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## Poly(methyloctadecylsiloxane) immobilized on silica by $\gamma$ radiation for use in solid-phase extraction

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### Abstract

This work presents a fast, easy and effective procedure to obtain silica-based  $C_{18}$  type sorbents for use in solid-phase extraction (SPE). The solid-phase was made by depositing a polymer, poly(methyloctadecylsiloxane) (PMODS), on the silica support followed by immobilization using  $\gamma$  irradiation. The method presents an application of green chemistry in the analytical laboratory, since there are no toxic residues after the synthesis. Water samples spiked with a mixture of pesticides (benomyl, tebuthiuron, diuron, simazine, atrazine and ametryn) were extracted in the off-line mode in order to evaluate the performance of this sorbent. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Solid-phase extraction; Sorbents; Gamma irradiation; Poly(methyloctadecylsiloxane); Pesticides

### 1. Introduction

Solid-phase extraction (SPE) is the most popular technique used in sample pre-treatment prior to analysis by high-performance liquid chromatography (HPLC) and gas chromatography (GC). It is used for both environmental [1] and biological [2] analysis. SPE has many advantages over traditional liquid-liquid extraction, such as use of less organic solvent, ease of automation and need for less time and money. It is a multistage rather than a single-stage process; organic compounds undergo multiple equilibrations, leading to good extractions [3]. SPE is used mainly for the following purposes: removal of interferences; preconcentration; sample storage and transport. Bonded phases with  $C_{18}$  on silica are the most used sorbents in SPE. Over the years, or-

ganochlorosilanes and organoalkoxysilanes have been used as sililating agents for the preparation of bonded phases [4]. The stability of the  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  bonds formed between the sililating agents and the hydroxyl groups on the silica surface is the main advantage of these reagents [5]. On the other hand, this method has some limitations, such as: high reagent cost, time consuming procedure, use of toxic solvents and reagents, need to an inert atmosphere and high temperature. A promising alternative method is substitution of the chemical reaction by depositing a polymer on the support and immobilizing using  $\gamma$  irradiation, as has been reported for several HPLC stationary phases, such as, poly(methyloctadecylsiloxane) (PMOS) on zirconized silica [6,7], titanium-grafted silica [8] and pure silica [9]. The main advantages of this procedure are good performance, lower cost, simplicity and reduction of toxic residues. In addition, this method includes the ability to promote reproducible changes and permits complete control of temperature, environment and

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additives [6]. Even so, no description was found in the literature using this process to produce sorbents for use in SPE. Thus, this work proposes a procedure to obtain silica-based C<sub>18</sub> type sorbents for use in SPE. This method is an application of “green” chemistry in the analytical laboratory since there is a considerable reduction of toxic residues during and after sorbent preparation. The solid-phases were made by depositing poly(methyloctadecylsiloxane) (PMODS) on irregular silica, immobilization using  $\gamma$  radiation in different doses followed by solvent extraction of excess polymer. The solid-phases were characterized by thermogravimetry, infrared spectroscopy and elemental (carbon) analysis. Water samples spiked with a mixture of pesticides (benomyl, tebuthiuron, diuron, simazine, atrazine and ametryn) were extracted, using the off-line mode, in order to evaluate the performance of these materials.

## 2. Experimental

### 2.1. Chemicals

The following solvents were used in the preparation of the sorbents: *n*-hexane (Mallinckrodt, HPLC-grade), methanol (Mallinckrodt, HPLC-grade) and *n*-pentane (Merck, analytical reagent-grade). Acetonitrile (Tedia, HPLC-grade), water (Milli-Q) and ammonium hydroxide (Synth, reagent-grade) were previously filtered, using a 0.45  $\mu\text{m}$  membrane, to prepare the mobile phase. The pesticide standards atrazine (97.7%), simazine (98.3%) and ametryn (96.8%) were obtained from Novartis, tebuthiuron (99.8%) was kindly donated by Dr Vera Ferracini (EMBRAPA, Brazil) and diuron (99.3%) was obtained from DuPont. The irregular silica was from Fluka; particle size 40–60  $\mu\text{m}$  (200–400 mesh) and pore size 10 nm. PMODS was from Petrarch Silanes and Silicones.

### 2.2. Preparation of C<sub>18</sub> loaded support

The support (silica) was dried at 120°C for 24 h. A sufficient quantity of support (silica) was added to a solution of PMODS dissolved in *n*-pentane to give a material with 40% (w/w) of PMODS, then the mixture was stirred gently for 3 h with magnetic

agitation at room temperature, after which the solvent was evaporated slowly at room temperature.

### 2.3. Irradiation

Two portions of the C<sub>18</sub> loaded support were placed in glass ampoules which were then sealed under air. The sealed samples were irradiated, using an industrial cobalt-60 source (IBRAS-CBO, Campinas, SP, Brazil), to obtain doses of 60 and 80 kGy.

### 2.4. Extraction procedure

After the  $\gamma$  irradiation treatment the materials were placed in a stainless-steel tube. This tube was connected to a Waters 510 pump for extraction of all soluble PMODS by passing approximately 25 ml of *n*-hexane per gram of sorbent, at a flow-rate of 2 ml/min. Then, 15 ml of methanol for each gram of material, were passed through the tube, at a flow-rate of 3 ml/min. To make sure that all soluble residues were removed, an extra extraction step was made using a high-pressure packing pump (Haskel), at 1000 p.s.i. (6.9 MPa), in a proportion of 20 ml of methanol per g of sorbent. After extraction, the solid-phase was removed from the tube and the solvent was evaporated at room temperature.

### 2.5. Solid-phase characterization

Prepared phase was characterized by elemental carbon analysis (using a Perkin-Elmer 240 CHN analyzer), infrared spectroscopy (Perkin-Elmer 1600 FT-IR spectrophotometer) and thermogravimetric analysis (TA Instruments 2050 TGA).

### 2.6. Cartridge preparation

The cartridges for off-line extraction were prepared using 0.5 g of sorbent packed in a 5 ml syringe made of polypropylene. The material was retained by two polyethylene frits (20  $\mu\text{m}$  pore size).

### 2.7. Breakthrough volume

To determine the breakthrough volume, a 20×4 mm trace enrichment column packed with sorbent, an auxiliary pump (Waters 510 model) and a six-port

switching valve coupled to a 1090 M LC system (Hewlett-Packard, Waldbronn, Germany), having a ternary gradient pump, a 25  $\mu$ l injection loop, a diode array detector (DAD) and Pascal WorkStation software was used. The sample was passed through a pre-column containing the prepared phase at a flow-rate of 5.0 ml/min. The pre-column was enriched with different volumes of sample (10, 20, 30, 50, 75, 100, 200, 300 ml) and a curve in which the peak area is plotted against the sample volume was constructed. After enrichment, the valve was turned to chromatographic column position and the separation was carried out. The analysis conditions were as follows: solvent A, 0.01% (v/v) aqueous  $\text{NH}_4\text{OH}$  (v/v) and solvent B, 0.01% (v/v)  $\text{NH}_4\text{OH}$  in acetonitrile. The gradient profile was: 95% A at 0 min, then linearly to 95% B in 20 min. The flow-rate was 1.0 ml/min. Two wavelengths were set, 220 and 252 nm, while absorbance spectra were recorded from 200 to 400 nm. Analytical separations were carried out on a 250 $\times$ 4.0 mm I.D. analytical column packed with 5  $\mu$ m Hypersil octadecylbonded silica.

### 2.8. Off-line extraction of pesticides

The cartridges were conditioned with 10 ml of methanol and equilibrated with 3 ml of Milli-Q water, without allowing the cartridges to dry. Two different volumes of water samples, connected by PTFE tubes to the conditioned cartridges, were passed through the cartridges at a rate of 5–8 ml/min. The cartridges were then suction dried for 10 min. The sample was eluted with 1 ml of methanol. The extract was evaporated to dryness under a gentle nitrogen stream. For HPLC analysis the residue was dissolved in methanol–water (1:1, v/v). For recovery studies, water samples spiked with 0.1, 1.0 and 10  $\mu$ g/l of pesticide were processed. Two replicates of each extraction were carried out.

A commercial SPE cartridge, Supelclean  $\text{C}_{18}$  (0.5 g) was obtained from Supelco.

HPLC separations were performed with a modular system consisting of the following components: Rheodyne model 7125 injector with a 10  $\mu$ l loop, a Waters 600E system controller, a Waters model 484 spectrophotometric detector (used at 235 nm) and a Waters model 746 integrator. The column (150 $\times$ 4.6 mm I.D.) was a Microsorb-MV  $\text{C}_{18}$ , 5  $\mu$ m, and the

guard column (20 $\times$ 2 mm I.D.) was Hypersil  $\text{C}_{18}$ , 5  $\mu$ m.

## 3. Results and discussion

### 3.1. Characterization of $\gamma$ -irradiated PMODS-loaded silica

Thermogravimetric analysis shows a % (w/w) decrease around 220 $^\circ\text{C}$ , which can be attributed to degradation of the polymer immobilized onto the silica. However, good thermal stability of these materials, in the temperature range generally used for extraction, is observed. A decrease in mass around 100 $^\circ\text{C}$  can be attributed to loss of adsorbed water.

Infrared spectra of the support (silica) and of the sorbents (60 and 80 kGy) were obtained. After depositing the polymer onto silica, immobilization and extraction of the excess of PMODS, the following main characteristic bands were observed: 975  $\text{cm}^{-1}$  due to silanols, and 2900  $\text{cm}^{-1}$  due to the PMODS, implying that the polymer was incorporated onto the support even after extraction with strong solvents such as *n*-hexane.

Table 1 shows the results of the characterization tests, by elemental carbon, of the solid-phases, obtained after immobilization of polymer, at two different doses (60 and 80 kGy), and after extraction of the excess polymer. The results were compared with some commercial sorbents. For commercial sorbents, the %C ranged from 10 to 17% and for the sorbents obtained in this work the value was 12%. Thus, the proposed method to obtain PMODS-loaded silica immobilized by gamma irradiation produces %C similar to the commercial sorbents, with the advantage of being a much easier, cheaper, less time consuming process, which uses less toxic solvent than the traditional methods (chemical reaction) [10].

### 3.2. Test of the performance of the $\text{C}_{18}$ sorbents

#### 3.2.1. Breakthrough volume

The breakthrough volume,  $V_b$ , represents the maximum sample volume which can be applied with a theoretical 100% recovery and this measurement can be used for predictions and comparisons among several solid-phases as well. However, the maximum

Table 1

Characteristics of the commercially available C<sub>18</sub> sorbents and the sorbents obtained by immobilization of PMODS onto silica using gamma irradiation

Commercial name	Company	Type of bonding	% C	End-capped	Pore size (nm)	Particle size (μm)
Supelclean LC-18	Supelco	–Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>18</sub> H <sub>37</sub> (monofunctional silane)	10	Yes	6	40–45
Bond Elut	Varian	–SiC <sub>18</sub> H <sub>37</sub> (trifunctional silane)	17	Yes	6	40–120
Sep-Pak C <sub>18</sub>	Waters	–Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>18</sub> H <sub>37</sub> (monofunctional silane)	12	Yes	13	55–105
Sep-Pak μC <sub>18</sub>	Waters	–SiC <sub>18</sub> H <sub>37</sub> (trifunctional silane)	17	Yes	13	37–55
Sorbents from this work						
C <sub>18</sub> (dose 60 kGy)			12	No	10	40–63
C <sub>18</sub> (dose 80 kGy)			12	No	10	40–63

amount that can be extracted corresponds to the application of a volume equal to  $V_b$ , but with a corresponding recovery lower than 100% [11]. Determination of the breakthrough volume is a major optimization step in the development of any analytical method using SPE. Measurement of breakthrough volume can be performed by monitoring continuously or discretely the UV signal at the outlet of a pre-column or cartridge. However, these methods are laborious and time-consuming and relatively high (mg/l) concentrations should be used, which do not reflect real-life situations [11]. Another method has been used for estimating  $V_b$  values, where various sample volumes are spiked with the analytes and curves in which the peak areas are plotted against the sample volume are constructed [12]. The point where the curve deviates from linearity is considered to indicate the breakthrough. Due to the advantages of this method, including that the  $V_b$  for several analytes can be measured simultaneously, under real experimental conditions, this method was used for determining the  $V_b$  of the six pesticides under study, in order to test the performance of the

new solid-phases. Table 2 shows the estimated breakthrough volume for benomyl, tebuthiuron, simazine, atrazine, diuron and ametryn.

According to Table 2, benomyl has the lowest  $V_b$ , due to its high polarity. A 200 ml sample volume, with each pesticide at 0.5 μg/l, was shown to be suitable for enrichment of all the other pesticides.

### 3.2.2. Water analyses using off-line extraction

The selected herbicides include three classes of pesticides widely used in Brazil. These pesticides have the potential to contaminate drinking water since they are soluble in water. The main concern in pesticide residue analysis is to reach detection limits as low as 0.1 μg/l, which is the maximum residue limit for drinking water [13]. SPE using C<sub>18</sub> is a sample preparation technique used to preconcentrate triazine and phenylurea pesticides in water [14]. Thus, cartridges packed with the sorbents prepared in this study were used to preconcentrate the selected pesticides. Three different concentrations (10, 1.0 and 0.1 μg/l) of each pesticide were spiked in samples of ultra pure water in order to calculate the

Table 2

Estimated breakthrough volumes ( $V_b$ ) of six pesticides at a concentration 0.5 μg/l in drinking water

Dose (kGy)	$V_b$ (ml)					
	Benomyl	Tebuthiuron	Simazine	Atrazine	Diuron	Ametryn
60	75	>300	200	200	200	>300
80	100	>300	200	>300	>300	>300

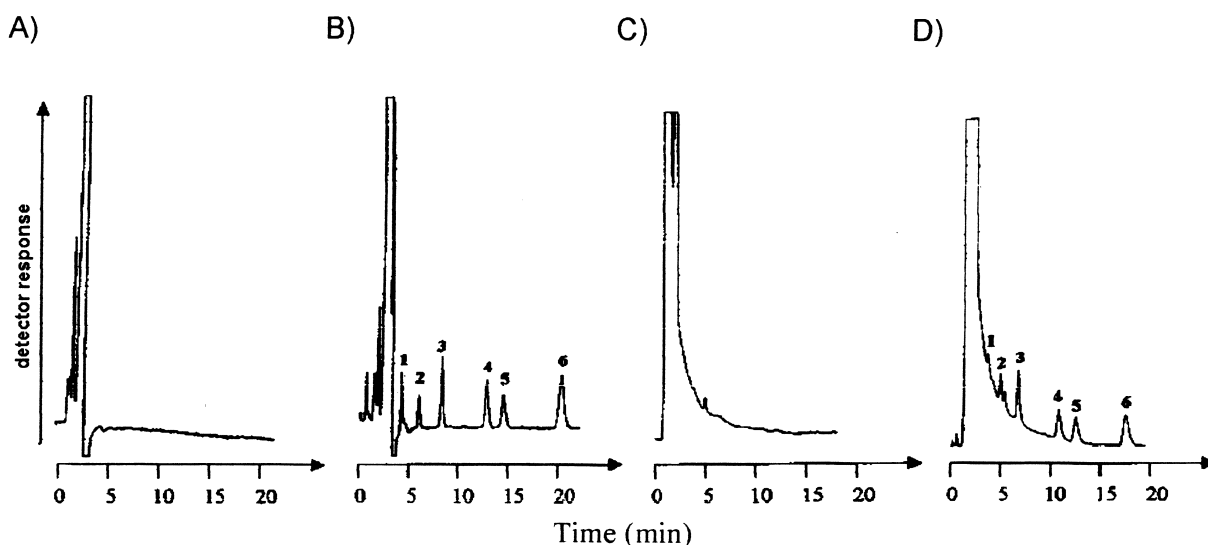


Fig. 1. Chromatograms obtained for a water sample spiked with pesticides. (A) Blank Milli-Q water, (B) spiked Milli-Q water, (C) blank tap water, (D) spiked tap water. 1=benomyl, 2=tebuthiuron, 3=simazine, 4=atrazine, 5=diuron, 6=ametryn. Chromatographic conditions: C<sub>18</sub> Microsorb-MV HPLC column, 150×4.6 mm I.D. Mobile phase: acetonitrile–water–NH<sub>4</sub>OH (40:60:0.1, v/v/v), isocratic elution. Spectrophotometric detection at 235 nm.

recovery for the extractions. Fig. 1 shows the chromatograms corresponding to unspiked samples and the same sample spiked with 0.1 µg/l of the pesticide standards, obtained after the preconcentration step. Tap water presented a broad peak at the beginning of the chromatogram, due to humic and fulvic acids present in this type of sample, interfering with the integration of the benomyl and tebuthiuron peaks. Thus, it is necessary to optimize the chromatographic separation, and a clean-up step could be used prior the elution of the sample from the

cartridge to decrease the peak from humic and fulvic acids. However, suitable recoveries and resolution for these peaks, by on-line preconcentration, have been obtained and these results, including method validation, will be presented in a future publication. The recovery values were calculated only for Milli-Q water spiked with the standards. Table 3 shows these results for the recoveries. Good results were obtained with sorbents prepared with radiation doses of both 60 and 80 kGy. Recoveries ranged from 73 to 103% and RSD<16% were obtained, using cartridges with

Table 3

Recoveries for Milli-Q water, in %, of tested pesticides using off-line SPE cartridges with PMODS on silica immobilized by  $\gamma$  irradiation at 60 kGy dose ( $n=2$ ) and 80 kGy dose ( $n=2$ )

Pesticide	Recovery (%)						Supelclean LC-18 0.1 µg/l <sup>a</sup>
	Dose: 60 kGy			Dose: 80 kGy			
	0.1 µg/l <sup>a</sup>	1 µg/l <sup>a</sup>	10 µg/l <sup>b</sup>	0.1 µg/l <sup>a</sup>	1 µg/l <sup>a</sup>	10 µg/l <sup>b</sup>	
Benomyl	81±11	76±12	99±4	89±1	73±10	96±4	79±2
Tebuthiuron	103±3	97±3	90±5	101±8	97±14	86±6	78±5
Simazine	84±12	101±2	94±8	86±0	85±9	95±3	78±9
Atrazine	96±10	94±2	98±1	85±3	88±3	103±3	74±4
Diuron	91±1	97±1	95±4	94±6	80±5	103±3	79±1
Ametryn	82±8	101±1	94±8	93±3	96±2	102±1	76±4

<sup>a</sup> Sample volume=200 ml.

<sup>b</sup> Sample volume=20 ml.

0.5 g of sorbent and sample volumes of 20 ml (10  $\mu\text{g}/\text{l}$ ) and 200 ml (0.1  $\mu\text{g}/\text{l}$  and 1  $\mu\text{g}/\text{l}$ ). A Supelclean C<sub>18</sub> (Supelco), 0.5 g, was used for sample enrichment in order to compare the results (recoveries ranged from 74 to 79%).

#### 4. Conclusions

This work presents a fast, easy and effective procedure to obtain silica-based C<sub>18</sub>-type sorbents for use in SPE.

The breakthrough volumes were estimated and water samples spiked with a mixture of pesticides (benomyl, tebuthiuron, diuron, simazine, atrazine and ametryn) were extracted in the off-line mode in order to test the performance of these sorbents. Good recoveries were obtained with both immobilized sorbents (60 and 80 kGy), which can be attributed to PMODS chain cross-linking, giving solid-phases with excellent retention for these pesticides. The main advantages of this procedure are good performance, lower cost, simplicity and reduction of toxic residues.

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