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Speciation of butyltin compounds by ion chromatography coupled to electrothermal atomic absorption spectrometry

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A new method for the determination of butyltin species by ion-exchange chromatography linked with graphite-furnace electrothermal atomic absorption spectrometry (ETAAS) is presented. The separation is achieved on a strong cation-exchange column with a 0.18 mol dm^{-3} solution of diammonium citrate at pH 6.5 with a step change to pH 4.0 in 60:40 methanol/water solvent. ETAAS detection is performed on-line using an oxidizing matrix modifier. Mono-, di- and tri-butyltin may be determined in a single experiment with detection limits of (respectively) 0.5, 1.1 and 0.8 ng (Sn). Applications to actual samples are reported.

Keywords: Butyltin, ion chromatography, speciation, electrothermal atomic absorption spectrometry (ETAAS)

INTRODUCTION

Trisubstituted organotin compounds are introduced in the aquatic environment through their use as biocides. Tri-n-butyltin (TBT) derivatives are currently the most used. The toxicity of TBT for some aquatic organisms is extremely high, and very sensitive detection methods are required for its determination. TBT is quite rapidly degraded in the environment into the much less toxic dibutyl- and monobutyltin cations. It is therefore necessary to couple a powerful separation technique to the specific detector to determine TBT specifically in naturally occurring mixtures.

Most of the multistage methods described in the literature (1–8) are based on the gas-chromatographic separation of volatile compounds previously obtained by some derivatization. These sample pretreatment procedures are often time-consuming and involve several steps, therefore increasing experimental errors. Published multistage methods involving liquid chromatography are scarce, being subject to the difficulty of finding separation conditions for organotin cations compatible with both the procedure of extraction of analytes from actual samples and the element-specific detection method. A review has recently been published.[9]

One-third of published procedures use ion-exchange chromatography,[10–16] the ionicity of alkyltin compounds being sufficient to achieve a separation in protic solvents. Typical conditions involve Partisil 10 μm SCX silica columns and a mobile phase containing methanol (60–90%) and ammonium ion (0.03–1 mol dm^{-3}) as developing cation. Detection is performed generally by electrothermal atomic absorption spectrometry (ETAAS) or, more recently, by inductively coupled plasma–mass spectrometry (ICP MS).

We have recently presented an HPLC–ETAAS procedure for the determination of TBT, using cyanopropyl-bonded silica columns for the separation of tropolone complexes of butyltin compounds.[17] However this procedure deals only with di- and tri-butyltin species (DBT and TBT), monobutyltin (MBT) being very strongly retained. McLaren *et al.*[18] also using an HPLC/ICP-MS procedure was not able to find a complete set of extraction/separation/detection conditions allowing the simultaneous determination of the three butyltin species in sediment samples.

This paper deals with a direct HPLC–ETAAS determination method for the three butyltin compounds (MBT, DBT, TBT) based on ion-chromatographic separation.

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Table 1 ETAAS temperature program

Step	Temperature (°C)	Time (s)	Gas flow ($dm^3 min^{-1}$)	Gas type	Read command
1	105	15	3	Normal	No
2	850	20	3	Normal	No
3	850	5	3	Normal	No
4	850	2	0	Normal	No
5	2600	1.1	0	Normal	Yes
6	2600	2	0	Normal	Yes
7	2600	1	3	Normal	No

MATERIALS AND METHODS

Reagents

Mono-, di- and tri-butyltin chlorides (MBTCl, DBTCl, TBTCl) were purchased from Merck or Alfa Products GmbH and tributyltin acetate (TBTAc) was furnished by the BCR (Brussels). These standards were used without further purification.

Stock solutions (1000 mg dm^{-3} as Sn) in methanol (Prolabo, Normapur) were stored at 4 °C in the dark; stability over several months has been checked. Working standards (10, 1 or 0.1 mg dm^{-3} as Sn) were obtained daily by dilution in the chromatographic eluent; they were stored in the dark. They were diluted further just before use.

Solutions of diammonium hydrogen citrate (Prolabo RP) in methanol and deionized water (Millipore) were prepared daily; pH was adjusted if necessary by addition of nitric acid (Merck, Suprapur) or ammonia (Prolabo, RP).

Potassium dichromate used for matrix modification in ETAAS determinations was purchased from Prolabo (RP). Pure acetic acid (Merck PA) was used for extractions from sediments.

The sediment reference material PACS-1 is available from the National Research Council of Canada (NRCC) Marine Chemistry Analytical Chemistry Standards Program.

Apparatus

A Varian 5020 liquid chromatograph with a Spherisorb SCX (250 mm × 4.6 mm) 5 μm multi strong cation column and guard column (10 mm × 3 mm) were coupled through a home-made interface (described fully in a previous paper[17]) to a Varian ETAAS assembly (AA30, GTA 96). The ETAAS matrix modifier, pushed by a Gilson Minipuls 2 peristaltic pump, was mixed in a T-tube with the chromatographic effluent before introduction to the interface.

RESULTS AND DISCUSSION

Optimization of the ETAAS detection

The GTA 96 automatic injection device automatically sampled 20 μl from the interface with a delay fixed by the temperature cycle of the graphite furnace and the software. This delay is a major limitation in the resolution of the overall analytical procedure. The temperature cycle reduced to a minimum (46.1 s) is presented in Table 1, the injection temperature being 60 °C.

Optimal ETAAS conditions have been found using a pyrolytic carbon platform in a pyrolytic carbon furnace. In these conditions the platform and the furnace may be used for approx. 700 and 400 atomizations, respectively. As in a previously described method[19] for ETAAS tin determination in aqueous solutions, the oxidizing matrix modifier adapted to the HPLC effluent giving the best results is 0.04% potassium dichromate in 2% nitric acid (Table 2).

As the flow rate of the chromatographic mobile phase is typically 1 $cm^3 min^{-1}$, a 0.12% (w/v) $K_2Cr_2O_7$ solution was added at 0.2 $cm^3 min^{-1}$ to minimize dilution.

Table 2 Variations of sensitivity with $K_2Cr_2O_7$ matrix modifier concentration

$K_2Cr_2O_7$ concentration (%)	Sensitivity (absorption units)
0.02	0.33
0.04	0.396
0.06	0.311

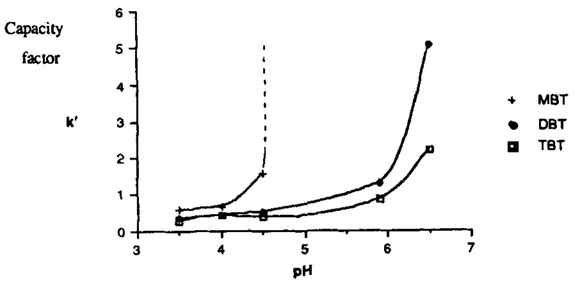

Figure 1 Effect of pH on capacity factors: mobile phase 0.18 mol dm^{-3} ammonium citrate, methanol/water (60:40, v/v).

Optimization of chromatographic conditions

Previous work on standard solutions by McLaren[18] using similar chromatographic conditions indicates that a pH variation from 6 to 3 after 1 min is necessary to obtain the separation of the three butyltin species. Moreover, the MBT peak appears over an ill-defined background peak arising from elution of inorganic tin.

Therefore McLaren[18] limited analysis of sediments to the determination of TBT and DBT by isocratic elution with a 0.18 mol dm^{-3} ammonium citrate solution in a methanol/water mixture (60:40, v/v) at pH 6.

Effect of pH

Very little is known on the aqueous chemistry of organotin cations in dilute solutions. A study of methyltin compounds[20] demonstrates that Me_3Sn^+ predominates up to pH 5, Me_2Sn^{2+} up to pH 4 and $MeSnOH^{2+}$ at pH 1.4, hydroxylated forms existing at higher pH values. At low pH Me_2SnCl_2 and Me_3SnCl are present respectively in the form of a dication and a monocation.[21,22] Et_2Sn^{2+} predominates at pH<3 and Et_2SnOH^+ from pH 3 to 5 least.[23] The less acidic butyltin compounds may be supposed to follow similar reaction patterns with some shifts in limiting pH values. Laughlin *et al.*[24] indicate that dissolved in seawater, TBT is present mainly as $TBTOH_2^+$ and TBTCl. Hydrated TBT cation behaves like a weak monoacid (pK_a 6.58 in 44% ethanol/water solution).[25]

However, Fig. 1 demonstrates that the retention of butyltin cations by the chromatographic ion-exchange column increases with pH in the range 3.5<pH<6.5, with abrupt variations around pH 4.5 for MBT, 6 for DBT and 6.5 for TBT. This behaviour cannot be linked directly to ion-exchange and acid–base equilibria. The eluent is a solution of ammonium citrate in water/methanol. Citric acid is a triacid (pK_a 3.13; 4.76; 6.40 in water[26]) and also a powerful complexing agent. The ability of butyltin cations to form stable complexes with oxygen-containing ligands is well known, tropolone (Trop) being the most often used complexing agent. MBT and DBT give very stable complexes with tropolone in toluene solutions (MBT $Trop_2$ and DBT Trop);[27] recently these complexes have also been shown to exist in a polar solvent,[28] but TBT seems less reactive. It may thus be suspected that the retention of butyltin moieties by the SCX column involves properties other than ion exchange, such as reverse-phase bond (RPB) character due to the hydrocarbon part, adsorption on uncovered Si–OH sites,[10] and the formation of complexes with citrate.

Using the mobile phase defined in Ref. 18, the capacity factors of butyltin species vary with pH (Fig. 1). At low pH values (≤4) the resolution is insufficient; at higher pH values resolution improves very sharply from pH 4.5 for MBT or pH 6 for DBT and TBT. There is thus a disagreement between optimal pH values for the resolution of TBT and DBT peaks and MBT determination and a compromise must be found or non-isocratic conditions used.

Effect of ionic strength (μ)

Varying the concentration of ammonium citrate at constant pH influences capacity factors of DBT and to a lesser degree TBT much more than that

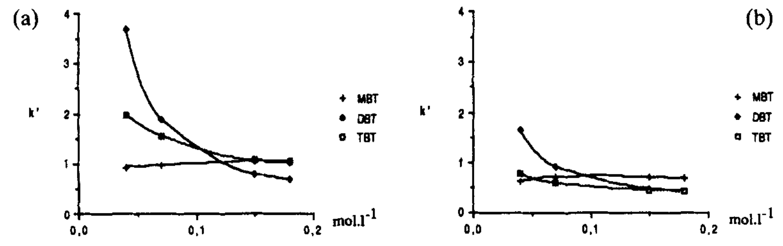

Figure 2 Effect of ammonium concentration on capacity factors: (a) pH = 4; methanol/water, 50:50 (v/v); (b) pH = 4; methanol/water, 60:40 (v/v).

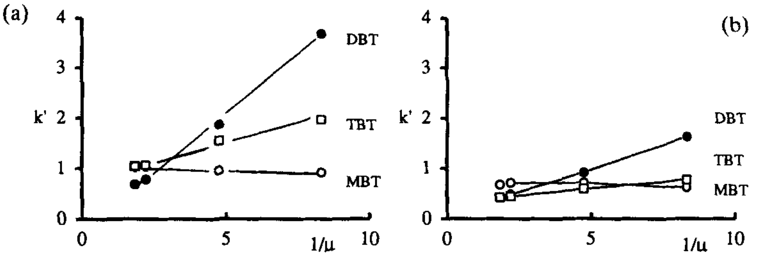

Figure 3 Variations of capacity factors with eluent ionic strength at pH = 4: (a) methanol/water, 50:50 (v/v); (b) methanol/water, 60:40 (v/v).

of MBT. Similar trends are observed at pH 4 with 50:50 (Fig. 2a) or 60:40 (Fig. 2b) methanol/water compositions, the effects being enhanced at lower methanol concentrations. Plots of the capacity factors versus the reciprocal ionic strength of the mobile phase at 50% methanol (Fig. 3a) yield straight lines of variable slopes and intercepts. The behaviour of DBT is nearly ideally suited to a purely ionic retention mechanism. TBT retention, with a positive intercept, indicates a non-negligible contribution of adsorption phenomena at high ionic strength. A similar conclusion on TBT behaviour in a relatively similar situation has already been published.[10] The retention of MBT, independent of or even negatively correlated with $1/\mu$, is purely dependent on adsorption phenomena. Results obtained with 60% methanol follow the same trends on a reduced scale (Fig. 3b).

Low ammonium citrate concentration and methanol percentage at pH 4 produce the best set of capacity factors; unfortunately a severe peak broadening is observed and selectivity is not satisfactory.

Effect of methanol concentration

The variations of the capacity factors were studied as a function of methanol percentage concentration at pH 4 for two different concentrations of ammonium citrate (Fig. 4). They show familiar hyperbolic relationships between the capacity factors and decreasing methanol concentration for all three butyltin compounds. Similar behaviour of TBT at pH ~7 has already been described.[10]

Optimized analytical conditions

Optimal conditions retained for practical analysis are as follows. The column is equilibrated with a 60:40 (v/v) methanol/water solution of 0.18 mol dm^{-3} diammonium citrate at pH 6.5 at 1.0 cm^{3} min^{-1} flow rate. Injection volume is 100 μl; after 28 min a step change in the eluent pH down to pH 4.0 is applied.

ANALYSIS OF STANDARD SOLUTIONS

Calibration graphs established from peak areas for the analysis of standard solutions containing the three butyltin compounds are perfectly linear in the range of concentrations studied (0–1200 ng cm^{-3}), but sensitivities are quite different (Table 3).

Repeatability of the chromatographic procedure was examined by eight replicate injections

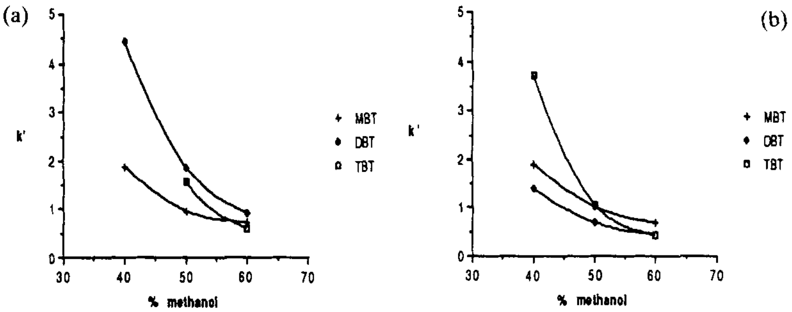

Figure 4 Effect of methanol percentage on composition capacity factors at pH = 4: (a) 0.07 mol dm^{-3} ammonium citrate concentration; (b) 0.18 mol dm^{-3} ammonium citrate concentration

Table 3 Calibration curve $y = i + mC$

Compound	i[a]	m[b]	r[c]
MBT	5	0.899	0.999
DBT	−8.4	0.405	0.998
TBT	−2	0.543	0.999

[a] Intercept of curve on absorbance axis; y and i are in milliabsorption units. [b] Calibration curve slope, in milliabsorption units ng^{-1} (Sn) cm^3. [c] Correlation coefficient.

of a 1 $\mu g\,cm^{-3}$ solution of TBTAc. The relative standard deviation was RSD = 9.6%. Reproducibility was evaluated to be 9.4% by the analysis of six independent TBTAc solutions (1 $\mu g\,cm^{-3}$). Detection limits (limit concentrations; C_L) have been estimated by the formula $C_L = 3\,S_B\,m^{-1}$ where S_B the blank standard deviations determined from 20 blank measurements (20 µl) sampled in the graphite furnace, is 1.5 milliabsorption units. C_L is, respectively, 5, 11 and 8 $ng\,cm^{-3}$ (as tin) for MBT, DBT and TBT.

APPLICATIONS TO ACTUAL SAMPLES

This analytical procedure, combined with suitable sample pretreatments, has been applied to the analysis of a leachate of commercial vegetal sponges and of a sediment reference material.

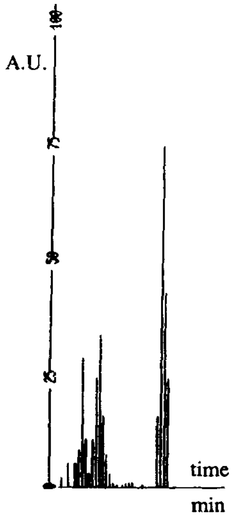

Figure 5 Chromatogram of PACS-1.

Table 4 Analysis of butyltin compounds[a] in PACS-1

Origin[b]	MBT	DBT	TBT	Total butyltin
A	0.28 ± 0.17	1.16 ± 0.18	1.27 ± 0.22	2.71 ± 0.57
B	0.42 ± 0.08	0.83 ± 0.04	1.23 ± 0.23	2.48 ± 0.35
C	—	1.19 ± 0.14	1.18 ± 0.15	—
D	0.59 ± 0.06	0.81 ± 0.07	0.91 ± 0.09	2.31 ± 0.22

[a] All concentrations are reported as µg (Sn) g^{-1} (dry wt) ± SD, except for A (certified values), where uncertainty is a 95% confidence level. [b] A, certified values; B, acetic and extraction directly followed by hydride generation–atomic absorption; [29]C, ion-exchange HPLC/ICP MS; D, this study: acetic acid extraction-evaporation-dissolution in mobile phase for HPLC/ETAAS.

Sponge leachates

Two extraction procedures have been used on the same commercial sample.

Aqueous leaching

A dry sample (1 g) was leached overnight under agitation in 15 cm^3 deionized water at room temperature. The leachate was evaporated to dryness at 30 °C under a flow of nitrogen[16] and the residue dissolved in 1 cm^3 of the chromatographic mobile phase. Water-leached butyltin compounds were determined by standard additions as MBT 690; DBT 30; TBT 50 ng (Sn) g^{-1}

Acetic acid leaching

A dry sample (0.5 g) was leached in 20 cm^3 of pure acetic acid overnight under agitation. After vacuum evaporation to dryness and redissolution in 10 cm^3 of mobile phase, butyltin compounds were evaluated as MBT 5400; DBT 2800; TBT 21400 ng (Sn) g^{-1}. The comparison of these analyses indicates that TBT, probably used as a fungicide, is strongly retained on solid material and escapes aqueous leaching.

Sediment reference material

The acetic acid extraction procedure has been applied to the analysis of the harbour sediment reference material PACS-1 (Fig. 5) certified for its content of butyltin compounds. Dry material (2 g) was extracted overnight with 20 cm^3 of pure acetic acid. A 5 cm^3 portion of the extract was dried at 30 °C under a gentle flow of nitrogen, following a procedure described in the literature,[16] then dissolved in 2 cm^3 of the chromatographic eluent at pH 6.5. The set of results presented in Table 4 with other available data needs some comment.

Comparison of lines C and D in Table 4 indicates that MBT determination in sediments that was not possible with the ion-chromatographic conditions of Ref. 18 is made possible with the procedure described above. Extraction of butyltins from sediments by acetic acid is efficient[19,30] this is confirmed by comparison of lines A and B. Now comparing lines A and D, we can say that the procedure described in this paper is as good as those previously described, especially for total butyltin. DBT and TBT values determined in this study are slightly lower and MBT concentration higher. Zhang *et al.*[30] indicate that none of the available extraction procedures has a convenient efficiency for MBT extraction from sediments. Low DBT and TBT values may be attributed to losses during the evaporation/redissolution step, as no losses have been observed during an identical treatment of standard solutions. This is most probably a matrix effect on the redissolution of the evaporated extract. Further investigations are in progress.

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