

EVALUATION OF MICROWAVE-ASSISTED EXTRACTION FOR ORGANOTIN DETERMINATION IN VEGETAL AND SOIL MATRICES

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ABSTRACT

A new method for the extraction of methyl-, butyl-, phenyl- and octyltin compounds from soil and vegetal samples was proposed. The extraction procedure is based on an acidic solution in methanol for both matrices using a microwave system. The optimal conditions for each matrix were determined using the experimental design methodology and the respective figures of merit were evaluated. In optimal conditions, the analytes can be detected between 0.1-2.9 ng g⁻¹ with repeatability lower than 6.5 % for both matrices. The extraction procedure was satisfactorily applied to spiked real samples, reaching recoveries ranged to 48.5-94.1% and 69-123 % for vegetal and soil samples, respectively. The proposed methodology is a promising alternative for control of organotin compounds in terrestrial ecosystems. Finally, the analytical performance of the proposed methodology was compared with published works in order to demonstrate its advantages and benefits.

Key words: Organotins; Vegetal matrices; Soil Extraction

1. INTRODUCTION

The organotin compounds (OTCs) are organometallic compounds, where one to four organic groups are covalently bound to a tin atom. The number and type of organic groups bounded to tin atom (methyl, butyl, phenyl, octyl, among others) influence their properties and toxicity, thus granting them a wide range of uses in the industry [1]. Their wide application range, such as polymer stabilizer, polymerization reaction catalyst and biocide has allowed the entry of such compounds to diverse ecosystems[2]. The most toxic trisubstituted compounds, such as tributyltin (TBT) and triphenyltin (TPhT), are commonly used as biocide, which are applied as active principle in antifouling paints, thus promoting their entry to the marine ecosystem [3-6]. In agriculture it has been used as fungicide, bactericide and herbicide, where the use of TPhT results remarkable, inducing a significant soil [7-9] and plant [10-11] contamination. The toxic effects of such compounds are extensively well-known in the marine biota, mammals and algae, where cases of imposex in gastropods, along with anomalies in the mollusk calcification process, algae growth problems and chlorophyll production alterations, among others[12-15]. The environmental problems resulting from these compounds have forced some countries to establish control programs for OTC emissions and their monitoring in different environmental matrices.

In general, the performance of several analytical methods has been evaluated for the determination of the OTC in environmental samples. Methods based on a derivatization step with sodium tetraethylborate (NaBEt₄), a pre-concentration using a liquid-liquid extraction (LLE) with isooctane, followed by gas chromatography (GC) and pulsed flame photometric detection (PFPD) have been widely studied, proving them suitable for the determination of OTC in environmental matrices [16-20]. Nevertheless, prior to the analysis, the OTCs must be extracted from the solid matrix. Thus, the assisted extraction through mechanical agitation [21-22], sonication [16-17] and microwaves [23-25] are among the main techniques assessed for this purpose, and which have been mainly used for the extraction of butyl- and phenyltin compounds from the sediment and marine biota. However, for soil and plant analysis, established analytical procedures for OTC extraction are not available and the procedures reported in literature are scarce or inexistent. For this reason, it is mandatory to evaluate some analytical alternatives to control the contamination for OTC in terrestrial environment.

In soils, ionic OTCs interact electrostatically with the negative charges of the surface of mineral particles, as clays for examples. While their interaction with the organic fraction of the soil mostly results from the complexation and adsorption in the hydrophobic medium formed with the complex organic structures from humic and fulvic acids [26,8,9]. In plants, on the other hand, OTCs are distributed within the cellular tissue through ionic and lipid interactions [27]. In order to extract the OTCs from these matrices, the cellular tissue must be hydrolysed from the plant tissue to break the interactions with the soil particles. The latter may be done using different substances, such as ethyl ethanoate and methanol, which result adequate for plants [19] and acetic acid for extraction from soils [28, 24]. It has also been reported the addition of organic ligands such as tropolone, which significantly increases

the performance of the extraction from different matrices and reducing the degradation specially for phenyltin compounds [23].

During the last years, microwave-assisted extraction has been used for different types of matrices. This technique presents several benefits, including high percentages of recoveries and short period sample treatment. This procedure allows a soft extraction of the analytes maintaining the chemical forms of the OTC [27]. Even though, cases have been reported where degradation of these compounds have been observed, mainly for the phenyltin compounds [29]. Therefore, the use of microwave-assisted extraction with closed vials is suggested, which permits digestion without losses of volatile elements, along with a quick warming of samples, above the normal boiling point of the solvents, thus achieving a higher performance during the extraction process [29]. However, the previous optimization of the most significant parameters during the extraction of the OTC is required in order to achieve quantitative extraction.

This study aims to develop an analytical method for the extraction of organotin compounds from soil and plants assisted by microwave and including methyl-, butyl- phenyl- and octyltin compounds. The experimental conditions for microwave-assisted extraction were studied and optimized using an experimental design. Finally, the optimized method was applied to spiked real samples of vegetables and soils.

2. EXPERIMENTAL

2.1 Apparatus

The extraction process of OTCs from environmental matrices was done using a microwave extraction system Milestone model Start D (Sorisole, Italy), which allows performing 12 simultaneous extractions in 100 mL PTFE vials.

For determination of organotin compounds, a Varian 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a PFPD system, Varian 1079 split/splitless injector and a capillary column CP-Sil 5 CB (30 m x 0.25 mm x 0.39 mm; Varian) with nitrogen as a carrier gas (flow-rate: 2 mL min⁻¹) was used. The oven temperature was initially held at 50 °C for 0.5 min, and then programmed at 10 °C/min to 200 °C and at 30 °C/min to the final temperature of 290 °C which was held for 4 min. A high transmission band filter (320-540 nm; BG 12, Schott, France) was selected to observe the emission from Sn-C, with a gate delay of 3.0 ms and a gate width of 2.0 ms.

A mechanical table with elliptical stirring (NB-101 M, N-Biotek Inc., Gyeonggi-Do, Korea) was used for the extraction of organotin compounds from solid samples and for the derivatization/extraction step.

Both glass and plastic materials used during this work were washed with running water, detergent and deionized water. They were subsequently treated with a HNO₃ solution at 15% v/v for at least 24 h. Then, the materials were twice washed with deionized water, dried at room temperature and stored on polyethylene bags until use.

2.2 Reagents and standards

High quality water (18 MΩ.cm) obtained from a Milli-pore system (Milipore, Bedford, MA, USA) was used to prepare the solutions. All solvents,

acids and tropolone (2-hydroxy-2,4,6-cycloheptatrienone, 98%) employed in this study were analytical grade or equivalent and were purchased from Merck S.A. (Darmstadt, Germany). The organotin standards, such as monomethyltin trichloride (MMT, 97%), dimethyltin dichloride (DMT, 97%), monobutyltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 96%), tributyltin chloride (TBT, 96%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), triphenyltin chloride (TPhT, 95%) and tripropyltin chloride (TPrT, 98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Monoctyltin trichloride (MOcT, 96%), dioctyltin dichloride (DOcT, 97%) and trioctyltin chloride (TOcT, 98%) were obtained from LGC Standards (Augsburg, Germany). Stock solutions of these reagents (1000 mg L⁻¹ of tin) were prepared in methanol and stored at -20 °C in the dark. Working standards were obtained by dilution with water, weekly for solutions of 10 mg (Sn) L⁻¹ and daily for 10-100 µg (Sn) L⁻¹.

Sodium acetate and acetic acid were obtained from J.T. Baker (Baker analyzed). Sodium chloride (Suprapur) was obtained from Merck and sodium tetraethylborate (NaBEt₄) was purchased from Sigma-Aldrich. Aqueous ethylating solution (2% m/v) was prepared just before a set of analysis and stored at 4 °C in the dark.

Finally, glassware was rinsed with deionized water, decontaminated overnight in 20% (v/v) nitric acid solution and then rinsed again with deionized water.

2.3 Samples

Vegetal (carrots and onions) and soil samples were collected in the Casablanca Valley (Central Zone, Chile). The vegetables were washed with deionized water and then were homogenized, lyophilized and stored in plastic containers until analysis. While, the soils were dried for 72 h at 60 °C, sieved to 250 µm and stored at 4 °C in dark until analysis.

2.4. Analytical performance evaluation

The figures of merit, limits of detection, limits of quantification and precision (expressed as % RSD) were evaluated according IUPAC criteria, and the results are presented in Table 1. Good linearity was obtained for all OTC in plants and soil, with determination coefficients (R²) ranging from 0.998 to 0.999. The detection limits obtained in soil and plants samples in this study are similar to those reported in previous works using different environmental matrices [20,18].

2.5 Analytical procedure

Extraction from environmental matrices was carried out through a solid-liquid extraction process assisted by the use of microwaves with closed vials. For both soil and plant samples, 0.5000 g of sample was weighted in PTFE containers, where 300 ng of tripropylchlorotin (TPrT) were added as internal standard. For soil samples, 10.0 mL of hydrobromic acid 0.25 mol L⁻¹ in methanol was added and each container was sealed under pressure. Then, the reactors were warmed during 3 min until reaching 80 °C, and during 2 min at maximum power of 600 W.

For vegetables, 10.0 mL of hydrochloric acid 0.05 mol L⁻¹ solution in methanol containing Tropolone (0.05% m/v) was added. Then, the samples were placed in the microwave system and subjected to extraction at 110 °C during approximately 12 min.

2.5.1 Derivatization

During this stage, the derivatization and pre-concentration of analytes were done simultaneously by ethylation and liquid-liquid extraction (LLE), as previously reported for other environmental samples [25, 28-30]. Therefore, 2.0 mL volume of acid extract was placed in a 50.0 mL glass reactor and mixed with 15.0 mL of acetate buffer (2.0 mol L⁻¹, pH 4.8) and 1.0 mL of isoctane were added. Then, 500 µL of a NaBEt₄, 2% m/v solution was subsequently added and each reactor was agitated at 400 rpm during 30 min. Then, the organic phase was recovered and 2.0 to 3.0 µL were injected to the GC-PFPD system for separation and quantification.

3. RESULTS AND DISCUSSION

3.1 Optimization of microwave extraction procedure

For microwave-assisted extraction, some influent factors for the extraction procedure could be temperature, extraction time, radiation power, nature of the extractant solution, and type and concentration of the complex agent, among others. In this study, the identification of influent factors on the extraction of OTC from soils and vegetables and their optimization was carried out in a sequential process using an experimental design approach. The level and

variable type were selected for each matrix according to previous studies found in the literature [19, 31-32] (Table 2). Finally, the experimental response studied for soil and plant matrices corresponds to the recovery percentages with respect to the quantities added at the beginning of the experience (spike).

3.1.1 Plant samples

The nature and levels of variables chosen for the extraction process from plants samples are presented in Table 3 and the influence of these factors were studied by using Plackett-Burman design. In a first step, only triorganotin compounds were considered in order to evaluate their potential degradation during microwave-assisted extraction. Figure 1 shows the Pareto charts obtained for the significance study. According to these results, HCl concentration presents a negative effect on the recovery percentage for all compounds and the extraction temperature produces a positive effect for TBT and negative for TPhT. In addition, the variable time was evaluated in two stages: heating time (Time 1) and temperature maintenance (Time 2).

According to the study, the first stage is not significant for the extraction process, while the second stage has a positive effect on the process. Considering these results, the time 1 was not considered for posterior studies and was fixed to '0' level (3.5 min), such as HCl concentration, which was set at 0.05 mol l⁻¹ for next experiments.

In according, with previous results, the optimization study of the extraction conditions of OTC; temperature and time 2 was carried out using a rotatable central composite design. The multivariate model obtained resulted statistical significant (p < 0.05; R² > 0.9). Therefore, the Derringer's desirability function was used, where a compromise function is constructed, determining the specific condition of the factors producing the total desirability (D), which is calculated combining the individual desirabilities (d) and applying the geometric mean (Eq.1)

$$D = (d_1 * d_2 * \dots * d_m)^{1/m} \quad \text{Eq. 1}$$

Applying this equation, the factors go from 0 to 1 establishing the highest recovery percentage for the analyte groups as the completely desirable value. Thus, the maximum convenience factor reached was 0.904.

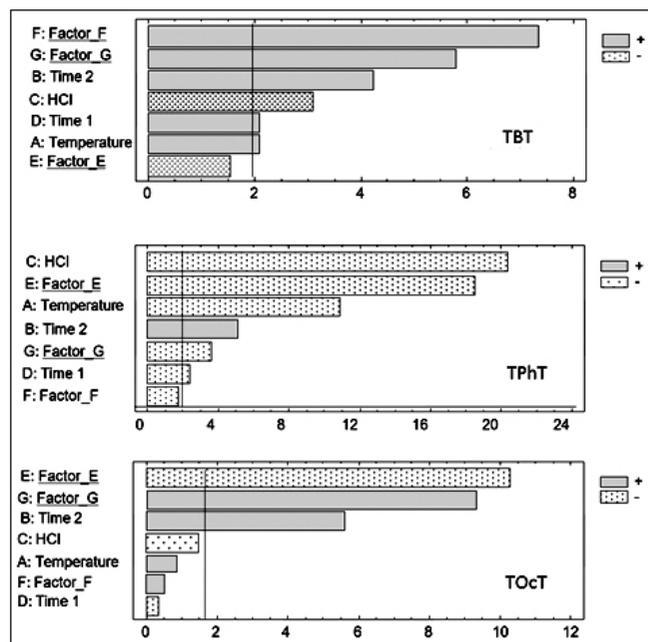


Fig.1. Pareto charts obtained for TBT, TPhT and TOcT in the significance study for plants. The variables with positive and negative effects are represented by black and grey bars, respectively.

3.1.2 Soil matrix

The nature and levels of variables chosen for the soil extraction process are presented in Table 3. Similar factors to vegetable samples were considered for soil samples, only bromhydric is different. This acid was chosen because it has been reported to achieve optimum recoveries extraction for OTC

from abiotic matrices, especially when monosubstituted is considered [33-34]. Besides, the addition of complex agents to extracting solution, such as Tropolone, has showed to improve the extraction performance [35]. In order to reduce the number of experiments to study four factors, a 2^{4-1} fractional factorial design were selected.

Figure 2 shows the Pareto charts obtained for the significance study. In according with results, HBr concentration presents a negative effect on the recoveries percentages for all trisubstituted compounds; besides, the temperature affects to the compounds TBT, TPhT and TOcT. The concentration

of the tropolona shows different responses depending on the nature of the compound, being negative for trisubstituted compounds. This effect was also observed in previous studies [24]. Considering the environmental concern for trisubstituted in environmental samples, the best extraction conditions for these compounds were considered. Then, the optimal conditions for the variables corresponds to the HBr 0,25 mol L⁻¹ in methanol, microwave-assisted extraction at 80 °C for 6 min, adding tropolona to 0.05% m/v, the minimum level.

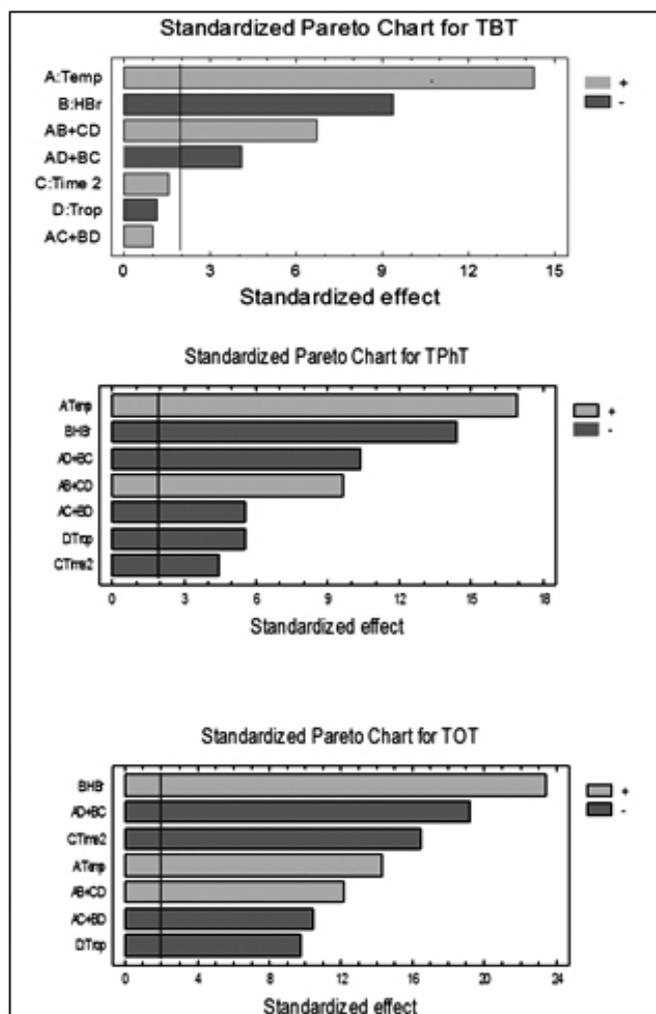


Fig.2. Pareto charts obtained for TBT, TPhT and TOcT in the significance study for soil. The variables with positive and negative effects are represented by black and grey bars, respectively.

The recovery percentages obtained for mono, di and trisubstituted compounds from these conditions are shown in Table 4. These results were satisfactory compared to that reported in the literature for similar matrices, where recoveries percentages lower than 85% have been reported [22].

3.2. Comparison of extraction procedures

The efficiency of the process in this study was compared with the main procedures found in the literature for the analysis of organotin compounds (Table 2).

This comparison showed that the optimal conditions for the OTC extraction process from plants and soil matrices are suitable. As can be observed in this study it reports a large number of extracted compound for soil and plants with high percentages of recovery (Table 4).

3.2. Application of the developed methodology

In order to evaluate the reliability of the extractions methods developed for soil and plant matrices, a recovery assays study were performed, spiked samples for each type of matrix. The analyses were done in triplicate, using the standard additions method with internal pattern (TPrT) for the quantification.

Recoveries are shown in Table 4 for soils and plants. In general, high recoveries were obtained for the extraction process reaching 48.5-94.1% for plants and 69-123% for soils.

In order to evaluate the reliability of the extractions methods developed for plants matrices, a recovery assays study were performed with spiked samples for each type of matrix. The analyses were done in triplicate, using the standard additions method with internal pattern (TPrT) for the quantification. In general, best results were obtained for extraction as in carrot root, which were on average 86.7 % for methylated, (84.5 %) butylated, (70.7 %) phenylated and (85.3 %) for phenylated compounds.

Table 1. Limits of detection (LOD), Limits of quantification (LC) and Repeatability (% RSD) of OTC (ng g⁻¹) in soil and plants.

Compounds	Soil				Plant			
	LOD ng g ⁻¹	LC ng g ⁻¹	%RSD	R ²	LOD ng g ⁻¹	LC ng g ⁻¹	%RSD	R ²
MMT	2,4	7,9	2,5	0,999	2,9	7,6	5,7	0,999
DMT	2,0	6,6	3,4	0,999	1,7	6,2	5,2	0,999
MBT	1,0	3,2	2,4	0,999	0,9	3,0	1,0	0,999
DBT	0,1	0,4	1,1	0,998	0,1	0,5	2,9	0,998
TBT	0,4	1,3	2,3	0,998	0,4	1,4	4,1	0,999
MPhT	0,3	1	2,2	0,999	0,5	1,7	2,8	0,999
DPhT	0,2	0,7	4,0	0,998	0,3	0,9	5,3	0,998
TPhT	0,3	0,9	3,6	0,998	0,2	0,6	2,9	0,999
MOcT	0,7	2,3	2,7	0,999	0,8	2,7	6,2	0,999
DOcT	0,3	0,9	3,5	0,998	0,2	0,7	4,8	0,999
TOcT	1,3	4,4	5,2	0,998	0,6	2,1	5,6	0,999

Table 2. Summary of Analytical procedures found in literature for the analysis of OTC.

Extraction method	Matrix	Compounds	Duration	Temperature	Analysis	Reference
Accelerated solvent extraction	Marine sediment	MBT DBT TBT	-	50	GC-FDP	[35]
Microwave assisted extraction	Plants	TBT TPhT	1h	-	GC- FDP	[19]
Microwave assisted extraction	Marine sediment	TBT DBT MBT	4 minutes	100	GC -MS	[36]
Microwave assisted extraction	Soil	TBT TPhT	32 days	20	GC- FDP	[31]
	Plant leaves	MPhT DPhT TPhT			GC- FDP	[32]
Microwave assisted extraction	Marine sediment	MBT DBT TBT DPhT TPhT	10 minutes	120	GC- ICP-MS	[33]
Microwave assisted extraction	Soil Plants	MMT DMT MBT DBT TBT MPhT DPhT TPhT MOcT DOcT TOcT	Soil (6 minutes) Plants (11 minutes)	110 80	GC- FPD	Present study plants

4. CONCLUSIONS

A new extraction method for methyl-, buthyl, phenyl- and octyltin compounds from soil and plant samples has been successfully developed using a microwave oven with closed-vessels. This method allows quantitative extractions of methylated, buthylated, phenylated and octylated tin compounds from soils and plants.

The application of the experiment designs allowed reliably and precisely to establish the best conditions for the extraction process, where the most significant factors were the nature of the extractant solution and temperatures of the microwave-assisted extraction system. The reagents efficiency showed

that HCl in methanol and Tropolone were particularly suitable for extraction of OTC from vegetal matrices and HBr and Tropolone for extraction of OTC in soils.

The results show that the method developed is reliable in the analysis of different organotin compounds from complex matrices such as soils, with applicability to different complex environmental matrices such as sediment or vegetal biota, after evaluation of the associated figures of merit.

Finally, the recovery study conducted in real samples demonstrated the performance of developed method reaching recoveries around 95 %. In this way, this method appears as a promising analytical tool to control the environmental levels of organotin compounds in terrestrial ecosystems.

Table 3. Studied variables and levels selected for the significance study in plant and soil matrices

Plant		Level		
Variable		-1	0	1
Temperature (°C)		60	90	120
HCl (M)		0	0.05	0.1
Maintenance Period, Temp. (min)		2	4	6
Maintenance Period, Temp. (min)		2	3.5	5
Soil		Level		
Variable		-1	0	1
Temperature (°C)		60	80	100
HBr (M)		0	0.25	0.5
Hold time (min)		2	6	10
Tropolone (%w/v)		0	0.05	0.1

Table 4. Percent of recovery of OTC obtained using the methodology developed in plants and soil.

Compounds	Carrot samples		Onion samples		Soil
	root	stem and leaf	bulb	stem and leaf	
DMT	86.3 ± 2.0	82.1 ± 9.2	65.2 ± 1.6	82.4 ± 5.9	75±11
MMT	86.5 ± 5.6	74.2 ± 8.2	78.5 ± 8.2	85.8 ± 4.5	100±12
MBT	82.9 ± 10.1	74.8 ± 3.3	82.9 ± 4.8	62.4 ± 5.1	113±8
DBT	95.3 ± 2.2	54.6 ± 3.9	83.3 ± 7.4	75.3 ± 5.0	86±7
MPhT	76.3 ± 0.7	48.5 ± 2.3	74.3 ± 4.7	57.5 ± 6.3	72±9
TBT	75.1 ± 5.5	94.1 ± 2.3	94.1 ± 4.1	75.2 ± 4.5	111±15
MocT	88.1 ± 3.1	45.6 ± 5.1	84.6 ± 4.6	73.4 ± 1.4	89±7
DPhT	45.9 ± 4.9	76.3 ± 3.6	63.8 ± 6.0	75.1 ± 8.1	69±8
DocT	83.5 ± 2.6	79.7 ± 6.3	83.7 ± 3.9	75.4 ± 6.2	123±6
TPhT	89.9 ± 5.2	79.2 ± 7.4	70.8 ± 3.9	61.5 ± 6.5	83±8
TOcT	84.3 ± 5.7	77.1 ± 1.2	84.3 ± 4.2	42.9 ± 5.0	114±11

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