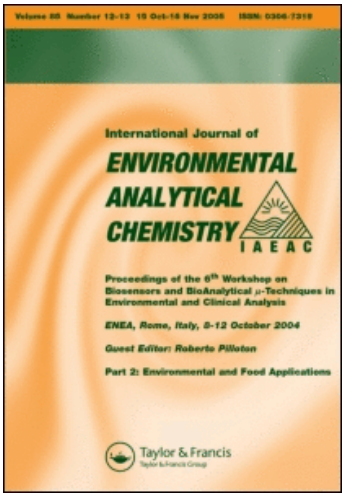

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IMPURITIES RELEASED FROM EXTRACTIVE PHASES USED IN THE ANALYSIS OF PESTICIDES

E. BENFENATI, S. GAROFANI, M. NATANGELO, S. MANGIAPAN and R. FANELLI

Laboratory of Environmental Pharmacology and Toxicology, Istituto di Ricerche Farmacologiche "Mario Negri", Via Eritrea, 62-20157 Milano, Italy

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Elution fractions relative to solid phase extraction (SPE) procedures using C-18 bonded silica and Carbopack B columns plus C-18 membranes have been analyzed by gas chromatography-mass spectrometry (GC-MS) for the characterization of interfering compounds from the phases. Alkanes, alkenes, phthalates and some silyl compounds (silanols, siloxanes) have been tentatively identified. Experiments on commercial C-18 phases prepacked in plastic tubes show that the increased interference compared to the phases alone comes from the polymer container. N-butylbenzensulfonamide (NBBSA) was identified as causing interference when the extraction device used for SPE involved plastic components. Increasing amounts of silanol interferences released from the C-18 phases were observed after passage of the water sample, depending on the acidic pH, as evidence of the hydrolysis of the bonded silica.

KEY WORDS: Solid phase extraction, water analysis, impurities, gas chromatography-mass spectrometry, N-butylbenzensulfonamide, silanols.

INTRODUCTION

Solid phase extraction (SPE) is gaining popularity for analysis of pesticides and organic pollutants[1,2]. SPE generally allows good recovery, speed of execution, simplicity and a reduction of cost. Emulsification is avoided with SPE and water samples can be extracted during the field campaign, bringing the extractive phase to the laboratory, not the whole samples. This is a practical and accurate method, because it has been reported that some pollutants are more stable once on the solid phase[3-5].

However, SPE presents some drawbacks. Impurities from the solvent are greatly reduced in comparison with liquid-liquid extraction, but contaminants from the phases and from the plastics used in the procedure are possible sources of interference. XAD and activated carbon materials have been reported to be contaminated by many impurities[6,7]. Silica bonded phases also present impurities[8] and in some cases this had to be purified with Soxhlet extraction

before use[9]. The release of impurities from the phase may be a problem in pesticide and other pollutants analysis.

We analyzed compounds released from C-18 and Carbopack B phases and from C-18 membranes during each step of our SPE procedures, for a tentative identification of the interferences observed in the analysis of water samples, so as to propose remedial action. We also studied other sources of interfering compounds like the extraction apparatus used, the plastic container of commercial prepacked SPE columns, and the influence of the pH of extraction on the nature and amount of interference released from the C-18 bonded silicas.

EXPERIMENTAL PART

Solvents, reagents and standards

All solvents (methanol, ethyl acetate and dichloromethane) were of analytical grade from Carlo Erba (Milan, Italy) and Merck (Darmstadt, Germany). Concentrated hydrochloric acid and ascorbic acid were from Carlo Erba. Glass-bottled mineral waters were used as the pure water for solid phase extractions. N-butylbenzensulfonamide (NBBSA) was prepared in our laboratory from benzensulfonylchloride and butylamine according to Brambilla *et al.*[10]; standard solutions were prepared in analytical grade methanol.

Dimethyloctadecylsilanol was synthesized starting from dimethyloctadecylsilyl chloride: NaOH 1 N in water was added to a n-hexane solution of this compound; the solution was stirred at ambient temperature for 4 hours, using tetrabutylammonium hydrogensulfate as phase transfer catalyst.

Methyl dimethyloctadecylsilyl ether was also synthesized from the above mentioned chloride: the starting material was dissolved in HPLC-grade methanol; after 4 hour the solvent was evaporated and the product redissolved in n-hexane.

C-18 bonded silica and Carbopack B (120/400 mesh) were purchased from Supelco (Bellefonte, PA, USA), prepacked C-18 SPE columns were from Waters (Milford, MA, USA), Empore C-18 extraction disks were from J. T. Baker (Phillipsburg, NJ, USA).

SPE experiments

Tests on the solid phases (C-18 bonded silica, Carbopack B) were made with an all-glass apparatus.

For C-18, starting from 500 mg of the phase, the procedure involved washing with 10 ml of ethyl acetate, activation with 10 ml of methanol and final elution with 10 ml of ethyl acetate, after or without passage of about 100 ml of pure water.

For Carbopack B (400 mg of starting material), the washing step involved elution with 10 ml of the mixture CH_2Cl_2/MeOH 8:2, activation with 20 ml of a water solution of 10 mg/ml of ascorbic acid at pH 2 with hydrochloric acid, and final elution with 10 ml of the mixture used in the washing step, after passage of about 100 ml of pure water.

For C-18 membranes, we used an all-glass system similar to that employed for the

ultrafiltration of the HPLC solvents. The elution procedure was similar to the C-18 columns procedure. We used a commercial Supelco extraction system for elution of the C-18 prepacked columns. All the elution fractions were injected into the gas chromatograph-mass spectrometer (GC-MS) after concentration to 1 ml.

Experiments on the stability of the C-18 phase at different pH during water extraction were made on 400 mg of the material, placed in glass columns, then washed and activated as above, and submerged in a pH 2 or pH 7 (for comparison) water solution for 3 hours; after washing with 10 ml of distilled water, the phases were dried in a Rotavapor, and 50 mg of each sample was analysed using GC-FID with on-line supercritical fluid extraction (SFE) with CO_2.

Instrumentation

Impurities present in the solid phases were identified using an HP 5971 MSD quadrupole MS coupled to an HP 5890 Series II gas chromatograph: the MS operated in the full scan mode (monitoring the ions from m/z 50 to m/z 500), the GC column was a Chrompack CP-Sil 8 CB (Middleburg, The Netherlands) 25 meter length, 0.25 mm internal diameter, 0.25 μm film thickness, GC program starting from 80°C (held for 2 min), then 15°C/min to 300°C (final temperature held for 4 min), GC column head pressure 30 kPa (helium), injector temperature 240°C; the splitless injection technique was used.

Samples relative to the C-18 extractions of about 2 litres of water were analysed using a VG-TS 250 mass spectrometer coupled to an HP 5890 gas chromatograph. The MS operated in the full scan mode (monitoring the ions from m/z 45 to m/z 600), the GC column was a CP-Sil 8 CB, 25 meter length, 0.32 mm internal diameter, 0.12 μm film thickness, GC program starting from 70°C (held for 1 min), then 20°C/min to 325°C, column head pressure 30 kPa (helium), injector temperature 240°C; the splitless injection technique was used. A Varian Saturn II ion trap detector, coupled to a Varian 3400 gas chromatograph, was also used in the same conditions.

The SFE experiments were conducted using a Chrompack Multi SFE-GC; SFE conditions were: temperature 50°C, CO_2 pressure 2.026×10^4 kPa, extraction time 10 min. On-line cryo-trapping conditions were: trapping temperature – 50°C, desorption temperature 280°C. GC conditions: GC column Cp-Sil 13 CB 25 meter length × 0.25 mm internal diameter and 0.2 μm film thickness; GC program 70°C initial temperature (held for 5 min) then 20°C/min to 300°C (final temperature held for 5 min), carrier gas pressure 75 kPa (helium), injector temperature 250°C, detector temperature 275°C. Methanol as a CO_2 modifier (10 μl for each sample) was added to the sample by syringe directly into the extraction vessel.

RESULTS

We used all-glass systems to assess the contribution of the phases without interference from the plastic tubes commonly used. Figure 1 shows the apparatus for the extraction with C-18 and Carbopack B, when not otherwise specified. An all-glass apparatus was also used for the C-18 membrane extraction.

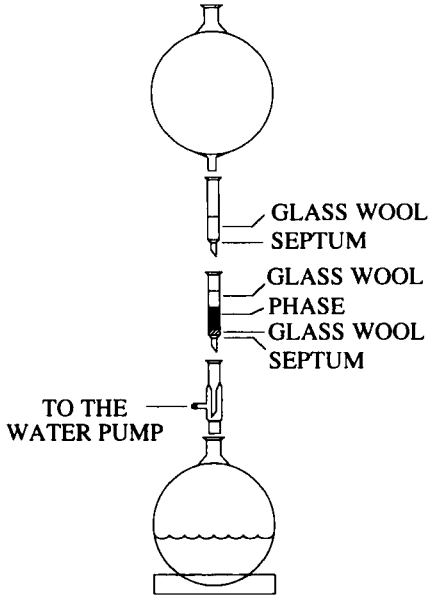

Figure 1 The all-glass extraction apparatus we used for SPE.

To gain a more detailed view of the release of impurities, we analyzed the washing and the activating fractions by GC-MS, when this was an organic solvent. To ascertain the influence of the water passage on the phase, we analyzed the eluting fraction with or without percolation of pure water. We also checked that the impurities found were not due to the solvent or to column ghost peaks, by analysing solvent blank samples.

Tables 1a and 1b shows the results from the C-18 phase, C-18 membrane and Carbopack B. Extensive washing appeared essential, since it removed many contaminants. On the other hand, methanol elution of the phase, useful to prepare the extractive material to the water

Table 1a Identified classes of compounds released from the SPE materials in the specific steps of our analytical procedures

	C-18 phase alone				*C-18 cartridge*			
	washing	activation	final elution		washing	activation	final elution	
	EtOAc	MeOH	EtOAc no H_2O	EtOAc H_2O passage	EtOAc	MeOH	EtOAc no H_2O	EtOAc H_2O passage
Alkanes (C_{18}–C_{29})	X							
Alkenes (C_{18})	X				X			
Phthalates	X		XX	X	X			X
Butylated hydroxy toluene (BHT)					X	XX	XX	X
Poly(alkylsiloxanes)	X		X	X	X	X	X	X
Dimethyloctadecylsilanol	XX			XX	XX	X	X	XX
Dimethyloctadecylsilanol, methyl ether	X		X	X		X		

X = positively identified, XX = identified class with the highest abundance in the chromatogram

Table 1b Identified classes of compounds released from the SPE materials in the specific steps of our analytical procedures

	C-18 membrane				*Carbopack B phase alone*	
	washing	*activation*	*final elution*		*washing*	*final elution*
	EtOAc	*MeOH*	*EtOAc no H_2O*	*EtOAc H_2O passage*	*CH_2Cl_2/MeOH 8:2*	*CH_2Cl_2/MeOH 8:2*
Alkanes (C_{18}–C_{29})	X					
Phthalates	XX	XX	XX	XX	XX	

X = positively identified, XX = identified class with the highest abundance in the chromatogram

extraction, was not important for cleaning the material, as already observed for the C-18 columns[8]. The eluent fraction was contaminated in all cases, but to different extents. Phthalates were among the most frequent contaminants.

The amount of dimethyloctadecylsilanol eluted from the C-18 phase during the last ethyl acetate elution step was markedly increased after passage of water, compared to the 'dry' experiment, and hydrolysis of the phase was thus assumed to be the primary source of this interference.

Of course the use of apparatus containing plastics, such as the commercially available prepacked columns, is a further source of impurities. Table 1a shows the results of analysis of a commercial prepacked C-18 column: compared to the phase alone, there were large amounts of specific compounds such as butylated hydroxytoluene (BHT), phthalates and alkyl siloxanes. BHT is an antioxidant compound and is released as an impurity from commercially prepacked C-18 SPE columns[8].

Besides the column itself, other sources of impurities may be found in the plastic joints used to couple the column with the glass reservoirs. Thus, we analyzed about 2 litres of pure water samples acidified at pH 2.5, extracted with a C-18 Sep-pak column and a similar sample prepared in an external laboratory, using the same column type but a different extraction apparatus, using plastic tubes. Both the samples gave intense peaks corresponding to silyl derivatives (see below), but we found a further peak in the one prepared in the external laboratory. The library search program identified this as N-butyl-benzensulfonamide (NBBSA). The major peaks appeared at m/z 77 (100), 141 (73), 170 (80), 213 (10). We confirmed its identity by comparison with the authentic standard, prepared in our laboratory. NBBSA is used as an additive in the production of some epoxide resins[10], and this clarifies its origin in the sample.

The major peak observed in these samples corresponds to dimethyloctadecylsilanol (the base peak at m/z 75 corresponds to the dimethylhydroxysilyl ion, the peak at m/z 313 to the M-CH3 ion, confirmed by comparison with the mass spectrum of the standard we synthesized). This compound has been reported to be an impurity of C-18 columns[8]. Another abundant peak is due to the methyl ether of the silanol (the base peak at m/z 89 corresponds to the dimethylmethoxysilyl ion, the peak at m/z 327 to the M-CH3 ion; confirmed by comparison with the mass spectrum of the standard we synthesized). This methyl ether has also been found as an impurity in the C-18 column, probably derived from the corrisponding alcohol if the column was eluted with methanol[8]. These observations are confirmed by the presence of these compounds in our experiments (Table 1a).

In order to clarify this question we started the characterization of the impurities released from extraction of acidic samples, using the SFE of the C-18 material. Experiments with pH 2 water solutions revealed two major peaks similar to those we found in GC-MS analysis of the extraction with solvent, using methanol as CO_2 modifier. If ethyl acetate was used instead of methanol we observed only one of these two peaks, probably the C18 silanol and its methyl ether; in fact, we assumed that the presence of methanol during the extraction process partially converted the silanol into its methyl ether, whereas this did not occur in the presence of ethyl acetate. The corresponding chromatograms relative to the experiments at pH 7 revealed the same two peaks, but with an intensity ten times less abundant than in the pH 2 experiments.

Acidification of the water released more of the impurities, because of the increased degradation of the C-18 phase. The manufacturer did in fact state that the material was not recommended for use with acidic water.

The most abundant of these impurities often reach more than 10 μg/l. For instance, working with 2 litres of water, the dimethyloctadecylsilanol and its ether corresponded to contaminants in the range of 5–80 μg/l. Their relative abundance varied, the acidity of the water being one reason. NBBSA was absent in some cases and in others corresponded to contaminants at 50 μg/l. Phthalates were often present (less than 10 μg/l). The other contaminants were generally found in smaller amounts.

For identification studies with contaminated waters we generally prefer to do a blank analysis simultaneously, in exactly the same conditions as for the samples, because we have noticed differences between batches and different brands of materials, as reported by others[8].

Impurities released by extraction materials may be a problem especially during identificative analysis of contaminants in waters; these compounds may be erroneously attributed to the samples and could hide contaminants co-eluting with them. As an example, Figure 2 shows the chromatogram of an extract with C-18 of a water sample: all the major peaks are due to the extraction procedure. In the quantitative analysis of pollutants these impurities are a minor problem, provided the detector is selective enough. In our case, the use of mass spectrometry as a detector achieved excellent selectivity.

A wide range of compounds are released from all the phases and an all-glass apparatus is recommended, especially if the analysis is aimed at general characterization of the pollutants in a water sample.

Carbopack B was the cleanest phase compared to the C-18 bonded silicas we considered, but no data is available about the influence of the pH of extraction or other variables (water salinity, oxidants levels or other reactive species in water) on the stability of this material.

Acknowledgements

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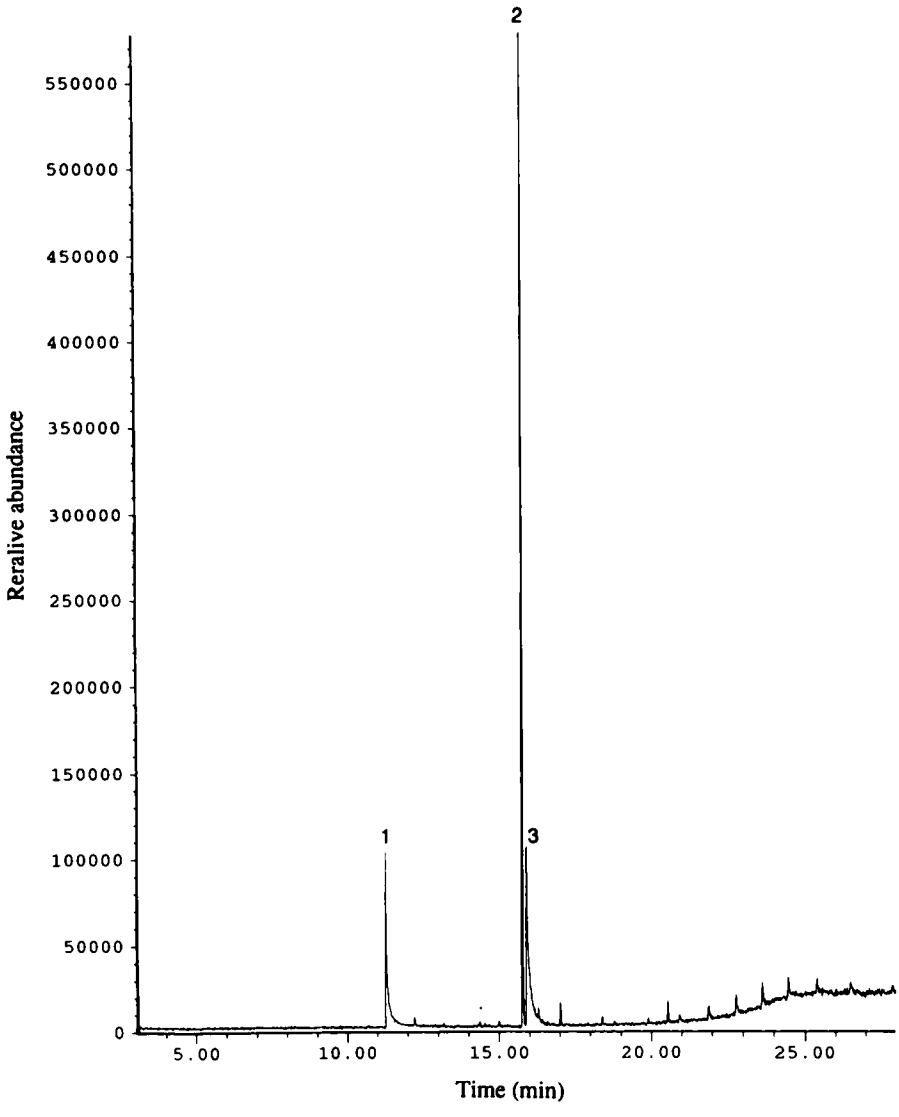

Figure 2 Chromatogram of a water sample extracted with a C-18 column. The major peaks are due to the extraction procedure: peak 1 corresponds to NBBSA, peak 2 is the methyl ether of dimethyloctadecylsilanol and peak 3 dimethyloctadecylsilanol.

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