PII:S1352-2310(97)00417-2

ANALYSIS AND STABILITY OF ALDEHYDES AND TERPENES IN ELECTROPOLISHED CANISTERS

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Abstract –Aldehydes and terpenes are important classes of polar VOC contaminants for which few sampling and analysis methods have been validated. This study reports on the analysis, stability and recovery of seven aldehydes (butanal, pentanal, hexanal, heptanal, octanal, nonanal and benzaldehyde) and four terpenes (α-pinene, β-pinene, limonene and 3-carene) prepared at trace levels (3-5 ppb) and stored in electropolished stainless-steel canisters. Humidified air, humidified N_2, and dry air were used to dilute three sets of canisters. A series of samples was withdrawn from each canister over a period of 16 days, and concentrations were determined by cryogenic preconcentration, gas chromatography and mass spectrometry. The VOCs were easily separated, but butanal and pentanal had high detection limits relative to the other compounds. While measurements were reproducible, concentrations decreased considerably in the first hour (19% in the humidified air-filled canister set), and losses continued over the measurement period, although at a slower rate. The estimated half-lives of aldehydes and terpenes were 18 d in humidified air-filled canisters, 24 d in humidified N_2, and 6 d in dry air. Loss mechanisms and analytical considerations for the target compounds are discussed. Like other VOCs, the collection and storage of aldehydes and terpenes in canisters require humidification; however; the absolute accuracy of samples and standards of mixtures of aldehydes and terpenes stored in canisters may be limited. © 1998 Elsevier Science Ltd. All rights reserved.

Key word index: Air sampling, aldehydes, chromatography, mass spectrometry, terpenes, volatile organic compound.

1. INTRODUCTION

Indoor and outdoor air can contain complicated mixtures of volatile organic compounds (VOCs), including polar compounds that can be chemically and biologically reactive with low odor thresholds and potentially significant health and comfort effects. (Wallace et al., 1986; Shah and Singh, 1988; Brown et al., 1994, Lewis and Zweidinger, 1992). While various methods exist for sampling and analyzing polar VOCs, procedures for many compounds are not routine and have not been validated. Critical issues include stability, recovery and effects of temperature, pressure and humidity in sample collection and storage, calibration, and management of water in sample analysis.

This paper examines the stability and analysis of aldehydes and terpenes collected and stored in electropolished stainless-steel canisters. Aldehydes and

terpenes are widely distributed at trace (ppb) levels. Many of these polar VOCs are natural constituents in wood (Rowe, 1989; Conner and Rowe, 1975; Conner et al., 1980). Outdoors, some aldehydes and terpenes are precursors of ozone. Indoors, emissions from wood materials (Sundin et al., 1982) and other sources may cause VOC concentrations to far exceed outdoor levels (Shah and Singh, 1988; Lewis and Zweidinger, 1992).

The collection of air samples in electropolished ("Summa") canisters, followed by cryogenic or sorbent preconcentration and analysis using gas chromatography and mass-selective detection, is an established U.S. EPA method (TO-14) which has proven to be flexible, reliable, sensitive and artifact-free for many nonpolar VOCs (U.S. EPA, 1988). A similar method (TO-15) has been recently published for polar VOCs (U.S. EPA, 1997). The collection and analysis of polar VOCs in canisters is convenient and advantageous given the simplicity of the method, the freedom from breakthrough, decomposition and desorption issues associated with the use of sorbents for

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some aldehydes, terpenes and other species (Roth-weiler *et al.,* 1991), and the opportunity for multiple analyses from the same sample. Also, the preparation and storage of concentration standards in canisters facilitates instrument calibration and quality assurance. However, VOCs must be shown to be stable in canisters, i.e. not undergo losses or compositional changes in samples stored over periods of typically two weeks, and recoveries must approach 100%, i.e. the concentration withdrawn from the canister must be near that originally loaded. Storage stabilities and recoveries depend on the VOC, the VOC mixture, humidity, canister pressure and other factors, and the total effect of these factors cannot be accurately predicted. (U.S. EPA, 1997; Coutant, 1993). In consequence, VOC recovery and stability must be experimentally determined. Recovery and stability studies for aldehydes and terpenes stored in canisters have not been found.

2. METHODS AND MATERIALS

2.1. *Study design*

The experimental design involved the preparation and storage of seven aldehydes (butanal, pentanal, hexanal, heptanal, octanal, nonanal and benzaldehyde) and four terpenes (α-pinene, β-pinene, limonene and 3-carene) in canisters at ppb levels. To evaluate effects of moisture, some samples were prepared in humid (~50% relative humidity) and dry air. To investigate possible effects with O_2 that might alter stability, samples were also prepared in humidified N_2. Toluene, a nonpolar vapor shown to be stable in humidified canisters over extended periods (US. EPA, 1988; Howe et al., 1988), was used for quality-assurance purposes. Table 1 provides information for these VOCs. All chemicals were obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI).

2.2. *Sample preparation*

Samples were prepared and stored in 14 spherical 6ℓ electropolished stainless-steel canisters (Andersen Samplers

Inc., Atlanta, GA). Canister cleaning procedures consisted of repeated cycles of pressurization with humidified zero air, followed by evacuation to < 0.1 Torr for 1 h. Canisters were heated to 120°C during each evacuation. To check cleanliness, each canister was filled with humidified zero air and analyzed as described below.

A high concentration standard was prepared by injecting 140 μl HPLC-grade water into a clean and evacuated canister. The canister was then filled to near atmospheric pressure (~ 2 in Hg) with ultra-pure N_2 (Scotts Speciality Gases, Troy, MI), and 5.8 μl liquid of each neat target compound was injected. Volume corrections of 0.8 μl were made to account for liquid in the syringe needle (Hamilton Co., Reno, NV) which was drawn into the canister. The canister was then filled to 1 atm with N_2. The high-concentration standard had a relative humidity (RH) of ~ 50% and concentrations of individual VOCs from 68 to 133 ppm (Table 2). A 110 ppm 50% humidity toluene external standard was prepared in a separate canister by injecting 140 μl HPLC water and 5.8 μl neat toluene.

Low-concentration canisters were prepared using double dilutions. Clean canisters were humidified by injecting 140 μl of HPLC-grade water and then filled with dry zero air to near atmospheric pressure. Using a gas-tight syringe, 500 μl of the high concentration sample was withdrawn and injected into the canister. The canister was then filled with dry zero air to 1 atm. These canisters had a RH of ~ 50% and VOC concentrations ranged from 2.9 to 5.6 ppb (Table 2). Five such low concentration canisters were prepared. A sixth canister was similarly prepared, but with half the VOC concentration. Three additional canisters were prepared using ultra-pure N_2 dilutions rather than air, and three more were prepared with air but without the water addition. Canisters in each set were prepared with toluene as an internal quality assurance (QA) measure by injecting 500 μl from the 110 ppm toluene standard.

2.3. *Sample analysis*

Sample recoveries were investigated by periodic analyses of canister contents at 30, 60, 90 and 120 min, and 1, 2, 4, 8 and 16 d following preparation. The nine samples withdrawn from each canister represented ~ 3ℓ, or 25% of the canister contents. The high concentration aldehyde/terpene mixture was analyzed immediately after preparation and at 1 d (five times), 5 d, 16 d (4 times), and 58, 59 and 60 d

Table 1. General information for the VOCs used in this study, including CAS number, chemical formula, molecular weight (MW), boiling point (BP), density and purity (from manufacturer)

Compound	Other names	Formula	CAS no.	MW	BP (°C)[a]	Density (g ml-1)	Purity (%)
Butanal	Butyraldehyde	C_4H_8O	123–72–8	72.1	75	0.800	99
Pentanal	Valeraldehyde	$C_5H_{10}O$	110–62–3	86.1	103	0.810	97
Hexanal	Caproaldehyde, Hexaldehyde	$C_6H_{12}O$	66–25–1	100.2	131	0.834	98
Heptanal	Heptaldehyde	$C_7H_{14}O$	111–71–7	114.2	153	0.818	95
Benzaldehyde		C_7H_6O	100–52–7	106.1	178	1.044	99
Octanal	Caprylic aldehyde, Octyl aldehyde	$C_8H_{16}O$	124–13–0	128.2	171	0.821	99
trans-2-Octenal		$C_8H_{14}O$	2548–87–0	126.2	84/19 mm	0.846	94
Nonanal	Pelargonaldehyde, Nonyl aldehyde	$C_9H_{18}O$	124–19–6	142.2	190	0.827	95
α-Pinene	(1R)-(+)-α-Pinene	$C_{10}H_{16}$	7785–70–8	136.2	155	0.857	99
β-Pinene	(1S)-(-)-β-Pinene	$C_{10}H_{16}$	18172–67–3	136.2	165	0.859	99
Limonene	(R)-(+)-Limonene	$C_{10}H_{16}$	5989–27–5	136.2	176	0.840	97
3-Carene		$C_{10}H_{16}$	13466–78–9	136.2	168/705 mm	0.857	95
Toluene		C_7H_8	108–883	92.1	111	0.865	99

[a] Boiling point given in °C except where mm denotes boiling point given as pressure (in mm) at 25°C.

Table 2. GC-MS parameters used to identify and quantify VOCs, including retention time, ions and their relative abundance (percent of base peak) in parentheses, concentrations in high and low canister standards, response factors and detection limits

Compound	Retention time (min)	Selected ions (Abundance)						Concentration standards				Response factor (ct ng^{-1})	Detection limit	
		(1)		(2)		(3)		Primary		Secondary				
								(ppm)	($\mu g\ell^{-1}$)	(ppb)	(ngℓ^{-1})		(ng)	(ppb)
Butanal	7.23	57	(25)	72	(60)			130	383	5.4	16.0	1724	0.57	0.600
Pentanal	8.66	57	(30)	58	(35)			110	388	4.6	16.2	644	0.94	0.821
Hexanal	9.52	56	(85)	57	(45)			97	399	4.1	16.7	2325	0.13	0.099
Heptanal	10.31	55	(75)	70	(85)			84	391	3.5	16.4	2676	0.08	0.051
Benzaldehyde	10.78	77	(100)	105	(95)	106	(95)	115	500	4.8	20.9	11900	0.02	0.011
Octanal	11.05	57	(80)	84	(55)			75	393	3.1	16.5	2105	0.12	0.073
trans-2-Octenal	11.52	55	(80)	70	(70)	83	(45)	78	405	3.3	17.0	3616	0.09	0.051
Nonanal	11.95	57	(100)	98	(60)			68	396	2.9	16.6	1447	0.14	0.074
α-Pinene	10.57	77	(20)	79	(18)	93	(100)	74	410	3.1	17.2	13294	0.02	0.008
β-Pinene	10.90	69	(20)	77	(18)	93	(100)	74	411	3.1	17.2	12577	0.02	0.012
Limonene	11.29	67	(65)	68	(100)	93	(60)	72	402	3.0	16.8	9135	0.03	0.016
3-Carene	11.15	77	(30)	91	(50)	93	(100)	74	410	3.1	17.2	10954	0.01	0.008
Toluene	9.23	91	(100)	92	(60)	65	(20)	110	414	4.6	17.3	11949	0.03	0.022

following preparation. Gas samples were concentrated cryogenically using a preconcentrator (PM EV, CDS Analytical Inc., Oxford, PA) and transferred via a heated transfer line and on-column cryofocus unit to a gas chromatograph (GC) (5890 Series II, Hewlett Packard. Palo Alto, CA). canister pressure drove the sample through the preconcentrator, and the sample volume was metered by a mass-flow controller and totalizer (Sierra Instrument Inc., Monterey, CA) placed at the cryogenic trap exit, thus eliminating the possibility of cross contamination. The gas flow was split 12:1 before cryofocusing. Separation was achieved using a HP-5 30 m fused silica capillary column (0.25 mm dia × 0.25 μm film thickness, Hewlett Packard). Column and split flows of He were controlled by the GC electronic pressure regulator. Analytes were detected using a quadrapole mass-selective detector (Model 5972A, Hewlett Packard). A PC workstation (G1034 C Chemstation, Hewlett' Packard) was used for data acquisition and manipulation.

In each analysis, a 320 ml gas sample from the canister was cryogenically trapped at - 100°C. A 25 μl syringe injection was used for the high concentration standards. The trap was heated to 150°C and the concentrated sample transferred and cryofocused at - 100°C at the inlet of the GC column. The cryofocus was then heated to 150°C and the GC temperature program initiated (- 20°C for 5 min, ramp at 25°C min^{-1} to 120°C, and hold at 120°C for 5 min). To achieve high sensitivity, selective-ion monitoring (SIM) was used, and groups of specific ion groups in multiple elution time windows (Table 2) were quantified. The dwell time of each ion group was 20 ms, and the electron multiplier voltage was 1624 V. Baseline correction and integration of ion spectra used the MS autoquantitation software, however, all results were manually checked. To determine concentrations, integrated counts of the fragmentation ions for each peak were summed, multiplied by the appropriate response factor, and divided by the sample volume. Response factors were determined from the high-concentration standard. Liquid standards in neat pentane and methanol were also prepared and analyzed but not used for calibration purposes due to losses (reaction) of several of the aldehydes. The 110 ppm toluene standard was analyzed periodically during the study period as a quality control measure. Beyond two leaky canisters, the equipment performed satisfactorily without any changes in performance, and all parameters remained unchanged throughout the study.

3. RESULTS

3.1. Sensitivity and ion responses

The fragmentation ions selected for each compound are listed in Table 2. Generally, molecular ions for the bicyclic terpenes were low and unsuitable for SIM usage. The outstanding feature of the terpenes (except limonene) was a base peak at $m/z = 93$ resulting from the loss of $C_3H_7^+$. For the straight-chain aldehydes, the relative abundance of the molecular ion was often low and decreased with increasing chain length (except for butanal). Most aldehydes had a relatively strong fragmentation ion at $m/z = 43$ derived from McLafferty rearrangement. Unfortunately, background noise (possibly comprised of the $C3H_7^+$ ion expected in the VOC mixture) often obscured the aldehyde ion. Therefore, secondary abundance fragmentation ions were chosen for many of the aldehydes. The aromatic aldehyde, benzaldehyde, showed relatively strong molecular ions and the (M-H)$^+$ ion, contributed by the stabilizing of the aromatic ring (Beynon et al., 1968) was selected. For certain compounds, ion abundances can vary with concentration and thus fragmentation ions must be carefully selected.

The selected compounds were easily separated by elution time and no overlap of chromatographic peaks occurred (Table 2 and Fig. 1). Some shifting of elution times was observed with humid samples due to the presence of water in the GC column. Because the sample humidity was controlled and a relatively small volume of air was sampled, no special water management technique was employed. While the elution time windows for the SIM analysis were broad enough to capture the full peaks, manual checks of autoquantitation results were sometimes needed. Table 2 shows limits of detection (LODs), both as a mass and as a concentration for the sample volume
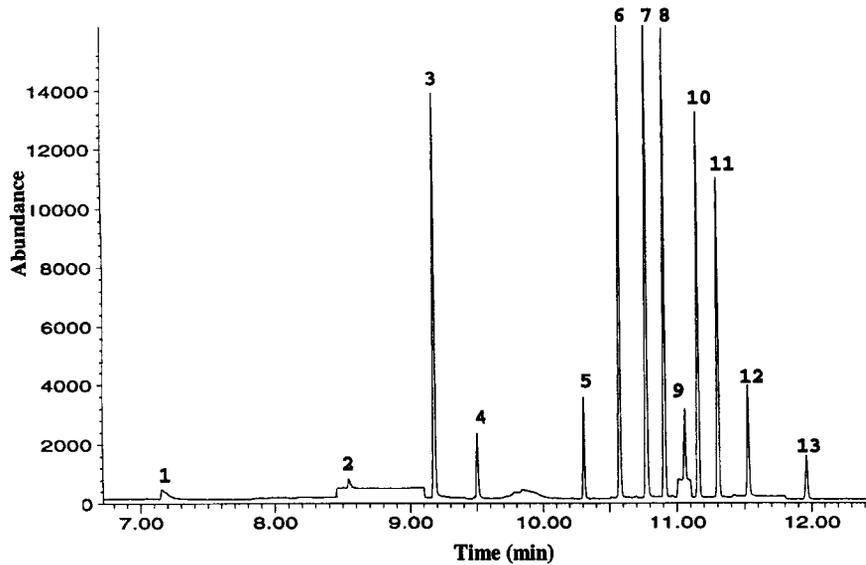
Fig. 1. Chromatogram of typical low concentration sample prepared in humidified air. The step changes in the baseline are caused by changes in SIM mode to different ion fragments. Peak identification: 1 = butanal, 2 = pentanal, 3 = toluene, 4 = hexanal, 5 = heptanal, 6 = α-pinene, 7 = benzaldehyd e, 8 = β-pinene, 9 = octanal, 10 = 3-carene, 11 = limonene, 12 = 2-octenal, 13 = 1-nonanal.
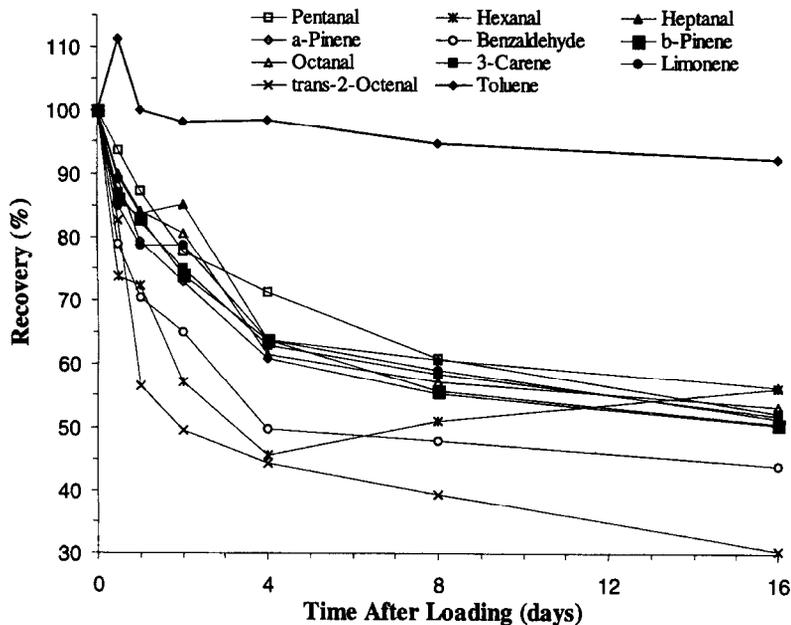
Fig. 2. Change in recovery over time for 10 compounds stored in humidified air. Samples are referenced to initial analysis (30 min after canister loading). Average of five canisters is plotted.

(320 ml). The LODs represent a peak size that exceeded by three times the baseline noise near the peak. LODs were high (> 0.6 ng) for butanal and pentanal in comparison to the other compounds studied (0.01–0.14 ng).

3.2. Recovery

Figure 2 displays recoveries for 11 VOCs prepared in humidified air. Recoveries are referenced to the initial analysis of each canister, and are averaged across the five canisters. A substantial drop in recoveries occurred within the first hour or two, followed by a more gradual decrease to the end of the 16 d study period. Across all terpenes and most aldehydes, recoveries dropped by an average of 19 ± 8% from 30 to 60 min after loading. For samples prepared in humidified N_2 and dry air, the decreases were 8 ± 10 and 39 ± 28%, respectively. These statistics exclude

pentanal and hexanal due to the poorer precision of these measurements. Over 16 d, Fig. 2 shows that recoveries of most VOCs decreased to ~ 50% of initial levels. Recoveries of 2-octenal declined more rapidly. In contrast to the polar VOCs, toluene showed small changes.

Variations in the initial decreases may have resulted from small differences in the interval between canister loading and the initiation of the GC-MS analysis, and possibly from incomplete partitioning and mixing in the canister, although this appears unlikely (Coutant, 1993). To minimize effects of initial variations, in subsequent analyses the initial two concentration estimates (30 and 60 min following canister loading) are averaged and used as a base or reference. While averaging improves the robustness of recovery estimates at longer time periods, it does not account for changes occurring in the first hour.

Table 3 shows recoveries for each set of low concentration samples over the 16 d period. For samples prepared in humidified air, recoveries of all compounds gradually dropped during the study period. After 16 d, recoveries averaged 49%. Samples prepared in humidified N_2 appeared slightly more stable, and recoveries averaged 61% after 16 d. This difference may not be statistically meaningful, however, as the smaller number of N_2 samples may not permit minor differences to be discerned. Recoveries for samples prepared in dry air averaged only 14% after 16 d.

Recoveries of the QA standard are also shown in Table 3. The results for humidified N_2 and dry air should be interpreted cautiously, as these are based on a small sample size (only 2 of 3 canisters in these sets had the internal QA standard). Results for humidified air are more reliable given the larger sample size. The humidified air samples had high recoveries (mean of 92% at 16 d). Toluene recoveries in N_2 and dry air were lower than expected (75 and 48% at 16 d, respectively), but still exceeded those of most aldehyde and terpene species.

At the conclusion of the experiments, canisters were cleaned using three pressurization–evacuation cycles. In four canisters tested to certify cleanliness, concentrations decreased by 60-90% from initial levels. A second cleaning sequence provided similar efficiency, and many target compounds remained at unacceptable levels. Canister valves were then removed and sonicated, and 5 ml of neat pentane was added to each canister. Canisters were then reassembled and cleaned again using three pressurization-evacuation cycles. This procedure reduced levels to below 1 ppb for nearly all compounds. These observations suggest that compounds absorbed on canister surfaces will be released very slowly, and that adding a high concentration of a volatile compound can help desorb recalcitrant compounds. It also suggests that an aggressive cleaning procedure may be necessary.

Table 3. Recoveries of VOCs as percent of initial two (30 and 60 min) measurements. Aldehyde and terpene recoveries based on five canisters for humid air, and three canisters each for humid N_2 and dry air. Toluene recoveries based on three canisters for humid air, and two canisters each for humid N_2 and dry air

Compound	Humid air								Humid nitrogen								Dry air							
	h 1	day 1	day 2	day 4	day 8	day 16			h 1	day 1	day 2	day 4	day 8	day16			h 1	day 1	day 2	day 4	day 8	day 16		
Butanal	90	87	74	79	49	51			72	108	84	74	48	41			98	83	72	37	33	28		
Pentanal	94	87	78	71	61	52			118	117	122	109	67	80			61	51	22	33	34	41		
Hexanal	74	72	57	46	51	56			54	28	69	90	54	42			79	23	37	13	14	8		
Heptanal	90	84	85	64	61	56			93	113	105	93	83	83			58	44	50	23	25	16		
Benzaldehyde	79	70	65	50	48	44			94	91	77	76	62	49			52	34	31	25	19	9		
Octanal	90	84	81	61	57	53			86	95	104	84	78	65			53	41	44	22	25	13		
trans-2-Octenal	83	57	50	44	39	30			86	83	75	69	67	65			42	29	35	16	14	8		
Nonanal	81	74	70	55	48	46			67	95	109	90	76	78			40	36	35	19	19	14		
α-Pinene	89	79	73	61	55	50			90	79	85	79	64	56			76	109	90	51	37	21		
β-Pinene	86	83	74	64	56	51			89	98	84	76	63	59			88	34	17	10	5	4		
Limonene	85	79	79	64	59	51			91	106	90	79	65	59			92	24	25	9	6	2		
3-Carene	87	83	75	63	58	52			88	101	87	77	63	55			89	44	38	17	11	4		
Average	86	78	72	60	54	49			86	93	91	83	66	61			69	46	41	23	20	14		
Toluene	111	100	98	98	95	92			103	91	64	88	74	75			NA	90	78	60	64	48		

3.3. *Half-life estimates*

A first-order model for VOC recoveries from canisters may be applicable for many compounds, at least for the period during which recoveries gradually decrease. The half-life τ is the time necessary for the recovery to decrease by 50%. For a first-order process, $\tau = -0.693/\beta$, where β is the slope of the regression line of the logarithm of recoveries versus time. Table 4 shows the half-life and R^2 for each compound in the three canister sets. Also shown are half-life estimates for the high concentration standard which was analyzed periodically (14 times, up to 60 d after loading). In many cases, the first-order model explained much (> 80%) of the observed variation. Low R^2 values indicate that the half-life estimate is not meaningful, a result which may arise from errors in analytical determinations. Also, the first-order model does not explain both fast and slow loss processes.

For the high concentration standard, the half-life and R^2 averaged 18 d and 82%, respectively. In humidified air-filled canisters, half-lives ranged from 11 to 21 d and averaged 18 d, the same as the high concentration standard. The canisters prepared with N_2 had slightly longer half-lives, ranging from 16 to 34 d and averaging 24 d. In dry canisters, the half-lives of all compounds were short, ranging from 3 to 8 d and averaging 6 d. Several observations (indicated in Table 4) were excluded from these statistics as the low R^2 indicated poor fit of the first-order model.

The internal toluene QA standard had half-lives of 91, 47 and 16 d in humidified air, humidified N_2 and dry air, respectively. The R^2 values were low for the humidified samples, however, and longer storage times are needed to improve the half-life estimate. The external toluene standard, stored alone in its own canister, was essentially "infinitely" stable, showing only small and apparently random changes in recovery up to 60 d following preparation. While the half-life of toluene in the aldehyde-terpene mixture exceeded that of other compounds in the same canister, toluene recoveries in the mixture appeared to decrease over time. A possible explanation is secondary adsorption of toluene on terpene and aldehyde reaction products that may have formed on canister surfaces.

3.4. *Inter-canister reproducibility*

Reproducibilities were calculated as the average coefficient of variation (COV) of concentrations measured among the 3-5 canisters in each set at sampling times of 4, 8 and 16 d after loading (Table 5). Samples stored for under 4 d were excluded to avoid any effects of the rapid concentration changes that occurred after canister loading. The only systematic change in reproducibilities during the study period was an increase in COVs observed at long storage times for the dry canisters. These samples generally had low reproducibility, and COVs exceeded 100% for α-pinene, limonene and 3-carene. As discussed earlier, recoveries in dry canisters dropped substantially, and the higher COVs resulted as concentrations approached quantitation limits.

For most of the aldehyde and terpene species in humidified canisters, reproducibilities were between 15 and 35%. Reproducibilities averaged 32% in humidified air and 19% in N_2. The two exceptions, butanal and hexanal, had reproducibilities from 36 to 66%. For hexanal, quantitation was based on secondary abundance ions. Both hexanal and butanal ion responses were relatively low, and butanal concentrations were only ~ 5 times higher than the

Table 4. Half-life and R^2 for each compound for high and low concentration canisters. Asterisk (*) denotes value excluded from average due to low R^2. Plus (+) denotes use of external standard which was stored in a separate canister

Compound	High conc. Half-life (d)	High conc. R^2 (%)	Humid air Half-life (d)	Humid air R^2 (%)	Humid nitrogen Half-life (d)	Humid nitrogen R^2 (%)	Dry air Half-life (d)	Dry air R^2 (%)
Butanal	26	96	16	78	12	80	8	76
Pentanal	24	92	18	89	24	53	26*	10*
Hexanal	17	86	29*	28*	33*	7*	5	65
Heptanal	18	69	21	75	47	54	7	72
Benzaldehyde	15	74	16	67	16	94	6	79
Octanal	13	85	19	76	28	79	7	74
trans-2-Octenal	15	82	11	71	34	59	6	72
Nonanal	13	93	17	72	68*	12*	8	59
α-Pinene	22	80	18	77	22	88	7	91
β-Pinene	20	75	18	80	21	84	4	72
Limonene	19	73	19	81	20	85	3	81
3-Carene	19	74	19	80	19	89	4	89
Average	18	82	18	77	24	76	6	76
Toluene	502+	7+	91	56	47	25	16	82

Table 5. Reproducibility of samples expressed as COV in percent. Low concentration samples measured at 4,8 and 16 d; high concentration standard measured at 1, 16 and 58-60 d

Compound	High conc.	Low concentration standards		
		Humid air	Humid N_2	Dry air
Butanal	43	48	36	76
Pentanal	28	35	11	53
Hexanal	17	66	49	9
Heptanal	19	26	8	9
Benzaldehyde	40	20	3	24
Octanal	25	27	16	10
trans-2-Octenal	35	18	21	33
Nonanal	25	25	18	18
α-Pinene	23	24	11	116
β-Pinene	28	27	19	49
Limonene	42	33	19	109
3-Carene	38	34	17	126
Average	27	32	19	53

LOD. Given small shifts in elution time (produced by excess water or other factors), noise, etc., autoquantitation results were inconsistent for these two compounds. While more reliable identification and quantitation were achieved by manually referencing elution time to a retention time index, COVs remained high.

The preconcentrator/GC/MS system generally appeared to meet the performance requirements of TO-14 and TO-15 i.e. LOD ≤ 0.5 ppb, replicate precision requirements within 25%, and audit accuracy within 30% (U.S. EPA, 1997). The COVs in Table 5 incorporate both analytical uncertainties and canister-to-canister differences. Based on tests using nonpolar VOCs and the same hardware, the analytical component of the uncertainty was 5-10%. The higher uncertainties may have resulted from variations in active sites on canister surfaces, differences in the amount of gas transferred from the high concentration standard, unequal pressurizations of canisters, and other factors (Wagoner et al., 1993).

4. DISCUSSION

Many nonpolar VOCs have been shown to stable and yield high recoveries when stored in humidified passivated canisters (Howe et al., 1988; Oliver et al., 1986; Jayanty, 1989; Miguel, 1995). Method TO-14 specifies a minimum "hold-time" of 14 d for negligible losses of VOCs in the canister (U.S. EPA, 1988), and some VOCs can be stored for much longer times without significant losses. Information regarding the stability of polar VOCs in canisters is comparatively rare. While theoretical analyses using Dubinin-Radushkevich isotherms predict competitive physical adsorption for several VOCs, data are insufficient to validate this model or to assess the effects of pressure,

humidity, temperature and VOC composition (Coutant, 1993). Several studies have indicated the critical role of water on recoveries of polar (and nonpolar) VOCs (U.S. EPA, 1988; Pate et al., 1992; Freeman et al., 1994). Likewise, we found low recoveries in dry air. Sampling in very dry environments can be easily accomplished by a small water addition to the evacuated canister prior to sampling. Some polar VOCs appear stable in humidified canisters, whether Summa polished or not (Shedlow and Schuyler, 1995). In a study of 27 polar VOCs stored up to 26 d, compounds were grouped into very unstable classes (e.g. vinyl acetate, acrolein), moderately unstable (e.g. benzonitrile, methanol) and stable classes, and lower responses and greater inter-canister variation was found for canisters at partial vacuum (12.7 cm Hg) as compared to pressurized (1.36 atm) canisters (Winslow et al., 1995). The same study reported that several compounds, e.g. ethylamine, paradichlorobenzene, cyclohexanone, 1,2-dibromoethylene, formaldehyde and aniline, were unstable at ppm levels. In contrast, a study of 14 polar VOCs, including alcohols, ketones and ethers prepared in humidified canisters, found high recovery and stability over a one month period. (Pate, 1992). These studies excluded the aldehydes and terpenes tested here, and differences in the tested mixtures are likely to account for the variation in results.

The half-life statistic summarizes VOC stability, allows easy calculation of the maximum storage times, and thus may complement daily drift statistics expressed as "percent per day changes (U.S. EPA, 1988)". For example, for a recovery of 75% and the 18 d half-life observed for VOCs in humidified air, the maximum storage time is 7 d. Such estimates omit losses observed in the first hour, effects of older or damaged canisters, and may only apply to laboratory conditions. It may be prudent to incorporate a "safety factor", perhaps halving the estimated maximum storage time.

4.1. Loss mechanisms and future research

VOC losses in canisters occur from several mechanisms The first is physical adsorption or chemical interaction of vapors on the nickel-chromium oxide canister walls, especially "active sites" that may be defects in the polishing (Freeman et al., 1994), or on carbonaceous material (particles) that may be present in the canister. Rapid decreases in recoveries over the first few hours or day of storage is generally attributed to physical adsorption, although these losses may also result from chemical reactions. (U.S. EPA, 1997). Adsorption may increase after the canister surface has been compromised, possibly from exposures to corrosive (HCl) and nonambient atmospheres, e.g. process streams. For many VOCs, water additions or humidity reduce adsorption losses, as water preferentially adsorbs on canister walls. However, polar VOCs may compete with water for surface sorption sites. The low recoveries found in dry canisters support

surface adsorption, and the enhanced recovery pro-
vided by the pentane addition following canister
cleaning supports competitive adsorption. A second
mechanism affecting recovery is the dissolution of
soluble compounds in condensed water present in the
canister. As canister pressure decreases due to sample
withdrawals, the amount of condensed water de-
creases and concentrations of any dissolved compo-
nents may increase (Coutant, 1993). This effect
depends on compound solubility and the presence of
condensed water in the canister. However, no water
condensation was expected in the laboratory-pre-
pared canisters and the solubility of compounds tes-
ted was low. A third mechanism is gas-phase reaction
and subsequent transformation and loss of target
compounds. Reaction would be enhanced by the pres-
ence of ozone or other reactive species. Additional
loss mechanisms include heterogeneous reactions
on the canister wall, polymerization (Pate et al.,
1992), hydrolysis (Shedlow and Schuyler, 1995), and
secondary adsorption, i.e. compounds adsorbed on
surfaces act as new active sites and adsorb other
compounds in the canister.

Unfortunately, evidence in the literature and this
study cannot identify specific loss mechanisms.
A common mechanism affecting all tested species
seems likely since the recovery and half-lives were
similar in each canister type. While dilutions in
N_2 increased sample longevity and reproducibility,
possibly because reaction rates decreased, these cha-
nges may not be statistically significant. Interestingly,
effects showed no effect of concentration. Most canis-
ters were prepared at concentrations (3-5 ppb) repre-
sentative of ambient levels. A canister prepared at half
this level and the high concentration (68-130 ppm)
standard showed similar half-lives. The small sample
size for the high and very low concentration standards
do not allow statistical analysis. Still, since adsorption
and dissolution have finite capacity, reaction may
account for some VOC losses.

Several areas for further investigations of factors
affecting VOC stability and recovery in canisters are
suggested. First, humidity may have a continuous
effect of VOC recovery, especially if dissolution in
condensed water is a major loss mechanism. Since
canister humidity generally cannot be controlled (ex-
cept increased by water additions), recoveries should
be determined over a range of humidities. This would
also help to confirm the roles of dissolution and ad-
sorption (water should coat canister surfaces at low
humidities). Second, ambient temperatures may fluc-
tuate widely and, to varying degrees, all loss mecha-
nisms depend on temperature. Also, some losses, e.g.
reactions, may not be reversible. Therefore, studies
should be conducted at typical and extreme temper-
atures, e.g. 0-40°C. Because adsorption potentials for
VOCs and water change at different rates with tem-
perature, these tests may help to separate sorption
losses. Third, while canister samples may be collected
and stored under partial vacuum or pressure, canis-

ters are usually pressurized prior to analysis. Pressur-
ization affects the amount of condensed water in the
canister. Pressurization with N_2 in this study ap-
peared to improve the stability. While probably less
critical than the previous factors, pressurization de-
serves further study. Fourth, stabilities of other im-
portant VOCs are unknown. Additional VOCs are
worth investigating, both in simple (single VOC and
water) and complex mixtures. The identification of
reaction products, if any, may help to confirm reac-
tion losses. Fifth, chromatography and MS quantitat-
ion may be adversely affected by water and the use of
secondary ions, and effective criteria and parameters
must be established for reliable quantitation. Finally,
this study could not quantify initial concentration
losses. Such losses could be measured using a dynamic
dilution system that allows sampling into the analyti-
cal system while canisters are being filled.

Laboratory tests may not necessarily represent con-
ditions where canisters are used, especially if the air
sample of interest contains a wide variety of VOCs
including reactive and/or unknown compounds.
A practical approach to determine VOC recovery and
stability in such applications might utilize two sets of
canisters, both of which contain the air sample of
concern. One set would be "spiked" with a known
concentration of the target compounds. VOC recov-
ery and stability would be based on the difference
between spiked and unspiked canister sets. (Repro-
ducibility would be determined using individual can-
ister sets as before, not the differences.) While this
procedure doubles the analytical work required, it
improves the relevance of results to the application of
concern. In this study, terpenes and aldehydes were
selected based largely on how frequently they are
encountered in several applications, and there was no
standard matrix or application. Further, while indi-
vidual aldehyde and terpene species were present at
only a few ppb, the total concentration of these species
was probably higher than that normally encountered
in ambient air. Additionally, the mixture used may
not be representative. These factors may have altered
and possibly lowered the recovery and stability of
VOCs. Tests of recoveries and stability using air sam-
ples of concern and the spiking procedure are sugges-
ted to determine the appropriateness of canister
sampling for polar VOCs in specific applications.

5. CONCLUSIONS

Based on numerous analyses of low concentration
standards, aldehydes and terpenes stored in elec-
tropolished canisters had lower recoveries and shorter
half-lives compared to the nonpolar aromatic control.
Losses occurred with short (hours) and long (days to
weeks) time scales. The results suggest that while the
precision is generally good, canister standards should
not be used as absolute references for mixtures of
some aldehydes and terpenes, and also that canister

sampling may not provide quantitatively accurate results for these species. Recoveries may be improved by short holding times, however, initial losses in the canister may be significant and absolute accuracies may be low. These conclusions are based on the protocols and conditions used in the experiments, and they must be viewed in light of issues associated with alternate sampling methods (collection on solid sorbents, chemical or thermal desorption, etc.) The accuracy, convenience and flexibility of canister sampling and whole air analysis can provide useful results in many applications. Laboratory tests using mixtures, concentrations and humidities typical of those in the application of interest are suggested to verify method performance prior to use.

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