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Using Strontium As A Matrix Modifier For Tin Determination In Environmental Water Samples By Graphite Furnace Atomic Absorption Spectrometry



Liang Shu-xuan
College of Chemistry and Environmental
Science, Hebei University,
Key Laboratory of Analytical Science and
Technology of Heibei Province,
Baoding 071002 (P.R.CHINA)
Tel: +86-312-507-9739
E-mail: liangsx168@yahoo.com.cn

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Sun Han-wen¹, Kang Wei-jun², Ha Jing³

¹College of Chemistry and Environmental Science, Hebei University,
Key Laboratory of Analytical Science and Technology of Heibei Province,
Baoding 071002 (P.R.CHINA) E-mail: hanwen@mail.hbu.edu.cn

²School of Public Health, Hebei Medical University,
Shijiazhuang, 050017 (P.R.CHINA)

³College of Chemical & Pharmaceutical Engineering,
Hebei University of Science & Technology, 050017 (P.R.CHINA)

ABSTRACT

The effectiveness of strontium nitrate as a modifier for the determination of tin in a variety of water samples by ETAAS was evaluated. The modifier allows the quantitative stabilization of Sn in water samples up to 1300 °C during the pyrolysis step. The modifier significantly enhances the sensitivity of Sn determination. The observed detection limit is 4.31 µg/L with a sample volume of 20 µL. The characteristic mass of the proposed method is 16.8 pg. The tolerable amounts of various interferences, such as chloride, sulfate and carbonate, are high enough for the determination of tin in a variety of waters in the presence of the modifier. The recoveries of spiked tin in tap water, extract solution from unplasticized polyvinyl chloride pipes, spiked water and contaminated water from a ditch were 96.4 – 102.0%. Calibration curves were parallel when using standard additions and standard curve.

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KEYWORDS

Tin;
Strontium;
Water samples;
Graphite furnace atomic
absorption spectrometry.

INTRODUCTION

The importance of tin and organotin compounds (OTC) as exogenous presence in environment and biota has become increasingly remarkable^[1]. As a

consequence, many analytical procedures have been developed. Because of its sensitivity, versatility, speed and specificity, graphite furnace atomic absorption spectrometry (GFAAS) has been extensively utilized in the direct analysis of water for numerous

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elements. However, problems arise in analyzing samples composed of complex matrices. Chemical interference encountered in a pulse-heated electrothermal atomizer frequently causes depression of absorbance signals due to the co-volatilization of the analyte with the matrices. Currently available ways of reducing such interferences include platform atomization, probe atomization, Zeeman effect background correction and chemical treatment of the sample in the graphite furnace^[2]. Chemical modification is preferred as simple approach to alleviating interferences encountered especially in the direct determination of volatile elements in samples with significant amounts of matrices. The modifiers can act as pyrolysis aids and delay the vaporization of the analyte before the graphite tube is nearly isothermal, the ideal condition for atomization.

Tin is not an easy element to determine by ETAAS as it volatilizes at temperatures below 700 °C^[3,4]. The direct determination has been fraught with problems, such as volatilization loss, interaction with the graphite tube, and vapor phase interference. A large number of different chemical modifiers have been proposed to overcome these problems^[5,6]. To date, a variety of modifiers have been suggested for Sn, the most common being palladium alone or in combination with magnesium nitrate^[7-9], refractory metal such as Hf, Nb, W, Zr^[10-13]. Despite considerable efforts having been made to search for valid Sn modifiers in the past, only limited success has been reported for modifiers that meet some or all the criteria of a suitable modifier.

In our previous study^[14], it has shown that strontium nitrate was a promising modifier for the tin in aqueous solutions. The main aim of this work was to optimize the method further and apply the proposal method to the determination of water sample. Furthermore, the influence of chloride, sulfite, carbonate and ions was examined.

EXPERIMENTAL

Instrument

The measurements were performed using a Perkin-Elmer Model Zeeman 5000 atomic absorp-

tion spectrometer (Perkin-Elmer Life and Analytical Sciences, Shelton, CT USA), equipped with a HGA500 graphite atomizer and a 3600 data processor. The light source was a hollow cathode lamp (Beijing Vacuum Electronics Research Institute), operating at 8 mA, using the 286.3-nm line and a spectral bandwidth of 0.7 nm unless indicated otherwise. Zeeman background correction and pyrolytically coated graphite tubes was used. The tubes were conditioned prior to use. For all measurements, integrated absorbance was used with an integration time of 4s.

When chemical modifiers were used, they were injected separately from sample solutions. Aliquots used for the samples and modifiers were 20 µl and 10 µl respectively in all cases except when indicated otherwise. The furnace program and instrumental conditions are given in TABLE1.

TABLE 1: Graphite furnace program for tin determination.

Step	Temp (°C)	Ramp time (s)	Hold time (s)	Gas flow (mL/min)	Read	Recorder
1	110	10	20	300		
2	1300	20	20	300		
3	2500	0	3	0	-1	-1
4	2600	1	3	300		

All glassware was kept in 5% nitric acid for at least 48 hours and before use was washed three times with de-ionized water.

Reagents

De-ionized water by sub-boiling distillation in an all-quartz apparatus was used for preparation of all standards and samples throughout. Chemicals with the highest available purity but at least of analytical-reagent grade were used to prepare solutions in de-ionized water. All glassware was soaked 5% nitric acid for 24 h and then rinsed with de-ionized water.

A stock solution of 1000 mg/L tin was prepared by the dissolution of precisely 0.5000g of high-purity tin powder in 50mL concentrated hydrochloride acid and diluted to 500mL solution. The working

standard solutions were prepared daily by serial dilution with 2% HCl.

The stock solution was diluted with 2% hydrochloric acid to generate working standards. A 1% solution of ultrapure hydrochloric acid served as the blank.

Chemical modifier of strontium nitrate solution was prepared by dissolving 0.2415g $\text{Sr}(\text{NO}_3)_2$ in 1% HNO_3 and diluted to 100mL, and the resulting solution was established as the 1000mg/L solution of Sr. A 20 μg amount of $\text{Sr}(\text{NO}_3)_2$ was used as a chemical modifier.

Water samples and their characterizations

All sample containers were new and acid-cleaned prior to use. Care was taken to avoid contamination at all stages.

Four kinds of water samples were used for the determination of tin. These water samples and their characterizations were described as follows.

Synthetic water sample: The spiked water was composed by Cd 100, Pb 1000, Cu 1000, Cr 500, Zn 5000, Ni 500, Sn 10.0 μg /L.

Extract solution from unplasticized polyvinyl chloride (PVC-U) pipes: PVC-U pipe is excellent for underground pressurized water delivery system and is extensively used for agriculture, municipal, and domestic applications. Certain stabilizers (organic derivatives to tin) of PVC-U may pass through the wall of the pipe. In order to verify that the extracted quantities do not exceed a certain concentration, tin of the water extract from PVC-U pipes was determined by the proposal method. The extract was performed according to the specified method of ISO 3114-1977 (Unplasticized polyvinyl chloride pipes for potable water supply—Extractability of lead and tin—Test method) and GB 9644-88 (Unplasticized polyvinyl chloride pipes fittings for drinking water supply—Extractability of lead, tin, cadmium and mercury occurring as impurities—Test method and permitted levels). The tubular test piece was prewashed during a fixed time. After this they were extracted with acidified (CO_2) water in three steps and the third extract was used for sample.

Contaminated water from a ditch: The waste water was taken directly from a ditch near the highway.

The surface and ground waters in the area have been substantially contaminated with fly ash wastes from local thermoelectric companies. The ditch water came from surface runoff, although mixing with the groundwater was possible before the water was discharged to the ditch. These samples were filtered through 0.45 μm syringe filters using a micropore filter assembly. They were kept at 4 °C for a brief period of time before analysis.

Tap water: The tap water used in this study was taken from the campus of Hebei University. The source of the water is Xidayang reservoir of Hebei province. The water sample was taken after running the tap for a few minutes and analyzed without further treatment.

Procedure

For the direct determination of Sn by ETAAS, quantitative results were obtained based on the peak heights produced from 20 μL aliquots of standard or sample solutions. A chemical modifier was injected separately from sample solution. A 40 μL of the aliquots (20 μL sample plus 20 μL chemical modifier) was pipetted into the pyrolytic graphite-coated tubes in all cases except when indicated otherwise. The internal gas flow was interrupted during an atomization stage. The atomic absorption signals of the elements were measured against blank standard solutions of 2% HCl. The quantification of the analyte in samples was achieved through aqueous standard calibration curve and the standard additions calibration method.

RESULTS AND DISCUSSION

Influence of strontium nitrate on signal

The influence of $\text{Sr}(\text{NO}_3)_2$ on the signal of tin was investigated at 286.3nm. The results in figure 1 show that the maximum number of Sn atoms is present in presence of Sr modifier. In the absence of modifier, absorption peak of tin is broader with a pronounced tongue (Figure 1a) and the peak height is suppressed when compared with the temporal profile of figure 1b.

The influence of different methods of preparing $\text{Sr}(\text{NO}_3)_2$ solution was studied. When $\text{Sr}(\text{NO}_3)_2$ was

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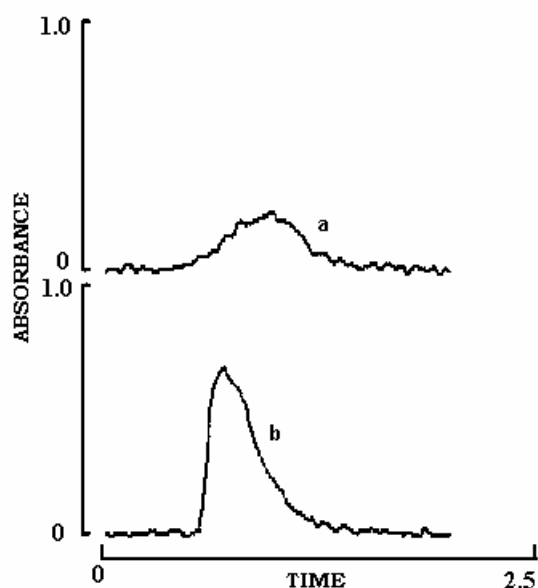


Figure 1: Effect of Sr modifier on absorption profile.
a-in the absence of any modifier;
b- in the presence of $\text{Sr}(\text{NO}_3)_2$

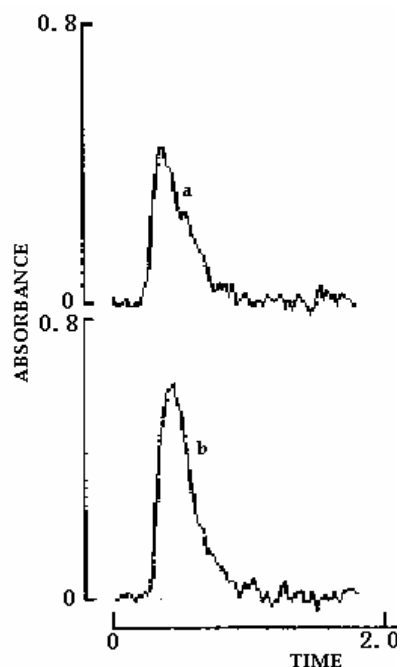


Figure 2: The influence of solvent of $\text{Sr}(\text{NO}_3)_2$.
a- H_2O ; b-1% HNO_3

dissolved in pure water, the absorption peak was lower than that of in 1% HNO_3 . The result was shown in figure 2.

The mass of $\text{Sr}(\text{NO}_3)_2$ was also optimized. When 1000mg/L Sr was used as modifier, a 20 μL of the modifier was sufficient.

Stabilization effect of strontium

The critical charring temperature for tin was 700°C in the absence of a modifier. In the presence of strontium, the critical charring temperature for tin was raised to 1300°C. The sensitivity was improved some dozens fold for tin in the presence of Sr modifier than in the absence of any modifier.

Influence of different wavelength

The influence of the wavelength of tin hollow cathode lamp on the Sn signal was tested by injection 20 μL 80 $\mu\text{g/L}$ Sn and 10 μL $\text{Sr}(\text{NO}_3)_2$ modifier. The difference of absorption profile was clearly observed as shown in figure 3(a), (b) and (c). The peak heights at three kinds of wavelength were 0.492, 0.160, 0.037, respectively. Thus 286.3nm was selected as absorption wavelength.

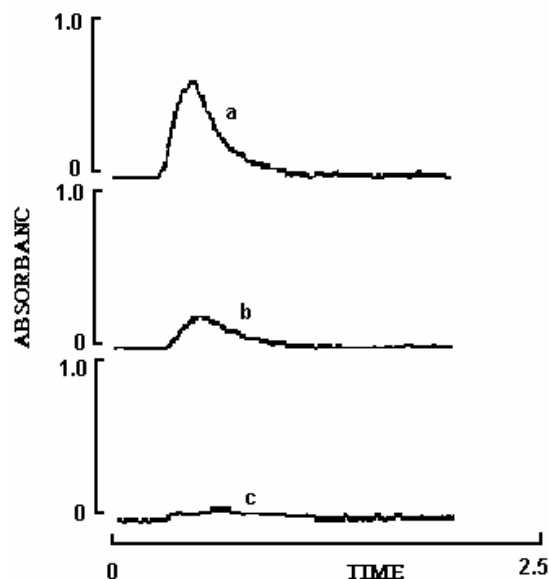


Figure 3: Absorption profile at different wavelength. a-286.3nm; b-284.0; c-224.6nm

Interference study

A comparison was made of the maximum amounts of interferents achievable with $\text{Sr}(\text{NO}_3)_2$ under the optimized ETAAS conditions. NaCl , Na_2SO_4 , and Na_2CO_3 , was selected as the repres-

tative interferences because of the potential spectral and nonspectral interference caused by Cl^- , SO_4^{2-} , and CO_3^{2-} ions or their compounds on tin signals. The results of tolerable Cl^- , SO_4^{2-} , and CO_3^{2-} interference are 30, 0.02, 3 μg , respectively.

Characteristic mass, detection limit and linearity

Characteristic mass (m_0) is an important concept in ETAAS analysis. It is widely affected by inherent instrumental parameters including spectral band width, lamp current, temperature program and so on^[15]. Generally, the graphite furnace temperature setting has a significant influence on analyte atomization. In the presence of the modifier, the modifier may delay vaporization of the analyte until after the furnace reaches a stabilized temperature. Therefore, the atomization efficiency is enhanced and a lower m_0 value could be expected. In our study, calibration curves with or without modifier were constructed using standard solutions. The characteristic mass (m_0) was calculated from the slopes of the calibration curves. The atomization temperature used for calibration was 2400°C in all cases, whereas the pyrolysis temperatures were 1000°C for the $\text{Sr}(\text{NO}_3)_2$ modifiers, and 500 °C for no modifier, respectively. When no modifier is present, the m_0 is 240pg, which implies that the method is the least sensitive. When

$\text{Sr}(\text{NO}_3)_2$ was used as modifier for tin, the m_0 value is 16.8pg. The smaller characteristic mass m_0 in the presence of $\text{Sr}(\text{NO}_3)_2$ modifiers corresponds to the higher sensitivity.

The detection limit for the proposed method is 4.31 $\mu\text{g}/\text{L}$, calculated as three times the standard deviation of a 20 μL of 10 $\mu\text{g}/\text{L}$ Sn solution for 11 determinations.

As a test for linearity, different masses of Sn were injected into the furnace. The relation between concentration and absorbance of tin was examined in the range of 0-200 $\mu\text{g}/\text{L}$ Sn with Sr modifier. Evidently, the absorbance-to-mass relationship was linear. The linearity regression equation for determination of tin is given by $A=0.00074+0.00445C$ with correlation coefficients of 0.9995.

Sample analysis

Using the optimum experimental conditions, calibration graphs obtained in aqueous media, spiked synthetic water sample solution, and extract solution from PVC-U pipe, are plotted in figure 4 for comparative purposes. To demonstrate instrumental precision, the relative standard deviation is included on the plot. In practice the slope is the same for the standard additional method and standard curve. The parallel of the three graphs was observed,

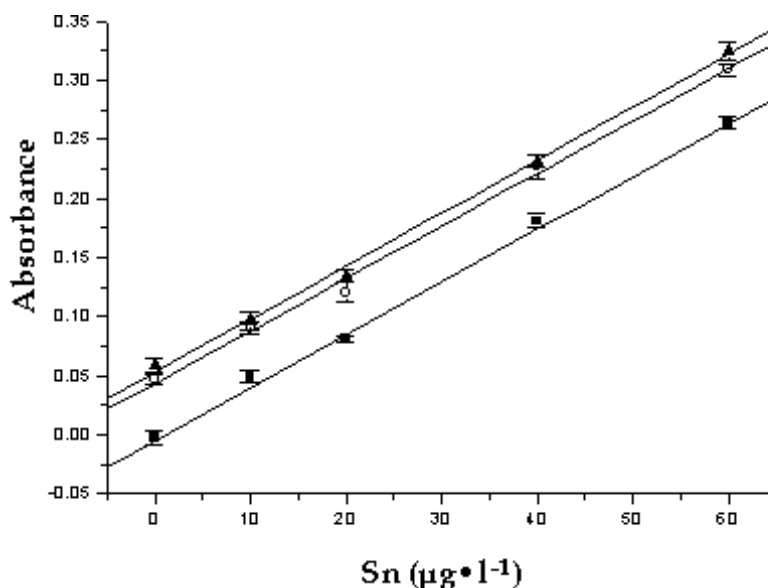


Figure 4: Comparative study of the calibration graphs obtained for Sn.

■-Sn in aqueous medium; ○-Sn in spiked synthetic water; ▲-Sn in extract from PVC-U pipe

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TABLE 2: The equations of the linear graph and in different samples

Sample	Equations of the linear graph	R
aqueous media	$A = -4.95 \times 10^{-4} + 0.00447C$	0.9990
spiked water sample	$A = 0.04361 + 0.00442C$	0.9982
Extract from PVC-U pipes	$A = 0.05303 + 0.00448C$	0.9989

TABLE 3: Recovery of Sn added to water sample as measured by ETAAS

Sample	Sn added ($\mu\text{g/L}$)	Sn founded ($\mu\text{g/L}$)	Recovery (%)
Spiked synthetic water	0.0	9.87	98.7
	10.0	20.11	100.6
	20.0	29.21	97.4
Extract from PVC-U pipe	0.0	11.84	—
	10.0	21.82	99.0
	20.0	30.67	96.4
Waster water	0.0	18.43	—
	10.0	29.01	102.0
	20.0	38.50	100.2
Tap water	0.0	ND	—
	10.0	9.78	97.8
	20.0	19.95	99.8

suggesting there is no observable interference. The equations of the linear graphs and correlation coefficient (R) are list in TABLE 2.

The accuracy of the procedure was investigated by determining the analyte content in spiked water and extract solution from PVC-U pipe. The results (TABLE 3) showed sufficiently high recoveries and a precision (RSD) of 3 – 7%. The precision was very good despite working close to the detection limit. The optimized methods were applied to determine Sn in a variety of water samples by using direct calibration with aqueous standards. The results of Sn found in samples are shown in TABLE 3.

CONCLUSION

It is reasonable to suggest that $\text{Sr}(\text{NO}_3)_2$ can act as an effective chemical modifier for the determination of Sn in several types of waters by ETAAS. Based on the experimental results, the pyrolysis temperature can be set to as high as 1300°C . The $\text{Sr}(\text{NO}_3)_2$ modifier also enhances the Sn signal and reduces matrix interferences. The recovery data for

different water samples appear to verify the effectiveness and applicability of the proposed method for the direct determinations of Sn in environmental water samples with complex matrices.

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