

# Purge and Trap Extraction with GC–MS Determination of Volatile Organic Compounds in Table-Ready Foods

David L. Heikes,\* Shannon R. Jensen, and Mary Ellen Fleming-Jones

Food and Drug Administration, 11510 West 80th Street, Lenexa, Kansas 66214-3338

A purge and trap procedure has been developed for the determination of volatile organic compounds (VOCs) in table-ready foods. VOC analytes are collected on a Vocab 3000 trap, thermally desorbed, and cryofocused directly on a capillary DB-624 column with GC–MS quantification. Adequate precision was achieved for 45 of the 60 analytes of U.S. EPA Method 524.2. Recoveries from 9 food samples fortified with these 45 analytes at 100 ppb and analyzed in duplicate ranged from 75.1 to 117% and from 61.3 to 160% for those fortified at 10 ppb. Average percentage of recovery standard deviation (%RSD) values were 11.3 and 20.4, respectively. Additionally, 234 table-ready foods of the FDA Total Diet Program were analyzed. A total of 77 foods showed residues > 50 ppb, 43 > 100 ppb. Only 47 items contained no residues. Toluene was the most common residue encountered, with residues in 91 foods. Cake doughnuts contained the highest total VOC residues (802 ppb).

**Keywords:** *Volatile organic compounds (VOCs); purge and trap; mass spectrometry*

## INTRODUCTION

Previous research efforts in this laboratory have resulted in methodology for the determination of eight volatile halocarbons (VHCs) and carbon disulfide in a variety of table-ready foods (Heikes, 1987). It was demonstrated that these VHCs were frequently encountered in table-ready foods as contaminant residues. Elevated levels (>1000 ppb) were found in foods high in fat content.

Volatile organic compounds (VOCs) are a loosely defined grouping of low molecular weight aliphatic and aromatic chemicals with low boiling points. Many are halogenated. The numerous and varied sources of VOCs include their use as chemical intermediates, solvents, dry-cleaning chemicals, degreasers, paints, and other industrial products. Additionally, VOCs are produced in certain combustion processes and chlorination of drinking water (Dunemann and Hajimiragha, 1993). It has even been determined that certain volatile chemicals are released from microwave heat-susceptor food packaging. McNeal and Hollifield (1993) identified 44 volatiles, including benzene and 1,1,1-trichloroethane, while testing packaging materials used for microwavable foods.

Because of their volatility, all VOCs are a potential source of contamination to both the environment and our food supply. Some are even allowed in foods as secondary and/or indirect food additives from components of commercial packaging, e.g. plastics (polymers), adhesives, coatings, paper, and paperboard (CFR, 1994a).

In recent years, a number of procedures have been developed for the determination of VOCs in foods. Several of these methods were directed at natural volatile components in soy sauce (Jitai et al., 1989), spices (Sashida et al., 1990), wines (Garcia-Jares et al., 1991), bottled beverages (Ridgeon, 1991), meat flavors (Ramarathnam et al., 1993a,b), cheese (Barcarolo et al., 1992; Barbieri et al., 1994), and grapefruit juice (Caddwallader and Xu, 1994). Interestingly, VOC monitoring in oranges (McCalley and Torres-Grifol, 1992) and milk (Cormier et al., 1991; Vallejo-Cordoba and Nakai, 1993, 1994) has been used as an indication of decomposition and freshness. Contaminant residues of VOCs have

been determined in eggs. Using headspace capillary GC with photoionization detection, Stein and Narang (1990) were able to determine nine volatile compounds including chlorinated ethenes, benzene, toluene, xylenes, and benzene derivatives at parts per billion levels. In 1989 McCown and Radenheimer presented a headspace GC–FID and GC–MS procedure for the determination of six VOCs in vegetable oils and fats fortified at 10 ppb. Chloroform, methylene chloride, and several benzene derivatives showed recoveries of 98–102%. Similarly, Thompson (1994) used purge and trap GC–MS to develop a method for the determination of volatile contaminants in bulk vegetable oils. A total of 20 volatile compounds were used to fortify 8 different oils. Recoveries ranged from 70 to 130% at low parts per billion levels.

The U.S. Food and Drug Administration (FDA) monitors residues of pesticides, industrial chemicals, metals, and nutrients in the nation's food supply through several programs. Of these, the Total Diet Program is one of the FDA's oldest residue surveillance studies, having been in existence since 1961. Only foods that have been rendered table-ready are examined. Selected foods are purchased from supermarkets in various regions of the United States and prepared as they would be in a domestic kitchen. Food lists based on surveys conducted by the U.S. Department of Agriculture are periodically updated to reflect existing food consumption habits (Pennington, 1983, 1992). The most recent revision of this study delineates the analysis of 265 food items which are representative of a 3571 item data base. Analytical data generated by this study are utilized to estimate dietary intakes for 14 age–sex categories of our national population. Results of this survey are published periodically (Yess et al., 1993).

Because VOCs are ubiquitous in the environment and many have specific health risks, it was deemed judicious that an analytical procedure be developed for the determination of these compounds in a variety of table-ready foods. The analytical data thus generated will allow toxicologists to reliably assess the significance of these VOCs in our nation's food supply on the basis of accurate dietary intake data. In this current effort, the 60 volatile compounds described in U.S. EPA Method

**Table 1. Composition of Foods Selected To Test Recovery and Reproducibility of the Developed Purge and Trap Procedure**

food item	% protein <sup>a</sup>	% fat <sup>a</sup>	% carbohydrate <sup>a</sup>
margarine	1	99	0
potato chips	7	38	55
bologna, sliced	27	66	7
Cheddar cheese	42	56	2
potatoes, boiled	8	0	92
cheeseburger, fast-food	28	33	39
spinach, boiled	43	4	53
chicken, fried	61	32	7
strained beef <sup>b</sup>	72	28	0

<sup>a</sup> Calculated on moisture-free basis from commercial labeling values. <sup>b</sup> Junior baby food.

**Table 2. Composition of Foods Selected for the Intralaboratory Collaboration of the Developed Purge and Trap Procedure**

food item	% protein <sup>b</sup>	% fat <sup>b</sup>	% carbohydrate <sup>b</sup>
French salad dressing <sup>a</sup>	1	69	30
black olives	5	60	35
half and half cream	16	61	23
ham lunch meat <sup>a</sup>	56	34	10
rice cereal <sup>c</sup>	5	1	94
cake doughnuts <sup>a</sup>	7	31	62
beef stew <sup>a</sup>	38	25	37
beef liver, fried <sup>a</sup>	63	19	18
haddock, fried	96	4	0

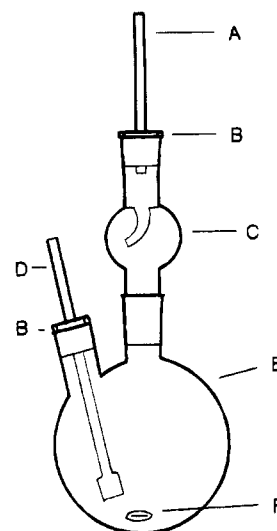
<sup>a</sup> Contained incurred residues of VOCs. <sup>b</sup> Calculated on moisture-free basis from commercial labeling values. <sup>c</sup> Junior baby food.

524.2 (Eichelberger and Budde, 1989) were used to fortify an array of table-ready foods. These 60 chemicals represent a range of volatility from gases (dichlorodifluoromethane, bp  $-29.8\text{ }^{\circ}\text{C}$ ) to semivolatiles (1,2,3-trichlorobenzene, bp  $221\text{ }^{\circ}\text{C}$ ). These purgeable analytes are varied in chemical structure and include  $\text{C}_1$ – $\text{C}_3$  saturated and unsaturated halogenated entities, alkylated and halogenated benzenes, and naphthalene.

## EXPERIMENTAL PROCEDURES

**Sample Selection and Preparation.** Of the 265 table-ready foods of the Total Diet Study, 9 items were selected as representative of each of 9 sectors of a food matrix paradigm developed by Ikins et al. (1993). Each sector describes foods with specific fat, carbohydrate, and protein content ranging from 0 to 100% on a moisture-free basis (Table 1). Similarly, an additional 9 food items were chosen for an intralaboratory collaborative study (see Table 2). Commercial labeling was relied upon to determine the composition of each food. Moisture determinations were made using an AVC-80 microwave, moisture–solids analyzer (CEM, Matthews, NC). Upon development of a suitable method, a survey of 234 of the 265 food items of the FDA Total Diet Program was conducted. Raw fruits and vegetables were eliminated from this study, as were alcoholic beverages. All samples were chopped or blended to form a homogeneous mixture and frozen prior to analysis.

**Standard Solutions.** An aliquot of  $5.0\ \mu\text{L}$  of a mixture of the 60 volatile analytes listed in U.S. EPA Method 524.2 ( $2000\ \mu\text{g}/\text{mL}$  in methanol) (AccuStandard, New Haven, CT) was added to 100 mL of purified deionized water to form a solution containing  $100\ \text{ng}/\text{mL}$  of each analyte. (Deionized water was purified by boiling for 1 h with a purge of helium at  $40\ \text{mL}/\text{min}$ .) Similarly,  $5.0\ \mu\text{L}$  of 1,4-difluorobenzene and  $5.0\ \mu\text{L}$  of 4-bromofluorobenzene (each,  $2000\ \mu\text{g}/\text{mL}$  in methanol) (Supelco, Bellefonte, PA) were diluted to 100 mL (puri-



**Figure 1.** Purge and trap apparatus: (A) Vocab 3000 trap; (B) universal adapters; (C) distillation trap; (D) gas dispersion tube; (E) 500 mL round-bottom flask; (F) magnetic stirring bar.

fied deionized water) to form an internal standard solution containing  $100\ \text{ng}/\text{mL}$  of each analyte. Aqueous solutions were prepared fresh daily.

**Adsorption Traps.** Stainless steel tubes ( $0.25\ \text{in. o.d.} \times 7\ \text{in.}$ ) were packed (in the direction of gas flow during adsorption) with 100 mg of Carboxen 1001, 300 mg of Carboxen 1000, and 400 mg of Carpack B, respectively, to form Vocab 3000 traps (Supelco). (Gas flows were reversed when traps were thermally desorbed.) Using a Tekmar 5100 thermal trap conditioner (Tekmar, Cincinnati, OH), traps were conditioned at  $350\text{ }^{\circ}\text{C}$  for 3 h with  $20\ \text{mL}/\text{min}$  He flow prior to each adsorption.

**Purge and Trap Apparatus.** The off-line purge and trap apparatus used in this study is depicted in Figure 1. The round-bottom, angled 24/40 double-neck, 500 mL flask was fitted with a 14 cm 24/40 distillation trap. A Vocab 3000 trap and  $7\ \text{mm} \times 300\ \text{mm}$ , porosity E, gas dispersion tube (Ace Glass, Vineland, NJ) were added through PTFE, 24/40, universal adapters (Kontes, Vineland, NJ). An egg-shaped, magnetic, stirring bar ( $5/8\ \text{in.} \times 1\frac{1}{2}\ \text{in.}$ ) was added to the flask.

**Purge and Trap Extraction.** Ten grams of homogeneous, frozen or partially thawed samples, 250 mL of purified antifoam-treated deionized water, 5.0 mL of internal standard solution, and any fortification aliquots were added to the 500 mL flask. After assembly, the flask was placed in a 1500 mL beaker containing 600 mL of rapidly boiling water on a stirring hot plate. Helium purging gas was added to the flask through the gas dispersion tube at a rate of  $25\ \text{mL}/\text{min}$  with rapid stirring to obtain a strong vortex. After 30 min, the adsorption tube was removed and analyzed using thermal desorption GC–MS. Reagent blank and fortification determinations were performed with each series of 14 samples. To avoid excessive foaming during purge and trap extraction, purified deionized antifoam-treated water was used. Ten drops/L 30% Antifoam A solution (Sigma Chemical Co., St. Louis, MO) was added to deionized water and then purified by boiling for 1 h with a purge of helium at  $40\ \text{mL}/\text{min}$ .

**Fortification of Samples.** Prior to fortification, any incurred residues were removed by performing a preliminary purge (see Purge and Trap Extraction) to form a blank sample with an authentic matrix. Each of the first set of 9 food items was fortified with the 60

**Table 3. Retention Times, Quantitation Ions, and Molecular Weights of Volatile Analytes Used in Recovery and Reproducibility Studies**

compound	$R_t$ (min)	Q ion(s) ( $m/z$ )	$M^+$ ( $m/z$ )	compound	$R_t$ (min)	Q ion(s) ( $m/z$ )	$M^+$ ( $m/z$ )
(1) dichlorodifluoromethane	1.61	85	120	(31) 1,2-dibromoethane	17.74	107, 109	172
(2) chloromethane	1.80	50	50	(32) chlorobenzene	18.91	112	112
(3) vinyl chloride	1.91	62	62	(33) 1,1,1,2-tetrachloroethane	19.14	131, 133	166
(4) bromomethane	2.29	94, 96	94	(34) ethylbenzene	19.21	91	106
(5) chloroethane	2.41	51, 64	64	(35) <i>m</i> -xylene <sup>b</sup>	19.49	91	106
(6) trichlorofluoromethane	2.72	101	136	(36) <i>p</i> -xylene <sup>b</sup>	19.49	91	106
(7) 1,1-dichloroethene	3.40	61, 96	96	(37) <i>o</i> -xylene	20.33	106	106
(8) dichloromethane	4.14	51, 84	84	(38) styrene	20.37	104	104
(9) <i>trans</i> -1,2-dichloroethene	4.61	96	96	(39) bromoform	20.71	173	250
(10) 1,1-dichloroethane	5.43	63	98	(40) isopropylbenzene	21.15	105	120
(11) 2,2-dichloropropane	6.79	77	112	4-bromofluorobenzene <sup>a</sup>	21.44	174, 176	174
(12) <i>cis</i> -1,2-dichloroethene	6.83	61, 96	96	(41) bromobenzene	21.72	156, 158	156
(13) bromochloromethane	7.47	130	128	(42) 1,1,2,2-tetrachloroethane	21.82	83	168
(14) chloroform	7.80	83	118	(43) 1,2,3-trichloropropane	21.86	75	146
(15) 1,1,1-trichloroethane	8.28	97	132	(44) <i>n</i> -propylbenzene	22.03	91	120
(16) carbon tetrachloride	8.83	117, 119	152	(45) 2-chlorotoluene	22.16	126	126
(17) 1,1-dichloropropene	8.86	75, 110, 119	110	(46) 4-chlorotoluene	22.40	126	126
(18) benzene	9.58	78	78	(47) 1,3,5-trimethylbenzene	22.41	105	120
(19) 1,2-dichloroethane	9.70	62	98	(48) <i>tert</i> -butylbenzene	23.09	119	134
1,4-difluorobenzene <sup>a</sup>	11.25	114	114	(49) 1,2,4-trimethylbenzene	23.19	105	120
(20) trichloroethene	12.02	95, 130, 132	130	(50) <i>sec</i> -butylbenzene	23.57	105	134
(21) 1,2-dichloropropane	12.66	63, 76	112	(51) 1,3-dichlorobenzene	23.75	146	146
(22) dibromomethane	13.00	93, 174	172	(52) <i>p</i> -isopropyltoluene	23.90	119	134
(23) bromodichloromethane	13.58	83	162	(53) 1,4-dichlorobenzene	23.96	146	146
(24) <i>cis</i> -1,3-dichloropropene	14.82	75	110	(54) 1,2-dichlorobenzene	24.79	146	146
(25) toluene	15.62	91, 92	92	(55) <i>n</i> -butylbenzene	24.82	91	134
(26) <i>trans</i> -1,3-dichloropropene	16.28	75	110	(56) 1,2-dibromo-3-chloropropane	26.62	157	234
(27) 1,1,2-trichloroethane	16.68	97, 99	132	(57) 1,2,4-trichlorobenzene	28.71	180	180
(28) tetrachloroethene	16.94	129, 166	164	(58) hexachlorobutadiene	29.21	225	258
(29) 1,3-dichloropropane	17.04	76	112	(59) naphthalene	29.32	128	128
(30) chlorodibromomethane	17.56	127, 129	206	(60) 1,2,3-trichlorobenzene	29.98	180	180

<sup>a</sup> Internal standard. <sup>b</sup> Unresolved GC peaks.

component standard solution at 100 and 10 ppb levels, respectively. Purge and trap TD-GC-MS analyses were performed in duplicate. For the intralaboratory collaborative study, an additional set of 9 food items was chosen. Four of the foods were fortified at 50 ppb, and analyses were performed in duplicate by each of two analysts. The remaining five items, which contained detectable levels of incurred residues, were analyzed in duplicate without fortification.

**Thermal Desorption GC-MS.** A Tekmar 6000 thermal desorber with 6016 autosampler and cryofocusing module was employed to focus the desorbed analytes on the head of a DB-624 column (0.32 mm × 30 m, 1.8 μm film) (J&W Scientific, Folsom, CA). The column was fitted in a Varian 3400 gas chromatograph (Sugar Land, TX), which was interfaced to a Varian Saturn II ion trap mass spectrometer through an open-split interface. Vocab 3000 traps were desorbed in reverse-direction flow at 335 °C for 20 min after having been swept (purged) at room temperature for 10 min with a helium flow of 40 mL/min. All transfer lines and valves were held at 200 °C. The analytes were first cryofocused at -150 °C utilizing liquid nitrogen and then injected by ballistically heating to 225 °C with a column flow of 1 mL/min (He). Through the use of multiramp programming nearly all 60 analytes were resolved. An initial temperature of 40 °C was held for 10 min, then ramped at 8 °C/min to 140 °C and at 5 °C/min to 180 °C, and held for 3 min. At the conclusion of the GC run (33.5 min) the column was baked by ramping at 20 °C/min to 200 °C and holding for 3 min. The eluants passed into the mass spectrometer through an open-split interface at 270 °C. Full scan mass spectra were obtained in the electron ionization mode at 70 eV, scanning from 50 to 300 Da at 0.5 s scan<sup>-1</sup>. Spectra were acquired for 31 min. A list of all 60

volatile compounds examined with retention times, quantitation ions, and molecular ions is presented as Table 3.

**Quantification.** Quantification was performed using the second-order regression algorithms of the Autoquan program of Saturn III revision 4 software. Nine-point standard plots (0–2500 ng) for each of the 60 volatile analytes were constructed from a simulated sample matrix consisting of 2.5 g of corn oil (100% fat), plus 2.5 g of gelatin (100% protein), plus 2.5 g of sugar (100% carbohydrate) in 250 mL of deionized water. Standard plots based on peak area ratios of samples and internal standards were deemed acceptable only if correlation coefficients exceeded 0.980. GC peaks were quantified only if full scan mass spectra matched those of respective standards with a fit confidence level > 800 and retention times matched within a window of 3 s. The first 20 analytes referenced 1,4-difluorobenzene as an internal standard; the remaining compounds were compared to 4-bromofluorobenzene. All validation determinations were performed in duplicate. If values varied by 20% or more, results were discarded and two new determinations were made. Sample weights were adjusted appropriately if incurred residue levels exceeded 250 ppb.

## RESULTS AND DISCUSSION

This study was comprised of three parts. The first examined the accuracy and reliability of the developed VOC method with tests of recovery and reproducibility. The second was an intralaboratory collaborative study that explored portability or ruggedness of the method. Finally, after the method was shown to be accurate, reliable, and rugged, a survey of 234 table-ready foods from the Total Diet Program of the FDA was conducted.

The nine table-ready food items selected for the initial recovery study and an additional nine items chosen for the intralaboratory collaborative study are presented as Tables 1 and 2, respectively. A wide range of matrices was chosen in an attempt to demonstrate the suitability of this purge and trap method for the analysis of 234 table-ready foods of the FDA's Total Diet Program.

Table 3 lists the 60 volatile analytes of U.S. EPA Method 524.4 with the quantitation ions used in this study. Even though multiramp GC temperature programming was used, some analytes were not completely resolved. However, except in the case of *m*- and *p*-xylene, all analytes were quantified through the judicious assignment of distinctive quantitation ions.

The average recovery values and %RSD from fortification of the nine initial food items at 100 and 10 ppb are given in Table 4. At 100 ppb the average %RSD for analytes 9–55 was 11.3. For these same analytes fortified at 10 ppb the average %RSD is 20.4. However, the remaining analytes possessed %RSD values that were unacceptable (>30 at 100 ppb). Most of the first eight compounds are gases at room temperature and, thus, present a special problem in preparation of standards in aqueous media and in purge and trap extraction. Similarly, the last five analytes can be classed as semivolatiles and as such are near the limits of this purge and trap technique. It is probable that for these reasons precision is lacking for these two sets of analytes. Because quantitation values for these 13 analytes are erratic, only analytes 9–55 are included in the final analytical scheme. Furthermore, analyte 52, *p*-isopropyltoluene (*p*-cymene), is a component of several essential oils and has been quantified at very high levels (>1000 ppb) in cake doughnuts, sausage, bologna, etc. Additionally, it has consistently proven difficult to construct a standard plot with a correlation coefficient >0.980 for 2,2-dichloropropane. A clear reason for this phenomenon has not been established. For these reasons *p*-isopropyltoluene and 2,2-dichloropropane were not considered for the remainder of the study. Of the remaining 45 analytes only 2, *m*-xylene and *p*-xylene, coelute and have essentially identical mass spectra. Consequently, they are quantified as one entity, and a total of 44 results are reported. Limits of quantitation (LOQs) are also listed in Table 4. These values were calculated as 3 times the standard deviation (SD) of recovery values for samples fortified at 10 ppb. Of the 45 analytes accepted for the balance of this study, 24 have LOQs under 5.0 ppb, while only 4 analytes have values in excess of 10 ppb.

The results of the intralaboratory collaboration are contained in Tables 5 and 6. Four food items (black olives, half and half cream, rice cereal, and haddock) were fortified with the 45 selected VOC analytes at a level of 50 ppb. The average recovery value for duplicate determinations performed by each of two analysts was 101.7% for the 44 values calculated (Table 5). Values for %RSD ranged from 2.76 to 24.3, with 38 of 44 being <20. Of the nine food items chosen for this study (see Table 2), five were found to contain detectable levels of incurred VOC residues (Table 4). Each was analyzed in duplicate (without fortification) by each of two analysts. The average %RSD value was 16.3 for a total of 19 residues. VOCs are not entirely removed from foods (especially those high in fat) by cooking (Heikes, 1985). Consequently, detectable levels of contaminant residues were found in fried beef liver, boiled beef stew, and baked cake doughnuts.

**Table 4. Average Recovery Values, %RSD, and Limits of Quantitation (LOQ) Resulting from the Fortification of the Initial 9 Table-Ready Food Items (see Table 1) with 60 Volatile Analytes at 100 ppb and 10 ppb (Analyses Performed in Duplicate)**

compound	av recovery (%)		% RSD <sup>a</sup>		LOQ (ppb) <sup>b</sup>
	100 ppb	10 ppb	100 ppb	10 ppb	
(1) dichlorodifluoromethane	57.7	176	99.4	30.1	— <sup>c</sup>
(2) chloromethane	52.6	103	81.5	52.7	—
(3) vinyl chloride	76.4	88.2	60.2	40.3	—
(4) bromomethane	59.0	141	58.8	59.1	—
(5) chloroethane	93.5	101	54.3	30.7	—
(6) trichlorofluoromethane	80.2	97.7	49.2	27.1	—
(7) 1,1-dichloroethene	80.0	78.4	33.2	66.6	—
(8) dichloromethane	168	195	64.5	80.0	—
(9) <i>trans</i> -1,2-dichloroethene	101	90.0	12.1	38.5	10.4
(10) 1,1-dichloroethane	98.1	112	17.3	31.8	10.7
(11) 2,2-dichloropropane	106	160	18.9	69.3	—
(12) <i>cis</i> -1,2-dichloroethene	103	89.8	10.6	14.0	3.78
(13) bromochloromethane	116	95.8	20.5	13.1	3.78
(14) chloroform	107	102	20.3	17.5	5.34
(15) 1,1,1-trichloroethane	93.4	104	10.9	23.7	7.41
(16) carbon tetrachloride	95.8	89.4	8.96	26.6	7.14
(17) 1,1-dichloropropene	103	92.0	12.4	24.3	6.69
(18) benzene	103	104	11.6	30.1	9.30
(19) 1,2-dichloroethane	117	103	6.54	13.4	4.14
(20) trichloroethene	101	114	13.4	21.5	7.35
(21) 1,2-dichloropropane	107	94.2	9.77	14.3	4.05
(22) dibromomethane	108	97.3	6.36	15.9	4.62
(23) bromodichloromethane	105	103	11.4	13.9	4.29
(24) <i>cis</i> -1,3-dichloropropene	101	108	9.68	14.1	4.56
(25) toluene	100	106	9.80	25.0	7.95
(26) <i>trans</i> -1,3-dichloropropene	101	98.6	11.3	24.0	7.11
(27) 1,1,2-trichloroethane	106	101	8.38	11.8	3.60
(28) tetrachloroethene	97.6	112	10.6	12.1	4.08
(29) 1,3-dichloropropane	98.2	129	7.56	10.9	4.20
(30) chlorodibromomethane	104	61.3	10.1	82.3	15.1
(31) 1,2-dibromoethane	101	107	13.0	20.0	6.42
(32) chlorobenzene	100	93.5	7.39	15.2	4.26
(33) 1,1,1,2-tetrachloroethane	102	102	14.5	24.5	7.50
(34) ethylbenzene	96.5	106	5.68	18.6	5.91
(35) <i>m</i> -xylene <sup>d</sup>	94.7	106	9.90	8.68	5.52
(36) <i>p</i> -xylene <sup>d</sup>					
(37) <i>o</i> -xylene					
(38) styrene	100	96.3	10.7	12.8	3.72
(39) bromoform	101	112	10.2	11.2	3.78
(40) isopropylbenzene	93.8	137	11.7	23.8	9.78
(41) bromobenzene	102	102	15.9	14.1	4.32
(42) 1,1,1,2,2-tetrachloroethane	98.8	109	6.88	5.59	1.83
(43) 1,2,3-trichloropropane	109	128	16.6	27.6	8.94
(44) <i>n</i> -propylbenzene	90.2	126	13.3	8.56	3.24
(45) 2-chlorotoluene	95.7	98.0	7.25	15.6	4.59
(46) 4-chlorotoluene	96.9	107	9.50	10.3	3.33
(47) 1,3,5-trimethylbenzene	93.3	100	8.83	10.9	3.27
(48) <i>tert</i> -butylbenzene	93.4	99.8	7.43	9.26	2.77
(49) 1,2,4-trimethylbenzene	99.2	103	9.80	11.4	3.54
(50) <i>sec</i> -butylbenzene	99.6	126	7.82	38.3	14.5
(51) 1,3-dichlorobenzene	88.4	105	10.4	10.8	3.39
(52) <i>p</i> -isopropyltoluene	86.4	106	13.5	11.7	3.72
(53) 1,4-dichlorobenzene	87.2	112	8.74	29.4	—
(54) 1,2-dichlorobenzene	90.8	95.6	13.2	14.8	4.26
(55) <i>n</i> -butylbenzene	97.0	94.9	15.0	18.9	5.40
(56) 1,2-dibromo-3-chloropropane	75.1	115	13.4	20.9	7.23
(57) 1,2,4-trichlorobenzene	93.3	272	31.9	20.1	—
(58) hexachlorobutadiene	59.3	105	35.1	32.6	—
(59) naphthalene	43.4	99.0	35.9	31.1	—
(60) 1,3,5-trichlorobenzene	50.5	104	57.0	27.4	—
	38.6	102	82.4	29.7	—

<sup>a</sup> *n* = 18. <sup>b</sup> Calculated as 3 times the SD at 10 ppb fortifications.

<sup>c</sup> Not calculated. <sup>d</sup> Reported as combined values (i.e. fortified at 200 and 20 ppb, respectively).

Of the 265 food items in the Total Diet Program, only 234 were surveyed for the presence of VOC residues. Raw fruits and vegetables, which a previous study (Heikes, 1987) had shown to be almost exclusively free of VOC residues, were excluded from this survey. Also,

**Table 5. Average Recovery Values and %RSD Resulting from the Fortification of 4 Table-Ready Food Items in an Intralaboratory Collaboration Study with 45 Selected Volatile Analytes at 50 ppb (Analyses Performed in Duplicate by Each of Two Analysts)**

compound	av recovery (%)		%RSD <sup>a</sup>
	analyst 1	analyst 2	
(1) <i>trans</i> -1,2-dichloroethene	90.2	90.4	15.2
(2) 1,1-dichloroethane	112	123	13.9
(3) <i>cis</i> -1,2-dichloroethene	98.4	104	13.0
(4) bromochloromethane	151	164	12.9
(5) chloroform	115	129	15.0
(6) 1,1,1-trichloroethane	107	113	20.5
(7) carbon tetrachloride	80.0	110	24.3
(8) 1,1-dichloropropene	89.4	90.2	15.1
(9) benzene	110	103	14.5
(10) 1,2-dichloroethane	107	114	7.40
(11) trichloroethene	115	103	17.7
(12) 1,2-dichloropropane	103	92.6	9.85
(13) dibromomethane	99.8	93.0	8.93
(14) bromodichloromethane	111	106	7.71
(15) <i>cis</i> -1,3-dichloropropene	95.6	96.0	14.8
(16) toluene	75.6	53.7	21.3
(17) <i>trans</i> -1,3-dichloropropene	89.0	94.7	21.6
(18) 1,1,2-trichloroethane	101	101	8.53
(19) tetrachloroethene	78.4	93.4	12.9
(20) 1,3-dichloropropane	95.8	100	11.4
(21) chlorodibromomethane	104	101	9.67
(22) 1,2-dibromoethane	100	98.2	14.7
(23) chlorobenzene	87.4	80.5	6.92
(24) 1,1,1,2-tetrachloroethane	102	105	16.4
(25) ethylbenzene	83.6	75.4	7.75
(26) <i>m</i> -xylene <sup>b</sup>	97.0	90.4	5.36
(27) <i>p</i> -xylene <sup>b</sup>			
(28) <i>o</i> -xylene	97.8	94.8	3.98
(29) styrene	105	101	5.71
(30) bromoform	112	103	17.0
(31) isopropylbenzene	108	102	11.3
(32) bromobenzene	99.4	101	2.76
(33) 1,1,2,2-tetrachloroethane	108	123	23.2
(34) 1,2,3-trichloropropane	109	111	10.5
(35) <i>n</i> -propylbenzene	102	99.8	6.42
(36) 2-chlorotoluene	100	99.4	4.99
(37) 4-chlorotoluene	113	106	5.54
(38) 1,3,5-trimethylbenzene	104	102	6.13
(39) <i>tert</i> -butylbenzene	102	101	5.73
(40) 1,2,4-trimethylbenzene	124	99.8	23.1
(41) <i>sec</i> -butylbenzene	103	92.9	8.56
(42) 1,3-dichlorobenzene	97.1	99.7	4.60
(43) 1,4-dichlorobenzene	98.5	103	3.47
(44) 1,2-dichlorobenzene	104	103	4.65
(45) <i>n</i> -butylbenzene	100	84.3	14.4

<sup>a</sup> *n* = 16. <sup>b</sup> Reported as combined value (i.e. fortified at 100 ppb).

it has been shown that alcohol from beer, wine, and whiskey samples interfere, with the adsorption of VOCs on the traps (Heikes, 1985). Consequently, alcoholic beverages were also eliminated from this study. Of the 234 items surveyed, over 20 recipe (combined) food items (e.g. lasagna, tuna noodle casserole) or fast-food items such as pizza or quarter pound cheeseburgers were included in this study. Thirty-six infant/toddler foods were represented.

A summary of the analytical data from this survey is presented as Table 7. Of the 234 foods analyzed, 187 items (80%) were found to contain at least one quantifiable VOC residue. A total of 708 incurred VOC residues were recorded: 80% of these were benzene or derivatives of benzene; the remainder were halogenated alkyl analytes. Of the 45 analytes determined according to this method, 29 were encountered in at least one food. Toluene, the most commonly occurring, was reported in 91 different items at an average level of 50.9 ppb.

A perspective on the significance of the results of this

**Table 6. Average Values and %RSD Resulting from the Analysis of Five Table-Ready Food Items in the Intralaboratory Collaboration Study for Incurred Residues of VOCs (Analyses Performed in Duplicate by Each of Two Analysts)**

food item compounds	av value (ppb)		%RSD <sup>a</sup>
	analyst 1	analyst 2	
beef liver, fried			
benzene	208	214	12.5
toluene	148	113	18.2
ethylbenzene	25.8	18.3	21.2
<i>m</i> -xylene <sup>b</sup>	109	82.2	18.0
<i>p</i> -xylene <sup>b</sup>			
<i>n</i> -propylbenzene	46.5	52.2	10.2
1,3,5-trimethylbenzene	4.34	5.57	18.6
1,2,4-trimethylbenzene	88.0	125	23.2
beef stew			
tetrachloroethene	7.03	9.89	20.5
<i>n</i> -butylbenzene	10.7	9.08	18.8
French salad dressing			
chloroform	5.36	8.11	25.9
ham lunch meat			
bromochloromethane	20.3	30.1	24.8
toluene	11.8	15.0	16.4
<i>n</i> -butylbenzene	9.95	14.0	20.9
cake doughnuts			
benzene	9.54	13.0	16.3
toluene	81.9	80.8	6.18
<i>m</i> -xylene <sup>b</sup>	16.9	20.7	14.5
<i>p</i> -xylene <sup>b</sup>			
styrene	20.4	20.2	2.71
1,3,5-trimethylbenzene	11.7	11.4	4.95
<i>n</i> -butylbenzene	18.0	20.0	16.4

<sup>a</sup> *n* = 4. <sup>b</sup> Reported as combined value.

survey can be gained with a comparison of the levels of these VOC residues with levels allowed in the nation's water supply. Drinking water standards of the U.S. EPA establish maximum contaminant levels (MCLs) for several VOCs (CFR, 1994b). For purposes of comparison, the appropriate values are included in Table 7. In terms of human exposure, the intake of drinking water far exceeds that of most foods. Furthermore, in most cases the levels of VOCs gathered from this study approximate or are far less than those allowed in drinking water. The most notable exception is in the case of benzene in sauerkraut (283 ppb). However, the source of benzene may be from fermentation of cabbage. In 1974, Lee et al. examined both the primary and complex fermentation products of fresh and cooked cabbage. Using gas chromatography, they separated over 40 compounds including several derivatives of benzene. The volatile nonpolar analytes determined in this study have an affinity for fatty foods. As expected, then, a close correlation was found between the levels of VOC residues and the fat content in the 234 food items analyzed. The average fat level of the 47 foods found to be free of incurred VOC residues was only 1.8%. Another 144 items with total residues <100 ppb had an average fat level of 7.8%, while foods with total residues in excess of 100 ppb (43 items) had an average fat content of 20%.

Cake doughnuts from this survey and those from the collaborative study of the validation were found to have high levels of VOC residues. In fact, of the 21 food items with total residues levels >200 ppb, cake doughnuts showed the highest level (802 ppb). Results of analysis of the four food items with the highest levels of VOCs, sandwich cookies, butter, margarine, and cake doughnuts, are presented in Table 8.

Since all of the samples examined in the FDA's Total Diet Program are analyzed as table-ready, dissipation

**Table 7. Results of Survey for 45 Volatile Organic Compounds in 234 Table-Ready Food Items from the FDA's Total Diet Study**

compound	occurrence <sup>a</sup>	av (ppb)	range (ppb)	highest level food item	U.S. EPA MCL <sup>b</sup>
(1) <i>trans</i> -1,2-dichloroethene	0				100
(2) 1,1-dichloroethane	0				
(3) <i>cis</i> -1,2-dichloroethene	0				70
(4) bromochloromethane	3	6.16	6.11–6.22	sandwich cookies	
(5) chloroform	44	18.6	5.53–110	cream cheese	
(6) 1,1,1-trichloroethane	2	12.7	12.1–13.3	butter	200
(7) carbon tetrachloride	0				5
(8) 1,1-dichloropropene	0				
(9) benzene	28	50.3	9.49–283	sauerkraut	5
(10) 1,2-dichloroethane	0				5
(11) trichloroethene	0				5
(12) 1,2-dichloropropane	0				5
(13) dibromomethane	0				
(14) bromodichloromethane	73	5.51	4.86–9.36	butter	
(15) <i>cis</i> -1,3-dichloropropene	0				
(16) toluene	91	50.9	7.96–344	cake doughnuts	1000
(17) <i>trans</i> -1,3-dichloropropene	0				
(18) 1,1,2-trichloroethane	0				5
(19) tetrachloroethene	7	20.1	5.23–50.4	butter	5
(20) 1,3-dichloropropane	0				
(21) chlorodibromomethane	0				
(22) 1,2-dibromoethane	0				
(23) chlorobenzene	2	22.5	4.87–40.1	clam chowder	100
(24) 1,1,1,2-tetrachloroethane	1	53.0	53.0	Cheddar cheese	
(25) ethylbenzene	15	14.6	6.37–38.7	margarine	700
(26) <i>m</i> -xylene <sup>c</sup>	64	19.9	6.20–114	margarine	10000 <sup>d</sup>
(27) <i>p</i> -xylene <sup>c</sup>					
(28) <i>o</i> -xylene	32	8.15	3.72–23.5	cake doughnuts	
(29) styrene	73	20.6	3.90–240	fruit yogurt	100
(30) bromoform	0				
(31) isopropylbenzene	8	19.2	4.72–92.1	fruit sherbet	
(32) bromobenzene	2	6.88	4.69–9.06	cake doughnuts	
(33) 1,1,2,2-tetrachloroethane	1	11.0	11.0	beef steak	
(34) 1,2,3-trichloropropane	9	4.21	3.53–6.12	sandwich cookies	
(35) <i>n</i> -propylbenzene	23	9.73	4.70–41.4	cake doughnuts	
(36) 2-chlorotoluene	11	10.1	3.99–32.3	dill pickles	
(37) 4-chlorotoluene	6	7.90	3.28–20.1	cake doughnuts	
(38) 1,3,5-trimethylbenzene	20	7.61	2.88–27.6	cake doughnuts	
(39) <i>tert</i> -butylbenzene	3	11.9	4.86–25.5	cake doughnuts	
(40) 1,2,4-trimethylbenzene	37	41.4	17.2–138	teething biscuits	
(41) <i>sec</i> -butylbenzene	5	5.67	3.88–7.76	sauerkraut	
(42) 1,3-dichlorobenzene	6	7.36	5.31–9.76	sandwich cookies	
(43) 1,4-dichlorobenzene	69	10.7	4.26–114	chocolate chip cookies	75
(44) 1,2-dichlorobenzene	45	9.47	7.80–24.4	cake doughnuts	600
(45) <i>n</i> -butylbenzene	28	15.9	7.26–93.7	cake doughnuts	

<sup>a</sup> Number of foods (of 234) in which the analyte was detected > LOQ. <sup>b</sup> Maximum contaminant levels for drinking water, presented as ppb. <sup>c</sup> Reported as combined value. <sup>d</sup> Allowable level for total xylenes.

of VOC residues during preparation (cooking) is of no immediate interest. However, losses that might occur during chopping, blending, or other manipulations designed to ensure homogeneity, will result in flawed conclusions regarding dietary intake and are, therefore, of concern. A limited investigation was conducted to gain an appreciation for the potential loss of analytes during sample preparation. Two samples, pumpkin pie and cake doughnuts, from the above survey were used in this test. Although both items contained high residue levels of VOCs, 264 and 802 ppb total, respectively, they varied in fat and moisture content. Pumpkin pie contained 52% moisture and 7.9% fat; cake doughnuts 38% and 19%, respectively. Both samples were first reanalyzed (in duplicate) using the developed procedure. They were then allowed to warm to room temperature, blended for 10 min, and reanalyzed in duplicate. The results of the reanalyses and the analyses after reblending were nearly identical. No detectable losses were incurred as a result of the reblending process. The %RSD for the total of 23 residues found in the two

samples was only 11.5 ( $n = 4$ ), approximating the precision established for this method.

## CONCLUSIONS

The procedure developed in this study represents a convenient means of obtaining an estimation of VOC levels in table-ready foods. The method is simple, rapid, and semiautomated. It presents no difficulty for the analysis of a wide variety of foods, even those with high fat content.

The results of the survey of 234 table-ready food items confirmed the suspicion that the VOCs that are ubiquitous in the environment are also present in our national food supply. The level of VOC residues appears to vary directly with the fat content of the food. This study also suggests that blending of foods containing moderate fat levels does not result in dissipation of incurred residues.

It is anticipated that this procedure will be incorporated into the FDA's Total Diet Program and that

**Table 8. Results of Analysis of Survey of 234 Food Items: 4 Food Items with Highest Levels (Parts per Billion) of Volatile Organic Compound Residues**

compound	sandwich cookies	margarine	butter	cake doughnuts
bromochloromethane	6.22	— <sup>a</sup>	—	—
chloroform	—	7.34	38.9	—
1,1,1-trichloroethane	—	12.0	13.3	—
benzene	—	—	—	11.0
bromodichloromethane	5.78	7.34	9.36	5.18
toluene	26.3	171	248	344
1,1,2-trichloroethane	3.78	—	—	—
tetrachloroethene	—	7.11	50.4	—
ethylbenzene	15.1	38.7	17.1	23.9
<i>m</i> -xylene <sup>b</sup> } <i>p</i> -xylene <sup>b</sup> }	12.9	114	54.8	35.0
<i>o</i> -xylene	6.31	21.7	12.5	23.5
styrene	216	9.28	22.4	23.0
isopropylbenzene	5.95	—	—	—
bromobenzene	4.69	—	—	9.06
1,2,3-trichloropropane	6.12	—	—	—
<i>n</i> -propylbenzene	6.76	9.42	6.54	41.4
2-chlorotoluene	6.69	5.63	—	—
4-chlorotoluene	7.41	—	—	20.1
1,3,5-trimethylbenzene	7.25	13.1	7.81	27.6
<i>tert</i> -butylbenzene	4.86	—	—	25.5
1,2,4-trimethylbenzene	—	31.3	22.9	94.3
<i>sec</i> -butylbenzene	6.00	3.88	—	—
1,3-dichlorobenzene	9.76	—	—	—
1,4-dichlorobenzene	12.0	—	—	—
1,2-dichlorobenzene	11.4	—	—	24.4
<i>n</i> -butylbenzene	8.61	16.2	14.4	93.7
totals	387	468	518	802

<sup>a</sup> —, residue level <LOQ. <sup>b</sup> Reported as combined value.

systematic generation of extensive VOC residue data for table-ready foods will result.

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