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Original Paper

Potential sources of background contaminants in solid phase extraction and microextraction

A study to identify the sources of background contamination from SPE, using a C-18 sorbent, and solid-phase microextraction (SPME), using a 70 μm carbowax/divinylbenzene (CW/DVB) fiber, was carried out. To determine the source of contamination, each material used in the procedure was isolated and examined for their contribution. The solid-phase column components examined were: sorbent material and frits, column housings and each solvent used to elute analytes off the column. The components examined in the SPME procedure were: SPME fiber, SPME vials, water (HPLC grade), and salt (sodium chloride) used to increase the ionic strength. The majority of the background contaminants from SPE were found to be from the SPE sorbent material and frits. The class of contaminants extracted during a blank extraction were phthalates and other plasticizers used during the manufacturing process. All had blank levels corresponding to measured concentrations below 2 ng/mL, except for undecane, which had a concentration of 5.4 ng/mL. The most prevalent contaminants in the SPME blank procedure are 1,9-nonanediol, a mixture of phthalates and highly *bis*-substituted phenols. All the concentrations were below 2 ng/mL, with the exception of *bis* (2-ethylhexyl) phthalate, which had concentrations ranging from 5 to 20 ng/mL.

Keywords: Background contamination / Sample preparation / Solid-phase extraction / Solid-phase microextraction

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1 Introduction

Advances in analytical instrumentation and methodology have considerably lowered analyte concentrations that are detectable [1, 2]. The ability to quantify very low concentrations allows for the determination of contaminants not previously identified by existing analytical techniques. This increase in sensitivity has substantial potential for environmental analysis where ambient concentrations of the contaminants in question are found at very low levels, often in the part *per* billion range, and lower. Not only are these methods capable of detecting low levels of environmental analytes, but also low levels of laboratory contaminants [3, 4].

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Abbreviations: BHT, butylated hydroxytoluene; **CAS,** chemical abstracts service; **CW/DVB,** carbowax/divinylbenzene; **EPA,** environmental protection agency; **GC,** gas chromatography; **SPME,** solid-phase microextraction

Laboratory contamination is usually addressed on a case-by-case basis, with the hope that contaminants will be removed by proper quality control laboratory procedures. The exception to this is a study by Junk *et al.* [3] that specifically looked at the sources of contamination arising from SPE. The authors found that the level of contaminants varied from column-to-column and lot-to-lot. The authors, however, did not examine contaminants arising from solid-phase microextraction (SPME). To date there is no study measuring SPME background contaminants or comparing the blank levels between SPE and SPME, two complimentary techniques for measurement of semivolatile organic analytes.

Laboratory contaminants, as a whole, can arise from a number of sources, including gas chromatographic (GC) columns, glassware, plastic ware, solvents, SPE columns, or any other reagents and laboratory ware used in the assay. Depending on the type of GC column used, degradation of the column can lead to benzoic acid, phenyl naphthalene, squalene, or the alkyl derivatives of benzene, styrene, naphthalene, and biphenyl showing up in chromatograms [5 – 8]. Polysiloxanes, which arise from bleeding of the septum or the column's stationary phase,

is a common problem for all the gas chromatograph users [8, 9]. A general rule is that the thicker the column the less uniform it is and the more that bleed will become a factor [10].

The most notorious class of laboratory contaminants are phthalates [11]. Phthalates are used as plasticizers in polyvinyl chloride (PVC) and other polymers such as polyethylene and polypropylene to enhance durability and flexibility [11 – 15]. Phthalates can be leached from any coated glass or plastic surface being used [16]. Environmental protection agency (EPA) method 525.2, which analyzes drinking water samples for semivolatile organic analytes by SPE, warns of phthalate contamination from leaching of polyethylene or polypropylene SPE columns when either ethyl acetate or methylene chloride are used [17]. Not only phthalates, but also other plasticizers can be leached from glass and plastic surfaces, including SPE columns [18, 19]. Plasticizers are additives to plastics and are not reagents, so they are not chemically bound to the polymer and can leach from the matrix [20, 21].

SPME is a relatively new analytical technique first derived in the 1990s and requires little sample preparation [22]. Sample preparation steps for SPME include changing the ionic strength of the solution *via* salt addition, and heating and agitation of sample. Since sample preparation and handling time is reduced, the number of contaminants is expected to be considerably less than when using SPE. Still SPME is not free from contamination [23]. Researchers have reported high phthalate backgrounds [16]. The epoxy glue used to hold the fiber in place with the stainless steel needle produces highly substituted *bis* compounds when high temperatures are used as part of the analytical method [24].

This study looks to classify the background contaminants present in an SPE and SPME extraction method that will be used to analyze ground and treated drinking waters for semivolatiles. Given the low concentrations of analytes targeted, and the low detection limits obtained while using an IT, it is important to determine if an analyte detected in field samples is actually coming from the environment or the materials or possibly both. Each method was broken down stepwise to isolate each component to determine the exact source of the contaminants.

2 Experimental

2.1 Chemicals and reagents

Ethyl acetate (pesticides grade), methylene chloride (Optima), acetone (HPLC grade), water (HPLC grade), and sodium chloride (Certified ACS) were obtained from Fisher Scientific (Fairlawn, NJ). Methanol (High Purity, chromatographic grade, Burdick and Jackson) was obtained from VWR (Bridgeport, NJ).

SPE columns (Supelclean ENVI-18, 6.0 mL, 1.0 g) and SPME fibers (70 μm carbowax/divinylbenzene (CW/DVB)) were obtained from Supelco (Bellefonte, PA). Twenty-milliliter SPME glass autosampler vials (Microliter Analytical Supplies) were purchased from Varian (Walnut Creek, CA) and used for analysis. The vials were capped and crimped with 20 mm magnetic crimp caps (Varian, Microliter Analytical Supplies, Teflon/white Silicone Septa).

2.2 Instrumentation

A Varian 3400 CX gas chromatograph coupled to a Saturn 2000 IT mass spectrometer (ITMS, Walnut Creek) was used for liquid injections to analyze for background contaminants from the SPE extraction protocol. A septum programmable split/splitless injector was used in the splitless mode. The gas chromatograph was equipped with a 30 m 5% phenyl/95% dimethylsilicone fused-silica DB-XLB capillary column with a 0.25 mm id and 0.25 μm film thickness (JW Scientific, Folsom, CA). Helium (BIP grade, Airgas, Radnor, PA) was used as the carrier gas with a flow rate of 33 cm/s.

The injector temperature program used for the 3400 CX was as follows: 100°C held for 1.5 min, increased at 140°C/min to 280°C and held for 20 min. The column temperature program used was as follows: inject at 35°C and hold in splitless mode for 1.5 min, at 4 min start temperature program: 35 – 130°C at 7°C/min, 130 – 200°C at 5°C/min, 200 – 260°C at 6°C/min, 260 – 340°C at 8°C/min and 8.43 min hold. Data acquisition was started at 5 min.

The ITMS was operated in EI positive mode and tuned with perfluorotributylamine (FC-43) as specified by the instrument manufacturer. The electron multiplier voltage, emission current, multiplier offset, and modulation amplitude are set at 1800 – 2100 V, 10 μA, ±0 V and 7.5 V, respectively. The transfer line was set to 270°C while the IT manifold was set to 225°C. The mass range was scanned from 45 to 450 *m/z* at 0.66 s/scan.

A Varian CP-3800 gas chromatograph coupled to a Saturn 2200 ITMS (Walnut Creek) was used to identify SPME background contaminants. A CTC Analytics Combi PAL Injector with SPME Agitator attachment (Zwingen, Switzerland) was used for agitation and heating of samples and injection into the GC/ITMS. The CP-3800 was operated in splitless mode with the same column type, carrier gas and flow rate as the 3400 CX.

The injector temperature of the CP-3800 was held at 250°C for the duration of the experiment. The following temperature program was used: inject at 60°C and hold in splitless mode for 5 min, 60 – 300°C at 15°C/min and hold for 10 min for a final run time of 31 min. Data acquisition was started at 6.80 min to prolong the lifetime of the filament.

The emission current of the CP-3800 was held at 40 μA while the multiplier offset was ±200 V, all other parameters were the same for both instruments. Data were acquired using Saturn GC/ITMS workstation Version 5.3 for the GC 3400 system and Version 5.51 Software for the Varian 3800.

2.3 SPE procedure

The general sample preparation scheme for SPE is: conditioning of the SPE columns, followed by sample loading and finally elution of the analytes off the solid-phase columns. In this study, the solvents were collected after the conditioning and elution stages. The solvents collected after conditioning were termed "prewash" and those collected after elution "postwash". In this experiment, there was no sample loading stage. EPA method 525.2's solvent scheme was used for the conditioning and elution of contaminants from the SPE columns. The solvent scheme was as follows: 5 mL of ethyl acetate, 5 mL of methylene chloride, and 5 mL of methanol for both the conditioning and elution stages [17].

The solvents were passed through the columns using a Visiprep DL disposable liner SPE vacuum manifold system (Supelco) and collected in 15 mL glass centrifuge tubes (Kimble). The solvents, from both the prewash and postwash stages, were evaporated separately, under vacuum (5 mm Hg), until a final volume of approximately 1 mL was obtained for each. Samples were transferred to GC vials containing glass inserts (National Scientific Company, Duluth, GA) to allow for quantitative removal of the small aliquot of the solution. One microliter of sample was injected into the GC/ITMS system.

The effect of solvent volume on column wash out (removal of contaminants from the column before adding sample) was examined by varying the volume of solvents used. Table 1 lists the volumes of each solvent used for wash out. The volume was changed for the prewash samples, and ranged from 1 mL of each solvent to 7 mL, but was held constant, at 5 mL of each solvent, for the postwash experiment. The solvents in the prewash stage were those used to clean the columns of contaminants, whereas the solvents in the postwash stage would be used to elute the analytes off the column after loading.

Each component of the SPE procedure was then isolated; solvents, centrifuge tubes, column housing, sorbent material, frits, and tubing. For each of the isolated components, six samples were analyzed.

To determine the background contaminants that were already present in the solvent, as well as in the centrifuge tubes, "solvent blanks" were generated. Five milliliters of each of three solvents (ethyl acetate, methylene chloride, and methanol) were pipetted directly into centrifuge tubes. These were then placed in the vacuum manifold and evaporated under vacuum until approximately 1 mL of sample remained. A 1 μL sub-sample was then injected onto the GC column for analysis.

Six milliliter filtration tubes (Supelco) were used to examine what contaminants came from the column housing. These tubes were the same as the columns used in previous experiments but without sorbent material and frits. To simulate the retention time that the solvents have on the SPE columns with sorbent material, each solvent was retained in the column for 5 min by restricting solvent flow by the flow control valve.

To isolate the sorbent and frits as potential contaminant sources, glass columns were specially ordered from Supelco to have the same specifications as the plastic SPE columns (Supelclean ENVI-18, 6 mL glass tube, 1 g). The results were then compared to 6 mL glass columns without sorbent and frits. The columns were prepared using EPA method 525.2, as outlined above.

2.4 SPME procedure

The SPME fiber was conditioned before use as *per* the manufacturer's instructions. The Combi PAL injection/sample preparation program was as follows: extraction time of 50 min, desorption time of 5 min, preinjection time of 1 min, incubation temperature of 45°C, agitation speed of 500 rpm, vial penetration 31.0 mm, and injection penetration of 54.0 mm.

Five components of the SPME process were evaluated: blank air injection, SPME fiber, SPME vials, SPME vials with water, and SPME vials with 10% NaCl. All the experiments were completed using three replicates.

A blank air injection consisted of the injection port being depressed and having the system run through the temperature program to determine the contribution of the GC/MS system (such as column bleed) to the measured contaminants. The blank SPME fiber experiment consisted of an unused, conditioned SPME fiber being placed in the GC injection port to the same depth as a fiber used for analysis, the injection port being depressed and the system running through the temperature program. This experiment was to determine the contaminants coming from the degradation of the SPME fiber.

The background contaminants from SPME vials were identified by sampling an empty crimped SPME vial. These vials were crimped and sampled at the same depth as vials that contained solution, *i.e.*, a direct sampling measurement; however, these vials contained only air. The Combi PAL extraction protocol outlined above was used to extract the contaminants from the air inside of the autosampler vials. After sampling the vial, the fiber was desorbed into the injection port and analyzed by GC/ITMS. To identify the background contaminants from the water and salt used, the autosampler vials were filled with 15 mL of HPLC grade water with and without NaCl

to make a 10% salt solution. The samples were extracted and analyzed as outlined above.

3 Results and discussion

3.1 SPE background contaminants

3.1.1 Effect of varying solvent volume

Solvents were initially used in SPE to remove any contaminants that are present in the columns from the manufacturing process. It was assumed that with an increase in the volume of solvents, more contaminants will be removed from the solid-phase material during the conditioning (washing) step. Compromise conditions had to be made since an increase in solvent volume also generates more waste. The volumes of solvents were varied from 1 to 7 mL to examine their effect on the number of contaminants removed. The most successful solvent scheme was defined for this work as one that had the least number of contaminants present in the final eluant.

Table 1 lists the number of compounds found by varying the volume of the conditioning solvent. As expected, an increase in the volume of solvent in the prewash step led to an increase in the artifacts seen in that eluant. EPA method 525.2 recommends 5 mL of each solvent. This volume extracted 60 contaminants from the columns while an increase to 7 mL of each solvent extracted a total of 116 contaminants. The 5 mL conditioning removed 25 contaminants more than what was removed using a smaller 3 mL volume. The data suggest that for the solvents examined, at least a combined 15 mL of conditioning solvents should be used to elute the adsorbed contaminants before the solid-phase columns can be used.

Increasing the volume of solvent in the prewash stage generally led to a decrease in the number of compounds seen in the postwash eluant. Total prewashes of 3, 6, and 9 mL (1, 2, and 3 mL of each solvent) yielded 13, 11, and 12 compounds in the postwash. A total prewash of 15 mL led to seven compounds detected in the postwash while a 21 mL prewash yielded eight compounds detected in the postwash. The data illustrate that a point of diminishing returns existed after about 5 mL of prewash. This suggests that there are either no more contaminants on column or more likely different solvents, based on polarity, are needed to remove those contaminants. For this experiment, new solvent schemes were not applicable since it was meant to follow EPA method 525.2.

The number of background contaminants seen in the postwash eluants of the lower volume solvent washes (3, 6, and 9 mL) were, however, lower than expected. The 15 mL prewash removed 60 compounds whereas the 9 mL prewash removed 35, a difference of 25 compounds. It was expected that these 25 compounds would still be on column and would be seen in the postwash of the 9 mL sample. This was not the case as the difference in the number of compounds seen in the postwash was only five. One possible reason was that the 15 mL volume used in the postwash stage was not enough to remove the compounds still on column.

Table 1. The volumes of each solvent used, in milliliters, along with the number of contaminants discovered. The experiment was to test the effect which the variation in the solvent volume had on background contamination. The term prewash represents the SPE column conditioning step

Prewash	Ethyl acetate	Methylene chloride	Methanol	Number contaminants prewash	Number contaminants postwash
1a	1	1	1	61	13
2a	2	2	2	39	11
3a	3	3	3	35	12
4a	5	5	5	60	7
5a	7	7	7	116	8

While an increase in the volume of solvents used during conditioning produced cleaner eluants, the increased solvent volumes also led to increased waste. The solvents used are often toxic and environmentally unfriendly. In this study, methanol and methylene chloride have toxicity warnings while ethyl acetate does not. With minimal gains in increasing the solvent volumes from 5 to 7 mL and with the generation of more waste it is recommended that the EPA method's 5 mL washing remain the same.

3.1.2 Components of SPE procedure

The first procedural components examined were the solvents used to condition the columns. Six replicates of the solvent blanks were analyzed. Two of the six replicates contained the contaminant dibutyl phthalate at an estimated concentration of below 1 ng/mL. This estimate is based upon a "counts" measurement that was compared to an injection of *bis*(2-ethylhexyl) phthalate standard. The other four replicate samples did not contain any contaminants. Dibutyl phthalate is a ubiquitous laboratory contaminant and almost unavoidable [12]. Dibutyl phthalate was probably leached from the centrifuge tubes or other glassware, such as the GC vials, inserts, and syringes that were used. All the six solvent blanks had peaks that were identified as siloxanes from column bleed. The results show that the only contribution to contaminants in the SPE process from the solvents and centrifuge tubes was dibutyl phthalate.

After the contaminants from solvents were determined, the contaminants from the sorbent material and plastic columns were examined. Figure 1 shows a chromatogram comparing artifacts identified from plastic

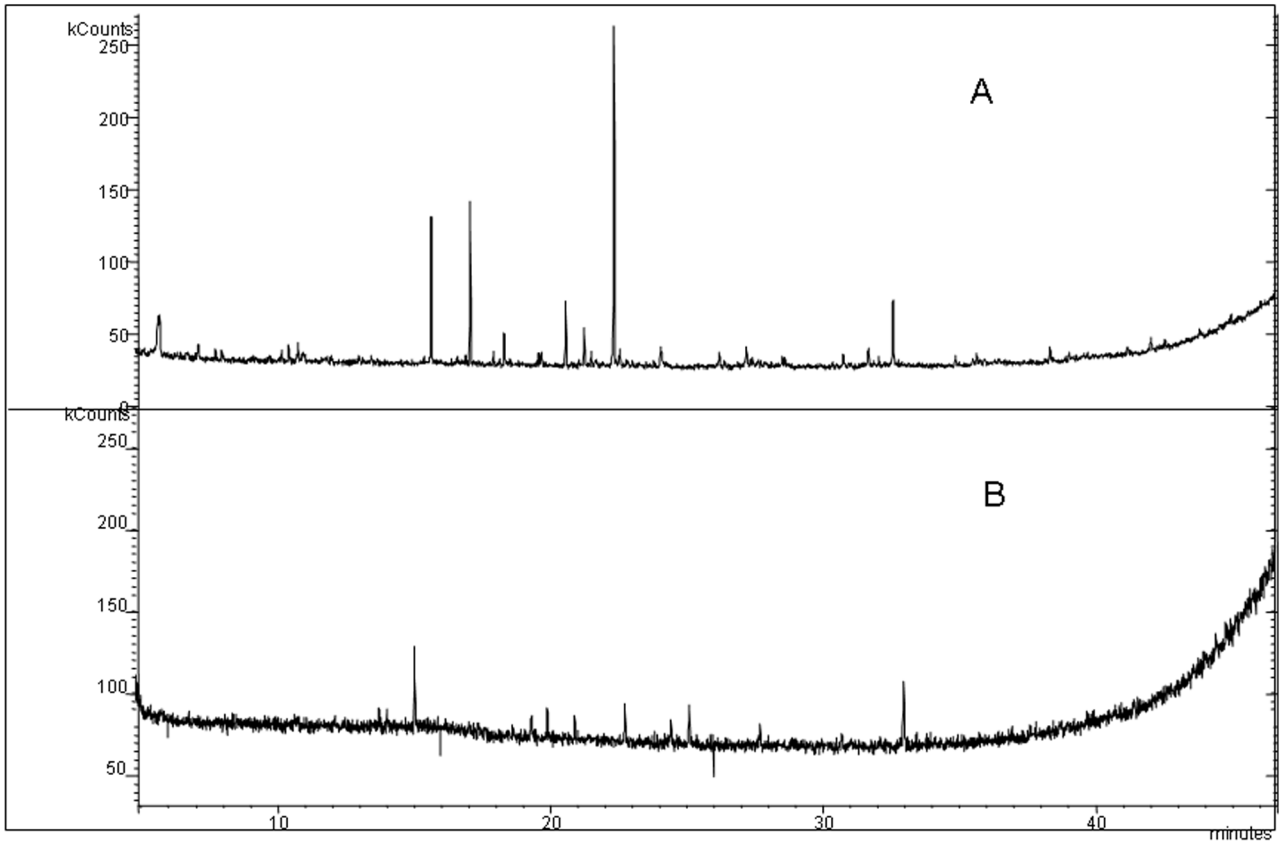

Figure 1. Postwash chromatograms for SPE blanks using (A) C-18 sorbent and (B) no sorbent material (empty SPE column housing). Both the chromatograms illustrate samples that were washed with 5 mL of each solvent (ethyl acetate, methylene chloride, and methanol). The chromatograms have been normalized to one another.

columns with sorbent material and frits *versus* plastic columns without sorbent material and frits. Both chromatograms represent prewashes of 5 mL of each solvent and have been normalized to each other based on the most concentrated peak. From the figure, it can be seen that plastic columns with sorbent not only contain more contaminants, but also in higher concentrations. The sorbent material being used, C-18, seems to be the major contributor to background contamination and not the plastic column housings. To further test this, glass column housings, with and without sorbent material and frits, were tested using the same procedure and solvent scheme.

Table 2 lists the number of contaminants extracted from the sorbent materials or column housings. The data show that the columns without sorbent material or frits produce only one or two contaminants in both the prewashes and the final eluant while those columns with sorbent yielded considerably more contaminants, 7 in the final eluant and 62 in the prewash for the plastic columns and 5 in the final eluant and 40 in the prewash for the glass columns. Since both the plastic and glass column housings contain a minimal number of background contaminants compared to the same columns with packing material and frits, it was concluded that the majority of contaminants identified were from the C-18 sorbent.

Table 2. Number of contaminants extracted from plastic and glass columns both with and without sorbent materials and frits

	Plastic columns		Glass columns	
	With sorbent	Without sorbent	With sorbent	Without sorbent
Prewash eluant	62	2	40	1
Postwash eluant	7	2	5	2

The contaminants identified in all the postwash eluants were butylated hydroxytoluene (BHT), dibutyl phthalate, and diethyl phthalate. These results once again illustrated the ubiquitous nature of these compounds. These compounds appeared in both the pre- and postwashes, so the conditioning of the columns does not fully remove them. Since they are not removed, they are expected to show up during the analysis of actual water

Table 3. Most commonly occurring background contaminants from SPE procedure

CAS number	Common name
128-37-0	BHT
111-87-5	1-Octanol
84-74-2	Dibutyl phthalate
37769-62-3	Ethenyloxyisooctane
104-76-7	2-Ethyl-1-hexanol
2511-91-3	Pentylcyclopropane
74630-65-2	Z-9-Methyl-5-undecene
1892-12-2	Cyclodecanemethanol
629-82-3	1,1′-Oxybisoctane
15890-40-1	1,2,3-Trimethylcyclopentane
765-05-9	1-Ethenyloxydecane

samples. The inability of the conditioning solvents to remove these compounds, and these analytes being of environmental importance, demonstrates how important it is to run blanks with each batch of samples.

3.1.3 Most prominent SPE contaminants

The most frequently observed contaminants arising from the SPE procedure are listed in Table 3. Given are both the common name and the chemical abstracts service (CAS) number for each compound. The majority of these compounds listed are plasticizers.

Dibutyl phthalate is used industrially as a light-stable and PVC auxiliary plasticizer [12 – 14]. Phthalates are an unavoidable laboratory contaminant and based on the method used throughout these studies, they were thought to arise from leaching of the polypropylene or polyethylene used to make SPE columns. They were extracted by both ethyl acetate and methylene chloride [17]. While the column housings were one source of dibutyl phthalate, the sorbent and frits also contributed to the levels of the phthalate seen in the final eluant. Phthalates are an important environmental contaminant since they can act as endocrine disruptors and synergistically activate the estrogen receptor [12, 14].

BHT is an antioxidant and used commonly as a preservative in the food industry [15]. Junk *et al.* [3] previously concluded that BHT arises from the polypropylene housing. From experiments performed here, it was concluded that BHT was not being leached from the polypropylene tubes themselves but from either the frits or the sorbent, because the isolated plastic SPE column housings showed no extracted BHT. 1-Octanol is used in industry to manufacture esters and perfumes. 2-Ethyl-1-hexanol is used as a plasticizer, specifically in the manufacturing of phthalate esters and may arise from the leaching of polyethylene and polypropylene by the solvents used to wash the columns.

Different solvents extract different plasticizers and contaminants from the SPE columns [8, 19]. Using a more polar solvent, such as methanol, should leach a more polar contaminant than a less polar solvent, like ethyl acetate. The concentration of the identified contaminants was also affected by the solvent scheme (type and volume of solvents used). Plasticizers are unavoidable in blanks since they are often necessary additives to the manufacturing process of SPE columns and other laboratory equipment. For each method, an analytical laboratory contaminant library should be created so that these analytes are easily identified when analyzing environmental samples.

3.2 SPME contaminants

Only phthalic anhydride and siloxanes from column bleed were detected in the blank air injections. They were present at concentrations below 1 ng/mL. Phthalic anhydride eluted early in the process and often during the dead time of the mass spectrometer for this method. The source of phthalic anhydride contamination is most likely the septum. Siloxanes are easily identifiable, so do not generally yield false positives in environmental analysis. While they will usually not be mistaken for analytes of environmental interest, if they have similar retention times they can mask such analytes. To prevent septum degradation and lessen the affects of column bleed, the septum should be changed after 60 injections. Column bleed should be monitored to determine the proper time to change the GC column and very low bleed GC columns, like the DB-XLB, should be used. The data show that the GC system's contribution to contaminants was minimal.

The blank SPME fiber, defined as placing the needle into the GC injection port without sampling any vials and deploying the fiber to the desorption depth, generated two artifacts, 1,9-nonanediol and a highly substituted *bis* phenol. Comparing the respective structures of 1,9-nonanediol and the components of the CW/DVB fiber, it can be seen that enough similarities exist between them to conclude that the contaminant was probably coming from that phase of the fiber. The contaminant was present at an equivalent concentration between 1 and 2 ng/mL. If a fiber is used that does not contain carbowax as one of its phases then 1,9-nonanediol should not be a concern. It is, however, possible that other breakdown products from other fibers used may also present themselves. It was observed in a previous study that highly substituted *bis* phenols arise from hydrolysis of the epoxy glue holding the fiber into the stainless steel needle at high temperatures [24]. The substituted *bis* phenols arise regardless of the fiber used since all the fibers are held into their respective needles by the same epoxies. The level of the *bis*-substituted phenols can be a concern and should be monitored appropriately.

Table 4. Most frequently occurring background contaminants from SPME

Common name	CAS number	Source(s)
1,9-Nonanediol	3937-56-2	Carbowax phase of SPME fiber
Bis-substituted phenols		Epoxy glue of SPME needle
Cyclodecanol	1502-05-2	SPME vial or crimp top
Dibutyl phthalate	84-74-2	SPME vial or crimp top
Isopropyl myristate	110-27-0	SPME vial or crimp top (leached by water)
Isopropyl palmitate	142-91-6	SPME vial or crimp top (leached by water)
(Z)-6,10-dimethyl-5,9-undecadien-2-one	3879-26-3	SPME vial or crimp top

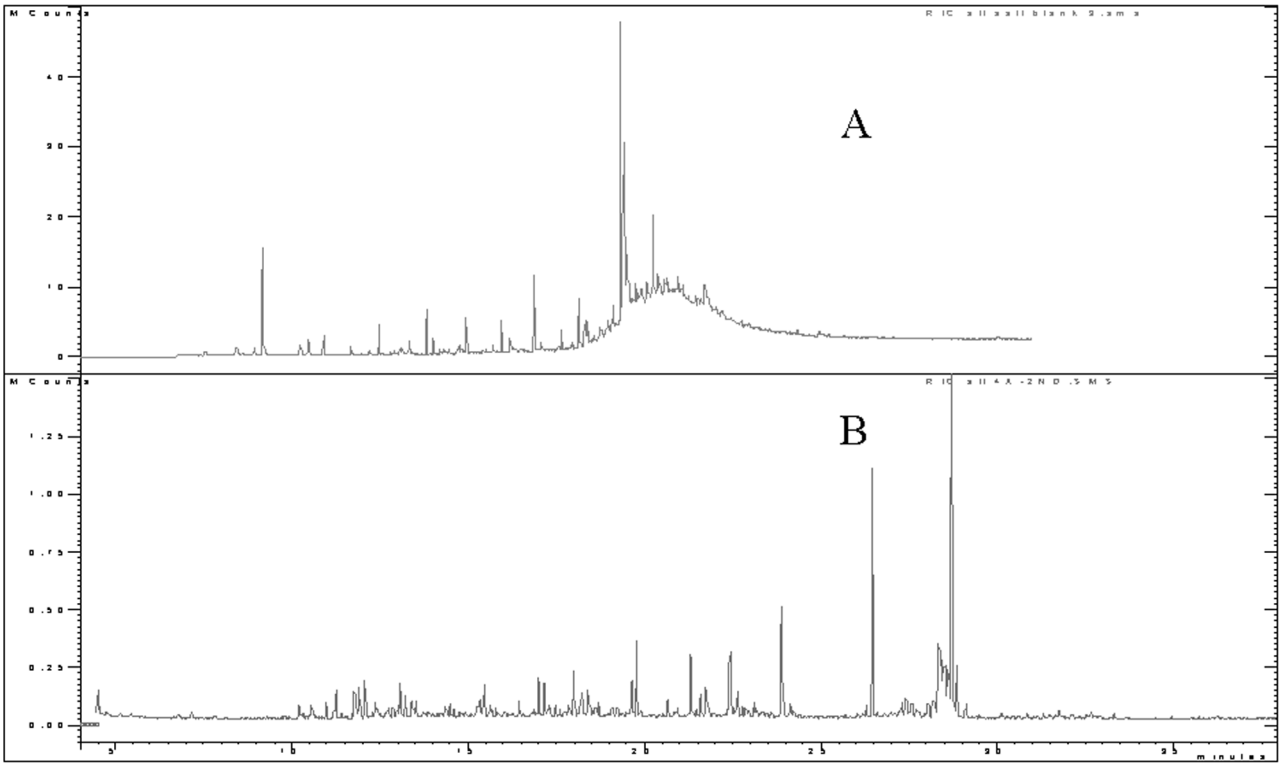

Figure 2. Chromatograms for SPME (70 μm CW/DVB fiber) and SPE (C-18 sorbent) blanks. The blanks represent (A) 10% salt-water solution for SPME and (B) 5 mL of each washing solvent for SPE. The chromatograms have not been normalized to illustrate baseline stability.

The most commonly observed SPME artifacts from this study, along with their CAS registry number and likely source, are listed in Table 4. The number of contaminants observed increased when the SPME vials containing only air were sampled. Besides the 1,9-nonanediol and the *bis*-substituted phenol seen from the SPME fiber, dibutyl phthalate, an alcohol (cyclodecanol), a ketone (Z-6,10-dimethyl-5,9-undecadien-2-one) as well as a compound not identified by the library system, were also detected. Since these four compounds were not detected in the previous experiments (fiber blank or instrument blank), they were likely to have evolved from out gassing of either the crimp top used or the glass vial. Use of other types of vials can remove these compounds but is likely to contribute different contaminants.

Sampling of water blanks added a number of phthalates, and increased the number of diols. Two esters, isopropyl myristate, and isopropyl palmitate were also observed. The compounds not previously detected were either from the water or on the walls of the vials that were not volatilized. Sampling of the blank air inside of an SPME vial is essentially a headspace measurement. A compound that is not likely to partition into the headspace generally would not out gas but would remain adsorbed to the walls of the vial. The addition of water may leach the compound from the walls of the vial and thus allow it to be sampled *via* a direct SPME measurement. These compounds are ubiquitous and may be found in the water as well.

In addition to contaminants found in water alone, saltwater blanks contained a highly substituted propanoic acid species. The concentrations of the contaminants also increased when the ionic strength of the solution was changed. For example, dibutyl phthalate had an equivalent concentration less than 1 ng/mL before salt addition and was 4.4 ng/mL after salt addition. Salt is added to increase the ionic strength of the solution, decreasing an analytes' water solubility and increasing its partitioning into the SPME fiber.

3.3 SPE/SPME comparison

Figure 2 shows nonnormalized chromatograms comparing the background contamination from both SPE and SPME procedures. The chromatograms were not normalized so that baseline stability could be compared. The SPME chromatogram represents contaminants from a 10% salt solution while the SPE chromatogram is for plastic column with C-18 sorbent material and 5 mL solvent prewashes. These two sets of conditions are those that would be used for analysis of field samples. The blank levels for SPME are higher overall for the majority of contaminants when compared to SPE. Equivalent concentrations for SPE were below 2 ng/mL for most compounds except for undecane. SPME concentrations were also often below 2 ng/mL except for the phthalates which ranged from 2 to 20 ng/mL. In a previous study, lower detection limits for some phthalates were obtained using SPME compared to SPE [25]. The primary reason for phthalates being more concentrated in the SPME blanks may be because SPME is a more efficient concentration method for this compound class.

4 Concluding remarks

The sources of background contaminants from two extraction methods, SPE and SPME were determined. The majority of contaminants from SPE were plasticizers and were attributed to the frits and C-18 sorbent material used in the SPE columns. The majority of contaminants from SPME are highly substituted *bis* phenols, 1,9-nonanediol, and phthalates. The carbowax phase of the fiber used was believed to be the source of 1,9-nonanediol. If a different fiber is used, this contaminant may be eliminated but may introduce other contaminants. The other major contaminants were not fiber specific and must be monitored using laboratory blanks.

Many factors play into the concentration and type of contaminants seen: volume and type of solvents used, make of SPE column, type of SPME fiber used, *etc*. This study demonstrates the importance of characterizing the compounds that arise from laboratory contamination and the need for a library to be made of these compounds specific to each laboratory and experimental method.

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