

**FINAL REPORT**

**APPLICABILITY OF CANISTER SAMPLING FOR HAZARDOUS AIR POLLUTANTS**

by

**Thomas J. Kelly and Michael W. Holdren  
BATTELLE  
505 King Avenue  
Columbus, Ohio 43201**

**March 1994**

**Contract Number 68-D0-0007  
Work Assignment No. 45, Subtask 4**

**Project Officer  
William McClenny  
Atmospheric Research and Exposure Assessment Laboratory  
U.S. Environmental Protection Agency  
MD-44  
Research Triangle Park, North Carolina 27711**

## ABSTRACT

This paper evaluates the applicability of sampling with evacuated canisters for volatile organic compounds listed among the 189 Hazardous Air Pollutants (HAPs) in the 1990 U.S. Clean Air Act Amendments. Nearly 100 HAPs have sufficient vapor pressure to be considered volatile compounds. Of those volatile organic HAPs, 52 have been tested previously for stability during storage in canisters. The published HAP stability studies are reviewed, illustrating that for nearly all of the 52 HAPs tested, canisters are an effective air sampling approach. However, the published stability studies used a variety of canister types and test procedures, and generally considered only a few compounds in a very small set of canisters. A comparison of chemical and physical properties of the HAPs has also been conducted, to evaluate the applicability of canister sampling for other HAPs, for which canister stability testing has never been conducted. Of 45 volatile HAPs never tested in canisters, this comparison identifies 9 for which canister sampling should be effective, and 17 for which canisters are not likely to be effective. For the other 19 HAPs, no clear decision can be reached on the likely applicability of canister sampling.

## INTRODUCTION

The collection of whole air samples in canisters for determination of volatile organic compounds (VOCs) in the atmosphere is common practice. Passivated stainless steel canisters are used in a variety of air monitoring programs, and form the basis for the U.S. Environmental Protection Agency's Compendium Method TO-14 (Winberry *et al.*, 1988; McClenny *et al.*, 1991a). The stability of volatile alkanes, alkenes, aromatic hydrocarbons, and their halogenated derivatives in canisters is well established (McClenny *et al.* 1991a, and references therein).

Recently attention has been focused toward volatile organic compounds containing oxygen, nitrogen, and sulfur. Such compounds are often collectively called polar VOCs (PVOCs). In part, this attention results from the recognition that atmospheric reactions of VOCs often produce PVOCs as products, and that PVOCs in turn may be quite reactive. Thus understanding of atmospheric chemical processes requires measurement of PVOCs. In addition, the potential toxicity of PVOCs in air has led to regulatory efforts directed toward them. For example, Title III of the 1990 Clean Air Act Amendments (CAAA) defines as hazardous air pollutants (HAPs) a list of 189 diverse chemicals and chemical groups, and mandates control and reduction of the human health risks from these compounds in ambient air (Clean Air Act Amendments, 1990). Nearly 100 of the HAPs are sufficiently volatile (i.e., vapor pressure  $>0.1$  mm Hg at room temperature) to be considered VOCs (Kelly, *et al.*, 1994). Some of those HAPs are common aromatic and halogenated VOCs, but over half of the volatile HAPS can be classified as PVOCs.

To meet the requirements of the CAAA, measurements of the diverse HAPs are needed. This requirement has prompted surveys of the existing and potential measurement methods for the HAPs (McClenny *et al.*, 1991b; Keith and Walker, 1992; Kelly *et al.*, 1994). The application of canister sampling to volatile HAPs would seem a natural extension of the existing methods for VOCs, and indeed the methods surveys noted above consider that approach. However, reactivity and water solubility, more than polarity, are the defining characteristics of most PVOCs. As a result, the stability of the PVOCs during storage of sampled air in canisters is not assured. Several experimental studies have tested the stability

of PVOCs and VOCs in canisters (e.g., Westberg *et al.*, 1981; Gholson *et al.*, 1990; Merrill and Zapkin, 1991; Pate *et al.*, 1992; Oliver, 1993; Kelly *et al.* 1993), and stability in canisters has also been evaluated from a theoretical standpoint (Coutant and McClenny, 1991; Coutant, 1993). These studies particularly indicate the importance of humidity in reducing the loss of volatile compounds to the canister walls.

The purpose of the present paper is to summarize published information on the stability of volatile HAPs, both VOCs and PVOCs, during storage in canisters. A comparison of chemical and physical property data then identifies additional HAPs for which canisters should be an effective atmospheric sampling approach. That same comparison also indicates volatile HAPS for which canisters are not likely to be useful.

## REVIEW OF STABILITY STUDIES

In this section several experimental studies are summarized, with the intent of identifying HAPs for which canister stability has been demonstrated, or alternatively shown to be inadequate. This review concentrates on the stability of VOCs and PVOCs designated as HAPs by the 1990 Clean Air Act Amendments. In summarizing the experimental studies, guidance has been drawn from theoretical considerations (Coutant and McClenny, 1991; Coutant, 1993) and from anecdotal evidence as to the parameters that may affect the stability of VOCs and PVOCs stored in canisters. As a result, indication is provided (when available from the original references) on the material, age, or history of the canisters used; the degree of humidification of the stored samples; the number of compounds in the stored test mixtures; the duration of the test; canister pressure during storage; and the concentrations of the compounds tested. Canister stability testing has also been conducted by researchers other than those cited here. However, the results of those tests have not been compiled or were unavailable for this review (R. Rasmussen, Oregon Graduate Institute; L. Ogle, Radian Corp.; personal communications, 1993).

**Westberg *et al.*, (1981):** In this study 6 L Summa polished stainless steel canisters were used to assess the stability of a variety of VOCs and PVOCs. In one test four canisters

were spiked with low concentrations of four terpene compounds during pressurization with ambient air. The canisters were analyzed for a total of 28 VOCs (including 8 HAPs), 24 of which were native in the ambient air and 4 of which were the spiked terpenes. Analysis was conducted at weekly intervals for comparison to an initial analysis at the time of filling the canisters. The initial concentrations were 1 to 30 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). Most of the tested compounds were stable within 10 percent over a two-week storage period, with the terpenes exhibiting poorer stability. In a second test, 11 PVOCs (including one HAP) were spiked into ambient air at concentrations of 20 to 40  $\mu\text{g}/\text{m}^3$ . Most of the PVOCs were stable within about 10 percent over one week of storage, and within 30 percent over 3 weeks. Considerable variability in results was noted from one canister to another. Low molecular weight (i.e.,  $\text{C}_1$  to  $\text{C}_6$ ) alcohols were reported to be unstable in canisters, even within a one day storage period.

**Holdren *et al.* (1984):** This study evaluated the stability of 16 VOCs, including 14 HAPs but no PVOCs, in seven new Summa polished stainless steel canisters of 6 liter volume. The stored mixture contained all 16 compounds, at concentrations of 0.6 to 2.7 ppbv, in humidified air. Storage was conducted for 7 days, with determination of the canister contents on the day the canisters were filled (day 0), and on days 2, 4 and 7. The bias of measured concentrations on day 7 relative to those on day 0 was less than 5 percent for 13 of the 16 VOCs, and the maximum bias was -18.8 percent, for benzyl chloride.

**Oliver *et al.* (1986):** This study employed a combination of new and previously used 6 L and 3 L Summa polished canisters in evaluating the stability of 18 VOCs, including 16 HAPs but no PVOCs. Concentrations of all the VOCs were less than 2 ppbv in all tests, and ambient air was the matrix for filling the canisters, up to 30 psig. Fifteen of the VOCs were spiked into ambient air in filling the canisters; three others (benzene, toluene, and o-xylene) were used at the levels native in the ambient air. Four new 6 L canisters, four new 3 L canisters, and five used 6 L canisters were used in a 7-day storage test, with measurements made on days 0, 2, 4, and 7. A 30 day storage test was also conducted with three other used 6 L canisters; measurements were made on days 0, 1, 15, and 30. All

compounds were found to be reasonably stable in the canisters, with most exhibiting mean rates of change of less than 1 percent per day of storage in both the 7 day and 30 day tests.

**Jayanty (1989):** In this study a single 6 L Summa polished stainless steel canister was used to test the stability of 18 VOCs, including 17 HAPs but no PVOCS. The 18 VOCs were prepared together at concentrations of 4 to 12 ppbv in air humidified to an unspecified level. The canister was filled to an initial pressure of 30 psig. Stability was tested during an 11 day storage, with the VOC content of the canister determined on days 0, 1, 7, and 11. For all of the 18 VOCs, concentrations measured on day 11 agreed well (i.e., typically within 5 percent) with the day 0 concentrations and with the expected concentrations put into the canister.

**Gholson *et al.* (1989):** In this study the stability of VOCs in canisters was evaluated under conditions simulating the sampling of dispersing emissions from hazardous waste incinerators. New 6 L stainless steel Summa polished canisters were used in several tests with up to 18 VOCs, including 17 HAPs but no PVOCS. In an initial test, 5 VOCs (all HAPs) were stored at concentrations of 10 to 15 ppbv in three canisters pressurized to 15 psig with dry air. Analyses were conducted on all three canisters after 4 days, and on one canister after 11 days of storage. No loss of any of the 5 VOCs was found. The same VOC mixture in air was also tested in one canister containing 2,800 ppm of water and 120 ppm of HCl, over a 14 day period with measurements on days 0, 1, 5, 8, and 14. All 5 VOCs were found to be stable within about 8 percent over the 14 day period. In a separate test, a mixture of 18 VOCs (17 HAPs) were tested in a single canister at concentrations of 5 to 12 ppbv in nitrogen, in the presence of 5,600 ppm of water and 120 ppm of HCl. The water content was stated to exceed the saturation vapor pressure in the canister. Storage over 14 days, with testing on days 0, 1, 3, 7, and 14, showed stability generally within 10 percent for the tested compounds. However, large positive artifacts were observed for a few compounds, possibly due to gas chromatograph column degradation caused by the water/HCl in the canister. The test most pertinent to ambient sampling was an 11-day study of the same 18-component mixture, in nitrogen with 150 ppm H<sub>2</sub>O but with no HCl, which showed

stability generally within 15 percent for all compounds, with no positive artifacts.

**Gholson *et al.*, 1990:** This study was conducted using four new 6 L aluminum canisters and one new 6 L stainless steel canister. The investigation of aluminum canisters was motivated by previous work (Allen *et al.*, 1987) that indicated improved chromatographic peak shapes for PVOCs when an aluminum sample loop was used, relative to those obtained with a stainless steel sample loop. Two of the aluminum canisters and the one stainless steel canister were Summa polished, the others were not. In one test, a mixture of 18 VOCs (17 HAPs, no PVOCs) each at about 4 ppbv in air was stored in the four aluminum canisters. Two of the canisters (one Summa polished, one not) were humidified with 2,000 ppm of water, whereas the other two contained dry samples. Storage was conducted over 10 days, with analysis of canister contents on days 0, 1, 4, 7, and 10. In a second test, seven compounds (4 HAPs, 2 PVOCs) were stored at 10 to 20 ppbv levels in one polished aluminum canister, one unpolished aluminum canister, and the one stainless steel canister, with 170 ppm of water added to all three canisters. This mixture was stored for 14 days, with analysis on days 0, 1, 3, 7, and 14. Storage stabilities for the VOCs were poor in dry canisters, but good in humidified canisters. Summa polishing of the aluminum canisters was found to have only a small effect on VOC stability. Aluminum canisters were found deficient relative to stainless steel for storage of PVOCs, and showed no advantage for storage of VOCs.

**Holdren *et al.* (1991):** This study was one of the most comprehensive, addressing the stability of a variety of compounds in nine new Summa-polished canisters obtained from three different vendors. Three separate tests were conducted, using purified air of 70 percent relative humidity, over storage periods of up to 33 days. The first test involved 42 VOCs (the 41 compounds on the TO-14 target list, plus 1,3-butadiene), including 31 HAPs. A mixture containing nominally 10 ppbv of each compound was analyzed on days 0, 20, and 32, and a separate 2 ppbv mixture was analyzed on days 0, 15, and 33. The second test involved 18 VOCs, including 15 PVOCs and 12 HAPs. A 10 ppbv mixture was analyzed on days 0, 10, and 33, and a 2 ppbv mixture on days 0, 11, and 30. The third test was of 13

toxic compounds, including 8 PVOCs and 9 HAPs. A 10 ppbv mixture was analyzed on days 0, 10, and 30, and a 2 ppbv mixture on days 0, 20, and 32. Ignoring duplication in the three tests, a total of 67 compounds, including 47 HAPs, were tested in this study. Most compounds tested showed good stability over 30 days storage, though some polar compounds were more stable at the nominal 10 ppbv level than at 2 ppbv.

**Parmar (1991):** This study tested the stability of four volatile sulfur compounds, including the HAPs carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>), in one Summa polished stainless steel canister. Initial concentrations of 1,200 ppbv COS and 1,400 ppbv CS<sub>2</sub> were stored in dry nitrogen for 3 days. The loss of COS in the canister was reported to be 8.3 percent in one day, 12.3 percent in 2 days, and 17.5 percent in 3 days. The corresponding losses for CS<sub>2</sub> were reported to be 1.1 percent, 1.5 percent, and 4.2 percent.

**Merrill and Zapkin (1991):** This study used three 6 L Summa polished stainless steel canisters to test the stability of four PVOCs (including the HAP methanol) over a 35 day period in air of 60 percent relative humidity. The initial concentrations were 20 to 30 ppbv, except for methanol which was at 60 ppbv. Analysis of the canister samples on days 0, 7, 15, 20, and 35 showed no significant losses of any of the four PVOCs.

**Pate *et al.* (1992):** In this study five 6 L stainless steel canisters, three Summa polished and two not polished, were used to test the stability of 12 VOCs, including 8 HAPs and 10 PVOCs. The compounds were present at levels of 5 to 13 ppbv in both dry and humidified mixtures. The humidified mixtures exceeded saturation for water vapor. Canister pressure was indicated as 3 atmospheres. Storage was conducted over 31 days, with analyses on days 0, 1, 3, 7, 14, and 31. Stability in humidified canisters was very good, whereas that in dry canisters was relatively poor. Summa polishing had little apparent effect on the stability of the tested compounds.

**Oliver (1993):** This study tested the stability of 9 PVOCs, including 5 HAPS, using four new 6 L Summa polished canisters. The PVOCs were spiked into ambient air to



fill the canisters. Testing was conducted over 7 days, with analysis on days 0, 2, 4, and 7, in two separate tests. The first test used PVOC levels of 1 to 4 ppbv, the second 3.5 to 8 ppbv. All the tested PVOCs were stable within 25 percent over 7 days of storage, with most exhibiting stability within 15 percent.

**Kelly *et al.*, (1993):** As part of a method development and ambient sampling effort for PVOCs, canister stability was tested for 15 VOCs, including 9 HAPs and 13 PVOCs, with used 6 L Summa polished stainless steel canisters. A mixture of these 15 compounds at about 4 ppbv each, in air of 80 percent relative humidity and 5 psig pressure, was analyzed after 4 days and after 12 days of storage. Linear regression of the day 4 results relative to the day 0 results for all 15 compounds indicated 13 percent loss over the 4 days of storage. Individual compounds showed losses of 2 to 38 percent over that time period. The PVOC compounds showed relatively poor stability after 12 days of storage.

**Holdren *et al.* (1994):** This study was intended primarily to evaluate differences in storage stability among nine new Summa polished stainless steel canisters, treated in three different ways. Three of the canisters underwent no further treatment, three underwent the Silcosteel® surface deactivation process, and three were treated with the Silcosteel treatment plus an added deactivating reagent. A target group of 9 VOCs, including 6 PVOCs and 7 HAPs, was prepared at nominal levels of 20 ppbv each, and of 2 ppbv each, in humidified high purity air. Actual concentrations of individual compounds in the 20 ppbv mix were 10.7 to 30.4 ppbv, and in the 2 ppbv mix were 1.1 to 3.0 ppbv. The 20 ppbv mixture was evaluated with both 52 percent and 21 percent relative humidity air (RH measured at 1 atm pressure); the 2 ppbv mixture was evaluated with 21 percent relative humidity only. Analyses were conducted on days 0, 4, and 7 of storage. No significant differences were observed among the three canister treatment processes. Stability of the target compounds was within the 25-30 percent uncertainty of the measurement method.

## HAPs STABILITY RESULTS

The reported degree of stability of a VOC in a canister is the end product of several factors, not all of which have been properly documented in the published studies. To begin with, the preparation and introduction of low levels of VOCs into canisters may introduce variability and uncertainty in stability testing, particularly for PVOCs. For example, the precision of replicate standards has been shown to be poorer for PVOCs than for VOCs (Kelly *et al.*, 1993), and initial concentrations reported in canisters do not always agree with those expected (Pate *et al.*, 1992). Furthermore, the stability of a compound in air within a canister is affected by a complex interaction of factors, including the vapor pressure, polarizability, water solubility, and aqueous reactivity of the compound; the characteristics of the canister surface; the past use of the canister itself; the reactivity of the compound with other species present in the air sample; the humidity of the air; the canister pressure; the temperature of the canister during sampling and storage; and the competitive adsorption of the compound relative to that of water vapor and trace chemicals in the sample (Coutant and McClenny, 1991; Coutant, 1993). Finally, the reported stability in a canister is based upon an analytical measurement, and thus is subject to uncertainties from that source. Methanol, for example, has been found to be stable in canisters in some studies (Merrill and Zapkin, 1991; Pate *et al.*, 1992), but in others analytical difficulties have prevented its determination (Westberg *et al.*, 1981; Oliver, 1993). In actuality, the reported studies have determined the overall recoverability of VOCs in the respective test and analysis systems, not merely the stability of VOCs within a canister. From an analytical standpoint, overall recoverability is the more important factor. However, the impact of analytical capabilities on reported stability results has rarely been discussed (Oliver *et al.*, 1986; Holdren *et al.*, 1994).

The summaries presented above show that canister stability testing has generally been limited in nature. Most of the reported stability tests have addressed relatively few compounds, and most have used very few canisters. The comparability of results among the various studies is uncertain, because of differences in the performance of the tests. For example, storage tests have been conducted for as little as 7 days, and for as long as 33

days. Most studies have used purified air or nitrogen as the diluent gas, but in a few studies ambient air was used. Thus the potential range of other chemicals present in the canister with the target VOCs has varied widely. The degree of humidification of the test mixtures and the pressurization of the canisters differ among the studies, and in some studies these parameters are not well documented. Stability studies have usually been conducted with VOC concentrations ranging from about 1 ppbv to 20 ppbv, but one study (Parmar, 1991) used levels of over 1 ppmv. The size, age, surface treatments, and even materials of construction of the canisters used have also varied. As a result, the published results do not constitute a single cohesive data set.

Despite the ambiguities in reported tests of VOC canister stability, the results of those tests are of interest as indications of the applicability of canister sampling for HAPs. Table 1 summarizes the canister stability results for the 52 HAPs for which such testing has been reported. Table 1 lists the HAPs in the same order as in the CAAA list, and indicates the stability reported, the concentration level tested, the pertinent literature, and any comments on the results. Because of the diversity of the stability tests, as noted above, Table 1 shows results for each study cited, rather than a summary stability value for each HAP.

The diversity of the reported stability tests requires explanation of the entries in Table 1. Unless otherwise noted, the entries in Table 1 refer to tests using Summa polished stainless steel canisters, with humidified, purified air as the diluent gas. When a published study included more than one stability test, the entries refer to the longest period of storage within each study. Results shown in Table 1 were also selected to be those most pertinent to ambient sampling of HAPs. For example, results in Table 1 from reference 5 (Gholson *et al.*, 1989) are from a test conducted without high levels of HCl in the canister. A few studies reported stability results using parallel flame ionization and electron capture gas chromatographic detectors, and for some compounds reported contradictory trends in canister stability from the two detectors (Oliver *et al.*, 1986; Jayanty, 1989, Gholson *et al.*, 1989). In such cases, the worse-case result, i.e., that indicating poorer stability, is shown in Table 1. The means of calculating the stability of VOCs in canisters also differed among the

TABLE 1. SUMMARY OF CANISTER STABILITY TESTS ON CAAA HAZARDOUS AIR POLLUTANTS

Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>	Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>		
Acetaldehyde	30/4	30.4	13		Carbon disulfide	1/30	17.9	7			
	30/7	3.0				21/32	3.7				
Acetonitrile	4/33	20.5	7			4/3	1400	8	[6]		
	14/30	4.3				15/7	28.2			13	
	25/7	8.6				15/7	2.8				
	38/4	4									
Acrylonitrile	5/33	16.3	7		Carbon tetrachloride	1/7	2.0	2			
	6/30	3.4				15/30	0.9			3	[2]
	5/31	13.9				5/11	4.5			4	
	12/7	4.3				8/11	4.7			5	[4]
	15/7	7.3				48/10	4.0			6	[7]
	14/4	4				3/10	4.0				[8]
	20/7	25.8				10/32	12.8			7	
	20/7	2.6				13/33	2.7				
Allyl chloride	2/32	13.1	7		Carbonyl sulfide	18/3	1200	8	[6]		
	15/33	2.7									
Benzene	19/21	2.1	1	[2]	Chloro- benzene	3/7	1.4	2			
	5/30	0.6				7/30	1.0			3	[2]
	2/11	4.7				10/11	10.0			4	
	9/11	4.7				14/11	10.0			5	[4]
	1/10	4.3				14/10	4.2			6	[9]
	6/32	12.0				24/14	10.2				[10]
	16/33	2.5				5/14	10.2				[11]
	5/33	12.1				9/32	11.0			7	
	7/30	2.5				14/33	2.3				
	14/4	4									
	10/7	19									
20/7	1.9										
Benzyl chloride	19/7	1.0	2		Chloroform	2/7	1.9	2			
	11/30	0.75				34/30	1.2			3	[2]
	9/32	10.9				3/11	4.8			4	
	36/33	2.3				1/11	4.8			5	[4]
Bromoform	5/32	12.3	7		Cumene	5/10	4.4	6	[5]		
	13/33	2.6				10/32	14.1			7	
						7/33	2.9				
1,3-Butadiene	4/11	4.7	4			10/32	7.7	7			
	2/11	4.7				13/33	1.6				
	9/10	9.3									
	14/32	11.8									
	34/33	2.5									
	19/33	11.0									

TABLE 1. (Continued)

Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>	Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>
1,4-Dichlorobenzene	11/32	9.8	7		Ethylene dichloride	1/7	1.9	2	
	14/33	2.0				12/30	0.9	3	[2]
1,3-Dichloropropene	7.3/7	0.82 (cis)	2		2/11	5.1	4		
	1.6/7	0.64 (trans)			10/11	5.1	5	[4]	
	4/30	0.49 (cis)	3	[2]	2/10	4.0	6	[5]	
	15/7	0.39 (trans)			9/32	13.8	7		
	12/32	12.9 (cis)	7		9/33	2.9			
	13/33	2.7 (cis)			Ethylene oxide	26/33	11	7	
	8/32	13.9 (trans)				Ethylidene dichloride	9/32	12.8	7
	15/33	2.9 (trans)			11/33		2.7		
1,4-Dioxane	100/4	19.2	6	[10]	Hexachloro- butadiene	11/7	1.3	2	
	77/14	19.2		[11]		35/30	1.0	3	[2]
	25/30	12.6	7			16/32	6.2	7	
	22/32	2.6				10/33	1.3		
Ethyl acrylate	3/33	9.9	7		Hexane	16/21	1.6	1	[2]
	19/30	2.1				Methanol	<5 <sup>d</sup> /35	60	9
	3/31	4.9	10		46/31		131	10	
	2/7	1.1	11	[2]	Methyl bromide		4/11	8.5	4
	3/7	3.6				15/11	8.5	5	[4]
15/4	4	12		4/10		4.1	6	[5]	
Ethyl benzene	16/21	0.6	1	[2]		6/32	12.7	7	
	12/11	9.4	4			34/33	2.6		
	17/11	9.4	5	[4]	Methyl chloride	19/32	10.1	7	
	50/10	3.9	6	[5]		17/33	2.1		
	10/32	9.5	7		Methyl chloroform	1/7	1.9	2	
17/33	2.0			11/30		1.4	3	[2]	
Ethyl chloride	12/32	11.4	7		4/11	10.1	4		
	29/33	2.4			1/11	10.1	5	[4]	
Ethylene dibromide	2/7	1.4	2		1/10	4.1	6	[5]	
	3/30	1.2	3	[2]	17/32	6.1	7		
	11/11	9.7	4		6/33	1.3			
	6/11	9.7	5	[4,12]	3/31	5.3	10		
	20/10	4.3	6	[5]					
	14/32	13.5	7						
	12/33	2.8							

TABLE 1. (Continued)

Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>	Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>	
Methyl ethyl ketone	14/21	13	1	[2]	1,1,2,2- Tetrachloro- ethane	9/32	10.1	7		
	4/33	12.0	7			15/33	2.1			
	94/30	2.5								
	7/31	26	10							
	58/7	1.2	11	[2]		Tetrachloro- ethylene	3.2/7	1.6	2	
	1/7	4.1				10/30	1.0	3	[2]	
	14/14	4	12			10/11	5.2	4		
	30/7	19.0	13			3/11	5.2	5	[4]	
	20/7	1.9				6/10	4.6	6	[5]	
				13/32	10.8	7				
				13/33	2.2					
Methyl iso- butyl ketone	21/30	8.6	7							
	24/32	1.8								
Methyl methacrylate	7/30	10.1	7		Toluene	20/21	3.9	1	[2]	
	15/32	2.1				20/30	1.0	3	[2]	
	1/7	1.2	11	[2]		4/11	9.5	4		
	4/7	3.9				6/11	9.5	5	[4]	
				5/10	4.3	6	[9]			
Methyl t-butyl ether	9/33	9.1	7		33/14	10.1		[10]		
	12/30	1.9			16/14	10.1		[11]		
	3/31	7.1	10		8/32	10.4	7			
	18/4	4	12		11/33	2.2				
	14/7	14.2	13		5/33	10.1				
	30/7	1.4			8/30	2.1				
				6/31	5.0	10				
Methylene chloride	3/11	5.2	4		15/4	4	12			
	4/11	5.2	5	[4]	25/7	16.0	13			
	55/10	4.3	6	[5]	30/7	1.6				
	26/32	17.1	7							
	27/33	3.6			1,2,4-Tri- chloro- benzene	5/32	7.1	7		
					7/33	1.5				
Nitrobenzene	26/30	10.4	7							
Propylene dichloride	3/11	10.5	4		1,1,2-Tri- chloroethane	12/32	12.1	7		
	6/11	10.5	5	[4]		18/33	2.5			
	<1/10	4.1	6	[5]						
	12/32	11.4	7			Trichloro- ethylene	2/7	1.8	2	
	17/33	2.4				11/30	1.0	3	[2]	
				5/11	5.4	4				
Propylene oxide	17/33	15.4	7		9/11	5.4	5	[4]		
	9/4	4	12	[13]	1/10	4.3	6	[5]		
					14/32	11.6	7			
Styrene	8/32	9.6	7		18/33	2.4				
	34/33	2.0								

TABLE 1. (Continued)

Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>	Compound	Stability <sup>a</sup> (% Change/Days)	Tested Conc. (ppbv)	References <sup>b</sup>	Comments <sup>c</sup>
2,2,4-Trimethyl- pentane	22/21	0.6	1	[2]	m-Xylene	17/21 7/32 17/33	2.3 9.3 1.9	1 7	[2,14]
Vinyl acetate	39/33 55/11 3/31 31/4	11.6 2.4 7.3 4	7 10 12		o-Xylene	12/21 120/30 15/7 16/11 10/11 59/10 9/32 10/33	0.8 0.14 0.15 11.7 11.7 4.1 9.8 2.0	1 3 4 5 6 7	[2] [2]
Vinyl chloride	3/7 11/7 <1/11 8/11 83/10 10/32 25/33	1.8 0.8 5.9 5.9 3.9 28.3 5.9	2 3 4 5 6 7	[2] [4] [5]	p-Xylene	17/21	<2.3	1	[2,15]
Vinylidene chloride	4/7 4/30 6/14 7/14 7/32 11/33	2.1 1.1 9.4 9.4 12.9 2.7	2 3 6 7	[2] [10] [11]					

a Stability indicated as absolute value of percent change from initial concentration value/duration of storage in days.

b References: 1, Westberg et al., 1981; 2, Holdren et al., 1984; 3, Oliver et al., 1986; 4, Jayanty, 1989; 5, Gholson, et al., 1989; 6, Gholson et al., 1990; 7, Holdren et al., 1991; 8, Parmar, 1991; 9, Merrill and Zapkin, 1991; 10, Pate et al., 1992; 11, Oliver, 1993; 12, Kelly et al., 1993; 13, Holdren et al., 1994.

c Comments:

- [1] Coeluted with ethanol.
- [2] Ambient air used as diluent.
- [3] Coeluted with 2-propanol.
- [4] Humidified nitrogen used as diluent.
- [5] Aluminum canisters.
- [6] Test conducted in dry N<sub>2</sub>.
- [7] Al passivated cans.
- [8] Al unpassivated cans.
- [9] Al canisters, 2000 ppm H<sub>2</sub>O.
- [10] Al canister, 170 ppm H<sub>2</sub>O.
- [11] Stainless steel canister, 170 ppm H<sub>2</sub>O.
- [12] Corrected for instability of control canister.
- [13] Coeluted with acetone.
- [14] Coeluted with p-xylene.
- [15] Coeluted with m-xylene.

d Estimated; based on lack of a significant concentration trend with time.

studies. Most studies reported canister results for each individual day on which measurements were made. The final day's results are shown in Table 1. However, Oliver *et al.* (1986) instead performed a linear regression with time over all canister analysis days. Canister stability was then reported in terms of a mean percentage change per day of storage (Oliver *et al.*, 1986). Results from Table 1 were calculated as the product of the mean percent change per day and the total number of days of storage. Several studies conducted tests at more than one initial concentration level; separate entries are shown in such cases, in Table 1. Separate results are also shown for the cis- and trans- isomers of 1,3-dichloropropene, which have been tested separately (the CAAA HAPs list makes no distinction between these isomers).

From an analytical standpoint, the important factor in canister stability is the absolute change in concentration of a volatile compound, relative to its initial concentration in the canister. The direction of any change in concentration, i.e., positive or negative, is less important. As a result, the stability results in Table 1 are shown as absolute values of the percentage change during storage. However, the results tabulated are based on both positive and negative changes reported in the cited studies. A negative change in concentration during storage, i.e., a loss of compound within the canister, is the more commonly expected result. Such loss can result from adsorption on the canister surface, or from chemical reactions with water or other chemicals in the canister (Coutant, 1993). A positive change, i.e., an increase in measured concentration, can also occur, as a result of the partitioning of volatile compounds between the gas phase and condensed water on the canister surface (Coutant, 1993). The extent of this effect depends on the Henry's law equilibrium of the volatile compound between the aqueous and gas phases. In this scenario, a volatile compound may be partitioned largely into condensed water on the canister surface, under the initial canister conditions of pressure, temperature, and relative humidity. However, as sample (and water vapor) is removed during successive analyses of the canister, changes in pressure result which may reduce the amount of condensed water, and consequently shift the partitioning of the volatile compound toward the gas phase. As a result, later analyses appear enriched in the volatile compound, and a positive trend in concentration with time is observed. In addition, normal variability in preparation of test



mixtures and in canister analysis may cause either positive or negative variations in canister stability results. All of these factors may play a role in any given stability study, but in general cannot be resolved based on the published information.

The quantitative stability results in Table 1 may be normalized in a sense by comparison to a quantitative criterion of the stability required to conduct ambient sampling. Although rapid transfer of canisters from the field to the lab has been employed to minimize storage times (e.g., Kelly *et al.*, 1993), a longer storage schedule is more typical. For the present discussion, we assume that stability within 25 percent over a two-week storage period is sufficient for the great majority of ambient measurements. For many HAPs, the reported stability results show considerable variation. However, relative to this criterion, Table 1 indicates that nearly all of the HAPs tested to date are sufficiently stable that canister sampling is an effective approach to ambient measurements. Possible exceptions are carbonyl sulfide and acetaldehyde, for which storage times of only a few days cause large changes in concentration. However, very limited testing has been done for these compounds, and further tests would be valuable, especially for carbonyl sulfide, which has only been tested during storage in dry nitrogen. In addition, Table 1 shows variable stability results for methyl ethyl ketone, propylene oxide, and vinyl acetate; further testing is also needed for these HAPs. Some of the variability in reported canister stability for these compounds undoubtedly arises from difficulties in the analysis step.

## DISCUSSION

The canister stability reported for the HAPs (Table 1) is largely the product of the chemical and physical properties of the HAPs. Consequently, the usefulness of canister sampling for other HAPs, not yet tested for stability, should correlate with their respective properties. In this section, comparisons of HAPs properties are used to identify HAPs for which canisters are, and are not, likely to be useful for sample storage.

Chemical and physical properties of volatile HAPs were compiled in a recent survey of proven and potential ambient measurement methods for the 189 HAPs (Kelly *et al.*, 1994), and in a modelling study of VOC canister stability (Coutant, 1993). The

properties compiled were vapor pressure, boiling point, polarizability, water solubility, Henry's law equilibrium constant, aqueous reactivity, and reactivity in the atmosphere. The latter two properties were quantified in terms of the typical half-life for reaction in each matrix (Spicer *et al.*, 1993; Kelly *et al.*, 1994). Data on chemical and physical properties of HAPs were compiled from a variety of reference materials. Key references for vapor pressure were Jones and Bursey (1992) and Weber *et al.* (1991); for polarizability Sansone, *et al.* (1979), CRC (1979), and Keith and Walker (1993); for water solubility Mackay *et al.* (1993) and Verschueren (1983); for Henry's law equilibrium Hine and Mookerjee (1975), Mackay and Shiu (1981), Yaws *et al.* (1991), Eklund *et al.* (1991), and Betterton (1992); and for reactivity data Howard *et al.* (1991) and Spicer *et al.* (1993). The overall ranges of properties found for the volatile HAPs were: vapor pressure, 0.15 to 3,800 mm Hg; polarizability, 8 to 50 cm<sup>3</sup>/mole; water solubility, <0.1 to >100 g/L at 25°C; and dimensionless Henry's law partition coefficient ( $C_{\text{water}}/C_{\text{air}}$ ),  $2 \times 10^2$  to  $2.5 \times 10^6$ . Reactive lifetimes in water and in the atmosphere ranged from a few minutes to many months. Reactivity with water was considered the more important factor, since atmospheric reactivity depends upon factors (e.g., radical reactions, photolysis) which are of no consequence in a canister. Henry's law partitioning was also given much greater weight than simple bulk solubility, because of its greater relevance to the behavior of volatile compounds in a canister.

In the present study, the properties of HAPs never tested for stability in canisters were compared to those of HAPs shown to be reasonably stable in canisters (Table 1), to infer the likely stability of the untested HAPs. An example of such a comparison is shown in Table 2. Table 2 compares the properties of 1,2-dibromo-3-chloropropane, which has not been tested for canister stability, to those of 1,4-dichlorobenzene (see Table 1). As Table 2 shows, the vapor pressure of the dibromochloropropane is low, but essentially the same as that of the dichlorobenzene. The two compounds also have the same polarizability, very similar water solubility, and very similar Henry's law partitioning. Both chemicals are non-polar compounds, and are relatively unreactive both in air and water. As a result, it is reasonable to conclude that the stability of 1,2-dibromo-3-chloropropane in a canister should

TABLE 2. EXAMPLE COMPARISON OF HAPs PROPERTIES

HAP	Vapor Pressure (mm Hg at 25°C)	Polarizability <sup>c</sup> (cm <sup>3</sup> /mole)	Water Solubility (g/L at °C)	Henry's Law Partitioning <sup>d</sup> (c <sub>w</sub> /c <sub>a</sub> )	Reactive Half-Life (Days)	
					Aqueous	Air
1,2-Dibromo-3-chloro- propane <sup>a</sup>	0.8	36.3	<0.1 at 18	20	14-180 <sup>e</sup>	6-61
1,4-Dichlorobenzene <sup>b</sup>	0.6	36.3	<1 at 23	15	28-180 <sup>e</sup>	8-84

a: Not tested for canister stability.

b: Tested for canister stability (see Table 1).

c: Polarizability =  $(MW/\rho) (n^2-1)/(n^2+2)$ , where MW = molecular weight,  $\rho$  = density, and n = refractive index.

d: Entries are dimensionless Henry's law constants, concentration in water/concentration in air (C<sub>w</sub>/C<sub>a</sub>). Value for 1,2-dibromo-3-chloropropane is based on data for 1,2-dibromopropane (Hine and Mookurjee, 1975; Yaws *et al.*, 1991).

e: Hydrolysis rate is negligible; indicated lifetime based on aqueous aerobic biodegradation.

be comparable to that of 1,4-dichlorobenzene, i.e., canister sampling should be effective for 1,2-dibromo-3-chloropropane.

Similar comparisons have been made for other HAPs, both by close similarity of properties, as in Table 2, or by ranking properties of chemically analogous HAPs. Examples of the latter approach include comparison of vinyl bromide with vinyl chloride, or of hexachloroethane with carbon tetrachloride, hexachlorobutadiene, and other highly chlorinated HAPs. A clear conclusion is not possible for all HAPs, due to the ambiguity or absence of some chemical and physical property data. In addition, some HAPs are relatively unusual compounds for which it is difficult to find suitable comparisons among the HAPs previously tested in canisters. However, for many of the untested HAPs some assignment can be made as to the likely effectiveness of canister sampling. The results of this comparison of properties are shown in Table 3. This table lists the volatile HAPs which have not been tested for stability, in the same order as in the CAAA list. Shown in Table 3 are an indication of the likely canister stability for each HAP, and comments or supporting information. The likelihood of canister stability is indicated as "Y", i.e. stability is likely; "N", i.e., stability is not likely; or "?", stability is unknown or doubtful based on the available information. In most cases, the supporting comments call attention to specific HAP properties that strongly determine the conclusion reached concerning canister stability. In those cases where canister stability is likely, the comments in Table 3 indicate the HAPs used as the basis for a comparison of properties.

Table 3 lists 45 volatile HAPs not yet tested for canister stability. Of those HAPs, 9 are indicated as likely to be stable in canister sampling, and 17 as unsuitable for canister sampling. For 19 of the HAPs in Table 3, no clear decision can be made as to their likely stability in canisters. The 9 HAPs for which canister stability is likely are generally analogs of other HAPs previously shown to be stable in canisters (Table 1), or are known to be unreactive. The other 36 compounds are polar, water-soluble, and potentially reactive compounds. For these HAPs, little or no canister testing has been done on analogous compounds. Canister sampling for the 17 HAPs designated by "N" in Table 3 is strongly discouraged. Reliance on canister sampling for the 19 HAPs designated by a "?" is not recommended, even for short storage periods, without prior canister stability testing.

**TABLE 3. VOLATILE HAPs NOT TESTED FOR CANISTER STABILITY, AND INDICATIONS OF LIKELY STABILITY**

HAPs	Likely Stability in Canister <sup>a</sup>	Comments <sup>b</sup>
Acetophenone	?	Low vapor pressure, substantial solubility
Acrolein	?	High water solubility
Acrylamide	N	Low vapor pressure, high water solubility
Acrylic acid	N	High water solubility
Aniline	?	High water solubility, low vapor pressure
bis(Chloromethyl)ether	N	Reacts with liquid water
Catechol	N	Substantial water solubility, low vapor pressure
Chloroacetic acid	N	High water solubility
Chloromethyl methyl ether	N	Reacts with liquid water
Chloroprene	Y	By comparison to 1,3-butadiene
Cresols/Cresylic acid	N	Only o-cresol has vapor pressure > 0.1 mm Hg
o-Cresol	N	Minimally volatile, highly soluble
Diazomethane	N	Reactive
1,2-Dibromo-3-chloropropane	Y	By comparison to p-dichlorobenzene
Dichloroethyl ether	Y	By comparison to 1,4-dichlorobenzene, benzyl chloride, and methyl iso-butyl ketone
Diethyl sulfate	N	Reacts with liquid water

TABLE 3. (Continued)

HAPs	Likely Stability in Canister <sup>a</sup>	Comments <sup>b</sup>
N,N-Dimethylaniline	?	Low vapor pressure
Dimethyl carbamoyl chloride	N	Reacts with liquid water
N,N-Dimethyl formamide	?	High water solubility
1,1-Dimethyl hydrazine	N	High water solubility, reactive
Dimethyl sulfate	N	High solubility and reacts with liquid water
Epichlorohydrin	?	Substantial water solubility, minimal previous stability testing of epoxides
1,2-Epoxybutane	?	High water solubility, minimal previous stability testing of epoxides
Ethyl carbamate	?	Minimal vapor pressure, high water solubility
Ethyleneimine	?	Potentially reactive, high water solubility
Formaldehyde	?	Soluble, potentially reactive
Hexachloroethane	Y	By comparison to hexachlorobutadiene, carbon tetrachloride, and other highly chlorinated compounds
Isophorone	Y	By comparison to benzyl chloride and nitrobenzene
Methyl hydrazine	?	Reactive, high water solubility
Methyl iodide	Y	By comparison to methyl chloride and methyl bromide
Methyl isocyanate	N	Reactive
2-Nitropropane	Y	By comparison to nitrobenzene

TABLE 3. (Continued)

HAPs	Likely Stability in Canister <sup>a</sup>	Comments <sup>b</sup>
N-Nitroso-N-methyl urea	N	Reacts with liquid water
N-Nitroso-dimethylamine	?	Soluble and possibly reactive
N-Nitrosomorpholine	?	Minimal vapor pressure, substantial solubility
Phenol	?	Minimal vapor pressure, substantial solubility
Phosgene	N	Reactive
1,3-Propane sultone	?	Reacts with liquid water
beta-Propiolactone	?	Reacts with liquid water
Propionaldehyde	?	By comparison to acetaldehyde
1,2-Propyleneimine	N	Reactive, high water solubility
Styrene oxide	N	Reacts with water
Triethylamine	?	Potentially reactive, substantial solubility
Xylenes (mixed)	Y	Individual isomers previously tested
Vinyl bromide	Y	By comparison to vinyl chloride

a: Y = Yes, likely to be stable in a canister.

N = No, not likely to be stable in a canister.

? = Canister stability uncertain, due to absence of some chemical and physical property data, or due to lack of appropriate compounds with which to make comparisons.

b: Comments summarize quantitative comparisons of several chemical and physical properties; see text.

The present study has focussed on volatile organic HAPs, and has not considered the several volatile inorganic compounds also on the HAPs list. The volatile inorganic HAPs include chlorine, hydrogen fluoride, hydrogen chloride, hydrazine, and phosphine. Although exhibiting high vapor pressures, these HAPs are generally too reactive, water soluble, and/or polar to be amenable to canister sampling.

## CONCLUSIONS

A review of canister stability tests shows such testing has addressed 52 compounds designated as HAPs in Title III of the CAAA. For nearly all of the tested compounds, stability during storage and analysis is sufficient to make canisters an effective sampling approach. However, additional stability testing under carefully documented conditions is needed to establish and understand the stability for some of the 52 HAPs. Further improvements in analytical methods for some HAPs are also needed, because determination of canister stability is dependent upon analytical measurements.

Comparisons of chemical and physical properties of the HAPs have identified 9 HAPs, never tested for canister stability, which are likely to be stable in canisters. Such comparisons also identified 17 HAPs for which canister stability will certainly be poor. For 19 other HAPs, available property information and stability testing of analogous compounds are insufficient to determine the likely effectiveness of canister sampling.

The canister stability tests reported in the literature have employed a great variety of procedures, and have generally addressed small numbers of compounds with a small set of canisters. Greater standardization of test procedures, and improved documentation of test conditions, are needed to integrate test results and allow application of models of chemical behavior in canisters.



## ACKNOWLEDGMENT

This work was conducted under the support of the U.S. Environmental Protection Agency, Contract No. 68-D0-0007. The involvement of William McClenny of the U.S. EPA in this study is gratefully acknowledged, as are helpful discussions with Robert Coutant. Although the work described here was funded by the U.S. Environmental Protection Agency, it has not been subjected to Agency review, and therefore does not necessarily represent the views of the Agency, and no official endorsement should be inferred.

## REFERENCES

- Allen, J.M., Jayanty, R.K.M., and von Lehmden, D.J. (1987) Comparison of sample loops constructed of several different materials for gas chromatographic analysis of parts-per-billion-level organic gas mixtures. Anal. Chem., 59, 1982-1984.
- Betterton, E.A. (1992) Henry's law constants of soluble and moderately soluble organic gases: Effects on aqueous phase chemistry, in Gaseous Pollutants: Characterization and Cycling, J.O. Nriagu Ed., John Wiley & Sons, Inc., New York.
- Clean Air Act Amendments of 1990, Conference Report to Accompany S. 1630, Report No. 101-952, U.S. Government Printing Office, Washington, DC, 1990, pp 139-162.
- Coutant, R.W. and McClenny, W.A. (1991) Competitive adsorption effects and the stability of VOC and PVOC in canisters. In Proceedings of the 1991 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants, EPA-600/9-91/018, Publication No. VIP-21, Air and Waste Management Association, Pittsburgh, PA, pp 382-388.
- Coutant, R.W. (1993) Theoretical evaluation of stability of volatile organic chemicals and polar volatile organic chemicals in canisters. Final Report to U.S. EPA, Contract No. 68-D0-0007, Work Assignment No. 45, Subtask 2, Battelle, Columbus, OH.
- CRC Handbook of Chemistry and Physics (1979) R.C. Weast, ed., 59th Edition, CRC press, Boca Raton, FL.
- Eklund, B., Smith, S., and Hunt, M. (1991) Air/Superfund National Technical Guidance Study Series: Estimation of air impacts for air stripping of contaminated water, EPA-450/1-91-002, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Gholson, A.R., Storm, J.F., Jayanty, R.K.M., Fuerst, R.G., Logan, T.J., and Midgett, M.R. (1989) Evaluation of canisters for measuring emissions of volatile organic air pollutants from hazardous waste incineration. J. Air Waste Manage. Assoc., 39, 1210-1217.
- Gholson, A.R., Jayanty, R.K.M., and Storm, J.F. (1990) Evaluation of aluminum canisters for the collection and storage of air toxics. Anal. Chem., 62, 1899-1902.
- Hine, J. and Mookerjee, P.K. (1975) The intrinsic hydrophilic character of organic compounds, correlations in terms of structural contributions, J. Org. Chem., 40, 292-298.
- Holdren, M., Rust, S., Smith, R., and Koetz, J. (1984) Evaluation of cryogenic trapping as a means for collecting organic compounds in ambient air. Final report to U.S. Environmental Protection Agency, Contract No. 68-02-3487, Work Assignment 22, prepared by Battelle, Columbus, OH.

Holdren, M.W., Matthews, M.C., Orban, J.E., and Smith, D.L. (1991) Stability of volatile organic compounds in Summa polished canisters. Final report to U.S. Environmental Protection Agency, Contract No. 68-D0-0007, Work Assignment 2, prepared by Battelle, Columbus, OH.

Holdren, M.W., Skarpness, B.O., Strauss, W.J., and Keigley, G.W. (1994) Effectiveness of Silcosteel treatment of canisters. Final report to U.S. Environmental Protection Agency, Contract No. 68-D0-0007, Work Assignment 45, Task 3, prepared by Battelle, Columbus, OH.

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M. 1991 Handbook of Environmental Degradation Rates, ISBN-0-8371-358-3, Lewis Publishers, Chelsea, MI.

Jayanty, R.K.M. (1989) Evaluation of sampling and analytical methods for monitoring toxic organics in air. Atmos. Environ., 23, 777-782.

Jones, D.L. and Bursey, J. (1992) Simultaneous control of PM-10 and Hazardous Air Pollutants, II: Rationale for selection of Hazardous Air Pollutants, II: Rationale for selection of Hazardous Air Pollutants as potential particulate matter, EPA-452/R-93/012, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Keith, L.H. and Walker, M.M. (1992) EPA's Clean Air Act Air Toxics Database. Volume I: Air Toxics Chemical and Physical Properties, ISBN-0-87371-819-4, Lewis Publishers, Boca Raton, FL.

Keith, L.H. and Walker, M.M. (1993) EPA's Clean Air Act Air Toxics Database. Volume II: Air Toxics Chemical and Physical Properties, ISBN-0-87371-820-8, Lewis Publishers, Boca Raton, FL.

Kelly, T.J., Callahan, P.J., Pleil, J.D., and Evans, G.E. (1993) Method development and field measurements for polar volatile organic compounds in ambient air. Environ. Sci. Technol., 27, 1146-1153.

Kelly T.J., R. Mukund, Gordon, S.M., and Hays, M.J. (1994) Ambient measurement methods and properties of the 189 Title III Hazardous Air Pollutants. Final report to the U.S. Environmental Protection Agency, Contract No. 68-D0-0007, Work Assignment 44, prepared by Battelle, Columbus, OH, March 1994.

MacKay, D. and Shiu, W-Y. (1981) A critical review of Henry's law constants for chemicals of environmental interest, J. Phys. Chem. Ref. Data, 10, 1175-1199.

Mackay, D., Shiu, W.Y., and Ma, K.C. (1993) Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume III: Volatile Organic Chemicals, ISBN-0-83731-973-5, Lewis Publishers, Chelsea, MI.

McClenny, W.A., Pleil, J.D., Evans, G.F., Oliver, K.D., Holdren, M.W., and Winberry, W.T. (1991a) Canister-based method for monitoring toxic VOCs in ambient air. J. Air Waste Manage. Assoc., 41, 1308-1318.

McClenny, W.A., Evans, G.F., Oliver, K.D., Daughtrey, E.H., Jr., Winberry, W.T., Jr., and Decker, D.L. (1991b) Status of VOC methods development to meet monitoring requirements for the Clean Air Act Amendments of 1990. In Measurement of Toxic and Related Air Pollutants, proceedings of the 1991 EPA/AWMA International Symposium, Report No. EPA/600/9-91/018, publication number VIP-21, Air and Waste Management Association, Pittsburgh, PA, pp. 367-374.

Merrill, R.G., Jr., and Zapkin, M.A. (1991) Application of canister sampling and analysis methodology to volatile polar organic compounds. In Measurement of Toxic and Related Air Pollutants, proceedings of the 1991 EPA/AWMA International Symposium, Report No. EPA/600/9-91/018, publication number VIP-21, Air and Waste Management Association, Pittsburgh, PA, pp. 602-606.

Oliver, K.D., Pleil, J.D., and McClenny, W.A. (1986) Sample integrity of trace level volatile organic compounds in ambient air stored in Summa polished canisters. Atmos. Environ., 20, 1403-1411.

Oliver, K.D. (1993) Sample integrity of trace level polar VOCs in ambient air stored in summa-polished canisters. Technical Note TN-4420-93-03, submitted to U.S. EPA under Contract No. 68-D0-0106, by ManTech Environmental Technology, Inc., Research Triangle Park, NC.

Parmar, S.S. (1991) A study of holding times for H<sub>2</sub>S, COS, and CH<sub>3</sub>SH samples (gas phase) in different containers. In Measurement of Toxic and Related Air Pollutants, proceedings of the 1991 EPA/AWMA International Symposium, Report No. EPA/600/9-91/018, publication number VIP-21, Air and Waste Management Association, Pittsburgh, PA, pp 544-551.

Pate, B., Jayanty, R.K.M., Peterson, M.R., and Evans, G.F. (1992) Temporal stability of polar organic compounds in stainless steel canisters, J. Air Waste Manage. Assoc., 42, 460-462.

Sansone, E.B., Tewari, Y.B., and Jonas, L.A. (1979) Prediction of removal of vapors from air by adsorption on activated carbon. Environ. Sci. Technol., 13, 1511-1513.

Spicer, C.W., Pollack, A.J., Kelly, T.J., and Mukund, R. (1993) A literature review of atmospheric transformation products of Clean Air Act Title III Hazardous Air Pollutants, Final Report to U.S. Environmental Protection Agency, Contract No. 68-D80082, Battelle, Columbus, OH.

Verschueren, K. (1983) Handbook of Environmental Data on Organic Chemicals, Van

Nostrand Reinhold Company, New York.

Weber, R.C., Parker, P.A., and Bowser, M. (1981) Vapor pressure distribution of selected organic chemicals, EPA-600/2-81/021, U.S. Environmental Protection Agency, Cincinnati, OH.

Westberg, H.H., Holdren, M.W., and Hill, H.H., Jr. (1981) Analytical methodology for the identification and quantification of vapor phase organic pollutants. Final report to the Coordinating Research Council, Project No. CAPA-11-71, prepared by Washington State University, Pullman, WA.

Winberry, W.T., Jr., Murphy, N.T., and Riggin, R.A. (1988) Method TO-14. In Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Report No. EPA-600/4-89-017, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Yaws, C., Yang, H-C., and Pan, X. (1991) Henry's law constants for 362 organic compounds in water, Chem. Eng., pp 179-185, November.

**TECHNICAL REPORT DATA**  
(Please read instructions on the reverse before completion)

1. REPORT NO. EPA/600/A-94/239		2.	3. R
4. TITLE AND SUBTITLE Applicability of Canister Sampling for Hazardous Air Pollutants		5. REPORT DATE	
7. AUTHOR(S) T.J. Kelly and M.W. Holdren, Battelle, Columbus, OH		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Laboratories 505 King Avenue Columbus, OH 43201.		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO.	
		13. TYPE OF REPORT AND PERIOD COVERED	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT <p>→ The report evaluates the applicability of sampling with evacuated canisters for volatile organic compounds listed among the 189 Hazardous Air Pollutants (HAPs) in the 1990 US Clean Air Act Amendments. Nearly 100 HAPs have sufficient vapor pressure to be considered volatile compounds. Of those volatile organic HAPs, 52 have been tested previously for stability during storage in canisters. The published HAP stability studies are reviewed, illustrating that for nearly all of the 52 HAPs tested, canisters are an effective air sampling approach. However, the published stability studies used a variety of canister types and test procedures, and generally considered only a few compounds in a very small set of canisters. → A comparison of chemical and physical properties of the HAPs has been conducted, to evaluate the applicability of canister sampling for other HAPs, for which canister stability testing has never been conducted. Of 45 volatile HAPs never tested in canisters, this comparison identifies 9 for which canister sampling should be effective, and 17 for which canisters are not likely to be effective. For the other 19 HAPs, no clear decision can be reached on the likely applicability of canister sampling.</p>			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC		19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
		20. SECURITY CLASS (This paper) UNCLASSIFIED	22. PRICE