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Method Development and Field Measurements for Polar Volatile Organic Compounds in Ambient Air

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This paper reports on a program which had two main objectives: (1) to develop an analytical method for polar volatile organic compounds (PVOCs) in ambient air using sample collection in canisters and (2) to perform PVOC analysis on ambient air samples collected at two sites formerly used in the U.S. EPA's Toxic Air Monitoring Study (TAMS). The analytical method consists of gas chromatographic separation of PVOCs with quantification by a quadrupole ion trap mass spectrometer. In order to achieve proper chromatographic resolution of the PVOCs, it was necessary to use a two-stage adsorbent trap to separate water from the sample prior to GC analysis. Detection limits for a group of 14 target PVOCs range from 0.2 to 1 ppbv in atmospheric samples, using electron impact (EI) ionization in the ion trap detector. The method has been used on canister samples collected over 24-h intervals on a regular basis over 1 year at former TAMS sites in Boston and Houston, and on occasional samples collected in other studies. The PVOCs most often found in ambient samples include methanol, ethanol, acetone, 2-propanol, methyl ethyl ketone, and 1-butanol. Measured levels of these species often substantially exceed the levels of benzene and toluene present in the same samples. The performance of the method in field sampling for PVOCs is comparable to that of the TO-14 method for nonpolar VOCs, though variability in canister sampling appears greater for the PVOCs, presumably due to the adsorptive behavior of these compounds. Possible improvements in PVOC sampling and analysis are also suggested.

Introduction

The measurement of low concentrations of organic compounds in the atmosphere has been a subject of research for many years. Measurement methods are well established for relatively nonpolar volatile organic compounds (VOCs) such as chlorinated and aromatic hydrocarbons. For example, EPA compendium method TO-14 involves sampling with stainless steel canisters, followed by cryogenic sample preconcentration, gas chromatographic (GC) separation, and measurement with a sensitive detector, and can provide detection limits for many VOCs well below 1 ppbv in air (1). Recently, attention has been focused on toxic and reactive oxygen- and nitrogen-containing organic compounds present in air, in part by the inclusion of many such compounds on the list of 189 Hazardous Air Pollutants in the 1990 Clean Air Act Amendments, and on state air toxics lists such as that for California's Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65). Such compounds may originate from a variety of industrial processes, automotive

emissions, and consumer products, and some may be formed in the atmosphere by photochemical oxidation of hydrocarbons. These compounds are collectively called polar VOCs (PVOCs), though in truth it is their reactivity and water solubility, more than simple polarity, which makes their measurement difficult with current methods. As a result, sampling and analysis methods for PVOCs are not as well developed as those for VOCs, and very few ambient data exist for many PVOCs, as a review of the National Ambient VOC database (2, 3) shows. The need for sensitive measurement of PVOCs in air has led to numerous recent efforts in analytical methods development (e.g., refs 4-10), and the feasibility of sampling PVOCs in canisters has been evaluated from both an experimental (11, 12) and a theoretical (13, 14) standpoint. Of particular interest has been the application of quadrupole ion trap mass spectrometry as a potential detection method for PVOCs (4, 6, 8). This detection scheme is attractive because the ion trap detector is largely unaffected by water vapor in the sample, unlike conventional mass spectrometer GC detectors, which require drying of the sample before analysis. Currently available drying methods used in VOC analysis (1) also remove large fractions of the PVOCs from the sample, preventing adequate measurement of these species.

Despite the current level of effort in method development for ambient PVOCs, results to date have been almost entirely limited to laboratory work; i.e., reported atmospheric measurements of PVOCs with the developing methods are virtually nonexistent. In contrast, the aims of the present study were to perform method development for PVOCs and then to apply the method in ambient measurements at selected urban sites. The specific goals of this study were (1) to develop and test a measurement method for PVOCs in air based on canister sampling, with analysis by gas chromatography and detection by ion trap mass spectrometry and (2) to conduct ambient PVOC sampling over a period of 1 year at sites in Boston and Houston formerly used in the U.S. EPA's Toxic Air Monitoring Study (TAMS). This paper presents the results of both the method development and the field measurements. The results of PVOC analyses from a variety of other less extensive sampling efforts are also reported.

Experimental Section

Method Development. This study employed a Hewlett-Packard 5880-A GC and a Finnigan MAT Model 700 ion trap detector (ITD). The target list of compounds addressed in this study is shown in Table I. Among the 17 compounds listed are 14 PVOCs, including alcohols, ethers, esters, and nitrile species, plus 1,3-butadiene,

Table I. Target Compounds for Analysis of PVOCs and VOCs in Canister Samples by GC/ITD

no.	target compd	ITD quantification mass
1	1,3-butadiene	39
2	methanol	31
3	ethanol	31
4	acetonitrile	41
5	acetone	43
6	propylene oxide	43
7	acrylonitrile	52
8	2-propanol	45
9	methyl <i>tert</i> -butyl ether	73
10	vinyl acetate	43
11	methyl ethyl ketone	43
12	ethyl acetate	43
13	ethyl <i>tert</i> -butyl ether	59
14	benzene	78
15	1-butanol	31
16	ethyl acrylate	55
17	toluene	91

benzene, and toluene. The latter two compounds are important and commonly measured nonpolar toxic VOCs, which were included as a point of comparison for the PVOC measurements. Also shown in Table I are the ion masses used to quantify each compound with the ITD.

Tests were conducted using a calibration mixture prepared from the pure compounds and containing 200 ppbv of each of the target compounds in dry, high-pressure nitrogen in an aluminum cylinder. The 200 ppbv mixture was analyzed at intervals throughout the program by both GC/ITD and GC/MS and was found to be stable in all components. This mixture was diluted to low ppbv levels with either dry or humidified air, using mass flow controllers on both calibration and diluent flows. When diluted with humidified air, the final calibration mixtures had a relative humidity of about 80% at room temperature. This humidity level was chosen for calibration and test mixtures, because of the high humidities expected in the near-coastal locations of both the Boston and Houston sites. The presence of humidity is expected to favor the stability of VOC and PVOC species during storage in canisters (12).

Initial laboratory tests with the diluted target mixture showed that although the ITD was relatively insensitive to water vapor present in the sample, the chromatographic analysis was not. In order to achieve proper chromatographic resolution of the PVOCs, it was necessary to separate water from the sample prior to analysis. A two-stage trap, commonly used in purge-and-trap analysis of water samples (Supelco 2-0321), incorporating Carboxpack B (60/80 mesh) and Carbosieve S-III (60/80 mesh), was found to provide the best combination of transfer of PVOCs and separation of PVOCs from water. The optimum trapping and drying procedure consisted of first flowing 320 cc of sample through the trap at room temperature. The trap was then subjected to a 13-min dry purge cycle in which dry nitrogen flowed through the trap at a rate of 100 cc/min at room temperature. Then the trap was heated to 220 °C and back-flushed with helium to thermally desorb the PVOCs onto the GC column for analysis. The amount of water removed by this procedure was not directly measured, but from chromatographic behavior we infer that over 90% of the water was removed.

Gas chromatographic analysis of the target compounds used a 50 m × 0.32 mm capillary column with a 1.0-μm HP-1 coating (cross-linked methyl silicone). The tem-

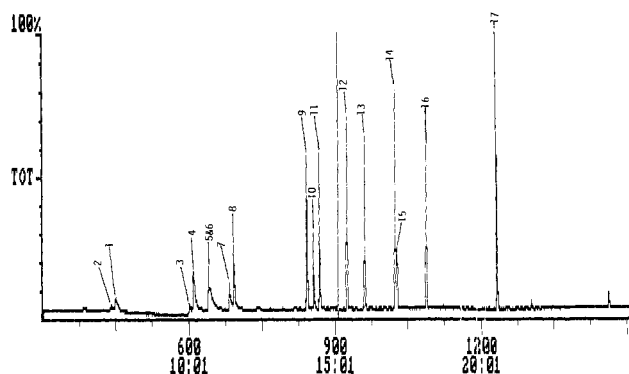


Figure 1. Total ion GC/ITD chromatogram of a humidified standard containing 8 ppbv of each of the target compounds. Peaks are numbered as listed in Table I.

perature program started at -50 °C for 5 min, then ramped to 200 °C at 8 °C/min. Carrier gas was helium, at a flow velocity of 72 cm/s. After each sample transfer, the two-stage trap was baked at 260 °C and back-flushed with dry N₂ for 5 min prior to the next run. All sample transfer lines were heated, and canister samples were also heated to approximately 40 °C prior to analysis by means of a heating mantle placed over the can. Figure 1 shows the ITD total ion signal chromatogram of a humidified calibration mixture of 8 ppbv of each of the target compounds, obtained using the analytical approach above. The peaks are numbered as in Table I. Quantification of the target compounds used selected-ion monitoring, detecting the ion masses listed in Table I. Note that only acetone and propylene oxide cannot be resolved chromatographically; these compounds also cannot be resolved on the basis of ion mass. Because of the inability to resolve these two compounds, and the expected low stability and atmospheric concentrations of propylene oxide, it is assumed that only acetone contributes to the response. Detection limits of the method using selected-ion mode are about 1 ppbv in air for compounds 1-8 in Table I, and 0.2 ppbv for compounds 9-17.

The effectiveness of the two-stage trap for transferring PVOCs to the GC was tested by analyses of humidified air samples containing the target compounds at levels below 10 ppbv. The ITD response to target mixtures was compared for (a) humidified mixtures transferred via the two-stage trap, (b) dry mixtures transferred via the two-stage trap, and (c) direct syringe injections of the 200 ppbv standards. These tests showed that for most of the target compounds, the efficiency of transfer from the humidified sample to the GC by way of the trap was 70-100%. However, for 1,3-butadiene and vinyl acetate, recoveries of only 40% and 10% were observed, respectively. These results indicated that the GC/ITD approach with the two-stage trap was acceptable for analysis of the target compounds in air samples, with the exception of the low recoveries found for 1,3-butadiene and vinyl acetate. Development of a canister-based method for the target compounds thus appeared feasible, provided the target compounds were sufficiently stable in air stored in canisters.

The stability of the target compounds in canisters was tested by analyzing humidified mixtures stored in Summa polished canisters and by comparing responses to those from the same mixture supplied directly to the two-stage trap. Canisters were filled with a test mixture and analyzed immediately and at intervals of 4 and 12 days after filling.

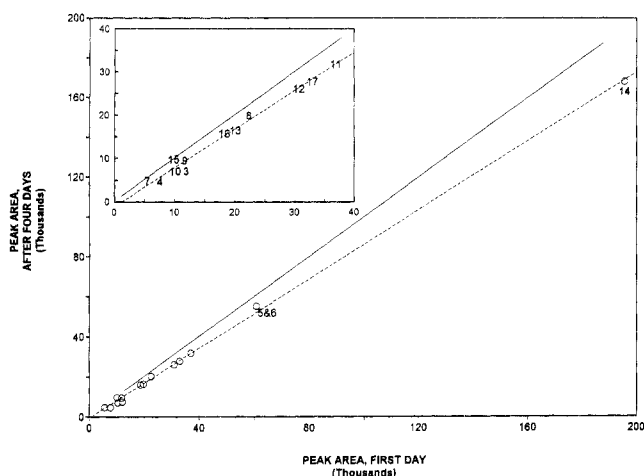


Figure 2. Test of storage stability of PVOCs in humidified air in a canister. Chromatographic peak areas for individual target compounds after 4-day storage are plotted against the corresponding areas measured shortly after filling the canister; the 1-to-1 line (solid) and linear regression (dashed) are shown. Target compounds are numbered as in Table I.

All canisters used in this test had previously undergone several cycles of air sampling and cleaning, in a variety of air sampling programs. Blank runs with humidified air showed no response from any of the target compounds. Canisters were filled using standard samplers equipped with stainless steel metal bellows pumps; as a result, this comparison evaluated the ability to sample the PVOCs as well as their stability during storage. The results of the canister stability tests are illustrated in Figure 2, which shows the peak areas found by analysis of a humidified mixture after 4 days of storage in a canister, plotted against the corresponding results on the day the canister was filled. The data points shown are the average of duplicate analyses; the numbers represent the target compounds as listed in Table I. Canister stability testing was done early in this study when removal of water by the two-stage trap was still under development. As a result, the early eluting compounds methanol and 1,3-butadiene were not quantified and are not shown in Figure 2. However, good stability of those compounds for several days in canisters has been demonstrated in previous studies (11, 12). Figure 2 shows that good stability of the target compounds was observed over 4 days of storage. A linear regression to the data points has the form $Y = 0.867(X) + 433$ area counts, with $R^2 = 0.999$. Note that the data for benzene and toluene lie on this regression line. Those two compounds are known to be stable in canisters, suggesting that the slope of the regression may be due to a small systematic bias in filling the canister rather than a selective loss of PVOCs during storage. Analysis of the target compounds after 12 days of storage indicated relatively poor stability for several of the PVOCs. These results indicated that canister sampling for most of the target compounds could be successful, provided that sample analysis was performed within 4 days after sample collection.

Field Sampling. Based on the laboratory testing described above, a field sampling protocol was implemented at the two former TAMS sites. Local residents who had served as site operators during the TAMS measurements served in that capacity for these measurements as well. The Boston sampling site was on the roof of the Boston Fire Department Headquarters, 115 Southampton St., in an urban area of mixed industry and

office buildings, with high traffic density. The Houston site was on the roof of an air sampling station run by the Texas Air Control Board, in Deer Park, TX. The site is surrounded by several acres of open athletic fields in a semirural area. However, it lies only a few miles south of the refinery and industrial complexes along the Houston Ship Channel and about 10 miles east-southeast of downtown Houston. The Houston site is expected to receive emissions from industrial and, to a lesser extent, urban sources. The Boston and Houston sites are the same as those designated Boston 2 and Houston 2, respectively, in the original TAMS study (15), and the measurements reported here are those referred to as the "extended" TAMS study by McClenny et al. (1).

Field sampling was conducted by shipping cleaned, evacuated canisters to the field operators. After the collection of 24-h samples, the canisters were returned by overnight delivery for analysis. Sampling took place about every 14 days from August 1990 through April 1991 and from June through August 1991, for a total of 44 samples (22 from each site). All field samples were analyzed twice; the two analyses were averaged for calculation of ambient concentrations. Duplicate canister samples were also collected by means of an extra canister sampler set up at the Houston site in summer and at the Boston site in winter, to sample in the seasonal extremes of temperature. Five sets of duplicate canister samples were collected, three in Houston and two in Boston.

Canister samples collected in other ambient sampling studies were also analyzed for PVOCs as opportunities arose, in order to enlarge the PVOC database. In addition, analyses were conducted for methanol, benzene, and toluene in four canister samples from a preliminary study of fuel vapor concentrations from conventional gasoline and from 85% methanol (M85) fuel. Those samples were collected inside a closed residential garage after vaporization of the two fuels. Two audit canisters containing ppbv levels of the three target compounds were also provided by the EPA as part of that study.

Results and Discussion

Analytical Method. This study allowed evaluation of the sampling and analysis approach for PVOCs on the basis of field measurements as well as in laboratory tests. In general, the analysis of canister samples from the field was convenient and routine, requiring about 1 h for performance of two analyses on a single canister. The two-stage trap was durable in extended use and showed no degradation in its behavior over the course of the study. No carryover (i.e., memory effect) was observed in blank samples analyzed immediately after field samples containing relatively high levels of PVOCs. The use of express canister shipment was found to be a reliable and easy means of assuring analysis of the samples soon after collection. The precision of the sample introduction and chromatographic procedures was evaluated in two ways: by repetitive analysis of the diluted, humidified standard in the laboratory and by comparison of the duplicate analyses performed on all samples collected in the field. These two data sets allowed the estimation of analytical precision both with controlled laboratory standards and with real-world samples, respectively. In addition, the combined sampling and analytical precision was assessed by comparisons of results from the five pairs of duplicate samples collected in the field. The results of these three evaluations

Table II. Precision as Percent Coefficient of Variation of PVOC Sampling and Analysis

target compd	obsd coeff of variation (% CV)		
	repetitive lab calibrations ^a	replicate analysis of field samples ^b	analysis of field duplicates ^c
1,3-butadiene	13.9	— ^d	—
methanol	29.2	25.3	45.0 (5)
ethanol	32.1	16.2	96.1 (3)
acetonitrile	15.9	—	—
acetone	23.4	17.9	56.1 (5)
2-propanol	38.3	26.5	45.3 (3)
acrylonitrile	15.8	—	—
methyl <i>tert</i> -butyl ether	20.1	9.4 ^e	62.5 (1)
vinyl acetate	42.7	—	—
methyl ethyl ketone	11.1	13.3	37.9 (5)
ethyl acetate	19.0	—	—
ethyl <i>tert</i> -butyl ether	22.8	—	—
benzene	13.3	13.3	16.0 (5)
1-butanol	29.6	15.7	—
ethyl acrylate	22.8	—	—
toluene	14.7	5.5	9.5 (5)

^a Based on 41 standards of 10 ppbv or less, run in sets of 2–5 replicates, on 14 test days between Dec 1990 and Aug 1991. ^b Average % CV value from replicate analyses routinely performed on all field samples. ^c Average % CV value from comparison of simultaneous duplicate samples collected in the field. Numbers in parentheses are the number of duplicate sets (out of 5) in which the indicated compound was detected. ^d Compound not detected. ^e Excludes nondetects; all other data include nondetects, as indicated in the text.

of the method are shown in Table II, in terms of the coefficients of variation (% CV) indicated for analysis of the target compounds.

The % CV values in Table II are calculated as the pooled standard deviation of the pertinent data set, expressed as a percentage of the overall mean of the data. In general, for N total observations in k groups, the pooled standard deviation is

$$S = \left[\frac{\sum_k \sum_i (x_i - \bar{x}_i)^2}{N - k} \right]^{1/2} \quad (1)$$

where \bar{x}_i is the mean within each group. This equation was used to treat the repetitive laboratory calibration data (41 calibrations in 14 groups) for all compounds. In the case of replicate or duplicate samples, eq 1 reduces to

$$S = \left[\frac{\sum_k (\Delta X_k)^2}{2k} \right]^{1/2} \quad (2)$$

where ΔX_k is the difference between the two observations within each group. Equation 2 was used to treat the replicate analysis and duplicate field sample data. With the latter data sets, nondetects were treated by setting one value of the pair to zero and the other equal to the detection limit for the compound in question. This approach tends to maximize % CV values, but is preferable to ignoring or assuming no variation in nondetect values. Treatment of nondetects in this way may have a significant effect on the % CV for a compound with numerous nondetects and a detection limit comparable to the detected concentrations, as noted below. The only exception to this approach is for the replicate analyses for methyl *tert*-butyl ether in Table II; the % CV value shown

is for the nine samples in which that compound was detected, excluding nondetects.

Table II shows that in runs of the low-level humidified standards in the laboratory, the method provided % CV values below 25% for most of the target compounds. The main exceptions to this finding were vinyl acetate and the alcohols, for which % CV values ranged from 29 to 38%. The poorer precision in analysis of the alcohols is due in part to an occasionally low response for these compounds in the first replicate of standard runs. This occurrence probably indicates a lack of complete equilibration of the laboratory calibration system caused by the presence of humidity and active surface sites in the dilution apparatus, since this effect was not observed in analysis of field canister samples. The data on replicate analyses in Table II also show that not all of the target compounds were present at detectable levels in canister samples from the field. For those compounds that were detected, the method achieved % CV values of about 5–27% in replicate analyses of individual samples from the field. In most cases, precision in replicate analysis of field samples was superior to that in the laboratory calibrations. This finding suggests, as noted above, that errors in preparation of dilute PVOC standards may contribute a large portion of the variability in laboratory standard runs. The possible effect of including nondetects as described above is exemplified by the replicate % CV for 2-propanol of 9.8%, excluding nondetects, versus the value of 26.5% in Table II.

The added effect of field sampling variability is shown in Table II by the % CV values found in analysis of the five pairs of duplicate canisters collected in the field. The % CV values are higher than those from the replicate analyses of individual field samples, and in nearly all cases higher than those from replicate laboratory calibrations. The % CV values range from about 10% for toluene to over 40% for several of the PVOCs. Although the five sets of duplicate samples are 10% of all the field samples taken, a reasonable rate of duplicate sampling, they comprise a small sample set and must be treated with caution. The most notable feature of the field duplicate data is the higher % CV for the PVOCs as opposed to benzene and toluene. These data suggest more variable behavior for the PVOCs in the duplicate samplers and canisters used in the field, a suggestion consistent with the known adsorptive behavior of PVOC compounds. However, the effect of including the nondetects in the PVOC data must also be considered. For example, excluding the nondetects for ethanol and propanol reduces their duplicate sample % CVs to 76.8 and 35.1%, respectively. Nevertheless, these values are still considerably larger than those for benzene and toluene. Given the small number of duplicate samples, it is also possible that individual duplicate sets exhibiting relatively high concentrations may dominate the calculation. This possibility has been addressed by deleting from the calculations the highest pair of samples for each compound. This change also reduces the % CV values for the PVOCs, particularly for ethanol, but not to less than 30%. Thus, the relatively higher duplicate % CVs for the PVOCs are not simply the result of individual samples within the small duplicate data set but appear to reflect a real difference in the behavior of the PVOCs relative to benzene and toluene. Further evaluation of field sampling variability for the PVOCs would be valuable, but the results do indicate that reasonable precision can be obtained in field

Table III. Summary of Ambient Air Measurements from Boston and Houston Sites

compd	Boston				Houston			
	N ^a	median ^b	mean ^b	range ^b	N ^a	median ^b	mean ^b	range ^b
methanol	22	12.9	17.4	7.2-47	22	13.2	16.6	5.6-31
ethanol	15	3.0	4.9	<1.0-38	15	2.2	2.9	<1.0-22
acetone	22	9.2	13.9	4.1-64	22	27.4	34.5	12.4-94
2-propanol	15	1.2	3.1	<1-20	6	<1.0	<1.0	<1.0-7.9
methyl <i>tert</i> -butyl ether	1	<0.2	<0.2	<0.2-0.49	8	<0.2	0.42	<0.2-2.8
methyl ethyl ketone	21	1.28	1.35	<0.2-4.9	22	0.99	5.1	0.47-58
benzene	22	1.06	1.24	0.69-3.1	22	1.73	2.08	0.55-6.3
1-butanol	0	<0.2	<0.2	<0.2	14	1.01	1.63	<0.2-5.4
toluene	22	2.07	2.29	0.66-5.5	22	1.62	2.57	0.79-16.3

^a Number of samples out of 22 in which the indicated compound was detected. ^b Median, mean, and range are in ppbv, calculated from 22 sample results. Values below detection limit were assigned a value of one-half the detection limit for calculation of the mean.

measurements of VOC and PVOC compounds in air with the present method. It is noteworthy that no ambiguity arose from the duplicate samples about the presence or absence of a target compound, i.e., in no case was a compound detected in one canister of a duplicate pair but not in the other.

The results shown in Table II are directly comparable to those calculated in the same manner for analytical replicates and field duplicates from the TO-14 method for nonpolar VOCs, in the previous TAMS measurements (15) and in the 1990 Urban Air Toxics Monitoring Program (16). Note that PVOC concentrations in the present study were higher in some cases than VOC concentrations in TAMS and UATMP. The TAMS data consist of 47 replicate pairs and 20 duplicate pairs for 13 compounds (15); the UATMP data are for 24 compounds or coeluting pairs and consist of from 2 to 90 replicate pairs and 1-45 duplicate pairs (16). The range of % CV values in replicate analyses of individual field samples in this study was 5.5-26.5%, whereas that reported from the TAMS measurements was 4-22% and from the UATMP measurements was 2.2-55%. Thus, the analytical precision of the present method is very similar to that of the TO-14 method. The % CV values in analysis of field duplicate canisters in this study ranged from 9.5 to 96%, whereas those from the TO-14 method ranged from 6 to 75% (TAMS; 15) and from 1.8 to 99% (UATMP; 16). Within the TAMS data set, the only % CVs exceeding 25% were for freon-11 and -12; a contamination source near the duplicate samplers (e.g., an air conditioner) was suggested as a likely explanation (15). In the present study, the only % CV values exceeding 16% from field duplicates are those for the PVOCs. This effect is thought to arise not from local contamination, but from sampling variability due to the sorptive behavior of the PVOCs. This hypothesis is supported by the fact that the field duplicate % CVs for the nonpolar compounds benzene and toluene in this study were the lowest for all the target compounds and, more importantly, were comparable to those found with the TO-14 method. The toluene % CV results, in particular, for both replicate analyses and duplicate samples, are almost identical to those found in the TAMS measurements (15) and lower than those from the UATMP data (16). Thus, the present field duplicate results, although few in number, are consistent with other results for nonpolar VOCs and indicate a difference between the nonpolar and polar target compounds in the degree of agreement in field duplicates. We ascribe this difference to the sorptive behavior of the PVOCs. Although improved field sampling techniques may minimize the variability in

PVOC duplicates, better precision for VOCs than for PVOCs may be a characteristic of any canister-based approach.

Field Measurements. The results of the ambient sampling program at the former TAMS sites are summarized in Table III, which lists the mean, median, and range of concentrations measured in the canister samples from each site. Also shown are the number of times each target compound was found above the detection limit in the canister samples. Note that several target compounds were never detected in these samples and so are not shown in Table III. For those compounds, ambient upper limits of 1 ppbv can be stated for acetonitrile and acrylonitrile and of 0.2 ppbv for ethyl acetate, ethyl *tert*-butyl ether, and ethyl acrylate. Vinyl acetate and 1,3-butadiene were also never detected in canisters from either site, but based on their low efficiencies of transfer from the two-stage trap, only ambient upper limits of about 2 and 3 ppbv, respectively, can be estimated.

Table III shows that methanol, acetone, and methyl ethyl ketone were the PVOCs found in all or nearly all samples from both sites. The VOCs benzene and toluene were also found in all samples. Ethanol was detected in most samples from both sites. Other PVOCs measured were found predominantly in samples from only one site. 2-Propanol was detected in most samples from Boston, but in only a few from Houston, whereas methyl *tert*-butyl ether and 1-butanol were detected in several samples from Houston, but not in those from Boston. The differences in occurrence of these PVOCs may be related to differences in the industrial and area emissions sources affecting the two sites. No significant seasonal trend was found for any of the PVOCs at either site. This observation may simply be an artifact of the infrequent sampling which led to the present data set or may indicate that the main sources of these compounds are area and industrial sources which do not have strong seasonal variations.

The medians and maximum values shown for benzene and toluene in Table III are consistent with the corresponding data for these species from the original TAMS measurements at the two sites (15), indicating that the sampling conducted here obtained a reasonably representative set of data from the two sites. The absolute concentrations observed for the PVOCs were generally similar at the two sites and were often higher than those of benzene and toluene, which are considered to be important toxic compounds in air. Methanol, ethanol, methyl ethyl ketone, 2-propanol, and acetone exhibit median values which equal or exceed those of benzene and toluene in most cases. The mean values for benzene,

Table IV. Analytical Results from Canister Samples from Various Environments (Concentrations in ppbv)

compd	furniture factory, North Carolina		outdoor air, paint incineration	machine shop indoor air	office area indoor air
	down- wind	up- wind			
1,3-butadiene	— ^a	—	7.8	—	—
methanol	297	212	78.5	41.1	60.0
ethanol	461	4.8	169	311	393
acetonitrile	—	—	—	—	—
acetone	64.8	19.5	51.0	31.1	89.6
2-propanol	21.2	9.3	—	13.7	197
acrylonitrile	—	—	8.1	—	—
methyl <i>tert</i> - butyl ether	—	—	—	—	—
vinyl acetate	—	—	—	—	—
methyl ethyl ketone	1.2	0.7	0.9	1.2	2.4
ethyl acetate	—	—	0.7	1.4	21.8
ethyl <i>tert</i> - butyl ether	—	—	—	—	—
benzene	0.8	0.8	23.4	0.6	0.3
1-butanol	39.1	7.5	4.4	2.7	7.5
ethyl acrylate	—	—	—	—	—
toluene	31.6	7.8	2.2	5.5	23.0

^a Not detected.

toluene, 1-butanol, and methyl *tert*-butyl ether at the Houston site (2.08, 2.57, 1.63, and 0.42 ppbv, respectively, Table III) are similar to the overall mean values (3.4, 4.1, <0.3, and <0.2 ppbv, respectively) reported from multiple sites in the Houston Regional Monitoring (HRM) study in 1987–88 (17, 18). However, the mean values for acetone and methyl ethyl ketone at the Houston site (35 and 5.1 ppbv) are much higher than the 6.1 and 0.8 ppbv overall means from the HRM data (17, 18). This comparison may be affected by site-to-site differences and by lack of simultaneity in the two data sets. Note also that in comparing the concentrations in Table III, it would be preferable to use the median values, rather than the means, since the medians are less subject to influence by a few high values. Review of the present data suggest that the highest PVOC levels observed (see range entries in Table III) occurred early in the study, when the analytical method was still under development, and measurement uncertainties were consequently high. This was particularly true for acetone and methyl ethyl ketone for which some elevated levels are shown in Table III.

Table IV lists the results from several additional canister samples collected in diverse environments. Included in Table IV are measurements made in outdoor air upwind and downwind of a furniture factory and near a furnace used for incinerating paint wastes, as well as in indoor air in a machine shop and a new office area. The compounds found in these samples are generally the same as those found at the TAMS sites (Table III), but some of the concentrations are much different. Table IV indicates that levels of ethanol, acetone, 2-propanol, 1-butanol, and toluene downwind of the furniture factory greatly exceeded those upwind, with the downwind ethanol concentration exceeding 450 ppbv. The impact of volatile emissions from the factory is evident. Interestingly, methanol concentrations in both samples exceeded 200 ppbv, with only a modest increase in the downwind sample relative to upwind. The presence of a substantial source of methanol in the area, unrelated to the factory, seems likely. The outdoor air sample taken near the paint incineration facility exhibited relatively high levels of methanol,

Table V. Results from Sample and Audit Canisters in Preliminary Fuel Vapor Measurements

sample	concentration, ppbv		
	methanol	benzene	toluene
M85, room temperature ^a	4 600	1.5	4.0
M85, elevated temperature ^b	17 000	6.4	25
M85, elevated temperature ^c	5 000	3.6	13
gasoline vapor ^d	1 500	190	480
audit canisters			
no. 1			
prepared	5.3	4.8	6.0
measured	5.9	4.4	6.1
% difference	11.3	-8.3	1.7
no. 2			
prepared	53	48	61
measured	44	42	52
% difference	-17	-13	-15

^a Evaporation of M85 from an open container at $\approx 20^\circ\text{C}$; grab sample. ^b Controlled evaporation of M85 at $\approx 39^\circ\text{C}$, simulating a hot vehicle; grab sample. ^c Same as *b*, but a 6-h integrated sample. ^d Obtained by parking a hot conventionally fueled vehicle in the test garage; grab sample.

ethanol, acetone, and benzene and was unique in that 1,3-butadiene and acrylonitrile were both present at concentrations of several ppbv. The indoor air samples in Table IV also show elevated concentrations of some target compounds. In the machine shop, methanol, acetone, 2-propanol, and especially ethanol (311 ppbv) were present at levels above 10 ppbv. The indoor air from the office area showed comparable levels of methanol, ethanol, and acetone, but also contained nearly 200 ppbv of 2-propanol, 23 ppbv of toluene, and over 20 ppbv of ethyl acetate, a compound never detected in the outdoor samples from the two field sites (Table III). The machine shop sample shows the presence primarily of light compounds associated with solvent use, whereas the office area sample suggests the possible presence of emissions from furnishings, coatings, or cosmetics as well. There are few other measurements with which to compare these data, however, the main finding of these measurements is that in various environments PVOCs are often present at substantial concentrations.

Table V shows the results from the sample and audit canisters in the fuel vapor study. The ppbv concentrations measured in each sample are shown, and for the audit canisters, the prepared concentrations and indicated measurement bias are shown as well. The sample results indicate that M85 vaporization produced low ppbv benzene and toluene levels, but methanol levels were in the ppm range. The effect of elevated temperature on methanol volatility is apparent from the first two samples. In contrast, the gasoline vapor produced benzene and toluene levels of 190 and 480 ppbv, respectively. Note that the methanol found in the gasoline vapor sample is believed to be largely residual in the garage air from the M85 tests done previously. The audit canisters indicate good performance of the present method for all three target compounds: measurement bias at the 5–6 ppbv level is -8.3 to +11.3% and at the 50–60 ppbv level is -13 to -17%. These bias values compare favorably to those reported for a variety of nonpolar VOCs with the TO-14 method (1): absolute bias values ranging from 4.6 to 18.6%, averaging 10.0%, from the TAMS data, and ranging from 4.2 to 31.4%, averaging 12.2%, from the Urban Air Toxics Monitoring Program. The present results for methanol

in the audit canisters are particularly encouraging, since it is one of the most difficult PVOCs to measure (see Table II).

Discussion of Method. In order to accomplish the dual goals of method development and field measurements, the present method development work was focused rather than exploratory in nature. The analytical method which resulted is simple, sensitive, and reliable and achieves the stated aim of accomplishing ambient PVOC measurements with canister samples. However, improvements or modifications are possible. The most important improvement is to extend the method to a greater variety of PVOCs in air. Development of a single analytical method encompassing both VOC and PVOC species is also desirable. The two-stage trap used in this work is effective at separating water from the sample prior to GC analysis, so an obvious modification of the method might be to conduct atmospheric sampling directly onto such a trap in the field. This approach would eliminate the sample transfer step currently conducted in the laboratory and would eliminate concerns about PVOC stability in canisters during sample storage. This approach might be useful in some situations, and, consequently, research on the use of two-stage and multistage sorbent traps for direct air sampling is currently in progress in our laboratory and elsewhere. However, use of such traps has some disadvantages relative to sampling with canisters. Most importantly, canisters allow multiple analyses to be made of a single sample, by one or more methods. In the current study this advantage of canisters allowed duplicate analyses of all field samples, using the GC/ITD method. Some field samples were also run on a conventional Hewlett-Packard GC/MSD instrument used for nonpolar VOC analyses—with the two-stage trap replacing the normal cryo-trap. These analyses indicated PVOC detection limits of about 5 ppbv using the GC/MSD. Such comparisons would have been difficult with only sorbent trap samples.

The somewhat poorer precision observed in analysis of laboratory standards relative to that with field samples indicates that further work is needed on the means of preparation of low-level PVOC standards. Difficulties in preparation of low ppbv multicomponent standards of polar compounds, in addition to analytical variability, appear to be an important cause of imprecision in standard runs. This effect may be due to incomplete equilibration of the PVOCs with the calibration system, as suggested by the results for the alcohols (see discussion of Table II). Possible improvements in the dilution system may include improved heating of the PVOC flow path, enhanced mixing of the air streams, and minimization of active sites and surface area in the system.

The ITD used in this work was not equipped to use water chemical ionization as the ionization source. Improved sensitivity in PVOC analysis should be achievable with existing ion trap instruments which can use this ionization approach, thereby making the presence of water in the sample an advantage. Furthermore, the potential exists for conducting direct air sampling with an ion trap by means of a glow discharge ionization source (e.g., ref 6) or a membrane sampling inlet. Such approaches may make it possible to analyze for PVOCs by MS/MS, rather than by GC/MS, thereby avoiding the troublesome chromatography of the polar compounds. Efforts in these directions are under way in our laboratories, using a Finnigan MAT ITMS instrument.

The present study results, although limited in scope, are generally consistent with previous efforts to assess the stability of polar compounds in sampling containers (11–14). The primary area of agreement is the finding of reasonable stability for PVOCs in Summa polished canisters under humidified conditions. The stability found here for the target PVOCs was adequate for field sampling and analysis, but was not as good as that reported by Pate et al. (12) in humidified canisters. The difference may be that Pate et al. supplied a larger amount of water (apparently exceeding saturation) to their canisters than was present in the humidified standards used here. Further work on the effects of intermediate humidities on PVOC stability appears to be needed. In any case, the important observation is that with the presence of reasonable levels of humidity, PVOCs can be sufficiently stable in canisters to allow proper sampling and analysis. Also note that the stability of the target standard, prepared in dry, high-pressure N₂, is consistent with theoretical evaluations of PVOC stability (13,14). Those evaluations indicate that PVOC stability is enhanced by both high concentrations and high absolute pressure, even under dry conditions.

Conclusions

Polar VOCs in ambient air can be sampled in Summa polished stainless steel canisters with sufficient stability for storage of at least 4 days. A relatively simple chromatographic procedure, using a two-stage sorbent trap for separation of water from the sample and a quadrupole ion trap detector, allows measurement of VOC and PVOC species in canister samples with detection limits of 1 ppbv or less. Thus, PVOC measurements could be implemented in existing field sampling programs which use canisters, provided analysis is conducted shortly after sampling. Use of this procedure on canister samples collected in Boston and Houston over a 1-year period shows that methanol, ethanol, acetone, 2-propanol, methyl ethyl ketone, and 1-butanol are among the main PVOCs present in ambient air. In most cases the concentrations of the PVOCs were higher than those of the toxic VOCs benzene and toluene measured simultaneously. Further work is needed to extend the method to a greater number of polar compounds and to improve calibration methods for PVOCs.

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Literature Cited

- (1) McClenny, W. A.; Pleil, J. D.; Evans, G. F.; Oliver, K. D.; Holdren, M. W.; Winberry, W. T. *J. Air Waste Manage. Assoc.* 1991, 41, 1308–1318.
- (2) Shah, J. J.; Heyerdahl, E. K. National Ambient Volatile Organic Compounds (VOCs) Data Base Update. Project

- Report EPA-600/3-88/010(a) to U.S. Environmental Protection Agency; Nero and Associates, Inc.: Portland, OR, Feb 1988.
- (3) Shah, J. J.; Singh, H. B. *Environ. Sci. Technol.* **1988**, *22*, 1381-1388.
 - (4) Gordon, S. M.; Miller, M. Analysis of Ambient Polar Volatile Organic Compounds Using Chemical Ionization-Ion Trap Detector. Report EPA-600/3-89/070 to U.S. Environmental Protection Agency; IIT Research Institute: Chicago, May 1989.
 - (5) Pierotti, D. J. *Atmos. Chem.* **1990**, *10*, 373-382.
 - (6) Gordon, S. M.; Chang, J. S. C.; Miller, M.; Pleil, J. D.; McClenny, W. A. Measurement of Polar Volatile Organic Compounds by Direct Air Monitoring Ion Trap Mass Spectrometry. In *Proceedings of the 1991 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants*; Report EPA-600/9-91/018; Air and Waste Management Association: Pittsburgh, PA, 1991; Publication VIP-21, pp 596-601.
 - (7) Fung, K. A Method for the Measurement of Alcohols and MTBE in Ambient Air. In *Proceedings of the 1991 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants*; Report EPA-600/9-91/018; Air and Waste Management Association: Pittsburgh, PA, 1991; Publication VIP-21, pp 770-775.
 - (8) Sykes, A.; Preston, W.; Howell, M. An Evaluation of Air Toxics Analysis Methods Using GC/Ion Trap Mass Spectrometry. In *Proceedings of the 1991 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants*; Report EPA-600/9-91/018; Air and Waste Management Association: Pittsburgh, PA, 1991; Publication VIP-21, pp 776-779.
 - (9) Ogle, L. D.; Brymer, D. A.; Jones, C. J.; Nahas, P. A. Moisture Management Techniques Applicable to Whole Air Samples Analyzed by Method TO-14. Presented at the 1992 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 3-8, 1992.
 - (10) Ciccioli, P.; Cecinato, A.; Brancaleoni, E.; Frattoni, M. J. *High Resolut. Chromatogr.* **1992**, *15*, 75-84.
 - (11) Gholson, A. R.; Jayanty, R. K. M.; Storm, J. F. *Anal. Chem.* **1990**, *62*, 1899-1902.
 - (12) Pate, B.; Jayanty, R. K. M.; Peterson, M. R.; Evans, G. F. *J. Air Waste Manage. Assoc.* **1992**, *42*, 460-462.
 - (13) Coutant, R. W. Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters. Report EPA-600/R-92/055 to U.S. Environmental Protection Agency; Battelle: Columbus, OH, Feb 1992.
 - (14) Coutant, R. W.; McClenny, W. A. Competitive Adsorption Effects and Stability of VOC and PVOC in Canisters. In *Proceedings of the 1991 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants*; Report EPA-600/9-91/018; Air and Waste Management Association: Pittsburgh, PA, 1991; Publication VIP-21, pp 382-388.
 - (15) Evans, G. F.; Lumpkin, T. A.; Smith, D. L.; Somerville, M. C. *J. Air Waste Manage. Assoc.* **1992**, *42*, 1319-1323.
 - (16) McAllister, R.; Bowles, E.; DeGarmo, J.; Rice, J.; Jongleux, R. F.; Merrill, R. G., Jr.; Bursey, J. 1990 Urban Air Toxics Monitoring Program. Report EPA-450/4-91-024; Radian Corporation: Research Triangle Park, NC, June 1991.
 - (17) LaGrone, F. S. *Environ. Sci. Technol.* **1991**, *25*, 366-368.
 - (18) Buchholtz, W. F.; Crow, W. L. Relating SARA Title III emissions to community exposure through ambient air quality measurements. Presented at the 83rd Annual Meeting of the Air and Waste Management Association, Pittsburgh, PA, June 24-29, 1990; Paper 90-170.11.

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