

Speciation of Lead in Environmental Waters by Preconcentration on a New Fullerene Derivative

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A novel fullerene derivative including a chelating group attached to the fullerene core has been prepared by photoreaction of C₆₀ and sodium diethyldithiocarbamate (NaDDC) in toluene–methanol medium. The optimization of the synthesis procedure was monitored by UV–visible spectroscopy using the spectrum of C₆₀ fullerene as reference; the new material, a C₆₀–NaDDC monoadduct, showed a shoulder at 430 nm and an increase in the absorption band comprised between 425 and 500 nm. The solid was obtained by photolysis reaction in ~24 h, requiring further purification by preparative chromatography. Characterization of the brown product was accomplished by XRD and solid-state ¹³C MAS NMR; chemical modification was confirmed through the appearance of peaks close to the fullerene core peak located at 146.9 ppm, which can be assigned to carbon atoms of C₆₀ that are covalently bonded to the diethyldithiocarbamate group to form a pyrrolidine ring-fused fullerene monoadduct. Using lead species as a model assessed the ability of the new material for the preconcentration of metallic and organometallic compounds, providing detection limits of 4–15 ng/L. The most interesting conclusions of the results were high adsorption efficiency, selectivity, and stability of the C₆₀–NaDDC derivative (the packed material can be used for at least six months).

Since the discovery of fullerene carbon clusters and their successful laboratory synthesis,¹ tremendous interest has been evoked in evaluating their structure and properties. The large-scale synthesis of fullerenes² has made C₆₀ readily available, and chemical modification of fullerenes has since attracted considerable attention.^{3–5} In particular, the combination of the unique molecular characteristics of fullerene with other compounds through chemical modification has increased their interest. A handful of patents cover possible fullerene applications in several fields such as physics, chemistry, and materials sciences, among others, although the holders agree that fullerene is not achieving

the original perspectives yet. Regarding analytical chemistry, C₆₀ itself and fullerene derivatives have been used as stationary phases in liquid chromatography (LC)^{6,7} and in gas chromatography (GC).^{8,9} In addition, the multiple redox states that C₆₀ exhibits enable its use as a promising electrochemical biosensor for several species.¹⁰ But maybe the most active research topic in this sense is the use of C₆₀ and C₇₀ fullerenes for preconcentration of metal and organometallic traces. Abraham et al.¹¹ demonstrated the analytical potential of fullerene for the adsorption of organic vapors using a surface acoustic wave (SAW) sensor. In independent studies, the characteristics of C₆₀ and C₇₀ fullerenes as sorbent materials for the preconcentration of metals in continuous systems were described;¹² further experiments showed both to be better sorbents in metal preconcentration than are conventional solid materials such as RP-C₁₈, activated carbon, or resins. Neutral chelates provided the best sensitivity and selectivity when compared to charged chelates or ion pairs.¹³

Derivatization of C₆₀ has played a key role in the studies of fullerene applications. The introduction of a suitable pendant group can not only modify the solubility of the fullerene but also provide a handle to anchor C₆₀ to a specific target analyte.¹⁴ During the past years, glycine esters have been directly added to C₆₀ under photolysis to form pyrrolidine ring-fused fullerenes;¹⁵ this reaction has also been applied to aminopolycarboxylic esters such as tetramethyl ethylenediaminetetraacetate (EDTA ester) and pentamethyl dimethylenetriaminepentaacetate (DTPA ester).¹⁶ The attachment of polydentate ligands to C₆₀ should open the scope for their potential applications. However, in the study of the chemical modification of the fullerenes, it has been found that well-characterized fullerenes are difficult to get, as multiple addition occurs readily yielding a mixture of multiple addition products. Some di-, tetra-, and hexa-adducts of C₆₀ have been reported.¹⁷

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The aim of this paper is the synthesis, characterization, and analytical application of a novel fullerene derivative based on the photolysis reaction between C₆₀ and a classical complexing reagent for metals such as sodium diethyldithiocarbamate (NaDDC). Through a simple procedure, a single and symmetric adduct is obtained that incorporates a molecule of NaDDC into the fullerene core, joining thus the chelating properties of the pendant group to the well-known sorbent capacity of fullerene.

EXPERIMENTAL SECTION

Reagents. All reagents were obtained from commercial sources, and, unless noted otherwise, were reagent grade or better. C₆₀ fullerene (99.999%) was provided by Dynamic Enterprises Ltd. (Berkshire, England). NaDDC, silica gel 40 (0.06–0.20-mm particle size), 4-chloro-2-methylphenol (as internal standard), and iodine monochloride were purchased from Sigma-Aldrich (Madrid, Spain). Trimethyllead (TML⁺) acetate and triethyllead (TEL⁺) chloride were supplied by Alfa (Barcelona, Spain). Sodium tetrapropylborate (NaBPr₄) was obtained from Galab (Geesthacht, Germany). Organic solvents such as toluene, acetone, ethanol, methanol, ethyl acetate, *n*-hexane, isobutyl methyl ketone, and other chemicals including sodium hydroxide and nitric acid were provided by Merck (Darmstadt, Germany).

Stock solutions of TML⁺ and TEL⁺ were prepared by dissolving the appropriate amounts of the respective salts in ultrapure Milli-Q water (Millipore) to yield a concentration of 0.5 mg/mL expressed as lead. Dimethyl- and diethyllead (DML²⁺ and DEL²⁺, respectively) were synthesized by reacting TML⁺ and TEL⁺ solutions with 0.1 mol/L iodine monochloride as described elsewhere.¹⁸ All organolead solutions were stored at 4° C in the dark to avoid their decomposition to inorganic lead, and diluted solutions were prepared daily from these standards. One gram of NaBPr₄ was dissolved in 1 mL of ethanol and stored at –20° C in the dark. Diluted solutions (7.5 mg/mL) were prepared in ethyl acetate on a daily basis.

Safety aspects concerning handling of toxic compounds (alkyl-lead species and NaBPr₄) such as the use of gloves and closed fume hood to prevent intoxication through dermal absorption or inhalation were considered.

Instrumentation. The elemental analysis used for the characterization of the C₆₀–NaDDC fullerene derivative was performed at the Elemental Microanalysis Center in the Complutense University of Madrid, Spain. A HP 8453 UV–visible spectrophotometer (Agilent Technology, Madrid, Spain) was used to record the UV–visible spectra of the target compound. Powder X-ray diffraction (XRD) data were collected by a Siemens D5000 diffractometer (Munich, Germany) provided with Cu K α radiation and graphite monochromator. Signals were recorded using step scans of 0.04° 2 θ step size and 2 s duration. Solid-state nuclear magnetic resonance (NMR) spectra were carried out using a Bruker ACP-400 spectrometer (Madrid, Spain) working at a spinning rate of 4100 Hz. For ¹³C magic angle spinning (MAS) NMR measurements, 10 500 transients were acquired using a repetition time of 5 s.

Organolead compounds speciation was accomplished by using a Fisons GC8000/MD800 GC/MS system (ThermoQuest, Madrid, Spain) with electronic pressure control and governed via MASS-LAB software (also from ThermoQuest). Separation of the analytes was achieved in a capillary column (30 m \times 0.25 mm i.d., 0.25 μ m) HP-5-MS (Supelco, Madrid, Spain) using ultrapure grade helium (6.0, Air Liquide, Seville, Spain) at a constant flow rate of 0.9 mL/min. The GC injection port, GC/MS interface, and MS source temperatures were kept at 250, 250, and 200 °C, respectively. The column temperature was initially set at 50 °C for 1 min and then raised at 30 °C/min to 250 °C, where it was held for 1.5 min. A 1- μ L aliquot of the sample was injected in the split mode (1:25). Mass spectra were obtained in the electron impact ionization mode at 70 eV, and the mass spectrometer was operated in the selective ion monitoring (SIM or SIR) mode, being the characteristic ions selected for identification and quantitation (underlined) of each analyte as follows: TML⁺ 208, 253, 281; DML²⁺ 208, 281, 309; TEL⁺ 208, 237, 309; DEL²⁺ 208, 251, 322; Pb²⁺ 208, 251, 337; 4-chloro-2-methylphenol 77, 107, 142.

The flow system comprised a Gilson (Villiers-le-Bel, France) Minipuls-2 peristaltic pump furnished with poly(vinyl chloride) tubes, two Rheodyne (Cotati, CA) 5041 injection valves, PTFE tubing of 0.5-mm i.d. for coils and a laboratory-made minicolumn containing the C₆₀–NaDDC derivative. The minicolumns were made from PTFE capillaries of 3-mm i.d. and sealed on both ends with small cotton beds to prevent material losses. Owing to its small particle size (~10–50 nm), the fullerene derivative is very prone to compaction when soaked in the flow system. To avoid abrupt changes in the column compacity that would stop the solution flow and disengage the system connections, every two C₆₀–NaDDC segments (~1.0 cm long) must be separated by additional ones of an inert material (e.g., glass beads, ~0.5 cm long, 0.9–1.2-mm o.d.).

Synthesis Procedure. All the reactions were carried out in open atmosphere without any special caution to exclude air. The derivative of C₆₀ was synthesized as follows: 50 mL of a NaDDC solution (90 mg/mL) in methanol was added into a 250-mL glass beaker containing 100 mL of a C₆₀ fullerene solution (37.5 mg/mL) in toluene. The mixture was magnetically stirred and exposed to a 60-W household light bulb as source light until the solution color changed from purple to dark red and the precipitation of a brownish byproduct was completed (~24 h); methanol was evaporated during this time. Then, the solution was placed in an extraction funnel and 100 mL of water was added; the mixture was manually shaken to remove the precipitate from the organic phase (this extraction/cleanup step was accomplished by triplicate treatment with fresh aliquots of water). Once separated from the aqueous phases, toluene was evaporated to air-dry in the dark at ambient temperature for 24 h, protected from draughts, and the dark brown solid obtained washed with 25 mL of acetone. The filtered residue was then dissolved in the minimum volume of toluene (~30 mL) and purified on a silica gel 40 preparative column (2.5 cm \times 15 cm) previously conditioned with ethanol. Toluene (~200 mL) was employed as mobile phase, being the eluate collected in a glass beaker and the solvent evaporated to air-dry in the dark; a dark brown solid (303 mg) was obtained as the final product of the synthesis (patent granted by University of Córdoba, Spain).¹⁹

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Speciation Procedure. Volumes of 5 mL of standard or sample solutions containing 0.1–200 $\mu\text{g/L}$ inorganic lead or organolead compounds at pH 7–10 were aspirated into a flow system similar to one described elsewhere²⁰ and pushed through the sorbent column located into the loop of an injection valve (preconcentration valve). In the preconcentration step, the different lead species were retained in the C_{60} –NaDDC derivative column (80 mg); in the meanwhile, the 200- μL loop of the elution valve was filled with ethyl acetate (eluent) containing the derivatizing reagent (NaBPr_4 , 7.5 mg/mL) and 4-chloro-2-methylphenol (10 $\mu\text{g/mL}$) as internal standard. In the elution step, both preconcentration and elution valves were switched; once the eluent reached the C_{60} –NaDDC column, the flow was stopped for 2 min to allow a deeper contact between the analytes and the eluent/derivatizing reagent, favoring thus the elution. After this time, the eluate was collected in a 0.5-mL PTFE vial and let to settle for another 2 min to ensure complete derivatization. Finally, a 1- μL fraction was injected into the GC/MS.

Solubility of C_{60} –NaDDC. The solubility of C_{60} fullerene is already established for the most common organic solvent and aqueous solution; C_{60} is essentially insoluble in polar and H-bonding solvents, sparingly soluble in alkanes, and quite soluble in aromatic solvents.²¹ However, since the addition of a functional group can modify the fullerene properties, evaluating the solubility of the C_{60} –NaDDC derivative is mandatory. In undertaking this work, aqueous solutions at different pH values, as well as several organic solvents (ethanol, acetone, ethyl acetate, *n*-hexane) were assayed as follows: ~10 mg of C_{60} –NaDDC was placed in a narrow glass bottle (2.5 cm long \times 0.5 cm diameter), and 1 mL of the aqueous solution or solvent was added. The solution was magnetically stirred in the dark by using a 5 mm \times 2 mm PTFE-coated stirring bar for 24 h to ensure equilibration. The saturated solution was then filtered through a 0.5- μm PTFE filter (Millipore, Seville, Spain) or paper (Whatman No. 1) filter for organic and aqueous solutions, respectively. The solid residue (nondissolved solid) was air-dried and then weighed. The solubility was established by difference between both weights.

RESULTS AND DISCUSSION

C_{60} –NaDDC Derivative. A careful selection of the initial reagents can make photolysis a simple and effective tool for the synthesis of active fullerene complexes. To select a suitable reagent to be bonded to C_{60} , yielding a product that showed chelating properties, a rigorous study of the classical reagents that form stable complexes with metallic cations was performed; the appropriate reagents must contain carbon atoms that are adjacent to an amine group (electron donor) and that are also available to be covalently bonded to C_{60} through the formation of a pyrrolidine-type ring, i.e., the unaltered chelating functional group. Taking into account these considerations, the sodium salt of the diethyldithiocarbamate acid was used as reagent since in addition its highly symmetrical structure would produce a single photolysis product by reaction with C_{60} . In this way, the adduct would show the ability to form stable complexes with a large

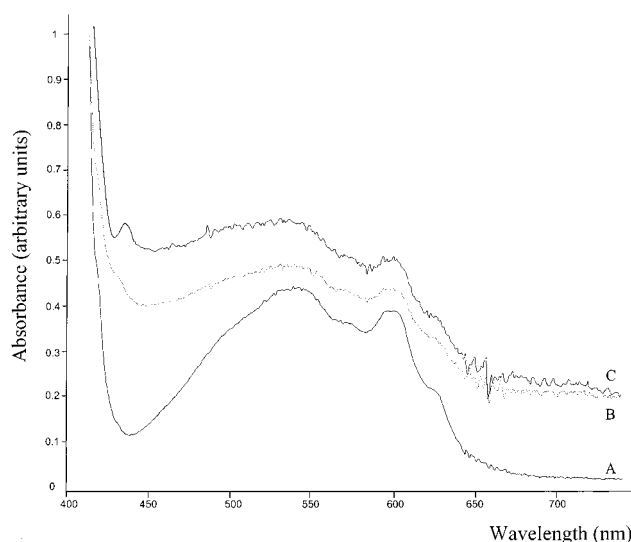


Figure 1. UV–visible absorption spectra of (A) C_{60} in toluene and C_{60} –NaDDC solution after a reaction time of (B) 2 and (C) 24 h.

number of metallic cations, besides the well-known sorption capacity of fullerene.

The solid adduct was prepared with different concentrations of NaDDC (30–90 mg/mL) in methanol and a constant concentration of C_{60} (37.5 mg/mL) in toluene. The mixture was irradiated with a household light bulb (60 W) to induce the photochemical reaction; photolysis was reflected by a color change from the characteristic purple of a C_{60} solution in toluene (reference solution) to dark red with the appearance of a brownish precipitate. The color changes became greater from a NaDDC concentration of at least 70 mg/mL. Thus, a concentration of 90 mg/mL was selected in order to ensure an excess of NaDDC versus C_{60} . On the other hand, several light sources (UV lamp, household light bulb, natural sunlight) were assayed, obtaining no significant differences when natural sunlight or household light bulbs with variable power supply were used. No reaction was observed with the UV source after 2 days, and therefore, a household light bulb of 60 W was selected. Optimization of the reaction time was accomplished by recording the UV–visible spectrum of the supernatant solution at short time intervals of 10 min that were increased up to 60 min as the reaction progressed; the obtained spectra were compared with those of the reference solution (C_{60} in toluene) under the same conditions. The absorption spectrum of the reference solution was found to be constant through the time, showing two intense absorption bands in the UV region ($\lambda_{\text{max}} = 213$ and 329 nm) and a broad band in the visible region from 450 to 650 nm. As can be seen in Figure 1, the absorption spectrum of the adduct (assigned to C_{60} –NaDDC) initially showed an increase in the absorption band observed between 425 and 500 nm that with time reached the intensity of the C_{60} maximum located at $\lambda_{\text{max}} = 540$ nm. On the other hand, the appearance of a weak shoulder at $\lambda_{\text{max}} = 430$ nm was also observed, assigned to addition at the [6,6] junction to form a pyrrolidine ring which is characteristic of fullerene adducts.^{16,22} The absorption spectrum of the product remained unchanged from 22 to 28 h, decreasing above this period of time. A reaction time of 24 h was selected.

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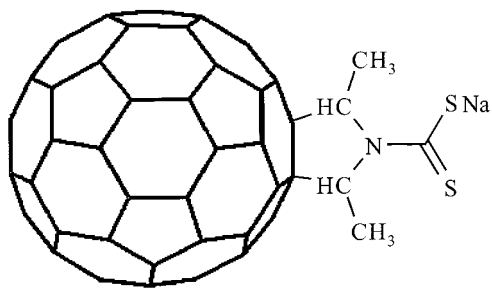


Figure 2. Structure of C_{60} -NaDDC derivative.

The solution containing C_{60} -NaDDC in toluene and the brownish precipitate was then purified in order to obtain a solid final product. The brownish precipitate was eliminated by extraction with water, taking into account its solubility in it; the UV-visible spectrum of the aqueous solution was also recorded to establish the precipitate composition, with the conclusion that it is probably a decomposition product of the great excess of NaDDC, since no fullerene bands were observed. The toluene phase was evaporated, washed, and purified by column chromatography using silica gel as stationary phase, as indicated in the synthesis procedure section. Toluene was first employed as mobile phase, and two different chromatographic bands were clearly observed inside the column: a reddish band, which was easily eluted and collected in a separated fraction, and a light brown band, which remained on the top of the column and was only eluted when ethyl acetate was employed as mobile phase. Again, UV-visible spectra were recorded, revealing that the characteristic fullerene bands only appeared in the reddish fraction of toluene. Thus, after the evaporation of toluene from this fraction, a dark brown product was obtained. Finally, this product was dissolved in toluene and the UV-visible spectrum also recorded, being similar to that obtained for the initial dark red solution.

Characterization of C_{60} -NaDDC Derivative. To elucidate the chemical structure of the synthesized dark brown product, several characterization techniques were employed. First, the presence of additional elements in C_{60} like nitrogen or sulfur was examined through elemental analysis revealing the following composition: C, 91.32%; H, 1.84%; N, 1.16%; S, 4.74%. This information agrees with the chemical structure proposed in Figure 2 for a yield of 66% on the basis of converted C_{60} , as reported for similar photoreactions involving fullerene.¹⁶

The XRD pattern of the C_{60} -NaDDC showed prominent peaks at $2\theta = 9.16, 10.40, 16.76, 17.64, 18.92, 19.56, 19.88, 20.28,$ and 21.20° , as can be seen in Figure 3A. The patterns of C_{60} and NaDDC are also shown (Figure 3B and C, respectively), both obtained from toluene solutions in order to detect a possible crystallization in a different phase owing to solvent molecule-fullerene interactions, as described for other organic solvents such as benzene²³ or tribromomethane.²⁴ By comparison it becomes evident that the fullerene derivative is entirely different in structure from C_{60} and NaDDC alone. If the product was a simple mixture of C_{60} and NaDDC, then the X-ray diffraction pattern would have shown peaks corresponding to both individual components exactly at the same positions; however, only a small contribution of

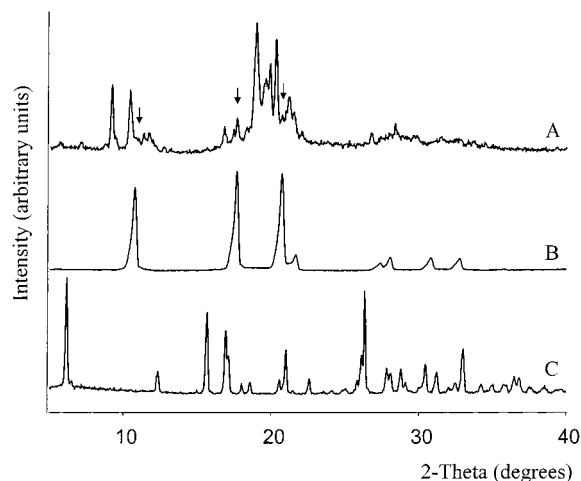


Figure 3. Powder XRD pattern of (A) C_{60} -NaDDC derivative, (B) C_{60} fullerene, and (C) NaDDC. All the compounds were obtained from toluene solutions.

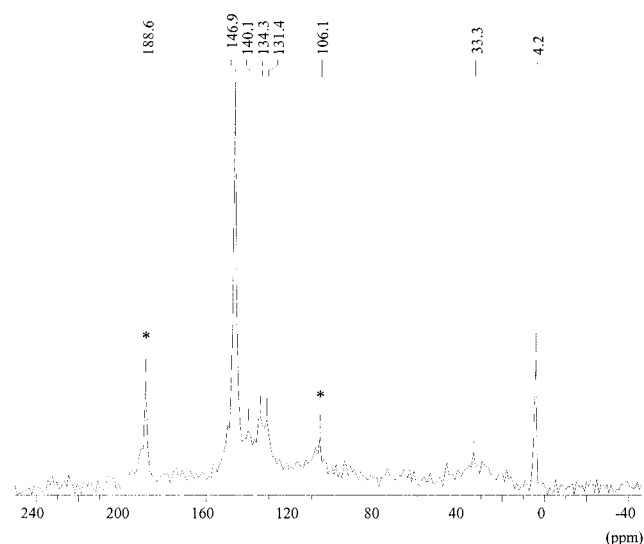


Figure 4. ^{13}C MAS NMR spectrum of C_{60} -NaDDC derivative.

unreacted fullerene is observed (peaks denoted with an arrow in Figure 3A). On the other hand, the presence of signals at 2θ values lower than those observed for free C_{60} can be interpreted as an indicator of a higher interplanar spacing in C_{60} -NaDDC derivative, as could be expected if a new derivative was formed. Nevertheless, the intercalation of NaDDC molecules between the planes of C_{60} fullerenes could also increase the interplanar spacing, leading to similar effects. For that reason, XRD must be considered in this case as a complementary characterization technique that provides useful, but not definitive information.

The ^{13}C NMR data enabled the elucidation of the structure of the mono-NaDDC adduct of C_{60} . The signals from saturated solutions were not intense enough to allow their assignment; thus, solid-state ^{13}C magic spin angle (MAS) NMR was employed. As can be seen from Figure 4, the solid-state ^{13}C MAS NMR spectrum of C_{60} -NaDDC showed two narrow peaks at 4.2 and 146.9 ppm and four wide peaks of carbon atoms at 33.3, 131.4, 134.3, and 140.1 ppm, respectively. The two peaks denoted with an asterisk at 106.1 and 188.6 ppm are the first spinning sidebands (SSB) of the main peak at 146.9 ppm. On the basis of the chemical shift data and intensity ratio of the peaks, we assign the peak at 146.9

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Table 1. Experimental Conditions and Analytical Characteristic for Speciation Analysis of Organolead Compounds in Aqueous Samples (5 mL)

exptl conditions	optimum range			selected value
sample pH	7–10			7–10
amt of sorbent (C ₆₀ –NaDDC), mg	50–80			80
NaBPr ₄ concn, mg/mL	7.5–10			7.5
eluent vol (ethyl acetate), μ L	200			200
elution/derivatization time, min	3–7			4
sample flow rate, mL/min	0.3–2.0			2.0
eluent flow rate, mL/min	0.6–1.2			0.6
analytical features	TML ⁺	DML ²⁺	TEL ⁺	DEL ²⁺
linear range, ng/mL as Pb	0.02–4	0.04–4	0.02–3	0.03–4
detection limit, pg/mL as Pb	5	15	4	10
RSD (%; <i>n</i> = 11, 0.5 ng/mL as Pb)	5.5	4.6	4.8	5.8

ppm to the fullerene core; the peaks at 140.1, 134.3, and 131.4 ppm can be assigned to carbon atoms of C₆₀ whose structural environment has been modified. Because these atoms are receiving electrons from the pyrrolidine ring, a shielding effect occurs, resulting in the appearance of these absorption peaks at lower chemical shift values. On the other hand, the peaks located at 4.2 and 33.3 ppm can be assigned to CH₃– (two groups) and C₆₀–CH–N= (two groups) respectively; the fact that two carbon atoms can be included in each signal implies that they seem to have the same structural environment, indicating the high symmetry of the molecular structure. We can also see that the signals have quite different spreads, the peak at 4.2 ppm being the narrowest one; this indicates that this group is the only one whose rotation is not quenched since it is not involved in the rigid pyrrolidine ring. As previously reported for other fullerene-based materials,²⁵ the peak assigned to the fullerene core is about +4 ppm upfield shift, i.e., deshielded, from free C₆₀, due to its participation in the bonding. Although the signal corresponding to =N–CS₂Na was not observed in the MAS spectrum due to the poor signal-to-noise ratio that is inherent to the technique, its presence was demonstrated in further experiments using ¹³C CP-MAS NMR as a signal in the characteristic region of C–S binding at 194.8 ppm.

Speciation of Organolead Compounds. To further demonstrate the ability of the novel fullerene derivative for preconcentration of metallic and organometallic compounds, C₆₀–NaDDC was used as a chelating material in the speciation of organolead compounds in rainwaters. For this purpose, the solubility of C₆₀–NaDDC in several organic solvents as well as its stability in aqueous solutions of different pH values was studied since those solutions were to be passed through the column during the preconcentration and elution steps. The solubility was lower than 0.1 mg/mL for ethanol, acetone, and ethyl acetate and notably higher (~0.8 mg/mL) for *n*-hexane. Regarding stability in acidic or alkaline solutions, the derivative showed great stability from pH 1 (hydrolysis of C₆₀–NaDDC occurred in an extension of only 1%, detected through UV–visible measurements of NaDDC) to pH 13 (no hydrolysis detected). Based on the previous results, a minicolumn packed with the C₆₀–NaDDC derivative was included into a continuous system. In this work, a slight modification of a recently developed flow system²⁰ was employed; a 5-mL sample

volume containing 0.5 μ g/L TML⁺, DML²⁺, TEL⁺, and DEL²⁺ was directly aspirated into the minicolumn (located into the loop of the preconcentration valve) and the analytes eluted with ethyl acetate containing the derivatizing reagent (introduced into the system by means of a second injection valve), as described in the speciation procedure section. Aliquots of 1 μ L of the derivatized eluate were injected into the GC/MS for analysis. The chemical and flow variables were optimized. The adsorption capacity was found to depend mainly on the pH of the sample solution; the optimum pH ranged between 7 and 10; thus, samples were adjusted to weak alkaline medium with dilute NaOH. Signals for alkyllead compounds decreased in strong acidic medium through decomposition of the organolead species to inorganic lead,^{18,26} which is observed as an increment of the signal assigned to tetrapropyllead. This peak also includes the contribution due to inorganic lead that could be present in the original samples. In weak acidic medium (pH 1–6), a plateau is observed in which the sensitivity is ~20% of that achieved in the optimal region (pH 7–10), as a consequence of the protonation of the DDC ligand prevailing over the chelate formation. Other variables such as amount of sorbent material (optimum range 50–80 mg), eluent volume, and sample and eluent/derivatizing solution flow rates were also studied; the selected values are listed in Table 1.

On the other hand, it is well known that derivatization time is a critical parameter in organolead speciation.²⁷ The elution of the analytes first implies their reaction with the derivatizing reagent in order to release the lead species from the chelating column; for this goal, an air stream (carrier of the eluent/derivatizing reagent, 200 μ L) of 0.6 mL/min was chosen, since lower flow rates resulted in less reproducible measurements and at higher flow rates the residence time of the eluent inside the column was not enough to complete the elution. Furthermore, the flow was stopped for 2 min. After the eluate was collected in a closed vial, an additional derivatization time of 2 min was also necessary to complete the propylation of all the organolead compounds; TML⁺ was especially affected by this variable. Under these working conditions, the column with C₆₀–NaDDC packing was reusable for at least six months.

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By using the selected conditions given in Table 1, several calibration graphs for all the organolead compounds were run. The figures of merit of the calibration graphs are also summarized in this table. Detection limits (calculated as three times the standard deviation of background noise) ranged from 4 to 15 ng/L. The precision (for 11 individual samples containing 0.5 $\mu\text{g/L}$ of each organolead compound) was found to be $\sim 5\%$ (within day).

The effect of the presence at significant concentrations in rainwater of metal ions that are able of forming complexes with NaDDC was also examined. Major elements (Ca^{2+} , Mg^{2+} , Na^+ , K^+) do not react with NaDDC; thus, only the common transition elements such as Fe^{3+} , Cu^{2+} , Co^{2+} , Zn^{2+} , and Mn^{2+} were studied at concentrations up to 0.5 mg/L, together with organolead compounds at 0.5 $\mu\text{g/L}$. As these elements could be precipitated in the weak alkaline medium in which samples are prepared (pH 7–10), a commercial HPLC filter was placed at the entry to the sample aspiration channel in order to prevent any particle from reaching the sorbent column and preclude its performance. No interferences were observed at the maximum concentrations assayed.

To examine the effect of the matrix on recoveries, an artificial rainwater¹⁸ was prepared by dissolving in Milli-Q water the following high-purity salts: NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2$, and $(\text{NH}_4)_2\text{SO}_4$. Samples were spiked in quintuplicate with 100 pg/mL of each lead species, giving satisfactory results for all the samples, with recoveries ranging between 92 and 96% for TML^+ , 95 and 99% for DML^{2+} and TEL^+ , and 94 and 100% for DEL^{2+} .

Finally, the proposed method was applied to the analysis of two rainwaters. Samples were collected in Spain in different seasons. Aliquots of 25 mL (breakthrough volume) of rainwater were preconcentrated onto the flow system. TML^+ was undetected ($< 1 \text{ ng/L}$) in both samples, probably as a result of environmental degradation to DML^{2+} and Pb^{2+} . All other species were detected, their concentrations being 20 and 80 ng/L (DML^{2+}), 30 and 150 ng/L (TEL^+), and 45 and 90 ng/L (DEL^{2+}), for samples 1 and 2, respectively.

Comparison of the C_{60} –NaDDC Derivative with C_{60} . C_{60} fullerene itself, and C_{70} , have proven to be effective sorbent materials for the preconcentration of metallic cations, after the formation of a suitable neutral chelate to be adsorbed via π – π interactions. Ammonium pyrrolidinedithiocarbamate¹² and NaDDC¹⁸ have been employed for the determination of lead and organolead compounds, among other metals, in flow systems similar to the one used in this work; those systems included an additional stream of the suitable chelating reagent that must be mixed with the sample stream and also a reaction coil long enough to ensure the complete formation of the chelate before retention onto the C_{60} fullerene column. However, by using a column packed with C_{60} –NaDDC the flow system is greatly simplified as the sample can be directly preconcentrated onto the column. On the

other hand, conditioning of the C_{60} column is needed for the retention of certain organolead compounds. Thus, the retention of TML –DDC chelate is enhanced when the C_{60} is conditioned with *n*-hexane;²⁸ the solvent molecules are adsorbed at the surface of the crystals of C_{60} ,²⁹ constituting a liquidlike phase in which TML chelate would be dissolved. The C_{60} –NaDDC derivative can overcome these difficulties, since owing to the different retention mechanism (chelate formation instead of π – π interactions), there is no reason for TML^+ to be retained in a lesser extension than the other lead species. The most relevant difference between both sorbent materials is the pH range in which formation of the chelate is favored. Thus, when C_{60} fullerene was employed, adsorption was maximal in a wider pH range (1–8) as the likely result of the chelate being formed in the aqueous medium (in excess of NaDDC) preceding its adsorption on C_{60} . In contrast, when using the C_{60} –NaDDC column, maximum analyte adsorption was achieved at a higher sample pH (7–10), but a previous plateau was obtained between pH 1 and 6, in addition to a decrease in the chromatographic signal by about 15% (for DML^{2+} and DEL^{2+}) and 30% (for TML^+ and TEL^+) relative to the first plateau. This displacement of the pH range toward the alkaline region related to C_{60} column is due to the enhancement of chelate formation on the C_{60} –NaDDC material in a weak alkaline medium in which the chelating reagent is negatively charged.

The main advantages of the new derivative relative to C_{60} are as follows: neither chelating reagents nor column conditioning are needed, since the flow system is notably simplified as a result of use of the C_{60} –NaDDC derivative. Regarding column stability, both columns have proved to be reusable for at least six months on a daily working basis.

CONCLUSIONS

From the foregoing, the following conclusions can be drawn: (a) C_{60} can be covalently bonded to classical chelating reagents, leading to stable fullerene derivatives that join the advantages of both compounds; (b) the C_{60} –NaDDC derivative synthesized in the present work can be employed as sorbent material for the preconcentration of metallic, organometallic, and probably organic compounds at trace levels; (c) typical drawbacks of previous NaDDC resins such as the hydrophobic bonding and the lack of pH stability³⁰ are circumvented by using the fullerene derivative, and (d) further applications of the novel material could be developed, such as immobilization on solid surfaces, assembling of optically transparent electrodes, or employment as a stationary phase in chromatographic processes.

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