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Ozone reaction with *n*-aldehydes ($n=4-10$), benzaldehyde, ethanol, isopropanol, and *n*-propanol adsorbed on a dual-bed graphitized carbon–carbon molecular sieve adsorbent cartridge

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Abstract

Ozone reacts with *n*-aldehydes ($n=4-10$), benzaldehyde, ethanol, isopropanol and *n*-propanol adsorbed on a dual-bed graphitized carbon–carbon molecular sieve adsorbent cartridge. Destruction of *n*-aldehydes increases with *n* number and with ozone concentration. In some sampling experiments both generation and destruction of *n*-aldehydes by ozone are observed. In field experiments the results of sample analysis for *n*-aldehydes and benzaldehyde are frequently not proportional to sample volume whereas results for toluene and isoprene, and sometimes for total carbon, are. A simple theory is developed to simulate the net result of three processes: the adsorption of compounds from an air stream onto a solid adsorbent, the generation of compounds by reaction of ozone with materials upstream of or on the adsorbent, and the destruction by ozone of pre-existing compounds and compounds adsorbed from the sample stream. The use of distributed volume pairs is recommended as a way to identify loss of sample integrity during air monitoring experiments. Published by Elsevier Science B.V.

Keywords: Ozone reaction; *n*-Aldehydes; Benzaldehyde; Ethanol; Isopropanol; *n*-Propanol

1. Introduction

The accuracy of monitoring for individual volatile organic compounds (VOCs) largely depends on the integrity of samples during the monitoring process. Concentrating VOCs by sampling onto solid adsorbents is frequently used in order to improve the detection limit, especially for ambient air measurements where individual concentrations of prevalent compounds are at or below 1 ppbv [1]. Ozone and

other airborne components in the sample stream may react with the adsorbed VOCs so that sample integrity is lost. For example, the three monoterpenes α -pinene, β -pinene and limonene were dramatically reduced while relatively non-reactive compounds such as benzene and toluene were not changed [2]. Other experiments [3,4] have shown that the analytical responses to terpenes and terpenoids collected from synthetic air samples and concentrated on Tenax solid adsorbent were significantly reduced when ozone was present.

This paper examines the effect of ozone on the integrity of a set of volatile *n*-aldehydes, benzaldehyde, ethanol, isopropanol and *n*-propanol ad-

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sorbed onto a solid adsorbent in synthetic samples and the effect of ozone and other ambient air components on some of these same compounds for samples taken at two field locations. In the synthetic and the field samples toluene and isoprene and, to a certain extent, total carbon were considered controls in that their results typically scale with the sample volume. In order to explain the experimental data, a simple theory based on the interaction of adsorbed VOCs with ozone and other reactive compounds is developed. Loss of sample integrity for the target VOCs from ambient air samples appears to be analogous to loss in the synthetic air samples except that reactive species other than ozone can also be present.

The study of *n*-aldehydes was undertaken because of their importance in photochemical processes and the apparent multitude of *n*-aldehyde sources. The occurrence of *n*-aldehydes in ambient air has often been noted in previous studies [5–7]. They can originate in ambient air by reaction of ozone or other oxidizing agents with organic material in airborne particles such as unsaturated fatty acids which typically result as natural products of biological decomposition. Aldehyde creation as a result of reactions of reactive atmospheric gases and the lipid materials in marine aerosols can be inferred from recent work [8]. The aggregate effect of *n*-aldehydes on reducing OH radical concentrations in the ambient air [9] is sufficient to warrant careful study of their source and sink inventories. *n*-Aldehydes are produced in the indoor environment through interaction of ozone with the organic components of dust [10,11] and during the process of alkyd-based paint drying [12]. Artifact formation of *n*-aldehydes has been noted in this laboratory when using a multi-component sorbent containing Tenax GR, Carbotrap and Carbosieve S-III for measuring ambient VOCs [13] and by others [14] when making ambient level measurements. Given the multitude of potential sources care must be taken in attribution of the *n*-aldehydes for any given sampling and analysis event.

2. Experimental

The sorbent tubes were glass tubes (90×4.0 mm

I.D.) packed with 160 mg of Carbotrap graphitized carbon black (20–40 mesh=420–840 μm grain sizes) followed by 70 mg of a Carboxen type carbon molecular sieve (60–80 mesh=180–250 μm grain sizes). The tubes were obtained from Perkin-Elmer (Wilton, CT, USA) and the sorbents were prepared by Supelco (Supelco Park, Bellefonte, PA, USA). The amount of graphitized carbon was sufficient to totally destroy ozone at concentration levels used in our experiments so that we expect the reactions of ozone with target compounds to occur as if only the graphitized carbon were present. The tubes were capped with Swagelok fittings and PTFE ferrules and stored inside glass tubes sealed against PTFE end disks. During shipping the glass tubes were placed in a clean metal can and cushioned with a packing of lint-free tissue paper. At the analysis location prior to processing, the tubes were placed in a refrigerator cooled to at least 10°C. Batches of tubes were automatically desorbed using the carousel arrangement and thermal desorption system of the Perkin-Elmer Model ATD-400. Details of the tube conditioning, thermal desorption conditions, and the GC–flame ionization detection (FID) analytical system used in most of the tests are given elsewhere [15]. For the more recent tests, samples were analyzed by GC–MS using a Varian Star 3400Cx gas chromatograph (Varian, Walnut Creek, CA, USA) equipped with a 60 m×0.32 mm×1.0 μm Rtx-1 capillary column (Restek, Bellefonte, PA, USA), and a Varian Saturn 2000 ion trap mass spectrometer. The GC oven temperature was programmed as follows: 35°C for 5 min, a 6°C/min ramp to 210°C, and a 0.84-min hold at 210°C, for a total analysis time of 35 min. The Saturn 2000 MS operating conditions were scan range, 26–300 amu; scan rate, 0.8 s/scan (3 μscans per analytical scan); background mass, 25 amu; segment breaks, 70,78,150; segment tune factors, 120/70/100/70 (segment time), 25.0/25.0/25.0/25.0 (segment RF); automatic gain control target, 15 000–20 000; emission current, 15 μA.

2.1. Laboratory tests using GC–FID

Synthetic air samples containing ozone in humidified air were sampled from a multiport glass manifold onto tubes either before, after, or during loading of the target compounds. To prepare a

sample of the target compounds for loading, neat compounds were added to 1 l of water and thoroughly mixed to form a solution. The amounts were chosen so that the gas phase concentration obtained by vaporizing 200 μ l of the water solution into an evacuated, SUMMA-polished, stainless steel canister (6 l) and thereafter pressurizing to 45 p.s.i.g. with nitrogen gave a nominal concentration of 10 ppbv, assuming complete solubility of the target compounds. Additional details are available in a technical note [16]. The actual canister concentrations were checked by GC–FID analysis referenced to the per-carbon response of a NIST propane standard after the application of correction factors to the FID response [17]. To adsorb VOCs onto the sorbent tubes either before or after sampling from the multiport manifold, a Tylan flow controller was attached to a pressurized canister containing the VOC mixture, the canister was opened and the flow-rate was allowed to stabilize, and then the tube was attached to the controller. A known amount of the VOC mixture was then passed onto the tubes, e.g. 1-l sample volumes were obtained by sampling 15 min at a flow-rate of 67 ml/min. In one case VOCs were mixed with ozonated, humidified air just upstream of the sampling tube so that both could be introduced simultaneously onto the sorbent. In all other cases ozone in zero air was passed over the surface of water contained within a round-bottomed glass beaker which provided relative humidity (RH) values in the range 40–60% at room temperature and then sampled onto the tubes from the multiport manifold. The ozone concentration was monitored from a port on the glass manifold. No particle filters were placed in front of the tubes. During sampling from the manifold, two sorbent tubes were placed on adjacent manifold ports and attached to a dual-port commercial air sampler (Bios International Corp., Pompton Plains, NJ, USA). This sampler was designed for applications of EPA compendium method TO-17 [18] in which a primary requirement is for sampling using a distributed volume pair (DVP), i.e. two tubes sampling at different flow-rates over the same time period. Each tube was used to sample air over a period of 1 h from the manifold, one tube sampling at a rate of 16.7 ml/min (1 l/h) and the second tube at 4 times this rate or 66.7 ml/min (4 l/h), this approach being that specifically recommended in Method TO-17.

2.2. Laboratory tests using GC–MS

GC–MS was also used in a series of tests designed to verify and expand the information obtained with GC–FID. In these tests, the tubes were preloaded with target compounds and then a humidified air stream containing ozone was sampled. Samples were taken from a reference canister containing a mixture of the *n*-aldehydes, three alcohols, and toluene; these samples were prepared and verified in the same manner as for the previous tests. After loading from the canister for 15 min at a flow-rate of 67 ml/min (1 l), the tubes were placed at ports on a sample manifold where samples of ozone in humidified scientific grade air (50% RH at room temperature of $25 \pm 3^\circ\text{C}$) were drawn through them for 1 h at 67 ml/min (4 l). The sample air stream was formed by adding ozone in air generated in a TEI Model 49PS (Franklin, MA, USA) ozone generator to a humidified air stream originating from a Miller Nelson Research (Monterey, CA, USA) Model HCS-401 humidifier. This arrangement provided levels of ozone from 0 to 150 ppbv.

2.3. Field tests

Ambient air samples were taken in the Research Triangle Park (RTP), NC, USA and Azusa, CA, USA in September 1997 and analyzed using the GC–FID system. These tests involved the same sampler and arrangement of distributed volume pairs as used in laboratory GC–FID tests except that the tubes were wrapped in aluminum foil to avoid sunlight and a 2- μ m 47-mm PTFE filter was placed in front of the sample inlet. Experiments were performed during midday at both locations with 30–34 $^\circ\text{C}$ and 30–52% RH at RTP and with roughly the same conditions in Azusa. In all field samples isoprene and toluene were used as indicators of the performance of the DVP since analysis results typically scaled with sample volume. Total integrated area count response of all GC peaks was also expected to be a good indicator of the attainment of a 4:1 sample volume ratio based on the documented stability of many VOCs in canisters [19]. Shipping and storage conditions prior to analysis were as noted above. Tests performed in RTP in 1998 were essentially the same. However, the Varian Model

3400CX gas chromatograph and the Varian Saturn 2000 ion trap were used in the analyses.

3. Laboratory test results

3.1. Tests using GC–MS

Table 1 shows the area counts for the quantitation ion for each compound including the alcohols ethanol, isopropanol and *n*-propanol as analyzed on the GC–MS ion trap system. The area counts for a zero ozone concentration, as in the first experiment, vary from compound to compound due to factors such as different ionization efficiency in the mass spectrometer and compound concentration levels in the canister. The results of these experiments for the four *n*-aldehydes, nonanal, octanal, heptanal, hexanal, and toluene are shown in Fig. 1 normalized to the initial value (no ozone). The *n*-aldehydes show a decreased response with higher ozone concentrations and higher *n* values while the results for toluene are essentially constant as ozone concentrations are changed. As indicated in Table 1, the alcohols also show a decreasing response with increasing ozone concentration although the responses begin to increase slightly at the highest ozone concentrations.

3.2. Tests using GC–FID

Interesting changes in the area counts were noted under different sampling scenarios. Five such

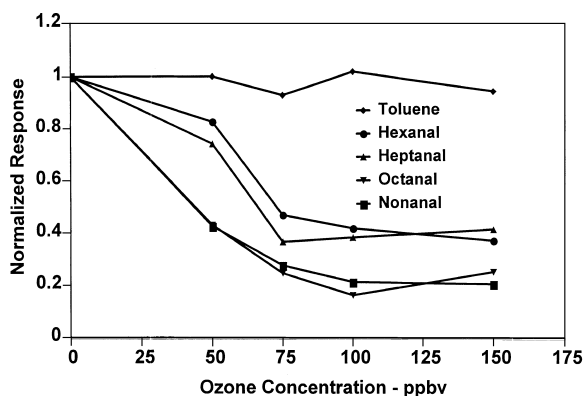


Fig. 1. Effect of sampling ozone in humidified zero air through tubes preloaded with aldehydes.

scenarios are listed in Table 2. The results show that the changes can be characterized as follows.

(1) Samples (4- and 1-1) of the set of aldehydes only (first lines under 4 l and 1 l in Table 2): results of analyses of the area counts of the *n*-aldehydes, *n*=4–9, and benzaldehyde, all at nominally 40 ppbv loaded for 15 min should give a response roughly proportional to carbon count. Because of uncertainties in preparing the synthetic samples in canisters, the actual concentration was not related to carbon count (as indicated by the area counts recorded in Table 2). However, this fact does not appear to affect the ratio value formed from results of analysis (4-l response/1-l response). Indeed, the ratios of results are approximately 4:1, the same as the sample volume ratio, as expected if sampling and retrieval of the target compounds by thermal desorption is

Table 1

Effect of sampling ozone in humidified air through a sampling tube containing graphitic carbon preloaded with aldehydes, alcohols and toluene

Ozone	0	50	75	100	150
Ethanol	66 283	51 381	38 854	46 659	56 982
Isopropanol	199 085	158 250	90 133	128 090	106 935
<i>n</i> -Propanol	149 991	109 175	65 733	99 738	83 378
Toluene	589 600	588 489	546 541	598 093	553 945
Butanal	38 719	39 929	40 657	40 533	36 371
Pentanal	89 647	97 001	67 213	80 639	48 402
Hexanal	51 974	42 855	24 448	21 746	19 346
Heptanal	23 253	17 225	8515	8943	9591
Octanal	115 225	49 476	28 767	18 926	29 243
Nonanal	31 007	13 262	8593	6622	6376

Ozone in ppbv; other results in area counts corresponding to the quantitation ion for each target compound.

Table 2

FID response in area counts to different scenarios for reaction of gas phase ozone with graphitic carbon solid adsorbents with and without adsorbed aldehydes

	Butanal	Pentanal	Hexanal	Heptanal	Benzaldehyde	Octanal	Nonanal
4-1 sample							
No O ₃	177 402	504 182	471 222	831 539	1 014 025	722 255	1 098 330
O ₃ , Al	1 175 481	578 882	1 467 158	2 124 257	2 790 043	1 248 111	1 553 052
Mix	125 573	251 030	296 278	91 238	271 011	62 278	124 707
Al, O ₃	601 875	1 219 070	371 491	340 483	924 891	197 105	148 116
Al, 1/2O ₃	577 416	1 514 987	1 074 139	1 757 152	2 532 691	502 364	144 399
1-1 sample							
No O ₃	45 828	143 006	124 518	224 919	303 248	185 428	262 763
O ₃ , Al	151 043	398 026	330 193	623 152	737 397	492 175	569 345
Mix	65 528	167 558	207 471	274 659	380 788	299 927	416 509
Al, O ₃	145 738	383 915	326 852	605 290	786 218	524 378	691 985
Al, 1/2O ₃	144 391	391 858	323 256	625 202	754 607	469 770	202 217

complete and if no artifacts are formed. The ratio of responses is as shown in Fig. 2 (“no ozone” plot).

(2) Sampling of O₃ prior to sampling of aldehydes: results of analyses show that artifact aldehydes are created when O₃ is sampled first. The amounts of artifact aldehydes are compound dependent but with no obvious systematic trend with *n*-values. This is evident in results as shown in Table 2 (line 2 under both 4-1 and 1-1). If the increases were proportional to the amount of O₃ passed through the sorbent tubes, then the ratio of responses would be 4:1. This is true as seen in Fig. 2 (“O₃ first, then *n*-ald.” plot) except that the response ratios for octanal and nonanal are somewhat lower than other compounds.

(3) Sampling of aldehydes prior to sampling O₃: results of analyses show that the FID responses due to the individual aldehydes decrease substantially for the 4-1 samples compared to the 1-1 results in (1) and (2) and that the decrease is greater for higher *n* values. The 1-1 samples also show decreases but to much less of a degree. The ratio shows a systematic decrease with *n* values (with a slight perturbation due to the inclusion of benzaldehyde) as noted in Fig. 2.

(4) Sampling of aldehydes and O₃ premixed before passing through the sorbent tubes: the ratios are similar to but slightly lower than situation (3) in which the compounds were loaded prior to sampling any ozonated air. This case is shown in Fig. 2.

(5) Sampling of aldehydes prior to sampling one half the amount of O₃ used in (3): results shown in Fig. 2B indicate that this case gives intermediate

ratios between those for (1) and (3), implying that the more O₃ used the more noticeable the effect. This fact is consistent with results shown in Fig. 1. Again, benzaldehyde causes a perturbation in the systematic change of response ratios with *n* value.

3.3. Field studies

The results from Azusa on 22, 23 September 1997 and shown in Fig. 3 as a series of 1-h, distributed volume sets taken during the late morning and afternoon are representative of results obtained on several other days in Azusa. Based on selected ozone concentration readings taken at a nearby network monitoring station the ozone concentrations during these sampling events are estimated at between 50 and 100 ppbv. Compounds 1–11 include the *n*-aldehydes (decanal to pentanal) and benzaldehyde (compound 4) along with isoprene (compound 9), toluene (compound 10), and total carbon (compound 11). In general, the pattern of ratios for the *n*-aldehydes does not show a 4:1 ratio and indeed is not even close to the ratio of 4 expected if sample integrity is maintained. For any single day, a rough pattern occurs in the relative ratios for the first six aldehydes while the ratios of pentanal, butanal, isoprene and toluene typically range between 3 and 5. Total carbon ratios vary significantly with hour of the day and are sometimes within specifications and sometimes moderately below the minimally acceptable ratio of 3.0 stated in the EPA compendium

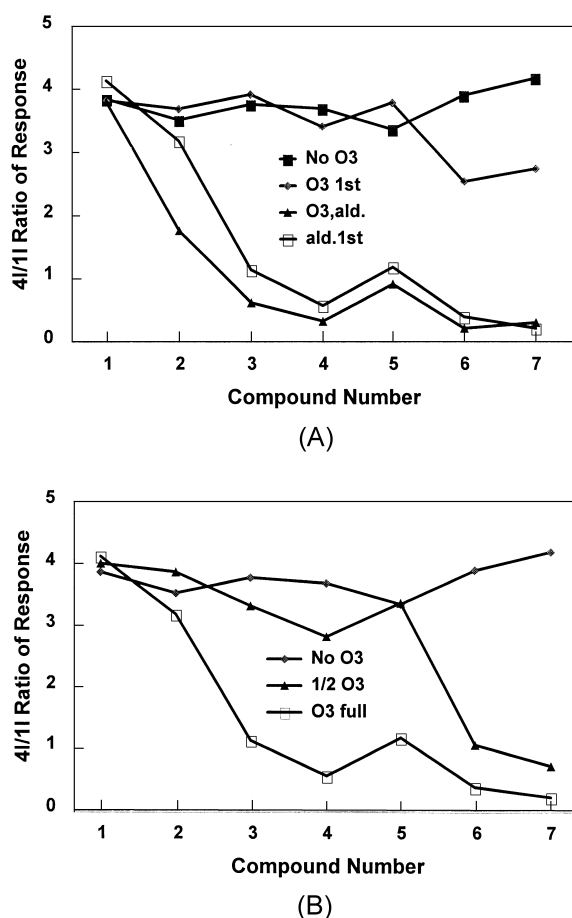


Fig. 2. DVP ratio vs. CPD no. for aldehydes: (A) different orders of collection; (B) different levels of ozone (100 ppbv ozone maximum in humidified synthetic zero air); Compounds from 1 to 7 are butanal, pentanal, hexanal, heptanal, benzaldehyde, octanal, and nonanal.

method TO-17 for sampling of VOCs with solid sorbents.

Ambient air samples taken during the summer at RTP in 1997 were taken during the days preceding the Azusa study and with the same sampling equipment. Ozone concentrations were not measured but are estimated to have been in the 50–100 ppbv range during the midday sampling runs. These samples showed significantly reduced DVP ratios for the aldehydes compared to toluene, isoprene, and total FID just as in the Azusa samples, but the pattern of the ratios for different n values was somewhat different.

Air samples taken at RTP in August and September of 1998 were taken directly from a heated manifold through which a high-velocity air stream was passing. No inlet particle filter was used in this arrangement and the air samples were pulled through the two tubes of a DVP set with a metal bellows pump fronted by Tylan flow controllers set for 1- and 4-l collections over an hour. The DVP ratio for octanal as a function of ozone concentration was recorded for all samples (12 DVPs) taken with a toluene concentration above 0.5 ppbv (an indication of higher pollution hours). The results show that the DVP ratio decreases from values between 2 and 4.7 at ozone concentrations below 40 ppbv to values between 0.4 and 1.2 for values above 80 ppbv using ozone measurements at the monitoring site. Although these data are limited, they are consistent with the laboratory data in indicating an octanal loss due to an ozone concentration increase.

4. Mathematical model of system

A theory was developed to model the features of the experimental observations. The theory includes the trivial case represented by the absence of any ozone or other reactive gas from the sample stream, i.e. scenario 1 represented above. The change in the quantity of a specific adsorbed aldehyde, A_i , is given as:

$$\Delta A_i = F_r C_{i0} \Delta t \quad (1)$$

where F_r denotes flow-rate of the sample air through the tube, C_{i0} denotes gas phase concentration of aldehyde entering the sorbent-filled tube, and Δt denotes an increment of time over which sampling occurs. The aldehyde accumulates linearly with time and flow-rate so that for a distributed volume pair over a period of time T , the total amount of aldehyde on the tube, A_i , equals $F_r C_{i0} T$, and the 4-1/1-1 response ratio is 4. In this case linear accumulation of the aldehyde occurs with no significant complications due to breakthrough of the compounds or to difficulty in retrieval of compounds from the sorbent bed.

To treat the case for collection of aldehydes in air containing ozone, the hypothesis was made that ozone reacts with adsorbed aldehydes such that the

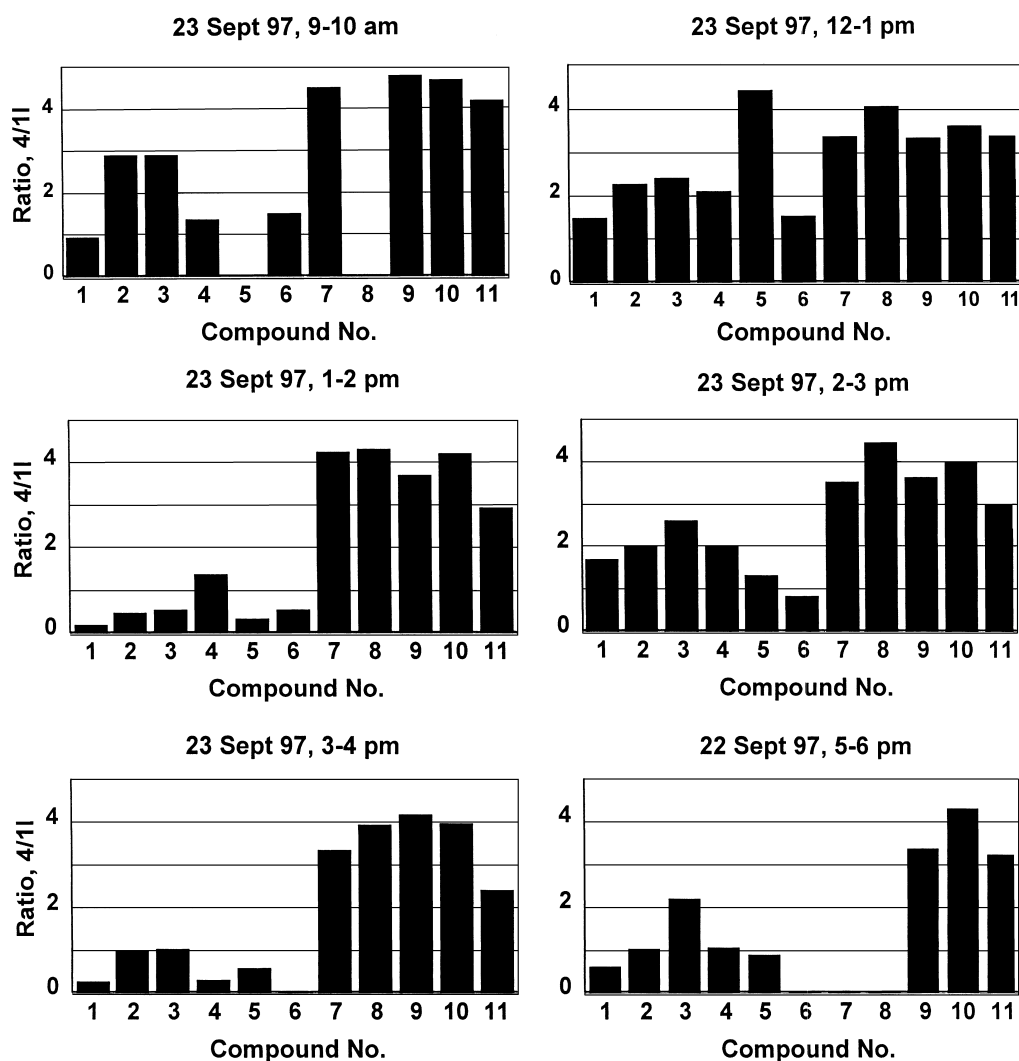


Fig. 3. Sequence of hourly samples: Azusa; compounds 1–11 are decanal, nonanal, octanal, benzaldehyde, heptanal, hexanal, pentanal, butanal, isoprene, toluene, and total hydrocarbons. Missing ratio values indicate that either the 1- or 4-l sample was not detected.

change in the quantity of adsorbed aldehyde, A_i , is affected by three terms, one for accumulation, one for generation, and one for destruction. Under certain assumptions, the change in A_i is given by:

$$\Delta A_i = F_r [C_{i0}] \Delta t + k_c F_r [O_3]_o \Delta t - \int k_d [A_i] F_r [O_3] \pi R^2 \Delta x \Delta t \quad (2)$$

In the generation term (second term on right), F_r denotes the gas flow-rate into the sorbent tube, $[O_3]_o$

denotes the concentration of ozone entering the tube, and k_c denotes the fraction of ozone molecules that result in the generation of aldehyde molecules. To use this form of generation term, the following conditions have been assumed.

(a) The availability of generation sites on the solid sorbent is assumed to be constant in time and to have a constant value along the sorbent tube length, i.e. no adsorption site depletion occurs.

(b) The ozone concentration profile along the sorbent tube length is assumed to be determined by a

first-order destructive interaction with the sorbent material, independent of aldehyde generation or destruction and of a significantly larger magnitude. Under this assumption, the ozone concentration profile with distance along the sorbent tube remains constant in time (if the sorbent surface does not change) for a given flow-rate and can be approximated as an exponential decay:

$$[\text{O}_3]_x = [\text{O}_3]_{x=0} \exp[-\alpha x] \quad (3)$$

However, no matter what the ozone profile, it remains constant in time. Under assumptions (a) and (b), the creation rate of aldehydes is simply a constant times the rate at which ozone flows into the sorbent tube, i.e. $k_c F_r [\text{O}_3]_o$, so that any given ozone molecule has a certain probability of creating an aldehyde molecule before being destroyed on the carbon surface. During the actual use of sorbents, the surface properties with respect to ozone destruction and to the generation of aldehydes probably change in time due to passivation of the surface, as experimentally observed for the case of ozone reacting with soot aerosol [20]. However, for this development the surface properties are considered constant in time.

In the destruction term in Eq. (2), the rate of destruction of aldehydes is proportional to the reaction rate of ozone with adsorbed aldehydes. If the exponential term in the expression for ozone concentration is expanded inside the integral, keeping only the first term, Eq. (2) reduces to:

$$\Delta A_i = F_r [C_{io}] \Delta t + k_c F_r [\text{O}_3]_o \Delta t - k_d F_r [\text{O}_3]_o A_i \Delta t \quad (4)$$

where A_i denotes the total number of aldehyde molecules adsorbed in the sorbent tube. Neglecting the additional terms in the expansion causes an overestimation of the loss of aldehydes and is essentially equivalent to assuming that ozone reactions with aldehydes occur very near the front of the sorbent. The treatment of the additional terms in the expansion can be addressed numerically or by imposing additional conditions on the variation of A_i with distance along the tube, although neither attempt has been made here.

4.1. Asymptotic solution

Assuming constant values of C_{io} , F_r , $[\text{O}_3]_o$, k_c ,

and k_d with time, a steady state is reached when $\Delta A_i / \Delta t = 0$ or equivalently when:

$$A_i = (C_{io} + k_c [\text{O}_3]_o) / k_d [\text{O}_3]_o \quad (5)$$

which is independent of flow-rate and initial aldehyde loading, e.g. from blank values or intentional loading before ozone exposure. The DVP ratio at steady state is 1.0, i.e. the ultimate result of the process of accumulation, generation, and destruction is an equal loading for tubes sampling at different rates.

4.2. General solution

Assuming an initial concentration of aldehyde A_{io} , the solution to Eq. (4) can be written:

$$A_i = A_{io} \exp(-k_d F_r [\text{O}_3]_o t) + [(C_{io} + k_c [\text{O}_3]_o) / k_d [\text{O}_3]_o] [1 - \exp(-k_d F_r [\text{O}_3]_o t)] \quad (6)$$

Special cases of this solution are now considered.

4.3. No initial loading

4.3.1. Aldehydes in sample, no ozone

If no ozone or initial loading of sample compounds is present, the quantity $A_i = F_r [C_{io}] T$ is accumulated after a time T and the DVP ratio is the ratio of sample volumes, i.e. a constant value of 4.0 corresponding to the 4- and 1-l sample volumes.

4.3.2. Ozone and aldehydes in sample

The net effects of accumulation, generation, and destruction in the presence of ozone occur more rapidly for the 4-l sample than for the 1-l sample as both terms approach their equilibrium values. When the results are plotted as distributed volume pair ratios, R , with no initial concentration of aldehyde, i.e. $A_{io} = 0$, and using the aldehyde destruction factor $\xi = k_d F_r [\text{O}_3]_o t$ as the abscissa, the results are:

$$R = [1 - \exp(-4\xi)] / [1 - \exp(-\xi)] \quad (7)$$

as shown in Fig. 4A. These results indicate that a 4:1 sampling rate gives a ratio of 4.0 in the limit of low samples volumes. The ratio decreases gradually towards an asymptotic value of 1.0. Inspection of Eq. (7) indicates that the destruction rate determines the rate of approach to the asymptotic value.

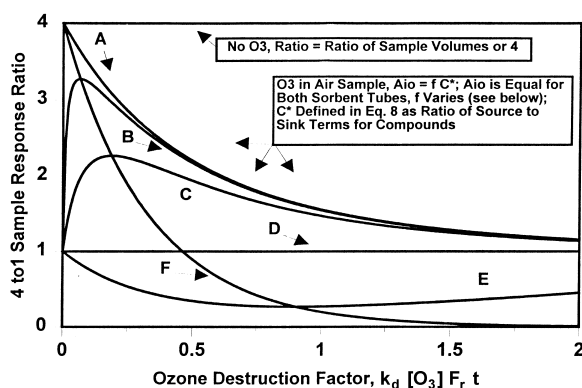


Fig. 4. Predicted 4:1 response ratio from Eq. (6) with sorbent initial loading values, A_{i_0} , equal; for (A–E), $A_{i_0} = f C^*$ where $f = 0.01, 0.1, 1.0, 10, 100$. In curve F the ratio of initial loadings is 4:1 and $C^* = 0$.

4.3.3. No aldehydes, ozone in sample

Aldehyde generation by the interaction of ozone with upstream elements or with unknown adsorbent material occurs linearly with sample volume such that $A_i = k_c F_r [O_3] t$. Experimentally, the rate of aldehyde generation for a given sampling event can vary considerably since the value of k_c is not known a priori and may change due to the history of the adsorbent and contamination of system components. The reaction between the aldehydes that are generated and ozone in the sample eventually limits buildup of aldehydes as the destruction term comes into play and the DVP ratio is the same as shown in Eq. (7).

4.4. Initial aldehyde loading present

4.4.1. Aldehydes and ozone in sample

If an aldehyde loading exists due to intentional loading or due to a blank value somehow developed on the adsorbent, then Eq. (7) is modified by the addition of two factors placed to multiply the exponential terms. These factors are of the form $B = [(A_{i_0} B C^*)/C^*]$; C^* denotes the ratio:

$$C^* = (C_{i_0} + k_c [O_3]_o) / k_d [O_3]_o \quad (8)$$

and the DVP ratio is written:

$$R = [1 - B_4 \exp(-4\xi)] / [1 - B_1 \exp(-\xi)] \quad (9)$$

where B_4 refers to the 4-l sample and B_1 refers to the 1-l sample (or equivalently to a 4:1 sampling rate

difference between the two samples). Fig. 4 shows curves corresponding to different initial loadings of the tubes where A_{i_0} is the same for both tubes. Curves A–E correspond to values of $A_{i_0} = 0, 0.01C^*, 0.10C^*, 1.0C^*$ (where the DVP ratio is a constant value of 1.0), and $10C^*$. The locus of extreme values coincides with curve F (see Section 4.4.2).

4.4.2. Ozone in sample, no aldehydes in sample

In this case $C_{i_0} = 0$, and Eqs. (8) and (9) apply. If the experimental situation is such that k_c is negligible so that only the first term in Eq. (6) remains, then a value of k_d can be estimated as $[\ln(A_i/A_{i_0})]/F_r [O_3] T$ (T denotes the specific time at which the response has decreased a fraction A_i/A_{i_0}) using the experimental data from Fig. 1. Fig. 4F shows the DVP ratios for samples with a 4:1 ratio of initial loadings and a 4:1 ratio of sampling rates where the tube with the higher initial loading has the higher sampling rate. In this case, the asymptotic value of the DVP ratio is not 1.0 as for all the other cases shown in Fig. 4 but is instead zero.

5. Discussion

When aldehydes were sampled onto adsorbent tubes and then ozone in air was sampled (Fig. 1 and Table 1 results), the aldehyde losses were greater the higher the n value and the greater the ozone concentration. The reaction of ozone with adsorbed aldehydes appears to be stronger by far than that with isoprene and toluene, although the opposite is apparently true for the gas phase reactions [21]. Based on these experiments, a kinetically-favored surface reaction is indicated where ozone reacts strongly with the aldehydes and alcohols (Table 1) that are adsorbed on graphitic adsorbent surfaces. The mechanism by which the adsorbed aldehydes were lost is probably direct ozonolysis as in the case reported for ozone reaction with a set of biogenic VOCs [4].

In Fig. 2 and Table 2, a net loss of aldehydes and alcohols was noted when ozone was co-collected or post-collected, and a net gain occurred if ozone in air was sampled prior to sampling aldehydes. These experimental data are consistent with the adsorption

of gases from the sample stream onto graphitic carbon, a generation of target compounds due to ozone, and destruction by ozone of the adsorbed target compounds. The evidence of significant generation of target compounds by ozone implies a reaction with material upstream of the adsorbent or with an unknown material on the adsorbent. The generation of the *n*-aldehydes by reaction with water used for sample stream humidification (in the GC–FID experiment ozone in air passed over a reservoir containing water) may be the source. However, attempts to reproduce this effect in a quantitative, predictable manner have not been achieved and the occurrence of this effect seems to be highly conditional, depending on factors such as the history of the adsorbent and the upstream sampling train components.

The occurrence of sampling artifacts originating from reactions of co-collected compounds results in a nonlinear response with sample volume. This circumstance is identified using the DVP approach to sampling. These artifacts are not detected using such quality assurance measures as duplicate sample collections or tandem tube sampling. For artifacts that scale with sample volume, other techniques, e.g. comparison with a different sampling approach, must be used to identify any artifacts. A nonconforming DVP ratio (outside the acceptable range of 3–5 as stated in EPA compendium method TO-17) also occurs if target compound blank values are comparable to the sample loading accumulated from the ambient sample. Our experience has been that the analysis of nominally clean tubes can, at times, show significant amounts of aldehydes. In these cases the cleanliness and history of the sorbent material and experimental arrangement are brought into question. For example, prior sampling in an arrangement where airborne particles can be introduced onto the sorbent or the sampling manifold surface might provide a source of aldehydes as a result of ozone reaction with fatty acids or other deposited organic material. If the blank values are dominant but random, a scatter of DVP ratios is expected depending on the range of blank values.

In the ambient air daytime samples taken at Azusa during September 1997, the DVP ratio of response indicates that compounds like propanal, butanal, isoprene, toluene and often total hydrocarbons

showed acceptable DVP ratios (3–5), while the DVP ratios for decanal, nonanal, octanal, heptanal, benzaldehyde and hexanal were often not acceptable under EPA Method TO-17 criteria and indicated significant problems such as target compound destruction by ozone or other ambient reactive compound, and/or tube blank value dominance. The DVP ratios were systematically low for the heavier *n*-aldehydes and appeared to move together and have a roughly similar response profile for different sampling runs. This behavior does not preclude blank value dominance as indicated in, for example, Fig. 4E where low DVP ratios are predicted. In fact, field blank values for the aldehydes were often comparable to the sample tube values in Azusa. The ambient samples taken at RTP indicate that the DVP pattern of response is not necessarily the same at different locations and may be related to a site-specific suite of reactions and/or to a different level of blank value dominance. At both field study locations, the DVP ratios showed low values often near and below 1.0 which indicate a dramatic departure from the 4.0 ratio necessary to insure a lack of sample integrity problems.

The simple theory presented here describes the general features of the experimental data as represented in Figs. 1 and 2 including the exponential decay of response due to ozone reaction with adsorbed aldehydes and the dependence of DVP ratios on the order of loading ozone and aldehydes. The simplifying assumptions used to derive Eq. (6) include neglect of the distributions of ozone and adsorbed VOCs along the length of the adsorption tube. As a result, the aldehyde destruction rates implied by comparison of experiment (Fig. 1) and theory represent estimates of the correct rates. Under the experimental conditions for field testing (no preloading of tubes), the simple theory with constant sampling conditions does not predict DVP ratio values lower than 1.0 unless blank value dominance is occurring. Other possible explanations of the experimentally observed low DVP ratios include a change in the surface properties of the graphitic carbon with exposure to ozone (adsorption site depletion) or the occurrence of a temporal variation in reactive compounds in the sampling stream. However, no experimental basis for either of these has been developed.

6. Conclusion

Ozone reacts with and destroys *n*-aldehydes and benzaldehyde as well as ethanol, *n*-propanol, and isopropanol adsorbed on graphitic carbon used in an air sampling tube. The destruction rate is compound dependent and for the *n*-aldehydes increases with higher *n* values (*n*=4–9) and with increasing ozone concentration. Apparent generation of aldehydes by ozone reaction with upstream system components or an unknown species on the adsorbent occurs but varies in magnitude depending on the experimental arrangement.

Artifact effects due to reactions of co-collected compounds can be determined during ambient monitoring by sampling two different air volumes over the same time period (a DVP) to determine if results are proportional to sample volume. The lack of proportionality for *n*-aldehydes, benzaldehyde, ethanol, *n*-propanol and isopropanol in laboratory tests is so significant as to preclude accurate monitoring of these compounds when co-collected ozone concentrations reach even modest levels of 30–50 ppbv. In field tests, the lack of proportionality for *n*-aldehydes and benzaldehyde appears to be due to a combination of reactions between ozone and adsorbed compounds and to the existence of blank values comparable to sample values. To successfully use adsorbents as part of monitoring these compounds, blank values must be suppressed well below the values accumulated in sampling and a selective scrubber for ozone and any other reactive compounds is required. Although a significant amount of information is available [22–26] on ozone scrubbers, the ideal ozone scrubber has apparently not yet been identified.

A simple model of the system simulates certain features of the experimental results. For reactive co-collected compounds and assuming insignificant tube blank values, a gradual reduction of the DVP ratio of responses (4:1 sampling rates) is predicted when co-collecting ozone, depending on the magnitude of the destruction factor $k_d F_r [O_3]_o t$ (see Fig. 4A). In this case the asymptotic value of the the DVP ratio is 1.0. If significant tube blank values occur, the DVP ratio varies due to the relative magnitude of the blank values, A_{io} , and the parameter C^* (see Eq. (8)) as shown in Fig. 4. For the case of tube pairs preloaded with a loading ratio of 4:1 and when

generation of compounds is not important, the presence of only ozone in the sample stream causes the DVP ratio to decrease exponentially towards a zero asymptotic value. Comparison of theory and experiment in this case gives an estimate of the reaction rates between ozone and adsorbed compounds.

Due to the presence of a distributed adsorbent in the ambient air (soot carbon with a concentration of $1.0 \mu\text{g}/\text{m}^3$ is not atypical) along with ozone and other reactive compounds and radicals, the results of these experiments should be considered as to their implications for atmospheric processes and health effects. To the extent that the small particles in the atmosphere (soot for example) constitute the adsorbent, the experimental equivalent of Fig. 1 can be used to estimate reaction rates with ozone. The products of these reactions on the surface of the small particles could travel with the particles to reach the deep lungs much more efficiently as an adsorbed compound than as a gas molecule. This would indicate a possible health effect related to the intensity of photochemical activity when ozone concentrations reach high values.

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