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Application of solid-phase microextraction to the headspace gas chromatographic analysis of halogenated volatiles in selected foods

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ABSTRACT

Solid-phase microextraction (SPME), with the poly(dimethylsiloxane)-coated silica fiber suspended and equilibrated in the headspace, has been applied to the capillary gas chromatographic (GC) analysis of 33 halogenated volatile contaminants in model aqueous solutions and in foods. With electrolytic conductivity detection, the limits of detection in water ranged from 1.5 μg/kg for vinyl chloride to ≤ 0.005 μg/kg for the tri- to hexachlorobenzenes. Headspace SPME–GC shows a much greater response for the less volatile analytes than those of greater volatility, a procedure complementing headspace GC with gas sampling. In model systems or foods, increasing lipid material decreased the headspace extraction. With 50 mg of lipid, the headspace extraction decreased about 50% for analytes with LODs about 0.1 μg/kg and by $\geq 99.5\%$ for the above chlorobenzenes. Standard addition was used to analyze a variety of beverages and dry foods and to determine the analyte partitions.

INTRODUCTION

Solid-phase microextraction (SPME) is a relatively new sampling technique first described by Belardi and Pawliszyn [1]. Their procedure employs a stationary phase, usually poly(dimethylsiloxane), coated on a fused-silica fiber to extract aqueous samples in completely filled sealed vials. After equilibration between the liquid and the coated fiber, the analytes are thermally desorbed in the injection port of a gas chromatograph, cryofocussed on-column, and separated and detected by established GC procedures. For protection and ease of handling the fiber is attached to a tube which replaces the plunger of a 5-μl positive displacement syringe. The fiber is extended only during sampling or desorption of the analyte.

Pawliszyn and co-workers have conducted extensive studies on SPME including its automation and optimization [2], the dynamics of adsorption [3], the analysis of benzene in water at trace levels [4], aromatic compounds in groundwater [5], and the analysis of caffeine in beverages using an uncoated silica fiber [6]. SPME has been applied to many of the volatile analytes included in the US Environmental Protection Agency Method 624. Some of these studies have recently been summarized and it is reported that a commercial SPME device is forthcoming [7].

In classical headspace gas chromatography (GC), the analyte equilibrates between a liquid and the gas phase in a closed system. At equilibrium, an aliquot of the headspace is taken and analyzed by GC. Apart from the chromatographic detection and separation, the sensitivity attained by headspace GC is dependant on several factors including the vapor pressure of the analyte, the activity coefficient of the analyte in

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the matrix in which it is present [8], as well as the volume of headspace sampled.

In our studies we have extended the classical two-phase headspace GC technique described above to include the SPME fiber coating as a third phase, suspended and equilibrated in the headspace. With the SPME sampling of the headspace, aqueous systems containing dissolved or suspended solids or non-volatile oil can be analyzed. Furthermore, salts may be added to the aqueous phase to increase the partition of volatiles into the headspace.

Using model aqueous systems, our studies compare the classical headspace GC procedure to the proposed headspace SPME–GC combination. The effect of non-polar non-volatile material on the headspace SPME–GC sensitivity in model systems is also studied. Practical application of SPME–headspace GC to a variety of foods, and the matrix effects of the food constituents on the partition into the coated fiber of the SPME device are studied and discussed.

EXPERIMENTAL

Solid-phase microextraction device

The SPME device was constructed as described by Potter and Pawliszyn [4] with minor dimensional modifications using either a Hamilton Model 7105 microliter syringe (Hamilton, Reno, NV, USA) or an SGE Model 5BR-7 microvolume syringe (SGE, Austin, TX, USA) and a 1 or 2 cm length of 100 μm thick poly(dimethylsiloxane)-coated fused-silica optical fiber (FLS100110300, Polymicro Technologies, Tuscon, AZ, USA). The stripped silica end of the coated fiber was cemented into 30 gauge (0.30 mm) stainless-steel tubing for the Hamilton syringe or 28 gauge (0.36 mm) tubing for the SGE syringe using a high-temperature epoxy resin (Epoxy-Patch No. 9340, Dexter, Seabrook, NH, USA). The fiber assembly is held in place in the SGE syringe using a 2×8 mm metric machine screw. After curing overnight the fiber assembly was heated at 250°C in the injector of the GC for 30 min before use. The needle tube with the attached fiber was adjusted so the end of the tube protruded 33 mm beyond the end of the needle when extended and the end of the fiber was 1 cm inside the needle when retracted.

A needle spacer for the Hamilton SPME syringe was fashioned from a 16 or 17 gauge luer tip hypodermic needle cut so the syringe needle protruded about 6 mm when the needle spacer was fitted to the external luer fitting of the syringe. The SGE syringe needle, however, does not have an external luer fitting so a similar spacer was used but did not attach firmly to the syringe. Needle spacers allow reproducible insertion of the needle without over-insertion.

Desorption and chromatography

The desorption of the analytes from fiber and the capillary separation was performed using a Varian Model Vista 6000 GC with cryogenic oven cooling. The GC was equipped with a Hall electrolytic conductivity detector operating in the reductive halogen mode for detection of the halogenated analytes. A disposable electrolyte system (N-Phase, Austin, TX, USA) was used with the detector. An attenuation of $8 \times$ was used for most samples; $2 \times$ was used when estimating sensitivity. The on-column injector of the Varian 6000 GC was replaced by that from a Varian 3400 GC to accommodate 0.53 mm I.D. tubing and further modified (Fig. 1) to permit proper positioning of the fiber for desorption. The glass alignment tube of the injector was

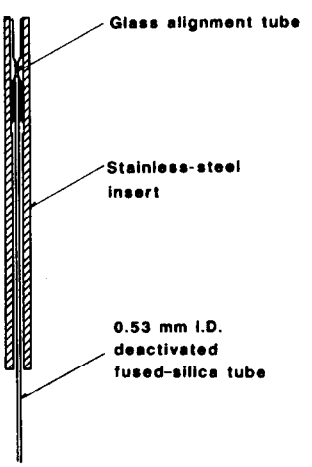

Fig. 1. On-column stainless-steel injector insert and alignment tube for smooth insertion of SPME fiber into 0.53 mm I.D. deactivated fused-silica tubing.

replaced by a 6.5 cm length of 2.1 mm I.D. stainless-steel tubing machined to 4.43 mm O.D. The upper end of the tube was drilled to 2.5 mm I.D. for a depth of 2.3 cm to accommodate a glass 0.53 mm to 0.53 mm press-fit capillary column union (Chromfit, Chromatographic Specialties, Brockville, Ontario, Canada) which acted as an alignment tube for fiber insertion into a 0.5 m × 0.53 mm I.D. piece of deactivated fused-silica tubing for desorption. The constriction in this union is wide enough to permit passage of the fiber assembly. For this purpose the union can also be prepared by carefully drawing out a piece of 2 mm pyrex tubing, cutting to 2 cm in length and fire-polishing the ends. The cap seal of the injector was enlarged to 9.53 mm I.D. to a depth of 6 mm to allow deeper entry of the SGE syringe. The Varian injector needle seal accommodated the SGE syringe but not the Hamilton syringe. For the latter syringe a 9.53 mm diameter HT-9 septum (Alltech, Deerfield, IL, USA) was modified to provide a needle seal using a short piece of 1.5 mm O.D. × 0.3 mm I.D. PTFE tubing flared at one end, inserted through a hole pierced in the center of the septum, and cut off flush. With the fiber assembly adjusted as described above, the syringe end of the fiber will be positioned 2.0 to 2.5 cm into the 0.53 mm deactivated tubing.

The halogenated analytes were separated on a 0.32 m × 30 mm DB-624 (J&W Scientific, Folsom, CA, USA) fused-silica capillary column (1.8-μm film) which was connected to the 0.5 m fused-silica tubing described above using a press-fit capillary column union. The exit of the GC column was connected to the detector by a 0.3 m length of 0.25 mm I.D. deactivated fused-silica tubing which was inserted 3–4 mm into the 0.5 mm I.D. nickel reactor tube. Helium at 2 ml/min (41 cm/s) was used as a carrier gas. The analytes were desorbed from the fiber in the injector by a temperature program from 0 to 250°C at 60°C/min with a 28-min hold. The oven was programmed from − 40°C (2 min hold) for SPME desorption [− 60°C (1.6 min hold) for gas sampling] to 30°C at 50°C/min and then to 250°C at 8°C/min (2 min hold). The detector base was at 250°C and the reactor at 850°C.

Standards

The volatiles determined and studied are listed in Table I. Primary stock solutions of standards were prepared as described by Environmental

TABLE I

VOLATILES STUDIED IN ORDER OF ELUTION AND THEIR REFERENCE NUMBERS

Volatile	No.	Volatile	No.
Vinyl chloride	1	Chlorodibromomethane	18
Methyl bromide	2	1,2-Dibromoethane	19
1,1-Dichloroethylene	3	Chlorobenzene	20
Dichloromethane	4	Bromoform	21
trans-1,2-Dichloroethylene	5	Bromobenzene	22
1,1-Dichloroethane	6	*o*-Chlorotoluene	23
cis-1,2-Dichloroethylene	7	*p*-Chlorotoluene	24
Chloroform	8	*p*-Dichlorobenzene	25
1,1,1-Trichloroethane	9	*o*-Dichlorobenzene	26
Carbon tetrachloride	10	1,2-Dibromo-3-chloropropane	27
1,2-Dichloroethane	11	1,2,4-Trichlorobenzene	28
Trichloroethylene	12	1,2,3-Trichlorobenzene	29
1,2-Dichloropropane	13	1,2,4,5-Tetrachlorobenzene	30
Dibromomethane	14	1,2,3,4-Tetrachlorobenzene	31
Bromodichloromethane	15	Pentachlorobenzene	32
1,1,2-Trichloroethane	16	Hexachlorobenzene	33
Tetrachloroethylene	17		

Protection Agency procedures [9] using chemicals purchased separately to give standards of about 2 mg/ml for each volatile. Hexachlorobenzene was prepared separately in acetone. Secondary standards were prepared by dilution of the primary standard in methanol to give concentrations of 10, 2, 0.4, 0.08, and 0.016 μg/ml for each analyte. Methanol, suitable for trace volatile analysis (Burdick and Jackson, Muskegon, MI, USA) was used to prepare all standards. Liquid chromatographic grade water (Milli-Q system, Millipore, Bedford, MA, USA) was used as required.

Headspace equipment and procedures

For headspace gas analysis and SPME sampling, 30-ml crimp-top headspace vials (actual capacity about 37 ml), 20 mm × 3 mm laminated silicone–PTFE (0.25 mm) septa, and aluminum seals (Supelco, Oakville, Ontario, Canada) were used. PTFE-coated, 25 × 7.5 mm magnetic stirring bars were used for stirring in the vials. The stirring rate was set to give a vortex depth of 1 cm.

The 1-ml headspace gas sampling and injection was conducted using equipment and procedures described previously [10]. The modified injector was used with this needle.

For headspace gas sampling by SPME, the vial septum was prepierced in the center, if required, with a sharp thin probe just before sampling to facilitate insertion of the SPME syringe needle. The needle was inserted so the spacer pushed firmly on the septum surface and the fiber assembly extended so the end of the fiber was about 1 cm above the surface of the liquid. The syringe was clamped in this position and the stirring commenced. After 30 min the fiber assembly was retracted, the syringe needle withdrawn from the septum, the needle inserted into the injector, the fiber extended, and the oven and injector temperature programs started. The fiber was left in place and desorbed for 15 min to ensure total desorption of the least volatile analytes. The procedure for liquid sampling by SPME was only employed with clean water and is the same as described above for SPME sampling of the headspace except that the end of the fiber was positioned about 0.5 cm above the stirring bar.

Studies in model systems

In these studies, unless noted otherwise, stirred vials containing 15 g of water and 6 g of sodium chloride and optimized equilibration times of 30 min and desorption times of 15 min at 250°C were employed. The vials were sealed and spiked through the septum using a 10-μl syringe to give 30 ng of each volatile. The resulting peak areas were either compared to those of another study, to an aqueous standard or to a 1-μl injection of the same volatiles at 1 μg/ml in cold (0°C) 2-pentane.

The relative sensitivity between headspace gas syringe sampling and headspace SPME sampling was studied. The sampled volatiles were either injected or desorbed, respectively, as described previously.

The repeatability of the headspace SPME–GC procedure was studied using six vials each containing 15 g of water, 6 g of sodium chloride and a stirring bar.

The limits of detection (LODs) of the headspace SPME–GC procedure were studied by spiking vials with 3-μl aliquots of standards containing 10, 2, 0.08, 0.04 and 0.016 μg/ml of each analyte.

Vials with no added salt and 25 g of water, required for complete fiber immersion, were used to evaluate the effect of fiber position on the analyte equilibration between the aqueous solution, the headspace gas and the poly(dimethylsiloxane) fiber coating. The SPME fiber was inserted into the spiked water or into the headspace over the water and equilibrated with stirring for 0.75, 1.5 or 3 h.

The effect of dissolved salt on the liquid–gas–solid equilibrium was studied with 6 g of either anhydrous sodium sulfate, sodium chloride or potassium chloride.

The decreases in sensitivity of the headspace SPME procedure were studied using 1.5, 12, 58, and 240 mg of a mixed vegetable oil as representative non-polar lipid food components.

Headspace SPME analysis of beverages and finely divided dry foods

The procedures for obtaining various types of beverage and food samples and their addition to the headspace vials for volatile analysis have been previously described [10–12] and were used in this study.

To analyze beverages, other aqueous samples or finely divided dry foods, three vials, each containing a magnetic stirring bar, 6.0 g of sodium chloride and loosely covered with the laminated silicone–PTFE septum were cooled in a water–ice bath for at least 15 min. For the dry foods, 15 g of water was also added to each vial. The cold liquid (4°C) or dry food (−20°C) samples were opened and, in succession, each vial was tared on a top-loading balance, 15 g aliquots of the liquid or 1.0 g sample of the dry food were added and each vial immediately sealed. After warming to room temperature, the first vial was sampled by headspace SPME for 30 min and analyzed as described above. Halogenated analytes were identified by comparison of retention times to those of external standards. To provide quantitation of any detected GC peaks and to evaluate the matrix effects on the headspace partition of various analytes from a particular sample, the second vial was spiked through the septum using a 10-μl syringe to give 30 ng of each volatile and sampled by headspace SPME as for the first sample. From the increase in peak area of a particular analyte, the concentration of that analyte in the sample can be calculated. When the analyte peak is greater than half that of the enhanced analyte peak (incurred plus added analyte) then quantitation should be conducted by a greater standard addition to the third vial. If the analyte response is too great, smaller, but representative samples of equal weight, can be taken analyzed using appropriate standard additions. Liquids are diluted in the headspace vial with water to give 15 g total liquid. Where the observed matrix effect on the headspace partition for the sample is the same as that for clean water, sample analytes can be quantitated from aqueous external standards.

A limited survey of locally purchased foods and beverages was conducted using headspace SPME–GC to study the analyte partitions and to determine the levels of any incurred chlorinated volatile contaminants.

RESULTS AND DISCUSSION

Headspace SPME–GC equipment

The SPME fiber assemblies were prepared according to Potter and Pawliszyn [4] for use with both the Hamilton and SGE syringes. The SGE syringe, with a blunt 0.63 mm O.D. needle was compatible with the existing Varian injector needle seal. Needle seals were considered preferable to septum injection which could inadvertently introduce pieces of septum into the GC column. For the Hamilton syringe a needle seal was fabricated in-house. All seals and syringes were tested to ensure the absence of leaks as suggested by Potter and Pawliszyn [4]. For best repeatability, the same fiber was used for replicate determinations as even two apparently identical fibers extracted and desorbed slightly different amounts of analytes from over identical solutions. Coated fibers of 2 cm were found to give peaks about twice those of the 1-cm fiber but for convenience and ease of handling, 1-cm fibers were used throughout. The constriction of the press-fit capillary unions used in the injector, permitted facile passage of the 30 gauge fiber assembly of the Hamilton syringe in 8 of 10 unions evaluated yet only 3 of the 10 permitted entry of the 28 gauge tubing required for the SGE syringe.

With on-column cryofocussing, desorption of the SPME fiber or headspace gas injection using the gas-tight syringe in the modified injector gave acceptable chromatograms for all analytes as shown in Fig. 2A and B. Oven cryofocussing, −60°C for the 1-ml headspace injection and −40°C for the desorption, was required to reduce peak broadening of the early eluting peaks. The peak widths were comparable to those obtained from a 1-μl liquid injection in the same injector. No carryover of undesorbed analytes was observed when the fiber was desorbed for a second time. The desorption temperature originally used was 230°C, however, when hexachlorobenzene was later included as one of the

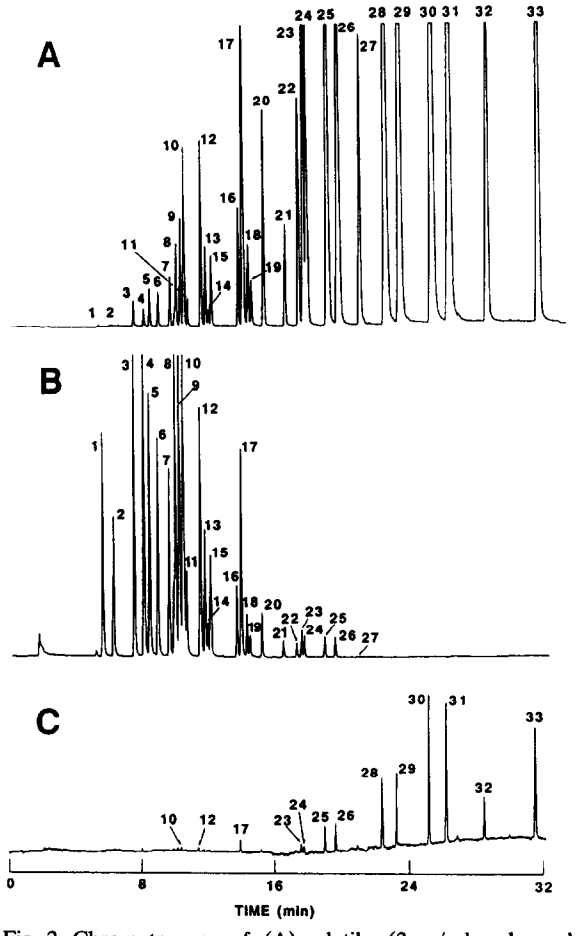

Fig. 2. Chromatograms of: (A) volatiles (2 ng/ml each, peak identities as in Table I) by headspace SPME over 15 ml NaCl saturated water; (B) as in (A) but 1 ml of the headspace injected; (C) as in (A) but at 0.016 ng/ml.

analytes, the desorption temperature was raised to 250°C. This increased temperature also gave complete desorption in 15 min. The equilibration time of the analytes, including hexachlorobenzene, between the liquid, gas and solid phases, when spiked into the liquid and analyzed by headspace SPME was found to be less than 30 min. Thus, when using the same SPME device, samples could be equilibrated and desorbed every 45 min. This turnaround time was only slightly greater than that for the GC.

Because the vial septum consists of a 0.25 mm thick PTFE layer on a silicone backing it was important to evaluate possible analyte adsorption by the silicone once the PTFE layer was pierced. Therefore, five additional punctures were made in the septum with a 20-gauge needle but without needles to plug the punctures. Headspace SPME analysis indicated about a 20% loss attributed to the exposed silicone. Thus, the loss to one puncture would be less than 5% and possibly even less when the SPME needle was in place in the puncture during the headspace SPME sampling.

Table I lists the volatiles studied in our laboratory using the SPME technique. Other halogenated volatiles which may co-elute with or not cleanly separate from those in Table I on the 30-m DB-624 column used in our studies were not included. If required, two possible co-eluting halogenated volatiles may be differentiated using specific detectors or other capillary columns capable of the desired separation.

Our interest in volatile halogenated contaminants concerns their determination in foods and beverages. Arthur *et al.* [7] had demonstrated the application of SPME to volatiles extracted with the coated fiber positioned in water. Our goal was to extend the application of SPME to beverages or to suspensions of dry foods in water. Except for clean water, however, sampling foods or beverages with the SPME fiber positioned in the liquid could possibly transfer non-volatile food material adsorbed by, or adhering to the fiber to the injector and the GC column. Therefore, for food analysis, we chose to evaluate SPME for sampling volatiles in the headspace followed by desorption in the injector and capillary GC separation with electrolytic conductivity detection.

Studies in model systems

The results of the studies in model systems are given in Table II with representative chromatograms presented in Fig. 2. The chromatograms of the analytes desorbed from the coated fiber or injected in 1 ml of headspace gas are shown in Fig. 2A and B, respectively. The percentage of each analyte transferred to the GC for analysis using these two techniques is given in Table II. Because of the different phase volumes, only 1 ml of the total 21.8 ml headspace gas is sampled and determined, yet all of the analyte in the 0.6-μl fiber coating is desorbed and determined.

TABLE II

STUDIES IN MODEL SYSTEMS: HEADSPACE SYRINGE *VS.* HEADSPACE SPME, THE EFFECT OF ADDED SODIUM CHLORIDE, PRECISION (R.S.D.) BY SPME ($n = 6$), LIMIT OF DETECTION (LOD, IN WATER), AND MATRIX EFFECTS OF ADDED NON-POLAR MATERIAL (*VS.* WATER)

No.	% of analyte sampled		% increase with salt by SPME	R.S.D. at 2 μg/kg	LOD (μg/kg)	Matrix effect (% rec. from veg. oil *vs.* water)			
	Syringe	SMPE				1.5 mg	12 mg	58 mg	240 mg
1	1.5	0.02	100	6.1	1.5	100	93.4	100	68.1
2	3.0	0.03	n.d.[a]	8.7	0.75	85.7	92.5	100	56.5
3	4.3	0.36	261	4.2	0.10	105	86.6	67.3	32.0
4	1.8	0.16	300	35	0.10	95.4	96.9	81.2	36.5
5	3.4	0.41	412	4.4	0.10	106	77.1	53.7	23.0
6	2.6	0.40	511	3.6	0.10	107	79.8	54.1	23.3
7	2.2	0.59	638	2.8	0.10	108	74.1	48.0	15.3
8	2.4	0.56	662	4.3	0.05	106	63.9	40.3	17.6
9	3.3	1.2	264	4.4	0.03	87.5	72.8	28.6	10.3
10	3.7	1.5	141	4.7	0.03	98.4	72.2	27.7	9.5
11	2.7	0.35	1160	5.1	0.15	114	75.8	56.0	23.3
12	2.9	1.9	353	4.1	0.02	99.3	59.1	19.4	5.8
13	2.2	1.2	710	3.6	0.05	107	64.1	27.2	7.2
14	0.28	0.24	300	6.1	0.02	114	59.5	40.2	15.0
15	1.5	0.84	843	3.4	0.20	106	57.5	23.4	6.8
16	0.69	1.0	958	4.1	0.07	107	60.2	22.0	5.2
17	2.6	5.7	127	5.8	0.04	85.2	37.8	7.2	2.0
18	0.47	0.97	865	4.8	0.08	99.5	46.8	14.2	3.7
19	0.32	0.80	1050	4.5	0.15	104	51.4	18.3	5.3
20	1.8	6.9	642	3.9	0.02	82.3	25.4	5.0	1.0
21	0.18	1.5	2173	4.9	0.08	94.8	38.0	10.0	2.5
22	0.84	12	1897	3.7	0.02	64.9	13.0	1.9	0.4
23	1.3	16	347	4.8	0.01	56.4	11.3	1.4	0.4
24	1.1	22	395	3.9	0.01	50.8	10.5	1.1	0.4
25	0.49	22	460	4.1	0.005	43.5	7.9	1.1	0.4
26	0.39	26	576	3.7	0.005	43	7.8	1.1	0.4
27	tr.[b]	4.3	1318	3.8	0.03	76.7	19.6	3.8	0.9
28	tr.	46	258	5.3	0.002	22.2	3.8	0.5	0.1
29	–[c]	57	297	4.7	0.002	22.2	3.6	0.5	0.1
30	–	56	121	7.6	0.002	17.2	3.1	0.5	0.2
31	–	72	144	7.7	0.002	17.0	3.7	0.5	0.2
32	–	57	69.7	9.9	0.005	8.1	3.3	0.3	0.2
33	–	n.d.	n.d.	15.2	0.002	2.8	3.0	0.2	0.2

[a] n.d. = Not determined: No. 2, peak detected only when salt added; No. 33 not included in standard.
[b] tr. = Trace level found, $< 3 \times$ baseline noise.
[c] Not detected.

These results relate to the practical sensitivity of each procedure and show the 1-ml headspace gas sampling technique to be progressively more sensitive as the volatility of the analyte, evidenced by earlier GC elution, increases. With SPME, however, as the analyte mass increases, the water solubility (polarity) and analyte volatility decrease, and increasingly more of any analyte that partitions into the headspace from the liquid will be extracted by the non-polar fiber and determined. SPME is progressively more sensitive as the analyte volatility, evidenced by later GC elution, decreases. Thus, headspace gas sampling and headspace SPME can be consid-

ered as complementary headspace sampling procedures.

The adsorption of the analytes with the fiber immersed in the water gave >90% of the peak areas obtained when the fiber was suspended in the headspace for the first 26 volatiles after 0.75 h. The later-eluting 7 volatiles gave 87–25% of the headspace response. Increasing the equilibration time to 1.5 and 3.0 h increased the water sampling to >90% of the headspace response for the first 29 analytes, with the tetra-, penta- and hexachlorobenzenes being found at 75–50%. There was little difference between the 1.5- and 3.0-h results. This study demonstrates that the liquid–solid (fiber in water) equilibration time is slower than the liquid–gas–solid (fiber in headspace) equilibration, even though the analytes are added to the water.

Table II also shows the relative standard deviation for replicate determinations from 15 ml of water containing 30 ng of each target analyte with all values below 10% except for *cis*-1,2-dichloroethylene (No. 4, 35%) and hexachlorobenzene (No. 33, 15.2%). The limit of detection (LOD), defined as 3 × the baseline noise, determined by headspace SPME in a 15-ml solution of water are given in Table II and parallel the percentage of each analyte sampled by headspace SPME as discussed previously. These LODs were extrapolated from several dilute standards with the detector at attenuation 2. Examples of these low detection limits for several of the less volatile analytes are shown in Fig. 2C. The limit of quantitation, defined as 10 × the baseline noise, or about 3 × the LOD, can be calculated from the LOD data.

The effects of aqueous saturation by various salts on the partition of the analytes into the coated fiber showed slightly smaller peaks for the earlier-eluting volatiles with sodium sulfate saturation compared to sodium chloride. The later-eluting volatile peaks were comparable. Potassium chloride gave smaller peaks for all the volatiles. Table II shows increases of the headspace SPME response by factors ranging from about 70 to 2170% when water is saturated with sodium chloride.

The matrix effects of increasing non-volatile non-polar food constituents, represented in Table II by a mixed vegetable oil, are given as the percent recovered compared to water. These reduced recoveries are to be expected, as vegetable oil, present in volumes of about 1.6 to 260 μl, competes with the 0.6-μl SPME fiber coating for the non-polar volatiles. The more volatile analytes are less affected by added oil as they partition significantly into the gas phase in addition to the combined non-polar phases. When large amounts, *e.g.*, 1 g of lipid material, are present, and 30 ng of each analyte are added, then only the first 17 peaks are above the LOD. The effects of proteinaceous material on the partition into the headspace was not studied.

Analytical results for selected foods

Table III reports the halogenated volatiles found in selected waters, fruit juices, fruit drinks, soft drinks and milks. Products to which water from public supplies could have been added, including water itself and the beverages listing water as an ingredient, were found to contain by-products of the water chlorination process, including chloroform (No. 8), bromodichloromethane (No. 15) and chlorodibromomethane (No. 18). Chloroform was found at levels ranging from 0.2 to 14.8 μg/kg. Of these eight samples four also contained bromodichloromethane. The other beverages in Table III, not listing water as an ingredient, were the grapefruit and the apple juice, and the three milks. In these five products, chloroform found was found only at low levels.

Standard addition provides for quantitation but also permits an evaluation of the partition of the target analytes between the SPME fiber and the particular sample matrix (5 g sample aliquot, 10 g water and 6 g of sodium chloride). The effect of non-polar non-volatile sample material parallels that of the vegetable oil noted above for Table II. Apple juice, the cola and ginger ale soft drinks and the cranberry–raspberry drink apparently contain little non-polar material as the analyte partition of all but the last two volatiles are generally >80%. The other juices and drinks, however, contain non-polar volatile and non-volatile material which reduce the partition of the volatiles into the fiber.

Of unique interest is *d*-limonene, a volatile

TABLE III

HALOGENATED VOLATILES IN μg/kg FOUND IN SELECTED BEVERAGES (5 g + 10 g WATER) AND THEIR HEADSPACE SPME PARTITION (%, IN PARENTHESES) COMPARED TO CLEAN WATER (15 ml, 2 μg/kg)

No.	Water[a]		Fruit juice				Soft drink			Fruit drink			Milk, % butterfat		
	Tap	Bottled	Pear	Orange	Apple	Grape-fruit	Orange	Cola	Ginger ale	Citrus	Cranb. rasp.	Lemonade	0.1	2.0	3.4
1	–	–	(117)	(85.7)	(111)	(114)	(75.0)	(100)	(100)	(100)	(100)	(109)	(100)	(60.0)	(83.3)
2	–	–	(89.3)	(96.3)	(94.4)	(132)	(78.5)	(75)	(75.0)	(71.5)	(95.2)	(68.7)	(88.0)	(55.2)	(85.7)
3	–	–	(109)	(92.4)	(106)	(109)	(96.8)	(90.4)	(94.0)	(96.6)	(74.4)	(100)	(82.4)	(29.4)	(26.7)
4	–	–	4.6(47.5)	(89.9)	(66.5)	(96.7)	(93.7)	(118)	(116)	(98.5)	(90.4)	(109)	(103)	(66.8)	(66.6)
5	–	–	(104)	(90.1)	(108)	(106)	(103)	(94.0)	(95.8)	(105)	(86.0)	0.49(93.5)	(77.2)	(28.0)	(21.5)
6	–	–	(98.3)	(83.4)	(102)	(98.1)	(94.5)	(86.1)	(91.8)	(91.7)	(82.4)	(95.5)	(81.3)	(28.8)	(23.8)
7	–	–	(95.4)	(84.2)	(102)	(94.3)	(88.9)	(86.7)	(94.4)	(90.7)	(84.9)	(94.8)	(73.2)	(27.0)	(20.1)
8	11.9	1.09	1.2(102)	2.18(86.5)	0.55(108)	(92.3)	2.62(97.7)	10.8(104)	1.56(103)	7.20(128)	14.8(97.0)	0.20(94.2)	0.33(85.5)	1.25(27.9)	(19.5)
9	–	–	(101)	(62.6)	(106)	(86.7)	(91.0)	(73.6)	(86.9)	(87.2)	(67.1)	(95.1)	(62.1)	(12.3)	(8.7)
10	–	–	(97.5)	(68.3)	(108)	(94.5)	(92.6)	(81.2)	(87.1)	(85.5)	(77.5)	(94.2)	(51.7)	(8.6)	(6.3)
11	–	–	(105)	(85.1)	(117)	(88.3)	(86.5)	(97.2)	(103)	(89.6)	(90.2)	(90.2)	(86.5)	(30.7)	(32.2)
12	–	–	(90.6)	(74.7)	(103)	(88.9)	(92.5)	(84.5)	(90.6)	(90.6)	(78.1)	(94.3)	(54.2)	(9.6)	(6.8)
13	–	–	(93.4)	(78.7)	(103)	(87.0)	(85.9)	(86.3)	(94.0)	(89.9)	(83.6)	(91.3)	(67.6)	(16.3)	(10.9)
14	–	–	(91.7)	(79.9)	(112)	(85.5)	(83.3)	(112)	(121)	(87.6)	(88.2)	(84.2)	(61.9)	(25.8)	(20.5)
15	0.53	0.39	1.2(97.1)	0.31(77.4)	(106)	(81.3)	1.72(94.2)	(98)	0.82(108)	(104)	4.7(96.0)	(90.6)	(56.4)	(11.9)	(8.9)
16	–	–	(89.3)	(73.3)	(107)	(77.2)	(81.7)	(91.2)	(103)	(93.8)	(85.7)	(86.4)	(59.4)	(12.2)	(8.3)
17	–	–	(80.0)	(47.7)	(106)	(74.1)	(84.9)	(87.3)	(92.7)	(64.8)	(77.8)	(85.0)	(33.2)	(3.5)	(2.3)
18	–	–	(80.5)	(66.1)	(107)	(73.0)	0.41(87.3)	(96.7)	(113)	(94.8)	1.8(91.7)	(85.6)	(40.8)	(7.7)	(4.9)
19	–	–	(90.1)	(74.8)	(113)	(78.9)	(87.5)	(98.9)	(111)	(101)	(90.0)	(82.8)	(55.6)	(10.4)	(6.6)
20	0.10	–	(69.2)	(49.5)	(102)	(64.8)	(80.0)	(80.3)	(89.8)	(67.4)	(80.5)	0.09(86.0)	(27.1)	(2.7)	(1.5)
21	–	–	(69.2)	(56.9)	(107)	(63.5)	(78.4)	(96.7)	(105)	(92.5)	(87.0)	(83.5)	(30.6)	(5.3)	(3.7)
22	–	–	(46.7)	(32.1)	(105)	(46.1)	(67.8)	(83.3)	(93.4)	(51.6)	(81.2)	(72.0)	(15.5)	(1.0)	(1.4)
23	–	–	(54.8)	(29.5)	(108)	(43.9)	(67.2)	(86.2)	(94.2)	(40.7)	(78.6)	(68.0)	(14.9)	(1.1)	(0.6)
24	–	–	(47.5)	(24.3)	(106)	(40.0)	(60.0)	(82.2)	(90.2)	(39.6)	(78.9)	(61.5)	(12.7)	(0.95)	(0.5)
25	–	–	(39.4)	(22.2)	0.16(103)	(34.6)	(46.6)	(84.1)	(93.7)	(6.3)[b]	(80.6)	(57.8)	(10.8)	(2.5)	(0.5)
26	–	–	0.02(38.6)	(18.9)	(102)	(28.9)	(53.5)	(78.8)	(92.7)	(31.1)	(79.1)	(56.5)	(8.9)	(1.4)	(0.4)
27	–	–	(57.2)	(40.1)	(102)	(51.1)	(67.9)	(90.9)	(98.7)	(68.0)	(85.8)	(70.8)	(22.1)	(2.4)	(1.1)
28	–	–	(23.9)	(9.3)	(111)	(16.1)	(32.4)	(94.8)	(100)	(16.8)	(85.1)	(32.2)	(4.8)	(0.45)	(0.2)
29	–	–	(21.5)	(7.4)	(114)	(13.4)	(30.6)	(88.3)	(98.2)	(15.4)	(82.0)	(31.6)	(3.7)	(0.40)	(0.1)
30	–	–	(15.3)	(4.4)	(121)	(8.6)	(17.2)	(101)	(106)	(7.8)	(89.8)	(18.8)	(2.7)	(0.20)	(0.1)
31	–	–	(12.9)	(3.5)	(123)	(7.1)	(16.3)	(90.7)	(105)	(7.8)	(82.8)	(18.1)	(1.8)	(0.18)	(0.08)
32	–	–	(5.8)	(1.2)	(110)	(2.7)	(7.2)	(71.6)	(101)	(7.5)	(71.2)	(6.7)	(0.7)	(0.13)	(–)[c]
33	–	–	(2.1)	(0.4)	(85)	(0.7)	(3.1)	(34.1)	(65)	(0.8)	(34.3)	(1.4)	(0.2)	(0.17)	(–)

[a] For water 15 g were analyzed. Partition data compared to clean water is 100% and is not reported.
[b] *d*-Limonene coelutes with *p*-dichlorobenzene and interferes its detector response.
[c] Peak not detected, partition not determined.

terpene associated with citrus products, which co-elutes with *p*-dichlorobenzene and disrupts its detection resulting in a small broadened peak for this analyte. To demonstrate that limonene causes this interference, an aqueous saline solution was spiked with 30 ng of each analyte and 1 mg of limonene, an amount chosen to slightly exceed the amount of limonene in 5 ml of processed orange juice [13]. The headspace SPME sampling failed with the Hamilton syringe, however, as the 0.3 mm O.D. fiber coating swelled so that it could not be retracted into the 0.33 mm I.D. protective needle. The SGE syringe, however, with the 0.37 mm I.D. needle readily accommodated the swollen fiber. The fiber swelling was observed with limonene only in model aqueous systems. Swelling was not observed in 5-g orange juice samples, even when spiked with limonene. Apparently non-volatile lipid material in the orange juice reduced the partition of limonene to the fiber. The swelling of the fiber appeared to be limited, as up to 25 mg of limonene in the vial did not restrict the fiber movement in the SGE syringe needle. The analyte capacity of the swollen fiber more than doubles for the more volatile analytes when compared to the unswollen fiber. The adverse chromatographic effects of limonene on the *p*-dichlorobenzene peak noted above were accentuated when limonene was present without juice.

Furthermore, the preceding two peaks were also broadened and not cleanly resolved. These findings with limonene also suggest that competitive adsorption, in which a benign volatile at high concentration may block or displace a target analyte from the fiber, is not an important consideration in headspace SPME.

Headspace SPME chromatograms of an orange juice, a cola soft drink and a fruit drink from Table III containing trihalomethanes are shown in Fig. 3A–C, respectively. There are no interferences evident. With the cola drink (Fig. 3B) there are a number of small peaks eluting between 18 and 30 min which do not correlate with any of the analytes studied. The chromatogram in Fig. 3D shows 15 ml of the blank water used for dilution of the juices, drinks and the milks at an attenuation of 2 × . Except for traces of dichloromethane (No. 4), there are no interferences.

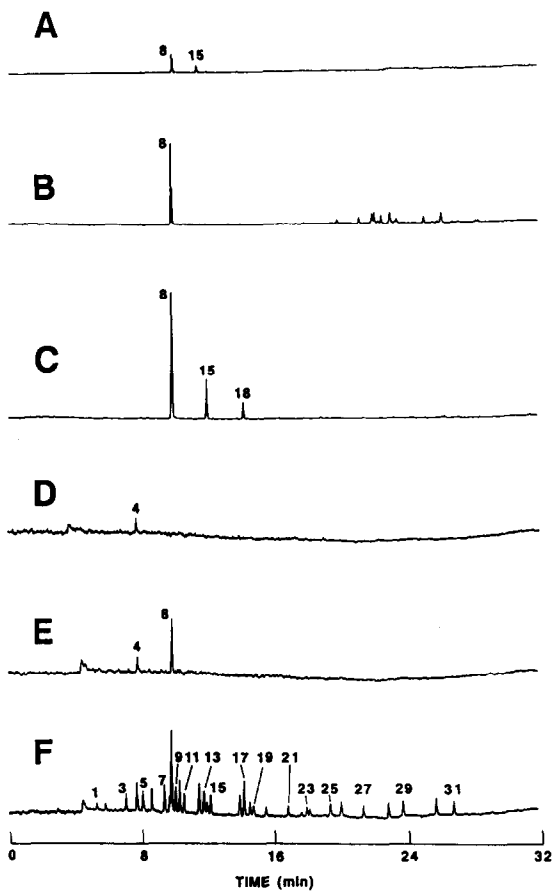

Fig. 3. Chromatograms of beverages, 5 g added to 10 ml of water: (A) orange juice containing chloroform (No. 8) and bromodichloromethane (No. 15); (B) cola soft drink containing No. 8; (C) cranberry–raspberry drink containing Nos. 8, 15 and chlorodibromomethane (No. 18); (D) water blank showing absence of interferences except for dichloromethane (No. 4); (E) 3.4% butter fat milk containing chloroform; and (F) as in (E) spiked at 4 μg/kg milk, only odd analytes numbered, peak identities as in Table I. Attenuation for (A), (B) and (C) 8 × ; others at 2 × .

The headspace SPME responses for the milk samples in Table III are reduced as the concentration of the butterfat increases. Fig. 3E shows the headspace SPME chromatogram at attenuation 2 × from 5 g unspiked 3.4% butterfat (about 170 mg) milk in 10 ml of water. Chloroform (No. 8) at about 9.3 μg/kg is detected in this sample. Fig. 3F shows this milk sample spiked with about 20 ng of each of the 33 analytes studied. An approximate 5-fold reduction of the chloroform response due to the butterfat is noted when Fig. 3F (milk at 2 ×) is compared to Fig. 3B (cola at 8 ×). Only about 10 of the volatiles in Fig. 3F can be considered as greater than the limit of quantitation (LOQ), others are between the LOQ and the LOD, and the volatiles Nos. 32 and 33 are not detected. Although the matrix effect varies considerably for the beverages studied, headspace SPME–GC can still detect and measure volatile contaminants at low μg/kg levels.

Table IV reports similar data to that of Table III for dry, finely divided foods. Most of these foods are reported [14] to contain appreciable lipid material: all-purpose white flour contains about 1.0% fat, the biscuit mix about 13%, the decaffeinated instant coffee 0.2% and the spices in Table IV, 0.5 to 36.3%. Comparable data for the decaffeinated teas and roasted and ground coffees were not available but the fat content of the non-decaffeinated products are 3% (dry weight, green leaf) [15], and 11.9% [16], respectively. In comparing these foods, the % partition from the food–water matrix to the SPME fiber is reduced with increasing food lipid content. Dichloromethane was found in the flour products and in the coffees and teas decaffeinated using dichloromethane. The biscuit mix was found to contain 1,1,1-trichloroethane at about 200 μg/kg. The origin of this contaminant was found to

TABLE IV

HALOGENATED VOLATILES IN μg/kg FOUND IN SELECTED DRY FOODS (1 g + 15 g WATER) AND THEIR HEADSPACE SPME PARTITION (%, IN PARENTHESES) COMPARED TO CLEAN WATER (15 ml, 2 μg/kg)

No.	Flour or flour-based		Decaffeinated teas			Decaffeinated coffees				Spices (% fat) [13]				
	All purpose	Biscuit mix	Brand A (DCM)[b]	Brand B (DCM)	Brand C (N.G.)[b]	Instant (Natural)	R&G[a] Brand A (Natural)	R&G Brand B (DCM)	R&G Brand C (DCM)	Paprika (12.9)	Ground pepper (3.3)	Cinnamon (3.2)	Onion flakes (0.5)	Nutmeg (36.3)
1	(124)	(77.7)	(81.9)[c]	–[c]	–	(100)	(69.0)[c]	–[c]	–	(107)	(88.2)	(87.3)	(100)	(100)
2	(71.6)	(107)	(69.5)	–	–	(107)	(75.3)	–	–	(80.4)	(90.0)	(100)	(75.2)	(85.0)
3	(96.2)	(50.8)	(51.1)	–	–	(83.2)	(24.5)	–	–	(74.7)	(31.6)	(68.0)	(90.2)	(32.7)
4	82.5(97.9)	70.3(10.1)	3.8(79.6)	58.6	13.5	(92.1)	(59.5)	308	76.5	(41.4)	(75.9)	(80.5)	(97.7)	(68.8)
5	(74.5)	(35.9)	(46.2)	–	–	(76.0)	(22.9)	–	–	(44.1)	(30.3)	(53.2)	(92.3)	(29.1)
6	(77.5)	(37.6)	(46.9)	–	–	(81.6)	(25.8)	–	–	(37.4)	(32.8)	(48.5)	(95.7)	(19.4)
7	(87.7)	(28.2)	(35.3)	–	–	(69.8)	(20.4)	–	–	(23.9)	(26.3)	(36.7)	(88.5)	(15.5)
8	(90.9)	(23.7)	(35.2)	–	–	(74.9)	(18.7)	–	–	(21.2)	(24.8)	(35.2)	(96.9)	(15.4)
9	(69.4)	206(15.4)	(31.2)	–	–	(66.3)	(10.0)	–	–	(41.5)	(12.8)	(41.5)	(70.9)	(14.3)
10	(52.1)	(17.0)	(26.1)	–	–	(56.6)	(9.6)	–	–	(40.2)	(9.3)	(37.1)	(62.6)	(14.6)
11	(74.7)	(30.5)	(39.6)	–	–	(65.6)	(26.2)	–	–	(23.7)	(30.4)	(33.0)	(86.7)	(20.4)
12	(52.9)	(9.1)	(23.8)	–	–	(55.3)	(9.1)	–	–	(23.9)	(8.2)	(28.3)	(64.7)	(8.0)
13	(66.9)	(11.9)	(27.3)	–	–	(60.0)	(13.5)	–	–	(14.2)	(18.8)	(29.6)	(80.5)	(8.4)
14	(63.2)	(20.6)	(26.9)	–	–	(54.1)	(17.6)	–	–	(16.3)	(38.9)	(26.6)	(96.6)	(17.4)
15	(44.2)	(9.1)	(20.4)	–	–	(49.8)	(10.9)	–	–	(10.5)	(18.7)	(21.7)	(76.8)	(7.3)
16	(47.2)	(10.4)	(18.4)	–	–	(47.8)	(9.4)	–	–	(8.6)	(12.4)	(16.7)	(70.6)	(5.5)
17	(28.0)	3.9(3.4)	(17.2)	–	–	(34.2)	(5.6)	128	–	(11.6)	(5.4)	(19.9)	(42.5)	(3.5)
18	(35.2)	(6.2)	(12.5)	–	–	(33.1)	(5.9)	–	–	(6.7)	(9.1)	(14.7)	(79.7)	(5.7)
19	(45.0)	(9.4)	(17.1)	–	–	(40.4)	(7.6)	–	–	(7.5)	(10.0)	(17.8)	(92.6)	(9.1)
20	(22.1)	(2.1)	(9.2)	–	–	(23.9)	(2.6)	–	–	(4.1)	(3.8)	(8.2)	(36.5)	(1.5)
21	(22.3)	(3.7)	(8.0)	–	–	(23.6)	(4.3)	–	–	(3.7)	(5.0)	(7.3)	(50.7)	(2.8)
22	(11.3)	(1.0)	(4.4)	–	–	(11.1)	(1.2)	–	–	(2.0)	(1.9)	(2.8)	(23.6)	(0.9)
23	(11.3)	(1.8)	(8.6)	–	–	(11.9)	(1.2)	–	–	(1.9)	(2.1)	(6.3)	(26.3)	(0.7)
24	(10.6)	19.6(0.7)	(7.1)	–	–	(11.9)	(1.1)	–	–	(1.3)	(1.3)	(3.6)	(18.0)	(0.3)
25	2.51(8.8)	31.9(1.4)	(5.3)	–	–	(8.0)	(1.0)	–	–	(1.6)	(1.8)	(3.2)	(15.9)	(0.8)
26	(7.4)	(0.2)	(4.2)	–	–	(6.7)	(0.7)	–	–	(1.3)	(1.4)	(2.4)	(13.7)	(0.4)
27	(17.0)	(1.7)	(5.0)	–	–	(11.7)	(2.2)	–	–	(7.2)	(2.0)	(3.8)	(28.6)	(0.9)
28	(4.2)	(0.2)	(4.6)	–	–	(3.0)	(0.3)	–	–	(0.9)	(0.8)	(1.7)	(6.9)	(0.2)
29	(3.6)	(0.2)	(3.5)	–	–	(2.3)	(0.3)	–	–	(1.1)	(0.7)	(1.3)	(5.5)	???
30	(2.9)	(0.2)	(6.1)	–	–	(1.0)	(0.1)	–	–	(1.7)	(0.6)	(1.8)	(4.5)	(0.2)
31	(2.4)	(0.2)	(4.5)	–	–	(0.8)	(0.1)	–	–	(2.1)	(0.5)	(1.4)	(3.2)	(2.2)
32	(1.1)	(0.2)	(4.8)	–	–	(0.3)	(–)[d]	–	–	(1.7)	(0.4)	(1.3)	(2.2)	(2.3)
33	(0.5)	(0.1)	(4.0)	–	–	(–)	(–)	–	–	(1.6)	(0.3)	(1.2)	(1.2)	(0.4)

[a] R&G = roasted and ground coffee.
[b] Decaffeination agent listed on package: DCM = dichloromethane; N.G. = not given; Natural = naturally decaffeinated (water or carbon dioxide).
[c] Partition data for Brands A averaged from 3 teas or 3 R&G coffees and not reported for other brands.
[d] Peak not detected, partition not determined.

be the paperboard adhesive of the retail package. Using headspace SPME, a small sample of the adhesive suspended in 15 g of water with added salt gave a massive off-scale GC peak for this volatile. Contamination of food by this source was first reported by Page and Charbonneau [17]. Others later reported similar incidents [18,19]. In the limited sampling of dichloromethane-decaffeinated teas and coffees, the levels of dichloromethane found are generally lower than those reported in an earlier survey [20]. Tetrachloroethylene was also found in one of the decaffeinated coffees at 128 μg/kg. Representative chromatograms of 1-g samples of the dry foods are shown in Fig. 4. Chromatograms of the biscuit mix, showing about 200 μg/kg of 1,1,1-trichloroethane (No. 9) and lower levels of other target analytes and a decaffeinated tea, showing 24 μg/kg dichloromethane (No. 4) and a number of unidentified low level responses are shown in Fig. 4A and B, respectively. Chromatograms of a naturally decaffeinated (water process) roasted and ground coffee, demonstrating the absence of halogenated volatiles, and the same coffee spiked with 30 μg/kg of the 33 analyte standard are displayed in Fig. 4C and D,

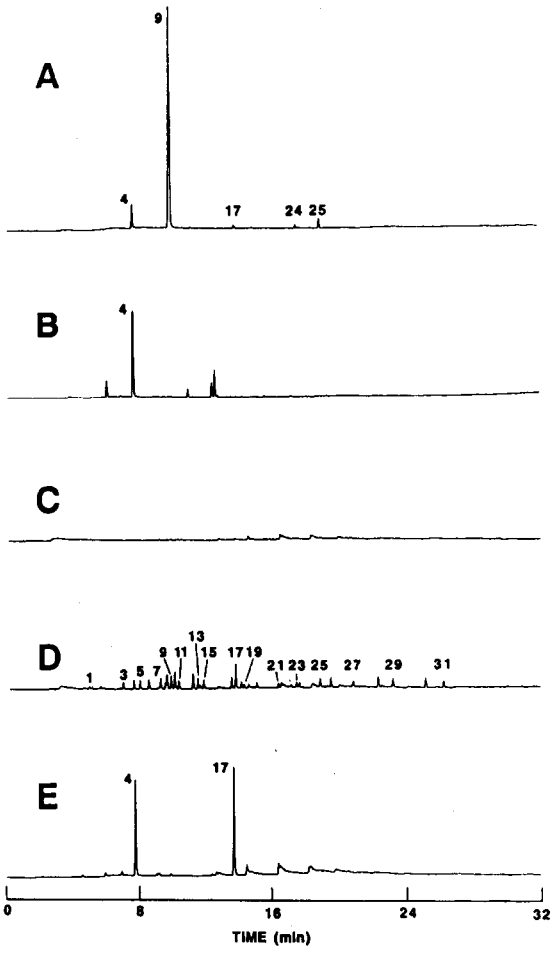

Fig. 4. Chromatograms of dry foods, 1 g added to 15 ml of water: (A) biscuit mix containing dichloromethane (No. 4) and 1,1,1-trichloroethane (No. 9); (B) dichloromethane-decaffeinated tea containing dichloromethane (No. 4); (C) roasted and ground naturally decaffeinated coffee; (D) as in (C) spiked at 30 μg/kg coffee, only odd analytes numbered, peak identities as in Table I; and (E) dichloromethane-decaffeinated roasted and ground coffee containing dichloromethane (No. 4) and tetrachloroethylene (No. 17).

respectively. The latter chromatogram demonstrates the expected reduction in method sensitivity due to the lipid material in the coffee. The last two peaks (Nos. 32 and 33) are not detected at the 30 μg/kg level and the other peaks are at or near the LOD or the LOQ. The final chromatogram (Fig. 4E) shows a dichloromethane-decaffeinated roasted and ground coffee with dichloromethane (No. 4) and tetrachloroethylene (No. 17) residues of about 300 and 130 μg/kg, respectively.

CONCLUSIONS

The application of a previously described SPME device to headspace sampling for capillary GC of a wide range of halogenated volatiles in model systems, water, beverages and finely divided foods is demonstrated. The headspace SPME–GC procedure is simple, robust, inexpensive, and uses existing or easily modified GC injectors. In water, detection of the tri- to hexachlorobenzenes at $\leq$0.005 μg/kg is attained. In water, the much greater response for the less volatile analytes than those of greater volatility complements headspace GC with gas sampling. When headspace SPME is applied to foods, increases in the lipid material markedly reduce the method sensitivity, the decrease being greatest for analytes of least volatility. Standard addition is required for quantitation of foods. Headspace SPME–GC should also be applicable to volatile non-halogenated analytes in similar matrices described above providing a suitable selective GC detector is used.

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