Analytical potential of fullerene as adsorbent for organic and organometallic compounds from aqueous solutions

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Abstract

In this work, the analytical potential of C_{60} fullerene as a sorbent for organic and organometallic compounds from aqueous solutions was studied for the first time. Fullerene adsorbs many types of organic substances (e.g., *N*-methylcarbamates, phenols, polycyclic aromatic hydrocarbons, amines) with efficiencies that depend on the nature of the compound concerned and never exceed 60%. Conventional sorbents such as XAD-2 or polyurethane foam are more efficient than C_{60} for this purpose. Organometallic compounds (viz. metalocenes and organoleads) are quantitatively adsorbed on C_{60} via the formation of neutral complexes or chelates; the adsorption constant is dramatically increased by the use of classical reagents such as pyrrolidinedithiocarbamate or diethyldithiocarbamate. A complementary comparative study on the adsorption of organometallic complexes on RP-C_{18} and silica gel 100, among others, showed C_{60} to be superior as sorbent. All experiments in this work were carried out by using continuous flow configurations and gas chromatography–atomic absorption spectrometry techniques.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic compounds are usually determined by using chromatographic techniques, the specific choice depending on their polarity, volatility and their risk of decomposition at high temperatures. In general, these determinations entail an enrichment/matrix separation procedure. Solid-phase extraction (SPE) is a convenient alternative to liquid–liquid extraction for this purpose as it can be performed off-line (using sorbents packed in disposable car-

tridges) or on-line with the chromatographic separation [1]. The basic principles of SPE are similar for off-line and on-line methods and are extensively documented [2]. The most popular sorbents are alkyl-bonded silicas (viz. C_8 or C_{18} silica), which are hydrophobic; nonpolar copolymers [3], the retention properties of which are also governed by a hydrophobic effect and π-electron interactions; and carbonaceous sorbents that act via different retention mechanisms, including hydrogen bonding [4,5]. The most selective sorbents are ion exchangers, metal-loaded sorbents and immunosorbents [1,6]. Recently, a solvation parameter model was used to characterize the intermolecular interaction responsible for retention of neutral organic compounds on active and graphitic carbons [7].

The currently endorsed approaches to the analysis

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of organometallic compounds are based on the coupling of a separation technique such as gas chromatography (GC) or high-performance liquid chromatography (HPLC) to an element-selective, sensitive detector [8]. Atomic absorption/emission spectrometry is a usual detection method [9–11]. However, some preliminary sample preparation (usually extraction and derivatization) is required for speciation analysis [10–12]. Solid-phase extraction is rapidly growing in popularity for preconcentration of trace metals. Thus, the SPE of organotin compounds in an aqueous acid medium was accomplished by using a copolymer as sorbent and methanol as eluent, the eluate being analyzed by HPLC–inductively coupled plasma (ICP) mass spectrometry (MS) [13]. Organomercury compounds have also been preconcentrated on solid sorbents by complexation with diethyldithiocarbamate (DDC), followed by elution with EDTA and analysis by HPLC [14]. The SPE of lead species usually relies on interactions based on chelate formation; the ligand can be immobilized on a stationary support or dissolved in a solution, the chelates formed being adsorbed on a non-polar sorbent for preconcentration. In this context, on-line SPE systems based on different materials have been developed for the preconcentration of organolead compounds [15].

Ever since fullerene was confirmed to exist [16], it has received considerable attention in various scientific fields [17,18]. The purity of fullerenes has also been determined; thus, precise data on trace element impurities in fullerene precursors and products have been reported [19]. Fullerenes occur as a wide variety of isomers and homologous series that are difficult to separate. Jinno and co-workers have published no fewer than 25 papers on the separation and isolation of fullerenes from carbon soot on ordinary and specialized stationary phases by HPLC [20,21]. These authors synthesized a chemically bonded C_{60} silica phase of use as a stationary phase for liquid chromatography [22], and retention behavior for various polycyclic aromatic hydrocarbons (PAHs) was evaluated [23]. The analytical potential of fullerene (packed into a chromatographic column as stationary phase) for the adsorption of organic vapors was demonstrated by Abraham et al. [24,25]. In independent studies, we described for the first time the characteristics of C_{60} fullerene as sorbent

material for the preconcentration of metals [26]; subsequent experiments with C_{60} and C_{70} fullerenes in continuous systems showed both to be better sorbents in metal preconcentration than are conventional solid materials such as RP-C_{18}, activated carbon and resins [27]. Better sensitivity and selectivity were obtained with neutral chelates than with ion pairs [27,28].

Our preliminary conclusions on the potential of fullerenes as sorbents for metal preconcentration were presented in previous papers [26–28]. In this work, we extended the analytical applications of C_{60} fullerene to the adsorption of organic and organometallic compounds from aqueous solutions. For this purpose, C_{60}-packed minicolumns were inserted into continuous flow systems and gas chromatography or flame atomic absorption spectrometry was used for detection, depending on the nature of the compounds assayed.

2. Experimental

2.1. Materials

The chemicals used as analyte standards and reagents were reagent-grade or better. Phenolic compounds were obtained from Aldrich (Madrid, Spain). PAHs, amines, ammonium cerium (IV) nitrate, ammonium perchlorate, surfactants, ammonium pyrrolidinedithiocarbamate and sodium diethyldithiocarbamate were supplied by Sigma (Madrid, Spain). *N*-Methylcarbamates and their hydrolysis products were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Bis(cyclopentadienyl)iron (II) (ferrocene) and bis(cyclopentadienyl)cobalt (II) (cobaltocene) were supplied by Strem (Barcelona, Spain). Trimethyllead acetate and triethyllead chloride were supplied by Alfa Product (Barcelona, Spain) and Sigma, respectively. All solvents were obtained from Romil (Loughborough, UK).

C_{60} fullerene (>99.4%) was obtained from Hoechst (Frankfurt am Main, Germany). Darco 20-40 activated carbon, polygosyl-bonded silica reversed-phase with octadecyl functional groups (RP-C_{18}, 60–100 μm) and XAD-2 styrene–divinylbenzene were purchased from Aldrich, Sigma and Serva (Heidelberg, Germany), respectively. Silica gel 100

and Florisil were purchased from Merck (Madrid, Spain) and Aldrich, respectively.

Standard solutions of each phenolic compound, PAH, *N*-methylcarbamate (in acetone) and amine (in water) were prepared at a concentration of 1 mg/ml and stored in glass-stopped bottles at 4°C. Organometallic compounds were prepared as follows: ferrocene and cobaltocene were dissolved in ethanol at metal concentrations of 1 mg/ml; trimethyl- and triethyllead were prepared by dissolving 37.8 and 40.0 mg of trimethyllead acetate and triethyllead chloride, respectively, in 1 ml of glacial acetic acid (100%) and diluting to 25 ml with water, which yielded a lead concentration of 1 mg/ml. A $3 \cdot 10^{-3}$ mol/l ammonium pyrrolidinedithiocarbamate (APDC) aqueous solution and a $3 \cdot 10^{-3}$ mol/l NaDDC solution in 0.03% acetic acid were also prepared that remained stable for three days. Surfactant solutions were prepared in ultrapure water.

2.2. Apparatus

Gas chromatographic experiments were carried out on a Hewlett-Packard 5890 A gas chromatograph equipped with a flame ionization detector. Chromatographic assays were performed on a cross-linked 100% poly(dimethylsiloxane) fused-silica column (15 m×0.53 mm I.D., 0.3 μm) supplied by Hewlett-Packard (HP-1). Peak areas were measured with a Hewlett-Packard 3392 A integrator. The injector and detector temperatures were maintained constant for each organic group at 160, 200, 225 and 300°C for *N*-methylcarbamates, amines, phenols and PAHs, respectively. The oven temperature was programmed according to the analyte groups to be chromatographed, namely: for phenols (60–200°C); for *N*-methylcarbamates (100–200°C); for PAHs (80–280°C); and for amines (50–130°C). The flow-rate of the carrier gas (nitrogen) was maintained at 15 ml/min.

A Perkin-Elmer 380 atomic absorption spectrometer equipped with a bead impact system in the burner chamber and single-element hollow cathode lamps was used. The wavelengths employed were 283.3, 240.7 and 248.3 for Pb, Co and Fe measurements, respectively; no deuterium arc background correction was used. The air–acetylene flame was adjusted to obtain a clean blue flame. The instrument output was

connected to a Radiometer REC-80 Servograph recorder.

The solid-phase extraction flow system consisted of a Gilson Minipuls-2 peristaltic pump, two Rheodyne 5041 injection valves and PTFE tubing of 0.5 mm I.D. for coils. A displacement bottle, poly(vinyl chloride) and Solvaflex pumping tubes for water and organic solvents, respectively, and custom-made sorption columns packed with different materials, were also employed. The columns were made from PTFE capillaries of 3 mm I.D. that were sealed on both ends with small cotton-wool plugs to prevent material losses. The sorbent column was washed by passing 0.5 ml of methanol or *n*-hexane for organic and organometallic compounds, respectively, followed by 1 ml of Milli-Q water.

2.3. Procedure

2.3.1. Organic compounds

The flow system used is shown in Fig. 1A. It operates in three steps: (1) 10 ml of aqueous standard solution of each individual group (phenols, PAHs, carbamates or amines) was passed through the sorbent column (located in the loop of IV$_1$) at 1 ml/min. (2) For GC analyses, IV$_1$ was switched and the sorbent column dried with a stream of nitrogen introduced via the carrier line of the second valve (IV$_2$) for 3 min; simultaneously, the loop of IV$_2$ was filled with the eluent. (3) Valve IV$_2$ was switched and 150 μl of eluent (ethyl acetate or toluene, inserted in a stream of nitrogen at a flow-rate of 1 ml/min) was passed through the column to elute retained analytes. Finally, the eluate was collected in glass vials containing anhydrous sodium sulfate, and 2-μl aliquots were manually injected into the chromatograph by means of a syringe. Peak area was used as the analytical signal.

2.3.2. Organometallic compounds

A continuous liquid–solid extraction system similar to the previous one was used for the preconcentration of organometallic compounds from aqueous samples (Fig. 1B). In the preconcentration step, 5 ml of standard solution was continuously pumped into the system at 1.5 ml/min and mixed thoroughly with a reagent solution (APDC or NaDDC) at 0.3 ml/min. The complex/chelate was formed in the coil (300 cm
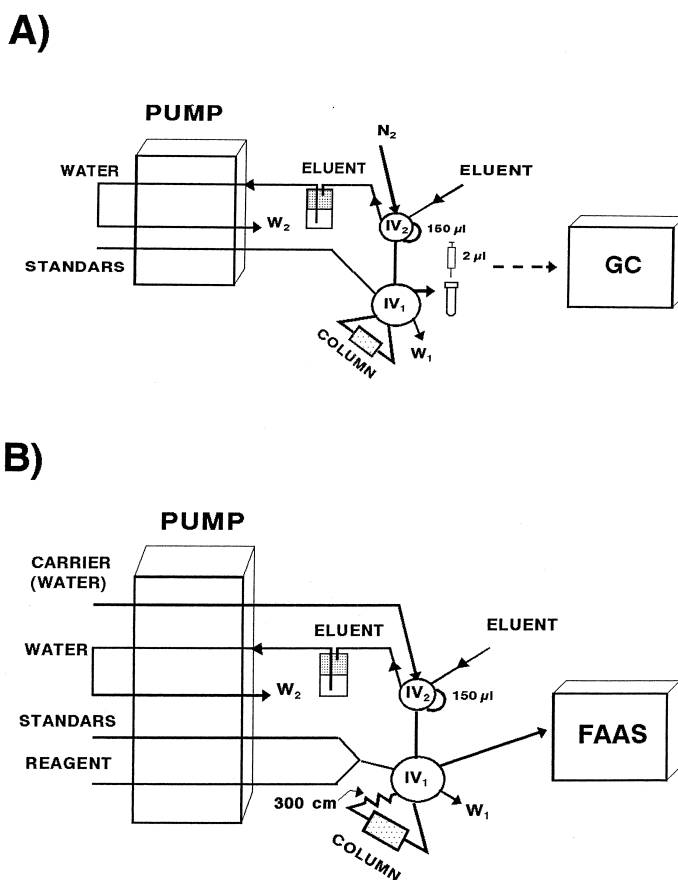
A)

B)

Fig. 1. Flow injection manifolds for on-line adsorption of organic (A) and organometallic (B) compounds. IV, injection valve; W, waste; GC, gas chromatograph (flame ionization detection); FAAS, flame atomic absorption spectrometer.

long) and then adsorbed on the sorbent column, located in the loop of the injection valve (IV_1). In this step, a water carrier was pumped at 4.0 ml/min to the atomic absorption spectrometer in order to flush the nebulizer after each measurement. In the elution step, both injection valves were switched simultaneously, so 150 μl of *n*-hexane (eluent) was injected into the water carrier and passed through the sorbent to desorb the complex/chelate and transfer it to the nebulizer of the atomic absorption spectrometer. A blank consisting of 150 μl of *n*-hexane was injected prior to preconcentration ($A\approx0.030$ units). Peak height was used as the atomic measurement.

3. Results and discussion

Fig. 1 depicts the manifolds used to determine the

analytical potential of C_{60} fullerene as sorbent for organic and organometallic compounds. The adsorption efficiency of fullerene was studied by analyzing four groups of organic compounds, namely: *N*-methylcarbamates and their hydrolysis products, phenols, PAHs and amines. The organometallic compounds assayed were two metalocenes and two organoleads. A column containing 80 mg of C_{60} fullerene was used in all experiments.

3.1. N-Methylcarbamates and their hydrolysis products

Chemical parameters influencing the determination of two carbamates (carbaryl and propoxur) and their hydrolysis products (1-naphthol and 2-isopropoxyphenol) were optimized using volumes of 10 ml of aqueous standards containing 25–300 ng/ml of both

pesticides and phenols. Pesticides exhibited a narrower linear pH range (3–4) owing to their hydrolysis to phenols; however, phenols (1-naphthol and 2-isopropoxyphenol) exhibited linear responses between 1 and 11. Different eluents (ethyl acetate, acetone, methanol, ethanol, *n*-hexane and toluene) were assayed, the most efficient being ethyl acetate (150 μl). The sorption efficiency was determined by using an aqueous standard solution containing 20 μg/ml of each of the four analytes and extracting the spiked sample (signals of 100% recovery) and the eluate from the column, with the same volume of ethyl acetate manually. The results are listed in Table 1; the sorption efficiency ($n=5$) was lower than 63% in all cases and similar for each carbamate and its corresponding phenols. In order to increase it, various surfactants (cationic, anionic and non-ionic) were spiked to the aqueous sample (pH 3) at concentrations of 10^{-3} mol/l and the above described experiments were repeated. It can be concluded that the addition of surfactants to the aqueous sample does not favor the adsorption of these compounds on C_{60} fullerene; on the contrary, it hinders it

Table 1
Sorption efficiency of organic compounds on C_{60} fullerene material

Compound	Sorption efficiency (%)
N-Methylcarbamates	
Carbaryl	57.6
Propoxur	60.2
N-Methylcarbamate phenols	
1-Naphthol	59.3
2-Isopropoxyphenol	62.6
Phenols	
Phenol	10.2
3,4-Dimethylphenol	48.3
2-*tert.*-Butylphenol	54.6
4-Chlorophenol	45.4
PAHs	
Naphthalene	22.1
Phenanthrene	37.4
Anthracene	42.3
Perylene	62.7
Amines	
Methylethylenediamine	10.2
Aniline	14.0
1,2-Phenylenediamine	27.9

– particularly cationic and non-ionic surfactants – the effect being more pronounced for pesticides than for phenols. A comparative study under the same chemical and flow conditions showed RP-C_{18} and C_{60} fullerene to have a similar adsorption efficiency, and the adsorption to be quantitative (ca. 100%) with XAD-2. This is the likely result of adsorption on XAD-2 resin taking place via hydrophobic surface and π-electron interactions [5]; on the other hand, adsorption on fullerene take places largely via π-electron interactions [29].

3.2. Phenolic compounds

Four phenols (phenol, 3,4-dimethylphenol, 2-*tert.*-butylphenol and 4-chlorophenol) were selected to study their adsorption capacity on C_{60}. Firstly the sample pH was studied over the range 1–11 using 10 ml of aqueous solution spiked with 100 ng/ml of analytes. The chromatographic areas obtained at a variable pH are shown in Fig. 2, which also compares the results with those provided by XAD-2 as sorbent and ethyl acetate as eluent. The optimal pH range was wider with C_{60} (1–9.5) than with XAD-2 (1–6.5); however, the signal obtained with C_{60} was lower as the likely result of its lower sorption efficiency for these compounds. Ethyl acetate (150 μl) was the best eluent for phenols. As can be seen from Table 1, the sorption efficiency for phenol compounds was lower than 55% at best. On the other hand, XAD-2 adsorbed all the phenols quantitatively (ca. 100%) – phenol excepted, with ca. 20%. The lower retention of phenols on C_{60} fullerene can be ascribed, as in other carbon sorbents, to its lack of interaction with solutes containing polar functional groups and to dispersion interactions governing its retention behavior [7].

3.3. Poycyclic aromatic hydrocarbons

Four representative PAHs, viz. naphthalene, phenanthrene, anthracene and perylene were used to examine the ability of C_{60} to adsorb this type of organic compounds. The method was optimized similarly to the previous ones and also the manifold of Fig. 1A was used. The sample solution, containing 100 ng/ml of PAHs, was initially prepared in distilled water; however, the low solubility of PAHs in water results in their adsorption on the manifold
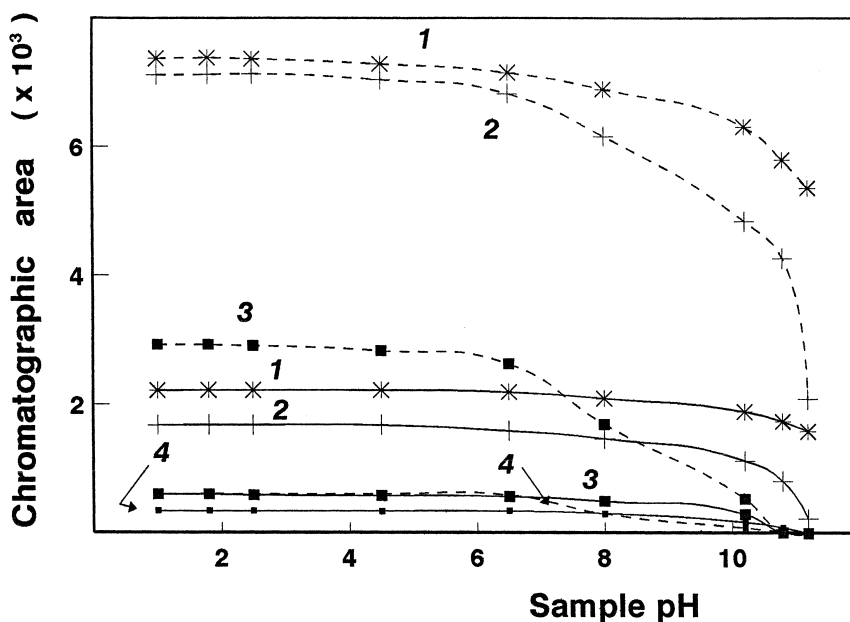
Fig. 2. Influence of the sample pH on the adsorption of phenols on XAD-2 (dashed line) and C_{60} fullerene (solid line) using the flow system of Fig. 1A: 1=2-*tert.*-butylphenol; 2=3,4-dimethylphenol; 3=4-chlorophenol; 4=phenol. Sample=10 ml of aqueous solution containing 100 ng/ml of each phenol compound.

tubes, as confirmed by the fact that toluene passed through PTFE tubing through which PAH solutions had been circulated eventually contained the PAHs. To avoid this pitfall, the aqueous standards of PAHs (100 ng/ml) were prepared in $3\cdot10^{-3}$ mol/l Triton X-100. The pH had no effect on the adsorption of PAHs on C_{60} fullerene over the range studied (1–10). Of the solvents assayed as eluents (methanol, ethanol, acetone, ethyl acetate, *n*-hexane and toluene), the best was found to be toluene, which resulted in chromatographic signals for the PAHs twice as high as those obtained with the other solvents. The sorption efficiency (Table 1) increased with increasing number of aromatic rings; however, it never exceeded 63%. XAD-2 and RP-C$_{18}$ provided recoveries of 60–90%. Fullerene is not a good sorbent for typical benzene compounds. PAHs in water are usually preconcentrated on polyurethane foam, which acts via three mechanisms, namely: hydrophobic effect, π-electron interactions and hydrogen bonding [5]. The adsorption of PAHs on fullerenes possibly takes place via π-electron interactions, which increase in strength with increase in the number of aromatic rings. Thus, perylene donates

electrons more readily easier than does naphthalene, so the former is more efficiently adsorbed on C_{60} (an electron acceptor).

3.4. Amines

The sorption on C_{60} fullerene of three amines (1,2-phenylenediamine, methylethylenediamine and aniline) was studied by using the flow injection (FI) system depicted in Fig. 1A. The method was optimized similarly to the previous ones. For this purpose, an aqueous solution containing the three amines (200 ng/ml each) was passed through the sorbent column, ethyl acetate being used as eluent. An exhaustive study of the sorption efficiency at variable pH in the presence of different surfactants was conducted; at best, however, the sorption never reached 30% (see Table 1).

3.5. Metalocenes: ferrocene and cobaltocene

C_{60} fullerene forms superconducting complexes by doping with an organic molecular ferromagnetic complex. Thus, structural stabilization through inter-

molecular interaction with no formal charge transfer between C_{60} and ferrocene complexes has been reported; the weak ferrocene–C_{60} charge transfer complex has a triclinic structure comprising eight ferrocene molecules [29,30]. Examples of the potential of C_{60} fullerene as a sorbent for ferrocene and cobaltocene (two parallel cyclopentane rings with a central Fe or Co atom located midway between the rings) are discussed below.

Preliminary adsorption experiments were conducted by aspirating 10 ml of ferrocene solution at different concentrations (1–5 μg/ml, expressed as iron concentration) and pH values (1–5) through a C_{60} fullerene column; the atomic signal for iron was recorded before and after passing the sample through the column. Similar signals were obtained in both cases, which suggests that ferrocene is not adsorbed on C_{60}. The 18 electrons available in ferrocene (10 from the two cyclopentadienyl ligands and 8 from the iron atom) make it rather inert and thus hinder adsorption on it. However, ferricenium ion is electron-deficient and introduces additional ligands that can contribute more electrons in order to complete the ''effective atomic number''. Thus, it has been suggested that ferricenium ion forms complexes with various anions in solution [31]. In order to test fullerene as sorbent for the preconcentration of ferrocene, this compound was oxidized to ferricenium ion and then complexed with various reagents. For this purpose, different oxidants [nitric acid, hydrogen peroxide and Ce(IV)] at concentrations of $2\cdot10^{-2}$ mol/l were assayed. The best oxidant was found to be Ce(IV), the action of which on ferrocene was instantaneous (hydrogen peroxide and nitric acid required 1 h and 8 h, respectively); also, the stability of the ferricenium ion was preserved for 15 days, as visually observed visually from its blue color. The ferricenium ion solution was prepared by mixing a solution containing 300 μg/ml ferrocene (corresponding to 90 μg/ml metal iron) and 10^{-3} mol/l (optimal amount) Ce(IV) in 60% ethanol. The flow system depicted in Fig. 1B was employed and 0.1% APDC was used to form a complex with ferricenium ion in it. Volumes of 150 μl of organic solvents [methanol, ethanol, acetone, isobutyl methyl ketone (IBMK) and *n*-hexane] were assayed as eluents and the best results (difference between the sample and blank signals) were provided

by *n*-hexane; the iron signal was 3- and 4.5-times higher than those in acetone and IBMK, respectively. In addition, the blank signal (150 μl of *n*-hexane) was low ($A\approx0.030$ units) and no dispersion occurred during transfer to the detector because *n*-hexane is immiscible with water. Negative results were obtained with both alcohols. Because PDC probably acted as counterion for ferricenium ion, two anionic species (sodium dodecyl sulfate, SDS; and ammonium perchlorate), at different concentrations, were assayed. The presence of the counterion favored adsorption (no signal was obtained in its absence); however, the signal decreased by a factor of 4 and 5 times with SDS and perchlorate, respectively, relative to PDC. Finally, NaDDC was also compared with PDC, but the adsorption/elution process exhibited lower efficiency (ca. 50%).

Once PDC was selected as the complexing reagent, the next step was to optimize the chemical and flow variables influencing the performance of the method. The atomic signal for iron decreased dramatically above pH 3, so aqueous solutions of ferricenium cation were prepared in 10^{-2} mol/l HNO_3 (pH 2). PDC concentrations above 0.02% were optimal, so 0.05% ($3\cdot10^{-3}$ mol/l PDC) was chosen for subsequent experiments. In order to ensure that the ferricenium–PDC complex would be formed and sorbed under the required conditions and that no Fe–PDC chelate would be formed by decomposition of organometallic compounds to iron cation, the ferricenium cation stream was replaced with a standard solution of iron (III) at pH 2. The Fe–PDC chelate was adsorbed, but slightly eluted with *n*-hexane (ca. 15%) and completely with IBMK. Therefore, the ferricenium–PDC complex was actually formed, sorbed on C_{60} and eluted with *n*-hexane.

The influence of the sample and reagent flow-rates on the adsorption of the ferricenium–PDC complex was examined at a constant sample volume of 5 ml. A sample flow-rate of 1.5 ml/min and a reagent flow-rate of 0.3 ml/min provided maximum adsorption efficiency. The optimum length of the preconcentration coil ranged from 250 to 450 cm (0.5 mm I.D.); a length of 300 cm was used throughout. The elution efficiency increased with increasing injected eluent volume up to 100 μl, above which the complex was eluted without carryover. At volumes higher than 200 μl, the atomic

signal decreased through dispersion of the eluted complex in the organic solvent; the volume of eluent finally selected was 150 μl. The aqueous flow-rate (eluent carrier) was found to affect the peak height up to 4.0 ml/min by increasing the nebulizer efficiency. A carrier flow-rate of 4.0 ml/min was adopted.

A comparative study under the same chemical and flow conditions was made with different sorbents (C_{60}, RP-C_{18}, activated carbon, XAD-2, silica gel 100 and Florisil), using columns packed with 80 mg of sorbent material in all instances. Several calibration graphs for each sorbent were constructed by using 5 ml of sample containing a ferricenium cation concentration between 20 and 500 ng/ml with the proposed FI method and from 1 to 5 μg/ml with direct aspiration (both are expressed as iron concentrations). Preconcentration factors were calculated by dividing the slope of the calibration graph (FI method) into that obtained with direct aspiration; the values thus obtained were 50, 30, 25, 20 and 15 for C_{60} fullerene, RP-C_{18}, silica gel 100, Florisil and activated carbon, respectively. Obviously, the highest sorption efficiency was obtained with fullerene, consistent with previous results for PDC–metal complexes [26]; the preconcentration factor of 50 was greater than the volume ratio (sample volume/ eluent volume=ca. 35) by virtue of the effect of the organic solvent on the atomization efficiency. The detection limit was calculated as three-times the standard deviation of the peak absorbance for 15 injections of 150 μl of *n*-hexane (blank). The precision was checked on 11 standard solutions containing 30 ng/ml ferricenium cation. The analytical features of the proposed FI method based on C_{60} fullerene are summarized in Table 2.

The following study involved cobaltocene. All metalocenes are oxidized easier than that ferrocene. This organometallic compound is soluble at concentrations of 300 μg/ml in water, so its oxidation to cobalticenium cation in this medium was examined. The best conditions for oxidizing cobaltocene were provided by a solution containing 300 μg/ml in 10^{-3} mol/l Ce(IV). The adsorption of cobaltocene on C_{60} fullerene was investigated by using the FI system of Fig. 1B; which was optimized similarly to that for ferrocene. The sample solution, containing 260 ng/ml cobalticenium cation (corresponding to 80 ng/ml cobalt cation), was mixed with PDC as reagent. Adsorption of the complex peaked at a low sample pH (below pH 3). A 10^{-2} mol/l nitric acid concentration was used to prepare the cobalticenium solutions (pH 2). The effect of the PDC concentration was similar to that on the ferrocene determination, so a concentration of $3 \cdot 10^{-3}$ mol/l was selected as optimal. *n*-Hexane proved the best eluent and was used in a volume of 150 μl. Flow variables were set at values similar those for ferrocene, so the same FI system was employed. As expected, the best sorbent material was C_{60} fullerene. Preconcentration factors for 5 ml of sample (calculated as the ratios of the slopes of the calibration graphs obtained by using the FI method and direct aspiration of cobalticenium ion) were 45, 27, 22, 10 and 8 for C_{60} fullerene, RP-C_{18}, silica gel 100, Florisil and activated carbon, respectively. Other analytical parameter values are listed in Table 2.

3.6. Organolead compounds

For this study, the FI system depicted in Fig. 1B was used. The sample solution, containing trimethyl- or triethyllead at concentrations equivalent to 100 ng/ml Pb, was prepared from a 1 mg/ml stock

Table 2
Figures of merit of the calibration graphs for the determination of organometallic compounds

Compound	Regression equation[a]	Range (ng/ml)	Detection limit (ng/ml)	RSD (%)	Preconcentration factor[b]
Ferrocene	$A=2.0 \cdot 10^{-3}+1.2 \cdot 10^{-3}x$	10–175	5	2.4	50
Cobaltocene	$A=-1.0 \cdot 10^{-3}+1.0 \cdot 10^{-3}x$	15–200	8	2.7	45
Trimethyllead	$A=2.0 \cdot 10^{-3}+0.35 \cdot 10^{-3}x$	35–550	15	2.9	20
Triethyllead	$A=-1.0 \cdot 10^{-3}+0.63 \cdot 10^{-3}x$	20–300	10	3.0	40

[a] *A*, Absorbance; *x*, in ng/ml metal.
[b] For 5 ml of sample.

solution. Two chelating reagents, viz. PDC and DDC, and two counterions [(A) SDS and ammonium perchlorate] were assayed. Formation of the (trimethyl or triethyl)lead-A ion pair was unfavorable under conditions assayed (sample pH 3 and reagent concentration $3 \cdot 10^{-3}$ mol/l). We thus chose to obtain chelates for organolead species. An exhaustive study of adsorption and elution of the chelates (using DDC and PDC) was conducted with both organometallic compounds. Adsorption experiments were done by aspirating aqueous solutions of trimethyl and triethyllead containing 2 μg/ml of lead at different pH values (1, 3 and 5), and mixing them with a stream of chelating reagent at a concentration of $3 \cdot 10^{-3}$ mol/l. The lead content was determined in the solution mixture before (total content) and after (unsorbed content) passage through the C_{60} column. Both organometallic compounds form strong complexes with PDC and DDC that are completely adsorbed on the column. The next step was to examine the elution of each chelate adsorbed; because lead was determined in the eluted fraction (150 μl, see Fig. 1B), the concentration of each organometallic compound in the sample was reduced to 100 ng/ml Pb in order to ensure quantitative measurements. On the assumption of 100% adsorption, the elution efficiency was assessed with IBMK and *n*-hexane as eluents (other solvents were discarded owing their miscibility with the water carrier stream). PDC as reagent and IBMK as eluent (150 μl) provided unsatisfactory results for both organometallic compounds; on the other hand, the chelate of triethyllead was completely eluted, but that of trimethyllead compound was only partly eluted by *n*-hexane. With DDC as chelating reagent, both chelates were quantitatively eluted by *n*-hexane. On the other hand, the chelate of inorganic lead (II)–DDC was completely sorbed on C_{60} and eluted with IBMK but only ca. 60% with *n*-hexane. Therefore, DDC and *n*-hexane were selected as reagent and eluent, respectively.

The effect of pH on the chelate adsorption for a concentration of organolead of 100 ng/ml Pb was studied over the range 1–11. A wide linear pH range (1–6.5) was obtained with both compounds because the chelate formation prevailed over DDC protonation as the likely result of a high adsorption constant for the fullerene [26]. In order to simplify the

operating procedure, solutions of both organolead compounds in ultrapure water at pH ca. 4 were used. The influence of the DDC concentration was examined over the range $6 \cdot 10^{-5}$–$6 \cdot 10^{-3}$ mol/l. Concentrations above 10^{-3} mol/l were required to ensure increased analytical signals, so a solution of $3 \cdot 10^{-3}$ mol/l was selected. The influence of flow variables was examined and no significant difference from metalocenes was observed, so the same FI system was adopted. The figures of merit of the calibration graphs obtained are listed in Table 2. The adsorption capacity of C_{60} fullerene for both organometallic compounds was compared with those of conventional sorbents. The procedure was done similar to that used in the previous method for metalocenes. The preconcentration factors for organolead compounds were better for C_{60} than that for the conventional sorbents (viz. RP-C_{18}, silica gel 100, Florisil and activated carbon).

4. Conclusions

C_{60} fullerenes have limited application as sorbents for organic compounds from aqueous solutions. The adsorption efficiency decreases with increasing polarity of the organic compound, consistent with the adsorption mechanism assigned to fullerenes (primary via π-electron interactions); in addition, with solutes containing polar groups, dispersion prevails over retention. Comparison with previous studies about sorption of nonpolar vapors on fullerene [24,25], is no an easy task because both the media (aqueous solution) and the analytes are different. Thus, in those studies, sorption is driven primarily by dispersion interactions but interactions of fullerene–water cannot be established.

Sandwich compounds (metalocenes) are stable to hydrolysis but can be oxidized to cations. In the form of cations, they can form complexes with ligands that favor their adsorption. Under these conditions, metalocenes–PDC complexes are quantitatively adsorbed on C_{60} fullerenes. The ionic trialkyllead compounds were found to behave similarly to inorganic Pb(II), so formation of chelates was necessary prior to their adsorption on C_{60}. In summary, C_{60} fullerenes possess a high analytical potential for preconcentrating organometals and is superior to

conventional solid materials, such as RP-C$_{18}$, silica gel 100, Florisil and activated carbon for this purpose.

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