and atomization curve were shown in Fig. 6.

Obviously, from the Fig. 6, it could be seen that VC was a quite effective matrix modifier for the determination of Sn. The sensitivity of determination was enhanced greatly.

#### Analytical Performance

By using the proposed method, the calibration graph for the GFAAS determination of Sn(IV) were linear over  $0\text{--}10.0 \mu\text{g} \cdot \text{mL}^{-1}$ . The corresponding coefficient of correlation was  $r = 0.9989$ . The relative standard



**Fig. 6.** Ashing curve ( $a_1$ ,  $a_2$ ) and atomization curve ( $b_1$ ,  $b_2$ ), Sn(IV) ( $c = 0.2 \mu\text{g} \cdot \text{mL}^{-1}$ ), Ascorbic acid (VC) ( $c = 5.0\%$ )

**Table 2.** Determination of tin in standard water sample

GBW(E)0805460408 <sup>a</sup>	Standard value ( $\mu\text{g} \cdot \text{mL}^{-1}$ )	Determination value ( $\mu\text{g} \cdot \text{mL}^{-1}$ )
Sn(IV)	1.00	$1.01 \pm 0.2$
Sn(II) <sup>b</sup>	1.00	$0.98 \pm 0.1$

<sup>a</sup> National reference materials (China).

<sup>b</sup> Spiked environmental water reference sample.

**Table 3.** Determination results of inorganic tin in water samples (n = 3)

Sample	$\mu\text{g} \cdot \text{L}^{-1}$			Recovery (Sn)** (%)
	Added Sn(IV)	Measured Sn(IV)	Measured Sn(II)*	
Tap water	0.00	0.37	0.12	
	1.00	1.34	0.12	98.7
	2.00	2.39	0.12	100.8
	0.00	1.81	0.21	
Lake water	1.00	2.83	0.21	101.7
	2.00	3.79	0.21	99.5

\* Calculated by subtracting Sn(IV) from total Sn.

\*\* The recovery of total tin.

deviation was 2.3% for  $n = 5$ ,  $c = 2.0 \mu\text{g} \cdot \text{L}^{-1}$ . The limit of detection by the described procedure was  $0.40 \mu\text{g} \cdot \text{L}^{-1}$ .

### Determination of Sample

The standard sample was determined according to procedure Section 2.2. The results were shown in Table 2. The analytical contents of Sn(II) and Sn(IV) in environmental reference materials are in good agreement with the certified value.

The proposed method was applied to the determination of speciation of inorganic tin in tap water samples and the Lake water samples, the recovery of total Sn was in the range of 98.7–101.7%. The results were shown in Table 3. The recovery was the value of recovery of total tin.

### Conclusion

Selective adsorption of Sn(IV) on the 717<sup>#</sup> anion exchange resin could be applied to separate Sn(IV)

from Sn(II). Use of the matrix modifier enhanced the sensitivity of the determination of tin. The method is characterized with simplicity, rapidity, selectivity, safety, low cost and high preconcentration factor, and is suitable for the speciation analysis of inorganic tin in environmental water samples.

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