Minimization of water vapor interference in the analysis of non-methane volatile organic compounds by solid adsorbent sampling

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Abstract

Water vapor can be a significant interference in the analysis of air for non-methane volatile organic compounds (NMVOCs) using solid-adsorbent sampling techniques. The adsorbent materials used in sampling cartridges have different hydrophobic characteristics, and it is therefore necessary to characterize solid-adsorbent cartridges over a wide range of humidity. Controlled humidity experiments were performed to assess the extent of water vapor interference when samples are collected onto AirToxics solid-adsorbent cartridges. It was found that elevating the temperature of the cartridge to 10 °C above the temperature of the air sample greatly reduced water vapor adsorption and interferences and resulted in ≥90% recovery of NMVOCs, biogenic VOCs and chlorofluorocarbons. Similar collection efficiencies were obtained at ambient temperature by reducing the relative humidity to ≤60% in the sample by dilution with dry, scrubbed ambient air. A procedure also was developed and optimized for dry-purging cartridges prior to analysis. However, under optimized conditions, significant losses of C_3–C_5 compounds still occurred under highly humid conditions. It was determined that these losses were due to reduced retention during sampling rather than loss during the dry purge procedure. The dry purge method was shown to be adequate at high humidities for sampling NMVOCs with retention indices greater than 500.
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1. Introduction

The analysis of air for anthropogenic and biogenic volatile organic compounds (VOCs) is made difficult by the complexity of the air matrix, which, in addition to the permanent gases, consists of water vapor and primary and secondary pollution products.

In the absence of a real-time method for analyzing air for VOCs, canisters frequently have been used for sample collection followed by laboratory analysis using gas chromatography (GC) [1–4]. While canister sampling is a well-established and reliable method in many VOC analysis applications, several limitations have been identified. Canisters are cumbersome where the mass and bulk limit the number of samples that can be collected; furthermore polar and high-molecular-mass compounds may be irreversibly adsorbed to the canister walls; some VOCs

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react within the canister with other air components (such as ozone) and inconsistent results have been observed for some light unsaturated compounds [5–8].

Solid-adsorbent sampling has proven its usefulness in atmospheric sampling and become an alternative technique for analysis of atmospheric VOCs. Particularly the advent of multi-stage adsorbent bed cartridges has led to major advances of solid-adsorbent techniques [9–16]. Solid-adsorbent sampling also offers convenience and the ability to develop small sampling packages for vertical profiling using kite, balloon and light aircraft platforms and for personal monitoring packages [17,18]. Solid adsorbents allow compounds of interest to be selectivity sampled. For example, Carbotrap C (Supelco, Bellefonte, PA, USA) selectively adsorbs C_{12}–C_{20} VOCs, Carbopack B (Supelco) adsorbs C_5–C_{12} VOCs, and Carbosieve S-III (Supelco) retains C_3–C_5 VOCs. Multi-bed sampling cartridges allow a wider range of compounds to be sampled, and many are offered pre-packed from the manufacturer. The AirToxics (Supelco) cartridges used in this study contain two adsorbent beds. This allows for the analysis of a wide range of compounds, non-methane hydrocarbons (C_3–C_{12}), as well as, TO-14 compounds [11,19]. The first bed is a Carbotrap (Supelco) graphitic adsorbent, and the second bed is a proprietary molecular sieve adsorbent for the collection of C_3–C_5 compounds.

The principal disadvantage of solid adsorbent cartridges is that problems can arise when sampling humid air [20–22]. Water vapor concentration varies considerably in atmospheric samples and can be as high as 4% (v/v) of the atmosphere. While the manufacturer states both solid adsorbents in the AirToxics cartridges to be relatively hydrophobic, a detrimental amount of water vapor can still be adsorbed. The substantial retention of water vapor on molecular sieve type adsorbents, such as used in the AirToxics cartridge, has been demonstrated in controlled humidity experiments [21]. Excess water vapor adsorbed during sampling and subsequently desorbed during thermal desorption can form an ice plug in a cryogenic focusing trap, or at the head of the GC column during subambient temperature programming. The injected water can also cause peak shifting due to restricted flow of carrier gas through the column, changes in carrier gas viscosity, and changes in the stationary phase polarity and split ratios. As the oven temperature increases, water vapor travels to the detector(s) causing noise spikes and/or extinguishing the detector flame [23].

Several methods to reduce the effect of high humidity by chemical drying using desiccants, drying with adsorbents, removal of water by cryotrapping and by permeation through membrane tubes have previously been examined [21]. Furthermore, elevating the temperature of the adsorbent cartridges while sampling humid air can decrease the amount of water vapor adsorbed. However, small, lightweight sampling packages (such as for use in personal sampling, work exposure monitoring and tethered balloon sampling [17,18]) are not amenable to sample cartridge heating due to power and weight restrictions. Drying salts such as K_2CO_3, used to dry the sample stream prior to collection on the adsorbent cartridge, have been studied for their efficiency [24]. A drying cartridge containing 10–20 g of K_2CO_3 was found sufficient to reduce a 90% relative humidity (RH) sample stream to 10% RH. Unfortunately, reactive biogenic compounds can be lost [5,24,26]. A Nafion membrane (Perma Pure Products, Oceanport, NJ, USA), which is semi-permeable to polar compounds, especially water, can be employed to dry the sample stream by either counter-flowing an inert dry gas around the outside of the membrane or by packing a drying agent around the outside of the membrane. Nafion dryers have been found to sufficiently dry humid sample streams, but reactive biogenic compounds can undergo rearrangement, polar compounds can be lost and contamination of the dryer due to carryover from one sample to another are serious problems [5,24–29].

Dry purging of the adsorbent cartridge prior to analysis is accomplished by flowing a dry inert gas through the cartridge in the sampling flow direction following sample collection at high humidity. If the gas is sufficiently pure, contamination is kept to a minimum and collected compounds will not undergo further reactions [20,26,30–33]. Of course, it is very important that compounds are not lost during the dry purge step. Using multibed adsorbent cartridges of Carbotrap C/Carbotrap B/Carbosieve S-III and Carbotrap C/Carbotrap B/Carboxen 569, Gawlowski et al. found no loss of polar VOCs with the

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exception of methanol when samples were dry-purged with 900 ml of dry helium at 30 °C [33]. McClenny et al. extensively tested Carbotrap B, Carbotrap C and Carboxen 1000 solid adsorbents and reported dry purge conditions for TO-14 compound analysis [34]. In this study, AirToxics solid-adsorbent cartridges were used for the investigation of several water management approaches. AirToxics adsorbent tubes have become a frequent choice for VOC analysis and have been characterized for various analysis applications [17,19,33,35].

The amount of water vapor adsorbed by sampling cartridges depends on the sample volume, adsorbent material, cartridge temperature, and relative humidity of the sampled air stream [21]. In this study, three methods to reduce or remove the water adsorbed during sampling were investigated. First, experiments were performed in which the solid adsorbent cartridges were slightly heated during sampling. Next, dry scrubbed air was mixed with the humid sample stream to lower the humidity below a threshold level. Lastly, experiments were conducted that determined the optimal conditions for dry-purging AirToxics solid adsorbent cartridges. Unfortunately, reduced recoveries of light hydrocarbons (C_1–C_5) were found in the latter experiments. Additional experiments were carried out to determine the extent to which the light hydrocarbons are lost during sample collection and during dry purging of samples collected at high humidity.

2. Experimental

2.1. Materials

Pure gases were purchased from Airgas Houston, Houston TX, USA: helium (99.999% purity), hydrogen (99.999% purity), nitrogen (99.999% purity), ultra zero grade air (THC<0.1 ppm, CO<1 ppm, CO_2<1 ppm, H_2O<5 ppm); and electron-capture detection (ECD) system make-up gas, 5% methane (99.97% purity), 95% argon (99.999% purity). In addition, two ambient air standards were collected into stainless steel cylinders with an oil-free compressor on (a) 6 June 1996 between 17:30 and 18:30 h in the city of Boulder, CO, USA (urban air standard) and on (b) 6 March 1998 at Niwot Ridge,

CO, USA (continental background air standard). A standard of 1 ppm isoprene, and a standard mixture containing methacrolein (MACR), methylvinylketone (MVK), α-pinene, β-pinene and limonene at mixing ratios of 78 ppb, 87 ppb, 33 ppb, 13 ppb, and 1 ppb, respectively, were used as representative biogenic compounds. Water used was doubly distilled and de-ionized. AirToxics adsorbent cartridges were purchased from Supelco and were used for all sample collections. The cartridges are stainless steel, 88.9 mm in length with a 4.8-mm inner diameter and contain a 35-mm length bed of Carbopack B plus 10 mm of a proprietary molecular sieve separated by glass wool. Supeltex M-2A Vespel ferrules were used with Swagelok fittings to seal the cartridges.

2.2. Sampling cartridges

AirToxics adsorbent cartridges were conditioned by flowing through the cartridges approximately 90 ml min^{-1} (all sampling flow-rates and sampling volumes are given normalized to STP conditions, 0 °C, 1013 mbar) of N_2 that had passed through oxygen traps and a hydrocarbon trap. Cartridges were backflushed for 60 min while heating to 350 °C and subsequently capped with Swagelok fittings and stored in glass mason jars until use.

2.3. Sampling apparatus

The humidity generator consists of a microporous polytetrafluoroethylene (PTFE) tube surrounded by a thermostatted water jacket (Fig. 1). Increasing the temperature of the water surrounding the PTFE tube increased the water vapor content of the air passing through it. Dry samples were obtained by bypassing the water-jacketed PTFE tube, thereby allowing a comparison between dry and humid samples. Relative humidity could be adjusted by changing the ratio between the bypass and the PTFE tube flow-rates in combination with the temperature of the water jacket. In the experiments reported here, a nitrogen flow of 340 ml min^{-1} passed through the humidity generator. This flow was combined with 38 ml min^{-1} of the ambient air standard. The humidity sensor downstream of the mix maintained the relative humidity at 95% by a feedback loop to the humidity generator heater. Samples were collected
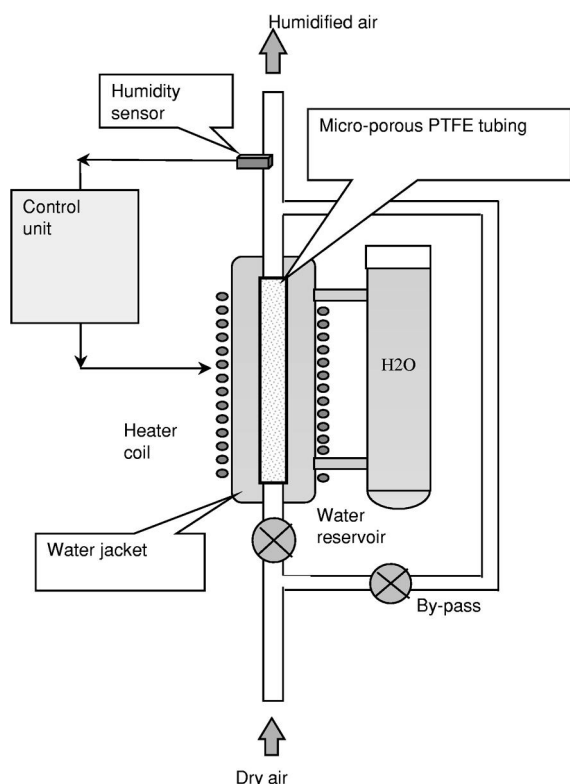
Fig. 1. Schematic diagram of the humidity generator.

onto the solid adsorbent cartridges by use of a mass-flow controlled sampler constructed in our laboratory. The sampler accommodated 10 sampling cartridges connected by Swagelok fittings. All tubing upstream of the sampling cartridge was silica-lined stainless steel (Silcosteel, Restek, Bellefonte, PA, USA). Electrically-actuated valves (4-port switching valve and 10-port sampling valve) (VICI, Houston, TX) controlled the sampling stream. The sampler valves were timed and switched by a computer running a BASIC program. Sample cartridges were weighed before and after sampling to determine the water mass gain. A unique feature of this apparatus is that cartridges can be temperature-controlled to 0–25 °C above ambient air temperature during the sampling procedure or for dry purge applications.

2.4. Dry purging

The 10-port sampler also was used for dry purging for various lengths of time using UHP nitrogen.

Following dry purging, sample cartridges were re-weighed prior to analysis to determine how much water remained on the cartridges.

2.5. Desorption and cryogenic focusing

Using a Perkin-Elmer ATD-400 autosampler, samples were desorbed at 300 °C for 15 min in a flow of UHP helium (25 ml min^{-1}) that had passed through oxygen traps and a hydrocarbon trap. Desorbed compounds were focused onto a microtrap held at -25 °C. With the GC oven at 0 °C, samples were injected on the GC column by rapidly heating the cold trap to 325 °C and held for 5 min. The sample was transferred from the cold trap to the GC column by a 0.53-μm I.D. deactivated fused-silica transfer line maintained at 150 °C.

2.6. GC separation and detection

Analytes were separated on a 30 m × 0.32 mm DB-1 capillary column with 5 μm film thickness (J&W Scientific, Folsom, CA, USA). Liquid nitrogen was used to maintain the GC oven at 0 °C for 5 min. The oven temperature was then ramped at 6 °C min^{-1} to 180 °C and held at that temperature for 5 min. A second ramp of 30 °C min^{-1} to 250 °C was used to clean the column prior to cooling the column to 0 °C for the next sample. The end of the GC column was split into two flows by a glass Y connector. A deactivated fused-silica capillary, of 100 cm × 0.18 mm I.D., directed 5% of the effluent to an ECD system. Another deactivated fused-silica capillary that has an internal diameter of 0.32 mm and 53 cm length, directed 95% of the effluent to a flame ionization detection (FID) system. The ECD system was operated at 375 °C with 40 ml min^{-1} 95% argon, 5% methane makeup gas. The FID system was operated at 300 °C with flows of 350 ml min^{-1} of air and 45 ml min^{-1} of hydrogen.

3. Results and discussion

3.1. Water retention as a function of sample relative humidity

In order to determine the amount of water ad-sorbed on the AirToxics solid adsorbent cartridges,
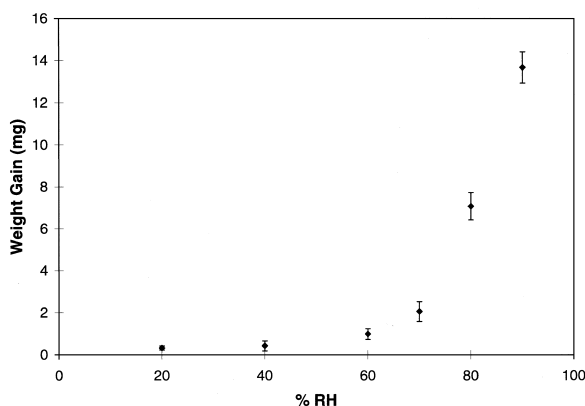
Fig. 2. Water uptake (mean of three measurements with standard deviation) of AirToxics solid-adsorbent cartridge as a function of relative humidity in the sampling air (3.8 l sampling volume).

the downstream relative humidity was monitored while the sample stream to the cartridges was varied from 0 to 95% relative humidity (RH). Cartridges were weighed before and after sample collection. Sample cartridges were loaded with 3.8 l of a standard gas mixture at a cartridge temperature of 23 °C. As seen in Fig. 2, there is a sharp increase in the mass of water retained above a relative humidity level of approximately 60%. Up to 20 mg of water

was accumulated on sample cartridges that collected 3.8 l of air at 95% RH, the highest humidity level tested. GC analysis of samples collected at 70% RH resulted in significant noise and peak shifting in the ECD chromatogram. For example, in the ECD chromatogram in Fig. 3, the chlorofluorocarbons (CFC) CFC-11 and CFC-113 peaks have shifted from the dry retention time, and noise spikes obscure the CFC-11 peak. Also, at this RH level enough water was adsorbed to cause the FID flame to extinguish.

3.2. Effect of cartridge collection temperature on water retention

The effect of collection temperature on retention of both water and VOCs was studied in the temperature range 25–45 °C for 80–90% RH sample streams. AirToxics sample cartridges were loaded with 3.8 l samples, and GC analysis was performed to assess compound recovery in comparison to dry samples collected at 25 °C. Mass data revealed the mass of water adsorbed at a particular humidity level and as a function of cartridge temperature. Fig. 4 shows that maintaining the sample cartridges approximately 10 °C above ambient temperature prevents
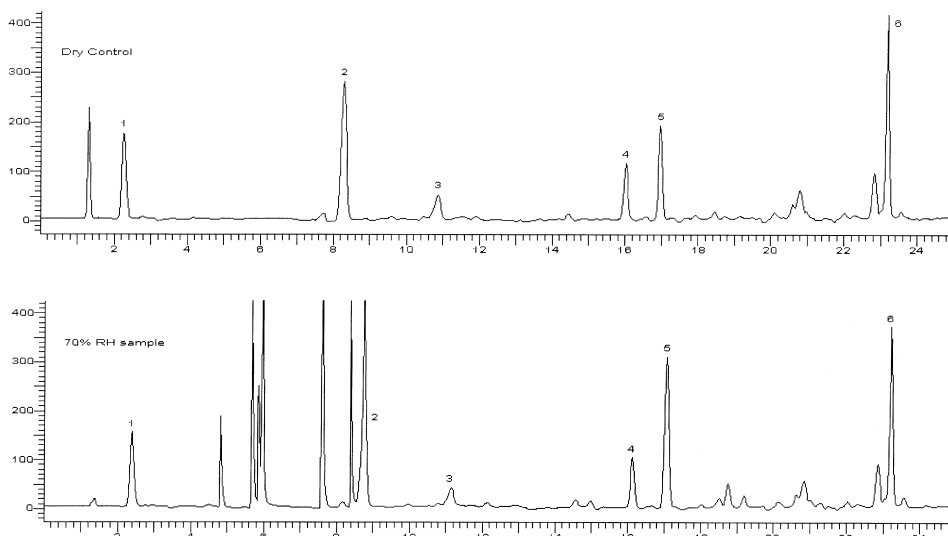

Fig. 3. Top: ECD chromatogram from a dry ambient standard (dry control). Bottom: chromatogram of the same standard humidified to 70% RH at 25 °C. Peak identifications: (1) CFC F-12, (2) CFC F-11, (3) CFC F-113, (4) methylchloroform, (5) carbontetrachloride, and (6) tetrachloroethylene. x-Axes: time in min; y-axes: response in mV.
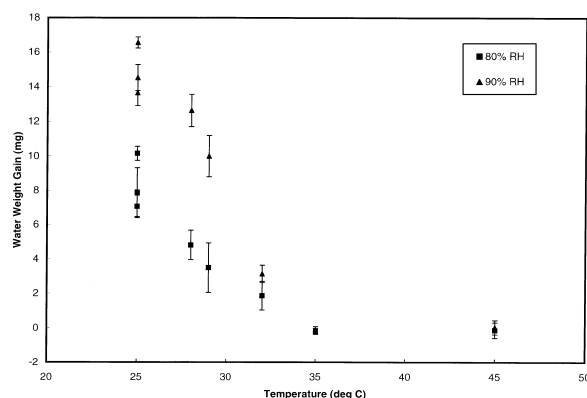
Fig. 4. Water uptake (mean of three measurements with standard deviation error bars) of AirToxics solid-adsorbent cartridges at 80 and 90% relative humidity (25 °C sampling air temperature). While the sample air temperature was kept constant the cartridges were heated during the sampling procedure. The resulting water gain is illustrated as a function of the adsorbent cartridge temperature.

the adsorption of water that would otherwise require a dry purge before analysis.

Experiments also were performed to determine the percent recovery of compounds sampled while varying both the sample stream humidity level and the cartridge temperature, as compared to dry samples collected at 25 °C. A summary of the experimental results is given in Table 1. Most VOCs were recovered from humid air streams with efficiencies

greater than about 90% when the solid-adsorbent cartridges were heated up to 35 °C (10 °C above the sampling air temperature). Only propane suffered slight losses at this temperature. Greater compound losses were experienced at 45 °C, and thus 35 °C was determined to be the optimal cartridge temperature for sample collection under humid conditions. Our findings are consistent with studies by Gawrys et al. [36], who tested four molecular sieve type adsorbents for their water uptake and similarly concluded that moderate heating of the sampling cartridge is a feasible technique for water management when using molecular sieve type solid adsorbents.

3.3. Effects of mixing dry air with the humid sample stream

Experiments were performed to determine whether very humid sample streams could be reduced below the threshold humidity level by mixing dry, scrubbed air into the sampling stream. Approximately 660 ml min^{-1} of a humidified ambient air standard (90% RH, Niwot standard) was diluted with approximately 400 ml min^{-1} of ambient air that passed through an ozone filter (prepared by soaking a glass fiber filter in a solution of $Na_2S_2O_3$ [37], a water trap (20 g of K_2CO_3) [24], and a hydrocarbon trap (Perkin-Elmer, Norwalk, CT, USA). This "dry" dilution effectively reduced the sample stream humidity from 90% RH

Table 1

Percent recoveries (means of three measurements) and standard deviation of non-methane hydrocarbons (NMHCs) and CFCs

Compound	Recoveries±SD (%)				
	50% RH; 30 °C	20% RH; 35 °C	70% RH; 30 °C	90% RH; 35 °C	70% RH; 45 °C
Propane	83.6±4.1	73.8±0.3	71.7±1.7	71.7±2.3	45.4±2.2
Methylpropane	89.0±2.3	89.9±1.9	94.4±3.6	97.3±7.7	94.0±4.7
CFC-12	94.3±1.6	92.1±1.1	90.0±1.4	89.9±1.3	73.3±0.9
Butane	96.6±1.3	97.0±2.5	98.4±2.1	99.4±5.4	97.2±2.6
CFC-11	89.2±4.5	92.9±8.0	93.3±8.6	91.2±8.8	97.8±4
Pentane	100.7±2.4	99.3±2.0	103.3±1.0	103.2±3.4	99.8±0.4
CFC-113	92.5±0.8	90.3±0.8	90.3±2.0	89.4±0.7	89.6±1.5
Hexane	98.2±1.6	101.3±3.3	107.7±2.0	106.4±5.1	107.8±4
Methylchloroform	87.3±3.8	91.8±1.3	87.2±3.6	90.8±4.3	76.5±4.7
CCl$_4$	94.9±1.0	95.4±0.6	94.5±1.2	93.0±4.1	87.3±1.2
Heptane	96.7±2.7	82.2±2.7	90.1±5.8	93.2±10.1	83.4±10.7
Octane	96.3±1.7	94.0±4.8	100.5±1.7	96.0±0.7	101.8±2.6
Cl$_2$C=CCl$_2$	95.5±1.5	97.0±1.2	98.3±1.1	95.5±0.5	102.2±1.8

Samples were loaded at 25 °C room temperature and under 20–90% RH, while the adsorbent cartridge was heated to 30–45 °C. Humidified samples were compared to a dry reference sample collected at 25 °C for the calculation of percent recoveries.

to 50% RH. Sample cartridges were loaded at ambient temperature with 6.4 l samples to account for the dilution. Water adsorption on the solid adsorbent cartridges was approximately 1 mg. Compound percent recoveries were determined by comparison to a dry ambient standard (Niwot) that was diluted in the same manner. The results of this experiment are illustrated in Table 2 and show good recovery ($>85\%$) of all compounds. Although this experiment suffered from high background levels, results indicate that ''dry'' dilution is a viable approach for water management. Therefore, for future applications of this technique a more rigorous scrubbing procedure for the dilution gas (for instance by applying a stronger adsorbent scrubber or a cryogenic trap) or by using ultra-high-purity nitrogen dilution gas from a gas cylinder is suggested.

3.4. Effects of dry purging the cartridge

Experiments were performed to investigate dry purge flow-rates and volumes. Following collection of 3.8 l air at 95% RH, samples were dry-purged in the sampling flow direction with UHP N_2 at 42 ml min^{-1} for 10–40 min with the cartridge temperature held at 35 °C. The sample cartridges were weighed before and after sampling and again after the dry purge to determine water mass gain and removal. The samples also underwent GC–FID–ECD analysis to monitor compound percent recoveries compared to dry samples that were collected as controls. The results of this experiment are shown in Fig. 5 and show that a 800 ml dry purge volume is sufficient to remove approximately 19 mg of water. Varying of the dry purge flow-rate in the range 42–84 ml min^{-1} (at constant total dry purge volume) revealed no increase in compound breakthrough at the higher flow-rates.

Chemical losses from dry purging were tested with the Boulder air and biogenic VOC standards. Cartridges were loaded with 3.8 l of standard at 90% RH, and subsequently dried by purging with 84 ml min^{-1} of UHP N_2 for 10 min. Under these conditions, 1 mg or less water remained on the cartridges. Percent recoveries were determined by comparing the results from the dry-purged wet samples to dry control samples. FID chromatograms of the Boulder air standard, given in Fig. 6, show only minor differences between the two experiments.

Percent recovery data of all the compounds studied are given in Fig. 7. From this figure it can be seen that some lighter compounds (retention index less than 500) are not fully recovered. The non-methane hydrocarbons propane, methyl propane, butane and methylbutane had significant losses, while pentane through decane did not. CFC-12 and CFC-11 also suffered losses under humid sampling conditions. The biogenic compounds isoprene, MACR, MVK, α-pinene, β-pinene and limonene
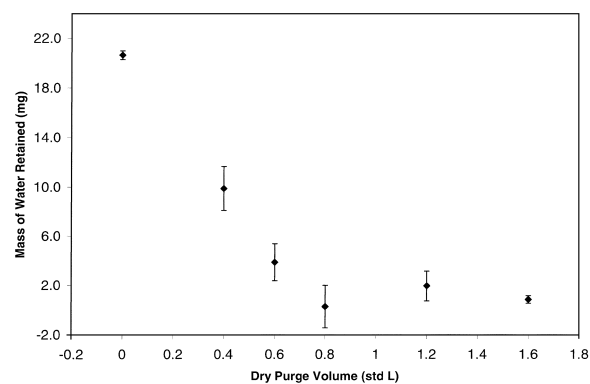
Table 2
Percent recoveries (mean of three measurements) and standard deviations of NMHCs and CFCs collected from a 90% RH sample stream that was reduced to 50% RH by mixing with dry scrubbed air

Compound	Retention index	Recovery ±SD (%)
Propane	300	87.3±5.2
Methylpropane	352	85.8±7.5
CFC-12	312	91.0±0.5
Butane	400	91.0±0.8
CFC-11	481	90.4±7.0
Pentane	500	94.9±0.8
CFC-113	533	89.1±1.8
Hexane	600	84.4±9.0
Methylchloroform	638	93.4±17.3
Carbon tetachloride	659	93.1±9.1
Toluene	761	86.1±6.0
Octane	800	95.5±3.7
Tetrachloroethylene	808	88.6±0.9

Compound recoveries were determined by comparison to an undiluted dry standard.

Fig. 5. Effect of dry purge volume (dry purge at 35 °C) on mass of water retained by the sampling cartridge ($n=3$, error bars represent 1 standard deviation).
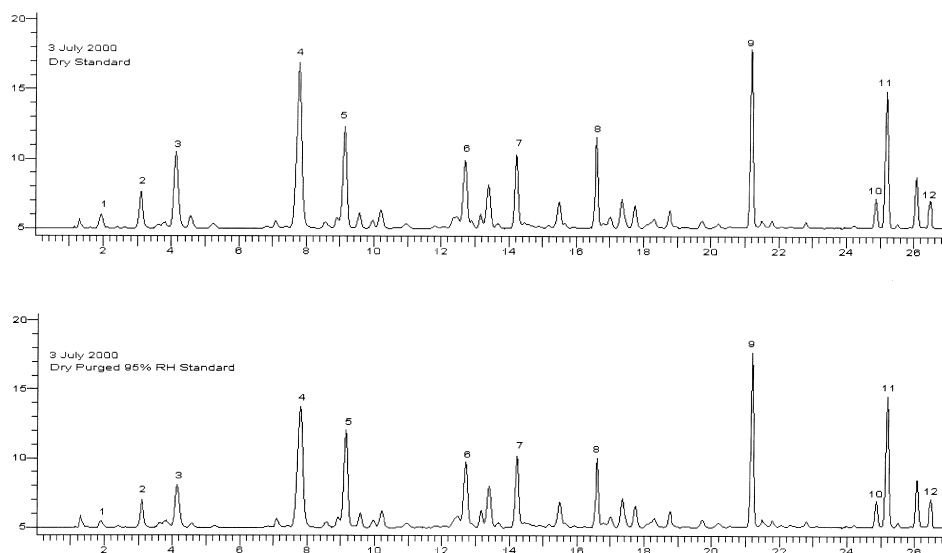
Fig. 6. Top: FID chromatogram of a 3.8 l ambient standard diluted with dry N_2 (dry control). Bottom: FID chromatogram of the same standard (3.8 l) which was diluted with humidified N_2 (wet sample) and subsequent dry-purged. Peak identifications: (1) propane, (2) methylpropane, (3) butane, (4) methylbutane, (5) pentane, (6) methylpentane, (7) hexane, (8) benzene, (9) toluene, (10) ethyl benzene, (11) *m/p*-xylene, and (12) *o*-xylene. *x*-Axes: time in min; *y*-axes: response in mV.

were fully recovered. There was rearrangement between α- and β-pinene (i.e. loss of β-pinene and gain of α-pinene) but we are not certain if this observation is a result from the dry purge procedure or from rearrangements occurring during thermal
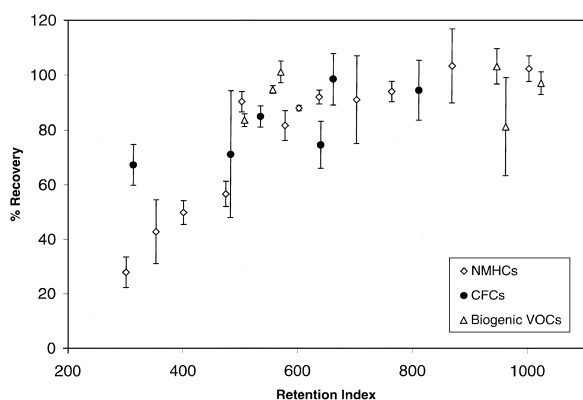

Fig. 7. Percent recoveries of non-methane anthropogenic hydrocarbons, biogenic VOCs and CFCs as a function of GC retention index (Table 3). The data represents samples collected at 95% RH and dry purged with 840 ml of UHP N_2 at 35 °C.

desorption, as previously observed by others [38]. It is expected that other biogenic compounds with a retention index greater than 500 will not suffer losses under high humidity sampling conditions followed by dry-purging.

In order to further investigate the observed loss of the light hydrocarbons, an experiment was designed to collect the effluent during dry purge. Standard samples (Boulder standard) and sample blanks (UHP N_2) were collected at a flow-rate of 315 ml min^{-1} for 12.5 min. The standard was collected at 95% RH ("wet") and 15% RH ("dry"). In addition, sample blanks (UHP N_2) were collected at both 95% RH ("wet") and 15% RH ("dry"). After weighing, the cartridges were reattached to the sampler and a second cartridge was placed in series with the cartridge undergoing dry purge (10 min at 84 ml min^{-1} at 35 °C) in order to collect the dry purge effluent on the second cartridge. The "wet" standard samples, the "wet" blanks and half of the "dry" standard samples underwent dry purge in series with a dry purge collection cartridge. The "dry" standard samples that were not dry-purged served as the control. Percent recoveries of compounds were de-

termined by comparing compound levels in the various samples to the levels found in the control. Thus, losses in the ''dry'' ambient standard that underwent dry purge can be attributed to breakthrough during the dry purge process. Any compounds lost from the ''wet'' or ''dry'' ambient samples during the dry purge would be retained in the dry purge backup cartridge. Any compound losses from the ''wet'' ambient samples that are not accounted for by breakthrough during the dry purge must be a result of reduced VOC retention on the cartridge from the sample humidity.

The results of these experiments are summarized in Table 3. The purge collection shows that propane suffers from breakthrough during the dry purge. However, the amount lost during the dry purge (20–30%) is less than half of the total loss. The remaining loss must have occurred during sampling. Methylpropane, butane and methylbutane have a loss of about 50% when the sample is wet. However, the purge collection cartridges contained only 4% or less of these compounds. Therefore, loss of these compounds is related to the water collected on the cartridge during sampling and not the dry purge. As seen in Table 3, some breakthrough may occur for

CFC-12 during dry-purging. Although significant losses occur under wet conditions for other CFCs, very little of this loss occurs as a result of dry-purging.

Compound losses at high humidity levels may be attributed to the water adsorbed during sampling. AirToxics sampling cartridges contain two adsorbent beds. The molecular sieve adsorbent retains the most volatile compounds (C_3–C_5), while the second adsorbent retains C_5–C_{12} compounds. It was concluded that the molecular sieve adsorbent fails to retain the light hydrocarbons (e.g. propane, methylpropane, butane and methylbutane) when significant water vapor is present in the sample stream. McClenny and Colen found that methylchloroform, carbon tetrachloride and tetrachloroethylene are completely adsorbed onto Carbotrap, while CFC-12, CFC-11, and CFC-113 are adsorbed onto both Carbotrap and Carboxen 1000 (molecular sieve adsorbent) [19]. This explains why CFC losses were not as great as for the light hydrocarbons. The structure of the molecular sieve adsorbent lends itself to water interference. Water vapor is able to condense in the small pores present in the molecular sieve [39,40]. Competition between analytes and water for active

Table 3
Percent loss (means of three measurements) of NMHCs and CFCs in a humidified (95% RH) standard

Compound	Retention index	Wet standard loss (%)	Purge collection (as % of dry spl)
Propane	300	−71.6	28.4
CFC-12	312	−31.4	24.8
Methylpropane	352	−56.4	3.6
Butane	400	−49.2	−0.2
Methylbutane	473	−42.2	0.1
CFC-11	481	−27.4	1.4
Pentane	500	−7.8	−0.1
CFC-113	533	−25.5	−0.6
Methylpentane	576	−16.7	0.4
Hexane	600	−10.2	−0.3
2,4-Dimethylpentane	635	−6.1	0.3
Methylchloroform	638	−56.4	1.1
Carbon tetrachloride	659	0.5	0.3
Heptane	700	−7.1	−8.6
Toluene	761	−4.1	−0.8
Tetrachloroethylene	808	−3.6	0.1
p-Xylene	866	5.5	0.0
Decane	1000	4.4	0.3

The third column shows the not-retained portion under this condition (wet standard loss) and the fourth column represents the percentage loss during the dry purge step.

adsorbent sites has been described previously [12,41]. Under very humid conditions, the pores may fill with water, thereby preventing the retention of VOCs and reduced recovery of those compounds that predominantly are trapped on the molecular sieve portion of the multi-bed cartridge.

4. Conclusions

Water retention in dual-bed AirToxics solid-adsorbent cartridges is predominantly determined by the second, molecular sieve adsorbent in these tubes. Three types of water management techniques for collection of humid air samples were investigated. (1) It was found that heating the cartridges to 10 °C above ambient temperature prevented the adsorption of water vapor and that VOCs and CFCs ranging from C_3–C_{12} (except propane) could be collected and analyzed with recoveries of ≳90%. The reduction of breakthrough volumes under the heated cartridge condition is acceptable for most VOCs of interest and is significantly less than the reduction of the breakthrough volume, respectively the loss of light VOCs that may occur from the co-adsorption of water in humid samples when the cartridge is not heated. (2) In addition, diluting a humid sample stream with scrubbed "dry" air successfully reduced the relative humidity and prevented water adsorption on the solid adsorbent cartridges even at ambient temperature. (3) Dry purging of sample cartridges to remove water vapor prior to analysis with 84 ml min^{-1} of N_2 for 10 min at 10 °C above the sample air temperature (e.g. 35 °C for 25 °C laboratory air experiments) was found to be adequate to remove all but approximately 1 mg of water from 3.8 l samples collected at 95% RH. Controlled humidity experiments, however, revealed significant losses of compounds that had a retention index less than 500. This loss was determined to be due to a lack of retention by the molecular sieve adsorbent during sampling at high humidity. Only the losses of propane and CFC-12 could be partially attributed to loss during the dry purge.

In conclusion the results from this study show that techniques (1) and (2) are advantageous because of higher recoveries for lighter VOCs and because they circumvent the additional analytical dry purge step.

Furthermore the technique of slight (10 °C) heating of the cartridge during sampling has the advantage of preventing possible contamination problems during an additional dry-purge step and from purging the adsorbent cartridge with a gas other than the sample air.

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