APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 425–433
DOI:10.1002/aoc.1236

A screening method for the determination of toluene extractable organotins in water samples by electrothermal atomic absorption spectrometry and rhenium as chemical modifier

Nikolaos S. Thomaidis[1]*, Athanasios S. Stasinakis[2] and Themistokles D. Lekkas[2]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 157 71 Athens, Greece
[2]Laboratory of Water and Air Quality, Department of Environmental Studies, University of the Aegean, University Hill, 81 100 Mytilene, Greece

Received 12 January 2007; Accepted 21 February 2007

A simple screening method for the determination of toluene-extractable organotin compounds in water samples was developed. Organotins [tributyl tin (TBT), triphenyltin (TPhT) and dibutyl tin (DBT)] were extracted from 2 l of water sample with 10 mL of toluene in the presence of 2.5% (v/v) CH_3COOH and 1.2% (w/w) NaCl. Aliquots of 240 μl of the toluene extracts were subjected to electrothermal atomic absorption spectrometry, utilizing the hot injection technique (injection temperature 120 °C) and chemical modification. Under these conditions, an enrichment factor of approximately 2000 was achieved. A comparative study of chemical modifiers was performed. Ten metals and mixtures of them were tested and the best results were obtained with 5 μg of Re. The characteristic mass was 90 pg and the instrumental limit of detection was 0.8 μg l^{-1} (as Sn), for all compounds tested. The overall limit of detection of the method was 2 ng l^{-1} (as Sn) for an injection aliquot of 240 μl. Quantitative recoveries were obtained for TBT and TPhT, whereas the DBT recovery was 70%. Addition of 0.5% (w/v) of tropolone in the extraction media resulted in 100% recovery of all organotins tested (TBT, DBT, monobutyl tin and TPhT), whereas, at the same time, inorganic tin was practically not recovered at 100-fold excess. The developed methodology was applied to fresh (lake) and marine waters of Greece and levels between <2 and 223 ng l^{-1} were determined.

KEYWORDS: ETAAS; chemical modifiers; organotin compounds; TBT; aquatic environment; screening method

INTRODUCTION

Organotin compounds (OTs), especially butyl and phenyl tin species, are used in many human activities, such as catalysts and stabilizing agents in industrial processes and as biocides in antifouling paints and in agriculture.[1,2] The nature and the number of organic groups bound with tin is critical for the chemical and toxic characteristics of these compounds. Moreover, the trisubstituted organotins are very toxic compared with the mono- and di-substituted.[1] Owing to their negative impact on aquatic environment and restrictions on their use, monitoring programmes are required to investigate the level of contamination.[3,4] In partlicular, the Water Framework Directive (WFD)[3] strongly demands, among other things, assurance of the quality of water bodies, both ground and surface waters. In this context, the availability of suitable, rapid, screening analytical methods before the implementation of WFD and the production of comparable and reliable analytical data at an affordable cost are key issues.

Several methods have been developed for the simultaneous determination of organotin species. Hyphenated

---

*Correspondence to: Nikolaos S. Thomaidis, Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 157 71 Athens, Greece.
E-mail: ntho@chem.uoa.gr

techniques are being used mainly, with a combination of a chromatographic separation technique and a sensitive and selective detector. Usually, the determination of the organotin compounds is based on gas chromatographic separation after a derivatization/extraction step with various selective detectors, such as conventional or pulsed FPD,[5–7] MS,[8,9] MIP-AES,[10,11] QF-AAS[12,13] and ICP-MS.[14,15] Many of these methods require special equipment, which may be expensive for a routine environmental laboratory. The experimental procedures are also quite lengthy and laborious and subsequently not convenient for use in routine analyses and monitoring programmes, where a large number of samples need to be analyzed. The increasing number of potentially harmful pollutants in the environment calls for fast, cost-effective analytical techniques to be used in extensive monitoring programs. Therefore, a simple screening method is required with low cost and high throughput, which could determine the total concentration of the required organotin species, the monitoring of which complies with European Community legislation, namely di- and tri- butyltin (DBT and TBT) and triphenyltin (TPhT). These compounds are included in catalog I of the 76/464 E.U. directive, as potential toxic compounds, and are considered as first priority pollutants in the new WFD.[3,4]

Electrothermal atomic absorption spectrometry (ETAAS) is a relatively low-cost technique, available in laboratories employed in environmental analysis. Even though it can been used for the monitoring of organotin compounds, few screening methods have appeared in the literature.[16–31] Screening methods based on ETAAS were developed for seawater,[16,19–21,24,26,29,31] freshwater, [20,27,30] wastewater,[25] marine organisms[17,18,22] and sediments.[18,22,23,28,31] However most of these methods were focused on TBT determination. Only two recent studies reported the combined determination of OTs.[29,31] Bermejo-Barrera *et al.*[29] determined total butyltins (TBT, DBT and MBT) in sea water by column preconcentration with tropolone-modified Amberlite XAD-2 resin and ETAAS determination, with adequate recovery and precision and a limit of detection (LOD) of 13 ng l^{-1}. Cámara and co-workers[31] reported the determination of TBT, DBT, MBT and TPhT in water and sediment samples by preconcentration in a polymeric sorbent and subsequent ETAAS determination. An LOD of 30 ng l^{-1} was reported.[31]

Generally, these ETAAS screening methods present the following problems: (a) OTs have very low concentrations, especially in aquatic samples, therefore an adequate preconcentration and a very low detection limit (a few ng l^{-1}) should be achieved; (b) OTs have different extraction properties in several extraction solvents or media, therefore a common procedure for all of them should be developed; and (c) different OTs present different thermal stabilities and different sensitivities in ETAAS. The volatility of the organotins, especially in organic extracts, is high. Therefore, adequate modifiers should be used in order to achieve the same thermal stabilities and the same sensitivity for all the compounds that have to be determined.

The main preconcentration procedure used is liquid–liquid extraction (LLE), mainly in toluene,[16,19–21,24–26] hexane[17,22] or isooctane,[28] with or without a back-extraction step into an aqueous solution.[17,18,22,23,28] Direct determination of the extracted OTs into the organic extract requires the mandatory use of chemical modifiers and adequate and carefully optimized conditions, taking into consideration the above-mentioned problems.

Several compounds were applied as chemical modifiers for the determination of organotins by ETAAS, $K_2Cr_2O_7$,[16,23] as a mixture with calcium,[26] $NH_4H_2PO_4$,[17] mostly as a mixture with $Mg(NO_3)_2$,[18,22] picric acid,[20] $Pd(NO_3)_2$ [28] and several coatings of carbide forming elements, like W,[19] V[21] and Zr.[29,30] Recently, a coating of Zr + W + Ir was used as permanent modifier.[31]

The aim of this study was the development of a simple screening method with sufficiently low method LOD for the determination of organotin compounds, monitoring of which in the aquatic environment is required by European legislation, namely TBT, TPhT and DBT. For this purpose, an ETAAS method was developed and optimized. The toluene extractable fraction of organotins was determined. The extraction step was optimized to recover only the organotins required by the EU legislation and not inorganic tin. A comparison of chemical modifiers was performed. The metals tested were W, Re, Zr, Mg, La, Pt, Rh, Ir, Ru and Pd. Some permanent modifiers, like mixtures of W and Zr with platinum group metals (PGMs), were also tested. The target was to achieve the same thermal stability and sensitivity for all organotin compounds. The developed methodology, which is a simple and sensitive screening method for routine analysis, was applied to fresh (lake) and marine waters of Greece.

EXPERIMENTAL

Instrumentation

A Perkin Elmer 5100PC atomic absorption spectrometer equipped with a THGA Zeeman graphite furnace (5100ZL) was used. Standard (80 µl) or sample solutions (3 × 80 µl) aliquots were dispensed into the graphite tubes utilizing hot injection mode (120 °C) with an AS-70 autosampler. The pipette speed was reduced at 40% to achieve smooth dispersion of the organic aliquot on the graphite surface. An HCl was used at 35 mA and the AA was monitored at 286.3 nm (bandwidth 0.7 nm). An alternative wavelength (235.5 nm) was also tested and produced similar results. The wavelength 286.3 nm was chosen as it produced less noisy signals. The instrumental parameters and the temperature programme are given in Table 1.

Reagents

All reagents were of analytical grade. Distilled, deionized water was used throughout. Bu_3SnCl (96%), Bu_2SnCl_2 (95%),

DOI: 10.1002/aoc

Table 1. Instrumental operating parameters and temperature programme for the determination of the toluene extractable organotins

Spectrometer	
Wavelength	286.3 nm
Bandwidth	0.7 nm
Lamp current	35 mA
BG corrector—graphite	Longitudinal Zeeman—THGA
Injection temperature	120 °C
Pipette speed	40%
Sample volume	80 µl
Modifier volume	5 µl

Temperature programme

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (ml min^{-1})	Read
Drying 1	120	5	15	250	
Drying 2	130	25	15	250	
Pyrolysis	*Variable*[a]	20	20	250	
Atomization	*Variable*[a]	0	4	0	ON
Cleaning	2400	1	2	250	

[a] *Variable:* T_{pyr} and T_{atom} are given in Table 2.

$BuSnCl_3$ (95%) and Ph_3SnCl were purchased from Sigma-Aldrich (Wisconsin, WI, USA). Stock standard solutions of OTs (approximately 1000 mg l^{-1} as Sn) were prepared in methanol. Working standards of OTs were prepared by dilution of appropriate volume of stock solutions in toluene, as described below. All standard solutions were kept in dark at 4 °C. Tropolone was purchased from Fluka (Buchs, Switzerland) and sodium chloride (NaCl), toluene and glacial acetic acid (CH_3COOH) from Merck (Darmstadt, Germany). Modifier stock solutions were prepared by dissolving appropriate amounts of their salts in acid media and diluting to a final volume with water. The modifiers studied were Mg and La (as nitrates), W (as Na_2WO_4), Re (as $HReO_4$, prepared by dissolving Re powder in H_2O_2), Zr (as $ZrOCl_2$) and Pd, Pt, Ir, Ru and Rh as their chloride salts ($PdCl_2$, $PtCl_4$, $IrCl_4$, $RuCl_3$ and $RhCl_4$). Rh was tested as its nitrate salt as well. All the modifiers were obtained from Merck.

Procedures

Comparison of chemical modifiers

The metals mentioned above were tested as chemical modifiers for the determination of organotin compounds. Eighty microlitres of the OT standard solution was dispensed into the graphite tube, followed by a separate injection of 5–10 µl of the modifier solution, to find the maximum permissible pyrolysis temperature and the optimum mass of the modifier. It was also tested whether the modifier could cause an 'isoformation' to all organotin species and stabilize them to the same extent.[32] This means that all OTs in the presence of a particular chemical modifier would show the same characteristic mass and the same thermal behaviour, so the same pyrolysis (T_{pyr}) and atomization (T_{atom}) temperatures could be applied.

Determination of toluene extractable organotins (TEOTs) in water samples

The extraction of tributyl- (TBT), triphenyl- (TPhT) and dibutyltin (DBT) was accomplished in the presence of 50 ml of acetic acid and 24 g of sodium chloride, from a 2 l water sample into a 10 ml toluene layer. For clean samples with low organic burden (i.e. seawater) these volumes/amounts could be 2-fold lower. The shaking time was 15 min and phase separation was achieved after 20 min. Normally, 80 µl of the extract was injected at an injection temperature of 120 °C and a pipette speed of 40%, along with 5 µg of Re (5 µl of 1 g Re l^{-1}, as a separate injection). To achieve a lower detection limit, the injection procedure of the sample extract was repeated three times, inserting a total volume of 240 µl. After each injection, a drying step at 130 °C was followed. After the third injection, the modifier solution was inserted and the temperature programme of the Table 1 was followed. The developed methodology was applied to lake- and seawater collected from various sites in Greece. Samples (2.5 l) were collected in dark glass bottles from four lakes (Doirani, Pamvotida, Major Prespa and Minor Prespa) around Greece, three gulfs of the Aegean Sea (Saronikos, Pagasitikos and Thermaikos) and two harbours (Mytilene and Rhodes), receiving merchant ships, pleasure crafts and fishing boats (large and small vessels), as a part of a wider monitoring programme. Samples from lakes and gulfs were collected in March 1999, whereas six samples at each harbour were collected during a one-year period (June 1999–May 2000). In general, samples were not filtered and were acidified with 50 ml of glacial acetic acid for preservation (pH 2.7–3.0). The samples were stored at 4 °C in the dark, until analysis (carried out after one week). Very turbid samples (i.e. wastewaters) may need filtration, but the addition of NaCl and use of centrifugation help to recover the toluene layer and overcome this problem.

Validation of the method

The calibration curves were constructed by injecting 80 µl of standard solutions containing 5.00, 10.0, 20.0, 30.0, 50.0, 100 and 200 µg l^{-1} as Sn (as a mixture of equal concentrations of TBT and TPhT in toluene), followed by 5 µl of the modifier solution (1 g Re l^{-1}) into the graphite tube. Calibration curves were also constructed with the same concentrations of DBT or MBT and the slope and the linear range were found to be the same as in the case of TBT and TPhT. Sensitivity was expressed as the characteristic mass, m_0, which is defined as the mass of analyte in picograms giving a signal of 0.0044 s as integrated absorbance. The characteristic mass, m_0 (pg), was calculated from the slope (b) of the calibration graph, using the equation $m_0 = 0.0044 \times 80/b$ for a sample volume of 80 µl. The

DOI: 10.1002/aoc

instrumental limit of detection, LOD (μg l^{-1}), was calculated from the equation LOD $= 3 \times S_{BL}/b$, where S_{BL} is the standard deviation of 10 replicate injections of a blank sample. The LOD of the method was determined from 10 replicate analyses of a blank sample (1 l of freshwater, with no detectable amount of organotins, extracted with 5 ml of toluene using the above-mentioned procedure). Precision experiments included the analysis of at least five replicate samples at three concentration levels (5, 20 and 100 ng l^{-1}) in two substrates (freshwater and marine water). Spiking experiments of each compound were used to assess the recovery of the method. Recovery of each organotin compound (TBT, TPhT, DBT and MBT) was tested at a level of 100 ng l^{-1} from a blank freshwater sample. The co-extraction of inorganic tin was tested in the same batch of experiments at a level of 10 μg l^{-1} (100-fold excess). The extraction of a TBT and TPhT mixture was also tested during the same experiments, at a level of 50 ng l^{-1} of each compound, resulting in a total organotin species concentration of 100 ng l^{-1}. To assess the recovery of the determination of TEOTs, spiking experiments were carried out in seawater and freshwater samples at two different concentration levels of TEOTs (100 and 10 ng l^{-1}, as a mixture of TBT and TPhT at equal concentrations), five times each. The solubility of toluene in water, under the optimized conditions of the extraction (i.e. in the presence of acetic acid and NaCl) was also tested, in order to correct the recoveries for reduced uptake of the organic layer. It was found that 9.6 ± 0.1 ml ($n = 3$) were recovered from a 10 ml toluene layer. The following correction was made to recoveries to account for the solubility of toluene: the concentrations found from the recovery experiments were multiplied with a correction factor of 0.96 (9.6/10), to account for the volume reduction of the final extract.

RESULTS AND DISCUSSION

Comparison of chemical modifiers

The primary role of a chemical modifier is the thermal stabilization of the analyte during the preatomization step. Organotins are volatile compounds that are lost from the graphite tube at temperatures higher than 400 °C in the absence of a modifier. Therefore the use of a chemical modifier is essential. The maximum T_{pyr} and T_{atom} of organotins were determined in the presence of various chemicals modifiers. The results are presented in Table 2.

In the absence of a chemical modifier, a different T_{pyr} for the organotin species was observed. This might be, due to the different volatility of the organotin species. The T_{pyr} of TBT and TPhT were lower than those of MBT and DBT. On the contrary, the T_{atom} was the same for all organotin species. The Sn–C bond was stable up to 200 °C.[2] Even this fact might not be generally applicable to conditions in the graphite atomizer; tin should be in inorganic form for temperatures higher than 200 °C, thus the T_{atom} should be the same for all tin species.

Table 2. Maximum permissible pyrolysis temperature (T_{pyr}) and optimum atomization temperatures (T_{atom}) of toluene solutions of organotins in the presence of various chemical modifiers

Modifier	T_{pyr} (°C)	T_{atom} (°C)
None	450 (TBT) 600 (DBT/MBT) 400 (TPhT)	2000 (all OTs)
3 μg W	1400 (all OTs)	2000
20 μg Zr	1400 (all OTs)	2000
5 μg Re	1400 (all OTs)	2100
5 μg La	1200 (TBT)	2000
2 μg Mg	1400 (TBT)	2200
0.3 μg Pt	1200 (TBT)	2200
0.5 μg Ru	1200 (TBT/TPT)	2200
0.2 μg Ir	1200 (TBT)	2200
1.0 μg Pd	1500 (DBT/TPhT) 1300 (MBT) 1000 (TBT)	2200
0.5 μg Rh	1300 (TBT/TPhT) 1200 (DBT)	2200
1 μg Pd + 5 μg Re	1300 (TBT) 1400 (DBT)	2200
0.5 μg Rh + 5 μg Re	1300 (TBT)	2200
240 μg W (coating)	1400 (all OTs)	2100
240 μg W + 5 μg Rh (coating)	1500 (all OTs)	2100
120 μg Zr (coating)	1300 (all OTs)	2100
240 μg Re (coating)	800 (TBT) 600 (DBT/MBT) 700 (TPhT)	2100 (all OTs)

The carbide forming elements, W, Zr and Re, stabilized all the OTs tested in the same extent. The T_{pyr} was 1400 °C in the presence of these modifiers and the sensitivity was similar for all species. The best sensitivity was achieved in the presence of W or Re with a characteristic mass of 90 pg. The T_{atom} was 2000 °C in the presence of W and Zr, but for Re was 2100 °C.

The addition of La and Mg also did not stabilize the organotin species. Only for TBT did the addition of Mg result in a T_{pyr} of 1400 °C and a characteristic mass equal to 95 pg.

The performance of PGMs was not satisfactory. The sensitivity was lower than the sensitivity achieved with the carbide forming elements with a T_{pyr} in the range 1200–1300 °C (Tables 2 and 3). Surprisingly, the addition of these metals as chemical modifiers did not stabilize to the same extent all the organotin species and the sensitivities were different. The general mechanism of action should be the same for all five PGMs tested, because they have similar properties. Their active form as modifiers is their elemental state. Palladium has been successfully used as a chemical modifier in the past,[25] but in this work it did not show similar good performance. It did not stabilize TBT at the same T_{pyr} as DBT, MBT and TPhT and the sensitivity was rather low

(Tables 2 and 3). The same results were observed when Pd used as a mixture with Re.

Some metals, such as W, Zr, Re and a mixture of W with Rh, have also been tested as permanent modifiers. Each coating was formed by successive injections of a modifier solution in order to insert the preferred amount of modifier on the graphite surface and subsequent thermal treatment of the graphite furnace after each injection. Permanent modification is an important recent development in chemical modification techniques, which is promising in view of increasing sample throughput with 'fast' programs, reduced reagent blanks, preliminary elimination of unwanted modifier components and, finally, lower detection limits.[32] Moreover, permanent modifiers were tested in this work to examine: (a) if the injection reproducibility for high volume aliquots could be improved; and (b) if sensitivity could be increased, so they could be used an alternative to modifiers in the form of solution. All of these permanent modifiers, except Re, gave the same T_{pyr} for all organotin species. The best T_{pyr} was achieved in the presence of W and Rh coating and it was equal to 1500 °C. Tungsten coating gave the same T_{pyr} as in solution. The Re coating did not stabilize at the same extent the organotin species and both DBT and MBT had the same T_{pyr} as they had in the absence of a modifier. One possible reason for this difference in behaviour between Re and the other permanent modifiers is that the former could be driven from the graphite tube during the pyrolysis step, due to the formation of volatile oxides (mainly Re_2O_7) in the temperature range 400–900 °C.[33]

Table 3. Comparison of chemical modifiers for the determination of toluene extractable organotins in terms of the obtained characteristic mass (m_0)

Modifier	m_0 (pg)
None	1200–1775 (TBT)
	229–503 (DBT/MBT)
	280–504 (TPhT)
3 μg W	90 (all OTs)
20 μg Zr	98 (all OTs)
5 μg Re	90 (all OTs)
5 μg La	117 (TBT)
2 μg Mg	95 (TBT)
1 μg Pd	150 (DBT/TPhT)
	165 (MBT)
	267 (TBT)
0.3 μg Pt	180 (TBT)
0.5 μg Ru	241 (TBT)
0.2 μg Ir	284 (TBT)
0.5 μg Rh	97 (DBT/TPhT)
	194 (TBT)
1 μg Pd + 5 μg Re	110 (DBT/TPhT)
	144 (TBT)
0.5 μg Rh + 5 μg Re	88 (DBT/TPhT)
	180 (TBT)
240 μg W (coating)	49 (DBT/TPhT)
	62 (MBT)
	82 (TBT)
120 μg Zr (coating)	62 (DBT/MBT)
	100 (TBT)
	85 (TPhT)
240 μg W + 5 μg Rh (coating)	56 (DBT/TPhT)
	72 (MBT)
	109 (TBT)
240 μg Re (coating)	211 (TPhT)
	238 (MBT)
	287 (DBT)
	620 (TBT)

Careful optimization of the mass of modifiers was carried out, because it is known that the mass of a modifier influences the sensitivity and T_{pyr} greatly, especially in the case of PGMs.[34] The optimum amounts of modifiers and the sensitivity achieved are summarized in Table 3. The characteristic mass (m_0) was compound dependent and this was also noticed in the presence of PGMs (Table 3). Nitrates of PGMs gave consistently better m_0 than their chlorides. This can be explained by the formation of the volatile chloride of tin. On the contrary, the same sensitivity for all compounds tested was observed in the presence of carbide-forming metals. Re and W gave consistently the best m_0 during the useful lifetime of a THGA (approximately 500–600 firings).

The influence of increasing masses of Pd, W and Re on the TBT signal is shown in Fig. 1. The integrated absorbance was recovered with 0.6–1.0 μg of Pd, with 3–6 μg of W and with 5–20 μg of Re. The modifiers showed a different effect on the peak height. The TBT signal was stable in the presence of Re or W in a relative wide optimum range. Experiments with Pd showed that the peak height signal of TBT increased sharply up to 0.6–1.0 μg. The signal of TBT decreased gradually when masses higher than 2 μg of Pd were used, but this decrease was more obvious with peak height measurements. In the

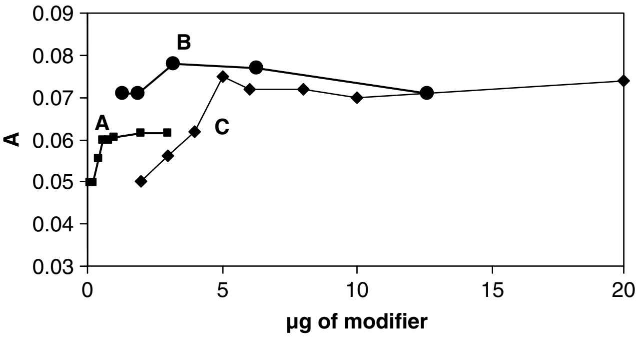

Figure 1. Influence of increasing amounts of Pd (A), W (B) and Re (C) on the integrated absorbance of 2 ng TBT (as Sn). The pyrolysis temperature was 1200 °C (W and Re) or 1000 °C (Pd) and the atomization temperature was 2100 °C (W and Re) or 2200 °C (Pd).

DOI: 10.1002/aoc

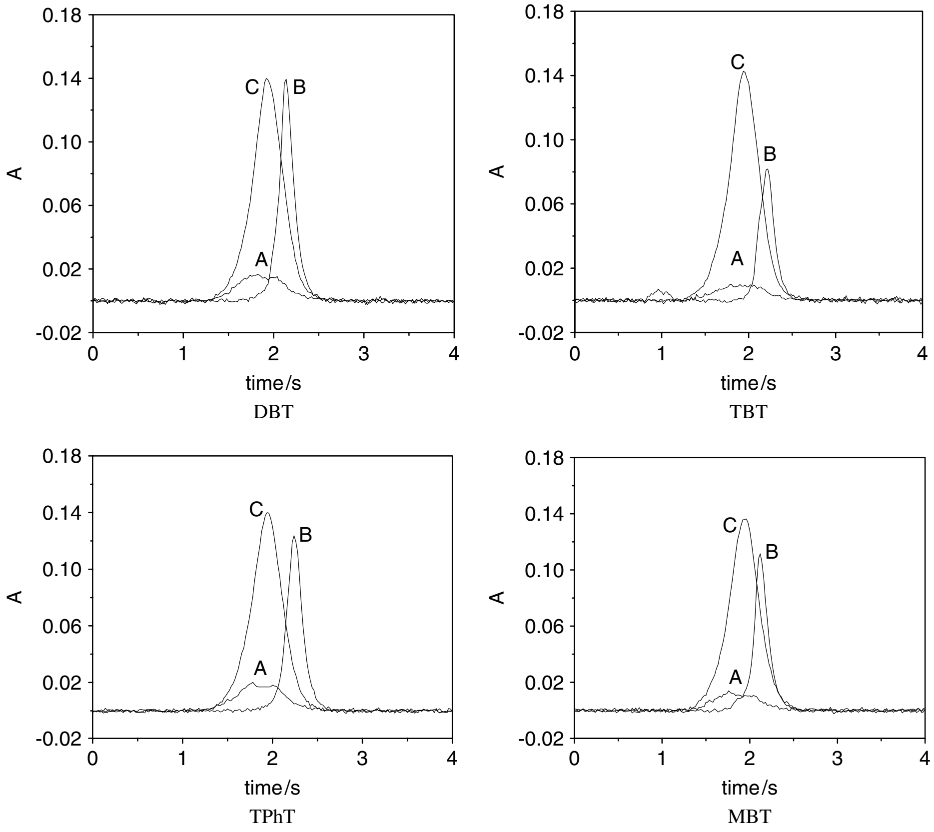

Figure 2. AA profiles of 50 μg l^{-1} (as Sn) of DBT, TBT, TPhT and MBT: (A) in the absence of modifier; (B) in the presence of 1 μg of Pd; and (C) in the presence of 5 μg of Re.

presence of Pd, organotin compounds are transformed to alloys and, depending on the pyrolysis temperature, different alloys are detected, such as PdSn, Pd_3Sn, Pd_3Sn_2, $Pd_3SnC_{0.5}$, Pd_2Sn and $PdSn_3$.[35,36] Moreover, organic materials seemed to help the formation of the alloys.[35] Five micrograms of Re or 3 μg of W were used for the remaining study.

The sensitivity of organotins in the absence of a modifier was very low (high characteristic mass). In the presence of the carbide forming elements, the sensitivity was satisfactory and similar among the species. In the presence of 3 μg of W or 5 μg of Re, the characteristic mass was 90 pg for all OTs. All the other modifiers gave values of m_0 higher than these of W, Re or Zr, except when W was used as a coating. This permanent modifier gave m_0 lower than 90 pg, but not the same value for all species. Palladium did not present good and equal characteristic mass for all the organotin compounds.

Figure 2 presents the peak profiles of the studied compounds in the absence and in the presence of Re and Pd. The integrated signal and the peak height of MBT, DBT, TBT and TPhT are equal in the presence of Re as chemical modifier. When Pd is used as chemical modifier, the absorbance peak shifted to higher temperatures. As discussed above, tin compounds interact strongly with Pd, forming intermetallic compounds or alloys, especially in the presence of the organic matrix. The better and equal sensitivity of OTs in the presence of Re or W or Zr could be attributed to their mechanism of action, taking into account the particular chemistry of tin in graphite furnaces. The role of refractory carbides as chemical modifiers appears to be the catalysis of the reduction of analyte oxides by the graphite atomizer.[37] Moreover, this is supported in that these compounds may promote the catalytic decomposition of organoelement compounds.[37] However, in the present study it was shown that W or Zr permanent modifiers were not as effective as the same modifiers added in solution. The reason for this difference could be the presence of oxygen in the latter case. In the case of W or Zr permanent modifiers, the main compound on the graphite surface is W or Zr carbide and the oxygen content is significantly reduced.[38] On the contrary, when Re, W or Zr modifier is added as a solution, oxygen is present at high concentrations at the time of dissociation of organotins, early in the drying and/or pyrolysis step. It seems that OTs can effectively be retained on the graphite surface and present the same sensitivity only if they are transformed into tin oxide at an early stage of the pyrolysis step. This was also the reason for the signal enhancement of TBT after the addition of water in the graphite tube[19] and the higher sensitivity of oxygen-containing organotin compounds in the presence of Pd.[35]

DOI: 10.1002/aoc

Optimization of the liquid–liquid extraction procedure

Liquid–liquid extraction procedure was optimized in order to achieve quantitative recovery of the required organotin compounds (DBT, TBT and TPhT). The recoveries obtained in the presence of various compounds are given in Table 4. Each extraction experiment was repeated at least three times. TBT and TPhT were easily extracted in toluene in the absence of an acid, at a pH normally found in environmental waters (pH 6–8). Under these conditions, DBT was recovered at a rate of 26 ± 4%. Addition of CH_3COOH and NaCl in the water sample resulted in 70% recovery of DBT. The pH of the samples after addition of CH_3COOH ranged between 2.7 and 3.0. These results are in agreement with a previous study that showed that addition of HCl and decrease of pH below 4 resulted in quantitative recovery of DBT, whereas the recoveries of TBT and TPhT were almost 100% in a wide range of pH (1–10).[19] However, this study showed that the addition of NaCl in freshwater samples was necessary in order to increase the recovery of DBT. Moreover, formation of emulsions reduced in the presence of NaCl. This can be a severe problem in some turbid samples, like wastewaters. Use of centrifugation for 15 min at 3000 rpm showed to produce a clear toluene layer. The recovery of DBT and MBT was almost quantitative in the presence of tropolone in the toluene layer. At the same time, the extraction of inorganic tin was nearly negligible (recovery 1.5%, at 10 µg l^{-1} of Sn^{IV}). Therefore, with this extraction scheme, all organotins could be extracted in the presence of inorganic tin with adequate selectivity. This method allows the analyst to have a clear indication of OT pollution and to perform speciation analysis only on polluted samples. No other phenyltins (MPhT and DPhT), apart from TPhT, were tested, because these compounds are present in very low concentrations in water samples,[1,2] generally below the LOD of the method, and it is expected to behave during extraction the same as the butyltins.

Optimization of the toluene volume was performed with different sample volumes (1 or 2 l). The volume of toluene was varied from 2 to 5 ml and from 3 to 10 ml for 1 and 2 l water samples and quantitative recoveries were obtained with 5 and 10 ml of toluene, respectively. In conclusion, organotin compounds were extracted from 2 l water sample, into 10 ml of toluene, an enrichment factor of 200. In addition, the sample volume injected in ETAAS was 240 µl, which can be considered as another 10-fold improvement of sensitivity compared with a conventional 20 µl sample introduction. With a total preconcentration factor of 2000, the method can determine TEOTs at concentration levels with environmental relevance.

Analytical figures of merit

The analytical characteristics of the developed method were determined with various chemical modifiers. The results are given in Table 5. The characteristic mass obtained, in the presence of Re and for an 80 µl sample, was 90 pg. The same m_0 was obtained in the presence of Zr or W modifier, whereas in the presence of Pd a higher m_0 was obtained (143 pg and only for DBT and TPhT), rendering this modifier inadequate for this application. The m_0 in the absence of modifiers ranged from 1620 (TBT) to 230 pg (DBT).

In order to achieve lower instrumental detection limit and a higher preconcentration factor, a multiple injection technique was used. The hot and multiple injection techniques were utilized in order to dispense 3 × 80 µl into the THGA. The optimum injection temperature was found to be 120 °C. However the characteristic mass was increased. This can be ascribed to the high volume of the injected sample (240 µl), which increases the organic matrix that, in turn, adversely affects (decreases) sensitivity. This phenomenon was also reported in the literature for an injection aliquot of 60 µl.[30] It was observed that, for a total injection volume of 240 µl, the characteristic mass decreased slightly, from 90 to 128 pg, but the instrumental limit of detection was 2-fold lower and equal to 0.42 µg l^{-1} (as Sn). The achieved instrumental LOD

Table 5. Characteristic mass, instrumental limit of detection and injection repeatability of the determination of toluene extractable organotins in the presence of various chemical modifiers

Modifier	m_0 (pg)	LOD (µg l^{-1})	RSD (%, $n = 5$)
5 µg Re	90 (80 µl) 128 (3 × 80 µl)	0.80 (80 µL) 0.42 (3 × 80 µl)	3.1 (0.8 ng as Sn)
20 µg Zr	92	2.0	4.0 (2 ng as Sn)
3 µg W	90	1.2	4.8 (2 ng as Sn)
1 µg Pd	143 (DBT/TPhT)	3.1	2.8 (4 ng as Sn)

Table 4. Extraction recoveries (%, $n = 3$, at least) of tin compounds from 1 l of a blank freshwater sample into the toluene layer (5 ml) in the presence of various extraction media. The concentration of the organotin compounds was 100 ng l^{-1} each, whereas inorganic tin was spiked at a level of 10 µg l^{-1}

A/A	Extraction media	TBT	TPhT	TBT + TPhT	DBT	MBT	Sn^{IV}
1	None	99 ± 5	104 ± 6	100 ± 3	26 ± 4	—	—
2	2.5% (v/v) CH_3COOH	98 ± 3	103 ± 4	104 ± 4	55 ± 4	0	—
3	2.5% (v/v) CH_3COOH + 1.2% (w/v) NaCl	99 ± 2	101 ± 2	—	70 ± 2	0	0
4	As in (3) + 0.5% (w/v) tropolone	—	—	—	96 ± 4	100 ± 6	1.5 ± 0.13

was in the same range or even better than those reported in the literature for the determination of TBT or total OTs in seawater.[20,29–31] For comparison, the LODs in the absence of modifiers ranged from 68 (TBT) to 9 (DBT) μg l^{-1} (as Sn). The method LOD was determined as three times the standard deviation of 10 replicate analyses of a blank freshwater sample. Using the optimized conditions (with Re modifier), the LOD of the overall procedure, for an injected aliquot of 240 μl, was found to be 2 ng l^{-1}, adequate for environmental applications.

The linear range of the calibration curves was 5–200 μg l^{-1} and the correlation coefficient was always higher than 0.999 in the presence of Re. It was observed that the sensitivity was surface-dependent. It increased constantly during the first 30 firings and stabilized until the breaking of the THGA. This was apparent mostly in the absence of modifier or in the presence of the PGMs.

The injection repeatability, expressed as the relative standard deviation (RSD) of five replicate measurements was always below 5% (Table 5). In the presence of 5 μg of Re the RSD was 3.1% (at 0.8 ng of Sn, $n = 5$), whereas at the same time in the absence of modifiers, RSDs ranged from 11% (TPhT) to 5% (DBT) at a level of 8 ng of Sn. Precision experiments were performed after the optimization of the extraction procedure. A seawater sample spiked with 100 ng l^{-1} of a mixture of TBT and TPhT of equal concentrations ($50 + 50$ ng l^{-1}) was extracted five times and the RSD (%) was 3.5%. A seawater sample with a concentration of approximately 19 ng l^{-1} of toluene extractable OTs was analysed five times and resulted in a mean concentration of 18.9 ng l^{-1} with an RSD of 5%. A freshwater sample with a concentration of approximately 5 ng l^{-1} of toluene extractable OTs was analysed five times and gave a mean concentration of 4.9 ng l^{-1} with an RSD of 11%, a satisfactory precision at this concentration level.

Owing to the lack of a water reference material with a certified concentration of OTs, recovery experiments were performed for the evaluation of the accuracy of the developed procedure. Recoveries were corrected taking into account the solubility of toluene in water samples acidified with acetic acid and in the presence of NaCl. As already mentioned, a loss of approximately 4% of the toluene layer was observed. Although extraction with toluene was reported in the literature,[16,19–21,24–26] only one early study corrected the TBT recoveries for toluene solubility.[19] A 10% loss of toluene was observed in that study.[19] However, the recoveries rates were not altered substantially after volume correction. The mean recoveries of the individual compounds at a concentration level of 100 ng l^{-1} each, from a blank freshwater sample, are given in Table 4. The mean recoveries of TEOTs from blank seawater and freshwater samples spiked with 10 and 100 ng l^{-1} of a mixture of TBT and TPhT of equal concentrations are given in Table 6. The recoveries ranged between 98 and 108 with adequate precision (RSDs <5%). Statistical analysis of the results had shown that there is no significant difference between the recoveries at both fortification levels and sample substrates.

Table 6. Mean recoveries (%) and relative standard deviations (RSD, %) of toluene extractable organotins in spiked seawater and freshwater samples

	Concentration level		
	10 ng l^{-1} in freshwater	10 ng l^{-1} in seawater	100 ng l^{-1} in seawater
Recoveries (%)	108	98	100
RSD (%, $n = 5$)	5.2	3.7	2.8

Table 7. Determination of the toluene extractable organotins (TEOTs) in water samples from the aquatic environment of Greece

Sampling site	[TEOTs] (ng l^{-1})
Lake water	
Doirani	<2
Pamvotida	13
Major Prespa	2.9
Minor Prespa	3.4
Seawater	
Saronikos Gulf (Perama)	19
Pagasitikos Gulf (Port of Volos)	19
Thermaikos Gulf (EKO)	5.4
Harbours	
Rhodes island harbour—June 1999	11.8
August 1999	77
November 1999	134
March 2000	102
April 2000	89.4
May 2000	92.4
Mytilene island harbour—June 1999	3.7
August 1999	<2
November 1999	116
March 2000	106
April 2000	223
May 2000	52

Screening determination of the toluene extractable organotins in the aquatic environment of Greece

An application of the developed methodology was performed on lake- and seawater samples collected from the aquatic environment of Greece, as a part of a wider monitoring programme of priority micropollutants. Some indicative results are presented in Table 7. The precision values (RSDs) found at two different levels (11% for a 5 ng l^{-1} level and 5% for a 19 ng l^{-1} level) could be applied as uncertainty estimates of the concentrations found. The presence of these compounds in seawater is correlated with their use as biocides in antifouling paints formulations. In particular, the analyses from Mytilene and Rhodes harbours revealed high concentrations of TEOTs during winter and springtime (November 1999 to May 2000). The increased concentrations in both ports could be attributed to two different reasons.[39] The increase in November could be attributed to fishing boats, which are used for fishing during summer and then are moored and cleaned during November. The second increase during springtime is attributed to the increased use of newly painted pleasure crafts and fishing boats. Both harbours have increased shipping activity during springtime and summertime, during the intense tourist period. However, the sharp dip in TEOTs concentrations during summertime (June to August) could be attributed to higher biological activity during summertime[40] and increased photolysis by sunlight.[1] The presence of organotins in the freshwater environment probably denotes their use for agricultural purposes. In particular, their detection in lakes could be attributed to both of these reasons.

CONCLUSIONS

A screening method for the determination of toluene extractable organotins (DBT, TBT, TPhT) as a sum parameter has been developed. The whole procedure includes a toluene extraction in the presence of 2.5% (v/v) CH_3COOH and 1.2% (w/v) NaCl and the determination of the analytes directly in the organic phase with ETAAS. Taking into account the increased volume (240 μl) of the extract that was subjected to ETAAS analysis, a preconcentration factor of approximately 2000 and a method LOD of 2 ng l^{-1} as Sn were achieved. A comparison of chemical modifiers was performed. The use of Re, as chemical modifier, gave adequate and similar stabilization for all the OTs tested ($T_{pyr} = 1400\,°C$) and the lowest instrumental LOD (0.42 μg l^{-1}, as Sn, for a 3×80 μl aliquot injection).

The advantages of this screening method are its simplicity and low cost. It is simpler and has lower method LOD than the previous screening methods that determine all OTs.[29,31] No resins are required and selectivity is achieved by appropriate selection of the extraction media. It can be developed in every laboratory involved in environmental analysis. Approximately four samples can be extracted per hour, giving a sample throughput of 30 samples over an 8 h working day. This method could be applied in monitoring programmes where a high number of samples have to be analysed in a short time. Its application helps the laboratory to perform speciation analysis only on samples that are contaminated with organotins and to avoid unnecessary, time-consuming and expensive procedures.

REFERENCES

1. Cima F, Craig PJ, Harrington C. In *Organometallic compounds in the Environment*, Craig PJ (ed.). Wiley: Chichester, 2003; 102–149.
2. Hoch M. *Appl. Geochem.* 2001; **16**: 719.
3. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for Community action in the field of water policy. *Off. J. Eur. Commun.* December 2000; **L327**: 1.
4. Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. *Off. J. Eur. Commun.* December 2001; **L331**: 1.
5. Montigny C, Lesper G, Potin-Gautier M. *J. Chromatogr. A* 1998; **819**: 221.
6. Bancon-Montigny C, Lesper G, Potin-Gautier M. *J. Chromatogr. A* 2000; **896**: 149.
7. Flavia Locateli Godoi A, Favorelo R, Santiago-Silva M. *Chromatographia* 2003; **58**: 97.
8. Stab JA, Brinkman UA Th, Cofino WP. *Appl. Organomet. Chem.* 1994; **8**: 577.
9. Caricchia AM, Chiavarini S, Cremisini C, Morabito R, Ubaldi C. *Int. J. Environ. Anal. Chem.* 1993; **53**: 37.
10. Lobinski R, Dirkx WMR, Ceulemans M, Adams FC. *Anal. Chem.* 1992; **64**: 159.
11. Schubert P, Rosenberg E, Grasserbauer M. *Int. J. Environ. Anal. Chem.* 2000; **78**: 185.
12. Thomaidis NS, Adams FC, Lekkas TD. *Mikrochim. Acta* 2001; **136**: 137.
13. Bowles KC, Apte SC, Hales LT. *Anal. Chim. Acta* 2003; **477**: 103.
14. Moens L, De Smaele T, Dams R, van den Broeck P, Sandra P. *Anal. Chem.* 1997; **69**: 1604.
15. Leach AM, Heisterkamp M, Adams FC, Hieftje GM. *J. Anal. Atom. Spectrom.* 2000; **15**: 151.
16. Parks EJ, Blair WR, Brinckman FE. *Talanta* 1985; **32**: 633.
17. McKie JC. *Anal. Chim. Acta* 1987; **197**: 303.
18. Stephenson MD, Smith DR. *Anal. Chem.* 1988; **60**: 696.
19. Apte SC, Gardner MJ. *Talanta* 1988; **35**: 539.
20. Pinel R, Benabdallah MZ, Astruc A, Astruc M. *J. Anal. Atom. Spectrom.* 1988; **3**: 475.
21. Donaghy C, Harriot M, Burns DT. *Anal. Proc.* 1989; **26**: 260.
22. Cardellicchio N, Geraci S, Marra C, Paterno P. *Appl. Organomet. Chem.* 1992; **6**: 241.
23. Mortensen G, Pedersen B, Pritzl G. *App. Organomet. Chem.* 1995; **9**: 65.
24. Fytianos K, Samanidou V. *Sci. Total Environ.* 1990; **92**: 265.
25. Dadfarnia S, Thompson KC, Hoult G. *J. Anal. Atom. Spectrom.* 1994; **9**: 7.
26. Gong B, Liu Y, Xu Y, Lin T. *Talanta* 1997; **44**: 1003.
27. Riepe HG, Erber D, Bettmer J, Cammann K. *Fresenius J. Anal. Chem.* 1997; **359**: 239.
28. Arambarri I, Garcia R, Millan E. *Fresenius J. Anal. Chem.* 2001; **371**: 955.
29. Bermejo-Barrera P, González-Campos G, Ferrón-Novais M, Bermejo-Barrera A. *Talanta* 1998; **46**: 1479.
30. Bermejo-Barrera P, Anllo-Sendin R, Cantelar-Barbazán M, Bermejo-Barrera A. *Anal. Bioanal. Chem.* 2002; **372**: 837.
31. Puri BK, Muñoz-Olivas R, Cámara C. *Spectrochim. Acta Part B* 2004; **59**: 209.
32. Tsalev DL, Slaveykova VI, Lampugnani L, D'Ulivo A, Georgieva R. *Spectrochim. Acta Part B* 2000; **55**: 473.
33. Haug HO. *J. Anal. Atom. Spectrom.* 1992; **7**: 451.
34. Thomaidis NS, Piperaki EA, Efstathiou CE. *J. Anal. Atom. Spectrom.* 1995; **10**: 221.
35. Li H, Gong BL, Matsumoto K. *Anal. Chem.* 1996; **68**: 2277.
36. Volynsky AB. *Spectrochim. Acta Part B* 2000; **55**: 103.
37. Volynsky AB. *Spectrochim. Acta Part B* 1996; **51**: 1573.
38. Volynsky AB. *Spectrochim. Acta Part B* 1998; **53**: 509.
39. Gomez-Ariza JL, Giraldez I, Morales E. *Water Air Soil Pollut.* 2001; **126**: 253.
40. Wade TL, Garcia-Romero B, Brooks JM. *Environ. Sci. Technol.* 1988; **22**: 1488.

DOI: 10.1002/aoc