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**DEVELOPMENT AND VALIDATION OF A METHOD FOR
MEASURING EXEMPT VOLATILE ORGANIC COMPOUNDS
AND CARBON DIOXIDE IN CONSUMER PRODUCTS**

Final Report

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16. ABSTRACT The report describes the development and validation of a method for measuring exempt volatile organic compounds (VOCs) and carbon dioxide in consumer products. (NOTE: Ground-level ozone can cause a variety of adverse health effects as well as agricultural and ecological damage. Controlling emissions of VOCs is important to reducing ground-level ozone; however, not all VOCs are photochemically reactive, and several have been exempted from control regulations. Currently, there is no standard method for measuring the exempt VOC content of consumer products.) The new method involves heating a sample in an oven at 110 C for 1 hour while purging the sample container with nitrogen gas. The resultant mixture of nitrogen and volatile compounds from the sample is then collected in a Tedlar bag and analyzed by gas chromatography with mass selective detection (GC/MSD). An internal standard is added to the sample container to permit quantitation without measurement of the purge gas volume. The method was evaluated by analyzing samples that were spiked with known amounts of the exempt compounds. Recoveries of spiked compounds were excellent, ranging from 86 to 107% for the compounds and products tested. This method should be applicable to other volatile compounds that might be present in consumer products and could be useful in evaluating the risk that these products pose.			
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FOREWORD

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The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

ABSTRACT

Ground-level ozone can cause a variety of adverse health effects as well as agricultural and ecological damage. Controlling emissions of volatile organic compounds (VOCs) is important to reducing ground-level ozone. However, not all VOCs are photochemically reactive and several have been exempted from control regulations. Currently, there is no standard method for measuring the exempt VOC content of consumer products. This report describes the development of such a method.

The new method involves heating a sample in an oven at 110°C for 1 hour while purging the sample container with nitrogen gas. The resultant mixture of nitrogen and volatile compounds from the sample is then collected in a Tedlar bag and analyzed by gas chromatography with mass selective detection (GC/MSD). An internal standard is added to the sample container to permit quantitation without measurement of the purge gas volume. The method was evaluated by analyzing samples that were spiked with known amounts of the exempt compounds. Recoveries of spiked compounds were excellent, ranging from 86 to 107 percent for the compounds and products tested. This method should be applicable to other volatile compounds that might be present in consumer products and could be useful in evaluating the risk that these products pose to the environment.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM	--	American Society for Testing and Materials
CAAA	--	Amendments to the 1990 Clean Air Act
CFC	--	chlorofluorocarbon
FID	--	flame ionization detector
GC	--	gas chromatograph or gas chromatography
HCFC	--	hydrochlorofluorocarbon
HFC	--	hydrofluorocarbon
MSD	--	mass selective detector
NAAQS	--	National Ambient Air Quality Standards
PCBTF	--	parachlorobenzotrifluoride (α, α, α -trifluoro, 4-chlorotoluene)
perc	--	perchloroethylene (i.e., tetrachloroethylene)
TCD	--	thermal conductivity detector
VOC	--	volatile organic compound

SYMBOLS

CO ₂	--	carbon dioxide
HCFC-22	--	chlorodifluoromethane
HCFC-123	--	1,1,1-trifluoro-2,2-dichloroethane
HCFC-124	--	2-chloro-1,1,1,2-tetrafluoroethane
HCFC-141b	--	1,1-dichloro-1-fluoroethane
HCFC 142b	--	1-chloro-1,1-difluoroethane
HFC-125	--	pentafluoroethane
HFC-134	--	1,1,2,2-tetrafluoroethane
HFC-134a	--	1,1,1,2-tetrafluoroethane
HFC-143a	--	1,1,1-trifluoroethane
HFC-152a	--	1,1-difluoroethane

SECTION 1

INTRODUCTION

Ground-level ozone can cause a variety of adverse health effects as well as agricultural and ecological damage (1). To control the levels of ozone in the environment, the U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for ozone. In 1990 there were 98 areas in the country that did not meet the NAAQS for ozone (1), with over 150 million Americans living in these areas. Volatile organic compounds (VOCs) are important contributors to the formation of ozone in photochemical smog. Control of VOC emissions is an important strategy for controlling ozone levels. The 1990 Amendments to the Clean Air Act (CAAA) require EPA to conduct a study of VOC emissions from consumer products. However, there was no standard method for measuring the VOC content of consumer products. Such measurements are needed to assess the risk posed by VOCs in consumer products to the environment. Such a method will also be needed if EPA determines that the risk associated with VOCs in consumer products is sufficient to require control regulations.

To address the need for measurement of VOCs in consumer products, EPA has established a research program. This program has already produced results in four previous phases:

- **Phase I** - Preliminary studies were performed on two candidate methods for VOC measurement (EPA Reference Method 24 and Gravimetric Purge and Trap Gas Chromatography).
- **Phase II** - A Consumer Products Test Methods Work Group was established with participation from a number of State and Federal agencies. This Work Group, after consideration of an initial list of 10 candidate methods, reached a consensus that further research should be concentrated on two methods: EPA Reference Method 24 and Gravimetric Purge and Trap Gas Chromatography.
- **Phase III** - A test method was developed to determine the total VOC content of consumer products. This method was based on EPA Reference Method 24, with added modifications for sampling and analysis of consumer products.

- **Phase IV** - The test method developed in Phase III was validated in an interlaboratory study. (3)

The validated total VOC method (Phase IV) for consumer products gravimetrically measures the total volatile content and determines the amount of water by gas chromatography with thermal conductivity detection (GC/TCD). The water content is then subtracted from the total volatile content to calculate the total VOC content. However, many VOCs have been exempted from the list of regulated VOCs (40 CFR 51.100, Table 1) due to their low photochemical reactivity and thus low ozone formation potential. Measurement of these exempt VOCs in consumer products would allow EPA to correct the total VOC measurements to better reflect the total ozone formation risk that consumer products pose to the environment. Table 2 in Section 4 of this report lists the thirteen target compounds selected for this study. The target compounds consist of 12 from Table 1 plus carbon dioxide. The reasons for selecting these compounds are given in Section 4. Since it is anticipated that determining these 13 compounds will be considerably more expensive and time consuming than measurement of total VOC content, a two-step approach to assessing the ozone formation risk posed by consumer products is envisioned. The first step would involve measurement of total VOC content for the product. Consumer products that might pose significant risks for ozone formation based on their total VOC content would then undergo a second step of having their exempt VOCs measured to provide a better assessment of their ozone formation risk. This report describes the development and validation of an exempt VOC measurement method that would be used as the second step of the VOC risk assessment process.

**Table 1. Organic Compounds Determined to Have
Negligible Photochemical Reactivity**

Compound Name
methane
ethane
methylene chloride (dichloromethane)
1,1,1-trichloroethane (methyl chloroform)
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
trichlorofluoromethane (CFC-11)
dichlorodifluoromethane (CFC-12)
chlorodifluoromethane (HCFC-22)
trifluoromethane (HFC-23)
1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114)
chloropentafluoroethane (CFC-115)
1,1,1-trifluoro-2,2-dichloroethane (HCFC-123)
1,1,1,2-tetrafluoroethane (HFC-134a)
1,1-dichloro-1-fluoroethane (HCFC-141b)
1-chloro-1,1-difluoroethane (HCFC 142b)
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)
pentafluoroethane (HFC-125)
1,1,2,2-tetrafluoroethane (HFC-134)
1,1,1-trifluoroethane (HFC-143a)
1,1-difluoroethane (HFC-152a)
parachlorobenzotrifluoride (PCBTF)
cyclic, branched, or linear completely methylated siloxanes
acetone
perfluorocarbon compounds that fall into these classes
Source: 40 CFR 51.100 (reference 2)

SECTION 2

CONCLUSIONS

The method for measuring exempt VOC content in consumer products shows good accuracy as measured by exempt compound spike recoveries. Recoveries for individual compounds were excellent, ranging from 86 to 107 percent, and are within project goals of 80 to 120 percent. The method is very versatile for the following reasons:

- The sampling method developed for this method is suitable for a wide variety of consumer products, including solid, liquid, and aerosol products.
- Detection with a mass selective detector permits identification and quantitation of exempt compounds, even in the presence of potential interferants.

A small (approximately 2 percent) but statistically significant positive bias was seen in total volatile measurements made with purge gas. Unless further research can resolve this problem, total volatile measurements should be made using the validated total VOC method (i.e., without purge gas).

SECTION 3

RECOMMENDATIONS

Although the current method should prove useful for EPA research efforts in assessment of VOC emissions from consumer products, the ability of other laboratories to use this method has not been established. An interlaboratory study would be desirable before implementation of this method in a regulatory context.

Modifications to this method would extend it to a wider range of compounds. Such work would be useful to evaluate emissions of a wide variety of volatile and semivolatile compounds from both consumer and industrial products. This information would help EPA to better assess the risk that these products pose to the environment.

The exempt VOC method (Appendix A), which uses a purge gas to collect volatiles, should not be used to measure total volatile content (which includes exempt and nonexempt VOCs as well as water and carbon dioxide). Total volatile content should be measured by the previously validated total VOC method (3).

SECTION 4

METHOD DEVELOPMENT AND TESTING

INTRODUCTION

History

A method to measure the volatile content of surface coatings (i.e., paints, varnishes, and lacquers) was developed by the American Society for Testing and Materials (ASTM), which issued it under the designation D 2369, "Standard Test Method for Volatile Content of Coatings" (4). This method determines volatile content based on the weight loss of a sample that is heated for 1 hour at 110° C. The industrial members of ASTM accepted this method as a reasonable simulation of volatile compound loss over the coating's lifetime. The method is easily performed and requires only an analytical balance and a suitable drying oven. Because this method was widely used and accepted by industry, EPA incorporated it (by reference) into EPA Method 24 (5) to measure the volatile organic content of surface coatings. ASTM D2369 measures all volatile compounds, including volatile organics and water. To obtain a measure of the volatile organic content, EPA incorporated (in Method 24) an ASTM water content method (6) for measurement of the coating's water content. The water content is then subtracted from the total volatile measurement to obtain the volatile organic content. Further development by RTI under sponsorship of EPA showed that this method is also suitable for other compounds such as printing inks.

EPA used its experience with surface coatings to develop a VOC method for consumer products (3) based on Method 24. Modifications were made to permit sampling of aerosol products (including aerosol-based foams) and to improve calibration for the water content analysis. An interlaboratory study (3) was conducted that indicated that the precision of the VOC consumer products method was comparable to EPA Method 24.

Not all VOCs contribute significantly to ozone formation. Specific VOCs have been designated as exempt VOCs due to their low photochemical reactivity (Table 1). EPA initiated the current work to develop a method to quantify these exempt VOCs in consumer products.

Knowledge of the exempt VOC content permits EPA to correct the total VOC measurements to better assess the actual ozone formation risk posed by the product.

Selection of Target Compound List

An early step in method development was to select the target compounds to be measured (Table 2). Several of the compounds on the exempt VOC list (Table 1) are not likely to be found in consumer products. Inclusion of them would lead to development of a more difficult, and thus more expensive, method than is actually needed.

Table 2. Exempt VOC Method Target List

Compound Name
carbon dioxide ^a
methylene chloride (dichloromethane)
1,1,1,2-tetrafluoroethane (HFC-134a)
pentafluoroethane (HFC-125)
1,1,2,2-tetrafluoroethane (HFC-134)
1,1,1-trifluoroethane (HFC-143a)
1,1-difluoroethane (HFC-152a)
acetone
tetrachloroethylene (perchloroethylene or perc) ^b
Class II ozone depleting chemicals ^c
chlorodifluoromethane (HCFC-22)
1,1,1-trifluoro 2,2-dichloroethane (HCFC-123)
1,1-dichloro 1-fluoroethane (HCFC-141b)
1-chloro 1,1-difluoroethane (HCFC 142b)

^a Carbon dioxide is not a VOC, but is measured by the total volatiles method (3) and has been added to the target list to permit correction of measured total volatiles.

^b Tetrachloroethylene was added to the exempt list during the course of this work (61 FR 4588, February 7, 1996).

^c Use of class II ozone-depleting chemicals (58 FR 65018, December 10, 1993) is currently restricted. These chemicals may be phased out in the future.

Parachlorobenzotrifluoride (PCBTf), siloxanes, and perfluorocarbons are not widely used in consumer products and were omitted from the method target list. EPA currently restricts use of, and will phase out most uses of chlorofluorocarbons and 1,1,1-trichloroethane (methyl chloroform) by January 1, 1996, due to their impact on stratospheric ozone (58 FR 65018, December 10, 1993). Exempt compounds affected include 1,1,1-trichloro-ethane, CFC-11, CFC-12, CFC-113, CFC-114, and CFC-115. Because these compounds are no longer available (except to licensed technicians for uses such as air conditioner repair), they were removed from the method target list. We were not able to obtain 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124) and this compound was also removed from the target list.

Several compounds on the exempt list have too high a vapor pressure to be useful in consumer products. Methane, ethane, and HFC-23 (trifluoromethane) all have high vapor pressures at room temperature (methane > 2000 psi, ethane \approx 560 psia at 70° F, HFC-23 \approx 650 psia at 70° F) (7). The high vapor pressures of these compounds make it difficult to incorporate substantial amounts in consumer products and precludes their use as propellants in aerosol cans. These compounds were omitted from the method target list.

In addition to the compounds on the exempt list at the start of this project, tetrachloroethylene (also called perchloroethylene or perc) was added to the method target list. At the time this project was begun, EPA had proposed adding this compound to the exempt VOC list (57 FR 48490, October 26, 1992). The final ruling adding tetrachloroethylene as an exempt compound was announced while the experimental work was being performed (61 FR 4588, February 7, 1996).

Although carbon dioxide (CO₂) is not a VOC, it is measured by the total VOC method (3). Carbon dioxide was added to the target list to permit correction of volatiles measured by the total VOC current method.

Although methylene chloride is included on the target list, it may be removed from consumer products in the future because of health concerns.

Overview of Approach

Assessing the ozone formation risk of consumer products is complicated by several issues

including:

- Consumer products consist of a number of different formulations.
- Products may be in liquid, solid, or aerosol form.
- Any one product may contain hundreds of individual chemical compounds.
- The exact chemical composition of many consumer products may not be well known, even by the manufacturer. For example, essential oils and fragrances contain large numbers of individual compounds, the identity and amount of which are generally unknown to the manufacturer.

Based on these considerations, development of a method to separate, identify, and quantify each individual VOC in a consumer product was considered unnecessarily difficult and expensive. Instead, a method was developed to separate, identify, and measure only the exempt VOCs and carbon dioxide present in consumer products. The exempt content can be subtracted from the total VOC content, as measured by the earlier consumer products VOC method, to obtain the nonexempt VOC content.

The overall method approach consisted of two parts -- sampling and analysis. Sampling consisted of capturing the volatile components from a consumer product in a Tedlar collection bag (Figure 1). The bag contents were then analyzed using gas chromatography with mass selective detection (GC/MSD).

SAMPLING

Development of sampling procedures required addressing the wide variety of consumer products available. These products may be packaged as a liquid, solid, or (propellant-driven) aerosol, and any single product may contain from one to hundreds of individual chemical compounds. Dealing with various forms of packaging was addressed in the development of the total VOC method. In this study a septum sealed vial was used. Liquid and solid samples were added before crimp sealing the vial. An adapter permitted the injection of aerosol products through a hypodermic needle into the sealed vial without loss of sample. This approach had been

verified in the interlaboratory study of the total VOC method.

Because many of the exempt products are condensable gases at room temperature, the sampling method had to accommodate both liquids and gases. Heating was used to convert all exempt compounds in the sample to the gaseous phase. Purging the sample with a purge gas would then sweep out the volatile components and leave behind any solids, tars, and resins that could complicate the analysis. The volatiles, now mixed with the purge gas, were collected in a Tedlar collection bag. A new Tedlar sample bag can be used for each sample, if desired, to prevent problems with contamination between samples and to reduce cleanup costs. Addition of a sufficient volume of purge gas prevented recondensation of the exempt compounds at room temperature. The collected gas in the bag was then analyzed by GC/MSD. A known amount of volatile internal standard (1,2,2-trichloro-1,1-difluoroethane [HCFC 122]) was added to the sample before purging. The use of an internal standard eliminated the need to make accurate dilution volume measurements and automatically compensated for differences in sample bag temperature and atmospheric pressure.

Estimated Minimum Dilution Volume

Previous tests on consumer products (3) indicated that water frequently is a major volatile component. Sampling of products requires that sufficient dry nitrogen diluent be used to prevent condensation of water during storage of the sample bag at room temperature. The final partial pressure of water must be less than the saturation vapor pressure. The minimum dry nitrogen gas purge volume (V) needed to prevent condensation of a 0.5 g sample composed of 100 percent water at 20° C would be:

$$V(L) = \frac{0.5(g) \times 293.15(K) \times 0.082(L\text{-atm/mol/K}) \times 760(\text{torr/atm})}{18(\text{molecular weight, g/mol}) \times 17(\text{vapor pressure at } 20^{\circ}\text{C, torr})} \quad (1)$$

or approximately 30 L. This would require a minimum flow rate of 0.5 L/min for the 1 hour evaporation time as used in EPA Method 24. Based on this minimum flow, a nominal flow of 1 L/min was selected for the study.

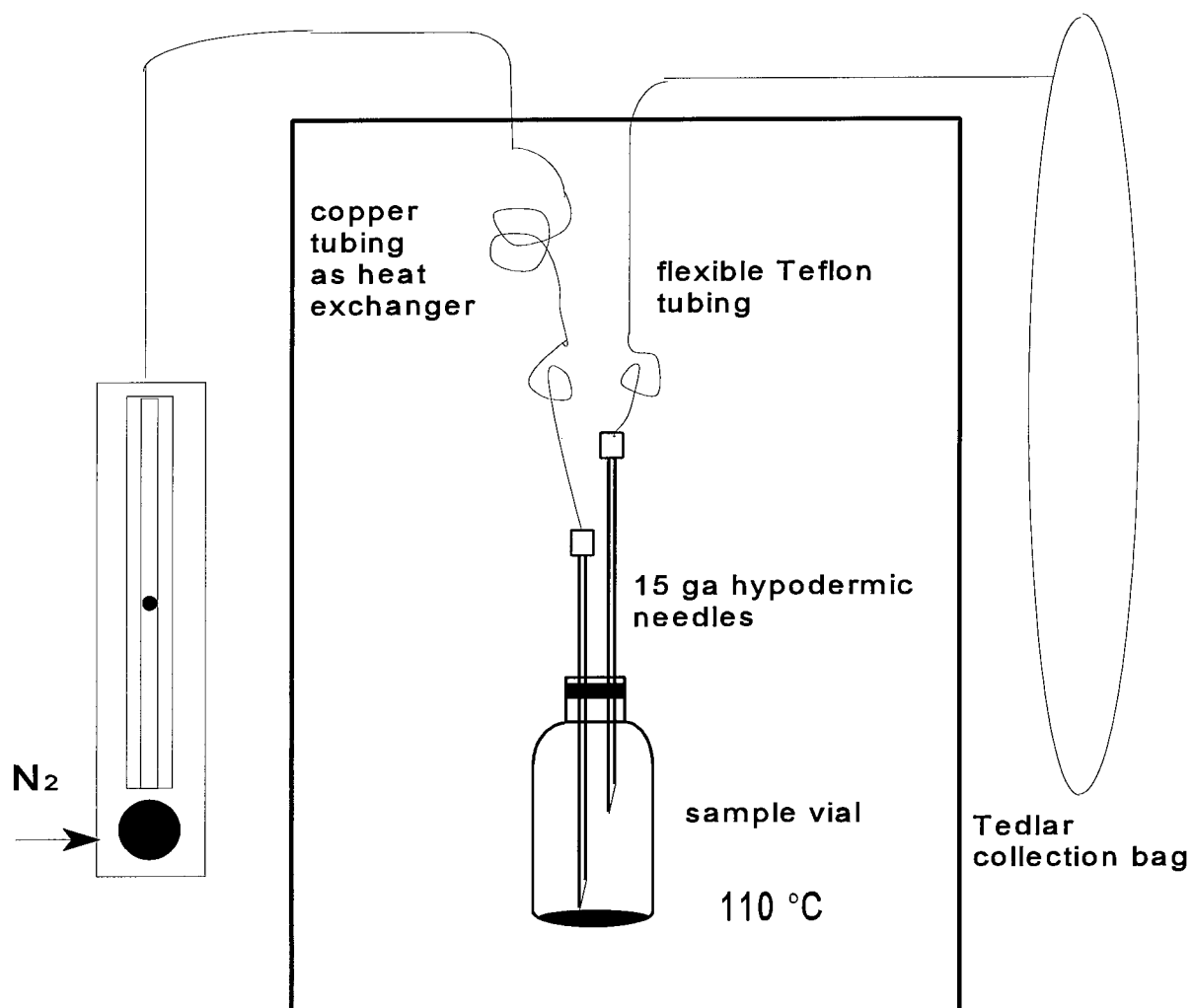


Figure 1. Sample purge and volatiles collection assembly

ANALYSIS

Because exempt VOC compounds are by definition volatile compounds, gas chromatography was most appropriate for separation. Mass spectral detection was selected due to its ability to obtain compound-specific information for each peak. Comparison of the measured mass spectrum with library spectra permitted verification of compound identity. Quantitation on specific target ions permitted the accurate measurement of exempt compounds, even if perfect chromatographic separation was not obtainable.

Selection of GC Column and Conditions

The goal for selection of a GC column for this method was to separate as many of the exempt compounds as possible in a reasonable chromatographic run time. Several capillary columns and conditions were evaluated. Table 3 summarizes columns and conditions that were evaluated:

Table 3. Chromatographic Conditions Evaluated

Column	Temperature Program
DB-624	-20° C for 1 min, 10° C/min. to 120° C
HP-5	-40° C for 1 min, 10° C/min to 120° C
	-60° C for 1 min, 10° C/min to 120° C
VOCOL	40° C for 4 min, 10° C/min to 120° C
	40° C for 1 min, 5° C/min to 180° C
	-20° C for 1 min, 5° C/min to 180° C
GS-Q	40° C for 1 min, 30° C/min to 220° C
	40° C for 1 min, 10° C/min to 220° C
	40° C for 1 min, 5° C/min to 150° C, 20° C/min to 220° C, hold for 4.5 min

^a All columns were 30 m by 0.53 mm ID.

After evaluation of each of these columns and conditions by analyzing a mixture of selected exempt compounds, the GS-Q column operating under the last set of conditions listed was

selected. The advantages of using the GS-Q column include:

- No subambient column temperatures are necessary.
- No cryofocusing of the sample is necessary.
- Carbon dioxide is separated from nitrogen, enabling quantitation of the CO₂ content.
- Most of the exempt compounds are separated.

Exempt Compound Detection

Because of the inability to achieve complete chromatographic separation of all the exempt compounds and the risk of other compounds in consumer products coeluting with the exempt compounds, a MSD was selected for this method. By careful selection of target ions for quantitation, it is feasible to measure exempt compounds with no interference from other compounds. The use of a nonselective detector such as a flame ionization detector (FID) would require chromatographic resolution of all exempt compounds in all consumer products, which is not feasible.

The use of an MSD also provides for identification of exempt compounds through the use of qualifier ion relative abundances.

Calibration

One of the first challenges faced in this project was the development of a suitable calibration procedure. One approach considered was to prepare calibration standards by loading a blank sample vial with known amounts of the exempt compounds. A calibration point would then be obtained by analyzing this vial as a normal sample. This approach was not used for several reasons. First, because the gas in the Tedlar bag cannot be kept for long periods of time (i.e., more than a few hours), it is impossible to analyze the same standard on different days to evaluate instrumental drift. Second, because the sample is effectively consumed, such an approach does not permit an independent evaluation of the calibration standard. Third, because many (i.e., five) of the compounds are gases that are easily condensed, it is necessary to spike the sample vial with each gas individually. This is a time-consuming procedure not generally

employed by commercial laboratories.

Based on these considerations, the use of a standard mixture of the exempt compounds in a compressed gas cylinder (with nitrogen as the diluent) for calibration was adopted. The use of such a mixture permits independent analysis of the calibration standards. Although preparation of such a standard may not be within the capabilities of many laboratories, a large number of commercial gas suppliers will produce such mixtures on request. Use of such a preprepared mixture greatly reduces the time required to perform daily calibration checks, and the fact that the same mixture can be used on different days permits better tracking of instrument response on a daily basis.

For this study, RTI prepared three calibration mixtures, each containing different concentrations of the exempt compounds in nitrogen. The internal standard (HCFC 122) was added during preparation to obtain approximately the same internal standard concentration in each mixture. The mixtures were prepared in Summa canisters. A known volume of exempt compound, either gas or liquid, was injected into an evacuated Summa canister of known volume. Gases were injected with a gas-tight syringe. Liquids were injected from a fixed volume sample loop into a vaporization zone which was swept with nitrogen into the canister. A schematic diagram of the calibration standard preparation system is shown in Figure 2.

The maximum concentration of the high-level standard was limited to that which would be feasible in a high-pressure (approximately 500 psi) commercial gas cylinder. The limit on concentration is due to the saturation vapor pressure of the exempt compound. Tetrachloroethylene had the lowest saturation vapor pressure of 13.9 torr at 20° C. Thus the maximum concentration that would not condense in a cylinder pressurized to 500 psig would be given by:

$$\text{Maximum Concentration (ppm)} = \frac{13.9 \text{ torr} * 0.0193 \text{ psi/torr}}{515 \text{ psia}} * 10^6$$

or approximately 520 ppm. To allow a reasonable safety margin, a practical maximum would be 250 ppm.

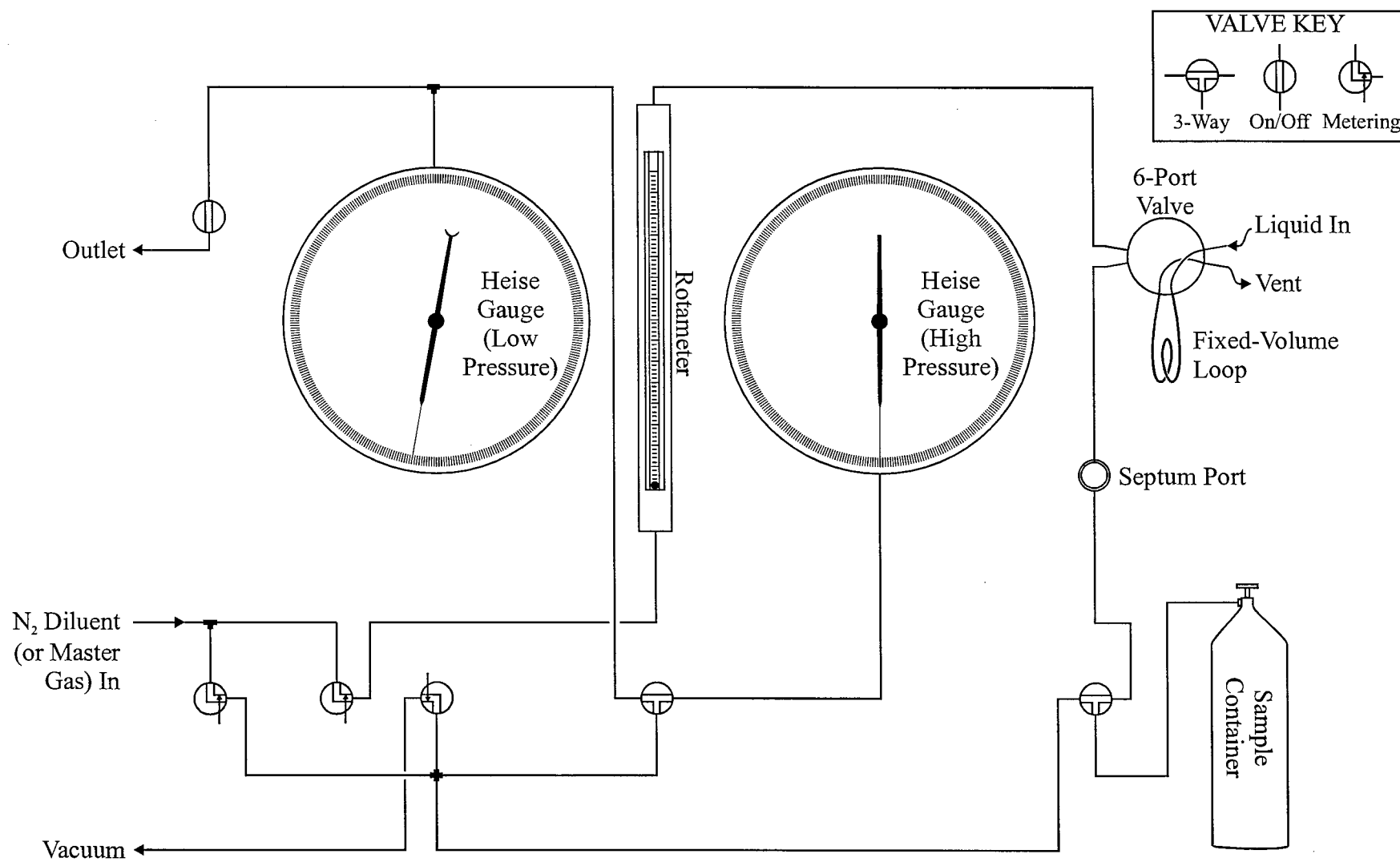


Figure 2. Schematic Diagram of Gas-Phase Standard Preparation System

The equivalent amount of tetrachloroethylene that would correspond to a 250 ppm concentration in a sample bag with a 1-L/min flow rate for a 1-hour purge time is given by:

$$\text{amount (g)} = \frac{250 \text{ ppm} * 1 \text{ L/min} * 60 \text{ min} * 1 \text{ atm} * 165.8 \text{ g/mol}}{0.08205 \text{ L-atm/mol K} * 298 \text{ K}} * 10^{-6}.$$

This corresponds to a weight of approximately 0.1 g or 20 percent by weight of a 0.5-g sample.

SELECTION OF PRODUCTS

It was not considered feasible to find current consumer products with exempt compounds and obtain information from the manufacturer(s) within the time available for completion of this project. With the exception of acetone, all of the other exempt compounds are synthetic as such are not likely to occur in consumer products (at least at percent levels). Most of the compounds on the target list are considerably more expensive than their nonexempt counterparts and, as such, are not generally added to consumer products unless they meet some special need (such as a reduction in flammability). For this reason, few currently available consumer products are expected to contain exempt compounds, although this could change rapidly if VOC regulations are imposed on consumer products. In addition, the composition of many consumer products is considered proprietary and some manufacturers would be unwilling to provide information on exempt concentrations (especially within the time constraints of this project).

Because products with known levels of exempt compounds were not available for this study, currently available products were spiked with known amounts of exempt compounds. This spiking permitted an estimate of the accuracy of the method. The products selected for this study were those used in previous work involving an interlaboratory study of the total volatile content of consumer products (3). The same product codes are used to refer to a given product in both studies.

SPIKING OF SAMPLES

Samples were spiked by adding the exempt compounds to the sample vial after the sample and internal standard had been added but before the vial had been heated. Five of the compounds

(tetrachloroethylene, methylene chloride, HCFC-141b, HCFC-123, and acetone) are liquids at room temperature. A mixture containing known amounts of four of these compounds (excluding acetone) was gravimetrically prepared and added to the sealed vial by a gas-tight microliter syringe. The amount added was gravimetrically determined. To avoid potential problems with solubility of acetone in the fluorocarbons, a separate solution of acetone (in methanol) was used to spike products with acetone.

The remaining eight exempt compounds are gases at room temperature. Preparation of a single spike mixture at the high levels required (approximately 50 to 100 mg loading per compound) was not considered feasible because many of these gases are easily condensed (all except CO₂, HFC-125, and HFC-143a were supplied as condensed gases in low pressure cylinders). Spiking a mixture with each of these compounds (at approximately 50 mg) individually involves adding a total of approximately 80 mL of gas to the 100-mL sample vial. It was not feasible to add this much additional gas to a container that was already pressurized with an aerosol sample. For these reasons, product samples were spiked with only one or two gases, although all gases were tested with at least one product.

EXPERIMENTAL MATRIX

Based on the calibration data for the lowest level calibration standard, a bag concentration of at least 25 mg per compound would be needed to produce bag concentrations greater than the lowest calibration standard. The samples were prepared and spiked with approximately 30 mg of each exempt compound (Table 4). As described above, only one or two gases were spiked for each given product. All liquids were spiked for each product, except for product FD (engine cleaner) which was only spiked with the liquid HCFC-141b (in hexane).

Table 4. Experimental Matrix

	AB	AC	FD	FB	LC	AA	SA
	aerosol	aerosol	engine	tire	pump	furniture	stick
Compound	hairspray	deodorant	cleaner	cleaner	hairspray	polish	deodorant
<u>gases</u>							
carbon dioxide	X						
HFC-125			X				
HCFC-22						X	
HFC-134a				X			
HFC-152a	X						
HFC-134					X	X	
HCFC-142b		X					
HFC-134a							X
<u>liquids</u>							
HCFC-123	X	X		X	X	X	X
HCFC-141b	X	X	X	X	X	X	X
methylene chloride	X	X		X	X	X	X
tetrachloroethylene	X	X		X	X	X	X
acetone	X	X		X	X	X	X

SECTION 5

RESULTS AND DISCUSSION

INTRODUCTION

Consumer product samples spiked with known amounts of exempt compounds were analyzed by the new method to evaluate the method's accuracy and precision. The percentage of spike measured (recovered) was used as a measure of the method's accuracy. The method's precision was evaluated based on the results of multiple aliquots and analyses of aliquots.

Three samples were taken from each product and each sample was spiked and processed to produce a gas collection bag containing the exempt compounds, internal standard, and any other volatile compounds from the sample. The variation in results of the analyzes for these three aliquots provides a measure of the method's precision. In addition, one of these bags was analyzed (injected) three times to estimate the precision of the GC/MSD system (which is one component of the total method precision).

RESULTS FOR MULTIPLE INJECTIONS OF ONE SAMPLE

Results for multiple injections of one sample are shown in Tables 5 through 11. Most analyses had recoveries within 10 percent of the prepared values. Only the analysis of tetrachloroethylene with product FB (tire cleaner) failed to meet the method accuracy goals of ± 20 percent spike recovery. This product is discussed further in the section on "Results for Multiple Aliquots of One Product". Analysis precision was also good with typical standard deviations for percent recovery being 2 percent or less.

**Table 5. Results of Multiple Injections for
Product AB - Aerosol Hairspray**

Compound	Spike mg	Injection 1, measured mg (%)	Injection 2, measured mg (%)	Injection 3, measured mg (%)	% Recovery	
		recovery)	recovery)	recovery)	Avg	Stdev
tetrachloroethylene	39.6	45.4 (114.6%)	44.7 (112.8%)	45.2 (114.0%)	113.8%	0.9%
methylene chloride	32	31.5 (98.5%)	31.4 (98.1%)	31.6 (98.8%)	98.5%	0.3%
HCFC-141b	30.1	30.9 (102.6%)	30.5 (101.3%)	30.4 (100.9%)	101.6%	0.9%
HCFC-123	35.2	35.4 (100.7%)	35.6 (101.3%)	35.6 (101.3%)	101.1%	0.3%
acetone	23.6	24.7 (104.7%)	24.7 (104.7%)	25.1 (106.4%)	105.2%	1.0%
carbon dioxide	18.3	17.4 (94.8%)	17.5 (95.4%)	17.6 (95.9%)	95.4%	0.5%
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	27.5	24.4 (88.6%)	24.2 (87.9%)	24.4 (88.6%)	88.4%	0.4%
HFC-134	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 6. Results of Multiple Injections for
Product AC - Aerosol Deodorant**

Compound	Spike mg	Injection 1, measured mg (%)	Injection 2, measured mg (%)	Injection 3, measured mg (%)	% Recovery	
		recovery)	recovery)	recovery)	Avg	Stdev
tetrachloroethylene	41.1	41.9 (101.9%)	41.5 (100.9%)	41.4 (100.6%)	101.1%	0.6%
methylene chloride	33.2	34.8 (104.8%)	34.6 (104.2%)	34.6 (104.2%)	104.4%	0.3%
HCFC-141b	31.3	31.9 (102.0%)	31.0 (99.2%)	31.9 (102.0%)	101.1%	1.7%
HCFC-123	36.5	36.7 (100.6%)	36.6 (100.3%)	36.9 (101.1%)	100.7%	0.4%
acetone	23.6	26.8 (113.6%)	26.1 (110.6%)	26.0 (110.2%)	111.5%	1.8%
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA
HCFC 142b	41.8	39.9 (95.4%)	39.7 (94.9%)	40 (95.7%)	95.3%	0.4%
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 7. Results of Multiple Injections for
Product FD - Engine Cleaner**

Compound	spike mg	Injection 1, measured mg (% recovery)	Injection 2, measured mg (% recovery)	Injection 3, measured mg (% recovery)	% Recovery Avg Stdev	
tetrachloroethylene	NA	NA	NA	NA	NA	NA
methylene chloride	NA	NA	NA	NA	NA	NA
HCFC-141b	11.9	12.7 (106.7%)	12.3 (103.4%)	12.0 (100.8%)	103.6%	2.9%
HCFC-123	NA	NA	NA	NA	NA	NA
acetone	NA	NA	NA	NA	NA	NA
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	49.3	46.6 (94.4%)	48.2 (97.7%)	46.9 (95.1%)	95.8%	1.8%
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 8. Results of Multiple Injections for
Product FB - Tire Cleaner**

Compound	Spike mg	Injection 1, measured mg (% recovery)	Injection 2, measured mg (% recovery)	Injection 3, measured mg (% recovery)	% Recovery Avg Stdev	
tetrachloroethylene	40.1	48.6 (121.3%)	48.4 (120.8%)	48.3 (120.6%)	120.9%	0.4%
methylene chloride	32.3	32.6 (100.8%)	32.9 (101.7%)	33.6 (103.9%)	102.1%	1.6%
HCFC-141b	30.4	30.2 (99.2%)	28.8 (94.6%)	30.4 (99.8%)	97.9%	2.9%
HCFC-123	35.5	35.4 (99.6%)	35.1 (98.8%)	35.3 (99.3%)	99.2%	0.4%
acetone	23.4	25.4 (108.5%)	25.3 (108.1%)	25.2 (107.6%)	108.1%	0.4%
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	41.4	36.5 (88.1%)	36.5 (88.1%)	37.2 (89.8%)	88.7%	1.0%
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 9. Results of Multiple Injections for
Product LC - Pump Hairspray**

Compound	Spike mg	Injection 1, measured mg (%)	Injection 2, measured mg (%)	Injection 3, measured mg (%)	% Recovery	
		recovery)	recovery)	recovery)	Avg	Stdev
tetrachloroethylene	59.1	60.5 (102.3%)	59.9 (101.3%)	59.8 (101.2%)	101.6%	0.6%
methylene chloride	47.7	47.0 (98.5%)	47.3 (99.1%)	47.2 (98.9%)	98.8%	0.3%
HCFC-141b	44.9	47.5 (105.7%)	47.3 (105.3%)	46.4 (103.3%)	104.8%	1.3%
HCFC-123	52.4	51.7 (98.6%)	52.4 (99.9%)	51.6 (98.4%)	99.0%	0.8%
acetone	23.3	24.5 (105.3%)	24.6 (105.7%)	24.7 (106.1%)	105.7%	0.4%
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	41.3	34.6 (83.7%)	34.9 (84.5%)	34.8 (84.2%)	84.1%	0.4%
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 10. Results of Multiple Injections for
Product AA - Furniture Polish**

Compound	Spike mg	Injection 1, measured mg (%)	Injection 2, measured mg (%)	Injection 3, measured mg (%)	% Recovery	
		recovery)	recovery)	recovery)	Avg	Stdev
tetrachloroethylene	39.1	36.2 (92.6%)	36.1 (92.4%)	36.7 (93.9%)	93.0%	0.8%
methylene chloride	31.5	30.3 (96.0%)	30.5 (96.7%)	30.5 (96.7%)	96.5%	0.4%
HCFC-141b	29.7	27.7 (93.3%)	28.2 (94.9%)	28.2 (94.9%)	94.4%	1.0%
HCFC-123	34.7	35.3 (101.8%)	35.6 (102.7%)	35.7 (103.0%)	102.5%	0.6%
acetone	23.3	24.4 (104.6%)	25.0 (107.2%)	24.8 (106.3%)	106.0%	1.3%
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	35.4	32.5 (91.8%)	33.4 (94.3%)	33.5 (94.6%)	93.6%	1.6%
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	41.8	44 (105.3%)	45 (107.7%)	44.7 (107.0%)	106.7%	1.2%
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

**Table 11. Results of Multiple Injections for
Product SA - Stick Deodorant**

Compound	Spike mg	Injection 1, measured mg (%) recovery)	Injection 2, measured mg (%) recovery)	Injection 3, measured mg (%) recovery)	% Recovery Avg Stdev	
tetrachloroethylene	36.5	34.6 (94.7%)	36.3 (99.4%)	36.7 (100.5%)	98.2%	3.1%
methylene chloride	29.5	29.0 (98.3%)	28.7 (97.3%)	28.6 (97.0%)	97.5%	0.7%
HCFC-141b	27.8	24.2 (87.2%)	24.2 (87.2%)	28.1 (101.2%)	91.8%	8.1%
HCFC-123	32.4	31.2 (96.3%)	30.7 (94.7%)	30.7 (94.7%)	95.2%	0.9%
acetone	23.6	25.3 (107.1%)	24.9 (105.4%)	24.7 (104.6%)	105.7%	1.3%
carbon dioxide	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA
HFC-143a	34.7	33.2 (95.8%)	32.6 (94.1%)	33 (95.2%)	95.0%	0.9%

NA = Not applicable, compound was not added as spike for this sample.

RESULTS OF MULTIPLE ALIQUOTS OF EACH PRODUCT

Results for multiple aliquots of each spiked product are shown in Tables 12 through 18. Results for all products are summarized in Table 19. Most analyses had recoveries within 10 percent of the prepared values. Only the analysis of tetrachloroethylene with product FB (tire cleaner) failed to meet the method accuracy goals of ± 20 percent spike recovery. The reason for the high recoveries seen with this product is not known; however, presence of tetrachloroethylene in the product is not a likely cause. Although the sample weights for this product varied between 0.23 and 0.79 g, the percent recoveries for these samples were within 1 percent. Clearly this would not be possible if the high recovery was due to the presence of tetrachloroethylene in the sample.

Precision was good with standard deviations for percent recovery typically less than 5 percent. Notably poorer precision was seen with a few gaseous exempt compounds, especially product LC (pump hairspray) with HCFC-134a and product SA (stick deodorant) with HFC-143a. This reflects good recoveries for two of the three samples, with the third sample

showing low recovery (approximately 60 to 70 percent). The poor recovery is believed to be due to problems with septum material from the apparatus used to fill the syringe with gas for spiking. This material tended to clog the syringe needle and produce a high backpressure and leakage around the hypodermic needle used to introduce spike gas into the vial.

Table 12. Results of Multiple Aliquots for Product AB - Aerosol Hairspray

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		%Recovery	
	Measured		Measured		Measured			
	Spike mg	mg (%) recovery)	Spike mg	mg (%) recovery)	Spike mg	mg (%) recovery)	Avg	Stdev
tetrachloroethylene	39.6	45.1 (113.8%)	39	44.9 (115.1%)	38.9	40.2 (103.4%)	110.8%	6.4%
methylene chloride	32	31.5 (98.5%)	31.5	31.5 (100.1%)	31.4	32.4 (103.2%)	100.6%	2.4%
HCFC-141b	30.1	30.6 (101.6%)	29.6	29.9 (100.9%)	29.5	30.1 (101.9%)	101.5%	0.5%
HCFC-123	35.2	35.5 (101.1%)	34.6	34.9 (100.9%)	34.5	34.9 (101.2%)	101.1%	0.2%
acetone	23.6	24.8 (105.2%)	23.4	25.3 (108.2%)	23.3	26.0 (111.7%)	108.4%	3.2%
carbon dioxide	18.3	17.5 (95.4%)	18.3	17 (92.7%)	18.3	16.2 (88.5%)	92.2%	3.5%
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	27.5	24.3 (88.4%)	27.5	24.9 (90.4%)	27.5	25.2 (91.7%)	90.2%	1.7%
HFC-134	NA	NA	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 13. Results of Multiple Aliquots for Product AC - Aerosol Deodorant

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery	
	Measured		Measured		Measured			
	Spike	mg (%)	Spike	mg (%)	Spike	mg (%)		
	mg	recovery)	mg	recovery)	mg	recovery)	Avg	Stdev
tetrachloroethylene	41.1	41.6 (101.1%)	38.2	39.2 (102.6%)	38.2	39.0 (102.1%)	101.9%	0.7%
methylene chloride	33.2	34.7 (104.4%)	30.8	32.6 (105.7%)	30.8	31.5 (102.1%)	104.1%	1.8%
HCFC-141b	31.3	31.6 (101.1%)	29	31.0 (106.7%)	29	29.5 (101.6%)	103.1%	3.1%
HCFC-123	36.5	36.7 (100.7%)	33.9	34.7 (102.4%)	33.9	33.2 (97.9%)	100.3%	2.2%
acetone	23.6	26.3 (111.5%)	23.7	25.7 (108.6%)	23.7	26.4 (111.6%)	110.6%	1.7%
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA	NA	NA
HCFC 142b	41.8	39.9 (95.3%)	41.8	41 (98.0%)	41.8	38.8 (92.8%)	95.4%	2.6%
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 14. Results of Multiple Aliquots for Product FD - Engine Cleaner

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery	
	Measured		Measured		Measured			
	Spike	mg (%)	Spike	mg (%)	Spike	mg (%)		
	mg	recovery)	mg	recovery)	mg	recovery)	Avg	Stdev
tetrachloroethylene	NA	NA	NA	NA	NA	NA	NA	NA
methylene chloride	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-141b	11.9	12.3 (103.6%)	22.8	22.3 (98.0%)	23.3	23.2 (99.8%)	100.5%	2.9%
HCFC-123	NA	NA	NA	NA	NA	NA	NA	NA
acetone	NA	NA	NA	NA	NA	NA	NA	NA
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	49.3	47.2 (95.8%)	49.3	47.3 (95.9%)	49.3	50.5 (102.4%)	98.0%	3.8%
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 15. Results of Multiple Aliquots for Product FB - Tire Cleaner

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery Avg Stdev	
	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)		
tetrachloroethylene	40.1	48.4 (120.9%)	39.6	48.0 (121.1%)	39.6	48.2 (121.8%)	121.3%	0.5%
methylene chloride	32.3	33.0 (102.1%)	32	33.0 (103.1%)	31.9	32.5 (101.7%)	102.3%	0.7%
HCFC-141b	30.4	29.8 (97.9%)	30.1	29.8 (98.9%)	30.1	30.2 (100.4%)	99.1%	1.3%
HCFC-123	35.5	35.3 (99.2%)	35.2	36.2 (103.0%)	35.1	35.7 (101.7%)	101.3%	1.9%
acetone	23.4	25.3 (108.1%)	23.8	25.7 (108.1%)	23.4	25.4 (108.4%)	108.2%	0.2%
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	41.4	36.7 (88.7%)	41.4	34.7 (83.8%)	41.4	35.9 (86.7%)	86.4%	2.5%
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 16. Results of Multiple Aliquots for Product LC - Pump Hairspray

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery Avg Stdev	
	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)		
tetrachloroethylene	59.1	60.1 (101.6%)	40.2	40.9 (101.9%)	40.3	41.7 (103.6%)	102.3%	1.1%
methylene chloride	47.7	47.2 (98.8%)	32.4	31.8 (98.1%)	32.5	32.3 (99.4%)	98.8%	0.6%
HCFC-141b	44.9	47.1 (104.8%)	30.5	30.7 (100.6%)	30.6	32.0 (104.6%)	103.3%	2.3%
HCFC-123	52.4	51.9 (99.0%)	35.6	33.0 (92.6%)	35.7	34.3 (96.0%)	95.9%	3.2%
acetone	23.3	24.6 (105.7%)	23.6	25.2 (106.6%)	23.5	24.7 (105.0%)	105.8%	0.8%
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	41.3	34.8 (84.1%)	41.3	27.3 (66.1%)	41.3	41.6 (100.7%)	83.6%	17.3%
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 17. Results of Multiple Aliquots for Product AA - Furniture Polish

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery Avg Stdev	
	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)		
tetrachloroethylene	39.1	36.3 (93.0%)	38.2	35.0 (91.7%)	37.3	35.3 (94.7%)	93.1%	1.5%
methylene chloride	31.5	30.4 (96.5%)	30.8	29.5 (95.8%)	30.1	27.7 (92.0%)	94.8%	2.4%
HCFC-141b	29.7	28.0 (94.4%)	29	27.6 (95.2%)	28.3	26.1 (92.1%)	93.9%	1.6%
HCFC-123	34.7	35.5 (102.5%)	33.8	34.1 (100.8%)	33.1	32.5 (98.3%)	100.5%	2.1%
acetone	23.3	24.7 (106.0%)	23.3	24.4 (104.7%)	23.4	24.2 (103.6%)	104.8%	1.2%
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	35.4	33.1 (93.6%)	35.4	33.3 (94.0%)	35.4	34.2 (96.6%)	94.7%	1.6%
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	41.8	44.6 (106.7%)	41.8	42.6 (102.0%)	41.8	44.1 (105.6%)	104.7%	2.5%
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	NA	NA	NA	NA	NA	NA	NA	NA

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 18. Results of Multiple Aliquots for Product SA - Stick Deodorant

Compound	Aliquot 1 ^a		Aliquot 2		Aliquot 3		% Recovery Avg Stdev	
	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)	Spike mg	Measured mg (%) recovery)		
tetrachloroethylene	36.5	35.9 (98.2%)	37.6	37.1 (98.7%)	40.2	37.6 (93.6%)	96.8%	2.8%
methylene chloride	29.5	28.8 (97.5%)	30.4	29.4 (96.8%)	32.4	30.5 (94.0%)	96.1%	1.9%
HCFC-141b	27.8	25.5 (91.8%)	28.6	24.3 (85.0%)	30.5	26.1 (85.5%)	87.4%	3.8%
HCFC-123	32.4	30.9 (95.2%)	33.4	31.1 (93.2%)	35.6	32.6 (91.5%)	93.3%	1.9%
acetone	23.6	25.0 (105.7%)	23.4	24.9 (106.5%)	23.3	24.3 (104.4%)	105.6%	1.1%
carbon dioxide	NA	NA	NA	NA	NA	NA	NA	NA
HFC-125	NA	NA	NA	NA	NA	NA	NA	NA
HCFC-22	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-152a	NA	NA	NA	NA	NA	NA	NA	NA
HFC-134	NA	NA	NA	NA	NA	NA	NA	NA
HCFC 142b	NA	NA	NA	NA	NA	NA	NA	NA
HFC-143a	34.7	32.9 (95.0%)	34.7	32.1 (92.6%)	34.7	24.4 (70.4%)	86.0%	13.6%

NA = Not applicable, compound was not added as spike for this sample.

^a Average of three injections.

Table 19. Comparison of Spike Recoveries by Product

Compound	AB aerosol hairspray	AC aerosol deodorant	FD engine cleaner	FB tire cleaner	LC Pump hairspray	AA furniture polish	SA stick deodorant	Average	Standard deviation
tetrachloroethylene	110.8%	101.9%	NA	121.3%	102.3%	93.1%	96.8%	104.4%	10.2%
methylene chloride	100.6%	104.1%	NA	102.3%	98.8%	94.8%	96.1%	99.4%	3.6%
HCFC-141b	101.5%	103.1%	100.5%	99.1%	103.3%	93.9%	87.4%	98.4%	5.8%
HCFC-123	101.1%	100.3%	NA	101.3%	95.9%	100.5%	93.3%	98.7%	3.3%
acetone	108.4%	110.6%	NA	108.2%	105.8%	104.8%	105.6%	107.2%	2.2%
carbon dioxide	90.8%	NA	NA	NA	NA	NA	NA	90.8%	NA
HFC-125	NA	NA	98.0%	NA	NA	NA	NA	98.0%	NA
HCFC-22	NA	NA	NA	NA	NA	94.7%	NA	94.7%	NA
HFC-134a	NA	NA	NA	86.4%	NA	NA	NA	86.4%	NA
HFC-152a	90.2%	NA	NA	NA	NA	NA	NA	90.2%	NA
HFC-134	NA	NA	NA	NA	83.6%	104.7%	NA	94.2%	14.9%
HCFC 142b	NA	95.4%	NA	NA	NA	NA	NA	95.4%	NA
HFC-143a	NA	NA	NA	NA	NA	NA	86.0%	86.0%	NA
average								95.7%	
maximum								107.2%	
minimum								86.0%	
median								95.4%	

NA = Not applicable, compound was not added as spike to this product.

MEASUREMENT OF TOTAL VOLATILES

Similar conditions are used to process consumer product samples in the method for measuring exempts and in the total VOC method (3) evaluated earlier. The major change is the use of a purge gas in the exempt VOC method. The change in sample weight due to the heated purge was used to calculate the total volatile content for the products used in this study. Results are shown in Table 20. The same product containers had previously been tested in an interlaboratory study of the total VOC method. The total volatile content as determined by these laboratories (using the total VOC method) is also included in Table 20. Comparison of the results using the purge gas to those obtained in the interlaboratory study (without purge gas) indicates a positive bias, which, although slight (around 2 percent), is statistically significant at 95 percent confidence. The reason for this bias is unknown but may be due to better volatilization when purge gas is used or to removal of a plug of septum by the large (16 gauge) needles used in the purge apparatus (this would incorrectly appear to be a loss of volatiles from the product). Because measurements of total volatiles by the total VOC method (3) are relatively easy to do and because this method has been validated in an interlaboratory study, it is recommended that the total volatiles for products be measured as described in the total VOC method.

ESTIMATED METHOD COST

The cost of analyses by this method will vary widely depending on a number of factors including:

- Number of analyses to be performed at one time
- Automation facilities available (e.g., automated multisample gas injection facilities)
- Sample handling problems (liquid and solid samples are easier to dispense than aerosols)
- Previous experience with this or similar laboratory methods
- Cost of labor

- Availability of facilities to make multi-component calibration standards (these can be bought commercially, if the laboratory does not have facilities to prepare their own).

Table 20. Comparison of Total Volatiles With and Without Purge Gas

Product ^a	Weight percent total volatiles (with purge)					Expected total volatile content	Difference
	Aliquot 1	Aliquot 2	Aliquot 3	Average	Std Dev	(Without Purge) ^b	
AB - aerosol hairspray	97.9%	94.0%	97.1%	96.3%	1.7%	95.6%	0.7%
AC - aerosol deodorant	103.8%	100.6%	97.1%	100.5%	2.7%	99.9%	0.6%
FD - engine cleaner	94.4%	95.6%	96.2%	95.4%	0.7%	93.4%	2.0%
FB - tire cleaner	72.0%	74.8%	76.4%	74.4%	1.8%	72.2%	2.3%
LC - Pump hairspray	95.0%	97.1%	95.4%	95.8%	0.9%	94.2%	1.6%
AA - furniture polish	96.1%	97.8%	97.5%	97.1%	0.7%	94.3%	2.9%
SA - stick deodorant	54.8%	55.6%	54.6%	55.0%	0.4%	53.0%	2.0%
Average							1.7%
Standard deviation							0.8%
t (difference = 0)							5.58
t at 95% confidence							2.45
Significant difference exists?							Yes

^a Product codes are those used in the interlaboratory study (3).

^b Average total volatiles value measured by eight laboratories in an interlaboratory study using the total VOC method (3).

No overall cost estimate per sample is given, because the actual costs will vary widely among different laboratories. However, estimates of equipment costs, expendable costs, and labor hours are provided to assist users in evaluating method costs.

Equipment Costs

Equipment costs for this method should be similar to other methods using GC with MSD. The largest single item is the GC/MSD itself, with costs for a GC with MSD and data system ranging between \$50,000 and \$100,000, depending on model and accessories. Additional equipment costs will include a drying oven (\$3,000 to \$5,000 for explosion resistant models, a standard model could be used if the samples are known in advance to be non-flammable). Most other reusable items of equipment used for this method are relatively inexpensive, by comparison, and should be less than \$200 in all.

Expendable Items

Expendable item costs are fairly small (less than \$10 per sample) if the collection bags are reused. Collection bags cost approximately \$20 each.

Labor costs

Total time for sample analysis is approximately 2.5 hours, of which 1.5 hours are used for sample preparation and 1 hour is used for GC/MSD analysis. This time does not include calibration and check samples (the number needed will depend on the stability of the system and the size of sample batches). The actual labor time for analysis is around 1.5 hours per sample, considerably less than the total sample analysis time, because the sample preparation and purge for one sample can be performed while the GC/MSD analysis of the previous sample is being performed.

SECTION 6

QUALITY ASSURANCE AND QUALITY CONTROL

INTRODUCTION

The major quality concern in methods development is to provide a method that promotes quality measurements. A key feature is to reduce the chances for error and minimize the number and types of measurements required. Discussions among project personnel during the initial stages of this project resulted in improvements that greatly affected the overall method quality.

The original method approach, contemplated during preparation of the QA plan, was to use a heated reservoir to collect the volatile components for later analysis by GC using either FID or MSD. The concentration of exempt compounds in the reservoir would be measured by GC using calibration based on analyzing standard samples. The measured concentration would then be converted to a total mass of exempt compounds by using measured reservoir volume, temperature, and pressure. This approach has several problems, chiefly the potential for reservoir contamination and the need to have accurate pressure and volume measurements. Selecting MSD as the detector permits measuring selected target ions for the exempt compounds. Measuring target ions provides a greater assurance that the correct compound is quantified, which is especially important with the number and complexity of consumer product samples. Problems with reservoir contamination were addressed by use of a Tedlar gas collection bag in place of the reservoir. Problems with volume and pressure measurements were eliminated by use of an internal standard (HCFC-122). In addition, internal standard methods are more tolerant of changes in total sensitivity that may occur between runs in GC/MS operation. The use of prepared cylinders for calibration and daily checks permits comparison of instrument response on different days and thus provides for better quality control.

CALIBRATION CHECKS

The high-level calibration standard was checked daily. Results are shown in Figure 3. All compounds were within 20 percent of the original calibration data, except for tetrachloroethylene. As a result, the reported recoveries for tetrachloroethylene may be biased

somewhat high. The limit for calibration drift of ± 20 percent was defined in the Quality Assurance Project Plan. This limit is a reasonable expectation for measurements performed by GC/MSD. The reason that the check for tetrachloroethylene exceeded the 20 percent criterion is not known.

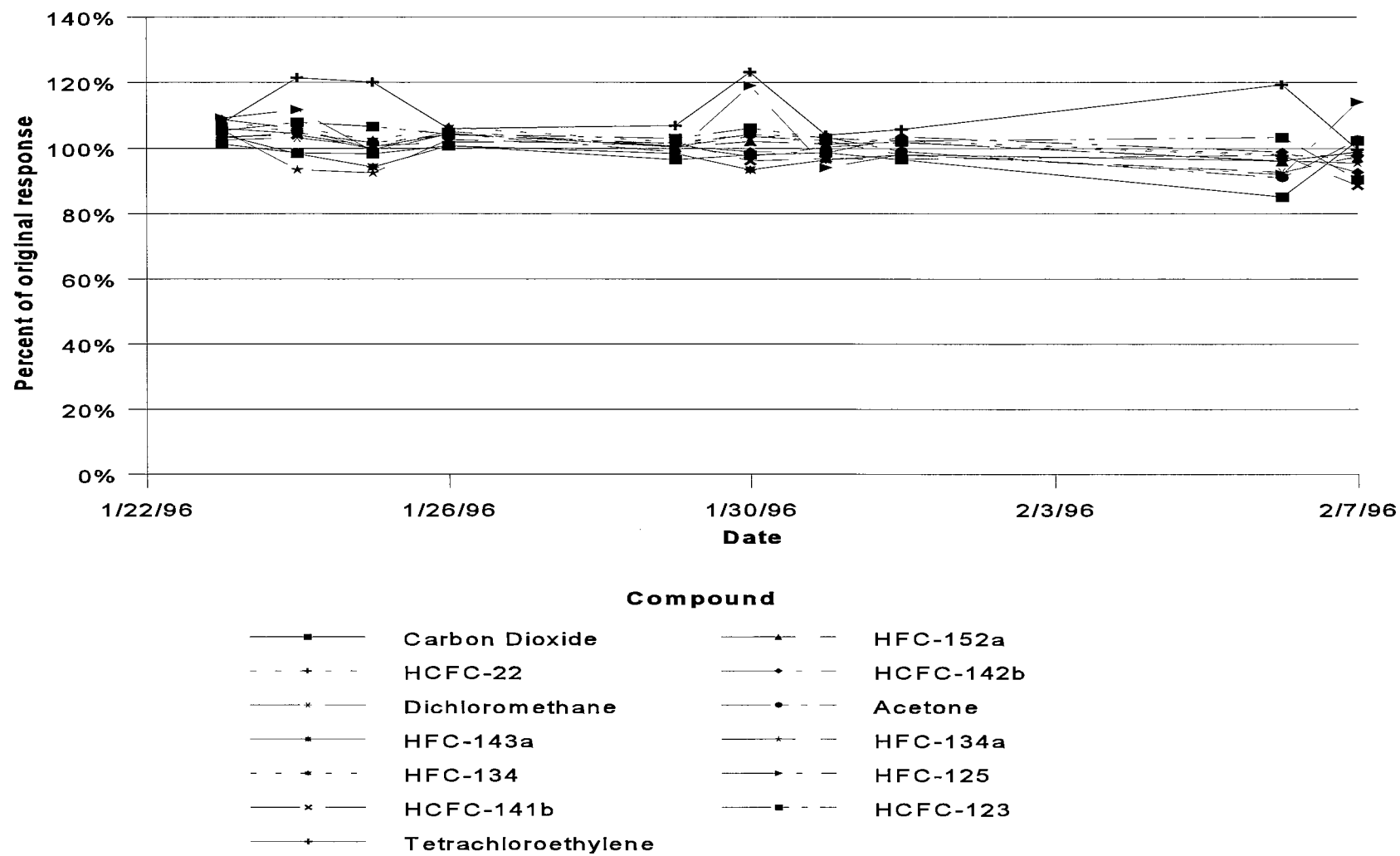


Figure 3. Calibration check data

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APPENDIX A

DETERMINATION OF EXEMPT VOLATILE ORGANIC COMPOUNDS AND CARBON DIOXIDE IN CONSUMER PRODUCTS

DETERMINATION OF EXEMPT VOLATILE ORGANIC COMPOUNDS AND CARBON DIOXIDE IN CONSUMER PRODUCTS

Notice

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.0 APPLICABILITY AND PRINCIPLE

1.1 Applicability

A previously validated method entitled "Determination of Volatile Organic Compounds in Consumer Products" (1) specifies a gravimetric technique for measuring total volatile content and a gas chromatographic technique with thermal conductivity detection for measuring water content. Subtraction of the water content from the total volatile content gives the apparent volatile organic compound content.

The method described here is for measurement of exempt volatile organic compounds (VOCs) and carbon dioxide (CO₂) in consumer products. Exempt VOCs are defined in 40 CFR 51.100. The total nonexempt volatile organic compound content is determined by subtracting the exempt compound content from the apparent volatile organic compound content.

It is assumed that the personnel employing this method have sufficient experience and training to properly evaluate any safety and technical issues that might arise from this method's use. Although some specific hazards have been noted, these do not represent all possible safety problems that might arise. The user should also be familiar with general laboratory procedures and the use of gas chromatography (GC) with mass selective detection (MSD).

This method has been validated for several exempt compounds, which are listed below:

Carbon dioxide

1,1,1-Trifluoroethane (HFC-143a)

Pentafluoroethane (HFC-125)

1,1-Difluoroethane (HFC-152a)

1,1,1,2-Tetrafluoroethane (HFC-134a)
Chlorodifluoromethane (HCFC-22)
1,1,2,2-Tetrafluoroethane (HFC-134)
1-Chloro-1,1-difluoroethane (HCFC-142b)
Dichloromethane
1,1-Dichloro-1-fluoroethane (HCFC-141b)
Acetone
1,1,1-Trifluoro-2,2-dichloroethane (HCFC-123)
Tetrachloroethene.

1.2 Principle

The consumer product sample is placed in a sealed septum vial. This vial is attached to a Tedlar collection bag and dry nitrogen is used to purge the vial while heating at 110°C for 1 hour (Figure 1). Volatile compounds in the sample are transferred to the collection bag by the purge gas. After the purge, the bag contents are analyzed by GC with MSD to determine the weight percent of exempt volatile organic compounds present in the original sample.

1.3 Accuracy and Precision Statement

The accuracy and precision of measuring exempt compounds has been determined by analyzing consumer product samples that were spiked with known amounts of exempt compounds. Recoveries for exempt compounds averaged 95.5 percent, with different compounds ranging from 86 to 107 percent recovery. Precision for spiked samples of the same product were typically less than 5 percent, expressed as the standard deviation of spike recovery. Interlaboratory precision and accuracy for this method have not been evaluated.

2.0 APPARATUS AND MATERIALS

2.1 Analytical Balance

A balance with capacity sufficient to weigh sample vials (approximately 100 g) to a precision of ± 0.0001 g.

2.2 Drying Oven

A forced-draft oven capable of maintaining a temperature of $110 \pm 5^\circ \text{C}$. This oven needs to be suitable for use with flammable vapors, if flammable samples are to be evaluated.

2.3 Sample Vials

A 100-mL disposable glass serum vial with crimp-type cap and septum.

2.4 Sample Shaker (optional but recommended)

A wrist-action shaker to mix the consumer product containers before sampling.

2.5 Transfer Pipets and Spatulas

Pipets and laboratory spatulas suitable for transferring solids and liquid samples to sample vials.

2.6 Thermometer

An oven thermometer capable of measuring 110°C with an accuracy of 1°C .

2.7 Purge Assembly

The sample is collected in a Tedlar bag for analysis by GC/MSD by using the purge assembly illustrated in Figure 1. This apparatus is composed of the following parts:

2.7.1 Hypodermic needles --

Two 15-gauge hypodermic needles of sufficient length for purging vial (approximately 3.5 in. long).

One 22-gauge hypodermic needle of sufficient length for relieving vial pressure (into the bag) before insertion of larger gauge needles.

2.7.2 Rotameter --

A rotameter capable of measuring a purge gas flow of approximately 1,000 mL/min.

2.7.3 Needle valve --

A needle valve to control purge gas flow.

2.7.4 Heat exchanger --

Ten feet of 0.25-in.-OD copper tubing with connecting fittings.

2.7.5 Flexible tubing --

Several feet of 0.25-in.-OD flexible (accordion pleated) Teflon tubing to connect input and output lines to the vial assembly.

2.7.6 Sample tubing --

Teflon tubing (0.25-in.-OD) to connect output hypodermic needle to sample bag.

2.7.7 Viton tubing --

A 2-inch length of 1/4-in.-OD Viton tubing for connecting the small gauge needle and Tedlar bag for relieving sample vial pressure.

2.7.8 Connecting adapter --

Two adapters to connect hypodermic needles to tubing. A Luer-lok to NPT adapter (Millipore part No. XX3002567) connected to an NPT to tubing fitting was used in development of this method; however, other fittings may be used as appropriate.

2.7.9 Support for sample vial --

Although not shown in Figure 1, a support to prevent the vial from turning over in the oven is recommended. A simple support might consist of a laboratory ring stand and clamp.

2.8 Aerosol Sampling Assembly

Aerosol sampling is accomplished using the apparatus shown in Figure 2. An aerosol can adapter (e.g., part No. 8048 from Alltech Associates or equivalent) and a double-ended syringe needle (e.g., part No. 5742 from Becton Dickinson or equivalent) are used to connect the sample vial to the product container. This adapter is designed to fit over the exit tube of an aerosol product (i.e., after the spray nozzle has been removed). Obtaining samples from containers with one-piece exit tube/spray nozzles will require a short length of appropriately sized plastic tubing to connect the can to the adapter.

2.9 Collection Bags

Tedlar bags capable of containing nominally 80 L of purged gas.

2.10 Vacuum Pumps

Two vacuum pumps are required. One pump should be suitable for evacuation of the Tedlar bags and the second pump should be suitable for filling the GC gas sample loop with gas from the collection bag. The sample pump must be installed on the downstream side of the sample loop.

2.11 Nitrogen Purge Gas

WARNING - EXPLOSION HAZARD: The presence of oxygen in the nitrogen purge gas may result in explosion. An explosion may result if air is used as the purge gas.
--

Nitrogen gas free from organic compounds, water, other condensibles, and oxygen. The nitrogen should be at sufficient pressure to permit a flow of approximately 1 L/min through the purge apparatus.

2.12 Gas Chromatograph

A gas chromatograph configured with an MSD, a gas sampling valve fitted with a sampling loop, and a data acquisition system. A 1-mL stainless steel loop was used in method development.

2.13 GC Column

A column that will provide adequate separation of most of the exempt compounds from each other and from other consumer product components. A 30-m, and 0.53-mm-ID PLOT column with GS-Q stationary phase was used successfully in development of this method.

2.14 GC Carrier Gas

Helium, ultra-high-purity grade.

2.15 Internal Standard

1,2,2-trichloro-1,1-difluoroethane (HCFC-122).

2.16 Microliter Syringe

A 100- μ L syringe with needle for use in adding the internal standard to the sample.

2.17 GC Calibration Standards

Compressed gas mixtures consisting of the exempt compounds of interest and the internal standard compound (see Section 2.15) in a nitrogen diluent. The concentration of the exempt compounds should bracket the concentration of exempt compounds expected in the collection bag from consumer product tests.

3.0 SAMPLING PROCEDURE

WARNING - EXPLOSION HAZARD: This procedure uses glass vials under pressure. Wear appropriate eye and face protection.

3.1 Consumer Product Sample Collection

3.1.1 Solids and liquids (nonpressurized products) --

This procedure is to be used for all nonpressurized products including pump aerosol products. Weigh a 100-mL glass vial with cap and septum and record the weight to the nearest 0.0001 g as "A" on the data sheet (Table 2).

Mix the consumer product thoroughly immediately before sampling. Using a spatula or pipet, transfer approximately 0.5 g of sample into the sample vial and weigh along with the designated cap and septum. (Note: Transfer of extremely volatile liquids may be made with a hypodermic syringe and needle through the septum of a sealed sample vial). Record the weight to the nearest 0.0001 g as "B" on the data sheet. Attach the septum (with the Teflon face up) and cap and securely crimp.

Weigh out approximately 100 mg of the internal standard and add through the septum to the sample. Reweigh the sample with the internal standard and record the weight as "C" on the data sheet.

3.1.2 Pressurized aerosol cans --

This procedure is to be used for all pressurized samples including aerosol cans, pressurized foam products, and gaseous products (special adapters may be needed for gaseous products). The sample vials are filled using an aerosol sampling adapter (Figure 2).

Weigh a 100-mL glass vial with cap and septum and record the weight to the nearest 0.0001 g as "A" on the data sheet. Affix the cap and septum (with the Teflon face up) and securely crimp the cap.

Mix the consumer product thoroughly by shaking the container vigorously for 1 to 2 min. Shaking should be performed with a wrist-action shaker (preferred method) or by hand. (NOTE: Aerosol and foam products contain an eductor tube that may be filled with propellant until the can is first used. Press the sample valve to dispense a short [about 1 second] burst of product to clear the eductor tube before continuing the sampling procedure. This step should be needed only upon initial sampling of the product.)

Immediately after shaking the container, insert one end of the double-sided needle into the aerosol sampling adapter (Figure 2). Remove the spray nozzle from the aerosol or foam container and connect the sampling adapter to the exit tube of the valve (i.e., in the place of the spray nozzle). (NOTE: Some containers may have a one-piece spray nozzle and exit tube. These containers require addition of an exit tube to the sampling adapter before the adapter can be connected to the container.)

With the product container oriented to dispense product (upright for products whose instructions specify upright use, inverted for products that specify inverted use), insert the other end of the needle through the septum on the sample vial. Depress the adapter, opening the container valve for a sufficient time to allow about approximately 0.5 g of sample into the vial. While maintaining a firm seal between the adapter and the exit tube, release pressure on the adapter to close the container's valve. Quickly pull the adapter needle out of the vial septum, so as to lose as little propellant as possible. (NOTE: A hissing sound will result as some gas escapes from the adapter assembly.) Reweigh the pressurized vial and sample and record the weight to the nearest 0.0001 g as "B" on the data sheet.

<p>WARNING: Glass vials under pressure may explode. Handle the pressurized sample vial carefully.</p>
--

Add approximately 100 mg of the internal standard through the septum. Reweigh the vial and internal standard and record the weight as "C" on the data sheet.

Clean the adapter with a suitable solvent between each set of products. Disassemble and allow the adapter to dry completely before reuse.

3.2 Purging Volatiles Into the Collection Bag

Attach one end of a 2-inch length of Viton tubing to the inlet of the empty gas collection bag. Attach the other end to a 22-gauge hypodermic needle. Pierce the sample vial with the needle and allow the propellant to transfer to the bag for approximately 5 minutes. Seal the bag inlet and then remove the needle from the sample vial. Remove the needle from the Viton tubing.

Next, preheat the oven to 110° C. Connect the collection bag to the output of the purge assembly and open the collection bag inlet. Open the oven door and, using a quick motion, insert the output hypodermic needle through the sample vial's septum. Insert the purge gas (input) hypodermic needle through the septum. Start the gas flow at approximately 1 L/minute. Record the time that the purge gas was started as "D" on the data sheet.

Adjust the input needle depth in the vial so that it is about 0.25 inch above the bottom of the sample vial. Adjust the output needle depth in the vial so that it is at least 1 inch above the end of the input needle. Place the vial in the oven and close the door. Allow the vial to be purged at 110° C for 1 hour.

At the end of the purge time, stop the purge gas flow and record the time as "E" on the data sheet. Seal the collection bag inlet, remove the vial from the oven and remove the needles from the vial. Allow the vial to cool before discarding.

4.0 ANALYSIS OF BAG CONTENTS TO MEASURE EXEMPT VOC

Details of instrument operation will vary with the individual apparatus and are not specified in this method.

4.1 Chromatographic Conditions

A column and chromatographic conditions should be selected to adequately separate the exempt compounds from each other and from other product components. The following conditions have proven suitable in tests of this method and may be used as a starting point.

4.1.1 GC column --

Thirty-meter, 0.53-mm-ID fused silica PLOT (porous layer open tubular) column with GS-Q stationary phase.

4.1.2 Column flow rate --

Set the flow rate to 4.0 mL/min. An effluent splitter must be used to limit the column effluent flow which passes into the MSD interface to 1 mL/minute.

4.1.3 Sample loop --

Stainless steel loop with nominal volume of 1 mL.

4.1.4 Sampling valve temperature --

Set the sampling valve temperature to 150° C.

4.1.5 Oven temperature program --

40° C for 1 minute, 5° C per minute to 150° C, 20° C per minute to 220°C, hold for 4.5 minutes.

4.1.6 Detector temperature --

Set the detector temperature at 280° C.

4.2 MSD Operating Conditions

Operating mode: scan

Low mass: 29

High mass: 200

Threshold: 250

A/D samples: 16

4.3 GC Calibration Procedure

Obtain three calibration standards containing the internal standard and exempt compounds of interest at a range of concentrations that includes the expected bag concentrations. Analyze each standard in triplicate or until no trend in component response is observed. Introduction of gas samples from compressed gas calibration standards is performed without the sample pump operating.

Determine one target ion for each exempt compound for use in quantitation. For closely eluting compounds, select a unique target ion for each compound. Determine one or more qualifier ions for each exempt compound for use in compound identification.

Prepare a quantitation database using an internal standard calibration and include retention times, target ions, qualifier ions, and compound amounts. Instead of entering compound amounts in parts per million (ppm), enter the product of ppm concentration and gram molecular weight. This will enable quantitation of the exempt compounds in the samples on a weight basis.

Using appropriate data analysis software, create a multilevel calibration using the three analyzed calibration standards.

A summary of exempt compounds, retention times, target ions, and qualifier ions used in development of this method is presented in Table 1. This information is to be used only as a guide in method implementation. The specific retention times may vary for other GC columns and operating conditions.

4.4 Collection Bag Analysis

Before injection of a gas sample from a collection bag for analysis, enter into the data system the amount (in grams) of internal standard that was loaded into the sample vial. Also enter the weight of product sample (in grams) being tested. This will enable reporting of the exempt compound amount directly in weight percent

Connect the sample bag to the gas sampling valve inlet tube and use the sampling pump to purge the loop at approximately 30 mL/min for 2 minutes. Stop the sample flow through the loop and inject the sample.

4.5 Quality Control Procedures

Analyze a calibration standard and blank after every eight sample injections. Before analysis, enter the product of the ppm concentration and gram molecular weight for the internal standard. The reported component amounts (ppm x gram molecular weight) should not vary by more than 10 percent from a previous value on the same day or more than 20 percent between days. If the response factor is outside of these limits, then recalibrate using all three calibration standards.

TABLE 1. EXEMPT COMPOUND ANALYSIS GUIDELINES

Compound	Retention time, minutes	Target ion mass	Qualifier ion mass
Carbon dioxide	3.26	44	
1,1,1-Trifluoroethane (HFC-143a)	7.21	69	65
Pentafluoroethane (HFC-125)	8.48	51	101
1,1-Difluoroethane (HFC-152a)	9.70	51	65
1,1,1,2-Tetrafluoroethane (HFC-134a)	9.84	69	83
Chlorodifluoromethane (HCFC-22)	10.57	51	67
1,1,2,2-Tetrafluoroethane (HFC-134)	12	51	83
1-Chloro-1,1-difluoroethane (HCFC-142b)	14.82	65	45
Dichloromethane	22.06	49	84
1,1-Dichloro-1-fluoroethane (HCFC-141b)	22.58	81	83
Acetone	22.69	43	58
1,1,1-Trifluoro-2,2-dichloroethane (HCFC-123)	23.53	85	69
1,2,2-Trichloro-1,1-difluoroethane ^a (HCFC-122)	27.16	83	133
Tetrachloroethene	29.76	85	69

^aInternal standard compound.

5.0 CALCULATIONS

5.1 Sample Weight

The sample weight (SW) is calculated as:

$$SW = B - A$$

where

B = weight of vial, cap, septum, and sample

A = weight of vial, cap, and septum.

5.2 Internal Standard Weight

The internal standard weight (ISTDW) is calculated as:

$$ISTDW = C - B$$

where

C = weight of vial, cap, septum, sample, and internal standard.

B = weight of vial, cap, septum, and sample.

5.3 Internal Standard Calibration

Because commercial GC-MSD systems include data analysis software that performs the necessary calculations to establish a multilevel calibration based on an internal standard, the calculations shown below are given only to describe the approach.

- Calculate an amount ratio and response ratio for each level and compound in the database.

$$\text{Amount ratio} = \text{Amount}_q / \text{Amount}_{\text{ISTD}}$$

$$\text{Response ratio} = \text{Resp}_q / \text{Resp}_{\text{ISTD}}$$

- Perform a linear regression analysis of Amount ratio versus Response ratio.

5.4 **Exempt VOC Weight Percent**

Because all commercial GC-MSD systems include data analysis software that performs the necessary calculations to determine the exempt VOC weight percent based on an internal standard, the calculations shown below are given only to describe the approach.

- Calculate a response ratio from GC-MSD analysis for each exempt compound.

$$\text{Response ratio} = \text{Resp}_q / \text{Resp}_{\text{ISTD}}$$

- Calculate an amount ratio for each compound based on the linear regression equation determined during calibration.
- Multiply the amount ratio by the known amount of internal standard that was added to the sample to determine the amount of exempt compound.
- Calculate the weight percent for each exempt compound by dividing the component amount (in grams) by the sample amount (in grams) and multiplying by 100.
- Calculate the total exempt VOC weight percent by summing the individual component weight percents.

6.0 **GLOSSARY**

CO ₂	Carbon dioxide
GC	Gas chromatograph, gas chromatography, or gas chromatographic
NPT	National Pipe Thread - used to specify the size and threads associated with a pipe fitting
OD	Outside diameter (of tubing, etc.)
VOC	Volatile organic compound
MSD	Mass selective detector.

7.0 **REFERENCES**

1. E.E. Rickman, Jr., G.B. Howe, and R.K.M. Jayanty, "Interlaboratory Study of a Test Method for Measuring Total Volatile Organic Compound Content of Consumer Products," U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, EPA-600/R-95-163(NTIS PB96-121652), November 1995, Appendix A.

TABLE 2. DATA SHEET FOR SAMPLE COLLECTION

Weighings		
A)	Weight of empty sample vial, septum and cap (g).	
B)	Weight of vial, septum, cap, and sample (g).	
C)	Weight of vial, septum, cap, internal standard, and sample (g).	
D)	Time purge started	
E)	Time purge ended	
Calculations		
G)	Sample weight (g) = B - A	
H)	Weight of internal standard (g) = C - B	

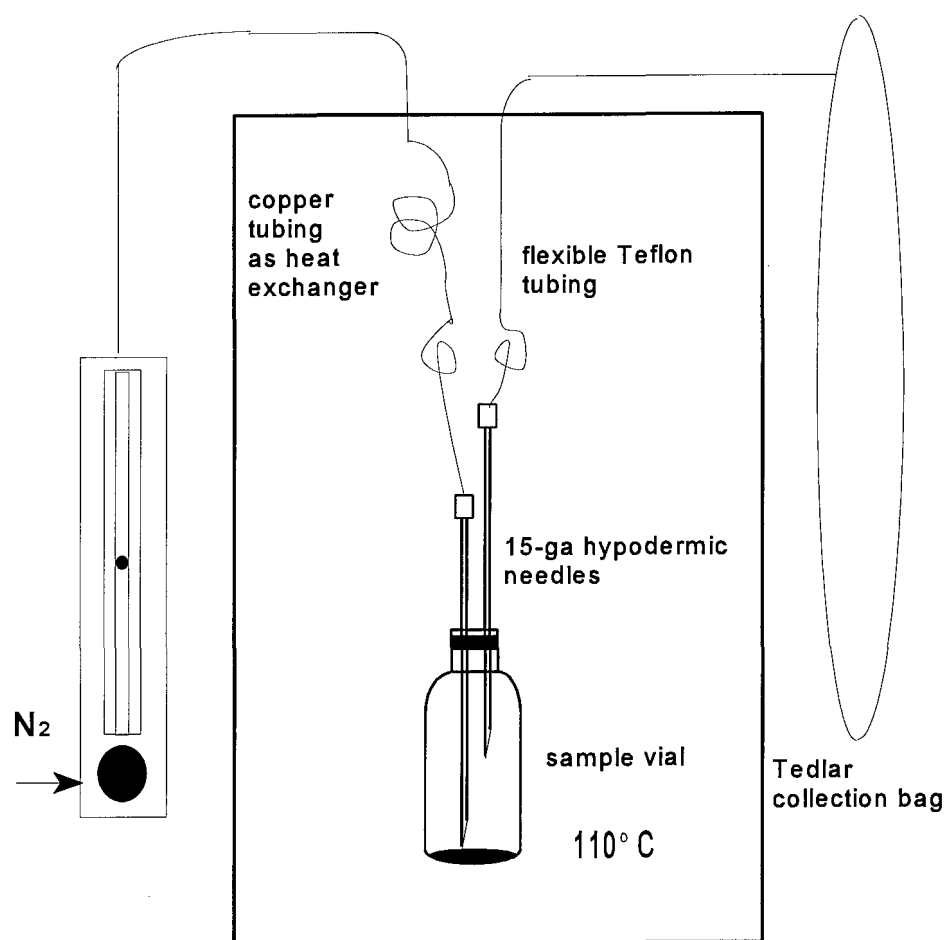


Figure 1. Sample purge and volatiles collection assembly.

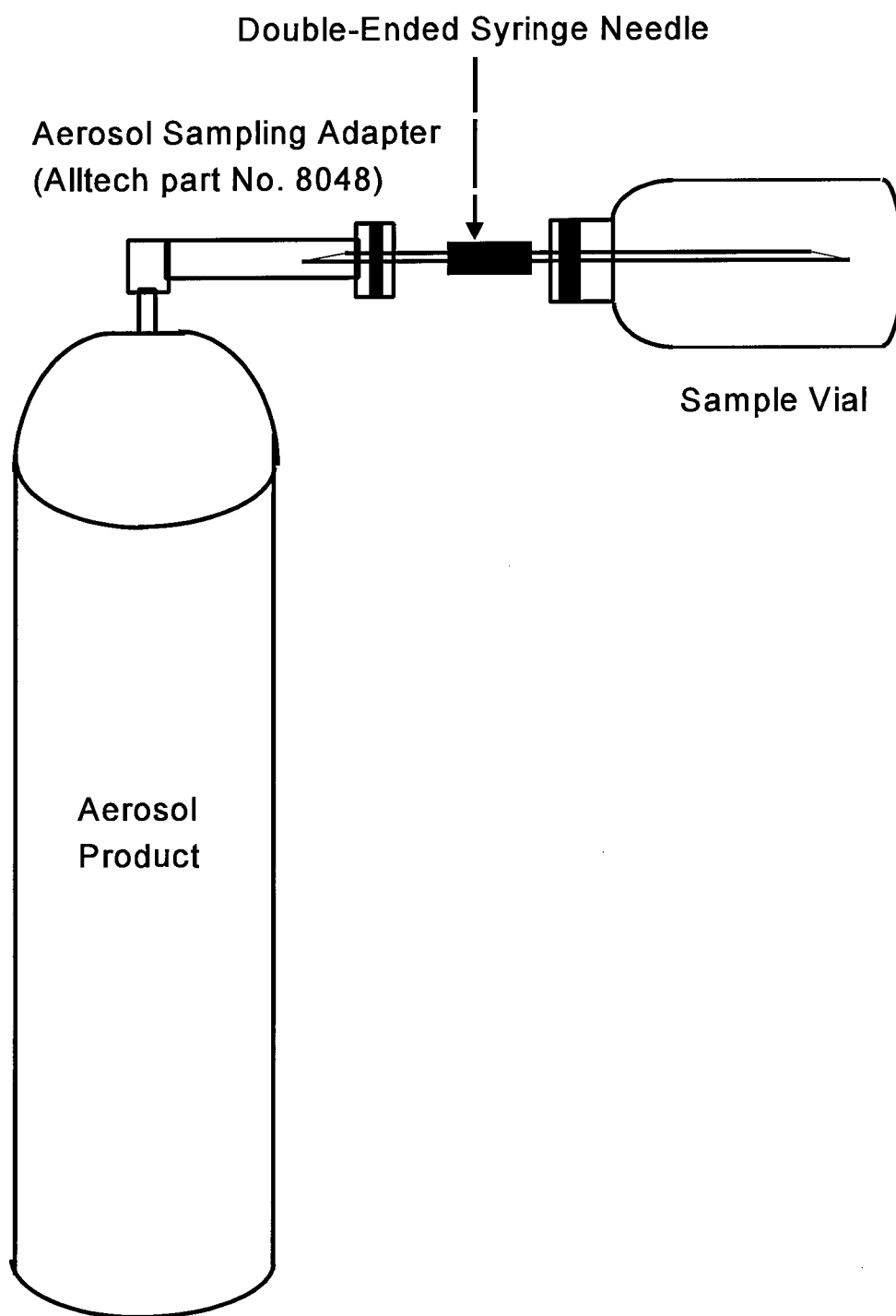


Figure 2. Aerosol sampling adapter.

Method Validation for Measurement of Selected Semivolatile Phenols in Dust and Soil

by

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Contract 68-D4-0023
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16. ABSTRACT

The objectives of this study were to evaluate and validate analytical methods for analysis of persistent organic pollutants (POP) in dust/soil and to obtain concentration profiles for the target POP in dust/soil samples from the homes of 13 low-income families.

The analytical method for determining p-pentylphenol, p-octylphenol, nonylphenols, and bisphenol-A consisted of sequential extractions of the dust/soil with 5 % acetic acid in methanol (MeOH), 100 % dichloromethane (DCM), and 5 % acetic acid in water; liquid-liquid partitioning the resulting extract with water; and analyzing the concentrated DCM extract by gas chromatography/mass spectrometry (GC/MS). With this method, quantitative recoveries (> 80 %) were obtained for the target phenols from the spiked soil samples. The estimated detection limits for the target phenols are 0.001 ppm.

The analytical method for determining 2-acetylaminofluorene (2AF) and 3-amino-9-ethylcarbazole (AEC) consisted of extracting dust/soil with 30 % water in MeOH at pH 10, and analyzing the extract by liquid chromatography with tandem mass spectrometry (LC/MS/MS). Recoveries for 2AF and AEC from the spiked soil samples ranged from 98 to 110 % and from 39 to 110 %, respectively. The estimated detection limits were 0.001 ppm for 2AF and 0.005 ppm for AEC.

Sums of the concentrations of target phenols ranged from 1.94 to 14.8 ppm in house dust samples, from 0.047 to 1.51 ppm in entryway dust samples, and from 0.021 to 0.265 ppm in pathway soil samples. The observed concentrations trend was house dust > entryway dust > pathway soil. There were no detectable amounts of 2AF and AEC in any dust/soil samples. Other compound classes found in dust/soil samples from one household were alkanes, aliphatic alcohols, fatty acids, fatty acid esters, and phthalates.

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FOREWORD

The mission of the National Exposure Research Laboratory (NERL) is to provide scientific understanding, information and assessment tools that will quantify and reduce the uncertainty in EPA's exposure and risk assessments for environmental stressors. These stressors include chemicals, biologicals, radiation, and changes in climate, land use, and water use. The Laboratory's primary function is to measure, characterize, and predict human and ecological exposure to pollutants. Exposure assessments are integral elements in the risk assessment process used to identify populations and ecological resources at risk. The EPA relies increasingly on the results of quantitative risk assessments to support regulations, particularly of chemicals in the environment. In addition, decisions on research priorities are influenced increasingly by comparative risk assessment analysis. The utility of the risk-based approach, however, depends on accurate exposure information. Thus, the mission of NERL is to enhance the Agency's capability for evaluating exposure of both humans and ecosystems from a holistic perspective.

The National Exposure Research Laboratory focuses on four major research areas: predictive exposure modeling, exposure assessment, monitoring methods, and environmental characterization. Underlying the entire research and technical support program of the NERL is its continuing development of state-of-the-art modeling, monitoring, and quality assurance methods to assure the conduct of defensible exposure assessments with known certainty. The research program supports its traditional clients -- Regional Offices, Regulatory Program Officer, ORD Offices, and Research Committees -- and ORD's Core Research Program in the areas of health risk assessment, ecological risk assessment, and risk reduction.

Human exposure to multimedia contaminants, including semivolatile organic compounds (SVOC) and nonvolatile organic compounds (NVOC) is an area of concern to EPA because of the possible carcinogenicity of these compounds. These compounds are present in a variety of microenvironments. The efforts described in this report provide an important contribution to our capability to measure and evaluate human exposure to toxic pollutants.

Gary J. Foley
Director
National Exposure Research Laboratory

ABSTRACT

The objectives of this study were to evaluate and validate analytical methods for analysis of persistent organic pollutants (POP) in dust/soil and to obtain concentration profiles for the target POP in dust/soil samples from the homes of 13 low-income families.

The analytical method for determining p-pentylphenol, p-octylphenol, nonylphenols, and bisphenol-A consisted of sequential extractions of the dust/soil with 5 % acetic acid in methanol (MeOH), 100 % dichloromethane (DCM), and 5 % acetic acid in water; liquid-liquid partitioning the resulting extract with water; and analyzing the concentrated DCM extract by gas chromatography/mass spectrometry (GC/MS). With this method, quantitative recoveries (> 80 %) were obtained for the target phenols from the spiked soil samples. The estimated detection limits for the target phenols are 0.001 ppm.

The analytical method for determining 2-acetylaminofluorene (2AF) and 3-amino-9-ethylcarbazole (AEC) consisted of extracting dust/soil with 30 % water in MeOH at pH 10, and analyzing the extract by liquid chromatography with tandem mass spectrometry (LC/MS/MS). Recoveries for 2AF and AEC from the spiked soil samples ranged from 98 to 110 % and from 39 to 110 %, respectively. The estimated detection limits were 0.001 ppm for 2AF and 0.005 ppm for AEC.

Concentrations of the sums of target phenols ranged from 1.94 to 14.8 ppm in house dust samples, from 0.047 to 1.51 ppm in entryway dust samples, and from 0.021 to 0.265 ppm in pathway soil samples. The observed concentrations trend was house dust > entryway dust > pathway soil. There were no detectable amounts of 2AF and AEC in any dust/soil samples. Other compound classes found in dust/soil samples from one household were alkanes, aliphatic alcohols, fatty acids, fatty acid esters, and phthalates.

This report is submitted in fulfillment of Contract Number 68-D4-0023, Work Assignment No. 1-08, Task 1 by Battelle under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1996 to September 1996, and work was completed as of September 1996.

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Chapter 1

Introduction

Persistent organic pollutants (POP), including polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and other semivolatile organic compounds (SVOC), nonvolatile organic compounds (NVOC) and some metals (M) are found in air, house dust, soil, food, and water (1-5). Many of these compounds are putative endocrine disrupters and are known mutagens or probable human carcinogens. Humans can be exposed to these pollutants through inhalation, dietary and non-dietary ingestion, and dermal adsorption, and adverse health effects have been linked to such exposures. The non-dietary pathway resulting from ingestion of soil and dust may be more important for young children because of their play activities.

Children of low-income families, or families living in urban environments may have increased exposure to POP and M. This may arise because of their proximity to areas of high traffic, industrial activities, or lifestyle aspects. Under Cooperative Agreement CR822073, a preliminary study to develop and evaluate field methods to estimate children's exposure to PAH was conducted. The results from the first two years of this study indicated that the loadings of house dust in several urban low-income households are more than one order of magnitude higher than those of middle-income families (4,6). Such high dust loadings can increase children's exposure to POP and M through the non-dietary pathway.

Many POP were not included in the Cooperative Agreement study. It is desirable to include these pollutants in the evaluation of the field exposure methods targeted at low-income families. Under Task 1 of this Work Assignment, two analytical techniques, gas

chromatography/mass spectrometry (GC/MS) and liquid chromatography with tandem mass spectrometry (LC/MS/MS) were evaluated for analysis of target POP that include putative endocrine disrupters. The GC/MS method was evaluated and validated for analysis of target phenols. The LC/MS/MS method was evaluated for analysis of all target POP, but only validated for the analysis of 2-acetylaminofluorene (2AF) and 3-amino-9-ethylcarbazole (AEC). House dust, entryway dust and pathway soil samples collected from 9 homes under the Cooperative Agreement study (6) and from 4 homes under Contract Number 68-D4-0023, Work Assignment 02 (7) were analyzed for target phenols, 2AF, and AEC using the validated analytical methods.

The objective of this study was to validate analytical methods for analysis of target POP in dust and soil, and to determine target POP in 39 dust/soil samples collected from the homes of 13 low-income families using the validated analytical methods.

The following tasks were carried out in this study:

- (1) Conduct GC/MS method evaluation/validation for analysis of p-pentylphenol, p-octylphenol, nonylphenols, and bis-phenol-A.
- (2) Conduct LC/MS/MS method evaluation/validation for 2-acetylaminofluorene, 3-amino-9-ethylcarbazole, 2,4-dinitrotoluene, anthraquinone, vinclozolin, and phenols
- (3) Analyze 39 samples and one method blank for target POP using the appropriate validated methods
- (4) Prepare a final report on the results of the study.

Chapter 2

Conclusions

An analytical method for the determination of phenols in dust and soil samples was validated. This method consisted of (1) sequential sonication of the dust/soil sample with 5% acetic acid in methanol, 100% dichloromethane (DCM), and 5% acetic acid in water, (2) liquid-liquid partitioning the resulting extract with water, and (3) GC/MS analysis of the concentrated DCM extract. With this method, quantitative recoveries (> 80 percent) of the phenols were obtained from the spiked soil samples and the estimated detection limits are 0.001 ppm of target phenols in dust/soil.

An analytical method consisting of extracting the sample with 30% water in methanol at pH 10 and analyzing the extract by LC/MS/MS was validated for the determination of 2-acetylaminofluorene (2AF) and 3-amino-9-ethylcarbazole (AEC) in dust/soil. The recoveries of spiked 2AF ranged from 98 to 110 percent in the soil samples. The recoveries of spiked AEC ranged from 39 to 110 percent and showed more variations than the recoveries of 2AF. The estimated detection limits for this method were 0.001 ppm for 2AF and 0.005 ppm for AEC. The LC/MS/MS method was evaluated but not validated for the analysis of other target POP because appropriate MS/MS conditions could not be established or inadequate detection limit.

The most abundant target phenols were nonylphenols and the least abundant one was, in general, p-pentylphenol in the dust/soil samples. The concentrations of target phenols ranged from 0.043 to 3.56 ppm in house dust, from < 0.001 to 0.974 ppm in entryway dust, and from < 0.001 to 0.204 ppm in pathway soil. There were no detectible levels of 2AF and

AEC in these dust and soil samples. Other compound classes found in the dust/soil samples from one household were alkanes, aliphatic alcohols, fatty acids, fatty acid esters, and phthalates.

The general concentration trend observed for phenols in these samples was: house dust > entryway dust > pathway soil. Similar relationships among dust/soil samples were also observed for PAH, alkyl PAH and phthalates from other EPA studies (4,6,7). This finding suggests that many persistent organic pollutants are enhanced in the house dust medium. Therefore human exposure to POP, especially that of young children, through non-dietary ingestion or dermal contact of house dust should not be overlooked.

Chapter 3

Recommendations

Levels of many persistent organic pollutants (POP) including nonylphenols, bisphenol-A, PAH, and phthalates found in house dust were much higher than those found in entryway dust and pathway soil. House dust is an easily accessible environmental matrix as opposed to air and food and can provide relevant information on human exposure to POP. Several important issues remain to be addressed to assess human exposure to POP due to house dust and soil. In future studies, we recommend:

- (1) Conducting a pilot field study to determine concentration profiles of POP that are potential endocrine disrupters by broad scan analysis, and to evaluate/validate a cost-effective method that can determine POP of different compound classes in house dust samples.
- (2) Conducting a pilot field study to determine concentration profiles of POP that are potential endocrine disrupters in multimedia samples; to determine the effects of geographic location and the social economic status of the households on POP exposures, and to determine if house dust can be used as a marker sample matrix for other sample media for human indoor exposure to POP.

Chapter 4

Experimental Procedures

Analytical Method for Phenols

Two extraction methods were evaluated for removing phenols from the dust and soil sample matrices. Initially, the soil samples were spiked with known amounts of target phenols and extracted with dichloromethane (DCM) in a sonication bath. This approach did not provide satisfactory recoveries. Another extraction method was then evaluated. For spike recovery, known amounts of target phenols were spiked into each aliquot of the soil samples. The spiked sample was extracted sequentially with 10 mL of 5% acetic acid in methanol, 10 mL of DCM, and 10 mL of 5% acetic acid in distilled water, in a sonication bath for 15 min of each type of solvent. The resulting extracts were combined and transferred to a separatory funnel. The DCM extract was transferred to another separatory funnel and washed with 20 mL of distilled water. The DCM extract was dried with sodium sulfate and concentrated to 2 mL for subsequent GC/MS analysis.

Thirty-nine dust/soil samples collected previously (4,6) from thirteen low-income households were analyzed for target phenols. The house dust samples were collected using the High Volume Small Surface Sampler (HVS3, Cascade Stack Sampling Systems, Bend, OR) in designated areas where the child's greatest play activity occurred. The entryway dust samples were collected from a doormat at the primary entrance of the house. The walkway soil samples were collected from a primary walkway into the home. Aliquots of the 39 dust/soil sample and one method blank were prepared by the above method except that the target phenols were not spiked into the samples prior to extraction. Known amounts of internal

standard, phenanthrene-d₁₀, were added to each concentrated DCM extract prior to GC/MS analysis. An aliquot of each DCM extract was also removed for residue weight measurement.

The extracts were analyzed by 70 eV electron impact (EI) gas chromatography/mass spectrometry (GC/MS). A Finnigan TSQ-45 GC/MS/MS instrument, operated in the GC/MS mode, was used. Data acquisition and processing were performed with an INCOS 2300 data system. The GC column was a DB-5 fused silica capillary column (60m x 0.25 mm, 0.25 μ m film thickness, J&W), and the column outlet is located in the MS ion source. Helium was used as the GC carrier gas. Following injection, the GC column was held at 70 °C for 2 min and temperature-programmed to 120°C at 20°C/min and then to 300°C at 8°C/min. The MS was operated in the selected ion monitoring (SIM) mode. Masses monitored were the molecular ions and their associated characteristic fragment ions. Identification of the target compounds was based on their GC retention times relative to those of the internal standard phenanthrene-d₁₀. Quantification of target compounds is based on comparisons of the respective integrated ion current responses of the target ions to those of the corresponding internal standards using average response factors of the target compounds generated from standard calibrations. The dust/soil sample extracts from household A were analyzed by GC/MS in full mass scan mode to identify major compounds tentatively. The MS was set to scan from m/e 45 to 450 am μ at 1 sec/scan. Tentative identification of the compounds was accomplished by manual interpretation of background-corrected spectra together with an on-line computerized library search. The on-line library was the most currently available EPA/NIH mass spectral data base, containing 42,197 unique reference spectra.

LC/MS/MS Method Evaluation

The following compounds were evaluated for analysis by LC/MS/MS using the Sciex TAGA 6000E with an atmospheric pressure chemical ionization (APCI) source: 2-acetylaminofluorene (2AF), 3-amino-9-ethylcarbazole (AEC), 2,4-dinitrotoluene (DNT), anthraquinone, vinclozolin, p-pentylphenol, p-octylphenol, nonylphenols, and bisphenol-A.

Each compound was analyzed in the single MS mode to identify the precursor ion formed by the APCI process. Once the precursor ion was identified, a fragment ion spectrum (MS/MS) was obtained by introducing energy to the collision cell. Standards of the above chemicals were introduced into the TAGA ion source as either vapors or liquids. Standards with sufficient vapor pressure were introduced by placing an open vial of the standard at the inlet of the TAGA sampling stream. For nonvolatile standards, solutions were prepared at known concentration levels. Aliquots of the standard solutions were introduced into the ion source through a Battelle-developed vapor jet system (8). Characteristic fragment ions for each standard were selected from the MS/MS spectrum, for use in the selected ion monitoring (SIM) mode. A series of standard solutions was analyzed by LC/MS/MS to establish calibration curves and to estimate detection limits. The initial evaluation results showed that the LC/MS/MS technique can provide adequate detection sensitivity for two of the above standards, namely 2AF and AEC. These two compounds were selected for further analysis in dust/soil samples.

Analytical Method for 2-Acetylaminofluorene and 3-Amino-9-ethylcarbazole

Extraction recovery experiments were conducted for 2AF and AEC. Two extraction methods were evaluated for removal of the AEC and 2AF from the dust/soil samples. The first method, sonication with methanol (MeOH), did not provide satisfactory recoveries for AEC. The extraction solvent was then changed to 30% water in MeOH at pH 10. A spike recovery study was conducted, where known amounts of the two target compounds were spiked into aliquots of selected soil samples. The spiked sample was extracted with 5 mL aliquots of 30% water in MeOH at pH 10 in a sonication bath for 15 min. This step was repeated four times. The resulting extracts were combined, filtered, and concentrated to 3 mL for LC/MS/MS analysis.

The LC gradient elution conditions for the analysis of the standards and sample extracts are:

Column:	Supelco LC-304 Guard Column
Flow Rate:	1.2 mL/min
Sample Loop:	50 μ L
Gradient Elution Scheme:	
0 - 2 min	100% H ₂ O
2 - 8 min	100% H ₂ O/0% MeOH \rightarrow 25% H ₂ O/75% MeOH
8 - 10 min	25% H ₂ O/75% MeOH
10 - 15 min	25% H ₂ O/75% MeOH \rightarrow 100% H ₂ O

The mass spectrometer was operated in the MS/MS (SIM) mode. Vaporized eluent from the LC was introduced into the APCI ion source, where the samples were ionized using a corona discharge. Protonated precursor ions were selected with the first quadrupole mass analyzer (thus eliminating all other possible interference ions). The precursor ions were then focused into the collision cell where they were fragmented at a collision energy of 35 volts (E_{lab}) with argon as the collision gas with a target thickness of approximately 350×10^{12} molecules/cm². Selected fragment ions from the isolated precursor ions were passed through the second MS and were detected by an electron multiplier. For 2AF, two precursor/fragment ion transitions were monitored, namely m/z 224/182 and 224/43. For AEC, three precursor/fragment ion transitions were monitored: m/z 211/182, 211/194, and 211/179. Identification of the target compounds was based on their correct LC retention times and their correct relative responses for each of the precursor/fragment ion transitions when compared with those from the standards calibrations. Quantitation of the target compounds was based on comparisons of the respective integrated ion current responses of the target compounds in the sample extract to those in the standard solutions.

Chapter 5

Results and Discussion

GC/MS Analysis of Dust and Soil Samples

The analytical method for analyzing target phenols consisted of sequentially extracting the samples by sonication with 5% acetic acid in methanol, DCM, and 5% acetic acid in water, followed by liquid-liquid partitioning, and analyzing the concentrated DCM by GC/MS.

Table 5.1 summarizes the recovery data for spiked phenols from the soil samples at three spiked levels. Quantitative recoveries (> 80 percent) of the spiked phenols were obtained. The recoveries ranged from 90 to 104 percent at 5 ppm spiked levels, from 84 to 101 percent at 0.2 ppm spiked levels and from 84 to 110 percent at 0.1 ppm spiked levels. The precision for the phenols for the triplicate spiked samples was within 13 percent (relative standard deviation).

Table 5.1. Recoveries of Phenols from Spiked Soil Samples

Compound	Recovery, % ^(a)		
	H	M	L
p-Pentylphenol	90	100 ± 8.7	87
p-Octylphenol	91	84 ± 2.6	100
Nonylphenols	104	91 ± 4.9	110
Bisphenol-A	98	101 ± 13	84

- (a) H denotes a single soil sample at 5 ppm spiked level
M denotes triplicate soil samples at 0.2 ppm spiked level
L denotes a single soil sample at 0.1 ppm spiked level.

The concentrations of phenols measured in the house dust, entryway dust, and pathway soil samples are summarized in Table 5.2. The data for individual samples are given in Appendix A. The reported concentrations were corrected for the background levels from the method blank and expressed in units of ppm ($\mu\text{g/g}$). The results of target phenols found in the method blank are given in Appendix B. Only trace amounts of phenols were found in the method blank. There are three major nonylphenol isomers present in the nonylphenol standard solutions, because only technical grade nonylphenols are available. The other target phenol standards are specific isomers, which are p-pentylphenol, p-octylphenol, and bisphenol-A. Note that one of the p-pentylphenol isomers was reported and this isomer eluted about 10 scans later than the p-pentylphenol from the GC column. This compound was estimated using the same response factor as p-pentylphenol.

Among the measured phenols, the most abundant phenols found were nonylphenols. The least abundant phenols were in general, p-pentylphenol and its isomer. The concentrations of phenols ranged from 0.043 ppm of p-pentylphenol to 11.1 ppm of p-octylphenol in house dust samples. Relative lower concentrations were found in entryway dust samples and ranged from < 0.001 ppm of p-pentylphenol to 0.974 ppm of nonylphenols. The concentrations of phenols in pathway soil samples were from < 0.001 ppm of p-octylphenol to 0.204 ppm of nonylphenols. The relative concentration trend within individual households was house dust $>$ entryway $>$ pathway soil.

Among the target phenols, nonylphenols and bisphenol-A are potential endocrine disrupters. Figures 5.1 and 5.2 show the concentration profiles of nonylphenols and bisphenol-A in the dust/soil samples. Levels of nonylphenols found in house dust samples were greater than 1 ppm, while those levels found in entryway dust and pathway soil sample are less than 1 ppm. The concentrations of nonylphenols ranged from 1.24 to 3.56 ppm in house dust, from 0.024 to 0.974 ppm in entryway dust, and from 0.015 to 0.204 ppm in pathway soil. The concentrations of bisphenol-A are lower than those of nonylphenols in the

Table 5.2. Summary of Concentrations (ppm) of Phenols in House Dust, Entryway Dust, and Pathway Soil

Compound	House Dust			Entryway Dust			Pathway Soil		
	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
p-Pentylphenol	0.120	0.043	0.088	0.073	<0.001	0.018	0.005	0.001	0.002
Pentylphenol isomer	0.270	0.060	0.129	0.085	0.004	0.019	0.011	0.003	0.004
p-Octylphenol	11.1	0.158	1.49	0.311	<0.001	0.059	0.019	<0.001	0.003
Nonylphenols	3.56	1.24	2.30	0.974	0.024	0.300	0.204	0.015	0.072
Bisphenol-A	3.50	0.322	1.19	0.335	0.019	0.120	0.036	<0.001	0.011
Sum of phenols	14.8	1.94	5.19	1.51	0.047	0.517	0.265	0.021	0.092

Nonylphenols In House Dust, Entryway Dust, And Pathway Soil

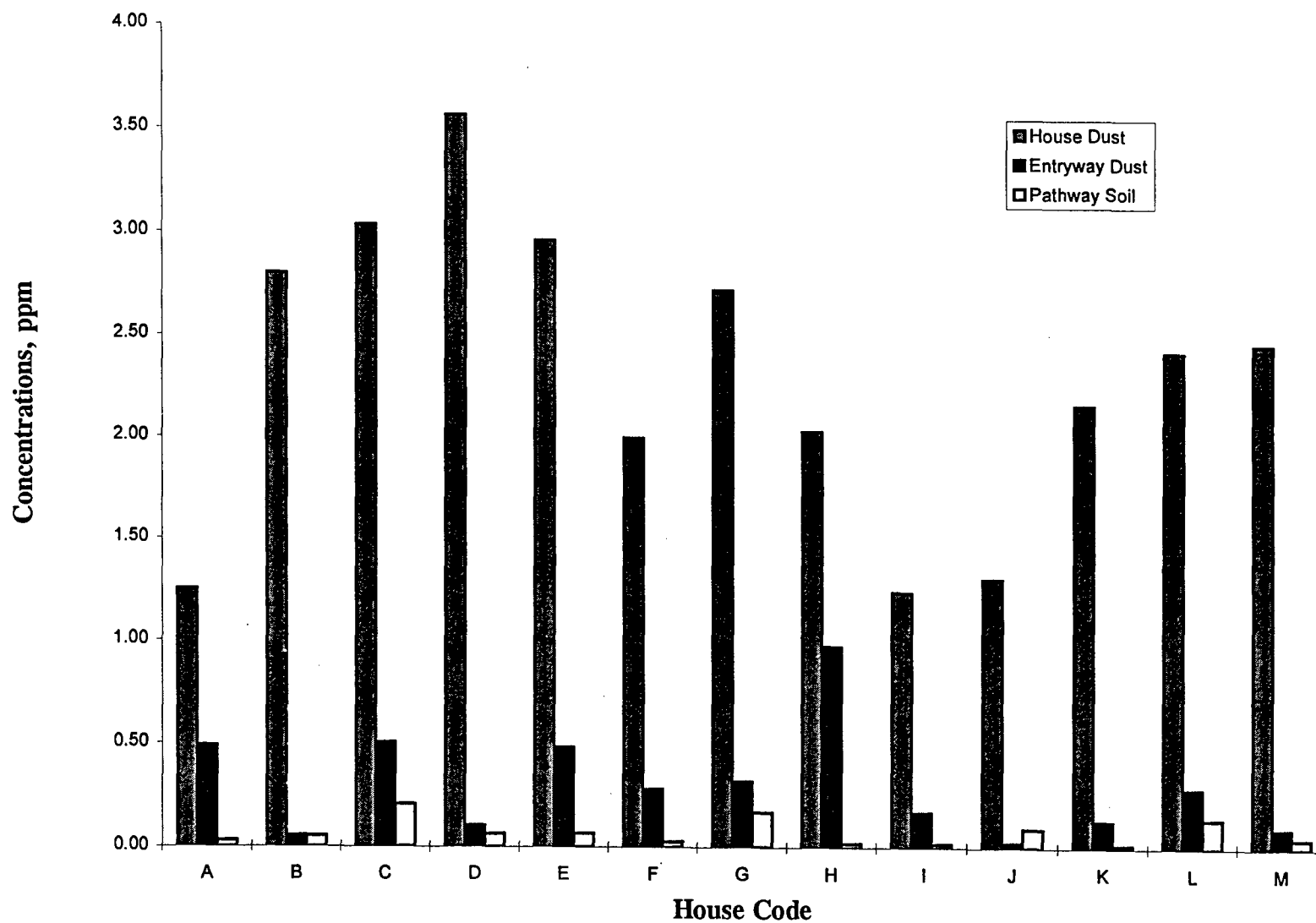


Figure 5.1. Concentrations of nonylphenols in house dust, entryway dust, and pathway soil samples.

Bisphenol-A In House Dust, Entryway Dust, And Pathway Soil

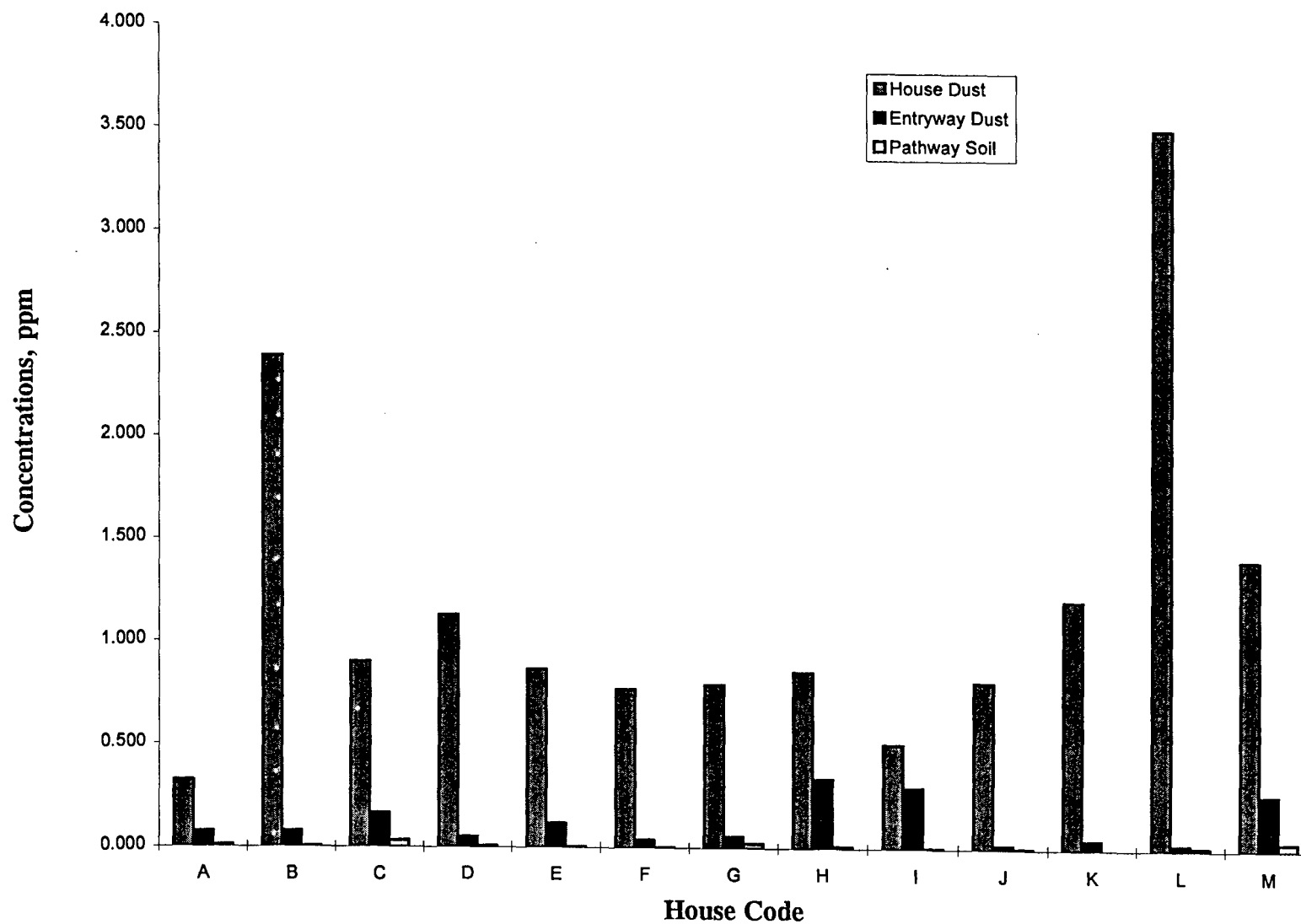


Figure 5.2. Concentrations of bisphenol-A in house dust, entryway dust, and pathway soil samples.

dust/soil samples. The levels of bisphenol-A ranged from 0.322 to 3.50 ppm in house dust, from 0.019 to 0.335 ppm in entryway dust, and from <0.001 to 0.036 ppm in pathway soil.

Sample extracts of dust/soil samples from Household A were analyzed by GC/MS in the full mass scan mode to determine the major components present. The compounds tentatively identified in these dust and soil samples are summarized in Tables 5.3 through 5.5. Total ion current chromatograms of the samples are shown in Figures 5.3 through 5.5. The major compound classes found in house dust were alkanes, fatty acids, fatty acid esters, phthalates, and aliphatic alcohols. Similar components including alkanes, fatty acid esters and phthalates were found in entryway dust at lower levels. Pathway soil exhibited the smallest number of compounds, among them aliphatic alcohols, alkanes, fatty acid esters, and phthalates.

LC/MS/MS Analysis of Dust and Soil Samples

In order for a compound to be ionized by APCI, its gas phase basicity (for positive ion mode) or gas phase acidity (for negative ion mode) should be greater than the gas phase basicity/acidity of water. For this reason, the MS/MS spectra of anthraquinone, phenols, and vinclozoline could not be obtained. Of all the compounds evaluated, MS/MS spectra were obtained for only three compounds, namely 2-acetylaminofluorene (2AF), 3-amino-9-ethyl carbazole (AEC), and 2,4-dinitrotoluene (DNT). The 2AF and AEC spectra were obtained under positive ion APCI conditions and the DNT spectrum was obtained by negative ion APCI. Standard solutions of 2AF, AEC and DNT were prepared in the range from 1 ng/mL to 1200 ng/mL (1 ppb to 12 ppm) and analyzed using LC/MS/MS. The estimated detection limits for 2AF, AEC and DNT were 1 ng/mL, 5 ng/mL and 500 ng/mL, respectively. Since an adequate overall method detection limit for DNT could not be obtained, only 2AF and AEC were selected as target analytes for the spike recovery study.

The analytical method for the analysis of 2AF and AEC consisted of extracting the sample with 30 % water in MeOH at pH 10, concentrating the extract, and analyzing the concentrated extract by LC/MS/MS. Table 5.6 summarizes the recovery data for the spiked 2AF and AEC from the soil samples. As shown in Table 5.6, quantitative recoveries were obtained for 2AF

Table 5.3. Compounds Tentatively Identified in House Dust from Household A

Scan Number	Tentative Identification
412	Aliphatic compound
428	Hexanoic acid
438	Aliphatic alkene
459	C5-alkyl furan
470	Aliphatic alcohol
489	Chlorine containing compound
522	Heptanoic acid
569	Aliphatic alcohol
618	Octanoic acid
645	Butoxyethoxy ethanol
657	Alkane (C ₁₂ H ₂₆)
665	Aliphatic alcohol
709	Nonanoic acid
748	Alkane (C ₁₃ H ₂₈)
772	Phthalate
795	Decanoic acid
817	Fatty acid ester
833	Alkane (C ₁₄ H ₃₀)
858	C2-naphthalene
881	Alkane
913	Alkane (C ₁₅ H ₃₂)
919	Aliphatic alcohol
949	Alkane
956	Tridecanoic acid
962	Alkane
968	Alkane
986	Phthalate
990	Alkane (C ₁₆ H ₃₄)
1023	Alkane
1036	Alkane
1062	Alkane (C ₁₇ H ₃₆)
1100	Tetradecanoic acid
1130	Alkane (C ₁₈ H ₃₈)
1148	Internal standard (phenanthrene-d ₁₀)
1175	Phthalate
1195	Alkane (C ₁₉ H ₄₀)
1232	Hexadecanoic acid
1257	Alkane (C ₂₀ H ₄₂)

Table 5.3. Continued

Scan Number	Tentative Identification
1310	Aliphatic alcohol
1316	Alkane (C ₂₁ H ₄₄)
1339	Aliphatic alcohol
1351	Octadecanoic acid
1373	Alkane (C ₂₂ H ₄₆)
1406	Phthalate
1427	Alkane (C ₂₃ H ₄₈)
1446	Alkane
1465	Phthalate
1481	Alkane (C ₂₄ H ₅₀)
1538	Alkane C ₂₅ H ₅₂)
1562	Phthalate
1597	Alkane (C ₂₆ H ₅₄)
1619	Phthalate
1645	Phthalate
1663	Alkane (C ₂₇ H ₅₆)
1692	Phthalate
1737	Alkane (C ₂₈ H ₅₈)
1756	Phthalate
1782	Phthalate
1823	Alkane (C ₂₉ H ₆₀)
1850	Unknown
1885	Unknown
1924	Alkane (C ₃₀ H ₆₂)
2046	Alkane (C ₃₁ H ₆₄)
2129	Mixture containing chrolostenol isomer
2193	Alkane (C ₃₂ H ₆₆)
2372	Alkane (C ₃₃ H ₆₈)
2512	Aliphatic alcohol
2593	Alkane (C ₃₄ H ₇₀)
2831	Alkane
2954	Fatty acid ester
2964	Aliphatic alcohol

Table 5.4. Compounds Tentatively Identified in Entryway Dust from Household A

Scan Number	Tentative Identification
395	Hexanoic acid
410	Benzaldehyde
440	C3-alkylbenzene
476	Methylphenol MW 108
547	Aliphatic alcohol
600	Octanoic acid
631	Butoxyethoxyethanol
645	Alkane (C ₁₂ H ₂₆)
700	Nonanoic acid
714	Alkane
742	Alkane (C ₁₃ H ₂₈)
786	Alkane
796	Fatty acid ester
805	Alkane
809	Alkane
814	Fatty acid ester
831	Alkane (C ₁₄ H ₃₀)
871	Alkane
881	Alkane
885	Alkane
890	Alkane
897	Alkane
914	Alkane (C ₁₅ H ₃₂)
919	Alkene
949	Alkane
954	Alkane
963	Alkane
968	Alkane
980	Nitrogen containing compound
986	Phthalate
991	Alkane (C ₁₆ H ₃₄)
1025	Alkane
1032	Alkane
1037	Alkene
1042	Aliphatic alcohol
1150	Internal standard (phenanthrene-d ₁₀)
1063	Alkane (C ₁₇ H ₃₆)
1127	Nitrogen containing compound
1132	Alkane (C ₁₈ H ₃₈)

Table 5.4. Continued

Scan Number	Tentative Identification
1137	Alkane
1177	Phthalate
1197	Alkane (C ₁₉ H ₄₀)
1238	Phthalate
1259	Alkane (C ₂₀ H ₄₂)
1279	Hydroxy methoxy benzoicacid methyl ester
1312	Aliphatic alcohol
1319	Alkane (C ₂₁ H ₄₄)
1341	Chlorine containing compound
1375	Alkane (C ₂₂ H ₄₆)
1408	Phthalate
1429	Alkane (C ₂₃ H ₄₈)
1467	Phthalate
1477	Fatty acid ester
1483	Alkane (C ₂₄ H ₅₀)
1539	Alkane (C ₂₅ H ₅₂)
1563	Phthalate
1599	Alkane (C ₂₆ H ₅₄)
1665	Alkane (C ₂₇ H ₅₆)
1725	Aliphatic alcohol
1739	Alkane (C ₂₈ H ₅₈)
1825	Alkane (C ₂₉ H ₆₀)
1927	Alkane (C ₃₀ H ₆₂)
2049	Alkane (C ₃₁ H ₆₄)
2132	Mixture containing chrolostenol isomer
2197	Alkane (C ₃₂ H ₆₆)

Table 5.5. Compounds Tentatively Identified in the Pathway Soil from Household A

Scan Number	Tentative Identification
369	Ethoxyethanol
431	Aliphatic compound
461	C3-alkyl benzene
581	Silicone
612	Silicone
649	Aliphatic alcohol
801	Fatty acid ester
818	Fatty acid ester
828	Alkene
889	Fatty acid ester
915	Alkane (C ₁₅ H ₃₂)
986	Aliphatic alcohol
1063	Alkane (C ₁₇ H ₃₆)
1128	Aliphatic alcohol
1151	Internal standard (phenanthrene-d ₁₀)
1238	Phthalate
1466	Phthalate
1477	Fatty acid ester
1539	Alkane (C ₂₇ H ₅₂)
1563	Phthalate
1665	Alkane (C ₂₇ H ₅₆)
1739	Alkane (C ₂₈ H ₅₈)
1825	Alkane (C ₂₉ H ₆₀)
2049	Alkane (C ₃₀ H ₆₄)

RIC
09/15/96 13:03:00 DATA: 96091653 #1 SCANS 1 TO 3000
SAMPLE: A-HD-X NONDILUTED FULL SCAN CALI: 960916ACL03 #5
CONDS.: 70(2)-290/10
RANGE: G 1.3121 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

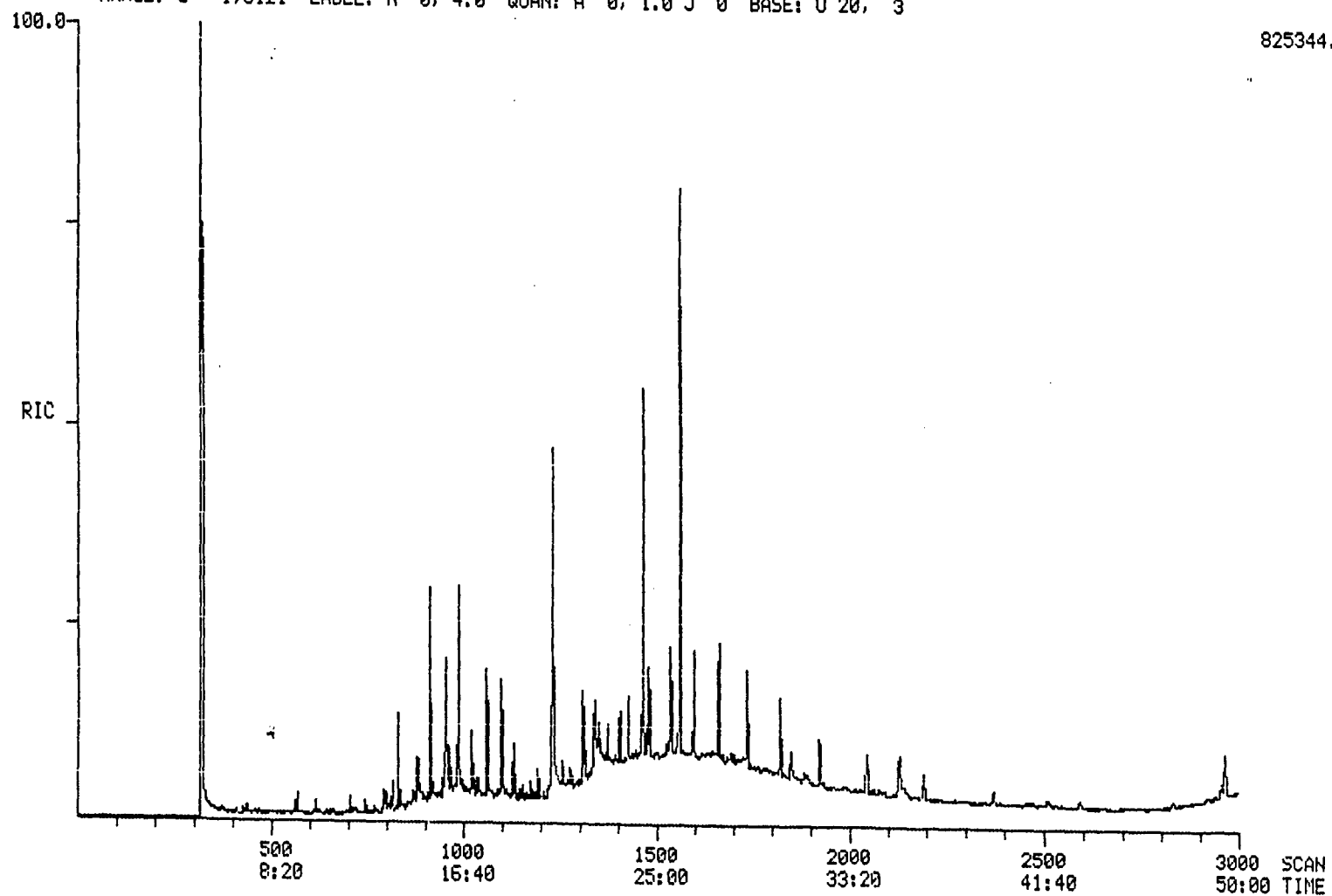


Figure 5.3. Total ion currents chromatogram of house dust sample from Household A.

RIC
09/15/96 13:59:00 DATA: 96091654 #1 SCANS 1 TO 2800
SAMPLE: A-ES-X NONDILUTED FULL SCAN CALI: 960916ACLQ3 #5
CONDOS.: 70(2)-290/10
RANGE: G 1.3100 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

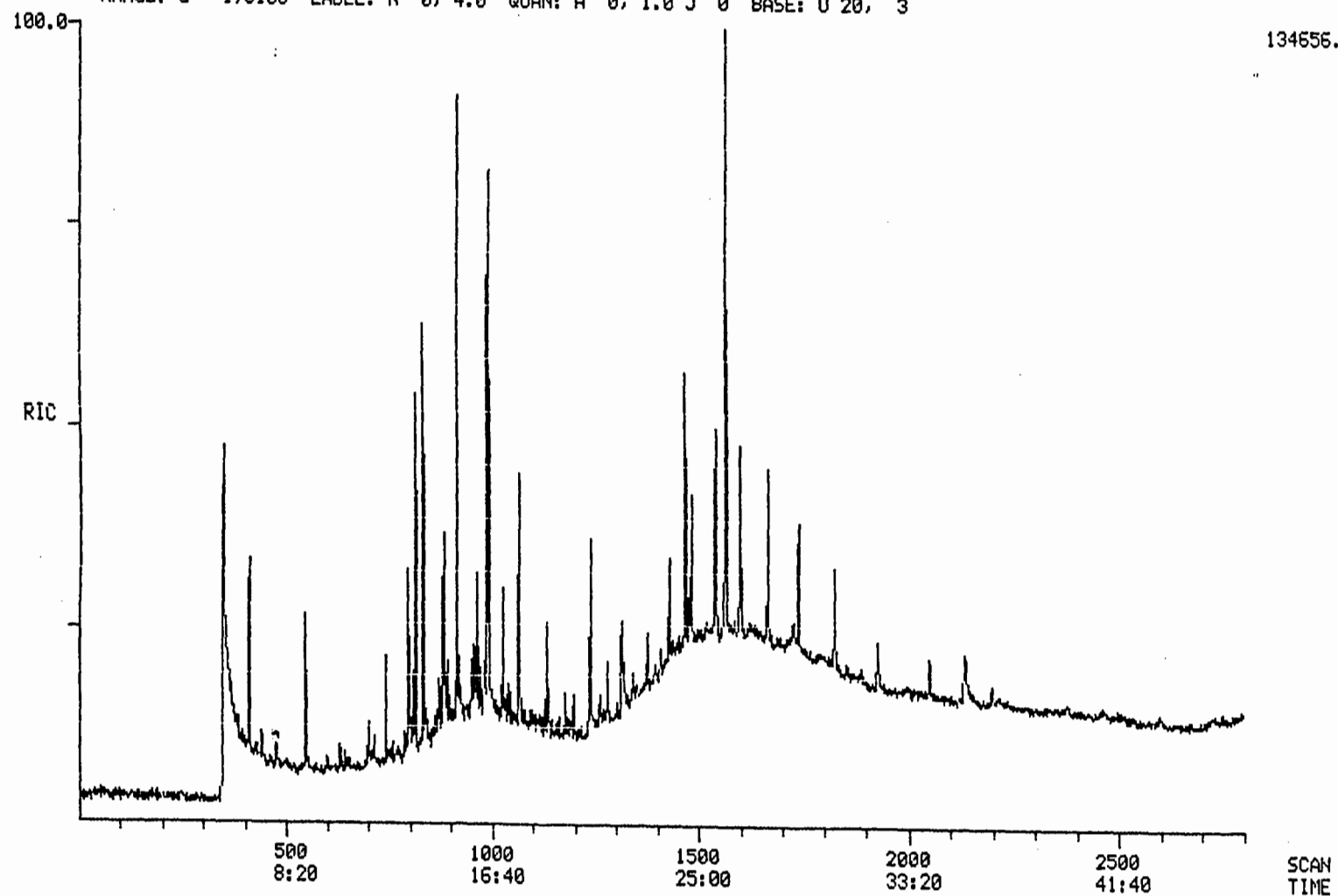


Figure 5.4. Total ion currents chromatogram of entryway dust sample from Household A.

RIC DATA: 96091655 #1 SCANS 1 TO 2800
09/15/96 15:02:00 CALI: 960916ACL03 #5
SAMPLE: A-PS-X NONDILUTED FULL SCAN
CONDS.: 70(2)-290/10
RANGE: G 1.3100 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

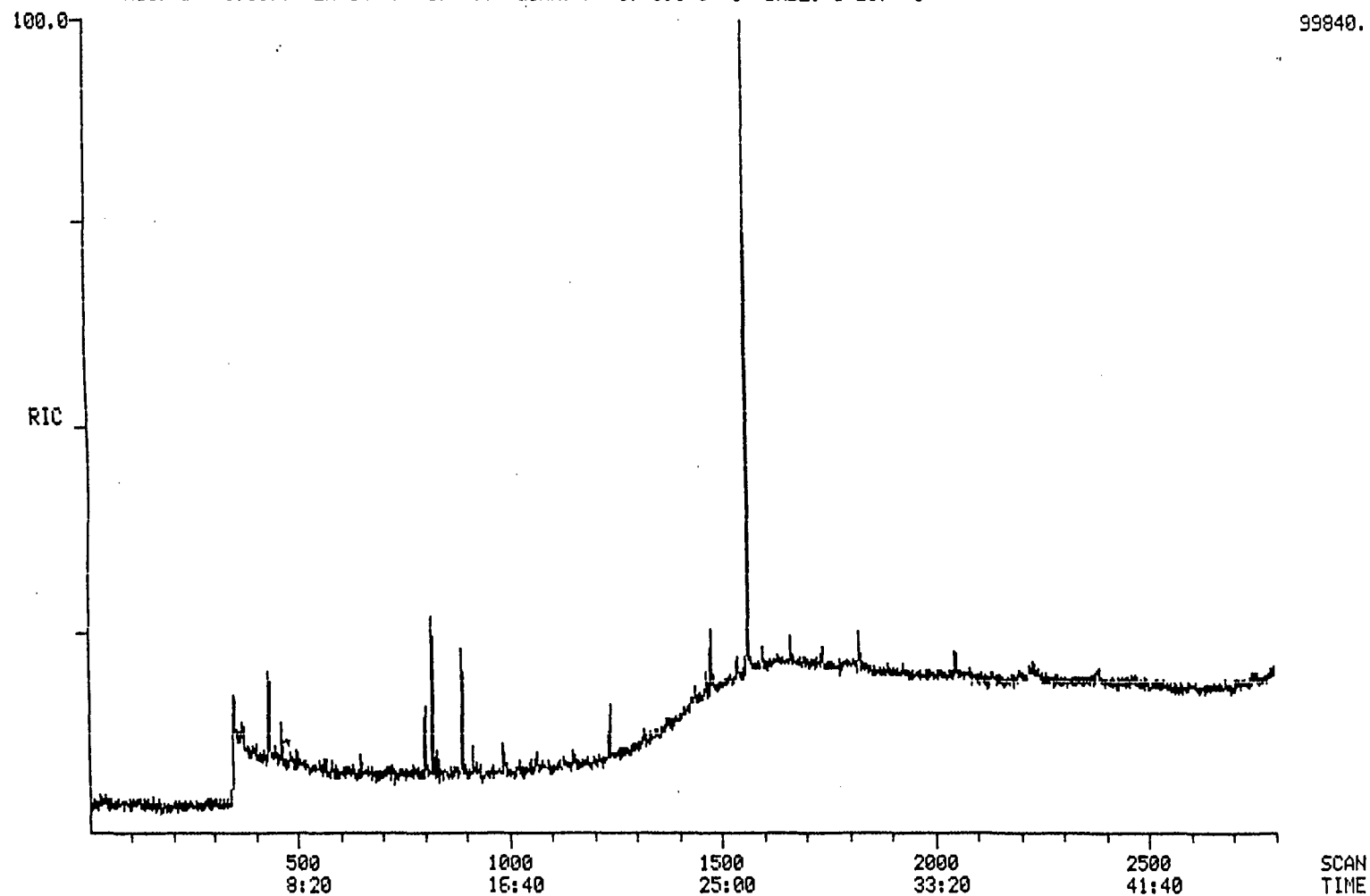


Figure 5.5. Total ion currents chromatogram of pathway soil sample from Household A.

from the spiked soil samples and ranged from 98 to 110 percent. The recoveries for AEC in the spiked soil samples ranged from 39 to 110 percent. The precision for determining AEC was not as good as that for 2AF. The estimated detection limits for 2AF and AEC were 0.001 ppm and 0.005 ppm, respectively. The 2AF and AEC were not detected in any of the dust/soil samples or in the method blank.

Table 5.6. Recoveries of AEC and 2AF from Spiked Soil Samples

Compound	Spiked Level, ppm	Recovery, %
AEC	2.0	100
	2.0	98
	1.0	98
	1.0	110
2AF	0.2	63
	0.2	110
	0.1	39
	0.1	64

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Appendix A. Phenol Data in House Dust, Entryway Dust, and Pathway Soil Samples

Compound	A-HD-X ppm	B-HD-X ppm	C-HD-X ppm	D-HD-X ppm	E-HD-X ppm	F-HD-X ppm	G-HD-X ppm	H-HD-X ppm	I-HD-X ppm	J-HD-X ppm	K-HD-X ppm	L-HD-X ppm	M-HD-X ppm
p-Pentylphenol	0.043	0.099	0.055	0.120	0.090	0.098	0.110	0.102	0.064	0.065	0.106	0.114	0.081
p-Pentylphenol isomer	0.072	0.270	0.113	0.181	0.169	0.101	0.128	0.180	0.087	0.060	0.183	0.061	0.072
p-Octylphenol	0.251	2.142	1.238	0.488	0.271	0.420	11.050	0.584	0.158	0.311	0.741	0.996	0.658
Nonylphenols	1.249	2.798	3.032	3.563	2.956	1.995	2.720	2.028	1.241	1.307	2.162	2.423	2.463
Bisphenol-A	0.322	2.389	0.899	1.127	0.865	0.769	0.793	0.854	0.505	0.807	1.206	3.505	1.409
sum of phenols	1.937	7.699	5.336	5.479	4.352	3.382	14.802	3.748	2.055	2.550	4.399	7.099	4.682
Compound	A-ES-X ppm	B-ES-X ppm	C-ES-X ppm	D-ES-X ppm	E-ES-X ppm	F-ES-X ppm	G-ES-X ppm	H-ES-X ppm	I-ES-X ppm	J-ES-X ppm	K-ES-X ppm	L-ES-X ppm	M-ES-X ppm
p-Pentylphenol	0.073	0.005	0.023	0.005	0.027	0.006	0.006	0.059	0.014	<0.001	0.011	0.006	0.001
p-Pentylphenol isomer	0.028	0.009	0.023	0.008	0.015	0.017	0.016	0.085	0.018	0.004	0.010	0.013	0.007
p-Octylphenol	0.072	0.021	0.311	0.006	0.239	0.009	0.004	0.060	0.005	<0.001	0.009	0.016	0.013
Nonylphenols	0.488	0.054	0.503	0.103	0.483	0.282	0.317	0.974	0.169	0.024	0.128	0.286	0.094
Bisphenol-A	0.075	0.077	0.164	0.050	0.117	0.038	0.056	0.335	0.294	0.019	0.045	0.025	0.265
sum of phenols	0.735	0.165	1.023	0.173	0.880	0.351	0.399	1.513	0.499	0.047	0.204	0.346	0.381
Compound	A-PS-X ppm	B-PS-X ppm	C-PS-X ppm	D-PS-X ppm	E-PS-X ppm	F-PS-X ppm	G-PS-X ppm	H-PS-X ppm	I-PS-X ppm	J-PS-X ppm	K-PS-X ppm	L-PS-X ppm	M-PS-X ppm
p-Pentylphenol	0.002	0.003	0.004	0.003	0.002	0.004	0.003	0.001	0.001	0.005	0.002	0.001	0.002
p-Pentylphenol isomer	0.004	0.004	0.006	0.006	0.004	0.003	0.004	0.011	0.003	0.003	0.004	0.003	0.003
p-Octylphenol	<0.001	0.001	0.019	0.002	<0.001	<0.001	0.002	<0.001	<0.001	0.004	<0.001	0.004	0.002
Nonylphenols	0.029	0.051	0.204	0.063	0.065	0.027	0.169	0.020	0.018	0.090	0.015	0.139	0.044
Bisphenol-A	0.008	0.003	0.032	0.007	0.004	0.002	0.023	0.009	0.002	0.003	<0.001	0.014	0.036
Sum of phenols	0.043	0.062	0.265	0.079	0.075	0.036	0.201	0.041	0.024	0.105	0.021	0.161	0.086

Sample Code: The first letter indicates the household; the next two letters indicate the sampled medium, HD = house dust, ES = entryway dust, and PS = pathway soil. The letter X indicates that the samples were obtained in April 1996 under cooperative agreement CR822073.

Appendix B. Levels of Target Phenols in the Method Blank

Compound	Total ng	ppm
p-Pentylphenol	1.263	0.001
p-Pentylphenol isomer	0.727	0.001
p-Octylphenol	7.045	0.007
Nonylphenols	13.489	0.013
Bisphenol-A	1.194	0.001
Sum of phenols	23.718	0.024