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Ozone Artifacts and Carbonyl Measurements Using Tenax GR, Tenax TA, Carbopack B, and Carbopack X Adsorbents

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ABSTRACT

Four popular thermally desorbable adsorbents used for air sampling (Tenax TA, Tenax GR, Carbopack B, and Carbopack X) are examined for the potential to form artifacts with ozone (O_3) at environmental concentrations. The performance of these adsorbents for the ketone and aldehyde species identified as O_3-adsorbent artifacts was also characterized, including recovery, linearity, and method detection limits (MDLs). Using gas chromatography/mass spectrometry, 13 different artifacts were identified and confirmed for both Tenax TA and Tenax GR, 9 for Carbopack B, but none for Carbopack X. Several O_3 artifacts not reported previously were identified, including: pentanal, 3-hexanone, 2-hexanone, hexanal, 3-heptanone, and heptanal with Tenax TA; pentanal, 3-hexanone, 2-hexanone, hexanal, and 3-heptanone on Tenax GR; and 1-octene and 1-nonene with Carbopack B. Levels of straight-chain aldehyde artifacts rapidly diminished after a few cycles of adsorbent conditioning/O_3 exposure, and concentrations could be predicted using a first-order model. Phenyl-substituted carbonyl artifacts (benzaldehyde and acetophenone) persisted on Tenax TA and GR even after 10 O_3 exposure-conditioning cycles. O_3 breakthrough through the adsorbent bed was most rapid in adsorbents that yielded the highest levels of artifacts. Overall, artifact composition and concentration are shown to depend on O_3 concentration and dose, conditioning method, and adsorbent type and age. Calibrations showed good linearity, and most compounds had reasonable recoveries, for example, 90 ± 15% for Tenax TA, 97 ± 23% for Tenax GR, 101 ± 24% for Carbopack B, and 79 ± 25% (91 ± 9% for n-aldehydes) for Carbopack X. Benzeneacetaldehyde recovery was notably poorer (22–63% across the four adsorbents). MDLs for several compounds were relatively high, up to 5 ng. By accounting for both artifact formation and method performance, this work helps to identify which carbonyl compounds can be measured using thermally desorbable adsorbents and which may be prone to bias because of the formation of O_3-adsorbent artifacts.

INTRODUCTION

Sampling of airborne volatile organic compounds (VOCs) using thermally desorbable solid adsorbents has proven its usefulness in many environmental applications and has become a routine technique[1] with compelling advantages over canisters, especially when a large sample volume or sample transport is needed.[2] Many adsorbents are available, and users are faced with the difficulty of selecting materials appropriate for specific applications.[3] The ideal adsorbent would have the following characteristics: (1) efficient adsorption and desorption of target compounds, potentially including very volatile, semivolatile, polar, and nonpolar compounds; (2) thermal stability; (3) low background levels of contaminants; (4) unaffected by storage; (5) capable of sampling at very low concentrations; (6) uninfluenced by humidity[4]; (7) high capacity and breakthrough volume; (8) limited back diffusion losses (especially important for passive and low-flow sampling); (9) minimal water uptake; (10) longevity, allowing numerous conditioning/sampling/desorption cycles; and (11) minimal adsorbent-oxidant reactions that yield artifacts. No single adsorbent fulfils all of these requirements and, increasingly, multisorbent tubes are used.

Air constituents like ozone (O_3) and nitrogen oxides (NO_x) can react with the adsorbent bed and analytes to form unwanted artifacts that can cause positive artifacts, whereas reactions with previously adsorbed compounds on the surface of the adsorbent can cause negative biases.[3,5–8] The most recognized and significant interference occurs because of reactions with O_3.[5] Although a number of positive artifacts have been documented,[9–12] the literature is limited and qualitative, and identifications of many suspected artifacts have not been confirmed. The importance of artifact formation is likely to increase as

IMPLICATIONS

The formation of artifacts in air sampling can lead to biases, especially for carbonyl compounds that may be both formed and destroyed by reactions between O_3 and adsorbents Tenax TA, Tenax GR, and Carbopack B. No positive O_3-adsorbent artifacts were identified with Carbopack X, although this adsorbent had poorer recoveries of carbonyls (other than n-aldehydes) and higher detection limits than the three other adsorbents. Concentrations of several artifact compounds will diminish with repeated adsorbent use; however, other compounds can be persistent. Thermally desorbable adsorbents can be used to measure carbonyls, although methods may require refinement to address sensitivity and artifact issues.

Table 1. Characteristics of the adsorbent materials in this study.

Adsorbent	Material	Mesh Size	Surface Density ($m^2\ g^{-1}$)	Maximum Temperature (°C)
Tenax GR	2,6-Diphenyl-*p*-phenyleneoxide with 23% graphitized carbon	60/80	24	375
Tenax TA	2,6-Diphenyl-*p*-phenyleneoxide	60/80	35	375
Carbopack B	Graphitized carbon black	60/80	100	<400
Carbopack X	Graphitized carbon black	60/80	240	<400

method detection limits (MDLs) improve and as the number of polar compounds targeted as analytes grows.

This work characterizes O_3-adsorbent artifacts for four popular adsorbents (Tenax GR, Tenax TA, Carbopack B, and Carbopack X) using well-controlled laboratory tests. A quantitative assessment of artifacts is provided using certified calibration standards and gas chromatography (GC)/mass spectrometry (MS) analysis, evaluating aging effects that result from repeated O_3 exposure, and exploring some of the potentially causative mechanisms. Two relatively new materials are evaluated: Carbopack B, which has not been tested previously for O_3 artifacts, and Carbopack X, which has been examined recently by McClenny et al.[7] O_3 breakthrough curves developed for the four adsorbents provide new information that helps to explain artifact formation. To quantify the artifacts, analytical methods (including calibrations, MDLs, and absorbent recoveries) were developed for the 15 carbonyls identified as O_3-adsorbent artifacts and for each of the four adsorbents.

BACKGROUND

Adsorbents used for thermal desorption can be classified into polymers, graphitized carbon blacks (GCBs), carbon molecular sieves, the carbon skeletal framework remaining after pyrolysis of a polymeric precursor, and other materials. In this paper, two polymeric materials and two GCB materials are evaluated. Characteristics of these adsorbents are shown in Table 1.

Polymer/Tenax Adsorbents

Tenax GC was the first adsorbent used for VOC analysis with thermal desorption.[13] This porous polymer is based on 2,6-diphenyl-*p*-phenylene oxide, a low bleed material originally used as a GC column packing. Problems recognized with Tenax GC when used for air sampling include a rather high background[14] and chemical decomposition in the presence of oxidants, such as O_3 and NO_x, that can produce VOC artifacts.[15,16] Often, however, no O_3 artifacts are reported.[17] Subsequently, Tenax TA was developed for air sampling purposes, a material with lower background, and some localized negative charges. Another variant, Tenax GR, which contains 23% graphitized carbon, is a more inert material with a higher breakthrough volume for C_5 compounds.[18] Although considered to be "weak" adsorbents given a surface density of only 35 $m^2\ g^{-1}$, Tenax adsorbents have many favorable properties for air sampling, for example, high breakthrough volumes of C_7 to C_{26} VOCs, good thermal stability, a maximum temperature of 390 °C, and low water

retention.[19] Tenax GR has a higher density (0.55 g mL^{-1}) than Tenax TA (0.25 g mL^{-1}) because of its graphite content and a somewhat larger retention volume for very volatile compounds.[20] On the other hand, higher background has been claimed for Tenax GR than Tenax TA.[18] Currently, Tenax GR appears to be the most commonly used solid adsorbent for thermal desorption of air samples.

Artifact formation with Tenax has been studied or reported for exposures to O_3,[16,21–24] nitrogen dioxide (NO_2),[16,22,24] nitrogen oxide (NO),[16,24] sulfur dioxide, hydrogen peroxide,[24] OH radical,[24] limonene oxidation products (with O_3 and NO_2),[22,24] and halogens (Cl_2 and Br_2).[25] Table 2 summarizes the O_3-Tenax artifacts identified in the literature. Phenyl-substituted carbonyl compounds, especially benzaldehyde, acetophenone, benzophenone, and benzeneacetaldehyde (Figure 1), have been reported as the principal O_3-Tenax artifacts. Additional artifacts identified include phenol, benzonitrile, C_9- and C_{10}-aldehydes, and compounds tentatively identified as "alkylated phenols."[10] Using relatively large O_3 doses (20 L at 50 ppb and 2 L at 1000 ppb), Klenø et al.[24] identified the largest number of O_3-Tenax artifacts. Pellizzari et al.[16] noted that O_3-Tenax GC artifacts decreased as adsorbents aged, for example, benzaldehyde declined from 670 to 65 ng and acetophenone from 300 to 20 ng from the first to the fifth exposure cycle. NO_2 exposure formed 2,6-diphenyl-p-benzoquinone and 2,6-diphenyl-p-hydroquinone; the latter compound was also found in the simultaneous presence of O_3 and limonene.[22] No significant differences between the two versions of Tenax have been reported.[10] However, the presence of graphite enhanced the decomposition of certain compounds, especially terpenes.[26] Tenax GR was also associated with the catalytic breakdown of some microbially related VOCs, for example, 2-methylisoborneol, geosmin, and 1-octen-3-ol.[4] Clausen and Wolkoff[22] have suggested that one artifact, phenylmaleic anhydride, might be a good indicator of exposure of Tenax TA to O_3.

GCB Adsorbents

These nonporous adsorbents are produced by heating carbon blacks to high temperatures (~3000 °C) under an inert gas.[27] Their surface is homogeneous with a very low number of polar groups; thus, GCBs are nonselective adsorbents that interact with molecules via nonspecific, nondirectional van der Walls' forces that depend on the polarizability, molecular weight, and geometric structure of the analytes.[28] GCBs demonstrate excellent thermal stability up to >400 °C.

Table 2. Summary of positive artifacts identified for four adsorbents at 100- and 1000-ppb O_3 exposures in the current paper and citations showing previously identified positive artifacts.

Compound	Tenax GC			Tenax GR			Carbopack B			Carbopack X		
	100 ppb	1000 ppb	Others (ref)	100 ppb	1000 ppb	Others (ref)	100 ppb	1000 ppb	Others (ref)	100 ppb	1000 ppb	Others (ref)
Pentanal	✓	✓		✓	✓		✓	✓		ND	ND	
3-Hexanone	✓	ND		✓	ND		ND	ND		ND	ND	
1-Octene	ND	ND		ND	ND		✓	✓		ND	ND	
2-Hexanone	✓	ND		✓	ND		ND	ND		ND	ND	
Hexanal	✓	✓		✓	✓		✓	✓		ND	ND	
3-Heptanone	✓	✓		✓	ND		ND	ND		ND	ND	
1-Nonene	ND	ND		ND	ND		✓	✓		ND	ND	
Heptanal		✓		✓	✓		✓	✓		ND	ND	
Benzaldehyde	✓	✓	14,16,21,23,24,25	✓	✓	21	✓	✓	15	ND	ND	
Phenol	ND	✓	16,22,24,25	ND	✓		ND	ND	15	ND	ND	
Octanal	✓	✓	21	✓	✓	21	✓	✓		ND	ND	
Benzeneacetaldehyde	✓	✓	22,24	✓	✓		ND	ND		ND	ND	
Acetophenone	✓	✓	14,16,21,23,24,25	✓	✓	21	ND	ND	15	ND	ND	
Nonanal	✓	✓	21,24	✓	✓	21	✓	✓		ND	ND	
Benzoic acid	ND	✓	22,24	ND	ND		ND	ND		ND	ND	
Decanal	✓	✓	22,24	✓	ND		✓	✓		ND	ND	
Phenylmaleic anhydride	ND	✓	22,24	ND	✓		ND	ND		ND	ND	
Benzophenone	✓	✓	24	✓	✓		ND	ND		ND	ND	
Phenylbenzoate	ND	✓		ND	✓		ND	ND		ND	ND	
Ethylene oxide			16									
α-Hydroxyacetophenone			16									
4-Bromobiphenyl			36			36						
Phthalate ester			36			36						
Dibutyl phthalate			22									
Benzoic anhydride			22,24									
Diphenyl propanetrione			22,24									
2,6-Diphenylphenol			22,24									
2,6-Diphenylcyclopentane-2,5-dione			22									
2,6-Diphenyl-4H-pyran-4-one			22,24									

Reported by ref 14 using Tenax GC	Pentane, hexane, heptane, octane, nonane, decane, undecane, 2-methylpentane, 3-methylpentane, 3-methylhexane, 2-methylhexane, 2-methylheptane, 2,2-dimethylhex-3-ene, cyclohexane, methylcyclopentane, methylcyclohexane, ethylcyclohexane, propyl of isopropylcyclohexane, benzene, toluene, ethylbenzene, butylbenzene, xylenes, a trimethylbenzene, c3 alkylbenzenes, a methylstyrene or indan, 1,1,1-trichloroethane, 1,1,2-trichchloro-1,2,2-trifluoroethane, tetrachloroethene, a dichlorobenzene, acetone
Reported by ref 21 using Tenax GC	Benzene, heptane, toluene, ethylbenzene and o,p-xylene (but also present in the O_3-free air)
Reported by ref 24 using Tenax GC	Formic acid, acetic acid, phenylglyoxal, p-hydroquinone, phenyl glyoxylic acid, phthalic anhydride, 1,2-diphenylethanone, diphenylethanedione, 2,4-diphenyl-4-cyclopentene-1,3-dione, 2,6-diphenyl-p-benzoquinone (DPQ), 2,6-diphenyl-p-hydroquinone (DPHQ)

Notes: ND = not detected. O_3 concentrations/doses, if available, by reference number: ref 15 used 500 ppb; ref 20 used 100 ppb and 30-L volume; ref 21 used 180 ppb with passive exposure for 1 week; ref 24 used 50 ppb and 20-L volume and also 1000 ppb and 2-L volume; ref 36 used 115 ppb and 1443-L volume. This and most other studies used Tenax TA; studies using Tenax GC are indicated.

GCBs are marketed under several names. Carbopack and Carbotrap, the products that have been available the longest, have the same composition but different mesh size (60/80 and 20/40, respectively). Both are available as low-surface density (10 $m^2\,g^{-1}$) versions called Carbopack C, Carbotrap C, and Carbograph 2. Other GCBs include a medium-surface density (100 $m^2\,g^{-1}$) version called Carbotrap B, Carbopack B, and Carbograph 1, a medium-surface density (240 $m^2\,g^{-1}$) 60/80 mesh version called Carbopack X, and a newer high-surface density (560 $m^2\,g^{-1}$) 20/40 version called Carbograph 5.[29]

Initially, GCB adsorbents were claimed to be inert and not to catalyze any reactions.[30] However, graphite has been found to have a catalytic effect and may breakdown terpenes and aldehydes during thermal desorption.[31] Carbotrap adsorbents preloaded with n-aldehydes showed aldehyde losses that increased with O_3 concentration and "n" number, as well as losses of preloaded alcohols (e.g., ethanol, n-propanol, and iso-propyl alcohol) after O_3 exposure.[6] Small negative biases have been noted for 1,1,2-trichloroethane and 3-chloropropene (of 27 compounds tested) in preloaded Carbopack X tubes exposed to O_3 in diffusive sampling.[7] Benzaldehyde, phenol, and acetophenone have been identified as positive artifacts resulting from O_3-GCB exposure (Table 2).[15]
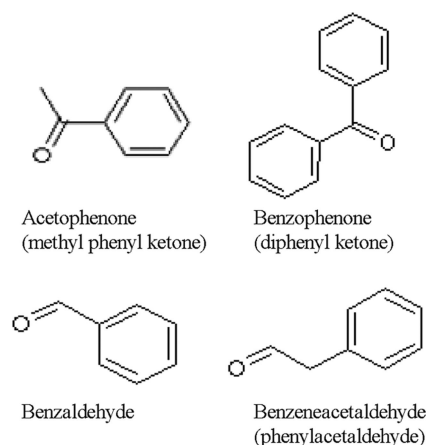
Figure 1. Structural diagrams for the phenyl-substituted carbonyl compounds found as O_3-Tenax artifacts and alternative names.

Comparison of Tenax and GCB Adsorbents

The performance of GCB and polymeric materials has been compared in many applications. For example, Ciccioli et al.[15] found Carbopack B to be more efficient than Tenax GC in sampling C_6-C_{10} alkyl hydrocarbons in the presence of O_3 without the formation of artifacts. Carbotrap also gave better performance than Tenax TA for 2-L samples of nonpolar hydrocarbons in tests by DeBortoli et al.,[32] but Tenax TA performed better for small (0.5 L) samples where it yielded better recovery (82%) of 1-butanol and lower background levels of benzene. Rothweiler et al.[31] obtained very low recoveries for many polar compounds using Carbopack B; higher, though not totally satisfactory, recoveries on Tenax TA for 1-L samples; and, as mentioned, noted catalytic activity involving aldehydes, α-pinene, and Carbopack B. Sunesson et al.[4] reported poor recoveries for many microbial VOCs sampled into Carbopack B, as well as the breakdown of 2-methylisoborneol and geosmin. However, Carbotrap was used successfully to analyze 46 VOCs released during composting but not 2-methylisoborneol and geosmin.[33] Trikonen et al.[34] concluded that Carbotrap has several disadvantages, including high background, poor performance for polar compounds, and formation of artifacts, especially terpenes. Cao and Hewitt[21] studied effects of O_3 on four adsorbents (Tenax GR, Tenax TA, Chromosorb 106, and Carbotrap); however, the GC/flame-ionization detector used could not identify or confirm many artifacts. Polymeric materials Tenax TA and GR were reported to form more artifacts than carbon-based adsorbents Carbotrap and Carbosieve.

EXPERIMENTAL WORK

Table 3 shows the major elements of the experimental design, including tests to examine effects of adsorbent aging, O_3 concentration and dose, adsorbent conditioning, O_3 breakthrough, and the method performance evaluation.

Adsorbents, Preparation, and Conditioning

New adsorbents were obtained from Supelco and loaded into stainless-steel tubes (10 cm long, 4 mm i.d.) with tapered screw threads on both ends (Scientific Instrument Services, Inc.). From upstream to downstream, each tube was packed with 3-mm silanized glass wool, 160 mg of the adsorbent, and 3-mm silanized glass wool. Packed tubes were conditioned at 325 °C in a 24-tube conditioning oven (Model A-24; Scientific Instrument Services) for 6 hr with a 60 mL min^{-1} reverse flow (opposite to sampling direction) of high purity helium gas (>99.999%). After conditioning, tubes were sealed using endcaps with Teflon gaskets and stored at 4 °C in a glass jar with a pouch of activated carbon. After conditioning, tubes were stored for <1 day before O_3 exposure in most cases and <7 days in all cases.

O_3 Exposure

Each adsorbent was exposed to a constant O_3 concentration at a controlled temperature (24 °C), relative humidity ([RH] 50%), and flow rate (160 mL min^{-1}) using an O_3 exposure system (Figure 2), which included an air generator (Model 737-12A; Addco Instrument, Inc.) that supplied hydrocarbon-free air to an O_3 generator (Model MZ-250; Clearwater Tech Inc.). The flow was diluted with 50% RH air, obtained using temperature-controlled bubblers, then split into eight identical streams using rotameters, seven of which were used to expose samples, and the last (noted as A-4 on Figure 2) was used to monitor O_3.

In the adsorbent aging tests, tubes were first conditioned, exposed to 100 ppb O_3 for 30 min (5-L sample), and then desorbed and analyzed by GC/MS. This conditioning/O_3-exposure/analysis cycle was repeated a second

Table 3. Overall experimental design for O_3-adsorbent artifact tests.

| Aim | Adsorbent | Ozone Exposure | Conditioning | | GC/MS Analysis[a] | No. Reps./ No. Blanks | No. Tubes | No. GC/MS Analyses |
			Duration	No. Cycles				
Aging/conditioning	Tenax TA and GR Carbopack B and X	100 ppb, 30 min (5 L)	6 hr	10	1, 2, 3, 10	3/1	16	64
Ozone concentration effect	Tenax TA and GR Carbopack B and X	1000 ppb, 30 min (5 L)	6 hr	1	1	3/1	16	16
Ozone dose effect	Tenax GR	100 ppb, 60 min (10 L)	6 hr	10	1, 2, 3, 10	3/1	4	16
Conditioning effect	Tenax TA	100 ppb, 30 min (5 L)	None	1	1	2/1	3	3
			3 hr	1	1	2/1	3	3
			6 hr	1	1	2/1	3	3

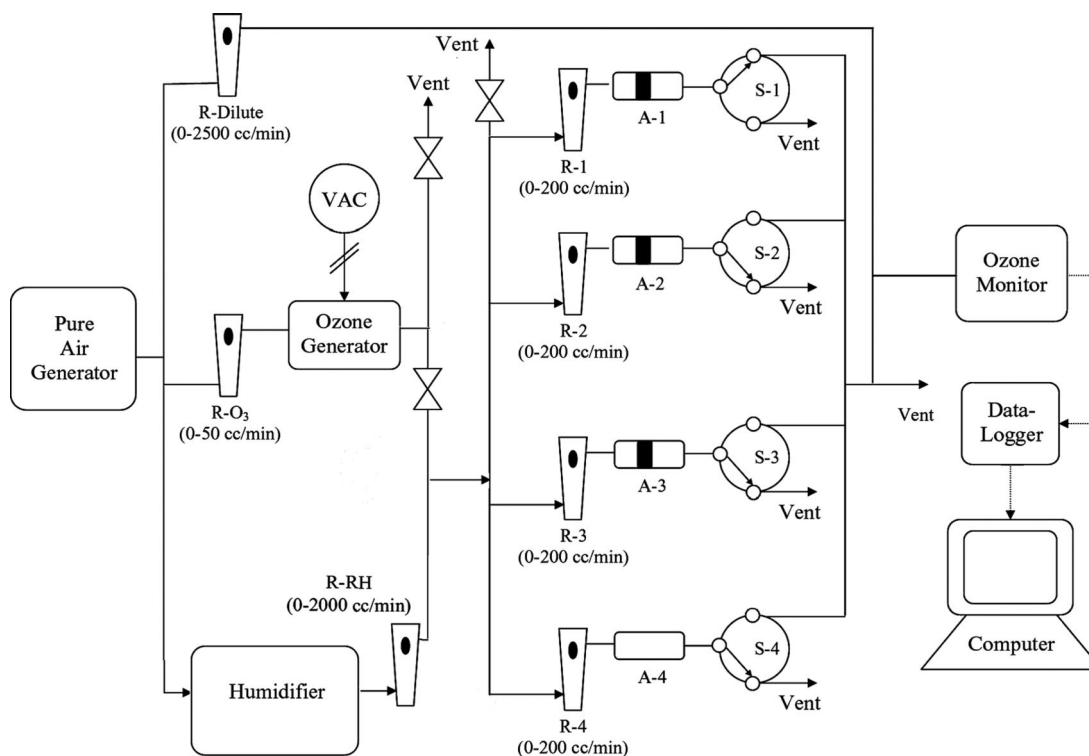*Notes:* [a]Analyses after the indicated conditioning/exposure cycle.

Figure 2. Ozone exposure and breakthrough monitoring system. Ports 5–8 omitted for simplification. Tube A-4 is a blank. R = flow rotameter; A = adsorption tube; S = solenoid valve.

and third time (Table 3). Each tube was then conditioned and exposed seven more times, but without GC/MS analysis. After the final conditioning/O_3-exposure cycle, tubes were analyzed once again for artifacts. Thus, each tube was analyzed immediately after preparation and the first, second, third, and tenth conditioning/O_3-exposure cycle. All of these tests used the same O_3 concentration, temperature, humidity, and flow conditions. To investigate the effects of O_3 dose, freshly prepared tubes were analyzed after their first exposure to the same (100 ppb) O_3 concentration but with a doubled exposure time/volume (30 min, 10 L). To investigate possible effects of O_3 concentration, 30-min 1000-ppb O_3 exposures were used. To determine whether artifacts were a result of manufacturing residues on the adsorbent, fresh adsorbent samples without any conditioning (contrary to manufacturer's guidance and at risk of overloading the GC/MS instrumentation) were analyzed, then with partial conditioning (heated and purged for 3 hr), and finally with full conditioning. In all of these experiments, multiple replicates and blanks were used, and averages and ranges are reported.

O_3 Breakthrough

The exposure system (Figure 2) had the capability of measuring O_3 breakthrough for each sample. The humidified 100-ppb O_3 test atmosphere was passed through thin cylindrical beds of each adsorbent; held in place using stainless steel screens, stainless retainers, and silanized glass wool (to catch any fine material); and all placed in Teflon tubes (4.8 mm i.d.). Bed masses were 20 mg for all four of the adsorbents (results are also presented for 30 mg

of Tenax TA). These masses were determined in part by trial and error so as to give reasonable breakthrough times. Two to four replicates of each adsorbent quantity were O_3 exposed for 45 hr, during which tube effluent was periodically diverted through a two-way Teflon solenoid valve for dilution with clean, dry air and measurement using a continuous O_3 analyzer (Model 400A; Advanced Pollution Instrumentation, Inc.). A computer operated the valves and logged the O_3 concentration in the effluent of each sample every 16 min. These data were processed to 1-hr averages that were then exponentially smoothed (damping factor = 0.2). Breakthrough curves were constructed using the relative penetration, expressed as C_t/C_0 (%) where C_t is O_3 concentration measured downstream of the filter at time t, and C_0 is constant upstream concentration, measured through an empty tube (A-4 on Figure 2).

Artifact Identification and Analysis

Air samples were analyzed using an automated short-path thermal desorption (TD)/cryofocusing system (Model 2000; Scientific Instrument Services), a GC/MS (Model 6890/5973 running Chemstation, G1701BA, Version B.01; Hewlett-Packard), and a validated VOC analysis protocol.[35] Adsorbent-O_3 artifacts were identified on the basis of retention time and ion spectra with confirmation using individual standards. Adsorbent tube samples were analyzed by screwing the downstream side of the tube onto a stainless-steel connector containing a check valve and small VOC trap. The upstream side of the tube was screwed onto a previously cleaned 3.5-cm-long stainless steel side-port needle. Graphitized Vespel seals (Scientific

Table 4. Characteristics of target compounds and GC/MS parameters for identification and quantification.

Artifact	Retention Time (min)	CAS Number	Molecular Formula	Molecular Weight (amu)	Quantitation Ion (m/z)	Confirmation Ions (m/z)
Pentanal	9.12	110-62-3	$C_5H_{10}O$	86.13	44	58, 41
3-Hexanone	13.28	589-38-8	$C_6H_{12}O$	100.16	57	43, 71
1-Octene	13.29	111-66-0	C_8H_{16}	112.21	70	55, 43
2-Hexanone	13.50	591-78-6	$C_6H_{12}O$	100.16	43	58, 100
Hexanal	13.85	66-25-1	$C_6H_{12}O$	100.16	56	44, 41
3-Heptanone	17.38	106-35-4	$C_7H_{14}O$	114.19	57	85, 114
1-Nonene	17.45	124-11-8	C_9H_{18}	126.24	56	43, 70
Heptanal	17.95	111-71-7	$C_7H_{14}O$	114.19	70	44, 55
Benzaldehyde	19.93	100-52-7	C_7H_6O	106.12	106	105, 77
Octanal	21.54	124-13-0	$C_8H_{16}O$	128.21	43	57, 84
Benzeneacetaldehyde	22.84	122-78-1	C_8H_8O	120.15	91	120, 65
Acetophenone	23.53	98-86-2	C_8H_8O	120.15	105	77, 120
Nonanal	24.79	124-19-6	$C_9H_{18}O$	142.24	57	41, 70
Decanal	27.80	112-31-2	$C_{10}H_{20}O$	156.27	57	43, 70
Benzophenone	35.67	119-61-9	$C_{13}H_{10}O$	182.22	105	182, 77

Notes: CAS = Chemical Abstracts Service. For comparison, retention time of internal standards, fluorobenzene and p-bromofluorobenzene are 7.98 and 18.53 min, respectively.

Instrument Services) sealed both ends of the sample tube. Excess water on the adsorbent tube was removed using a dry purge ($\sim$40 mL min^{-1} of helium carrier gas for 1 min). The sample then was heated to 200 °C, and a desorption flow of $\sim$20 mL min^{-1} transferred VOCs to the previously cooled ($-$140 °C) cryotrap at the head of the GC column. After 5 min of desorption, the trap was rapidly heated to 250 °C for 10 sec, providing a narrow injection band, and the GC/MS program started. Separations were achieved using an HP-5MS capillary column (30-m length, 0.25-mm diameter, 0.25-μm film thickness, and 5% phenyl methyl siloxane) and column temperature program started at $-$10 °C and held for 3 min, ramped at 8 °C min^{-1} to 20 °C and held for 3 min, ramped at 5 °C min^{-1} to 120 °C and held for 1 min, and finally ramped at 15 °C min^{-1} to 200 °C and held for 1 min. The MS scanned from 26 to 270 m/z at 3 scan sec^{-1} in the electron ionization mode, and ion source and quadrupole temperatures were 230 °C and 150 °C, respectively.

Standards and Method Performance
The carbonyls analyzed in this study are listed in Table 4. All of the chemicals were obtained as pure substances from Sigma-Aldrich and Lancaster Synthesis, Inc. with purities exceeding 98% with the exceptions of pentanal (97%), heptanal (95%), nonanal (95%), and benzeneacetaldehyde (90%). Stock solutions at 2000 μg mL^{-1} were prepared in methanol. Multicomponent standards were prepared from the stock solutions by dilution in pentane (99.9%; Sigma-Aldrich). Standards were prepared on the day of use and stored at 4 °C. Calibrations were performed by thermally desorbing and analyzing tubes loaded with 5, 10, 20, and 40 ng of each compound, using duplicates at each level. MDLs were calculated as 3.14 σ, where 3.14 is the Student's t value appropriate to a 99% confidence level with 6 degrees of freedom, and σ is the standard deviation of seven replicate analyses that used a loading of 5 ng per compound. This is higher than the typical loading (e.g., 0.2 ng) used for nonpolar VOCs[35]; thus,

only approximate MDLs are obtained for some of the carbonyls (see below). All of the quantitative determinations used normalized abundances, that is, ratios of abundances of the target compound to the internal standard in the same GC/MS run.

Adsorbent recoveries were determined by comparing abundances obtained from TD and direct injection obtained using the same GC/MS conditions and 40-ng injections. Recovery was calculated in percent using the average of two replicates. In an attempt to improve recoveries, desorption temperatures were boosted from 200 °C to 250 °C and then to 300 °C.

RESULTS
Artifact Formation at 100-ppb O₃
Typical chromatograms obtained from fresh adsorbents exposed to 5 L of 100-ppb O_3, and from Tenax TA exposed to 5 L of O_3-free air are shown in Figure 3. Chromatograms from adsorbents exposed to O_3-free air showed only a few very small peaks. As an example, Tenax TA (Figure 3E) showed column bleed (at retention time t_r = 15 min) and very small but detectable quantities of toluene. (As discussed below, toluene is likely a laboratory contaminant.) Otherwise, the four adsorbents exposed to O_3-free air were free of artifacts. In contrast, many compounds were observed for O_3-exposed Tenax A, Tenax GR, and Carbopack B, indicating artifact formation (Figure 3, A–C, respectively). No artifacts were detected with Carbopack X (Figure 3D). Identified artifacts are summarized in Table 2.

A total of 13 artifacts were detected from O_3-exposed Tenax TA, the most prevalent (based on peak height) being 3-heptanone, benzaldehyde, acetophenone, nonanal, decanal, and benzophenone. Significant quantities of benzaldehyde, phenol, and acetophenone on O_3-exposed Tenax GC have been identified previously; for example, Ciccioli et al.[15] reported these compounds detected on Tenax GC with a 5-L exposure with 500 ppb of O_3. Additionally, six carbonyl compounds not reported
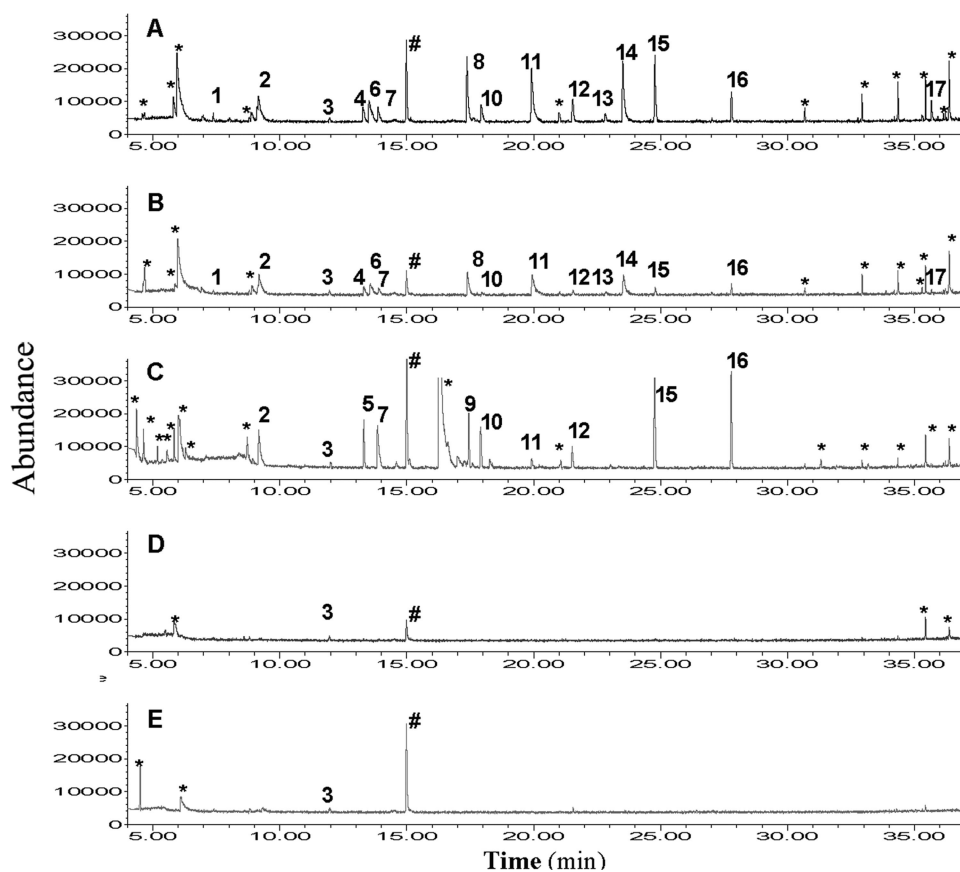
Figure 3. GC/MS chromatograms for four fresh adsorbents exposed to 5 L of 100-ppb O_3. A, Tenax TA; B, Tenax GR; C, Carbopack B; D, Carbopack X; E, Tenax TA with O_3-free air (blank). Peak identification: 1, benzene; 2, pentanal; 3, toluene; 4, 3-hexanone; 5, 1-octene; 6, 2-hexanone; 7, hexanal; 8, 3-heptanone; 9, 1-nonene; 10, heptanal; 11, benzaldehyde; 12, octanal; 13, benzeneacetaldehyde; 14, acetophenone; 15, nonanal; 16, decanal; 17, benzophenone. *Identification was unconfirmed; #Column bleeding.

previously were found, that is, pentanal, 3-hexanone, 2-hexanone, hexanal, 3-heptanone, and heptanal. Each was confirmed using individual standards.

O_3-Tenax GR artifacts included the same 13 compounds seen with Tenax TA, although the abundances were significantly lower. Five of the compounds (pentanal, 3-hexanone, 2-hexanone, hexanal, and 3-heptanone) have not been identified previously as O_3-Tenax GR artifacts. Two reasons for the lower artifact formation have been suggested: Tenax GR contains 23% graphitized carbon and, thus, a smaller amount of artifact-forming polymer than Tenax TA for the same weight of adsorbent[21]; and the carbon in Tenax GR might mitigate artifact problems associated with O_3.[36] The breakthrough experiments (described later) show that Tenax GR removes much more O_3 than Tenax TA, which the authors believe is the major reason for the difference in artifact formation between the two Tenax adsorbents.

Carbopack B showed seven of the same artifact compounds that were found for Tenax (Table 2). Several of these have been identified previously; for example, Ciccioli et al.[15] found benzaldehyde on Carbopack B after a 10-L exposure to 500-ppb O_3. In addition, two alkenes not reported previously, 1-octene and 1-nonene, were detected and confirmed.

Artifact Formation at 1000-ppb O_3

Chromatograms of fresh samples of the four adsorbents exposed to a 1000-ppb O_3 (Figure 4) showed four new artifacts on Tenax TA, that is, phenol, benzoic acid, phenylmaleic anhydride, and phenylbenzoate (= benzoic acid and phenyl ester), compounds not observed at the lower (100 ppb) exposure. Also, the relative levels of O_3-Tenax artifacts changed; for example, abundances of benzaldehyde, benzeneacetaldehyde, acetophenone, and benzophenone increased, but 3-hexanone, 2-hexanone, 3-heptanone, octanal, and nonanal decreased (Figure 4A and Table 2). Toluene was unaltered, confirming that toluene was not an artifact. Carbopack B showed the same artifacts when exposed to 100-ppb O_3 exposure but at reduced levels (Figure 4C). Again, Carbopack X showed no artifacts.

Linearity, Recovery, and MDLs for Carbonyls

Adsorbent performance was evaluated for the 15 carbonyls identified as O_3-adsorbent artifacts. Calibrations for most of these compounds showed excellent linearity (R^2 = 0.99) on the four adsorbents. Benzeneacetaldehyde, nonanal, decanal, and benzophenone had slightly lower linearity (R^2 from 0.95 to 0.98) and, in several cases, small nonzero intercepts. Recoveries varied by compound and,
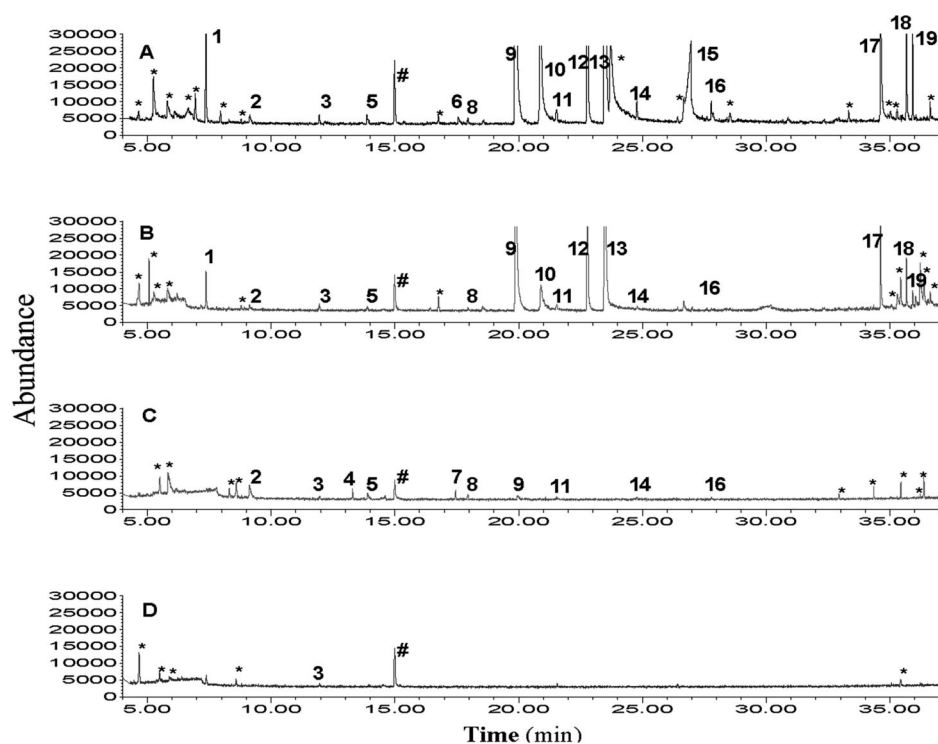
Figure 4. GC/MS chromatogram for four fresh adsorbents exposed to 5 L of 1000-ppb O_3. A, Tenax TA; B, Tenax GR; C, Carbopack B; D, Carbopack X. Peak identification: 1, benzene; 2, pentanal; 3, toluene; 4, 1-octene; 5, hexanal; 6, 3-heptanone; 7, 1-nonene; 8, heptanal; 9, benzaldehyde; 10, phenol; 11, octanal; 12, benzeneacetaldehyde (phenylacetaldehyde); 13, acetophenone; 14, nonanal; 15, benzoic acid; 16, decanal; 17, phenylmaleic anhydride; 18, benzophenone; 19, benzoic acid, phenyl ester (= phenylbenzoate). *Identification was unconfirmed; #Column bleeding.

to an extent, by adsorbent. Across the 15 compounds, recoveries by adsorbent averaged 89 ± 15%, 97 ± 23%, 101 ± 24%, and 79 ± 25% for Tenax TA, Tenax GR, Carbotrap B, and Carbopack X, respectively (Table 5).

Recoveries for most compounds were acceptable, comparable to that achieved for toluene (also shown in Table 5) often used as a reference compound. However, benzene-acetaldehyde had poor recovery, as low as 24% and 34%

Table 5. MDLs and recovery for target compounds.

Type	Compound	Tenax TA		Tenax GR		Carbopack B		Carbopack X	
		MDL (ng)	Recovery (%)	MDL (ng)	Recovery (%)	MDL (ng)	Recovery (%)	MDL (ng)	Recovery (%)
Targets	Pentanal	0.6	124	0.8	115	1.4	113	3.1	109
	3-Hexanone	0.6	115	0.5	115	0.5	125	1.9	110
	1-Octene	1.1	86	0.6	96	0.5	111	0.5	70
	2-Hexanone	1.2	79	0.4	79	0.7	92	2.1	88
	Hexanal	0.6	93	0.5	90	1.2	97	3.3	88
	3-Heptanone	0.6	98	0.3	112	0.8	119	1.6	89
	1-Nonene	0.4	88	0.2	115	0.7	104	2.7	70
	Heptanal	0.9	95	0.4	108	1.5	119	3.3	82
	Benzaldehyde	0.6	76	0.8	106	0.8	120	1.3	84
	Octanal	0.4	88	1.0	92	2.3	114	2.4	89
	Benzeneacetaldehyde	0.9	63	1.0	22	3.1	24	1.6	34
	Acetophenone	0.5	73	0.6	102	0.4	107	1.7	76
	Nonanal	1.4	85	1.6	91	1.8	107	1.5	91
	Decanal	2.4	82	4.0	90	2.2	84	1.1	90
	Benzophenone	0.6	84	0.5	120	3.4	80	1.1	10
	Average	0.84	89	0.88	97	1.43	101	1.93	79
	Standard deviation	0.50	15	0.90	23	0.93	24	0.82	25
Aromatic	Toluene	0.56	82	0.45	82	1.20	92	1.67	95

Notes: MDLs based on seven replicates and 5-ng loading for each compound. Recoveries based on average of two replicates of adsorbent tube analyses compared with two replicates using direct injections for each adsorbent.

on Carbopack B and X, respectively. The low average recovery for Carbopack X is mainly because of the poor recovery (10%) of benzophenone; recovery of n-aldehydes remained high (91 ± 9%).

Increasing the desorption temperature beyond the normal 200 °C did not significantly and consistently improve recoveries. For Tenax GR, recoveries of heavier compounds slightly improved at 250 °C, but not for benzeneacetaldehyde. At 300 °C, recoveries of the carbonyls (including benzeneacetaldehyde) and toluene were slightly reduced. Carbopack B recoveries followed the same pattern, although many of the changes were negligible. Carbopack X showed larger changes, again with most recoveries dropping at higher temperatures, and the recovery of benzeneacetaldehyde fell to only 6% at 300 °C. Thus, the maximum recovery of benzeneacetaldehyde and other target compounds in Tenax and Carbopack adsorbents was achieved at 200 °C. Higher desorption temperatures may result in the thermal degradation of analytes, although no evidence of degradation products was seen.

For many compounds, MDLs were <1 ng, but values depended on the compound and adsorbent (Table 5). MDLs across the 15 carbonyls averaged 0.84 ± 0.50 ng for Tenax TA and 0.88 ± 0.90 ng for Tenax GR. Nonanal and decanal consistently had the highest MDLs. MDLs for Carbopack B were higher, averaging 1.4 ± 0.9 ng, and MDLs exceeded 3 ng for benzoacetaldehyde and benzophenone. MDLs for Carbopack X averaged 1.9 ± 0.8 ng, higher than for Carbopack B, with several of the straight-chain aldehydes showing the highest MDLs. Ideally, MDLs are determined using injection masses similar to the MDL itself, otherwise, true values may not be obtained. For example, the authors estimated previously the MDL of toluene using seven replicates of 0.3-ng injection to be 0.065 ng, compared with the MDL of 1.67 ng estimated using 5-ng injections (as presented in Table 5). Smaller injection quantities were not tested, given the large range of MDLs encountered, and because the primary goal was investigation of artifacts. Thus, true MDLs using Tenax TA and GR, for example, are likely to be considerably smaller for most compounds (with the exceptions of decanal and nonanal). However, the calculated MDLs are helpful in quantifying the O_3-adsorbent artifacts, reported next, and as rough estimates of MDLs in air sampling applications. For example, a 1-ng MDL gives a 0.2-μg m^{-3} MDL for a sampling volume of 5 L.

Adsorbent Conditioning

Chromatograms obtained using Tenax TA without prior conditioning had numerous large peaks, presenting very high and potentially excessive loadings to GC/MS. (GC/MS systems normally should avoid such excessive loadings.) Without O_3 exposure, unconditioned tubes contained many of the same carbonyl compounds detected as O_3-Tenax artifacts but at much higher concentrations, approaching 100 ng for hexanal, benzaldehyde, nonanal, and decanal (Figure 5A). O_3 exposure generally increased concentrations of these carbonyls by ~20%, although the destruction process can exist simultaneously. Without O_3 exposure, partial conditioning largely eliminated these compounds (Figure 5B), and they
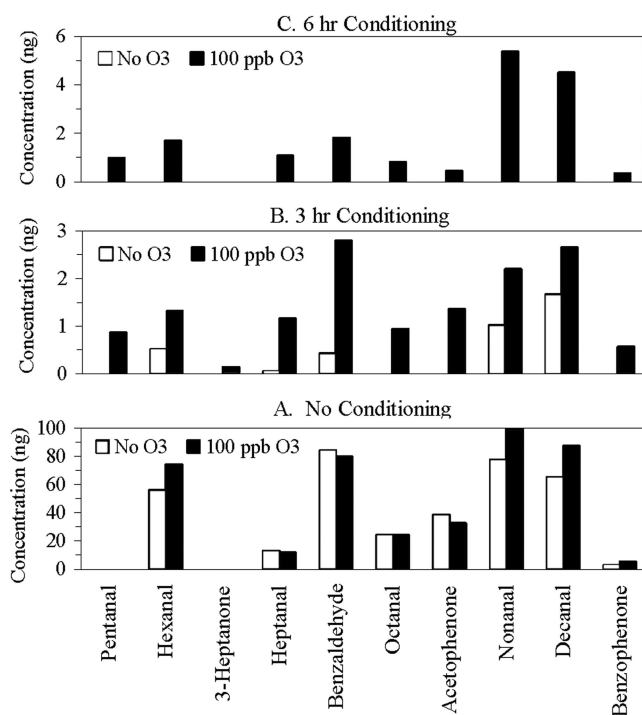

Figure 5. Compounds found on Tenax TA (A) before conditioning, (B) after partial (3 hr) conditioning, and (C) after full (6 hr) conditioning, with and without 5 L of O_3 exposure.

were not detected after full conditioning (Figure 5C). With O_3 exposure, the artifacts returned, as seen earlier. Thus, O_3 can generate artifacts from both partially and fully conditioned adsorbents. Clearly, to minimize positive artifacts, adsorbents need to be fully conditioned immediately before use.

Aging of Adsorbents

Table 6 lists the concentrations of O_3-adsorbent artifacts for three adsorbents (Tenax TA, Tenax GR, and Carbopack B) measured in tests designed to simulate repeated uses of adsorbents in applications where O_3 is present. Results for Carbopack X are not shown, because no artifacts were identified. Tenax TA and Tenax GR aged similarly. Levels of most artifacts on these adsorbents dramatically decreased after each conditioning/exposure/analysis cycle, and they either disappeared after three cycles or were present at trace levels. This applied to three ketones (3-hexanone, 2-hexanone, and 3-heptanone) and six chain aldehydes (pentanal to decanal). There were four exceptions to this behavior (structures shown in Figure 1): two aromatic aldehydes, benzaldehyde and acetophenone, showed modest (two-fold) reductions after repeated exposures on Tenax TA and relatively constant levels on Tenax GR. Benzeneacetaldehyde also showed modest reductions for both adsorbents. Finally, another ketone, benzophenone, was still detectable after 10 exposure-conditioning cycles, although levels were very low. The four phenyl-substituted carbonyl artifacts were more persistent on the Tenax polymers, although only benzaldehyde, benezeneacetaldehyde, and acetophenone are likely to be found at higher levels.

For Carbopack B, the seven aldehyde artifacts were greatly reduced after a single conditioning/O_3-exposure

Table 6. Artifacts (ng) detected on Tenax TA, Tenax GR, and Carbopack B after 1, 2, 3, and 10 conditioning/O_3 exposure cycles.

Adsorbent	Compound	Exposure 1			Exposure 2			Exposure 3			Exposure 10		
		Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Tenax TA	Pentanal	0.46	0.05	1.23	0.39	T	0.62	ND	ND	ND	ND	ND	ND
	3-Hexanone	2.03	1.94	2.11	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2-Hexanone	4.33	4.25	4.44	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Hexanal	1.32	0.57	2.16	0.51	0.91	0.91	0.04	0.02	0.1	ND	ND	ND
	3-Heptanone	6.47	6.05	6.74	0.02	T	0.04	ND	ND	ND	ND	ND	ND
	Heptanal	1.18	0.03	2.31	0.47	T	0.85	ND	ND	ND	ND	ND	ND
	Benzaldehyde	5.61	4.92	6.05	6.04	5.15	6.64	4.52	3.09	6.43	2.79	2.54	3.15
	Octanal	1.68	0.2	3.21	0.26	T	0.45	ND	ND	ND	ND	ND	ND
	Benzeneacetaldehyde	1.33	1.16	1.45	1.42	1.06	2	1.45	1.07	1.97	0.78	0.66	0.89
	Acetophenone	6.58	5.1	8.39	7.55	6.81	7.97	7.55	6.27	9.06	3.1	2.89	3.29
	Nonanal	2.65	0.11	5.8	0.58	T	1.09	0.22	0.03	0.35	ND	ND	ND
	Decanal	1.39	0.12	2.72	0.46	T	0.96	0.01	T	0.04	ND	ND	ND
	Benzophenone	0.68	0.62	0.72	0.56	0.5	0.6	0.41	0.29	0.52	0.09	0.06	0.12
Tenax GR	Pentanal	0.26	0.05	0.65	ND	ND	ND	ND	ND	ND	ND	ND	ND
	3-Hexanone	1.17	1.06	1.24	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2-Hexanone	2.5	2.21	2.86	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Hexanal	0.89	0.57	1.37	0.16	0.02	0.24	0.02	T	0.03	ND	ND	ND
	3-Heptanone	2.88	1.86	3.58	0.002	T	0.01	ND	ND	ND	ND	ND	ND
	Heptanal	0.11	T	0.34	0.07	T	0.22	ND	ND	ND	ND	ND	ND
	Benzaldehyde	2.93	2.55	3.55	3.12	3.07	3.15	2.34	1.01	3.14	2.15	1.76	2.43
	Octanal	0.48	0.06	1.37	0.01	T	0.06	ND	ND	ND	ND	ND	ND
	Benzeneacetaldehyde	1.21	0.57	1.8	0.93	T	1.83	1.19	0.98	1.58	0.45	0.13	0.71
	Acetophenone	2.06	1.68	2.26	1.77	T	2.04	1.61	1.34	1.86	1.87	1.72	2.01
	Nonanal	0.48	0.05	1.35	0.01	T	0.04	0.01	T	0.02	ND	ND	ND
	Decanal	0.39	T	1.17	0.04	T	0.06	ND	ND	ND	ND	ND	ND
	Benzophenone	0.1	0.05	0.12	0.07	T	0.09	0.06	0.05	0.06	0.002	T	0.01
Carbopack B	Pentanal	0.74	T	2.21	0.45	T	1.36	ND	ND	ND	ND	ND	ND
	3-Hexanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2-Hexanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Hexanal	0.78	T	1.46	0.37	0.03	0.7	0.39	0.03	0.72	ND	ND	ND
	3-Heptanone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Heptanal	0.37	T	0.7	ND	ND	ND	0.13	T	0.26	ND	ND	ND
	Benzaldehyde	0.5	0.11	0.81	0.06	0.01	0.15	0.33	0.01	0.51	ND	ND	ND
	Octanal	0.44	T	1.31	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Benzeneacetaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Acetophenone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Nonanal	0.79	T	1.57	0.02	T	0.07	ND	ND	ND	ND	ND	ND
	Decanal	0.63	T	0.97	0.01	T	0.04	ND	ND	ND	ND	ND	ND
	Benzophenone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Notes: Exposures used 100-ppb O_3 and 5 L. T = trace; ND = not detected; mean of three replicates.

cycle, and none were detected after 10 cycles. The most persistent were hexanal, heptanal, and benzaldehyde, lasting 3 cycles. Concentrations of the two identified alkene artifacts, 1-octene and 1-nonene, averaged 3.6 and 1.4 ng, respectively; however, these levels were not always reproducible.

Concentrations of several artifacts fell below the estimated (and conservative) MDLs (Table 5). However, all of the compounds listed in Table 6 were clearly detected, most were highly reproducible (precisions generally within 20%), and all were confirmed by ion spectra and retention time. The authors have not identified other studies that quantified concentrations of positive O_3-absorbent artifacts. Because artifact levels that are formed in a given application are likely to depend on many factors (discussed later), the range of concentrations in Table 6 is likely to provide better guidance regarding the magnitude of artifact concentrations than any single value.

For the chain aldehydes from hexanal to decanal, a regular decrease in artifact concentrations after each conditioning/O_3 exposure cycle was noted, and log-linear plots showed near linear decreases (Figure 6A). In contrast, concentrations of the phenyl-substituted carbonyls dropped initially but then stabilized (Figure 6B). A first-order model was fit to the n-aldehydes by normalizing concentrations to the level found before conditioning; pooling data for hexanal, heptanal, octanal, nonanal, and decanal; and using linear regression on log-transformed values to estimate a first-order coefficient with a fixed intercept of 1, giving the predictive equation:

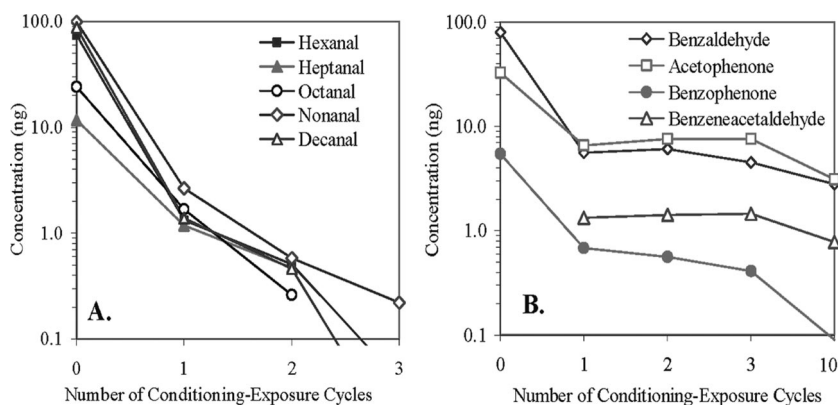$$C_n = C_0 \exp(-1.42\, n) \tag{1}$$

Figure 6. Reduction in concentrations of O_3-Tenax TA artifacts after 0, 1, 2, and 3 conditioning/O_3 exposure cycles. (A) Straight-chain aldehydes; (B) phenyl substituted carbonyls.

where C_n is the artifact concentration remaining after n conditioning/O_3 exposure cycles, and C_0 is the artifact concentration found before the first conditioning. Equation 1 provided good fit ($R^2 = 0.89$), and the estimated parameter was significant (standard error = 0.067). This model indicates that the initial levels of these artifacts will fall 4.14 times after each conditioning cycle, thus, only 1.4% will remain after three conditioning cycles, and extrapolating (because the model is based on 0, 1, 2, and 3 cycles) 0.00007% after 10 cycles. This decay rate is considerably more rapid than found in early work by Pellizzari et al.,[16] probably a result of more effective cleaning procedures. Although this simple model depends on the specific laboratory conditions, it suggests that a first-order process can represent the effect of conditioning/O_3 exposure for positive artifacts that are solely attributed to initial contamination of the adsorbent material, assuming that any adsorbent storage or other effects are negligible (see below). A practical result is that the number of conditioning cycles before adsorbent use can be optimized so that artifacts fall below MDLs. In most circumstances, two to four cycles will be sufficient.

O_3 Dose and Breakthrough

Doubling the O_3 dose (from 5 to 10 L of 100-ppb O_3) approximately doubled concentrations of benzaldehyde and acetaphenone, led to greater increases of chain aldehydes (nonanal and decanal), and did not much alter levels of benzeneacetaldehyde (Figure 7). These patterns were largely maintained regardless of the number of O_3 exposure-conditioning cycles. Thus, generally larger yields of artifacts are obtained with higher O_3 doses.

O_3 breakthrough curves for 20 and 30 mg of Tenax TA showed immediate breakthrough and little O_3 removal, for example, O_3 penetration exceeded 50% at 10 hr (Figure 8). In contrast, breakthrough for 20 mg of Tenax GR was much slower; for example, ~10 hr was needed to detect O_3 in the tube effluent. Carbopack B and X (20 mg of each) showed no breakthrough after 90 hr. These results were highly reproducible. Clearly, the carbon in Tenax GR and relatively large graphitic surface

density of both Carbopack B and X remove substantially more O_3 than Tenax TA.

The O_3 breakthrough tests used long exposures, large sampling volumes, and small quantities of adsorbent. The behavior in the first few hours of these tests may be most relevant to air sampling. The immediate breakthrough seen for Tenax TA indicates that the critical bed depth was not reached and that O_3 was available to essentially the entire amount of adsorbent. This appears to accelerate artifact formation as compared with adsorbents that rapidly remove O_3.

DISCUSSION

Phenyl-substituted carbonyl compounds (especially benzaldehyde and acetophenone), a reaction product of low molecular weight polymers and O_3,[21] have been reported as the main O_3-Tenax degradation compounds in several
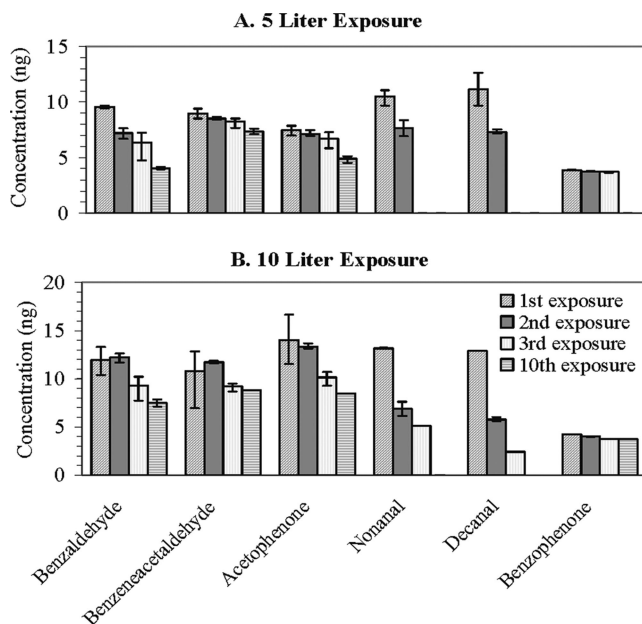

Figure 7. Comparison of O_3-Tenax GR artifacts (in toluene equivalents) after first, second, third, and tenth 100-ppb conditioning/O_3 exposure cycles. (A) 5-L exposures; (B) 10-L exposures.
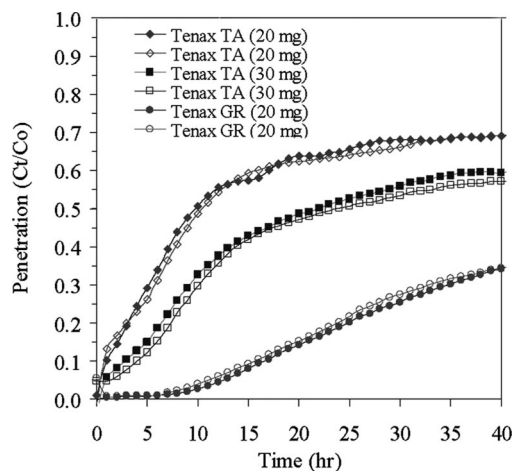
Figure 8. O_3 breakthrough curves for 20 mg of Tenax TA, 30 mg of Tenax TA, and 20 mg of Tenax GR. O_3 concentration = 100 ppb; flow rate = 160 mL min^{-1}. Two replicates shown for each case.

studies. Other compounds have been detected, but less regularly. The authors analyzed a large number of adsorbent samples and focused attention on 15 compounds that were regularly detected and confirmed by GC/MS. Three explanations for differences in the literature are suggested. First, artifact formation shows O_3 concentration and dose effects, and certain artifacts are found only at higher O_3 concentrations that may not be relevant to environmental applications. As examples, Klenø et al.[24] detected two compounds only at 1000-ppb of O_3 (but not at 100 ppb), and all of the results reported by Clausen and Wolkoff[22] were obtained at 330- and 500-ppb of O_3 using 13- and 48-L volumes, respectively. Second, several artifacts that have been reported may be because of incomplete conditioning. The authors demonstrated that conditioning at 325 °C for 3 hr is not sufficient to remove all residues from new adsorbents. Clausen and Wolkoff[22] used 3 hr at 300 °C; Klenø et al.[24] did the same but also included 0.5 hr at 340 °C. Earlier work by Walling et al.[23] used solvent cleaning of the adsorbents. MacLeod and Ames[14] used 250 °C and 275 °C and reported a very large number of artifacts; levels were greatly reduced at 340 °C. Third, not all of the studies confirmed the identity of compounds, and the optimization of the analytical method for specific compound classes may affect results.[22]

Artifact Formation Mechanisms

Adsorbent-O_3 artifacts can result from several mechanisms. O_3 may react with low molecular weight byproducts remaining on adsorbents after manufacturing, that is, low molecular weight polymers and impurities in the technical-grade reagents used in polymer production.[21] Even after cleaning and conditioning, adsorbents can still contain these contaminants. Pellizzari et al.[16] have suggested that oligomeric materials, which are readily degradable, react with O_3 to form artifacts like benzaldehyde, acetophenone, and phenol. As the adsorbent undergoes repeated conditioning/use cycles that may oxidize and desorb these reactive materials, reactive

materials will be depleted and the associated artifacts will diminish. This mechanism applies to the artifacts that appear on the initial exposure-conditioning cycles and that have a rapid and systematic decay with additional cycles, for example, n-aldehydes from hexanal to decanal that formed on Tenax. Concentrations of these artifacts were well represented using a first-order model.

A second mechanism that may form artifacts is O_3-mediated decomposition of the adsorbent itself and subsequent reaction of decomposition products with O_3.[34] This process is accelerated with exposure to higher O_3 concentrations and repeated O_3 treatments.[21] Indeed, the higher (1000 ppb) O_3 exposure led to several new artifacts on Tenax TA and Tenax GR, for example, phenol and benzoic acid. Degradation might cause levels of other artifacts to increase or at least not to very rapidly decrease, with repeated exposure and use. Levels of several compounds, for example, benzaldehyde and acetophenone in Tenax, declined little with adsorbent aging and increased with O_3 dose. Initially, these reactions would involve the polymer surface at the upstream side of the adsorbent bed where O_3 concentrations are highest. With repeated exposure, degradation may continue at the same sites and possibly elsewhere as O_3 penetrates further into the bed and increases secondary porosity, thus exposing new sites for reaction. With this mechanism, artifact formation may continue over the lifetime of the adsorbent.

A third mechanism forming artifacts is the reaction of O_3 with previously adsorbed analytes. Helmig's comprehensive review[5] discusses the substantial losses that may occur, especially for terpenoids. Other work also shows negative biases for styrene,[2] alcohols, n-aldehydes, and two chlorinated VOCs on GCB adsorbents,[6,7] and the formation of halogenated reaction products on Tenax.[16,23] O_3 exposure may form positive or negative artifacts depending on the relative rate of creation and destruction, that is, if the adsorbate is above or below an equilibrium concentration that represents a balance between creation and destruction. The present work does not examine such interferences (including negative artifacts), but instead focuses on the effect of O_3 on clean adsorbents. O_3 scrubbers may be the only way to address such problems (discussed later).

O_3 removal by the adsorbent itself may affect the production of O_3-adsorbent artifacts. The four adsorbents showed clear differences in O_3 breakthrough, which depend on the composition and surface area of the adsorbent. The authors do not believe that O_3 breakthrough in air-sampling adsorbents has been reported previously. O_3 breakthrough and removal by activated carbon (AC) has been extensively examined[37] and is believed to be a chemisorption process involving reactions that form hydroxyl, carbonyl, -C-O-, and -COOH surface functional groups and that structurally change the carbon matrix, causing enlargement of existing pores and creation of new pores (secondary porosity). Some of these processes may not produce VOC artifacts if reactions result in gasification; for example, O_3 oxidizes the AC surface forming CO_2. O_3 that is rapidly removed by adsorbents like Carbopack is unavailable for reaction with either compounds present on the adsorbent or possibly the adsorbent itself.

In contrast, the rapid penetration of O_3 through Tenax facilitates artifact formation throughout the adsorbent bed.

It is clear that there are many processes that can form or affect artifacts in adsorbent sampling. A full understanding of the controlling factors requires additional investigation. For example, the authors did not examine the effect of storage time for both conditioned and exposed absorbent tubes. Although tests of conditioned but unexposed (blank) tubes showed no O_3 artifacts, results might differ for longer storage times, especially if tubes are prepared weeks in advance of air sampling. The previous work by the authors for largely nonpolar VOCs on Tenax GR has shown that adsorbed compounds are stable for ≥ 6 weeks when appropriately stored[35]; however, the present work does not evaluate whether storage time after sample collection affects artifact concentrations. Elevated storage temperatures might also warrant consideration.

Applications

In practice, artifact formation on air sampling adsorbents is likely to be very complex; for example, O_3 penetration and artifact formation may be affected by VOC loadings on the adsorbent, which may block O_3 access to active adsorption or reaction sites. Furthermore, artifact formation may be affected by sampling rates, humidity, temperature, other oxidants, and other variables.[16] The results show that artifact formation depends on adsorbent material, O_3 concentration and dose, adsorbent age, and the conditioning method. Many, but not all, artifacts will decrease with adsorbent age. Future work might examine both lower and higher O_3 concentrations (the U.S. standards are 120 ppb for 1-hr average and 80 ppb for 8-hr average), other adsorbents, and the effect of VOC loadings.

Although many papers in the literature have noted adsorbent-O_3 artifacts, quantification of artifacts is the exception. Because artifact levels will depend on many factors, the quantification detailed here provides only approximate guidance to the artifacts that will be formed in practice. Still, knowledge of the identity and the rough magnitude of artifact concentrations is helpful in determining the applicability of a sampling method. As several aldehydes, specifically acetaldehyde and formaldehyde, have come under increasing scrutiny as priority urban hazardous air pollutants by U.S. Environmental Protection Agency (although none of the detected artifacts are so designated), better methods to detect aldehydes (and other compounds) would be valuable.

One method to minimize artifact formation is the use of an upstream scrubber for O_3. The authors and others have used previously, for example, scrubbers containing crystalline potassium iodide (KI) that remove O_3 and that do not appear to remove significant amounts of target VOCs.[37–39] O_3 scrubbers consisting of copper screens coated with MnO_2 may allow better quantification of oxygenated VOCs.[2,40] Helmig[5] discusses these and other O_3 removal approaches and indicates that no universally applicable technique exists. Although simple and often effective, scrubbers have disadvantages: materials must be conditioned before use,[41] they have limited lifetimes, they impose a pressure drop in active sampling, they may preclude passive sampling, and additional artifacts may

be formed, for example, KI can form organic iodine species (that are, however, easily recognized as artifacts).[42]

Finally, distributed sampling, often a good way to test data quality, may not reliably detect certain O_3-adsorbent artifacts, for example, phenyl-substituted carbonyls. For example, in atmospheric sampling, Walling et al.[23] observed that benzaldehyde concentrations remained roughly constant on adsorbents using low (6 L) to moderate (11 L) sampling volumes, but concentrations increased at higher volumes (up to 54 L was tested). This is consistent with the study results that O_3-adsorbent artifacts will increase with O_3 dose. However, because this is not the case for all artifacts, distributed volume sampling remains a good idea, handling at least some O_3-adsorbent artifacts, as well as providing checks on other compounds.

Method Performance

Each of the four thermally desorbable adsorbents tested can be used to sample carbonyls, although additional work may be necessary to address artifact formation and to improve sensitivity, important issues given the low levels of these compounds usually encountered in environmental sampling. Although Carbotrap X did not form O_3-adsorbent artifacts, recoveries and detection limits achieved with this material were somewhat poorer for several compounds compared with the three other adsorbents. Still, this work indicates that Carbotrap X avoids positive artifacts from O_3; other recent work indicates that this adsorbent also avoids negative artifacts from O_3 (that would decrease concentrations) for most compounds.[7] The authors did not optimize sampling and analytical methods for the carbonyls; rather, their goal was to provide information necessary to quantify artifact concentrations. Nor did they investigate reactions between O_3 and adsorbed (preloaded) VOCs, which, as noted earlier, also can produce artifacts. The use of other adsorbents, O_3 scrubbers, and changes to TD-GC/MS conditions may improve performance.

CONCLUSIONS

O_3-adsorbent interactions were examined for four adsorbents commonly used for air sampling. Environmental levels of O_3 are shown to form a number of artifacts that may be interpreted as false positives. After exposure to 100-ppb O_3, the authors identified, confirmed, and quantified 13 different compounds on both Tenax TA and Tenax GR and 9 compounds in Carbopack B. Carbopack X did not show any artifacts, even after exposure to 1000-ppb O_3. The pattern of artifacts differed among the adsorbents, although C_6 through C_{10} n-aldehydes were found on Tenax TA, Tenax GR, and Carbopack B. Tenax GR formed the same artifacts as Tenax TA, but at lower levels, likely because of enhanced removal of O_3 as determined in O_3 breakthrough experiments. The authors found six O_3-Tenax TA artifacts not reported previously (pentanal, 3-hexanone, 2-hexanone, hexanal, 3-heptanone, and heptanal), five new O_3-Tenax GR artifacts (pentanal, 3-hexanone, 2-hexanone, hexanal, and 3-heptanone), and two new O_3-Carbopack B artifacts (unsaturated alkenes 1-octene and 1-nonene). The phenyl-substituted carbonyls identified in earlier studies as O_3-Tenax artifacts were also found. The pure hydrocarbon artifacts reported

in earlier work were not seen, and their examination of conditioning practices suggests that some of the literature results may be a result of incomplete conditioning. They also developed calibration curves, recoveries, and MDLs for the 15 carbonyls identified as artifacts.

The mechanisms that form artifacts remain incompletely understood, although results reveal that formation is related to the adsorbent type and age, O_3 concentration and dose, and the degree of O_3 penetration through the adsorbent bed. High O_3 concentrations (1000-ppb O_3) yielded different artifact patterns: Tenax TA formed phenol, benzoic acid, phenylmaleic acid, and phenylbenzoate; Tenax GR formed phenol, benzeneacetaldehyde, phenylmaleic acid, benzophenone, and phenylbenzoate; and concentrations of artifacts on Carbopack B were diminished. Artifact concentrations were quantified after repeated O_3 exposure-conditioning cycles. Benzaldehyde and acetophenone on Tenax TA were reduced by half after 10 cycles. The same compounds on Tenax GR were largely unaltered after repeated cycling, but levels were lower than found on Tenax GR. Most other artifacts were significantly decreased to only trace levels after two or three exposure-conditioning cycles after a first-order (exponential) decrease.

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