METHOD DEVELOPMENT FOR THE DETERMINATION OF TIN IN A MARINE SEDIMENT AND A PRELIMINARY STUDY OF TIN DISTRIBUTION FROM LA PAZ, B.C.S., MEXICO

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ABSTRACT

Organotin compounds are used as fungicides and antifouling agents, which are incorporated into paints for use in sea vessels. These compounds have been found to be a threat to the environment. Method development for the determination of total tin in marine sediments by Zeeman GFAAS was studied. The optimum pyrolysis and atomization temperatures for tin analysis were 1100ºC and 2300ºC, respectively. When different matrix modifiers were evaluated, a mixture of $NH_4H_2PO_4/Mg(NO_3)_2$ and $Mg(NO_3)_2$ alone produced the optimum tin signal. No significant effect on the tin signal was observed when using HNO_3 as a diluent. The extraction of total tin from marine sediments was best performed by sample digestion with 6 M HCl and diluting the sample extracts with 1% HNO_3. Finally, the tin analytical and extraction method developed in our investigation was used to determine tin content in marine sediments from La Paz, Baja California Sur, Mexico. Tin concentrations in La Paz Bay area ranged from 320 to 5570 μg Sn/Kg of sediment (dry-weight).

KEY WORDS

tin, organotin, Zeeman GFAAS, marine sediment analysis, tin determination

INTRODUCTION

Organotin compounds have found a significant use as biocidal materials in such diverse areas as agriculture, skin care and anti-fouling paints [1]. In particular, tributyltin (TBT) derivatives have been widely used as anti-fouling components of marine paints since they are capable of preventing the attachment of barnacle, sea grass and other marine organisms to the hull of all types of ships. Such paints usually contain about 20% (w/w) of TBT, which is slowly leached into the surrounding water in the immediate vicinity of the hull, reaching normal concentrations at the part per trillion level (ppt) [2-7]. In spite of their excellent antifouling action, TBT antifouling paints have potential negative environmental effects because of the toxicity of this compound to non-target organisms [2-9]. Thus the observed introduction of organotins into mussels, various fish and the observation that they can be toxic to humans has led to a reappraisal of the overall utility of such materials [10-11]. Many nations have severely restricted the use of tin-containing paints for smaller marine craft. The general idea is that these can disproportionately create contamination in shoreline marine environments where a maximal damage to both marine and human life might be anticipated. Such concerns have been the

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driving force behind many world-wide studies that focused upon tin concentrations in both marina and inland lake environments.

A range of analytical techniques and methods have been used to determine inorganic and organotin compounds in the environment. Waite et al. reported using a toluene/tropolone extraction method followed by electrothermal atomic absorption spectroscopy, ETAAS, (graphite furnace atomic absorption spectroscopy, GFAAS) to obtain total tin content of sediments [4]. Quevauviller et al. used hydride generation atomic absorption spectroscopy (HGAAS) for the determination of tin followed by gas chromatography (GC) [12]. More recently gas chromatography has been used for the speciation analysis of organotin compounds [13]. Mortenson et al. have developed a simple screening which determines the organotin compounds in marine sediments by GFAAS [14]. In this method the sediment is extracted by a two-phase extraction procedure, and the organic extract is analyzed by GFAA. Furthermore, Elf Atochem North America, Inc., a major organotin supplier, uses several methods to extract total tin from complex organic matrices followed by determination with GFAAS. One method includes the use of concentrated sulfuric acid (H_2SO_4) to oxidize tin into stannic sulfate ($Sn(SO_4)_2$), followed by dilution to 50% H_2SO_4 and addition of hy-

drobromic acid (HBr). The inorganic tin is then extracted using a toluene/tropolone solution. In addition, Harriot et al. [15] used a 1:1 nitric acid (HNO_3)-HCl solution for digestion and total tin extraction from soil, even though HCl is known to cause interferences to the signal during metal analysis with GFAAS [16].

Thus, despite the considerable number of papers published in the last decade on the determination of organotin and total tin from soil samples, there appears to be a lack of a recognized standard procedure. This can lead to a serious problem when comparing data from different sources. Since we are presently engaged in a collaborative effort to investigate the environmental load of the La Paz Bay, B.C.S., Mexico, and its surrounding area, we have initiated a study to develop the optimum extraction and analytical method for inorganic tin analysis by using GFAAS with Zeeman background correction.

THEORY IN GFAAS

When performing metal analysis by GFAAS, five sequential operations are performed on the sample and instrumentation: drying, ashing (pyrolysis), atomization, cooling and cleaning. During this process the temperature is gradually increased in an attempt to remove most of the sample matrix while preventing loss of analyte. In

Wavelength	286.3 nm
Irradiation source	Tin electrodeless discharge lamp
Lamp current	310 mA
Slit width	0.7 nm
Mode	Zeeman background correction
Sample size	varying
Signal processing	Peak area
Tube	Transversely heated graphite tube (THGT)
Gas	Argon

Table 1. Zeeman Graphite Furnace AAS instrumental parameters.

the atomization step, the analyte is converted into the gas phase where it can absorb the light from the source. The measured absorbance ultimately permits determination of the analyte concentration. The relative volatilities of the sample matrix and target analyte in GFAAS are usually controlled through a method called "matrix modification." A chemical compound or "matrix modifier" is added to the sample prior to analysis, and the specific matrix modifier is selected to obtain either an increased matrix volatility or decreased analyte volatility during the pyrolysis step.

We wish to report the optimum digestion and extraction procedures for inorganic tin for sediments by using mineral acids; the optimum pyrolysis and atomization temperatures when analyzing tin by Zeeman-GFAAS; and the optimum sample size and matrix modifier composition (and modifier sample size). The developed method was employed to preliminarily quantify the total tin in marine sediment samples obtained from La Paz Bay, B.C.S., Mexico, a major recreational and commercial boating area, which to our knowledge has not been evaluated for environmental pollution due to organotin compounds.

METHODOLOGY

Instrumentation

All determinations were performed on a Perkin Elmer Model 4100 ZL Zeeman Atomic Absorption spectrometer equipped with a transversely heated graphite atomizer (THGA). A tin electrodeless discharge lamp was used as the resonance line source. Sample aliquots were injected into the furnace with a Perkin Elmer AS-80 autosampler. Pyrocoated graphite tubes were used throughout the work. The instrumental operating parameters are shown in Table 1. Argon was used as the purge gas. Quantification was performed using the peak area per second.

Reagents

Nitric and hydrochloric acid used were both Trace metal grade (Fisher Scientific). Deionized water was used to prepare the acid dilutions, tin standard solutions, and matrix modifiers. A standard tin solution, 1000 ppm (EM-Science), was used to prepare various diluted standards of tin for calibrating the GFAAS. The matrix modifiers used were prepared from the following solutions: 40,000 ppm ammonium hydrogen phosphate ($NH_4H_2PO_4$), 10,000 ppm magnesium nitrate ($Mg(NO_3)_2$), 4000 ppm nickel nitrate ($Ni(NO_3)_2$, and 5000 ppm palladium nitrate ($Pd(NO_3)_2$). These chemical modifiers were purchased from Inorganic Ventures Inc.

	amount of modifier used (μL)			
	3	5	10	15
15 μl of 200 ppb Sn std (Absorbance)	.054	.055	.054	.051
20 μl of 200 ppb Sn std (Absorbance)	.073	.067	.065	.064
25 μl of 200 ppb Sn std	.092	.087	.079	.071

Notes: The pyrolysis and atomization temperatures used were 1400ºC and 2200ºC, respectively. The matrix modifier used was a mixture of 0.005 mg Pd(NO)$_3$ + 0.003 mg Mg(NO)$_3$.

Table 2. Optimum amount of sample aliquot and matrix modifier use for tin analysis by GFAAS.

Sample collection, preparation and extraction

A total of eleven sediment samples were chosen from the La Paz Bay in Baja Cali-fornia Sur, Mexico, a popular recreational and commercial boating area. Samples were collected from surface sediments in clean glass bottles as recommended by the Environmental Protection Agency (EPA) method 3050 "Acid Digestion of Sediments, Sludges, and Soils" [17]. The samples were kept at 4°C after arrival to our laboratory in El Paso, Texas. Before digestion, the samples were air-dried and approximately 1 g sample size (sieved to pass the 10-mesh sieve) was digested and refluxed in either HCl or HNO_3 (this step is discussed further in the results and discussion section). The sample digestates were then filtered, and the final volume was brought up to 50 ml with the appropriate acidic diluent. Appropriate "spiking" experiments were performed on each sample. In such experiments a known amount of tin was added to the sediment to be extracted, thus upon analysis of the spiked and unspiked samples the difference should represent the added material. In our reporting (Tables 6 and 7) the % Sn recovery is that % of the added Sn that was obtained experimentally.

RESULTS AND DISCUSSION

There are two basic parts to the overall analytical procedure, extraction and analysis. We therefore investigated the various extraction methods and those parameters that control the operation of the GFAAS. The variables studied were (a) sample size, (b) temperature variation during GFAAS, (c) effect of HNO_3 upon the Sn signal, (d) matrix modifier composition, and (e) extraction method.

The method development consisted of optimizing the sensitivity check for inorganic tin under standard instrumental conditions (0.2 A-s/200 ppb Sn standard) by altering some steps in the furnace program as well as by using different matrix modifiers and acid solutions for the digestion step. The sensitivity check is a quality control parameter that assures that the GFAAS is functioning properly under standard instrumental operating conditions. If all the GFAAS parameters are correct, a 200 ppb tin standard should give an absorbance of 0.2 A-s (within a precision of 20%). The optimized conditions obtained were then applied to subsequent analyses during the method development, where recoveries of known amounts of tin added to the samples were used to further evaluate the method.

Pyrolysis step		Atomization step	
Absorbance	Temperature (ºC)	Absorbance	Temperature (ºC)
0.142	1000	0.024	2000
0.155	1100	0.032	2100
0.125	1200	0.035	2200
0.066	1300	0.037	2300
0.029	1400	0.039	2400
0.018	1500		

Notes: The matrix modifier used was a mixture of 0.005 mg $Pd(NO)_3$ + 0.003 mg $Mg(NO)_3$.

Sample size used was 25 µL, and 3 µL of matrix modifier.

Table 3. Effect of furnace temperature on tin signal.

Optimum amount of sample aliquot and matrix modifier

The first part of this work consisted of finding the optimum amount of aliquot (of standard solution as well as matrix modifier) that will maximize the absorbance of the tin signal. For this step the standard instrumental conditions were used (Table 1). The pyrolysis and atomization temperatures used were 1400°C and 2200°C, respectively. In addition, the recommended chemical matrix modifiers were utilized (0.005 mg Pd(NO)$_3$ + 0.003 mg Mg(NO)$_3$). Table 2 shows the absorption of tin as a function of sample size. The increase in absorbance is relative to the aliquot size. It can be observed, however, that as the amount of matrix modifier increases, the absorbance decreases. Aliquot samples for the tin standard larger than 25 μL were not used in order to prevent carryover and overfilling the tube. Aliquots of matrix modifier smaller than 3 μL were not used. The optimum aliquot size of the 200 ppb tin standard was found to be 25 μL although we later found that using 20 μL aliquots

gave an absorbance signal close to that of the first value. The optimum amount of matrix modifier to be used was determined to be 3 μL.

Effect of temperature on tin signal

The most critical steps for tin analysis by GFAAS are ashing and atomization, since the metal can be lost due to a lack of temperature control. Therefore, we investigated the effect of temperature on tin absorption during the ashing and atomization steps. We varied the temperature in the furnace program over a scale that allowed us to see the absorbance behavior. This part consisted of keeping all the other furnace parameters (i.e., temperatures, hold times and ramp times) unchanged while only altering one furnace step at a time. Results are shown in Table 3. The data show that there is a maximum absorbance when the pyrolysis temperature is at 1100°C and that there is a gradual absorbance increase when the atomization temperature increases. We selected 2300°C as the optimum atomization temperature instead of 2400°C (which produced higher absorption)

200 ppb Sn std in varying HNO$_3$ conc. (%)	Absorbance (3 replicates)
0.1% HNO$_3$	0.133
0.2% HNO$_3$	0.116
0.4% HNO$_3$	0.145
0.8% HNO$_3$	0.150
1.0% HNO$_3$	0.143
3.0% HNO$_3$	0.131
5.0% HNO$_3$	0.133
7.0% HNO$_3$	0.143

Notes: The pyrolysis and atomization temperatures used were 1100°C and 2300°C, respectively.

The matrix modifier used was a mixture of 0.005 mg Pd(NO)$_3$ + 0.003 mg Mg(NO)$_3$.

Sample size used was 25 μL, and 3 μL of matrix modifier.

Table 4. Effect of nitric acid concentration on tin signal.

to increase the longevity of the graphite tube. The higher the temperature, the lower the lifetime of the graphite tube. Our optimum pyrolysis and atomization temperatures differ from the ones recommended by the instrument manufacturer (1400°C and 2200°C, respectively).

Effect of HNO$_3$ concentration on tin signal

We decided to investigate the effect of nitric acid as a diluent solution for the 200 ppb Sn standard solution. Several solutions of a 200 ppb Sn standard were diluted in different acid concentrations and analyzed using GFAAS with Zeeman background substraction. The results are shown in Table 4. These results suggest that there is no significant difference in the effect of varying amounts of HNO$_3$ on the tin signal. We decided that a 1% HNO$_3$ diluent solution was the best to use, for it could provide the best enhancement to the Sn signal while keeping tube wearing low.

Effect of chemical matrix modifiers on tin signal

Several chemical sample matrix modifiers were prepared and used to analyze the 200 ppb Sn standard solution (in 1% HNO$_3$).

Table 5 shows the results. The data show that the chemical matrix modifiers consisting of ammonium-magnesium and of magnesium alone produce the highest and, thus, best signals. These absorptions are closer to the ideal absorbance (sensitivity check of 0.2 A/s) than the other modifiers. We proceeded to use the ammonium/magnesium matrix modifier for future analyses although the other modifiers produced absorptions which are not too low and could also be used. Other investigators have recently determined that HNO$_3$ was the best modifier for tin analysis by GFAAS [14]. We do not agree with the use of high concentrations of acid as a chemical modifier since damage to the graphite tube can occur very rapidly.

Optimization of the digestion and extraction of tin from sediments

From the results above (Table 4) nitric acid does not seem to affect the tin signal significantly. However, there is no clear evidence whether or not HNO$_3$ is a good acid to digest or extract tin from marine sediments. A mixture of HNO$_3$ and HCl or HCl alone have been used with inconsistent results. Even method 3050 from the U.S. Environmental Protection Agency for the

Matrix modifier	Absorbance (3 replicates)
NH$_4$-Mg (3000 ppb each)	0.188
NH$_4$-Mg (3000 & 2000 ppm resp.)	0.194
Magnesium (5000 ppm)	0.196
Ni-Mg (3000 & 2000 ppm resp.)	0.178
Ni-Mg (3000 ppm each)	0.163
Ni-Pd (3000 ppm each)	0.171

Notes: The pyrolysis and atomization temperatures used were 1100°C and 2300°C, respectively.

The matrix modifier used was a mixture of 0.005 mg Pd(NO)$_3$ + 0.003 mg Mg(NO)$_3$.

Sample size used was 25 μL, and 3 μL of matrix modifier.

Table 5. Effect of chemical matrix modifiers on tin absorption.

acid digestion of sediments for the extrac-tion of most metals does not include tin as a target analyte [17]. Thus, we investigated the effect of HNO_3, HCl and mixtures of both acids to digest and extract tin from a marine sediment sample. For performing this experiment we selected a sediment sample #9 from La Paz, Mexico. Approximately 1 g portions of the sample #9 were spiked with 50 ppm Sn standard solution. Subsequently, the spiked samples were digested using different acid solutions. The digesting solutions investigated were 6 M HCl, 6 M HNO_3 and 6 M HCl. Then the sample was brought to dryness and treated with 6 M HNO_3 and a mixture of 6 M HCl-6 M HNO_3. All the samples were heated at 95ºC for 15 min. For each sample after filtration, the sample digestate was diluted with 1% HNO_3 solution to a final volume of 50 ml. Sample extracts were analyzed by GFAAS with Zeeman background substraction by using the optimized conditions previously described. Table 6 shows the tin absorbances after digestion with the various acids. It is very clear that the 6 M HCl solution is the best acid to extract tin since 100% of the tin spiked in the sediment sample was recovered. As observed, the other tin extraction methods did not produce good recoveries. We attribute the low

tin recoveries perhaps to the production of the insoluble tin oxide (SnO) in the presence of high concentrations of HNO_3. Thus, we propose that the sediments for tin analysis should be digested in 6 M HCl, and then the digestate should be brought close to dryness, so that most of the HCl is eliminated (since it interferes with tin analysis by GFAAS). Finally, the sample digestates should be diluted with 1% HNO_3 prior to tin analysis by GFAAS.

Preliminary screening of tin concentrations in marine sediments in La Paz Bay area

After having developed the optimum tin extraction method from marine sediments and optimized the analytical method for tin by GFAAS with Zeeman background substraction, we decided to perform a preliminary screening of tin concentrations in La Paz Bay area. La Paz, located in the south of Baja California Sur, Mexico, has an intense commercial boat activity and, to our knowledge, no environmental monitoring studies for tin have been performed in the area. Since this was a preliminary screening study, we randomly selected 11 sampling sites around the Bay area (Figure 1), and samples were brought to our laboratory in El Paso, Texas.

digesting solution	Absorbance (3 replicates)	% Sn Recovery
6 M HCl	0.344	100.7
6 M HNO_3	0.244	61.1
6 M HCl then 6 M HNO_3	0.165	38.1
6M HCl & 6 M HNO_3 (mixed)	0.24	71.3

Notes: The pyrolysis and atomization temperatures used were 1100ºC and 2300ºC, respectively.

The matrix modifier used was a mixture of $NH_4H_2PO_4/Mg(NO_3)_2$.

Sample size used was 25 μL, and 3 μL of matrix modifier.

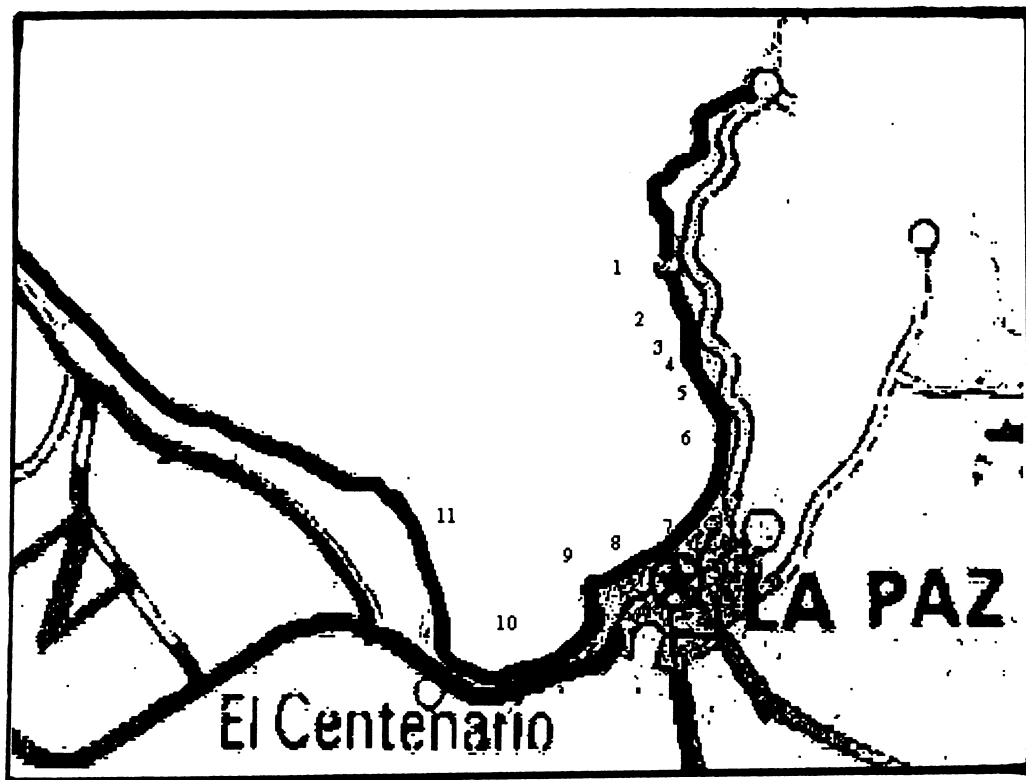Table 6. Recovery of tin by treatment with different digesting acids.

Figure 1. Sampling locations along the La Paz Bay area.

Samples were extracted and analyzed for tin. As part of our quality control, every single sample was treated individually, and a separate sample from the same site was spiked with 50 ppm tin. Table 7 shows the tin concentrations in the samples and the percent tin recovery. As observed, better than 88% tin recoveries were obtained. The tin concentrations varied from 320 to 5570 μg Sn/Kg of sediment (dry-weight). These concentrations are comparable to Sn concentration in other parts of the world. Tin concentrations reported in marine sediments in nine different places around the world are shown in Table 8. These concentrations reported by Maguire show tin concentrations based only on the extraction of tributyl tin [18]. We report tin concentrations based on the extraction of total tin.

SAMPLE	% Tin recovery	μg Sn/kg soil
1	100	4040
2	129	414
3	108	2330
4	109	3100
5	98	3620
6	88	5570
7	101	1840
8	97	2320
9	100	1775
10	128	320
11	112	2940

Table 7. Tin concentrations in sediments in La Paz Bay area.

SUMMARY AND CONCLUSIONS

At the present time the study of the environmental distribution of organotin compounds is of great concern. In this work we developed and optimized a method to analyze tin by GFAAS with Zeeman background correction. We found that the optimum pyrolysis and atomization temperatures for tin analysis were 1100ºC and 2300ºC, respectively. We determined that the best sample size to use is 25 μL and 3 μL for matrix modifier. On the other hand, the optimum chemical matrix modifiers to use were determined to be a mixture of $NH_4H_2PO_4/Mg(NO_3)_2$ or $Mg(NO_3)_2$ alone. The extraction of tin from marine sediments is best performed by digesting the samples with 6 M HCl and diluting the sample extracts with 1% HNO_3. The amounts of tin detected in La Paz Bay area are comparable to those found in other places around the world. This was a preliminary screening study in La Paz, Mexico. We plan to carry out a more complete study in the Bay area considering further the sediment sample size, the sampling depth, and the speciation of the organotin compounds. Finally, we wish to study the optimization of the analytical methods of the various organotin compounds when performing analysis by GFAAS with Zeeman background substraction.

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Location	Sn Conc. (μg Sn/Kg soil) dry weight
Rivers and lakes in Ontario, Canada	nd-200
Japanese river	400
Lakes Constance and Zurich, Switzerland	0.7-5.8
Detroit and St. Clair Rivers, Canada and USA	nd-70
Toronto harbour, Canada	nd-1800
San Diego Bay, USA	8-44
Across Canada	nd-11000
Lake Biwa, Japan	nd-0.9
Esquimalt harbour, BC, Canada	300-7000

Notes: nd stands for non-detected

[a] obtained from reference 18

Table 8. Tin concentrations in marine sediments around the world (as TBT) [a].

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