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Assessment of polycrystalline graphites as sorbents for solid-phase microextraction of nonionic surfactants

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Abstract

Two polycrystalline graphites (pencil lead and glassy carbon) were used as sorbents for solid-phase microextraction of a nonionic alkylphenol ethoxylate surfactant (Triton X-100). Analyses were performed by reversed-phase HPLC-fluorescence detection. The presence of the benzene ring in the congeners of Triton X-100 also allowed their direct detection at $\lambda_{ex}=230$ nm and $\lambda_{em}=310$ nm. Variables such as time of adsorption, time of desorption and concentration of surfactant in water were evaluated. The method limit of detection was found to be 0.5 μg/l for Triton X-100, with a linear dynamic range of 0.5–150 μg/l. Results were compared to those obtained using polymeric fibers such as PDMS/DVB and Carbowax/TPR. The chemical resistance and low cost of the polycrystalline graphites are advantageous over commercially available SPME fibers.

Keywords: Sorbents; Graphite; Glassy carbon; Pencil lead; Surfactants

1. Introduction

Solid phase microextraction (SPME) has been introduced in sample preparation as a solvent-free and easy to use technique. The development of new fibers has increased its scope not only in analysis by gas chromatography (SPME-GC) but also by capillary electrophoresis (SPME-CE) [1] and high-performance liquid chromatography (SPME-HPLC) [1,2,3,4]. However, use of HPLC has been limited due to the poor chemical resistance of commercially available fibers, carryover of the analyte from one analysis to the next, and stripping of the coating. Therefore a new solid phase is required, and graphite could be a suitable candidate since it provides a high surface area, high adsorption capacity and most importantly high chemical resistance.

The use of pencil leads as sorbents for SPME-GC analysis was first reported for the analysis of lindane, methyl parathion and 2-chlorophenol [5]. The authors achieved detection limits of parts per trillion, but carryover from one analysis to the next was reported. A different approach consisting of electrodeposition of diamines onto the pencil leads followed by GC analysis with detection limits of the order of parts per billion was reported by Conte et al. [6].

Glassy carbon has been mainly used as a material for working electrodes in electrochemistry. Because of its mechanical and chemical stability, as well as its high surface area, it has been used as a stationary

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phase for HPLC [7] and SFC [8,9]. Glassy carbons are polycrystalline graphites, and are obtained by carbonization of polymeric materials, polyacrylonitrile being the most commonly used. The polycrystalline products are aggregates of graphite crystallites which vary in size, orientation, degree of porosity and purity. As a consequence, their properties vary widely. For instance, their density may vary from 2.26 g/cm^3 for graphite to 1.54 g/cm^3 for glassy carbon.

Functional groups such as hydroxyl, carboxyl, and carbonyl have been reported present on the surface of graphite [10], carbon black [11] and glassy carbon [12]. The presence of such groups allows further modification of the surface via esterification or amidation. Reported modifications of the surface of glassy carbon include covalent attachment of groups such as alcohols [13], phenyl substituents [14], alkanes [15] and coating with polymeric materials such as polyethylene imine [7].

To the best of our knowledge, glassy carbon has not been used for SPME/HPLC. The aim of this work was to develop and study the applicability of two polycrystalline graphites (pencil lead and glassy carbon rod) as sorbents for SPME of a nonionic surfactant. Among the nonionic surfactant, alkylphenol ethoxylates (represented by Triton X-100) are the most important and extensively used. The breakdown products are considered more toxic than the parent compound and they have been found in effluents and river water in significant concentrations [16].

2. Experimental

2.1. Polycrystalline graphites

Pencil leads (60×0.5 mm) H grade, were obtained from Pentel (Tokyo, Japan). These were used as received (PLU) or after coating with graphite by carbon evaporative coating (ca. 5 nm thickness) (PLC). Both PLU and PLC were conditioned prior to analysis by immersion in acetone for 1 h. The geometrical surface area of these rods was 15.9 mm^2 per cm of length.

Glassy carbon rods (50×1 mm, Type 2) were obtained from Alfa ÆSAR (Ward Hill, MA, USA). They were used as received (GCU), or after a light polishing between extractions with 1000 grit sandpaper followed by sonication in deionized water for 10 min (GCP). Both were cleaned by immersion in acetone for 20 min. The geometrical surface area of the glassy carbon rods was 32.2 mm^2 per cm length.

2.2. SPME fibers

SPME fibers, 60 μm Polydimethylsiloxane/divinylbenzene (PDMS/DVB) and 50 μm Carbowax/TPR-100 were obtained from Supelco (Bellefonte, PA, USA). These fibers were conditioned by immersing them in acetonitrile with stirring for 1 h, followed by methanol for 1 h.

2.3. Analytical system

The HPLC system consisted of a Varian (Sunnyvale, CA, USA) model 9050 autosampler connected in series to a six port Valco valve. The sample loop in the valve was replaced by the SPME/HPLC interface (Supelco). A pump was used to deliver methanol into the SPME/HPLC interface for static desorption experiments [4]. The mobile phase was delivered by a gradient pump (Varian model 9010) to a 5 μm ODS-Zorbax column (250 mm×4.6 mm, (Chromatographic Specialties, Brockville, ON, Canada)) and an ODS-Zorbax guard column (4.6 mm×1.25 cm). The mobile phase was composed of 60% A and 40% B. (A: methanol and B: 30:70 water:acetonitrile) at a flow rate of 2.0 ml/min. Detection (Linear Instruments Co. LC 304 fluorescence detector) was done at λ_{ex}=230 nm and λ_{em}= 310 nm. Standard solutions in methanol were automatically injected (20 μl) by means of the autosampler into the HPLC column.

2.4. Reagents

Triton X-100 was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and used as received. All solvents used were Optima grade (Caledon Laboratories, Nepean, ON, Canada). A stock standard solution was prepared in methanol (500 mg/l) and diluted to obtain concentrations in the range of 0.010–10 mg/l, which were used to calibrate the response of the detector. Aqueous model solutions

were prepared by serial dilution from a stock solution containing 100 mg/l of Triton X-100 in deionized water (Milli Q systems, Mississauga, ON, Canada).

2.5. Extraction of Triton X-100

2.5.1. SPME fibers

Six ml aliquots of aqueous solutions with Triton X-100 concentrations from 0.005 to 0.150 mg/l were transferred to 7 ml vials sealed with Teflon lined septa which could be pierced by the needle of the SPME device. The solution was vigorously mixed with a magnetic stirrer, the speed of which was kept constant for all extractions. Extractions were performed at room temperature (23±2°C) for 60 min.

2.5.2. Polycrystalline graphites

Six ml aliquots of aqueous samples containing Triton X-100, at concentration from 0.005 to 0.150 mg/l, were transferred to 7 ml vials without a cap. Pencil lead and GC rods were mounted in a pencil holder allowing at least 4 cm of the rod to be exposed to the environment; however, only 1.0±0.1 cm length of the carbon rod was immersed into the stirred solution. Extractions were performed at room temperature (23±2°C) for 60 min.

2.6. Desorption of Triton X-100

2.6.1. Desorption of Triton X-100 from SPME fibers

The desorption process requires further description of the SPME/HPLC interface. The interface is composed of three parts; a stainless steel body (internal volume of ca. 65 μl) a stainless steel cap and a double tapered ferrule which is placed in between them (Fig. 1a). The design of the interface is such that the coating of the fiber is positioned just below the inlet of the mobile phase. By closing a clamp, the SPME fiber is compressed by the ferrule. The system is then sealed and it can withstand high pressures.

After extraction of the analyte from the aqueous sample, the SPME device was transferred to the interface and the procedure described above was followed. Desorption of Triton X-100 was performed in a dynamic mode in which the fiber was exposed to flowing mobile phase for 2 min.

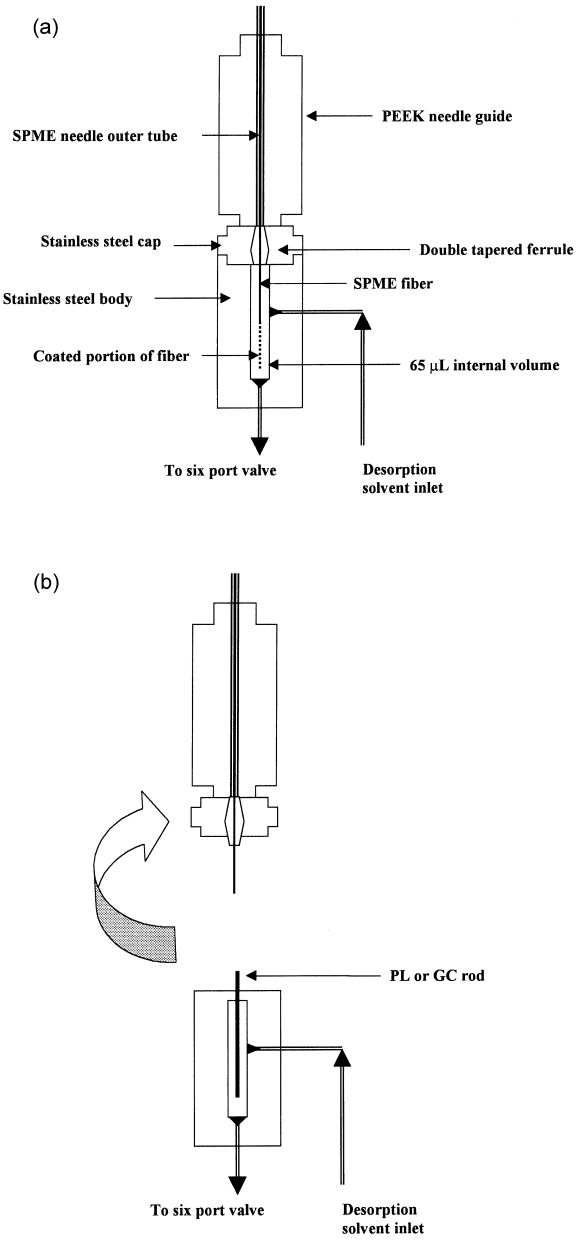

Fig. 1. (a) Cross-sectional diagram of the SPME/HPLC interface using a conventional SPME fiber. (b). Use of the interface for graphite rods.

2.6.2. Desorption of Triton X-100 from the polycrystalline graphites

Desorption took place in a static mode in the SPME/HPLC interface. The system was first sealed as above, using an SPME fiber without a coating, to allow filling of the interface with methanol just prior to the end of the extraction time. The stainless steel cap, PEEK needle guide and SPME fiber were then withdrawn together (Fig. 1b). The carbon rod with adsorbed analyte was transferred into the interface. Approximately 4 cm of the rod, including the 1 cm exposed to the aqueous solution, were then inside the body of the interface. After allowing time for desorption, the rod was withdrawn, the system sealed as above, and the mobile phase then flushed the contents of the desorption chamber onto the HPLC column.

2.7. Scanning Electron Microscopy

The scanning electron micrographs were obtained using a JSM 6400 system (JEOL, Japan).

3. Results and discussion

3.1. Optimization and evaluation of the solid support

Preliminary experiments were performed at room temperature with aqueous solutions containing 0.100 mg/l of Triton X-100 using a 60 min extraction and 60 min static desorption.

3.1.1. Pencil lead

Experiments performed using a single PLU rod showed poor reproducibility (74% RSD, $n=7$). The amount of Triton X-100 detected decreased with the number of extractions performed with a single rod which indicates incomplete desorption and consequently saturation of the surface. Better precision was attained (13% RSD, $n=4$) by using a new PLU for each extraction which suggests that at least their composition is consistent; therefore there is the possibility of using a single rod per sample. Still better precision (4% RSD, $n=4$) was obtained using the graphite coated (PLC) rods.

3.1.2. Glassy carbon

The precision obtained by using the same GCU rod for successive extractions was 16% RSD ($n=4$). Greater adsorption was expected using GCU because of its larger geometrical surface area (32.2 mm^2/cm length versus only 15.9 mm^2/cm length for the PLU). However, this was not the case, which may be explained by the apparently small porosity of the GCU surface as evidenced by the electron micrograph in Fig. 2a. The glassy carbon surface was then sanded followed by cleaning in ultrasound to detach any loose particles. Sanding of the surface likely increased the surface area (see the relatively porous surface shown in Fig. 2b) and when done between successive extractions provided a fresh surface free of the analyte.

After the preliminary results, the time of extraction profile (from 1 to 90 min) was obtained for GCP using Triton X-100 at 0.100 mg/l with a 60 min desorption time (Fig. 3). It was observed that analyte was being extracted even after 90 min of adsorption. A time of 60 min was selected as an optimum adsorption time for the remainder of the experiments.

3.2. Desorption

3.2.1. Desorption from SPME fibers

A problem of carryover (up to 10%) has been reported in the literature [3]. Desorption from the SPME fibers was done dynamically as outlined above. A second desorption showed that carryover was present (6% of the amount obtained in the first desorption). Therefore the fibers had to be cleaned prior to the next extraction by immersing them in methanol for 30 min. Blanks between extractions then showed no carryover of Triton X-100.

Although we measured the 6% carryover at only one concentration, the fact that the linear dynamic ranges are excellent (see Table 1) indicates that carryover is not a problem, as long as the cleaning procedure between successive runs is used. We also noted that swelling of the polymeric coating of SPME fibers frequently led to stripping of the coating from the silica fiber when the assembly was withdrawn through the double sided ferrule.

3.2.2. Desorption from polycrystalline graphite

As mentioned before, static desorption failed to

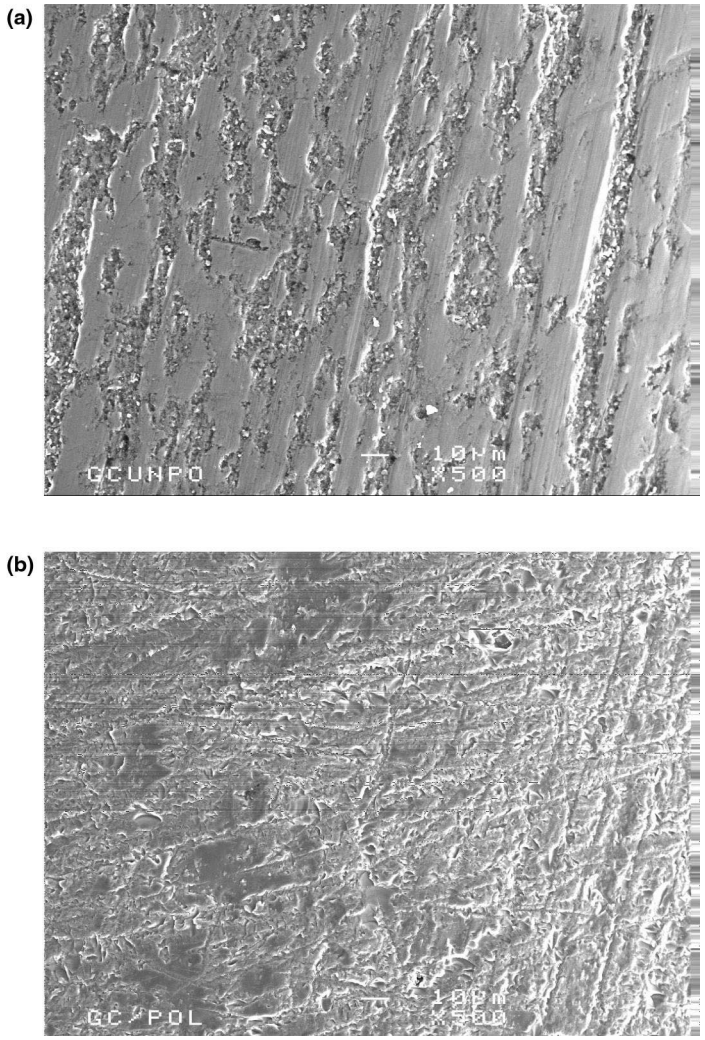

Fig. 2. (a) Scanning Electron Micrograph of a glassy carbon rod as received (GCU), 500× magnification. (b) Scanning Electron Micrograph of a glassy carbon rod after sanding (GCP), 500× magnification.

completely desorb Triton X-100 from PLU and GCU rods even after 60 min desorption time. After cleaning PLU and GCU rods with methanol for 30 min, the rods were placed in the SPME/HPLC interface and small amounts of Triton were still detected. This problem can be solved by using a new rod for each extraction, which is feasible because of their low cost and good reproducibility (as observed so far). In the case of GCU, carryover can be overcome by sanding the surface after which no analyte was found. Blanks were performed between extractions for GCP and no analyte was found.

3.3. Assessment of polycrystalline graphites as sorbents for analytical purposes by comparing their performance with SPME fibers

Analytical figures of merit were obtained for each type of SPME fiber (Carbowax and PDMS/DVB) and polycrystalline graphites and are shown in Table

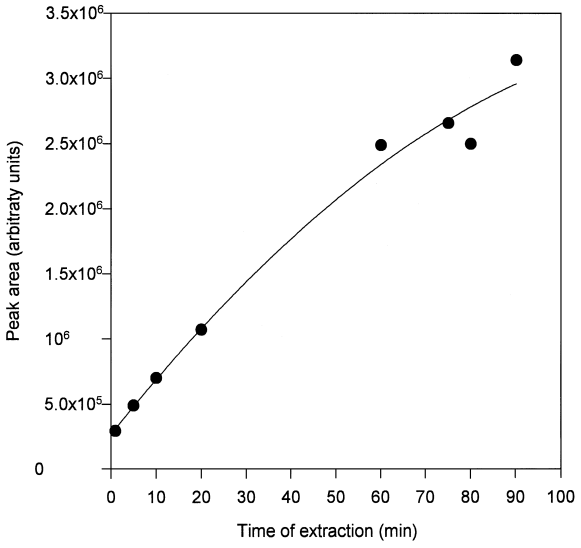

Fig. 3. Peak area of Triton X-100 versus adsorption time on a glassy carbon rod.

1. The analytical procedure for each solid support is presented in Table 2. The results are compared to those obtained by Boyd-Boland [3] which differ from our experiments only in the separation column and detection system used.

Because the exact composition of PLU is unknown, and in order to provide a homogeneous surface, PLU rods were coated with a 5 μm thick graphite layer, producing the PLC rods. The precision improved to 4% RSD and the detection limit by one order of magnitude to 0.50 μg/l. Improved detectability is attributed to more efficient desorption, since there was no carryover when using PLC.

The detection limit using GC was improved by two orders of magnitude to 0.50 μg/l when the surface was sanded. This is attributed mainly to the increase of the surface area since sanding roughening the surface. The precision was essentially unaffected by the roughening.

Also presented in Table 1 are data from the use of

Table 1
Figures of merit of the analysis method of Triton X-100 using different solid supports: pencil lead uncoated (PLU), coated (PLC), glassy carbon untreated (GCU), sanded (GCP) and SPME fibers

	LOD (μg/l)	LDR (μg/l)	RSD (%)
Uncoated (PLU), single rod for multiple extractions	5		74
Uncoated (PLU), new rod for each extraction	5		13
Coated (PLC)	0.50	0.50–150	4
GCU	50	50–	16
GCP	0.50	0.50–150	14
PDMS/DVB fiber	0.50	0.50–100	13
Carbowax/TPR fiber	0.50	0.50–100	15
PDMS/DBV and Carbowax/TPR[a]	1.57	100–100 000	2–15

[a] Boyd-Boland et al. [3].

Table 2
Experimental conditions used during the acquisition of the analytical figures of merit

	Extraction time (min)	Desorption mode	Column	Detection
Pencil lead	60	Static with methanol, 60 min	C_{18}	Fluorescence
Glassy carbon	60	Static with methanol, 60 min	C_{18}	Fluorescence
SPME in this study	60	Dynamic with mobile phase, 2 min	C_{18}	Fluorescence
SPME in Ref. [3]	60	Dynamic with mobile phase, 1 min	Normal phase	UV (220 nm)

conventional SPME fibers. Using a Carbowax fiber resulted in a detection limit, linear dynamic range and precision that are no better than those obtained using the carbon rods. Our results are similar to those obtained by Boyd-Boland et al. [3] who reported limit of detection of 1.57 μg/l, and a linear dynamic range of three orders of magnitude.

4. Conclusions

The performances of two polycrystalline graphites were assessed for analysis of a nonionic surfactant. Preliminary results showed that pencil leads and glassy carbon performed equally well as SPME fibers (PDMS/DVB and Carbowax-TPR) in terms of limit of detection, linear dynamic range and precision. Longer desorption times were necessary when using carbon rods than when using conventional SPME phases. Carryover was present in all the sorbents which affects the limit of detection because of incomplete desorption. Contamination of subsequent determinations was overcome by using a new pencil lead for each extraction or by sanding the surface of glassy carbon rods between extractions (which allows for about 100 extractions per rod). We have found the advantages of carbon, notably its chemical resistance and low cost, outweigh the disadvantages. It is believed that polycrystalline graphites can be more versatile since any derivatization reagent could be sorbed onto their surface. This would permit the analysis of compounds that require derivatization prior to detection such as alcohols and amines.

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