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Speciation of butyltin compounds by on-line HPLC–ETAA of tropolone complexes in environmental samples

A Astruc, M Astruc, R Pinel and M Potin-Gautier
Laboratoire de Chimie Analytique, CURS, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, France

Tropolone (Trop) forms in solution stable complexes with monobutyltin (MBT $Trop_2$) and dibutyltin (DBT Trop). This property has been used to develop a separation procedure of butyltin compounds by liquid chromatography on cyanopropyl-bonded silica columns with a solution of tropolone in toluene as eluent.

Tin-specific detection by on-line ETAA allowed the development of a simple procedure suitable for the determination of tributyltin and dibutyltin in water and sediment samples.

Keywords: Butyltin, HPLC–ETAA, tropolone complexes, water, sediment, environment, speciation, determination

INTRODUCTION

The introduction of the tributyltin cation (Bu_3Sn^+ or TBT) in the aqueous environment through the leaching of antifouling paints or other sources has adverse effects on aquatic life. Tributyltin is more or less rapidly transformed by photochemical or biologically mediated processes. The main products (but perhaps not the only ones) of this degradation are the dibutyltin cation (Bu_2Sn^{2+} or DBT), the monobutyltin cation ($BuSn^{3+}$ or MBT) and finally inorganic tin species. Methylated tin species seem to be ubiquitous but in tin-polluted areas they are found in concentrations much lower than the butylated ones[1, 1a, 1b]. As the various butyltin compounds have very different toxic effects on the biota, the determination of TBT, the most deleterious of them, in environmental samples has been the object of many investigations during the last decade (see Ref. 1*c*, for example, for a review).

Many of the procedures that have been published rely on a preliminary extraction step for butyltin compounds from the environmental samples by some organic solvent containing the ligand tropolone, $C_7H_6O_2$ (Trop).[2–9] Surprisingly enough, there is not in the analytical literature any detailed study on the chemical basis of this procedure, although there appear to be some discrepancies between the efficiencies obtained by the various authors. The extracts are submitted to a great variety of procedures (concentration, solid-phase extraction,[9a] derivatization, back-extraction) before the final analysis including a chromatographic separation followed usually by some element-specific detection. Gas chromatography is the most popular separation method. Many liquid-chromatographic procedures have been described, few of them being applied to real environmental samples. They use mainly the ion-exchange[10, 11] or ion-pairing[12] modes; both are hardly compatible with the presence of a complexing agent such as tropolone. The chromatographic separation of some organotin complexes on bonded-phase columns has been studied[13, 14] in conditions often remote from those encountered when dealing with environmental samples.

On-line detection of the individual butyltin species separated by the liquid chromatographic procedure may involve various methods such as flame[11, 15, 16] or electrothermal[10, 17–20] atomic spectrometry ETAA, inductively coupled plasma–atomic emission[21] or –mass[12, 22] spectroscopy. Flame AA and ICP-AE have too-high detection limits to deal conveniently with actual samples; ICP-MS is quite an expensive detector and hardly compatible with organic solvents.

This paper deals with a direct HPLC–ETAA method of determination of butyltin compounds

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in toluene–tropolone extracts of environmental samples, based on a study of their reactions with tropolone.

MATERIALS

Reagents

Mono-, di- and tri-butyltin chlorides (MBTCl, DBTCl, TBTCl) were used as supplied by Merck (for synthesis) or Fluka (purum).

Solutions of tropolone [Fluka (puriss)] were prepared daily in toluene (Prolabo R.P.) for chromatographic elution and dilution of the standards. Picric acid (Prolabo) solution (0.5 %) was prepared in toluene weekly.

Standards

Primary standard solutions (1000 mg dm^{-3} as Sn) were prepared by weighing mono-, di-, and tributyltin chlorides into volumetric flasks and diluting with methanol (Prolabo Normapur). They were stored at 4 °C in the dark. Every day, secondary working standard solutions (10 mg dm^{-3}) were obtained by dilution of the primary standards with an appropriate tropolone solution in toluene. They were stored in the dark at ambient temperature all day long. Calibration curves or standard additions were obtained by dilution of the secondary standards in the 0–1 mg dm^{-3} range just before utilization.

Apparatus

AA determinations reported here were made with various equipment. ETAA was performed with either an IL assembly (IL 451 spectrometer, IL 555 graphite furnace atomizer, IL Fastac injection device) or a Varian assembly (Spectrometer AA 30, GTA 96 atomizer). Hollow cathode lamps were used throughout this study at a wavelength of 235 or 286.3 nm.

On-line HPLC–ETAA chromatograms were obtained with one of the two instruments, combining a Varian 5020 HPLC chromatograph with either the IL or the Varian ETAA assembly through a home-made interface.[23]

Spectrophotometric determinations were performed with a Hewlett–Packard 8450A UV spectrophotometer using 1 cm quartz cells.

METHODS

Extraction procedure

Water samples

Aqueous samples (100–1000 cm^3) acidified by 10 % hydrochloric acid (HCl) are shaken vigorously with 10–50 cm^3 of a 0.05 % (w/v) solution of tropolone in toluene during 10 min in glass separatory funnels wrapped in aluminium foil with Teflon stopcocks and plugs. After a 30 min rest period the extract is separated, rinsed three times with de-ionized water, dried on anhydrous sodium sulphate and filtered on Durieux ash-free filter paper.

Sediment samples

Dry sediment (0.1–1 g) is mixed (1 h) on a magnetic stirrer with 5–10 cm^3 of a 0.2 % (w/v) solution of tropolone in toluene in a Pyrex flask wrapped in aluminium foil. After decantation the extract is filtered on Durieux ash-free filter paper, and evaporated to near-dryness under vacuum at 40 °C. The residue is dissolved in a known volume (usually 1 cm^3) of 0.2 % tropolone solution in toluene. Sediment samples used in the study have all been air-dried, crushed and sieved (63 μm).

Determination of total tin

The water or sediment extracts may be analysed for total tin by ETAA after matrix modification (addition of 0.1 % picric acid) following a previously published procedure.[24] The detection limit (IUPAC $k=3$) is 1.0 ng cm^{-3} in toluene. Assuming 100 % extraction yields, and considering the concentration factors involved in the extraction steps (×100 for water, ×1 for sediment), detection limits of *ca* 1 ng dm^{-3} in waters or 1 ng dm^{-3} in sediments may be calculated.

On-line HPLC–ETAA speciation of butyltins

The water or sediment extracts may be submitted to an on-line HPLC–ETAA speciation procedure.

Chromatographic separation of butyltins

Experiments were carried out with several chromatographic conditions.

Using pure toluene as eluent, Micro Styragel 500 and 100 Å columns allowed a separation of high concentrations (200 mg dm^{-3}) of Bu_3SnCl,

Bu_2SnCl_2, $BuSnCl_3$ (in this order). However, at trace levels (0–1 mg dm^{-3}), apparently random peaks appeared and a fast evolution of the separation properties of the gels was noted.

When solutions of tropolone in toluene were used as eluent, butyltins eluted in the order Bu_2Sn^{2+}, Bu_3Sn^{+}, $BuSn^{3+}$ but both the shape of the peaks and the reproducibility of the retention times were not satisfying.[25]

Cyanopropyl-bonded silica columns

Experiments were then performed with columns (250 mm × 4 mm Nucleosil, 5 μm particle size), using solutions of tropolone in toluene as eluent.

As pointed out by Langseth,[13] tailing of alkyltin compound peaks due to adsorption on residual silanol groups of the bonded-phased material may be avoided by converting them to chelates, thus reducing the reactivity of the tin atom. 3-Hydroxyflavone[26] and morin[5] were found to be suitable reagents for HPLC separation of dialkyltins and monoalkyltins[14] (the ligand being incorporated in the mobile phase) and fluorescence detection.

Tropolone being a ligand (see below) very often used for the extraction of butyltins from environmental samples, we studied in some detail the HPLC separation of these compounds using solutions of tropolone in toluene as eluent. Modification of the solvent by addition of this polar modifier was found efficient. With a 0–5 % gradient of methanol and 0.005 % tropolone, a very good separation of the whole series of butyltin compounds was obained in the order tetrabutyltin (not retained)/dibutyltin/tributyltin/monobutyltin (Fig. 1). However, in the presence of methanol a slow degradation of the retention properties of the column was noted. It may be attributed to a slow increase of the density of residual free silanol groups on the bonded phase. The phenomena already mentioned[13,14] preclude routine applications of this method.

In isocratic conditions using tropolone solutions in pure toluene as eluent, the tributyltin and dibutyltin peaks are well separated, monobutyltin does not produce any detectable peak, being strongly adsorbed on silanol groups, and tetrabutyltin has the same retention time as tributyltin. As tetrabutyltin is scarcely present in environmental samples and has toxicological properties similar to those of TBT, this method was judged convenient for the determination of tributyl- and dibutyl-tin and to compare with the results of other methods.

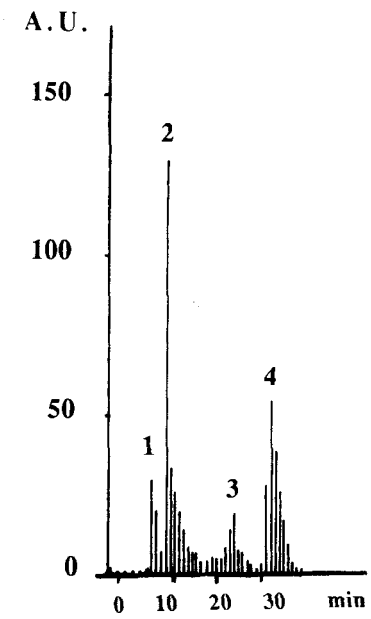

Figure 1 Chromatogram of a mixture of four butyltin compounds on cyanopropyl-bonded silica columns. 1, Tetrabutyltin (100 mg dm^{-3}); 2, dibutyltin dichloride (400 mg dm^{-3}); 3, tributyltin chloride (400 mg dm^{-3}); 4, monobutyltin trichloride (400 mg dm^{-3}). Eluent: 50 mg dm^{-3} tropolone in toluene during 5 min (flow: 1 cm^3 min^{-1}), then methanol gradient (0 to 5 % in 30 min).

Optimum chromatographic conditions for the drawing of HPLC–ETAA chromatograms were defined as 1 cm^3 min^{-1} flow rate of a 0.001 % solution of tropolone in toluene; the retention times were then 6 min (Bu_3Sn^{+}, Bu_4Sn) and 18 min (Bu_2Sn^{2+}). The tropolone-containing eluent may not be left overnight in contact with the column as it degrades, producing a brown residue, so that a daily cleaning with pure toluene is necessary.

Detection

The concentration of tropolone in the HPLC effluent was monitored by UV adsorption at 350 nm (Varian UV50). The effluent was then mixed in a T-connection with the AA matrix modifier (0.5 % picric acid in toluene, 0.2 cm^3 min^{-1}), pushed by a peristaltic pump (Gilson Minipuls 2) and conducted to the HPLC–ETAA interface. A low-volume interface (200 μl) was chosen to prevent a further broadening of the already rather broad HPLC peaks obtained.[23] The ETAA automatic injection device periodically sampled 20 μl out of the interface, the period being determined by the temperature cycle of the ETAA determination (Table 1) and

Table 1 Temperature and time conditions of the ETAA determination of total tin in toluene with 0.1 % picric acid as matrix modifier (Varian ETAA assembly; see text for description)

T (°C)	Time (s)	Gas flow ($dm^3\ min^{-1}$)	Read Command
60	5	3	No
110	5	3	No
700	4	3	No
750	4	3	No
750	1	0	No
2450	1.1	0	Yes
2450	1.0	0	Yes
2450	1.0	3	No
60	11.7	3	No

the delay introduced by the automatic injection device. This delay represents one-half of the total time interval between two ETAA measurements; it is thus a major limitation to the resolution of the HPLC–ETAA chromatographic peaks. This delay could be seriously reduced (perhaps to a few seconds) by modification of the software of the equipment.

A special BASIC program was written for the Varian Data Station DS15 that allows data storage, transformation and print-out as bar graphs on an Epson printer, thus producing HPLC–ETAA chromatograms directly (Fig. 1).

RESULTS AND DISCUSSION

Complexes of butyltin compounds and tropolone

The determination by ETAA of tin environmental samples cannot be realized directly, even for total tin determination, because of the low concentrations involved and the quite low sensitivity of AA for this element. A preconcentration step is necessary in every situation. Solvent extraction is one of the most often used procedures for this purpose.

As early as 1977, M&T Chemicals described a method where tin compounds are extracted from water by a solution of tropolone in toluene prior to an ETAA determination of total tin, with an overall detection limit of about 0.1 ng cm^{-3} in the water sample.

The reactions of organotin compounds with tropolone have scarcely been studied[27, 28, 28a] despite their frequent use[4, 29] and there are no thermodynamic data available allowing us to evaluate the importance of these reactions in the very dilute solutions of butyltin species that are likely to occur in environmental studies.

Muetterties and Wright[28] evidenced the production of $Trop_2SnX_2$ from aqueous or non-aqueous solutions of SnX_4 and tropolone and attributed to it a seven-coordinate structure. Action of tropolone on $PhSnCl_3$ gives $PhSnClTrop_2$. They also prepared $Trop_3SnCl$ by reaction of $Trop_2SnCl_2$ and the silver salt of tropolone, $PhSnTrop_3$ by reaction of $PhSnCl_3$ with sodium tropolonate and $SnTrop_4$, and $Trop_3SnOH$ from $SnCl_4$ and sodium tropolonate. Craig and Rapsomanikis[27] prepared $Me_3SnTrop$ from the reaction of Me_3SnOEt on tropolone and demonstrated its dismutation to Me_4Sn and $Me_2SnTrop_2$ in quite mild conditions.

We have realized a spectrophotometric study of the complexes between butyltin compounds and tropolone in dilute solutions in toluene using the method of continuous variations (often called Job's method[30]) to evaluate their physicochemical characteristics. When only one complex is formed this simple method allows the determination of the number of ligands involved in the equilibrium $A + nB \Leftrightarrow AB_n$ and an evaluation of the stability constant. Separate solutions of A and B of identical molarities (8.42×10^{-5} mol dm^{-3} for TBTCl and 4.21×10^{-4} mol dm^{-3} for DBTCl and MBTCl) are prepared and mixed in different proportions from 0 to 100 %. For each mixture a quantity characteristic of the complex AB_n and linearly dependent on its concentration is measured; it is maximum when the ratio of original solutions is $1/n$, so that n may be determined from the position of this maximum. The stability constant is evaluated from the shift to linearity of the plot around this maximum.

The molecular absorption spectrum (300–500 nm) of a solution of tropolone in toluene presents five more-or-less structured absorption bands with very different molar absorptivities. The addition of TBT to a solution of tropolone in toluene does not modify this spectrum. But with DBT and MBT additions some bands appear or disappear. This lack of reactivity of Bu_3Sn^+ with organic ligands has already been evidenced (oxine;[31] 3-hydroxyflavone or morin[14]) although complexes with 3-hydroxyflavone or morin can be synthesized[26] but decompose in dilute solution.

The results summarized in Table 2 evidence the lack of a sufficiently stable complex of Bu_3Sn^+ with tropolone in solutions representative of what

Table 2 Reactions between butyltin chlorides and tropolone in toluene in dilute solutions

Complex	Concentration (M)	Structure of complex	log K
$BuSnCl_3$ + tropolone	8.42×10^{-5}	ML_2	10.8 ± 0.3
Bu_2SnCl_2 + tropolone	4.21×10^{-4}	ML	5.2 ± 0.2
Bu_3SnCl	8.42×10^{-5}	No complex detected	

may occur in conditions of environmental analysis. Monobutyltin forms a very stable compound involving two molecules of tropolone per $BuSn^{3+}$ cation, with a conditional stability constant ($\log K = 10.8 \pm 0.3$) high enough to ensure a good stability of the complex provided that tropolone concentration in the solutions is maintained in the low ppm range (only 1 % dissociation in a 5 mg dm^{-3} solution of tropolone). This compound may be similar in structure to $PhSnClTrop_2$ described in the literature[27] and to the 1/2 complexes with morin advocated by Langseth.[14]

Dibutyltin forms a stable 1/1 compound with tropolone. The conditional equilibrium constant ($\log K = 5.2 \pm 0.2$) is such that a good stability of the complex necessitates higher tropolone concentrations (1 % dissociation in a 75 mg dm^{-3} solution of tropolone). Complexes of similar composition with morin and 3-hydroxyflavone have been mentioned.[14]

Besides thermodynamic properties, the kinetic aspects of these reactions may be of interest for practical purposes. Reaction kinetics have not been the object of any detailed study. However, no evolution of the spectra of the solutions of butyltin chlorides and tropolone were noticed on the time scale of these experiments (from a few minutes after mixing to several hours of conservation at room temperature). This indicates that there is no further slow evolution of the complexes initially produced. We may therefore conclude that no kinetic complication occurs on the time scale of extraction procedures that involves long extraction delays. However, this study does not exclude the possibility of a moderately rapid formation of these complex species, involving reaction times in the order of up to one minute, that may play a role in the chromatgographic elution of extracts of butyltin compounds by a solution of tropolone in toluene.

These data on the formation of complexes between butyltin species and tropolone in an organic solvent may be compared with published studies on the recovery by solvent extractions from environmental samples.

Extraction of butyltin compounds

Water samples

The absence of any complex between TBT and tropolone stable at low concentrations is consistent with the observation of several authors that the yields of extraction of Bu_3Sn^+ from water samples by low-polarity solvents are not significantly affected by the presence of tropolone. The liposolubility of the tributyltin species, such as Bu_3SnCl, Bu_3SnOH or $(Bu_3Sn)_2O$, that are most likely present in aqueous samples, seems high enough to allow direct extraction by toluene even without addition of a complexing agent. Meinema *et al.*[4] demonstrated that TBT in the low mg dm^{-3} range is quite well (80–95%) extracted into non-polar solvents such as benzene or chloroform from synthetic water samples. DBT extraction is enhanced to over 80 % by strong HBr acidification. The presence of tropolone increases MBT recovery from 0 to the 70–90 % range. In 1986, Maguire *et al.*[32] published recoveries of TBT by an extraction with a solution of tropolone in benzene varying from 96 ± 4 to 103 ± 8 % for spiked water samples (1–10 mg dm^{-3}).

The recovery of Bu_2Sn^{2+} from neutral aqueous solutions by benzene is improved from 0 to 80–90 % by 0.05 % tropolone,[4] in good agreement with the stability of the complex formed.

In Table 3 are presented typical results obtained in this study. All of them are comparable with those of the literature even those obtained at much lower concentrations of the analytes and by HPLC–ETAA determinations.

We note (Table 3) an important decrease of recovery when analysing natural raw sea-water, even after spiking. The most likely explanation is a lack of extractant efficiency in mobilising TBT

Table 3 Recovery experiments for TBT extraction from various water and sediment samples

Sample	TBT concn (ng Sn cm^{-3})	Extractant TT[a] (mg dm^{-3})	Detection method	Recovery (%)
TBTCL				
In ultra-pure water	20	100	ETAAS	95 ± 2
In synthetic water	5	500	ETAAS	96 ± 3
Raw brackish water (Cap Breton harbour)	*X*	500	ETAAS	33[b]
id + TBTCl spike	*X* + 0.5	500	ETAAS	45 ± 12[b]
Round robin test BCR				
Solution A (TBTAc)	8.76[c]	50	HPLC–ETAA	91 ± 5
Solution C [TBTAc + DBT + MBT + Sn(IV)]	9.32[c]	50	HPLC–ETAA	62 ± 9
Spiked sediment	1[d]	2000	ETAA	81 ± 9
	1[d]	0	ETAA	47

[a]TT: solution of tropolone in toluene. [b]Recovery evaluated by comparison with the results of an independent hydride generation/GC/AA method. [c]Mean of all selected individual values in BCR round robin test.[35] [d]Concentration expressed in mg (Sn) kg^{-1}.

adsorbed on solids suspended in the water sample. This difficulty has been noted with other procedures.[33] These data demonstrate that the extraction yield of TBT from water samples is independent of its concentration in the sample and of the concentration of tropolone in the extractant. Therefore, the major factor conditioning this extraction is the lipophilicity of TBT and not its complexation by tropolone.

Sediment samples

On the contrary, the extraction of TBT from sediments by pure toluene seems less efficient than in the presence of tropolone, despite the lack of stable complex formation.

When extraction of TBT from dry sediments is considered, the recovery of tributyltin from a dry spiked sediment is improved in the presence of 2000 mg dm^{-3} tropolone (81 % rather than 47 % with pure toluene; Table 3).

This improvement may be due either to an unknown action of tropolone on the matrix or more likely to the formation of a weak TBT/tropolone complex, unstable in the solutions with low tropolone concentrations used in the spectrophotometric or the chromatographic separations but appearing at the higher tropolone concentrations used for extractions from sediments (a value of the conditional stability constant such as $3 > \log K > 2$ for a 1/1 complex would be coherent with this hypothesis).

Data in Table 4 indicate that the extraction time has no significant influence on TBT recovery between 0.5 and 3 h. No more influential in the range studied is the ratio of sample weight to extractant volume. The concentration of tropolone has been maintained at 0.2 % (200 mg dm^{-3}) throughout this test but it is not critical above 100 mg dm^{-3} as ascertained by other data.[34]

Table 4 Influence of extraction time and volume of extractant on the recovery of TBT from a spiked sediment
Extractant: 0.2 % (200 mg dm^{-3}) tropolone in toluene
Sample: Vasière Ouest Gironde, a muddy, TBT-free marine sediment spiked with 1 mg (Sn) kg^{-1} Bu_3SnCl.

Ratio, sediment/extractant (g cm^{-3})	Extraction time (h)	Recovery (%)
0.0125	1.5	82
	3	92
0.024	0.5	90
	1	86
0.05	1.5	81
0.1	0.5	85

Speciation of butyltins in toluene extracts by on-line HPLC–ETAA

Following the extraction–concentration procedures previously described, the concentrations of butyltin compounds in toluene, representative of the actual concentrations obtained from environmental samples, are in the low mg dm^{-3} range. The concentrations of tin species in the effluent of the HPLC column are necessarily lower (high ng cm^{-3} range), justifying the choice of a very

Table 5 HPLC/ETAA retention times of tributyltin chloride and dibutyltin dichloride at various concentrations of tropolone in toluene (flow: 1 $cm^3 min^{-1}$)

Concentration of tropolone ($mg\ dm^{-3}$)	HPLC–ETAA retention times (min)	
	TBTC	DBTC
10	6	18
15	6	15
20	6	13
25	6	11

sensitive element-specific detector such as ETAA.

A simple procedure has been established using isocratic elution by a 10 $mg\ dm^{-3}$ solution of tropolone in toluene through a Nucleosil N 5 CN column already equilibrated with the eluent (Table 5). In these conditions tetrabutyltin and tributyltin species that are not complexed by tropolone are only very slightly retained. DBT is retained more strongly, the lower the tropolone concentration in the eluent. MBT is so strongly retained that it is eluted only as a nearly imperceptible shift of the base line in ordinary analytical situations (Fig. 2). The ability of butyltins eluted in tropolone solutions to react with the bonded nitrile groups of the stationary phase increases in the order tri- <di- <mono-butyltin, i.e. when the number of substituents linked to tin decreases.

Some tailing is observed with dibutyltin. The retention time of this compound decreases when the tropolone concentration is higher. This may be attributed to the variations of the ratio of free to complexed DBT species, which is strongly dependent on ligand content (from 1.5 to 29 when the ligand concentration varies from 1 to 20 $mg\ dm^{-3}$). The very stable complex of monobutyltin is so strongly adsorbed on residual silanol groups that this reaction does not seem reversible in the range of tropolone concentrations investigated, a behaviour similar to morin or flavonal complexes of the same cation.[14]

This method has been applied to the analysis of an unknown solution circulated by BCR in a round-robin test (Table 6). The result obtained is fully satisfying.[35]

Two kinds of problem appear during the analysis of the extracts of sediment samples by the HPLC–ETAA procedure.

(1) Toluene extracts a large part of the organic material and, during the analysis or organic-rich sediments, clogging of the precolumn and even of the column may occur. A preliminary cleaning of the extracts on Sephadex or deactivated alumina columns is efficient but induces TBT losses that are not negligible (up to 30 %). It is therefore necessary to take into account the overall recovery of the extraction–cleaning procedure in the determination of TBT.

(2) The extracted organic matter contained in the subsample injected in the HPLC column is, at

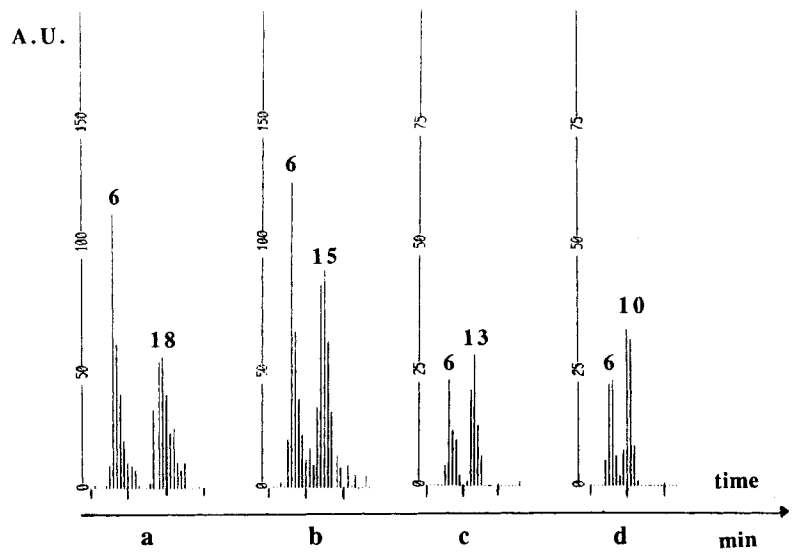

Figure 2 Isocratic HPLC–ETAA chromatograms of solutions of Bu_3SnCl and Bu_2SnCl_2. Eluent: various concentrations of tropolone in toluene: **a**, 10 $mg\ dm^{-3}$; b, 15 $mg\ dm^{-3}$; **c**, 20 $mg\ dm^{-3}$; **d**, 25 $mg\ dm^{-3}$; flow, 1 $cm^3 min^{-1}$.

Table 6 Determination of tributyltin in a water sample (BCR round robin test[35]) Concentrations are expressed in mg (Bu_3SnOAc) dm^{-3}, where OAc = acetate.

	HPLC–ETAA[a]	HG/GC/AA[a]	BCR round robin test, mean of all selected individual values
Water sample containing Bu_3SnOAc			
Solution A	2.36 ± 0.09	2.60 ± 0.03	2.58 ± 0.33
Solution C	1.71 ± 0.16	2.30 ± 0.13	2.74 ± 0.34

[a]Data obtained in our laboratory.

least in part, not retained and elutes simultaneously with TBT. This may have a negative effect on the sensitivity of the detection by on-line ETAA, probably through a chemical reduction of the matrix modifier (picric acid). Cleaning of the extract on Sephadex or alumina columns seriously reduces this effect. This difficulty in TBT determination is avoided by application of a standard addition procedure but with the same reduced sensitivity. A careful study (as for other methods) of the experimental conditions in relation with the nature of the analysed sediment samples is thus necessary. This method has been successfully applied to the speciation of butyltin compounds in sediment samples (Table 7): this intra-laboratory comparison of methods gave very good results like others already published,[36] thus validating this method and a hydride/GC/AA procedure developed in the laboratory.

CONCLUSION

The ligand tropolone has been used for over a decade to enhance extraction of butyltin compounds from environmental samples. Tropolone forms rapidly stable complexes with mono- and di-butyltin cations. However, its association with tributyltin is much weaker or does not exist.

Extraction of dissolved butyltin compounds from acidified waters by a solution of tropolone in toluene is characterized by a good recovery; however, the presence of suspended particulates may seriously decrease its efficiency.

Extraction of tributyltin from spiked dry sediments is made with good recoveries (80–100 %). Extraction yields of tributyltin and dibutyltin from 'naturally' polluted sediments are very close to those of the acetic acid extraction procedure used as a preliminary step for the hydride generation: GC AA speciation method.

The direct HPLC separation of butyltins in the toluene–tropolone extracts of environmental samples is a fairly fast and simple method compared with many published procedures that involve numerous preliminary sample handling steps (extractions and back-extractions, evaporations, derivatizations etc.).

This on-line HPLC–ETAA tin procedure has been applied successfully to aqueous solutions and sediment samples in several intra- and inter-laboratory exercises.

Table 7 Speciation of butyltins in sediment samples (data obtained in our laboratory by two different methods)

Sample	Methods	TBT	DBT	MBT
Orwell river, UK	HG/GC/AA	390 ± 80	210 ± 32	348 ± 56
(polluted estuarine sediment)	HPLC–ETAA[a]	350 ± 56	190 ± 38	
Rhine estuary sediment	HG/GC/AA	324 ± 52	173 ± 31	53 ± 10
(Netherlands)	HPLC–ETAA[a]	295 ± 50	186 ± 30	
Rhine estuary (Netherlands)	HG/GC/AA	332 ± 50	262 ± 44	162 ± 29
(suspended matter)	HPLC–ETAAS[a]	348 ± 63	234 ± 45	

[a]Extractant: TT 2000 mg dm^{-3}.

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