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ISSN: 0974-4908
Res. Environ. Life Sci.
5(1) 17-24 (2012)

Evaluation of stability of volatile organic compounds in SUMMA canisters at different humidity levels

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(Received: September 09, 2011; Revised received: January 22, 2012; Accepted: January 24, 2012)

Abstract: Volatile organic compounds (VOCs) occur in traces in atmosphere and even in trace levels, these compounds pose serious health hazard. Sample stability, recovery, effect of temperature and moisture management are a few critical points taken into consideration while sampling and analysis of polar and non polar VOCs. In the present work, stability study was carried out for polar and non polar VOCs in SUMMA stainless steel canister. Compounds recoveries were assessed in dry and humid canisters. Canister samples were prepared with 0, 25, 50 and 100% humidity. Moreover, the study with each humidity level was performed with two different concentrations (approx 50 & 500 μgm^{-3}) of each compound to evaluate the influence of lower/higher concentration. Before starting experiment, various parameters used for the measurement of VOCs from canister system were optimized and method detection limit was calculated as the accuracy of analytical measurement is the key part of stability study. Polar compounds like alcohols were poorly recovered from dry canisters. Sulfur and chloro compounds were recovered in the range of 12-68% over one month period. Aromatic and aliphatic hydrocarbons appeared to be unaffected. In presence of humidity in canister, alcohols showed better recovery but recovery was sometime irregular especially if they are in low concentration. Recovery of sulfur compounds improved significantly in presence of humidity while chloro compounds were recovered about 60-70% even if humidity is there. Overall, humidity is proved to be essential for the recovery of alcohols, sulfur and chloro compounds and 50% humidity was the best suitable humidity. Nonpolar compounds remained unaffected irrespective of humidity level.

Key words: VOCs, Canister, Gas Chromatography, Mass Spectrometry, Sample Stability

Introduction

Volatile organic compounds (VOCs) occur in ambient air in trace concentrations, yet remain important air pollutants. In addition to being photochemical smog precursors, some VOCs can pose significant risks to human health, particularly the so-called "air toxics" VOCs, of which some are known or suspected carcinogens or known to result in other serious human health and/or environmental effects (Wang and Austin, 2006; Kumar *et al.,* 2008; Malkina *et al.,* 2011).

With the growing concern for the quality of the environment, demand for reliable and sensitive monitoring technique for organic compounds in atmosphere has increased in recent past. The collection of air samples for the analysis of trace-level constituents, however, demands highly skillful approaches relative to ones contained in other environmental media (Kumar *et al*., 2011; Yamamoto *et al.,* 2000). This is especially the case, when highly reactive, or unstable, gaseous components like VOCs are concerned (Derwent *et al.*, 2003, Zabiegala and Namiesnik, 2010). Sample stability, recovery, effect of temperature and moisture management are a few critical points taken into consideration while sampling and analysis of polar and non polar VOCs analysis.

Among various sampling techniques, canister sampling is used in a variety of air monitoring programme and form the basis of USEPA TO-14 (USEPA TO-14A, 1999; Kelly and Holdren, 1995). One of the advantages of canister samples is that they do not need any refrigeration or special handling until they are analyzed. It has been recognized that certain levels of humidity are necessary for good recoveries of VOCs from SUMMA canisters (Ochiai *et al.,* 2002). It is also clearly indicated in the past studies that certain amount of water is necessary for stability of polar and non-polar VOCs in canister because water is required to cover the active sites on the interior surface preventing physical adsorption or chemical interaction, whereas high water content can cause the dissolution of target compounds in condensed water (Coutant, 1993; Pate *et al*., 1992; Winslow *et al.,* 1995).

Only few stability studies have been done on several compounds and further studies on various compounds were suggested. Kelly and Holdren evaluated the applicability of canisters for storage of VOC listed among the 189 hazardous air pollutants (HAP) in the 1990 U.S. Clean Air Act Amendment (CAAA) (Kelly and Holdren, 1995). Nearly 100 HAP have sufficient vapour pressure to be considered volatile compounds. Among these 100 VOC, 52 have been tested only for stability. Canisters were found to be a suitable approach for sampling and storage of most of the tested compounds. However, for many compounds canister stability data are extremely insufficient or widely differing. Therefore, additional stability testing of volatile organic compounds is advisable.

In this study, Stainless steel SUMMA canisters were used to evaluate the recovery and stability of volatile organic compounds over a period of one month. Polar and non polar hydrocarbons, alcohols, sulfur and chloro compounds were used for the study to cover a wide range of compounds. Two concentrations of samples were used for various humidity levels in canisters.

Materials and Methods

Gas standards: Standard gas mixtures were freshly prepared prior to use. Intermediate gas standard was prepared on the principle of static dilution bottles (USEPA TO-15, 1999). During the preparation of the standard the vessel was heated to about 65ºC to vaporize the VOC (Harington, 2003). Gaseous standard mixture consisted of polar, nonpolar and reactive compounds including methly alcohol, ethyl alcohol, propyl alcohol, carbon tetrachloride, n-pentane, benzene, dimethil sulfide, dimethyl disulfide and tetrahydrothiofen. All of the compounds were of GC analytical reagent grade obtained from Lachema, Brno, Czech Republic with purity above 99%. Intermediate gas standards were prepared by injecting predetermined aliquots of liquid standards into a 6 liter SUMMA Canister (Tekmar – Dohrman, USA) filled with known volume of zero grade nitrogen as the diluting gas. Concentration of intermediate standard was around 1.00 mg m^{-3} for each compound.

The concentration of compounds in gas mixture was calculated (Wu *et al.,* 2004) from equation 1:

$$Cppmv = 22.4 \times 10^{6} (\rho.V1 / MV) (T / 273) (760/P) \text{...........(1)}$$

where Cppmv is the concentration of the VOC sample (ppmv), 22.4 is the molar volume of gas at STP (l mol^{-1}), ρ is the density of the liquid sample injected (g mol^{-1}), V1 is the volume of liquid sample injected (ml), M is the molecular weight of the analyte (g mol^{-1}), V is the total volume of the dilution gas (l), T is the temperature (K) and P is pressure (Torr).

Two different concentrations of the working standard gas mixture were prepared in 6 liter SUMMA stainless steel canister. The first concentration was around 500 µg m^{-3} and the second was 50 µg m^{-3} to study the effect of humidity and long term stability of VOC in SUMMA canisters. Canisters were connected to zero grade nitrogen through a tee piece. One opening of the tee was closed with a septum and a gas-tight syringe was used to inject the primary standard into the tee. Intermediate standard gas mixture was injected into 6 liter SUMMA stainless steel canister with the help of gas tight syringe (Hamilton gas tight syringe). Dilution gas (zero grade nitrogen) was flowing during the injection process. The gas sweeps the VOC into the humidified canister and prevents them from being adsorbed to the tee or the lines. Exact concentration of each compound in standard gas mixtures, corresponding concentration in ppb for each compound, retention time (RT) and selected ions for analysis in SIM mode are given in Table -1. Qualitative identification of VOC was based on RT and two ions for each compound were selected for quantification to ensure the high quality of data. n-Heptane was used as internal standard for calibration and quality assurance and to compensate any drift in instrument sensitivity.

25%, 50% and 100% humidity canisters were prepared for lower concentration while 0% (dry), 25%, 50% and 100% humidity canisters were prepared for higher concentration gas mixtures by injecting appropriate amount of ultra pure water at 25ºC room temperature. Effects of humidity on recovery of compounds from canisters were evaluated on day 0,1,2,4,8,15 and 30. 50% humidity canisters were chosen for calibration and used as a reference for further calculations.

Canisters: 6 liter Summa stainless steel canisters (Tekmar – Dohrman, USA) were used for study. Summa canisters are specially treated stainless steel canisters. Interior surface of canisters are passivated by SUMMA polishing. Canister cleaning system (Meriter: Cycle Clean™, Model 214 GP, USA) was used for the canister cleaning and evacuation. Canisters were cleaned by evacuation and pressurization cycle as in compendium method TO-14.

Analysis: Canister method: An aliquot of canister content was transferred to Gas Chromatograph/Mass Spectrometer via automatic cryofocusing unit (Autocan Tekmar, USA). Sample was transferred at the flow rate of 100 ml min^{-1} to a cryotrap (glass bead trap) maintained at -165°C by liquid nitrogen. The trapped analytes were then heated to be transferred to a capillary cryofocusing unit via a transfer line maintained at 200°C. The temperature of the second cryofocusing unit was also kept at -165°C to trap all the analytes. Finally this cryofocusing unit was flash-heated to transfer all the analytes to a GC column.

Gas Chromatography / Mass Spectrometry parameters: VOCs were analysed with Gas Chromatography (Fisons instruments GC 8000 series) / Mass Spectrometry (Fisons MD 8000). A capillary column (Vocol, Supelco, USA) with dimensions 60m × 0.32mm × 3µm was used for the separation of analytes. GC oven temperature was programmed as follows: initial oven temperature was set to 40°C for two minutes, and then ramped by 10°C min^{-1} to 230°C for a hold time of 10 minutes. Source and interface temperature were set to 180°C and 220°C respectively. Electron ionization conditions were as follows: ion energy - 70eV, scan range from 10 to 300 AMU (atomic mass unit), scan rate 0.5 scan sec^{-1}, tune reference compound was heptacosa (perfluoro-tributyl-amine). The GC/MS set up was connected to a computer to store and evaluate the output data.

Results

Two ions for each compound were selected for analysis in SIM mode. In order to obtain the best results and optimum response for the studied compounds, all analytical parameters of canister system were optimized (Kumar and Viden, 2007) and statistical parameters for each compound were determined.

Method detection limits: Method detection limits (MDL) estimated by seven replicate analyses of the standard gas mixture following CFR, 1993 at the concentration of about 5 µg m^{-3} (1-4 ppb) are compiled in Table-2. MDL were found in the range of 0.07 to 0.96 ppb for the studied compounds. Benzene, toluene, n-hexane and

1,2-dichloroethane showed the values under 0.1 ppb. Alcohols showed higher values followed by dimethyl disulfide and tetrahydrothiophene. Higher deviations in alcohol determination caused higher values of their respective MDL. The humidified blank zero gas was checked for contamination and no analyte was found to exceed MDL.

Statistical evaluation of the methods: Standard gas mixture at the concentration level of 50$\mu g\ m^{-3}$ was applied to canister system to evaluate the method precision statistically. The results are shown in Table - 2. All three alcohols showed quite high values of standard deviation and relative standard deviation. All compounds except for alcohols showed reasonable values of standard deviation and relative standard deviation. Standard deviation was in the range of 2.22 $\mu g\ m^{-3}$ (toluene) to 31.79 $\mu g\ m^{-3}$ (methanol). Relative standard deviation was in the range of 4 to 13% except for alcohols. Alcohols showed very high relative standard deviation. The confidence interval shown in Table 4 was calculated for the significance level of 95%. It also shows the same behavior like other parameters. The confidence interval was in the range of 2.17 $\mu g\ m^{-3}$ (toluene) to 31.15 $\mu g\ m^{-3}$ (methanol). Alcohols exhibited quite high values of confidence interval in comparison to other compounds.

Alcohols give poor reproducibility unless moisture is removed effectively before sample is transferred into chromatographic column. The probable reason is their polar nature. Solubility of alcohols in water has significant influence as well. Standard gas mixture was prepared in canister with 50% relative humidity as some moisture level in canister has been reported to be quite essential for their recovery (Ochiai *et al*., 2002; Winslow *et al.,* 1995). Tekmar Autocan canister system contains MCS to avoid entering moisture from sample into chromatographic column. As discussed in optimization study (Kumar and Viden, 2007) MCS is also not efficient enough for all moisture removal. A part of moisture enters into chromatographic column even after the use of MCS at optimum temperature condition. Alcohols and other polar compounds elute out with moisture and influence their quantitation substantially. Change in detector response encountered as a consequence of humidity - peak splitting, variability in the retention time and sensitivity suppression- was reported by Ochiai *et al*. (2002) and Castellnou *et al*. (1998).

Effect of humidity on recovery of VOC in SUMMA canisters: SUMMA canisters were prepared for higher concentration (500 $\mu g\ m^{-3}$) of standard gas mixtures with 0 (dry), 25, 50 and 100% humidity and for lower concentration (50 $\mu g\ m^{-3}$) with 25, 50 and 100% humidity and they were analysed and compared on the same day (day zero). Instrument was calibrated by 50% humidity canister standard and these data were taken as reference for evaluating the influence of humidity. n-Heptane was selected as internal standard. Results are compiled in Table -3.

Recovery of alcohols was found much lower in all standard samples having different humidity and concentrations. The only way to recover alcohols substantially was to have humidity inside the samples to a minimum of 50%. All three alcohols were recovered by 65-80% in lower concentration samples having 25 and 100% humidity in comparison to 50% humidity canisters. 1-propanol was almost not recovered in dry canister. Sulfur compounds were also weak in recovery under 0% (dry) humidity conditions and 30 and 40% loss of dimethyl disulfide and tetrahydrothiophene, respectively, was observed in dry canisters. The rest of the compounds showed above 80% recovery under 25% and 100% humidity conditions and no significant difference was observed between lower and higher concentrations.

Since 50% humidity was taken as a reference, no other humidity gave considerably higher recovery. It indicates that 50% can be taken as optimum humidity. Zero percent humidity resulted in significant loss of sulfur and alcohol-compounds. For alcohols, 25% and 100% humidities were also not sufficient to have high recovery if these compounds were in low concentrations, though some humidity is proved to be quite essential for better results. The deviations in alcohol analyses were significantly high because of water content as shown in Table-2.

Long term stability and recovery of VOC in SUMMA canisters at various levels of relative humidity: Recoveries of VOC stored in SUMMA canisters at 0%, 25%, 50% and 100% relative humidity were studied on day 0, 1, 2, 4, 8, 15 and 30. Recovery of VOC was calculated as a comparison between the initial values (concentration on day zero) of the studied VOC prepared in a canister having 50% humidity and the respective samples on various time intervals. As discussed in the above section 50% humidity showed the highest response for most of the VOC investigated. This is the reason why VOC gas mixture prepared in canister with 50% humidity was selected as a reference for other humidity canisters.

Dry canisters: Table-4 shows the recoveries of VOC from SUMMA canisters under 0% (dry) humidity condition. Alcohols were the most affected compounds with the lowest recovery. 1-Propanol was almost not recovered followed by better recovery of ethanol (39%) and methanol (51%). All three alcohols were poorly recovered in dry canisters on day zero and thereafter recovery became constant with almost no difference with increasing time.

Sulfur compounds were observed to be unstable and their recovery started to decrease from initial day. Dimethyl disulfide and tetrahydrothiophene were recovered only 51 and 12%, respectively, over one month. Their recovery was in the range of 60-70% even on day zero. Tetrahydrothiophene was very weak in absence of humidity and its recovery decreased drastically. Regarding chloro-compounds, both 1,2-dichloroethane and carbon tetrachloride were recovered above 80% on day zero and day 1 but from day 2 they both started decreasing in recovery gradually until 61 and 68% recovery, respectively, on day 30. Aromatic and aliphatic hydrocarbons like benzene, toluene and n-hexane were not influenced by humidity at all and recovered in the range of 85 – 106% during the studied period.

Table - 1: VOC and their selected ions in standard gas mixture.

Compounds	Lower concentration µgm^{-3} (ppb)	Higher concentration µgm^{-3} (ppb)	RT minutes	Q Ions
Methanol	49.60 (37.97)	495.99 (379.74)	1.86	31, 32
Ethanol	49.29 (26.19)	492.85 (261.93)	2.43	31, 45
1-Propanol	50.16 (20.45)	501.64 (204.50)	4.70	31, 59
n-Hexane	49.72 (14.13)	497.25 (141.33)	6.34	57, 86
Benzene	50.83 (15.97)	508.30 (159.66)	8.14	77, 78
Toluene	50.83 (13.54)	508.30 (135.36)	11.43	91, 92
1,2-Dichloroethane	50.23 (12.43)	502.27 (124.35)	7.33	62, 64
Carbon tetrachloride	51.91 (8.27)	519.10 (82.69)	8.30	117, 119
Dimethyl disulfide	49.91 (12.98)	499.11 (129.84)	10.61	45, 94
Tetrahydrothiophene	50.23 (13.96)	502.27 (139.57)	12.36	60, 88
n-Heptane (Internal standard)	-	505.69 (124.02)	9.80	57, 100

Note: Q Ions = Quantification Ions (selected ions used for quantification)

Table - 2: MDL, Standard deviation, Relative standard deviation and Confidence Interval describing method precision for various compounds

	MDL (ppbv)	Standard Deviation (SD) (µg m^{-3})	Relative S.D. (RSD), n=6 (%)	Confidence Interval (µg m^{-3})
Methanol	0.73	31.8	63.6	49.6 ± 31.2
Ethanol	0.96	15.1	30.3	49.3 ± 14.8
1-Propanol	0.96	29.2	58.4	49.7 ± 28.6
n-Hexane	0.11	3.8	7.7	50.2 ± 3.8
Benzene	0.08	4.2	8.4	50.8 ± 4.1
Toluene	0.09	2.2	4.4	50.8 ± 2.2
1,2-Dichloroethane	0.07	3.9	7.9	50.2 ± 3.9
Carbon tetrachloride	0.22	6.5	12.9	51.9 ± 6.3
Dimethyl disulfide	0.53	2.7	5.4	49.9 ± 2.6
Tetrahydrothiophene	0.23	3.3	6.6	50.2 ± 3.2
n-Heptane	-	3.6	7.2	50.6 ± 3.5

Table - 3: Effects of relative humidity on recovery of VOC in SUMMA canisters.

Compounds	Recovery for lower concentration [%]		Recovery for higher concentration [%]		
	25 %	100%	00% (Dry)	25 %	100%
Methanol	*66*	*78*	*47*	*71*	*102*
Ethanol	*82*	*67*	*31*	*66*	*104*
1-Propanol	*72*	*68*	*1*	*118*	*105*
n-Hexane	100	105	104	92	95
Benzene	105	107	98	96	98
Toluene	98	104	90	101	103
1,2-Dichloroethane	99	92	91	95	94
Carbon tetrachloride	85	82	105	86	95
Dimethyl disulfide	91	83	*73*	106	105
Tetrahydothiophene	95	101	*60*	99	96

Note: 50% RH was taken as reference; Values in italics indicate recovery below 80%

25% Relative humidity canisters: Recoveries of lower and higher concentrations of VOC at 25% humidity on day 0,1,2,4,8,15 and 30 are given in Table 5. Methanol and ethanol showed irregular behavior particularly in lower concentrations. Methanol was recovered by 66% on day 0 while recovery increased on day 1, 2 and 4 up to 94% and again decreased to 57% on day 30 for lower concentration gas mixture. Methanol and ethanol exhibited little better results in higher concentrations and they were recovered in the range of 60-85%. 1-Propanol showed drastic decrease in lower concentration and around 20% of 1-propanol could be recovered on day 30, while in higher concentrations a significant loss (40%) was observed during one month period.

On day zero, recovery of dimethyl disulfide was 91% and than it decreased to 47% on day 30, while in higher concentration it was fairly stable. Another sulfur compound, tetrahydrothiophene, was quite stable for 15 days with above 80% recovery for both types of concentrations. Only on day 30 it indicated

Table - 4: Recoveries of VOC from SUMMA canisters with 0% (dry) relative humidity for one month period.

Compounds	Recovery for higher concentration [%]						
	Day 0	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30
Methanol	*47*	*52*	*55*	*52*	*51*	*47*	*51*
Ethanol	*31*	*26*	*16*	*20*	*27*	*38*	*39*
1-Propanol	*1*	*1*	*1*	*1*	*1*	*1*	*1*
n-Hexane	104	106	100	110	97	92	94
Benzene	98	100	101	107	102	96	105
Toluene	90	90	96	92	88	85	89
1,2-Dichloroethane	91	83	*72*	*72*	*61*	*61*	*61*
Carbon tetrachloride	105	87	*76*	*72*	*71*	*68*	*68*
Dimethyl disulfide	*73*	*64*	*70*	*63*	*59*	*53*	*51*
Tetrahydrothiophene	*60*	*54*	*54*	*49*	*38*	*27*	*12*

Note: 50% RH was taken as reference, Values in italics indicate recovery below 80%

Table - 5: Recoveries of VOC from SUMMA canisters with 25% relative humidity for one month period.

Compounds	Recovery for lower concentration [%]							Recovery for higher concentration [%]						
	Day 0	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30	Day 0	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30
Methanol	*66*	85	94	86	*65*	81	*57*	*71*	*67*	80	*74*	80	81	84
Ethanol	182	99	85	115	107	115	176	*66*	*63*	*70*	*59*	85	*77*	*73*
1-Propanol	*72*	*47*	*38*	*19*	*22*	*21*	*24*	118	98	97	90	*63*	*55*	*77*
n-Hexane	100	100	108	108	102	112	109	92	95	98	102	97	102	99
Benzene	105	101	112	99	103	107	103	96	96	103	108	105	103	107
Toluene	98	96	100	89	96	93	99	101	97	105	110	99	97	102
1,2-Dichloroethane	99	85	82	*70*	*60*	*64*	*59*	95	87	*77*	*76*	*63*	*64*	*63*
Carbon tetrachloride	85	82	81	*64*	*72*	*69*	*59*	86	83	*72*	*70*	*63*	*67*	*63*
Dimethyl disulfide	91	*68*	*61*	*48*	89	*59*	*47*	106	102	105	110	102	100	107
Tetrahydrothiophene	95	96	97	90	87	91	*77*	99	92	96	100	91	81	*79*

Note: 50% RH was taken as reference, Values in italics indicate recovery below 80%

Table - 6: Recoveries of VOC from SUMMA canisters with 50% relative humidity for one month period.

Compounds	Recovery for lower concentration [%]						Recovery for higher concentration [%]					
	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30
Methanol	140	92	104	*77*	80	85	99	84	91	*77*	*64*	*69*
Ethanol	181	118	122	143	122	170	*59*	*51*	*61*	*78*	*56*	*59*
1-Propanol	*54*	*35*	*33*	*22*	*19*	*15*	104	*74*	*59*	*51*	*68*	*67*
n-Hexane	106	102	103	100	108	101	96	97	101	91	92	87
Benzene	105	105	103	101	106	101	96	99	104	99	97	92
Toluene	98	101	94	87	98	93	99	99	99	95	89	90
1,2-Dichloroethane	88	*74*	*68*	*58*	*61*	*59*	83	74	74	61	61	55
Carbon tetrachloride	85	*73*	*68*	*65*	*77*	*67*	80	*75*	*68*	*67*	*65*	*55*
Dimethyl disulfide	*64*	*54*	*48*	80	*68*	*69*	88	89	96	81	82	86
Tetrahydrothiophene	105	102	95	94	92	91	95	92	97	91	82	85

Note: 50% RH was taken as reference; Values in italics indicate recovery below 80%

slight loss in concentration with 75-80% recovery for both concentrations. 1,2-dichloroethane and carbon tetrachloride had almost similar behavior for both concentrations with good stability for the first 2 days (>80%) and recoveries were in the range of 59-63% on day 30. Non-polar compounds like benzene, toluene and n-hexane were perfectly recovered in the range of 92-112% with both concentrations on all days of study.

50 % Relative humidity canisters: Recoveries of lower and higher concentrations of VOC at 50% humidity on day 1,2,4,8,15 and 30 are given in Table 6. Alcohols showed irregular behavior particularly with lower concentration sample. Methanol was recovered in the range of 77-140% and 64-99% for lower and higher concentration, respectively. Ethanol appeared to be more influenced by water content in canister with lower concentration. In case of higher concentration of ethanol, its recovery was in the range of 51 – 78% during one month period. Similar to the recovery results of 1-propanol having 25% humidity as discussed in above section, 1-propanol with 50% humidity in lower concentration showed

Table - 7: Recoveries of VOC from SUMMA canisters with 100% relative humidity for one month period.

Compounds	Recovery for lower concentration [%]							Recovery for higher concentration [%]						
	Day 0	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30	Day 0	Day 1	Day 2	Day 4	Day 8	Day 15	Day 30
Methanol	*78*	*59*	*55*	85	88	*56*	*49*	102	*76*	*71*	*72*	*64*	*67*	*58*
Ethanol	*67*	211	114	184	185	144	133	104	101	*56*	*55*	*54*	*71*	*63*
1-Propanol	*68*	*40*	*38*	*27*	*28*	*26*	*23*	105	*69*	85	82	*62*	*62*	*73*
n-Hexane	105	113	112	114	114	108	97	95	98	97	98	94	91	96
Benzene	107	111	113	113	109	105	99	98	102	103	102	104	100	104
Toluene	104	105	105	103	94	95	89	103	105	105	101	98	97	102
1,2-Dichloroethane	92	89	*77*	*68*	*63*	*61*	*56*	94	84	*73*	*70*	*61*	*60*	*62*
Carbon tetrachloride	82	80	80	*60*	*68*	*79*	*67*	95	80	*66*	*69*	*68*	*66*	*73*
Dimethyl disulfide	83	*67*	*49*	*52*	90	84	*64*	105	101	99	99	90	93	98
Tetrahydrothiophene	101	103	99	100	90	87	89	96	98	98	95	93	90	97

Note: 50% RH was taken as reference; Values in italics indicate recovery below 80%

very low recovery (15%) over one month period. 1-Propanol in higher concentration was recovered in the range of 51-104% during one month period.

The recovery of dimethyl disulfide in lower concentration decreased down to 69% over one month period. In higher concentration dimethyl disulfide was quite stable with more than 80% recovery over one month period. Another sulfur compound (tetrahydrothiophene) was recovered above 80% for both types of concentrations over one month period and did not show any sign of depletion. Carbon tetrachloride and 1,2-dichloroethane were stable only for the first two days (day 0 and day 1) followed by gradual decrease in their concentration(up to 40-45%) irrespective of their concentration. Acceptable recoveries (>80%) were obtained for all other non-polar compounds over 30 days.

100 % Relative humidity canisters: Results of recoveries of VOC for both lower and higher concentrations with 100% humidity are summarized in Table -7. Methanol was recovered in the range of 49-78 and 58-102% for lower and higher concentration, respectively. Ethanol was observed in the range of 67-211% during one month study period for lower concentration, while for higher concentration it was well recovered from 104 % on day zero to 63% on day 30. 1-Propanol was poorly recovered for lower concentration and only 23% could be recovered on day 30, while for higher concentration it was recovered in the range of 62-105 %.

Dimethyl disulfide showed decreasing recovery trend within lower concentration range with 100% humidity. It was recovered above 80% only on day zero followed by 67% on day 1 to 64% on day 30. Higher concentration of this compound was quite stable (>90%) over one month period. Tetrahydrothiophene was stable for both types of concentrations with the recovery of 87-103% over one month period. Both chloro-compounds showed similar trend irrespective of concentration and humidity level. They were recovered above 80% for the first two days with subsequent loss of 30-40% during study period (one month). n-Hexane, benzene and toluene were recovered for both concentrations almost without any loss over one month study period.

Alcohols were poorly recovered in dry canisters. 1-Propanol was almost not recovered with 0% humidity while recovery of ethanol and methanol was in the range of 15-50%. In case of lower concentrations of alcohols their content was found to vary much more than in case of more concentrated samples. Ethanol showed more than 100% recovery in the presence of humidity while 1-propanol showed very low recovery in lower concentrations. Overall, recovery of alcohols improved in the presence of humidity. Apparently, it seems that some humidity is necessary for alcohols recovery irrespective of humidity content. The most probable reason in variation of alcohols' recovery is their co-elution with moisture. Water is not well removed from the sample and co-elutes with alcohols influencing their quantitation. Statistical evaluation of the method as discussed in the above section also showed poor reproducibility of alcohols' content. Kelly *et al*. (1993) showed poor precision for polar VOC than for non-polar VOC. Pate *et al.* (1992) reported that the expected concentration (i.e. the injected amount of standard VOC) in canisters did not always agree with their actual concentration. Ochiai *et al.* (2002) showed in their work that ethanol and 1-propanol were not recovered in dry canisters, while ethanol was stable and 1-propanol was poorly recovered with 8% humidity. 1-Propanol was even not fully recovered with 27 and 53% humidity over 28 days. On the other hand, too much humidity (99%) caused significant decrease in alcohols recovery. The results of the presented study for alcohols in higher concentrations are comparable with the results of Ochiai et al. except for 100% humidity results. The recovery of alcohols with 100% humidity does not decrease in comparison to the 25 and 50% humidity. Hoshi *et al.,* (2007) revealed that the RH in the canister should be maintained high and water should not be allowed to condense in the canister while measuring oxygenated samples.

Dimethyl disulfide was quite stable with acceptably high recovery (>80%) for higher concentration samples under all conditions of humidity, while for lower concentration samples its recovery decreased significantly. The recovery of dimethyl disulfide in dry canister was only 51% over one month period. Humidity is necessary for recovery of this compound in higher concentrations, although lower concentration samples are unstable irrespective of humidity. Tetrahydrothiophene was very unstable in dry canister with only 12% recovery over one month period. It showed indication of slight decrease in recovery on day 30 with 25% humidity for both concentrations. 50 and 100 % humidity was found to be sufficient for its almost full recovery.

Chloro-compounds were well recovered on day 0 and day 1 under all conditions of humidity including dry canisters. Recovery of chloro-compounds was found in the range of 60-70% after 2 days with all humidity levels and both lower and higher concentrations. The recovery of chloro-compounds does not decrease further and it can be recovered in the same range over one month period. In the past studies, carbon tetrachloride has shown poor recovery in 0% (dry) humidity condition, though it showed good recovery with some level of water content (Ochiai *et al.,* 2002). Yokohata *et al.* (1985) also reported that carbon tetrachloride tends to be strongly adsorbed on the canister interior surface under relatively dry condition.

Benzene, toluene and n-hexane were quite stable with more than 85% recovery in all experiments. Lower or higher concentration and presence or absence of humidity did not have almost any influence on the recoveries of these non-polar compounds.

Stability of compounds in canisters may be influenced by many factors such as vapor pressure, polarity, water solubility and aqueous reactivity of the compounds. A negative change in concentration during storage (loss of compounds stored in canisters) is either a result of the adsorption on the inner canister surface or dissolution of soluble compounds in condensed water present in canister. Additional loss mechanisms include gas-phase reaction and subsequent transformation in canister, particularly in the presence of ozone or other reactive species, polymerization, hydrolysis and secondary adsorption, i.e. compounds adsorbed on canister surface act as new active sites and adsorb other compounds in the canister (Pate *et al.*, 1992). Increase in measured concentrations of compounds in canisters with the time increase (positive change in concentration) is due to partitioning of VOC between gas phase and condensed water on the canister surface. The extent of this effect depends on Henry's Law of equilibrium of VOC between aqueous and gas phases (Coutant, 1993). In this case, a volatile compound may be partitioned largely into condensed water on the canister surface under the initial canister conditions of pressure, temperature and humidity. However, as sample (and water vapor) is removed during successive analyses of the canister, change in pressure may reduce the amount of condensed water and consequently shift the partitioning of the volatile compound toward the gas phase. As a result, later analysis appears enriched in the volatile compound's concentration (Kelly and Holdren, 1995).

Canister system was optimised and the effect of humidity levels on sample recovery from canisters, one of the most sought-after problems during canister sampling and analysis, was investigated. For a range of compounds, 50% humidity was observed to be the best for their recovery over one month period followed by 100% and 25% humidity. Benzene, toluene and n-hexane were the only compounds that were recovered above 80% over one month period in dry canisters. Some losses of chloro-compounds (30-40%) were observed after two days with all humidity conditions including dry canisters and with both lower and higher concentrations of VOC. Dimethyl disulfide and tetrahydrothiophene were not stable in dry canisters. Dimethyl disulfide was not recovered satisfactorily when it was in lower concentration irrespective of humidity levels while higher concentration of this compound ensures sufficiently high recovery. 50% and 100% humidity was found to be sufficient for the almost full recovery of tetrahydrothiophene. Alcohols were poorly recovered in dry canisters. 1-Propanol was almost not recovered with 0% humidity while recovery of ethanol and methanol was in the range of 15-50%. Recovery of alcohols improved in the presence of humidity. Higher concentrations of polar compounds can ensure better stability of these compounds in canisters.

Acknowledgment

The authors wish to acknowledge and thank Institute's internal project (ID: 216080015) and Czech Government Fellowship to support this research.

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