

Stability of Trace-Level Volatile Organic Compounds Stored in Canisters and Tedlar bags

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Fifty-six volatile organic compounds (VOCs), known to be ozone precursors, were stored in three media (SUMMA and Silocan canisters and Tedlar bags) to evaluate their stability in these storage media. An analysis of samples of air followed the procedures described in the US EPA Method TO-15, and was performed using gas chromatograph (GC) equipped with a mass spectrometer (MS). The first-order decay model matched 87 % of the observations. These 56 VOCs were classified into four groups-alkanes, alkenes, aromatics and biogenics. Alkenes and biogenics exhibited lower recovery rates than those of alkanes and aromatics. After a seven-day (7-d) storage period, 87 % of alkenes could be recovered from canister storage and 82 % were recovered from Tedlar bag storage. Isoprene, a major component in biogenic VOCs, exhibited a recovery rate of only 75 ± 8 % after storage for seven days in canisters and Tedlar bags. Storage conditions (humidity and temperature) affected the degradation constant of each VOC. The calculated average half-lives of 56 VOCs for SUMMA canisters, Silcocan canisters, and Tedlar bags were 45 ± 6 , 52 ± 6 , and 37 ± 4 days, respectively. The VOCs stored in Tedlar bags had a lower recovery than those stored in canisters.

Keywords: air samples, chromatography, mass spectrometry, first-order decay, recovery

1. Introduction

Many diverse media are used for collecting gaseous or whole air samples, including for example, stainless steel canisters and Tedlar bags. Different analytical methods may require different sampling media. The Compendium Method TO-14 targets 41 VOCs (U.S. EPA, 1988). These compounds have been successfully stored in canisters over periods of several days to months at ppbv (parts per billion by volume) levels. Method

TO-15 (U.S. EPA, 1997) is used to measure 97 VOCs that represents 189 hazardous air pollutants (HAPs) listed in the Clean Air Act Amendment of 1990. Method TO-14 has been used to measure non-polar VOCs, while TO-15 is used for both non-polar and polar VOCs. The stability of several compounds to which Method TO-15 applies, has been evaluated under different storage conditions. The loss of VOCs may be due to the physical adsorption of VOCs on canister walls, the dissolution of VOCs in water condensed in the canisters, chemical reaction, hydrolysis and biological degradation (Coutant, 1993).

To support calibration and performance audits, the stability of 39 and 34 VOCs in compressed gas cylinders was determined from 1 ppbv to 10 ppmv

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(parts per million by volume) and 5 to 700 ppmv, respectively (Jayanty et al; 1992). The results indicate that the concentrations of several VOCs varied by under 10 % over several months, but that several compounds were found to be unstable at the ppbv or even the ppmv level. The unstable compounds at the ppbv level were ethylene oxide, propylene oxide and trans 1,4-dichloro-2-butene. Six other compounds were found to be unstable in compressed gas cylinders at the ppm level (aniline, cyclohexane, p-dichlorobenzene, ethylamine, 1,2-dibromoethylene, and formaldehyde). A review of the literature on the stability of 52 HAPs stored in stainless steel canisters showed that canister stability data were widely variable for a dozen compounds (Kelly and Holdren, 1995). The stability of 194 compounds stored in SUMMA® canisters at the ppbv level was examined (Brymer et al, 1996). Although the concentrations of 168 of the 194 compounds studied did not change, a few of the compounds studied including methyl mercaptan, ethyl mercaptan, butyl mercaptan, dimethyl acetal and bis ether) exhibited high variability, low recovery or poor storage stability. Seven aldehydes and four terpenes stored in SUMMA® canisters were recovered at concentrations of 3-5 ppbv (Batterman et al., 1998). The concentrations of all terpenes and most aldehydes decreased markedly during the first hour. On the 16th day, the recovery of most compounds was reduced to 50% of the initial concentration.

An alternative method for collecting air samples involves Tedlar bags. Tedlar bags are used according to EPA Method 18 for measuring the emission of VOCs from high-concentration process streams (U.S. EPA, 1993). The bags are made of a chlorinated substance and are resistant to corrosion by most solvents and chemicals. However, some VOCs have been reported to degrade significantly. (For example, 70 % of methanol degrades after being stored in 10L Tedlar bags for 6 hrs and ethylbenzene and o-xylene degrades to 13% and

11% concentrations, respectively after 2 days) (Lipari, 1990). In contrast, methanol and formaldehyde stored in 60L Tedlar bags tend to degrade slowly (Andino and Butler, 1991), apparently because they have a smaller surface-to-volume ratio than other substances.

The accuracy, convenience and flexibility of canister or bag sampling can yield useful results in several contexts. This study extends previous studies on stability of compounds in storage, by assessing the storage stability of 56 VOCs (referred to as ozone precursors) stored in SUMMA® canisters, Silcocan canisters and Tedlar bags. The recovery rates at two temperatures and two humidity conditions, were compared to determine the performance of each method of storage.

2. Materials and Methods

The research included the preparation and storage of these 56 VOCs. These 56 VOCs are classified into four categories-alkanes, alkenes, aromatics and biogenics. Table 1 lists 56 VOCs along with their CAS numbers, boiling points, method detection limits (MDL), and whether they are listed in EPA Methods TO-14 and TO-15. Only nine of these 56 compounds have been evaluated in EPA Methods. The effects of two RHs (30 and 90 percent) and two temperatures (25 and 35 °C) on the stability of the stored compounds were investigated. Triplicate samples were used. VOCs were prepared at ppbv levels (5-30 ppbv) and stored in 6L sampling media, including 12 SUMMA® canisters (Anderson Samplers Inc., Atlanta, GA), 12 Silcocan® canisters (RESTEK Co., Bellefonte, PA) and 12 6L Tedlar bags (SKC Inc., Eighty Four, PA). According to the manufacturer's information, the interior of each SUMMA® canister was subjected to an electropolishing treatment to reduce the surface adsorption of VOCs. Each silcocan® canister had been subjected to siloxane to impart resistance and

Table 1. Properties of targeted VOCs

Cat.	VOC Number	VOCs	CAS-No.	MW	BP.	TO-14A	TO-15	MDL (ppb)	Calibration R ²
Alkenes	1	1-Butene	106-98-9	56.1	-6.25			0.4	0.995
	2	trans-2-Butene	624-64-6	56.1	1.0			0.4	0.998
	3	cis-2-Butene	590-18-1	56.1	3.7			0.6	0.998
	4	3-Methyl-1-Butene	563-45-1	70.1	20.0			0.4	0.995
	5	1-Pentene	109-67-1	70.1	30.0			0.6	0.997
	6	trans 2-Pentene	646-04-8	70.1	36.0			0.5	0.997
	7	cis 2-Pentene	627-20-3	70.1	37.0			0.6	0.999
	8	2-Methyl-2-Butene	513-35-9	70.1	35.0			0.5	1.000
	9	Cyclopentene	142-29-0	68.1	68.1			0.4	0.995
	10	4-Methyl-1-Pentene	691-37-2	84.2	53.0			0.3	0.999
	11	2-Methyl-1-Pentene	763-29-1	84.2	53.0			0.4	0.996
	12	trans-2-Hexene	4050-45-7	84.2	62.0			0.7	0.998
	13	cis-2-Hexene	7688-21-3	84.2	62.0			0.5	0.998
Alkanes	14	Isobutane	75-28-5	58.1	-12.0			0.5	0.995
	15	n-Butane	106-97-8	58.1	-0.5			0.5	0.998
	16	Isopentane	78-79-5	72.0	34.0			0.5	0.998
	17	n-Pentane	109-66-0	72.2	36.0			0.6	0.999
	18	2,2-Dimethylbutane	75-83-2	86.2	50.0			0.4	0.999
	19	Cyclopentane	287-92-3	70.1	49.5			0.5	0.995
	20	2,3-Dimethylbutane	79-29-8	86.2	57.9			0.6	0.999
	21	2-Methylpentane	107-83-5	86.2	60.0			0.4	0.999
	22	3-Methylpentane	96-14-0	86.2	63.0			0.5	0.996
	23	n-Hexane	110-54-3	100.0	69.0			0.6	0.999
	24	Methylcyclopentane	96-37-7	84.2	72.0			0.6	0.995
	25	2,4-Dimethylpentane	108-08-7	100.2	81.0			0.5	0.999
	26	Cyclohexane	110-82-7	84.2	81.0			0.7	0.997
	27	2-Methylhexane	591-76-4	100.2	90.0			0.6	1.000
	28	2,3-Dimethylpentane	565-59-3	100.2	90.0			0.5	0.995
	29	3-Methylhexane	589-34-4	100.2	100.0			0.4	1.000
	30	2,2,4-TMP	540-84-1	114.2	99.0		x	0.5	0.996
	31	n-Heptane	142-82-5	100.2	98.0			0.5	0.999
	32	Methylcyclohexane	108-87-2	98.2	101.0			0.5	0.995
	33	2,3,4-TMP	565-75-3	114.2	112.0			0.6	1.000
34	2-Methylheptane	592-27-8	114.2	118.0			0.6	0.995	
35	3-Methylheptane	589-81-1	114.2	119.0			0.5	0.999	
36	n-Octane	111-65-9	114.0	126.0			0.5	0.998	
37	n-Nonane	111-84-2	138.0	151.0			0.6	0.998	
Aromatics	38	Benzene	71-43-2	78.1	80.0	x		0.4	0.997
	39	Toluene	108-88-3	92.1	110.6	x		0.6	0.999
	40	Styrene	100-42-5	104.2	145.2	x		0.4	1.000
	41	Ethylbenzene	100-41-4	106.2	136.0	x		0.5	0.995
	42	m,p-Xylene	108-33-3/106-42-3	106.2	138.5			0.7	0.998
	43	o-Xylene	95-47-6	106.2	144.4	x		0.6	0.998
	44	Isopropylbenzene	98-82-8	120.2	152.4		x	0.7	1.000
	45	n-Propylbenzene	103-65-1	120.2	159.0			0.5	0.998
	46	1,3,5-TMB	108-67-8	120.2	165.0	x		0.6	0.999
	47	1,2,4-TMB	95-63-6	120.2	169.0	x		0.5	1.000
Biogenics	48	Isoprene	78-79-5	68.1	34.0			0.5	0.999
	49	alpha-Pinene	80-56-8	136.2	155.5			0.5	0.997
	50	beta-Pinene	127-91-3	136.2	164.0			0.5	0.999
	51	Methacrolein	78-85-3	70.1	68.4			0.7	0.996
	52	Hexanal	110-54-3	100.0	128.6			0.5	0.998
	53	2-Heptanone	110-43-0	114.0	151.5			0.6	0.996
	54	p-Cymene	99-87-6	134.0	176.5			0.4	0.998
	55	1-Decene	872-05-9	140.0	172.0			0.6	0.999
	56	1-Dodecene	112-41-4	168.0	213.0			3.8	0.995

MW: molecule weight (g); BP: boiling point (°C); TMP: trimethylpentane; TMB: trimethylbenzene

improve sample-wetting characteristics. The TO-14 canister cleaning procedure consisted of repeated cycles of pressurization with humidified zero air, followed by evacuation to 0.1 torr for 1h, with heating to 120 °C. Each canister was first filled with humidified zero air and analyzed by the procedure described below to determine its cleanliness.

Samples prepared according to the procedures of Batterman et al. (1998). Clean evaluated canisters were humidified by injecting 69 µl and 207 µl of HPLC-grade water and then filled with dry zero air to near atmospheric pressure, to make up 30 and 90% RH at 25 °C, respectively. Volumes of 108 µl and 323 µl of HPLC-grade water were injected into clean evaluated canisters to yield 30 and 90 % RH at 35 °C, respectively. The samples thus prepared were stored in an oven to maintain the target temperature.

Organic compounds were prepared using a gas standard (Environ-Mat Ozone Precursor Mixture, Matheson Gas Products, Georgia, USA) and biogenic compounds were prepared using a liquid standard (Supelco, PA, USA). The gas sample was diluted with dry zero air in Tedlar bags and then transferred into stainless steel canisters. Liquid samples were diluted in methanol. Then, the mixture was injected into Tedlar bags and canisters, with proper dilution. All samples thus prepared were heated using an infrared lamp to keep VOC in the vapor phase. Most samples were prepared at concentrations (5 to 30 ppbv) similar to ambient levels. All Tedlar bags were kept in black bags to prevent photochemical reactions.

The procedures described in Method TO-15 were followed to analyze the samples. Samples of air were concentrated cryogenically using a preconcentrator (7100, Entech Instrument, Inc., CA) and transferred by a heated transfer line and a cryofocus unit to a gas chromatograph (GC) (5890 Series plus, Hewlett Packard, Palo Alto, CA). The flow of a 400ml sample of air was metered by a mass-flow-controlled meter (Sierra Instrument

Inc., Monterey, CA). The GC used a HP-1 60m capillary column (0.25-mm diameter x 1.8-µm film thickness, Hewlett Packard) and nitrogen as the carrier gas. VOCs were detected by mass-spectrometry (MS) (Model 5972, Hewlett Packard). The MS scanned a wide range of mass to charge ratios (40-200). A PC workstation (G1034C Chemstation, Hewlett Packard) was used to acquire and manipulate data. The starting temperature in the GC oven was 10 °C and was maintained for 3 min. The temperature was then increased at 8 °C per min to 130 °C, at which it was maintained for 5 min. Subsequently, the temperature was increased at 5 °C per min to 180 °C, at which it was maintained for 5 minutes.

Quality control and quality assurance requirements involved establishing GC retention times, calibration curves and MDLs, as well as studying the reproducibility of the results for all compounds analyzed. Furthermore, an internal standard (toluene-d8) was used for each analysis to verify the stability of the MS. Additionally, cyclohexanal-d12 was analyzed daily as a reference standard for determining the performance of the instruments used. A response deviation of more than 15% resulted in full instrument recalibration. Good results were achieved. Table 1 shows MDL and linearity coefficient (R²) for each VOC. Triplicate samples were prepared and analyzed, so the reported concentrations are the average measured concentrations of the compounds.

3. Results and Discussion

This study has investigated at two humidity levels (30 and 90%) and two temperatures (25 and 35 °C), representative of environmental conditions in Taiwan island affect the stability and recovery of stored compounds. Thus, four storage conditions, as determined by temperature and RH, (25 °C, 30 percent RH), (35 °C, 30 percent RH), (25 °C, 90 percent RH) and (35 °C, 90 percent RH), were

Table 2. Correlation coefficients ($R^2 > 0.7$) for 1st order decay under four storage conditions.

Cat.	VOC NB	VOCs \ (T, RH)	Summa C1				Silcocon C2				Tedlar Bags (TB)			
			(25,30)	(35,30)	(25,90)	(35,90)	(25,30)	(35,30)	(25,90)	(35,90)	(25,30)	(35,30)	(25,90)	(35,90)
Alkenes	1	1-Butene	0.73	0.87	0.80	0.90		0.92	0.89	0.93	0.93	0.86	0.98	0.75
	2	trans-2-Butene	0.74	0.87	0.80	0.80	0.74	0.89	0.83	0.90	0.75	0.95	0.89	0.90
	3	cis-2-Butene	0.75	0.93	0.86	0.77		0.82	0.91	0.89	0.88	0.89	0.98	0.83
	4	3-M-1-Butene	0.87	0.83	0.78		0.77	0.75	0.72	0.72	0.72	0.86	0.92	0.85
	5	1-Pentene	0.92	0.82	0.75	0.97	0.85	0.73	0.73			0.71	0.85	0.96
	6	Trans 2-Pentene	0.92	0.92	0.72	0.97	0.73	0.88		0.75	0.93	0.82	0.94	0.88
	7	cis 2-Pentene	0.98	0.94	0.92	0.74	0.92	0.92		0.92	0.77	0.85	0.94	0.92
	8	2-M-2-Butene		0.88	0.71	0.70	0.83	0.71	0.87		0.89	0.92	0.93	0.94
	9	Cyclopentene				0.93	0.71	0.71	0.81	0.92	0.81	0.89	0.93	0.79
	10	4-M-1-Petene	0.84		0.82	0.86	0.74	0.91	0.93	0.86	0.96	0.85	0.89	0.86
	11	2-M-1 Petene	0.88	0.95		0.77	0.87	0.90	0.90	0.71	0.94	0.92	0.88	0.92
	12	Trans-2-Hexene	0.93	0.72		0.83	0.95		0.95	0.70	0.72	0.82	0.92	0.89
	13	cis-2-Hexene			0.78	0.85	0.83	0.96	0.88	0.95	0.89	0.88	0.89	0.85
Alkanes	14	Isobutane	0.95	0.80	0.82	0.96	0.92	0.93	0.94	0.86	0.88	0.72	0.85	0.88
	15	n-butane	0.72	0.72	0.77	0.93		0.81	0.89	0.82	0.90	0.83	0.98	0.81
	16	Isopentane	0.78		0.90	0.80	0.88	0.81		0.91	0.91		0.93	0.81
	17	n-Pentane	0.89			0.92	0.71		0.93	0.73	0.88		0.71	0.74
	18	2,2-DM-butane	0.77	0.90		0.91	0.72		0.87	0.85	0.84		0.83	0.89
	19	Cyclopentane	0.85	0.61	0.93	0.94		0.89	0.80	0.84	0.96	0.81	0.88	0.93
	20	2-M-pentane	0.71	0.79	0.74	0.82	0.94	0.81	0.80	0.94	0.74	0.91	0.86	0.86
	21	3-M-pentane	0.90	0.85	0.72		0.87	0.77		0.90	0.83	0.83	0.95	0.83
	22	2,3-DM-butane	0.81				0.90	0.85	0.72	0.94	0.74	0.91	0.92	0.78
	23	n-Hexane		0.75		0.82	0.95		0.72	0.72		0.87	0.89	
	24	M-cyclo-P	0.73	0.72	0.73	0.86	0.95		0.90	0.82	0.81	0.75	0.70	0.78
	25	2,4-DMP	0.88	0.71		0.90	0.91		0.83	0.71	0.72	0.80	0.83	0.87
	26	Cyclohexane		0.72		0.93	0.94		0.90	0.75		0.85	0.88	0.87
	27	2-M-hexane	0.98	0.70	0.71	0.83	0.95	0.90	0.86	0.90		0.92	0.82	0.92
	28	3-M-hexane	0.95	0.72	0.76	0.83	0.94		0.90	0.73		0.90	0.93	0.88
	29	2,3-DMP	0.88	0.93	0.80		0.81		0.89	0.92	0.87	0.81	0.88	0.91
	30	2,2,4-TMP	0.93			0.93	0.81	0.77	0.82	0.83	0.94	0.89	0.87	0.85
	31	n-Heptane	0.93	0.74	0.80	0.84	0.74	0.83	0.92	0.73	0.87	0.92	0.81	0.86
	32	M-cyclohexane	0.86			0.89	0.76	0.82	0.97	0.79		0.85	0.81	0.90
	33	2,3,4- TMP	0.93	0.92		0.77	0.87	0.81	0.97	0.81	0.78	0.93	0.88	0.92
	34	2-M-heptane	0.80	0.82		0.86	0.78	0.90	0.86	0.69	0.87	0.79	0.86	0.89
	35	3-M-heptane	0.86	0.71	0.79	0.88	0.95	0.73	0.77	0.73		0.89	0.92	0.71
	36	n-Octane	0.92	0.90		0.93	0.80	0.71	0.88	0.75	0.84	0.87	0.81	0.95
	37	n-Nonane	0.75	0.87	0.74	0.91	0.87	0.84	0.80	0.69	0.89	0.89	0.86	0.89
Aromatics	38	Benzene	0.96		0.83	0.91	0.87	0.78	0.81	0.97	0.91	0.91	0.96	0.92
	39	Toluene	0.74		0.71	0.98	0.86	0.85	0.72	0.86	0.76	0.90	0.81	0.93
	40	Styrene	0.82	0.90	0.85	0.93	0.86	0.75	0.91	0.91	0.86	0.91	0.77	0.93
	41	Ethylbenzene	0.96	0.86	0.90	0.95	0.83		0.87	0.88	0.83	0.94	0.87	0.89
	42	m,p-Xylene	0.82	0.85	0.95	0.88	0.87	0.83	0.80	0.87	0.91	0.96	0.91	0.92
	43	o-Xylene	0.91	0.93	0.92	0.90	0.89	0.74	0.78	0.79	0.87	0.95	0.74	0.96
	44	Isopropyl-B	0.96	0.88	0.74	0.76	0.88				0.97	0.94	0.88	0.96
	45	n-Propyl-B	0.89		0.85		0.87		0.97	0.74	0.96	0.93	0.90	0.89
	46	1,3,5-TMB	0.94	0.85	0.94		0.82		0.83	0.78	0.94	0.94	0.95	0.92
	47	1,2,4-TMB	0.85	0.83	0.85				0.73	0.76	0.85	0.94	0.91	0.93
Biogenics	48	Isoprene	0.99	0.88	0.75	0.87		0.88	0.90	0.71	0.74	0.74	0.70	
	49	Alpha-Pinene	0.85	0.90	0.79	0.91	0.83		0.82	0.77	0.83	0.86	0.89	0.88
	50	beta-piene	0.94	0.82	0.85	0.74	0.72	0.86	0.92		0.70	0.90	0.97	0.96
	51	Methacrolein	0.79	0.82	0.77		0.67		0.74	0.70	0.96	0.87	0.86	
	52	Hexanal	0.81			0.74	0.75		0.85	0.82	0.81	0.96	0.82	0.96
	53	2-Heptanone	0.82	0.79				0.77	0.72	0.94	0.94	0.95	0.88	0.84
	54	p-Cymene		0.76	0.76	0.82	0.88	0.89	0.85	0.73	0.86	0.94	0.86	0.91
	55	1-Decene	0.94	0.87		0.88	0.86	0.76	0.79	0.78	0.92	0.92	0.89	0.94
	56	1-Dodecene	0.88	0.90		0.81	0.83		0.73		0.77	0.96	0.90	0.96

RH: relative humidity (%), B: benzene, M: methyl, DM: dimethyl, TM: trimethyl, B: butane, P: pentane, NB:VOC number

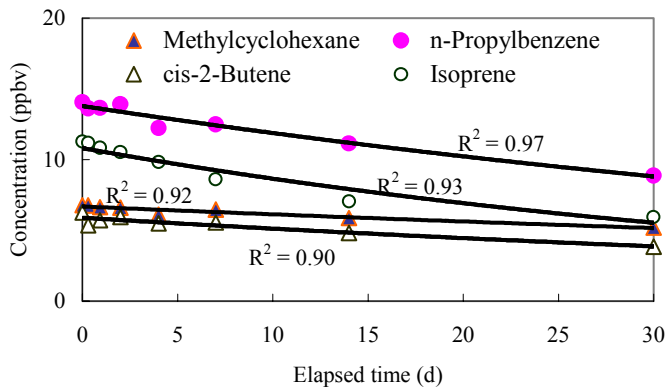


Figure 1. Concentration against time on a semi-log plot.

considered. The first-order decay model of VOC recovery from sampling media may be applicable to most compounds. The first-order decay model is expressed as

$$C_t / C_0 = \exp(-k t) \quad (1)$$

where C_0 represents the initial concentration; C_t is VOC concentration at a storage time of t (d), and k is the degradation constant (d^{-1}). The ratio of C_t to C_0 in Eq.1 is defined as the recovery rate, which is typically used to evaluate the stability of compounds stored in the containers over a certain period. Figure 1 shows typical VOC recovery variations with time for one compound in each category of VOCs. Recoveries refer to the initial analysis of each canister, and are averaged across the three sets of samples. Table 2 summarizes the correlation coefficients for fitting the first-order decay model under the four storage conditions. Clearly, several compounds have relatively high R^2 values. Observations of R^2 below 0.7 were excluded from the table as the low R^2 indicated a poor fit of the first-order model. Overall, the first-order model explained 87% of the observations. Tedlar bags yielded a higher R^2 than the canisters, perhaps because the first-order model fits fast processes better, such as are supported by Tedlar bags.

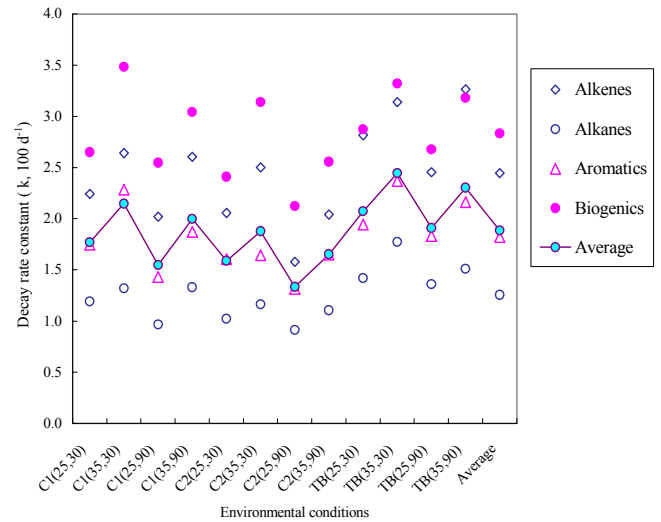


Figure 2. Decay rate constants for four categories of VOCs under various storage conditions.

3.1 First-order Decay Kinetic Constant

The first-order model of VOC decay in storage media may be valid for several compounds, at least over the period during which recoveries slowly decline. Table 3 shows the first-order degradation constants for those compounds with $R^2 > 0.7$. Low R^2 values indicate that the estimated decay kinetic constant is not significantly related to errors in the analytical determinations. The highest and lowest k values are obtained at 35 °C with 30 % RH and 25 °C at 90 % RH, respectively. The VOCs stored in Tedlar bags tend to exhibit higher k values. Samples stored in canisters at high humidity and low temperature are generally more stable than those stored in canisters at low humidity and high temperature.

For illustration, Figure 2 shows the average k values of categorized VOCs. Among the four categories of compounds, biogenics exhibit the highest k values, and alkanes the lowest; aromatic VOCs have k values close to the average k value of the 56 compounds. Since the k values of compounds stored in SUMMA® and Silcocan canisters do not statistically significantly differ, Table 4 presents the mean k values for the two kinds of canisters was tabulated, and compared

Table 3. Degradation constant (k, 100 d⁻¹) of 56 VOCs in three media for R² > 0.7

Cat.	VOC NB	VOCs \ (T, RH)	Summa C1				Silcocon C2				Tedlar Bags (TB)			
			(25,30)	(35,30)	(25,90)	(35,90)	(25,30)	(35,30)	(25,90)	(35,90)	(25,30)	(35,30)	(25,90)	(35,90)
Alkenes	1	1-Butene	1.7	2.8	2.3	1.8		2.0	1.7	2.3	3.6	4.6	2.6	2.5
	2	trans-2-Butene	2.0	2.8	2.0	2.8	1.7	2.8	1.3	2.4	2.9	3.0	3.0	3.5
	3	cis-2-Butene	1.9	3.2	1.9	1.7		1.9	1.4	2.0	3.2	3.2	3.0	4.6
	4	3-M-1-Butene	2.4	2.3	2.0		1.5	2.2	1.2	2.6	2.6	3.3	2.6	3.0
	5	1-Pentene	2.1	3.6	1.5	2.7	2.4	2.8	1.7			1.2	2.3	3.5
	6	Trans 2-Pentene	2.6	2.8	2.2	2.6	1.7	2.6		1.3	3.3	2.7	2.6	3.5
	7	cis 2-Pentene	2.9	2.5	2.3	2.3	2.9	3.0		2.0	2.9	2.6	2.6	2.7
	8	2-M-2-Butene		2.3	2.3	2.6	2.6	3.0	1.9		2.1	2.0	2.3	3.3
	9	Cyclopentene				2.0	2.8	3.3	2.0	1.7	2.3	3.3	2.0	1.9
	10	4-M-1-Petene	2.4		2.2	7.7	2.3	2.7	2.0	1.3	4.3	3.3	2.3	5.0
	11	2-M-1 Petene	2.2	2.8		2.6	1.9	2.3	1.7	2.0	2.6	2.8	2.3	3.0
	12	Trans-2-Hexene	2.1	2.2		1.7	2.0		1.9	1.9	2.8	5.3	2.3	3.5
	13	cis-2-Hexene			1.7	1.9	1.7	1.9	1.5	2.2	1.9	3.6	2.1	2.7
Alkanes	14	Isobutane	1.7	2.8	1.4	1.8	1.4	2.6	1.4	1.5	1.9	3.2	1.7	1.8
	15	n-butane	0.8	0.9	0.8	1.0		1.2	0.7	0.9	1.4	1.5	2.8	1.1
	16	Isopentane	0.9		0.9	1.0	0.7	1.4		1.3	2.3		1.0	2.0
	17	n-Pentane	1.3			1.3	0.8		0.7	1.0	1.4		1.0	1.2
	18	2,2-DM-butane	1.4	1.0		1.9	0.8		0.6	0.8	0.9		1.0	0.9
	19	Cyclopentane	1.5	1.2	0.9	1.4		1.2	0.9	1.0	2.1	1.6	1.2	1.6
	20	2-M-pentane	1.2	1.2	1.0	1.2	1.1	1.2	0.9	1.4	2.5	2.2	1.3	1.4
	21	3-M-pentane	1.5	1.2	0.8		1.1	1.1		1.0	1.1	1.9	1.9	2.0
	22	2,3-DM-butane	1.5				1.6	1.7	0.9	1.5	1.5	2.5	1.4	1.6
	23	n-Hexane		1.5		1.2	0.8		0.8	0.9		1.5	1.3	
	24	M-cyclo-P	1.0	1.5	0.9	1.2	0.9		0.9	1.0	1.1	1.2	1.7	1.3
	25	2,4-DMP	1.1	1.3		1.2	0.8		0.9	1.1	1.1	1.7	1.0	1.4
	26	Cyclohexane		1.1		1.1	0.9		0.8	1.0		1.5	1.1	1.3
	27	2-M-hexane	1.4	1.3	1.1	1.4	1.1	1.4	1.0	1.2		2.0	1.1	1.6
	28	3-M-hexane	1.2	1.2	1.2	1.2	1.1		1.0	1.1		1.7	1.2	1.4
	29	2,3-DMP	1.1	1.2	1.0		1.0		0.9	1.1	1.3	1.5	1.2	1.4
	30	2,2,4-TMP	1.2			1.3	1.2	1.1	1.0	1.1	1.5	1.9	1.2	1.6
	31	n-Heptane	1.1	1.2	1.0	1.3	0.9	1.0	0.9	0.9	1.4	2.2	1.4	1.9
	32	M-cyclohexane	1.0			1.2	1.0	1.1	0.9	1.0		1.6	1.1	1.3
	33	2,3,4- TMP	1.2	1.3		1.2	1.1	1.1	0.9	0.9	1.3	1.8	1.5	1.7
34	2-M-heptane	1.1	1.2		1.2	1.1	1.2	1.0	1.1	1.7	1.7	1.3	1.7	
35	3-M-heptane	1.4	1.4	1.1	1.5	1.2	1.3	1.0	1.3		1.4	1.2	1.2	
36	n-Octane	1.2	1.3		1.3	1.2	1.2	1.1	1.1	1.5	1.9	1.4	1.7	
37	n-Nonane	1.3	1.5	1.7	1.7	1.2	0.9	1.0	1.1	1.4	1.8	1.7	1.7	
Aromatics	38	Benzene	1.2		1.0	1.4	1.0	0.9	0.9	1.1	1.1	1.3	1.2	1.3
	39	Toluene	1.3		1.1	1.4	1.2	1.3	1.0	1.1	1.1	1.7	1.3	1.9
	40	Styrene	1.7	3.3	1.9	2.1	2.3	2.2	1.5	2.0	2.5	3.3	2.2	2.4
	41	Ethylbenzene	1.6	1.7	1.3	1.6	1.2		1.1	1.4	1.8	2.0	1.7	2.0
	42	m,p-Xylene	1.9	2.0	1.5	1.8	1.6	1.7	1.4	1.7	1.9	2.5	1.4	2.1
	43	o-Xylene	1.8	2.1	1.5	1.8	1.4	1.7	1.5	1.6	1.7	2.4	1.7	2.2
	44	Isopropyl-B	1.4	1.5	0.9	1.3	1.2				1.7	1.9	1.3	1.9
	45	n-Propyl-B	1.9		1.1		1.4		1.3	1.7	2.4	2.5	2.0	2.4
	46	1,3,5-TMB	2.3	3.9	1.7		2.2		1.7	2.2	2.4	2.6	2.6	2.6
	47	1,2,4-TMB	2.3	3.5	2.2				2.0	2.5	2.8	3.5	2.9	2.9
Biogenics	48	Isoprene	3.2	5.3	3.0	4.6		7.7	2.2	3.6	3.0	5.3	3.3	
	49	Alpha-Pinene	2.2	2.5	2.1	2.4	1.9		1.8	2.2	2.5	2.6	2.3	2.5
	50	beta-piene	2.0	2.4	1.9	2.2	1.9	2.0	1.7		2.8	3.0	2.3	3.0
	51	Methacrolein	3.3	3.5	3.2		3.5		3.0	3.2	3.6	3.6	3.6	
	52	Hexanal	2.9			3.5	3.2		2.7	2.8	3.5	3.6	3.2	3.5
	53	2-Heptanone	3.6	4.1				3.3	2.9	3.9	3.5	3.9	3.3	3.9
	54	p-Cymene		2.4	2.1	2.4	1.9	2.4	1.5	1.7	2.2	2.2	1.7	1.7
	55	1-Decene	2.1	2.2		2.2	1.6	1.6	1.4	1.3	2.4	2.7	1.8	2.9
	56	1-Dodecene	2.8	3.3		3.0	2.2		1.8		2.5	3.0	2.6	2.8

RH: relative humidity (%), B: benzene, M: methyl, DM: dimethyl, TM: trimethyl, B: butane, P: pentane, NB:VOC number.

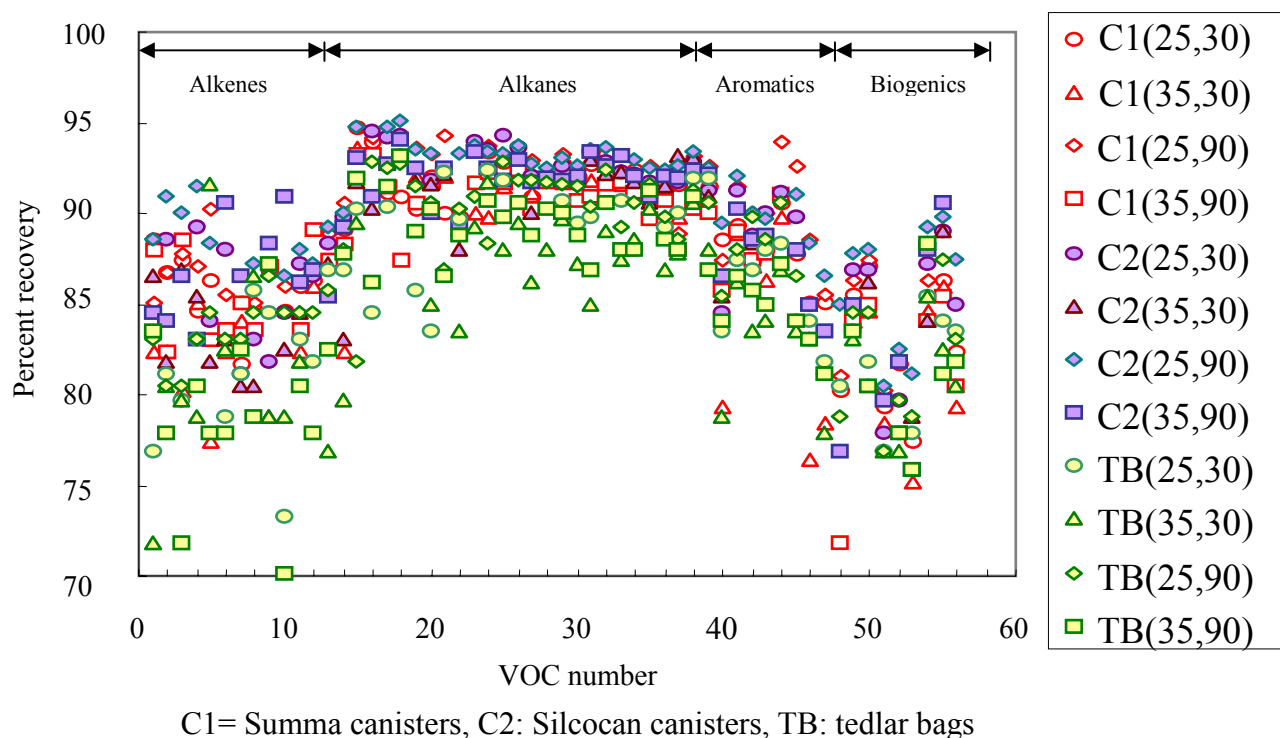


Figure 3. Recovery rates of 56 VOCs under various storage conditions after seven days

them with those obtained for Tedlar bags under the four storage conditions. The effect of humidity on the stability of samples has been reported elsewhere (MacClenny et al., 1991; Batterman et al., 1998): water vapor promotes sample stability because it fills active adsorption sites on the canister's interior surface, reducing the adsorption of VOCs.

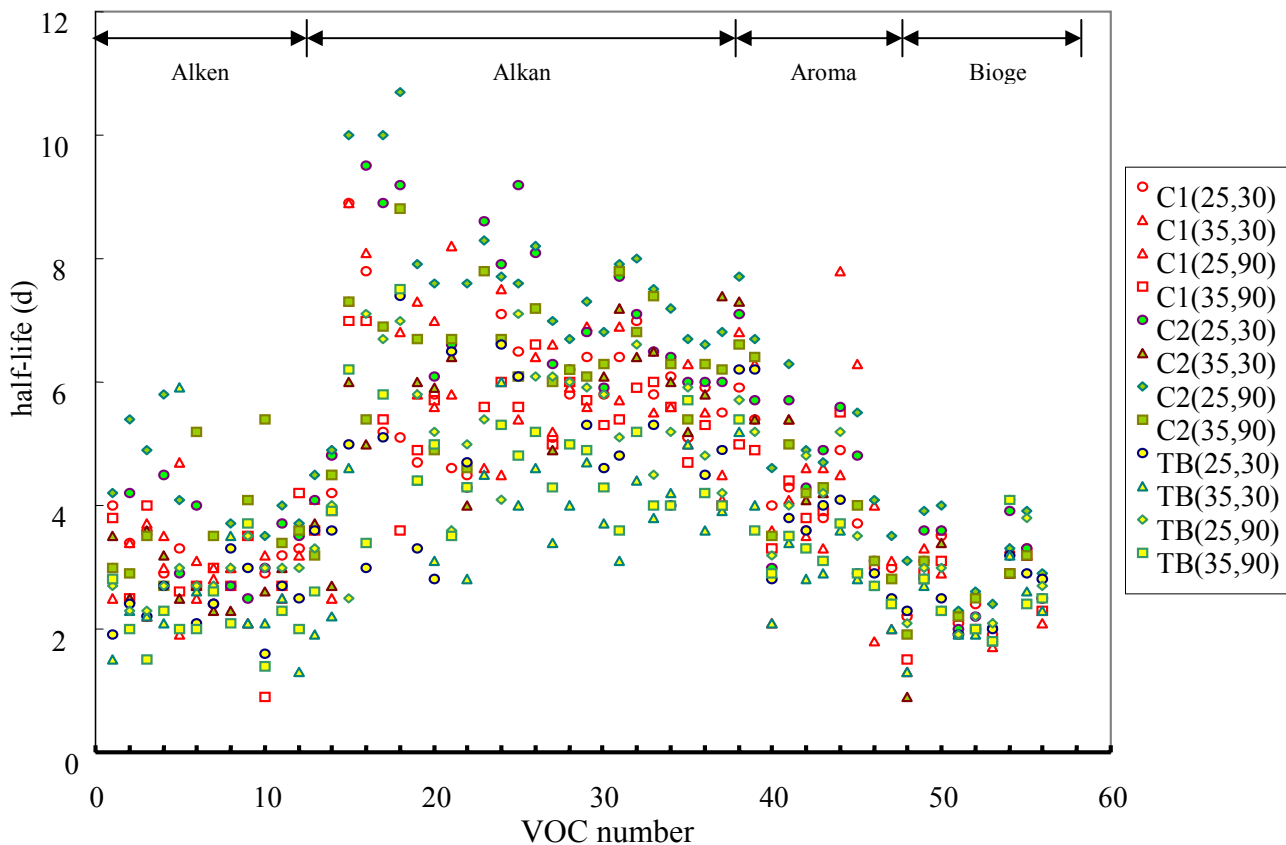
3.2 7-day Recovery Estimates

A storage period of seven days was used for evaluating stability since this is the period typically required to complete collection, transportation and analysis of such samples. Recoveries are obtained from the initial analysis of each sample, and are averaged across the three samples. The decay kinetic constants in Table 3 were used to estimate the recovery of the VOCs with $R^2 > 0.7$. The results shown in Fig. 3 show that the recovery of each VOC varies widely among the three media (SUMMA® canister, Silcocon® canisters and

Tedlar bag). Of the four categories, the highest recovery was obtained for alkanes (middle in Fig. 3) and lowest was of biogenics. Isoprene, as one of the most importantly reactive hydrocarbons in atmospheric chemistry, with a boiling point of 34 °C, had the lowest recovery (75 ± 8 percent) rate of any of the nine biogenics evaluated in this study.

3.3 Half-life Estimates

The VOC decay kinetic constants can be further used to estimate the compound's half-lives, which are defined as the time for 50 % of the initial concentration to disappear. Figure 4 shows the calculated half-life ($\tau = 0.693/k$) of VOCs stored in three types of containers (SUMMA® canister, Silcocon canister and Tedlar bag). The half-life data summarize VOC stability, and support straightforward calculation of the maximum storage times may match daily drift expressed as, "percent change per day (U.S. EPA, 1988)". The calculated mean half-lives of 56 VOCs in SUMMA



C1=Summa canisters, C2=Silcocon canisters, TB: tedlar bags

Figure 4. Half-life of 56 VOCs under various storage conditions.

canisters, Silcocon canisters, and Tedlar bags were 45 ± 6 , 52 ± 6 and 37 ± 4 days, respectively. The half-lives could be used to calculate the maximum storage periods. However, such estimates may be too low because losses at the beginning of the storage and the effects of old or damaged canisters are neglected; rather, the estimates apply under laboratory conditions. Thus, a “safety factor” should be included, by, say, halving the estimated maximum storage time (Batterman et al., 1998).

3.4 Inter-canister Reproducibility

Reproducibility was calculated as the average coefficient of variation (COV) of concentrations measured among the three types of canisters (or bags) for each set of samples. Table 5 shows the mean COV for each of the four groups under different storage conditions. Reproducibility was in all cases between 9 and 30%. The reproducibility

during the study period COVs observed under storage conditions of high temperature and low humidity. Among the four categories, biogenic had the highest COVs.

The preconcentrator/GC/MS system used in this study appeared to meet the performance requirements of TO-14 and TO-15, using a standard calibration of $R^2 > 0.995$, meeting precision requirements within 25% (U.S. EPA, 1988 & 1997). The COVs in Table 5 incorporate both analytical uncertainties and differences among canisters. The higher uncertainties may have resulted from variations in active sites on surfaces of the sampling media, differences among the amounts of gas transferred from the highly concentrated standard, unequal pressurization of canisters and other factors (Wagoner et al., 1993).

3.5 Loss Mechanisms

Table 4. Degradation constant (k , 100 d^{-1}) of four categories VOCs under different environmental conditions.

VOCs	RH T	Canisters		Tedlar Bags	
		<u>30</u>	<u>90</u>	<u>30</u>	<u>90</u>
Alkenes	25	2.2 (0.5)	1.8 (0.3)	2.8 (0.7)	2.5 (0.3)
	35	2.6 (0.5)	2.3 (1.0)	3.1 (1.0)	3.3 (0.8)
Alkanes	25	1.1 (0.2)	1.0 (0.2)	1.4 (0.4)	1.4 (0.4)
	35	1.3 (0.4)	1.2 (0.2)	1.8 (0.5)	1.5 (0.3)
Aromatics	25	1.7 (0.5)	1.4 (0.4)	1.9 (0.6)	1.8 (0.6)
	35	2.0 (0.5)	1.8 (0.5)	2.4 (0.7)	2.2 (0.4)
Biogenics	25	2.6 (0.7)	2.4 (0.6)	2.9 (0.5)	2.7 (0.7)
	35	3.3 (1.8)	2.8 (0.9)	3.3 (0.9)	3.2 (0.9)

T: Temperature (), RH: Relative Humidity (%)

(): Standard deviation

VOC losses in canisters and Tedlar bags may proceed by several possible mechanisms. Physical adsorption is the first loss mechanism. Rapid declines in recoveries over the first few hours or days of storage are normally associated with physical adsorption, although such losses may be related to chemical reactions (U.S. EPA, 1997). Adsorption was considered as the chemical interaction of vapors on "active sites" at the canister walls (Freeman et al., 1994). The results imply that Silcoan canisters had fewer active sites and thus adsorbed less. Tedlar bags gave more active sites than canisters, and thus absorb more. A second mechanism that affects recovery is the dissolution of soluble compounds in condensed water present in the canister. As the pressure in a canister drops because of withdrawal of a sample, the quantity of condensed water falls and concentrations of dissolved compounds may thus

Table 5. Average reproducibility of four groups under for storage conditions expressed as COV in percent.

VOCs	RH T	SUMMA canisters		Silcoan canisters		Tedlar bags	
		<u>30</u>	<u>90</u>	<u>30</u>	<u>90</u>	<u>30</u>	<u>90</u>
Alkenes	<u>25</u>	18	13	17	13	21	16
	<u>35</u>	21	15	20	13	25	21
Alkanes	<u>25</u>	13	9	12	10	15	11
	<u>35</u>	15	12	14	11	16	14
Aromatics	<u>25</u>	12	9	11	9	14	12
	<u>35</u>	14	11	13	10	15	13
Biogenics	<u>25</u>	24	18	23	18	28	23
	<u>35</u>	28	21	28	22	30	25
Average		18	14	17	13	21	17

T: Temperature (), RH: Relative Humidity

increase (Coutant, 1993). This effect depends on the compound's solubility and the presence of condensed water in the canister. A third mechanism involves a gas-phase reaction and the subsequent transformation and loss of objective compounds. Such a reaction may be promoted by the presence of ozone or other reactive species.

Information available in the literature and in this study is insufficient to identify the details of the loss mechanisms. A general mechanism that affects all tested compounds is expected since compounds stored at a lower temperature are more stable and their are more reproducible, probably because the reaction rates are lower. Moreover, adding water or increasing humidity may also reduce adsorption losses of several VOCs. The low recoveries in dry canisters verify the occurrence of physical adsorption.

Those storage conditions applied in this study were limited to typical environmental conditions in the Taiwan area. Since the potential for adsorbing VOCs and water in a canister changes with temperature, recovery must be further investigated over a range of temperatures (such as 0-40 °C) and humidities, to separate out sorption losses.

4. Conclusions

Storage conditions importantly affect the decay kinetic constant of VOC mixtures. The results indicate that a stored compound exhibits a higher recovery and half-life at lower temperature and a higher RH. Most alkenes and biogenics exhibit lower recoveries and half-lives than alkanes and aromatics. Not all sampling media should be used as absolute references for mixtures of some biogenics (especially isoprene). Organic compounds stored in Silcoan canisters are slightly more stable than those stored in SUMMA® canisters, but relatively more stable than those in Tedlar bags. The short-term degradation of samples with low concentrations of VOCs cannot be ignored since sample degradation is noted early on during storage. Thus, the holding period between VOC collection and analysis should be minimized to improve the recovery of VOC mixtures.

Acknowledges

We gratefully acknowledge the financial support of the Taiwan EPA (EPA-88-SA21-03-0012 and EPA-89-FA11-03-100). This paper has not been subject to Taiwan EPA policy review and should not be construed to represent the policy of agency.

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Received for review, November 11, 2002

Accepted, June 8, 2003

AAQR-2003-03