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Influence of Tropolone on Voltammetric Speciation Analysis of Butyltin Compounds

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Analysis of organotin compounds in environmental matrices is usually performed by chromatographic or spectroscopic techniques. Only a few papers dealing with organotin voltammetric determination have so far been published and this technique does not seem very promising for organotin speciation. The reasons are likely to be found in the very low organotin concentration levels in the marine environment, in the complexity of environmental matrices and in the presence of several organotin compounds (butyl- and phenyltins), together with other metals, in samples; the latter leads to peak overlapping. In this paper we present a study of the influence of tropolone (2-hydroxycyclohepta-2,4,6-trienone) on the voltammetric speciation of butyltin compounds. Results suggest that tropolone, being able to form complexes of different stability with tin and its compounds, improves the applicability of voltammetry to organotin determination by enhancing sensitivity and resolution.

Keywords: Organotins, speciation, tropolone, differential pulse polarography (DPP), differential pulse anodic stripping voltammetry (DPASV)

INTRODUCTION

Marine environment tributyltin (TBT) contamination has been reported over the last 20 years[1,2] following the introduction of this compound as the main component in antifouling paints.[3,4]

The release of TBT directly into the water, together with its high toxicity toward marine organisms and its high tendency to be bioaccumulated, can cause malformities and even high mortality of these organisms, as happened in France at the end of the 1970s (Arcachon Bay).[5]

Studies on the environmental distribution of TBT and its degradation products, dibutyltin (DBT) and monobutyltin (MBT), have been carried out and several analytical methods have been developed to determine butyltins in environmental matrices.[6–15] These methods usually required a pre-treatment of samples, including extraction and derivatization. A wide variety of different extraction methods have been published in the literature; many of them involve the use of tropolone to enhance the extraction efficiency for less-substituted organotin compounds.[7,12–15] Tropolone is able to form stable complexes with tin and its compounds, making them more liposoluble. Chromatographic and spectroscopic techniques are the most used methods for the final determination of organotin compounds. Papers dealing with the electrochemical behaviour of different (type and number of substituents) organotin compounds[16–27] as well as their electroanalytical determination[28–34] have also been published. However, in these papers organotin compounds are mainly determined as inorganic tin after mineralization[31–33] and this technique does not seem very promising for organotin speciation in environmental matrices. The reasons are likely to be found in the very low organotin concentration levels in the marine environment, in the complexity of environmental matrices and in the presence of several organotin compounds (butyl- and phenyl-tins), together with other metals, in samples that lead to peak overlapping.

The study of the influence of tropolone, which has been already used in voltammetric determination of inorganic tin,[31–33,35] in voltammetric determination of butyltin compounds is now presented and discussed for speciation purposes.

Results suggest that the use of tropolone improves the applicability of voltammetry to organotin determination by enhancing sensitivity and resolution.

EXPERIMENTAL

Differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) analyses were performed by a compu-

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Table 1 Experimental conditions for DPP of TBT, DBT and MBT

	TBT, DBT	MBT
Solvent	Water/methanol, 1:4	Water/methanol, 1:4
Support electrolyte	0.1 mol l^{-1} NH_4NO_3	0.1 mol l^{-1} NH_4NO_3 + 0.03% tropolone
pH	5.5	5.5
Initial potential (V)	−0.4	−0.4
End potential (V)	−1.1	−1.1
Scan rate (mV s^{-1})	3	3
Dropping time (s)	1	1
Pulse height (mV)	−50	−50
Pulse width (ms)	50	50
Sampling time (ms)	8	8

terized polarographic analyser AMEL model 433A (AMEL, Milan, Italy). The working electrode [dropping mercury electrode (DME) for DPP and hanging drop mercury electrode (HDME) for DPASV] potential was referred to a saturated Ag/AgCl reference electrode and a Pt wire was used as counter-electrode. Experimental conditions for DPP and DPASV are summarized in Tables 1 and 2, respectively. pH measurements (all pH values given for mixed solvents have to be considered as apparent values) were performed by a Crison model 2002 pHmeter.

Standard solutions (in methanol) of different butyltin compounds and tropolone were prepared by weight from Fluka (TBT), Aldrich (DBT) and Janssen (MBT and tropolone) products. The products were used without further purification. Whenever possible, highly pure reagents ('suprapur' Merck products) were used; in the other cases analytical-grade products from either Merck or Carlo Erba were used. Deionized water from Milli-Q Millipore system ($\rho \geq 18\ M\Omega$ cm) and mercury distilled twice were also used.

All the experiments were performed on 10 ml solutions. Before running the polarogram the solutions were deoxygenated for 5 min under stirring (at 500 rpm) by high purity nitrogen and the gas was maintained above the solutions during the experiment. As voltammetric determination was performed in a methanol/water system, nitrogen was previously saturated in a solution of the same composition in order to avoid changes in concentration due to methanol evaporation.

RESULTS AND DISCUSSION

A preliminary study to verify the best experimental conditions for DPP determination of butyltin compounds was carried out. At low concentration levels ($<5 \times 10^{-5}$ mol l^{-1}), TBT and DBT show well defined peaks: DBT ($V = -615$ mV) at less negative potential than TBT ($V = -820$ mV).

Different compounds (ammonium chloride,

Table 2 Experimental conditions for DPASV of DBT and TBT (as inorganic tin)

	TBT	DBT
Solvent	Water	Water/methanol, 1:1
Support electrolyte	0.1 mol l^{-1} acetate buffer + 5×10^{-5} mol l^{-1} tropolone	0.1 mol l^{-1} acetate buffer + 5×10^{-5} mol l^{-1} tropolone
pH	4.7	3.7
Deposition potential (V)	−1.0	−1.0
Deposition time (s)	120	60
Stirring speed (rpm)	500	500
Initial potential (V)	−1.0	−1.0
End potential (V)	−0.2	−0.4
Scan rate (mV s^{-1})	20	20
Pulse amplitude (mV)	50	50
Pulse width (ms)	50	50
Sampling time (ms)	8	8

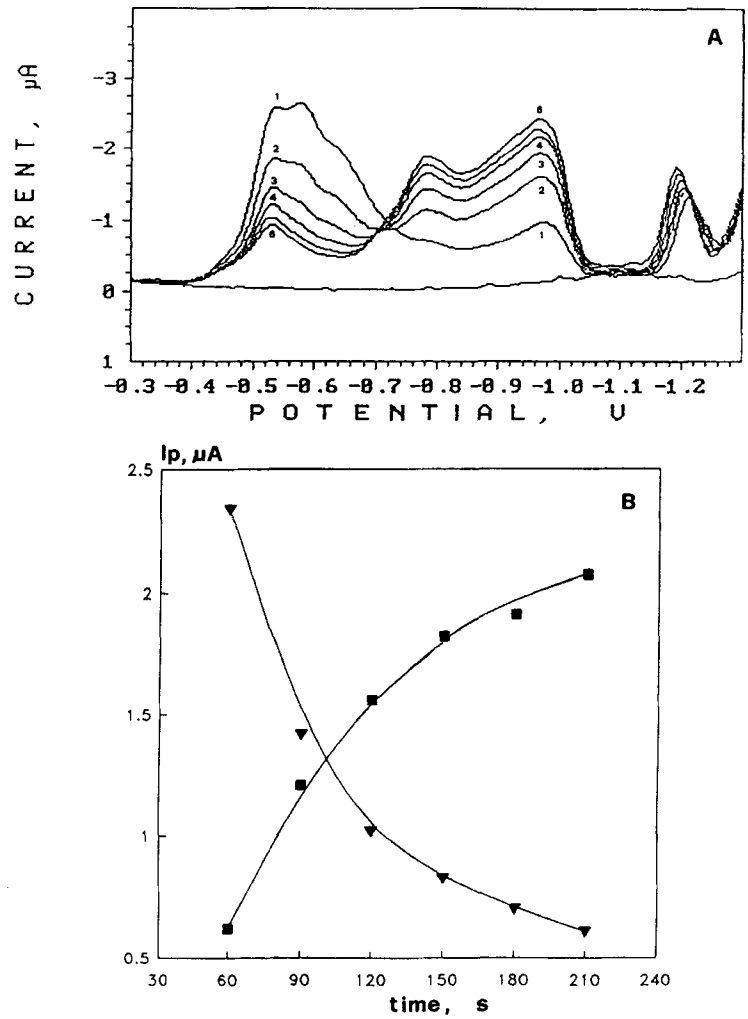

Figure 1 1.8×10^{-5} mol l^{-1} MBT. Medium: 0.1 mol l^{-1} NH_4NO_3 in water/methanol (1:4). (A) Successive polarograms; (B) variation of intensity peak of MBT (▼) and of its hydrolysis product (■) versus time.

ammonium perchlorate, potassium chloride, lithium chloride, ammonium nitrate, sodium acetate and ammonium acetate) were tested as support electrolytes: ammonium nitrate allows the best sensitivity for both compounds, and particularly for DBT, which shows higher sensitivity than TBT.

The addition of methanol improves the sensitivity for both compounds. Furthermore, the resolution also improves because the TBT peak is shifted towards more negative values while the peak potential of DBT remains quite constant (−615 mV). The highest sensitivity and separation ($\Delta V = 200$ mV) of peaks is obtained for a 4:1 methanol/water ratio.

A wide range of pH ($1 < pH < 8$) was investigated: pH 5.5 was chosen as the best one as it allows a good resolution of TBT and DBT, avoiding meanwhile the possible interference of phenyltin compounds.

Contrary to TBT and DBT, MBT gives a rather complex polarogram: several peaks are present whose intensities change with time as shown in Fig. 1(a). In Fig. 1(b) the intensity versus time of the two most relevant peaks is reported. As can be seen, with increasing time the intensity of the peak at less negative values decreases, whereas the peak at more negative values increases. Similar behaviour has been already observed for other mono-organotin compounds[20,23,24] and it has been explained on the basis of a slow hydrolysis process and the adsorption of the products

formed. The hydrolysis, influenced by pH and composition of the solution, leads to the formation of polycondensed species.

Under these conditions it is not possible to achieve a correct determination of MBT; furthermore, the presence of MBT, leading to peak overlapping with the DBT and TBT peaks, hinders their simultaneous voltammetric determination, unless there have been suitable separation steps. Actually, in the absence of MBT, TBT and DBT could be determined simultaneously by DPP but such determination is characterized by a poor detection limit for environmental purposes; nevertheless, it could be used advantageously both for analysis of highly polluted sediments and for a quick check of the extent of degradation of TBT standard solutions.

Complexing agents are very often applied to improve the peak resolution in voltammetric analyses. Tropolone has been largely used, in

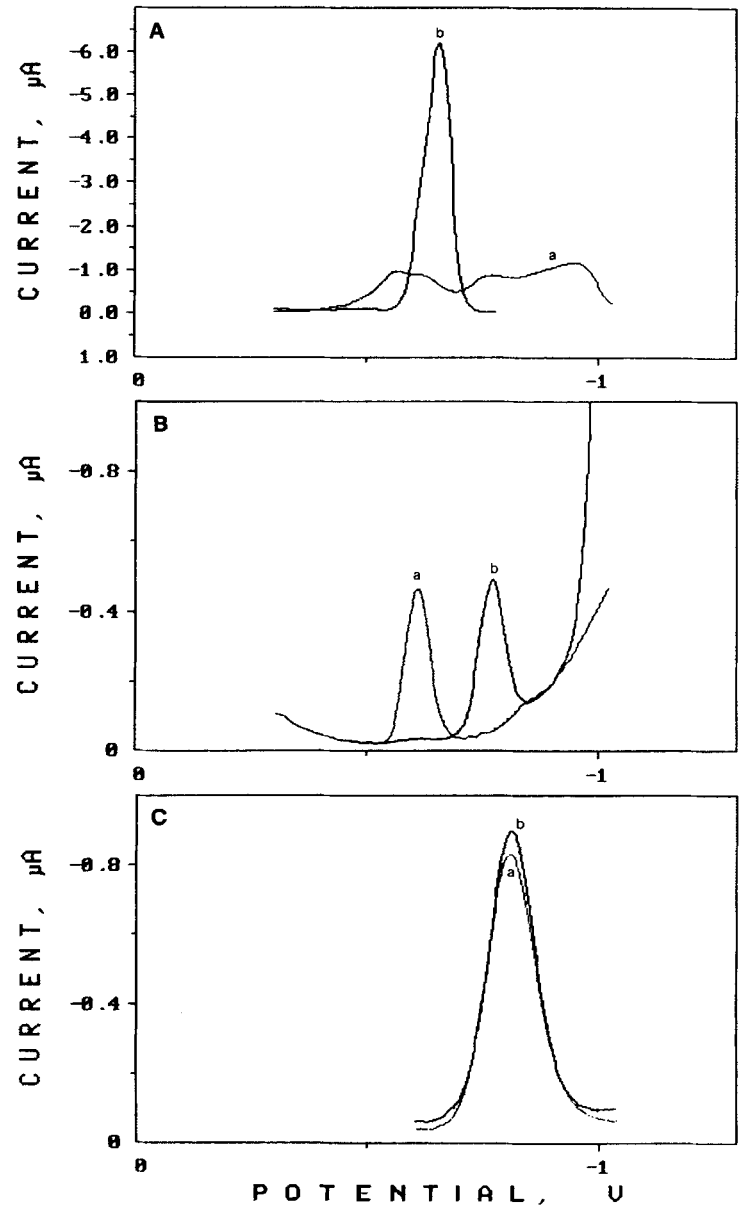

Figure 2 DP polarograms of 1.8×10^{-5} mol l^{-1} MBT (A), 4×10^{-6} mol l^{-1} DBT (B) and 3.7×10^{-5} mol l^{-1} TBT (C). Medium: (a) 0.1 mol l^{-1} NH_4NO_3 in water/methanol (1:4); (b) as (a), plus tropolone. Other experimental conditions as in the text.

combination with several organic solvents so as to improve the yield of organotin extraction. In spite of its frequent usage, very little information is available in the literature about thermodynamic and kinetic details of its complex formation with organotin compounds.

The formation of phenyltin–tropolone and methyltin–tropolone complexes was studied by Muetterties and Wright[36] and Craig and Rapsomanikis,[37] respectively. Recently, Astruc *et al.*[12] have published a spectrophotometric study of the butyltin–tropolone complexes to evaluate their physicochemical characteristics. The main conclusions of this study were: (1) monobutyltin forms a very stable complex, involving two molecules of tropolone per molecule of monobutyltin, with a conditional stability constant of $10^{10.8\pm0.3}$; (2) dibutyltin forms a stable compound, involving one molecule of tropolone per molecule of dibutyltin, with a conditional stability constant of $10^{5.2\pm0.2}$; tributyltin does not form a complex with tropolone. On this basis, it would be expected that the presence of tropolone should modify the butyltin peaks in a different way.

The addition of an excess of tropolone significantly changes the polarographic curve of MBT; in this case, $BuSnTrop_2Cl$ shows only one very intense peak at a rather low negative potential (Fig. 2a). This means that tropolone stabilizes MBT by a strong complexation preventing its hydrolysis. The formation of the MBT–tropolone complex is also coupled, as for inorganic tin, with a strong enhancement of the DPP signal of MBT.

Different results were obtained for DBT and TBT. The addition of tropolone shifts the DBT peak towards more negative values ($\Delta V = 160$ mV) but the sensitivity remains unchanged (Fig. 2b). As can be seen from Fig. 2c, the addition of tropolone does not affect either the potential value or the sensitivity of the TBT peak.

Such behaviour may be explained by the complexing properties of tropolone towards the differently substituted organotin compounds (the stability of the complexes decreases with the extent of substitution of tin, according to Astruc *et al.*[12]). However, the polarographic curve of MBT in the presence of tropolone cannot be explained by considering the complexation reaction alone, but other processes should also play an important role, for instance the strong adsorption of reduction products. With regard to detection limits, tropolone makes the DPP determination of MBT sensitive enough for environmental purposes, but more sensitive voltammetric techniques, such as anodic stripping methods, should be used for TBT and DBT.

In these cases too, the addition of tropolone improves the detectability. For instance, the anodic stripping peak of DBT ($V = -615$ mV) is usually overlapped by that of cadmium ($V = -610$ mV); the addition of tropolone at pH 3.7 (acetate buffer) shifts the DBT peak to a zone ($V = -735$ mV) where cadmium does not interfere. Furthermore, DPASV sensitivity of TBT is not high enough and it seems better to determine TBT, after separation from other tin compounds, as the more sensitive inorganic tin, after mineralization; however, the presence of lead ($V = -410$ mV) strongly interferes with inorganic tin ($V = -410$ mV). In this case also the presence of tropolone, shifting the inorganic tin

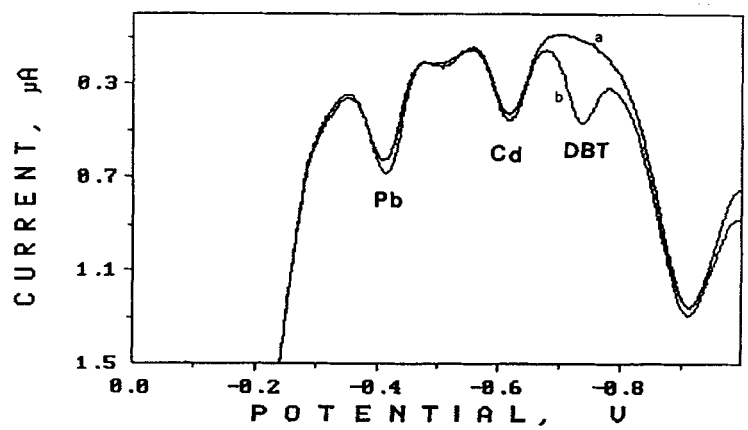

Figure 3 DPASV of sediment methanol–tropolone extract before (a) and after (b) 7.6×10^{-8} mol l^{-1} DBT. Electrolyte: 0.1 mol l^{-1} acetate buffer, pH 3.7 + tropolone. Other experimental conditions as in the text.

Table 3 Characteristic parameters for determination of different butyltins by voltammetric techniques

Analyte	Technique	E_p (mV)	Linearity range (ppb)	Sensitivity (nA ppb^{-1})	Det. limit[a] (ppb)
TBT	DPP	−820	196 ÷ 1120	0.07 ± 0.01	196
	DPASV[b]	−520	0.8 ÷ 168	95.7 ± 3.6	0.8
DBT	DPP	−615	18 ÷ 95	0.69 ± 0.09	18
	DPASV	−735	1.8 ÷ 326	45.9 ± 0.4	1.8
MBT	DPP	−660	2.8 ÷ 35	2.44 ± 0.06	2.8

[a] Determined as inorganic tin.
[b] Analysed volume 10 ml.

peak to more negative values ($V = -550$ mV), permits achievement of good resolution.

It is worth noting that cadmium and lead are usually present in environmental matrices. As an example, Fig. 3 shows the voltammetric curves of a methanol/tropolone extract of an organotin free sediment before (curve a) and after (curve b) addition of DBT. The figure suggests the possibility of determining DBT, after addition of tropolone, in samples containing cadmium and lead.

Table 3 summarizes the characterisic parameters of DPP and DPASV of the compounds considered. Regarding the detection limits achieved for the different compounds by the various techniques, it is possible to conclude that the use of tropolone permits speciation analysis of butyltin compounds. In particular, MBT can be determined by DPP, while DBT and TBT (after separation and mineralization to the more sensitive inorganic tin) can be determined by DPASV.

The use of suitable solid phases (LC18, Carbopack) makes possible the separation of TBT from other tin compounds, as described elsewhere[14] for seawater samples. In this case, 1 litre of sample can be easily extracted on graphitized carbon black (Carbopack). All the butyltin compounds are retained on this adsorbent while inorganic tin is not retained at all. TBT is eluted by 2 ml of methanol and DBT and MBT are successively eluted by 2 ml of methanol/tropolone. To the first fraction is added 1 ml of concentrated HNO_3 to convert TBT to inorganic tin; after mineralization the pH is adjusted to 5.5 with NaOH and the solution is brought to 10 ml with methanol and analysed by DPASV after tropolone addition. Under these conditions, the detection limit of TBT is 8 parts per trillion (ppt). The second fraction is brought to 10 ml, by adding 6 ml of methanol and 2 ml of water, and analysed by DPP for MBT and DPASV for DBT with a detection limit of 28 ppt and 18 ppt, respectively. The method was tested on synthetic seawater samples spiked with suitable amounts of butyltin compounds. The method has not yet been applied on natural samples.

Sediment samples may be extracted by methanol/HCl under sonication for 15 min. The extracts are placed in water and processed as above. In this case, however, substances present in sediments, e.g. chlorophyll, can strongly interfere with the voltammetric determination and further studies are taking place.

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