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Comparison of two derivatization reagents for the simultaneous determination of organolead and organomanganese compounds using solid-phase microextraction followed by gas chromatography with atomic emission detection

Rosa Peñalver, Natalia Campillo, Manuel Hernández-Córdoba*

Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, E-30071 Murcia, Spain

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ABSTRACT

Two procedures for the simultaneous determination of organolead (tetraethyllead, triethyllead and trimethyllead) and organomanganese compounds (cyclopentadienyl manganese tricarbonyl (CMT) and methylcyclopentadienyl manganese tricarbonyl (MMT)) are studied. Both procedures involve sample preconcentration by solid-phase microextraction and capillary gas chromatography coupled to atomic emission detection, the main difference being the derivatizing agent used for the ionic alkylated lead species: sodium tetrapropylborate ($NaBPr_4$) and sodium tetraphenylborate ($NaBPh_4$). The parameters affecting the derivatization and preconcentration steps, chromatographic separation as well as detection of the compounds were optimized. Higher sensitivity was attained for all compounds with the method involving propylation derivatization. In this case, detection limits ranged between 0.04 and 0.1 ng L^{-1}, depending on the compound. Detection limits of between 0.1 and 24.5 ng L^{-1} were obtained, when using phenylation derivatization. A low CMT concentration was found in one of the seawater samples analyzed.

1. Introduction

The use of alkyllead compounds, introduced as anti-knocking agents in petrol almost 90 years ago, has been restricted or even banned in many countries. However, fuel is entitled as unleaded when its lead content is lower than 26 mg L^{-1} [1], which means that organolead compounds are still released to the atmosphere, even without taking into account that leaded gasolines are still used in some parts of the world [2]. Alkyllead compounds appear in the environment not only as a result of human activity but also naturally via the so-called biomethylation processes [3]. The toxicity of these species has been widely demonstrated, tetraalkyllead compounds being more toxic to animals, and ionic alkyllead compounds more toxic to plants [4], with both showing higher toxicity than inorganic lead, mainly due to their liposolubility.

Methylcyclopentadienyl manganese tricarbonyl (MMT) was first used in 1976 in Canada as an alternative to triethyllead (TEtL) in petrol. Both MMT and cyclopentadienyl manganese tricarbonyl (CMT) are present in many petrols, raising their octane rating. The combustion of these species results in various carbon and manganese compounds, although the airborne concentrations of manganese as a result of car emissions represent no health hazard [5]. Nevertheless, if MMT and CMT are released to the environment, their high stability in the absence of light supposes a real problem due to their toxicity to humans [6,7]. Consequently, the determination of organolead and organomanganese compounds constitutes an important feature of environmental monitoring.

Gas chromatography (GC) separation coupled to a variety of detectors is the most commonly used strategy for determining organolead and organomanganese compounds. Whereas a wide number of references can be found dealing with the analysis of organolead compounds using GC with atomic emission detection (AED) [8–20], atomic absorption spectrometry (AAS) [21,22], mass spectrometry (MS) [23–26], inductively coupled plasma mass spectrometry (ICP-MS) [2,20,27–35] or flame photometric detection (FPD) [36], the references dealing with MMT and/or CMT analysis are scarce [37]. In this case, a number of detectors have been coupled to GC, mainly AED [38–42], AAS [43], FPD [44], among others [6,45,46].

Two of the organolead compounds determined in the present work, trimethyllead (TMeL) and TEtL, require previous transformation into species suitable for GC. A variety of commercially available Grignard reagents [9,24,29] have been recommended for the purpose, in spite of requiring the use of water-free organic solvents. Although hydride generation allows the reaction to be carried out in aqueous phase, the derivatives formed with organolead

* Corresponding author. Tel.: +34 868 887406; fax: +34 868 884148.
E-mail address: hcordoba@um.es (M. Hernández-Córdoba).

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compounds show low stability [13]. In situ ethylation with sodium tetraethylborate is probably the most widely used because of the stability of the resulting products and the ease with which the reaction is performed [10,11,16,21,23,25,27,34,47]. Nevertheless, this reagent is not suitable for the speciation of ethylated compounds, or for distinguishing them from inorganic lead. However, such discriminations can be attained with $NaBPr_4$ [15,19,20,22,26,31,33,48] and tetrabutylammonium tetrabutylborate [13].

In any case and due to the low concentrations to be expected, the determination of organolead and organomanganese compounds in waters requires the inclusion of a preconcentration step. The inherent characteristics of solid-phase microextraction (SPME) make it an interesting way for this purpose when dealing with species derivatized in aqueous medium [49]. To the best of our knowledge, the conjunction of SPME with GC–AED has not been applied for the simultaneous analysis of organolead (TeEtL, TEtL and TMeL) and organomanganese compounds (CMT and MMT) in waters and soils, and the procedures reported here could be of interest to those involved in environmental analysis.

2. Experimental

2.1. Chemicals

Cyclopentadienyl manganese tricarbonyl (97% purity) and (methylcyclopentadienyl) manganese tricarbonyl (97% purity) were obtained from Aldrich (Milwaukee, WI, USA). Individual stock solutions of the solid compounds were prepared using pure methanol as a solvent (1000 $\mu g\,mL^{-1}$). Trimethyllead chloride (98% purity) and triethyllead chloride (98% purity) were obtained from ABCR GmbH (Im Schlehert, Karlsruhe), and 1000 $\mu g\,mL^{-1}$ standard solutions were prepared in Milli-Q water. Tetraethyllead solution (TeEtL, 50% (w/v) in xylene) was provided by Aldrich (Milwaukee, WI, USA), intermediate standard solutions being prepared in methanol. Concentrated standard solutions were stored and manipulated separately in order to prevent possible transalkylation reactions. Working standard solutions were prepared daily in Milli-Q water. All solutions were stored at 4 °C in the dark. Sodium chloride, sodium acetate and sodium phosphate were purchased from Sigma (St. Louis, MO, USA). Acetic acid (99.8% (v/v), Fluka, Buchs, Switzerland) and phosphoric acid (85% (v/v), Panreac, Barcelona, Spain) were used to prepare buffer solutions.

The derivatizing agents were prepared as follows: 5.0% (w/v) aqueous solutions of sodium tetrapropylborate ($NaBPr_4$, ≥95%, GALAB, Geesthacht, Germany) or sodium tetraphenylborate ($NaBPh_4$, 98% purity, Strem Chemicals, Newburyport, MA, USA) were prepared daily in ethanol and water, respectively. Fractions of these solutions were stored in the dark at −20 °C, at which they remained stable for one month.

The plasma gas and carrier gas used for GC was helium, while the reagent gases for the AED were oxygen and hydrogen. Nitrogen was used for purging the AED system. All the gases (99.999% purity) were supplied by Air Liquide (Madrid, Spain).

2.2. Instrumentation

The SPME device for manual sampling consisted of a holder assembly and several replaceable fibers, all obtained from Supelco (Bellefonte, PA, USA). SPME fibers coated with non-bonded polydimethylsiloxane (PDMS) of 100 μm thickness, bonded polydimethylsiloxane/divinylbenzene (PDMS/DVB) of 65 μm and bonded Carboxen/polydimethylsiloxane (CAR/PDMS) of 75 μm were used. The fibers were conditioned prior to use by heating in the injection port of the chromatographic system under the conditions recommended by the manufacturer for each fiber coating.

Table 1
Experimental conditions of the SPME system with both derivatizing agents assayed.

	$NaBPr_4$	$NaBPh_4$
Fiber material	PDMS 100 μm	PDMS 100 μm
Extraction time and temperature	30 min at 80 °C	15 min at 25 °C
Extraction mode	Headspace	Headspace
Desorption time and temperature	3 min at 280 °C (splitless)	3 min at 280 °C (splitless)
Extraction solution	10 mL buffered at pH 4	10 mL buffered at pH 7
Derivatizing agent concentration	0.05% (w/v)	0.05% (w/v)
Reaction time	5 min	5 min

Whenever needed, the conditioning step was repeated for fiber cleanup. All analyses were performed in 15 mL amber glass sealed vials. An RH-KT/C magnetic stirrer (IKA, Staufen, Germany) and a home-made heating system consisting of a drilled block provided with an electronic temperature control system were used for stirring and heating, respectively, during the extraction step. PTFE-coated magnetic stir bars (10 mm × 6 mm O.D.) were used for stirring the samples.

An Agilent 6890 gas chromatograph was directly coupled by a transfer line to a G2350A microwave-induced plasma atomic emission detector (Agilent, Waldbronn, Germany). Specific software provided by the dealer was used to control and automate many features of the GC and AED systems, and for data acquisition and treatment. The chromatograph was fitted with a 25 m × 0.32 mm HP-1, 100% dimethylpolysiloxane non-polar capillary column (Agilent) with a 0.17 μm film thickness. Table 1 summarizes the experimental conditions used for derivatization with $NaBPr_4$ and $NaBPh_4$ as well as the SPME preconcentration parameters. A SPME liner (Supelco) of 0.75 mm I.D. and a general-purpose septum (Agilent) of 11 mm were used. The GC program began at 60 °C, which was maintained for 1 min, increasing to 150 °C at a rate of 20 °C min^{-1}, where it was held for 0.5 min. Helium was used as the carrier gas and as AED make-up gas at 4 and 300 mL min^{-1}, respectively. Oxygen and hydrogen were used as the scavenger gases at 25 and 30 psi, respectively. The transfer line and the cavity temperatures were set at the same value as recommended by the manufacturer, 325 °C. Filter and backamount (baseline correction parameter) adjustment in the AED system were set according to Agilent default specifications. The spectrometer was purged with a nitrogen gas flow rate of 2.5 L min^{-1}. Lead and manganese compounds were monitored at 261.4 and 259.0 nm emission lines, respectively, and quantified in both cases using peak area as the analytical parameter. Taking into account the time of 30 min adopted for the SPME adsorption step by using sodium tetrapropylborate and since the more retained analyte (TEtL) eluted with a retention time of 5 min, the analysis of each sample lasted about 35 min. In the case of sodium tetraphenylborate, the analysis lasted about 20 min.

2.3. Samples and analytical procedures

Five seawater samples were obtained from several harbours and beaches of southeast Spain. Four river water samples and two water samples collected from a gully were also analyzed. Five different soil samples were obtained from several locations in Murcia (Spain), all collected from sites near service stations. All the samples were collected in amber recipients and stored at 4 °C in the dark until analysis, which was normally performed within 24 h of arrival at the laboratory.

To carry out the extraction when using the tetrapropylborate reagent, 10 mL of water sample (or 0.25 g of soil) was placed in a 15 mL SPME glass vial. For water samples 0.5 mL of 2 mol L^{-1}

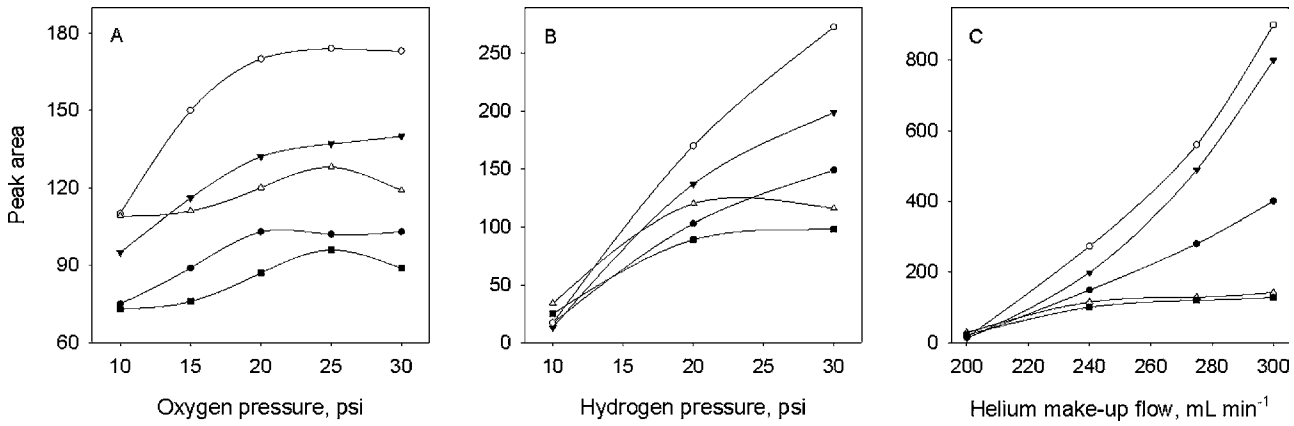

Fig. 1. Effect of: (A) oxygen pressure, (B) hydrogen pressure and (C) helium make-up flow rate on peak area of TeEtL (●), TMeL (○), TEtL (▼), CMT (△) and MMT (■).

acetate/acetic buffer solution (10 mL of 0.1 mol L^{-1} acetate/acetic buffer solution for soil samples) was added to adjust the pH to 4. Then, 100 μL of 5% (w/v) $NaBPr_4$ solution was added. After introducing the magnetic bar, the vial was immediately sealed with the cap and placed in the home-made heating module previously programmed to 80 °C, maintaining the stirring speed at 1300 rpm for 5 min. Then a PDMS 100 μm fiber was exposed to the headspace over the aqueous mixture for 30 min, with the temperature at 80 °C.

A recovery study was carried out by fortifying three water samples (two seawaters and one gully water) and two soils at three different concentrations. Fortification levels for waters ranged between 0.5 and 15 ng L^{-1} and for soils from 0.15 to 1 ng g^{-1}, depending on the compound. The spiked samples were set aside for 30 min at room temperature before being submitted to the above-described propylation procedure in duplicate.

When $NaBPh_4$ was used, 10 mL of water sample was placed in a 15 mL SPME glass vial and 0.5 mL of 2 mol L^{-1} phosphate buffer solution was added to adjust pH to 7. Then, 100 μL of 5% (w/v) derivatizing solution was added to the samples solutions and the vials were sealed immediately after introducing the magnetic stir bar. The vials were then placed in the home-made heating module previously programmed to ambient temperature, maintaining the stirring speed at 1300 rpm for 5 min. Then the 100 μm PDMS fiber was exposed to the headspace vial for 15 min at ambient temperature.

The retained compounds were desorbed in both cases by heating the 100 μm PDMS fiber at 280 °C for 3 min in the GC injection port.

3. Results and discussion

3.1. Optimization of the chromatographic separation and the detector conditions

Preliminary experiments were carried out using $NaBPr_4$ as derivatizing reagent, which was added at a concentration of 0.1% (w/v) to 10 mL of an aqueous solution containing the analytes at concentration levels ranging from 0.05 to 3 μg mL^{-1}, depending on the compound, in order to optimize the chromatographic separation and detection conditions. The derivatized TMeL and TEtL, as well as the rest of the compounds, were then extracted into 1 mL of hexane, 0.2 μL of the organic phase being injected in the GC in the splitless mode, with the solvent venting step switched on for 1.5 min immediately after injection into the GC.

The selected program temperature as well as the flow rate of the mobile phase allowed elution of the organolead compounds, which showed retention times of 2.1, 3.7 and 5.0 min in the case of TMeL, TeEtL and TEtL, respectively, while CMT and MMT eluted at 4.2 and 4.7 min, respectively. Separation was carried out using a constant helium flow rate of 4 mL min^{-1}, which reduced the analysis time necessary, with no peaks overlapping.

Because emission lines selected for monitoring lead and manganese compounds did not differ by more than 20 nm and both required the same scavenger gases, all the studied analytes could be simultaneously detected in one sample injection step. The detector parameters investigated were reagent gas pressure and make-up gas flow rate. The pressures used for the two required scavenger gases were optimized independently. No significant differences were observed in terms of sensitivity for lead compounds between 20 and 30 psi of oxygen, whereas manganese compounds showed a slight increase in sensitivity at 25 psi (Fig. 1A), so that 25 psi was adopted. The influence of hydrogen pressure was studied between 10 and 30 psi. Since the signals for lead compounds increased over the whole range studied, while the peak area for manganese hardly varied at hydrogen pressures above 20 psi (Fig. 1B), 30 psi was selected. The total make-up flow was varied between 200 and 300 mL min^{-1}, and measured with the window purge gas flow open. Higher flow-rate values were not assayed because the plasma lost its stability, resulting in poor repeatability. As shown in Fig. 1C, the make-up flow rate strongly affected the sensitivity for all the studied analytes. Sensitivity of the manganese compounds increased up to 240 mL min^{-1} and then remained practically constant, whereas the sensitivity of the lead compounds increased up over the whole of the studied range. Therefore, 300 mL min^{-1} was the value adopted.

As regards chromatographic separation using tetraphenylborate as derivatizing reagent, preliminary experiments were carried out under conditions identical to those used for $NaBPr_4$ and extracting the derivatized compounds in hexane. The previously optimized furnace program for the method involving propylation now allowed elution of the analytes at 3.7, 4.8 and 6.9 min for TeEtL, TMeL and TEtL, respectively, while CMT and MMT, as expected, eluted at 4.2 and 4.7 min, respectively. Therefore, the same oven program and carrier gas flow rate were used. The selected conditions for the AED using $NaBPr_4$ were also seen to apply to $NaBPh_4$.

3.2. Optimization of the procedure for propylation derivatization

To optimize the SPME stage, 10 mL of an aqueous solution containing the analytes at concentration levels ranging between 10 and 50 ng L^{-1}, depending on the compound, was used in the presence of a 0.1% (w/v) of the derivatization reagent. The reaction was allowed to proceed for 5 min and then the analytes were preconcentrated for 10 min at ambient temperature.

The 100 μm PDMS fiber in the headspace mode was selected, providing the highest sensitivity for the organolead compounds.

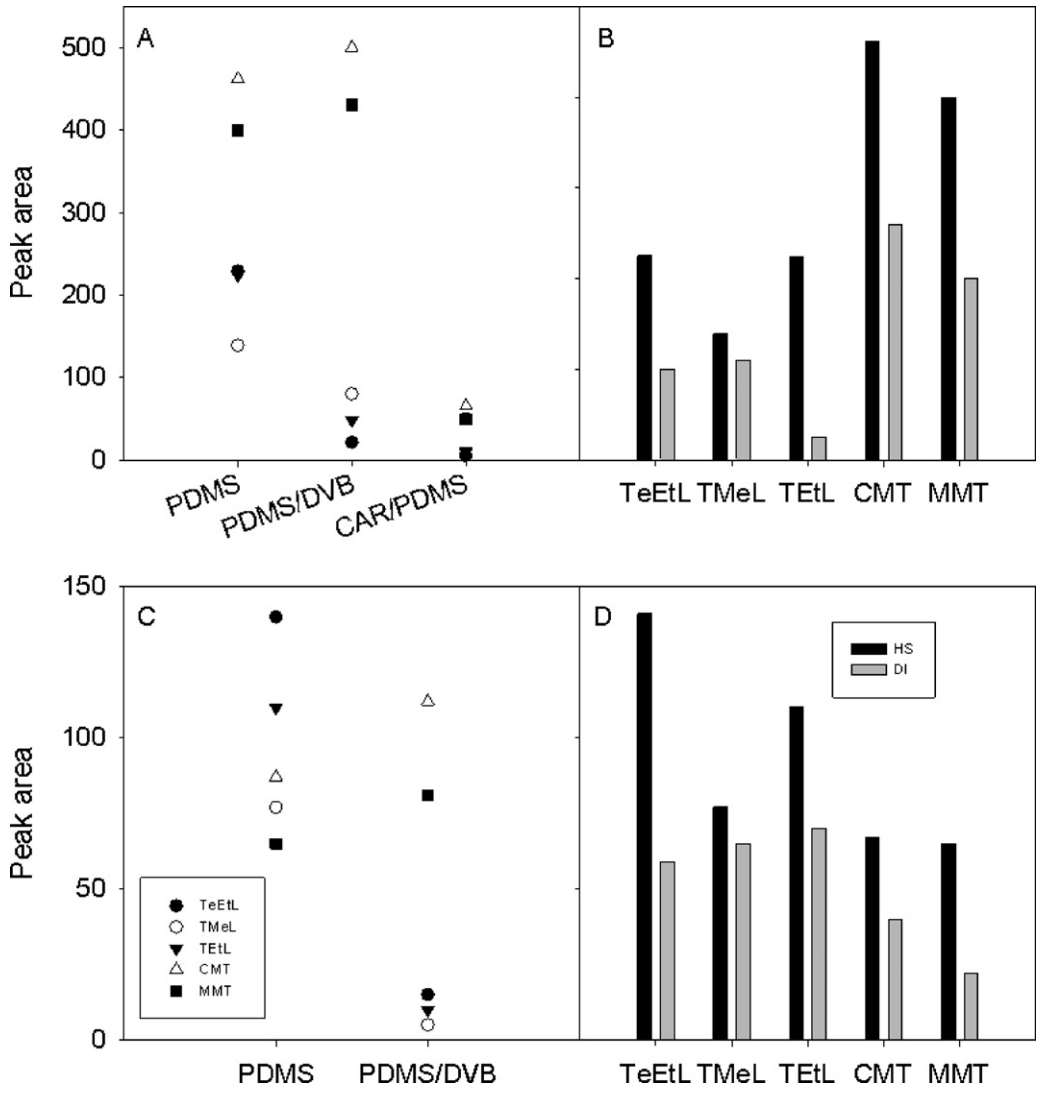

Fig. 2. Influence of the type of fiber coating and extraction mode on the extraction efficiency of the analytes when using (A and B) $NaBPr_4$ and (C and D) $NaBPh_4$ as derivatizing agents.

No great differences between the selected stationary phase and PDMS/DVB were attained for manganese compounds (Fig. 2A and B).

The pH of the extraction medium was studied by adding acetate or phosphate buffer solutions. In all cases, 200 μL of the 5% (w/v) derivatization agent solution was added and the reaction allowed to proceed for 5 min. As previously demonstrated [15], the derivatization efficiency was dependent on the pH. Fig. 3A shows that maximum sensitivity was obtained at pH 4 for the organolead compounds, while this parameter had practically no effect in the case of CMT and MMT.

The influence of the ionic strength was studied by adding different masses of sodium chloride ranging from 0 to 10% (w/v) to 10 mL of an aqueous solution, containing the analytes, and buffered to pH 4. The presence of salt decreased the SPME extraction efficiency in the case of TeEtL, TMeL and TEtL. Consequently, the addition of salt was discarded.

The amount of sodium tetrapropylborate necessary to carry out the derivatization step was studied by adding different volumes ranging from 50 μL to 200 μL of a 5% (w/v) solution of the reagent, to 10 mL of the sample previously buffered at pH 4, roughly corresponding to concentrations of 0.025 and 0.1% (w/v), respectively (Fig. 3B). As expected, the reagent concentration did not affect the sensitivity of CMT, MMT or TeEtL, while the highest signals were obtained for TMeL and TEtL, with 0.05% (w/v) being this concentration selected.

The effect of extraction temperature was evaluated by applying temperatures ranging from 25 to 98 °C with an adsorption time of 10 min. In the case of lead compounds, the extraction efficiency was significantly enhanced as the temperature increased up to 80 °C, above which it decreased. In the case of CMT, the highest sensitivity was attained at 60 °C, whereas no significant differences were observed between 60 and 80 °C for MMT (Fig. 4A). Therefore 80 °C was selected.

The influence of the extraction time was studied between 5 and 60 min. As can be observed in Fig. 4B, equilibrium between the gaseous phase and the fiber coating was reached at 30 min for most compounds, and so 30 min was selected for the extraction step. The stirring speed was varied between 0 and 2000 rpm, the highest signals for all compounds being obtained at 1300 rpm, which was the value selected.

The sample volume was studied between 3 and 10 mL for a standard mixture solution buffered at pH 4 contained in 15 mL SPME-vials and spiked with the analytes at concentrations between 5 and 10 ng L^{-1}, depending on the compound. A 10-mL volume was finally selected.

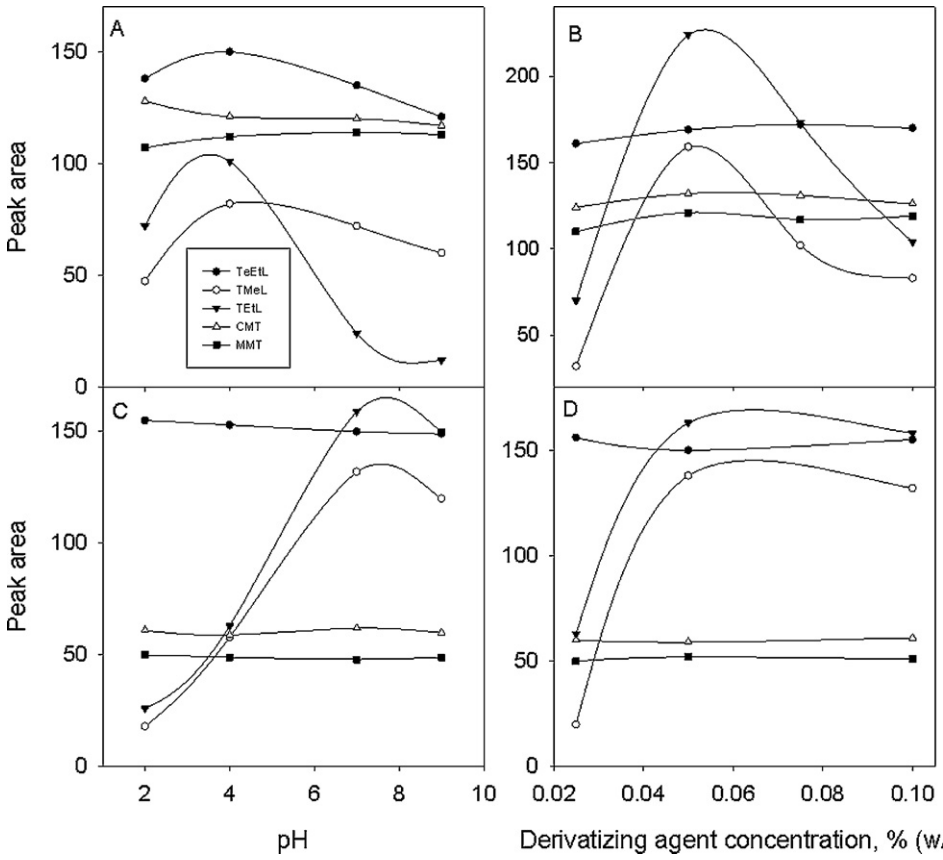

Fig. 3. Influence of the pH (A and C) and concentration of the derivatization agent (B and D) on the peak area, when using $NaBPr_4$ (A and B) and $NaBPh_4$ (C and D).

When the desorption temperature was investigated between 200 and 280 °C (the maximum temperature recommended by the manufacturer for 100 μm PDMS fibers), sensitivity increased with temperature for most compounds. Therefore, 280 °C was selected. As regards the desorption time, 3 min was found to be sufficient to desorb the trapped analytes. An injector temperature of 280 °C and 3 min desorption time assured complete desorption of all the investigated compounds from the fiber and hence optimum sensitivity as well as the absence of blanks originating from sample carry-over.

3.3. Optimization of the procedure for phenylation derivatization reaction

Preliminary experiments were carried out by submitting to SPME preconcentration, 10 mL of an aqueous solution containing the analytes at concentrations ranging between 0.01 and 5 ng mL^{-1}, depending on the compound, in the presence of a 0.05% (w/v) of sodium tetraphenylborate. The reaction was allowed to proceed for 5 min and then the analytes were preconcentrated for 10 min at ambient temperature.

The 100 μm PDMS fiber was again used in the headspace mode (Fig. 2C and D).

The pH of the extraction medium was studied between 2 and 9. In all cases 100 μL of tetraphenylborate solution at 5.0% (w/v) was added to 10 mL of buffer, the final concentration of the derivatizing agent being 0.05% (w/v). The reactions were allowed to proceed for 5 min. A pH of 7 was selected because the phenyl derivatives of TMeL and TEtL showed their maximum extraction efficiencies at this value, while no significant differences in sensitivity were observed for the rest of the compounds with pH (Fig. 3C).

The influence of changing the ionic strength of the extraction solution was studied by adding sodium chloride between 0 and 10% (w/v) to 10 mL of buffer solution, pH 7. Sodium chloride decreased the sensitivity of the organolead compounds, so its use was discarded.

The amount of sodium tetraphenylborate was studied by adding different volumes ranging between 50 μL and 200 μL of a 5% (w/v) solution of the reagent to 10 mL of aqueous standard mixture. As shown in Fig. 3D, sensitivity increased up to 0.05% (w/v) for TMeL and TEtL and then remained constant, while the presence of this reagent did not affect the sensitivity of the rest of the compounds. Consequently a $NaBPh_4$ concentration of 0.05% (w/v) was adopted.

The effect of the sample temperature during the adsorption step was tested in the 25–98 °C range. Fig. 4C shows the influence of this variable on the peak area when the fiber was maintained in the headspace vial for 10 min. Even though sensitivity increased with temperature for the manganese compounds up to 60 °C, a substantial decrease in sensitivity was observed for the lead compounds in the studied range. Therefore, room temperature was adopted for further experiments.

The adsorption time was studied by increasing the time of the PDMS fiber exposure from 5 to 60 min, maintaining the vial at 25 °C. The compounds that did not undergo derivatization reached the equilibrium partition at 15 min (TeEL and CMT) or 30 min (MMT); nevertheless, peak area increased up to 15 min for TMeL and TEtL, but strongly decreased at longer times (Fig. 4D). Consequently, 15 min was adopted as the adsorption time. The decomposition of the phenylated derivatives might explain this decrease in sensitivity. Nevertheless, controlling the adsorption time, the RSD values obtained when using this derivatization reagent are similar to those obtained with propylation.

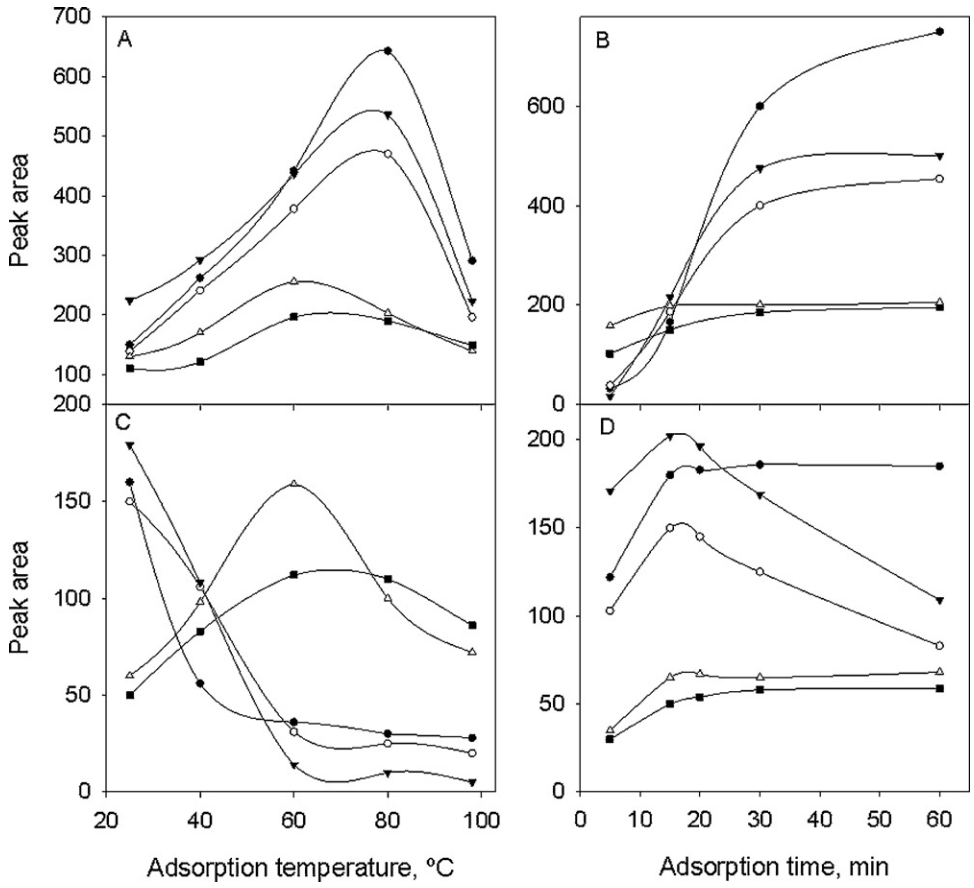

Fig. 4. Effect of temperature (A and C) and time (B and D) of the adsorption stage on the peak area when using $NaBPr_4$ (A and B) and $NaBPh_4$ (C and D). Symbols correspond to: TeEtL (●), TMeL (○), TEtL (▼), CMT (△) and MMT (■).

Different volumes ranging between 5 and 10 mL of a standard mixture solution buffered at pH 7 contained in 15 mL SPME-vials and spiked with the analytes at concentrations between 0.01 and 0.25 ng mL^{-1}, depending on the compound, were submitted to derivatization and SPME preconcentration. A 10-mL volume was selected because it provided the highest sensitivity for most compounds. As regards desorption parameters, the best results were obtained in conditions similar to those adopted for the propylation method, 280 °C for 3 min.

3.4. Analytical characteristics and validation of the methods

For calibration, aqueous standard solutions of 10 mL were buffered to pH 4 and 7 by adding acetate or phosphate buffer solutions, respectively, and then submitted to the corresponding optimized derivatization procedure with $NaBPr_4$ or $NaBPh_4$, respectively, as well as to the SPME preconcentration step. Six concentration levels were assayed in duplicate, using peak areas for calibration purposes. Table 2 shows the characteristics of the calibration graphs obtained for each compound for the two studied procedures. Correlation coefficients higher than 0.998 were obtained in all cases. The detection limits were calculated using a signal-to-noise ratio of 3 (Table 2). The quantification limits, calculated using a signal-to-noise ratio of 10, ranged between 0.13 and 0.33 ng L^{-1} for CMT and TMeL, respectively, when derivatizing with $NaBPr_4$ and between 0.33 and 82 ng L^{-1} for CMT and TMeL, respectively, when using $NaBPh_4$. The repeatability was calculated using the relative standard deviation for 10 successive injections of an aqueous standard solution containing the analytes in the concentration ranges 2–5 ng L^{-1} and 5 ng L^{-1}–1 ng mL^{-1} depending on the compound, for $NaBPr_4$ and $NaBPh_4$, respectively. The RSD values are shown in Table 2.

Table 2
Analytical characteristics of the studied methods.

Compound	$NaBPr_4$				$NaBPh_4$			
	Slope ± SD[a] (L ng^{-1})	Detection limit[b] (ng L^{-1})	Linearity range (ng L^{-1})	RSD[c] (%)	Slope ± SD[a] (L ng^{-1})	Detection limit[b] (ng L^{-1})	Linearity range (ng L^{-1})	RSD[c] (%)
TMeL	14.02 ± 0.45	0.10	0.5–50	8.5	0.053 ± 0.001	24.5	100–10,000	7.3
TeEtL	17.02 ± 0.32	0.09	0.5–50	5.2	0.640 ± 0.002	2.00	10–1000	5.0
TEtL	19.95 ± 0.39	0.08	0.5–50	7.9	0.098 ± 0.004	11.2	50–10,000	5.5
CMT	28.46 ± 0.31	0.04	0.2–10	7.2	11.06 ± 0.15	0.10	0.5–20	5.0
MMT	26.20 ± 0.36	0.05	0.2–10	6.6	7.25 ± 0.10	0.15	0.5–20	6.1

[a] Mean value ± standard deviation (n = 6).
[b] Corresponding to S/N = 3.
[c] Calculated for concentrations about 15 times the corresponding quantification limits.

Table 3
Slopes[a] ($L\,ng^{-1}$) of the standard additions calibration graphs for three different seawaters.

Compound	$NaBPr_4$			$NaBPh_4$		
	Seawater 1	Seawater 2	Seawater 3	Seawater 1	Seawater 2	Seawater 3
TMeL	7.53 ± 0.10	7.42 ± 0.19	7.61 ± 0.24	0.028 ± 0.002	0.026 ± 0.002	0.027 ± 0.002
TeEtL	9.72 ± 0.15	9.68 ± 0.12	9.58 ± 0.16	0.566 ± 0.003	0.562 ± 0.003	0.565 ± 0.003
TEtL	12.21 ± 0.22	12.52 ± 0.18	12.68 ± 0.15	0.065 ± 0.003	0.063 ± 0.003	0.062 ± 0.004
MMT	23.16 ± 2.44	22.98 ± 2.91	22.63 ± 1.98	11.12 ± 0.13	10.99 ± 0.17	11.53 ± 0.10
CMT	25.95 ± 3.15	26.37 ± 2.58	24.63 ± 2.90	7.30 ± 0.10	7.22 ± 0.08	7.20 ± 0.11

[a] Mean value ± standard deviation ($n = 6$).

Table 4
Analytical characteristics of the propylation-based procedure for soils.

Compound	Slope ± SD ($L\,ng^{-1}$)	Detection limit[a] ($pg\,g^{-1}$)	Quantification limit[b] ($pg\,g^{-1}$)	Linearity range ($pg\,g^{-1}$)	RSD (%)
TMeL	5.57 ± 0.42	10.8	36.0	30–300	9.4
TeEtL	7.12 ± 0.25	6.68	22.24	30–300	9.1
TEtL	10.98 ± 0.20	5.83	19.4	25–250	5.3
MMT	21.96 ± 3.1	2.54	8.46	10–100	7.0
CMT	25.92 ± 3.6	2.12	7.06	10–100	4.5

[a] Corresponding to S/N = 3.
[b] Corresponding to S/N = 10.

3.4.1. Water samples

When the slopes of the aqueous calibration graphs were compared with those obtained when the standard addition method was applied to five different water samples (three seawaters and two river waters), significant differences were found for the lead compounds in seawaters (Table 3). The presence of a matrix effect was corroborated by applying a paired *t*-test (95% confidence level). The matrix effect was not eliminated when seawaters were diluted in the proportion 1:1 and submitted to the above optimized procedures. Nevertheless, *p* values higher than 0.05 were recorded when the slopes obtained for three different seawater samples were compared; therefore, a seawater sample free of analytes could be used for calibration purposes. Water samples obtained from the gully did not show a matrix effect, meaning that their analysis, as well as the analysis of seawaters if only manganese compounds are to be analyzed, can be carried out against aqueous standards. Taking into account the obtained results, it can be concluded that the matrix effect obtained in seawaters is directly related with the salt content. Detection limits for lead compounds in seawaters were between 0.17 and 50 $ng\,L^{-1}$ for TMeL using $NaBPr_4$ and $NaBPh_4$, respectively. Repeatability was checked for a seawater sample fortified with the analytes at concentration levels of about 15 times the corresponding quantification limits, and RSD values ($n = 10$) lower than 9% were obtained in all cases.

3.4.2. Soil samples

Because the propylation procedure showed the best performance, it was extended to the analysis of soil samples. 10 mL of a pH 4 buffer solution was added to different sample masses between 0.1 and 1 g, and the derivatization and SPME enrichment steps were carried out as described above. The best results were obtained when using 0.25 g of sample, and so this mass was adopted. Again, calibration was carried out with a soil sample free of the organocompounds because a matrix effect appeared for the lead compounds. Six concentration levels were assayed in duplicate, using peak areas for calibration purposes. Table 4 shows the analytical characteristics obtained for each compound in the analysis of soil samples. The repeatability was calculated using the relative standard deviation (RSD) for a soil sample free of the analytes and fortified at concentration levels of about 1 $ng\,g^{-1}$ for lead compounds and 0.25 $ng\,g^{-1}$ for manganese compounds, the RSD values being lower than 10% in all the cases.

3.5. Analysis of samples and recovery studies

Finally, the method based on the propylation reaction was applied to the analysis of eleven water and five soil samples. None of the compounds was found in the soil samples, while CMT was detected in one of the seawater samples at a concentration close to the quantification limit ($0.18 \pm 0.01\ ng\,L^{-1}$).

Average recoveries ± standard deviations of 96.3 ± 7.8 ($n = 90$) and 98.6 ± 9.1 ($n = 60$) were obtained for water and soil samples, respectively.

4. Conclusion

The procedure involving derivatization with $NaBPr_4$ is recommended because it provides higher sensitivity for lead compounds. A significant matrix effect was observed for organolead compounds in seawater and soil samples, but the possibility of using a sample free of the analytes simplified notably quantification of the samples, the matrix effect for gully waters being negligible. A shorter SPME preconcentration step can be selected when using $NaBPh_4$, because the derivatives compounds were unstable at adsorption times longer than 15 min, although this procedure can be used if lower sensitivity is required. The analytical characteristics of the recommended procedure make it suitable for routine monitoring of the samples studied.

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