



Project Summary

GC/MS Analysis of Ambient Aerosols in the Houston, Texas, Area

Catherine H. Skintik

This study was designed to provide information on the organic aerosol pollutants in the Houston, Texas, area. The Research Triangle Institute (RTI) was responsible for qualitative and quantitative analysis of ambient air aerosols and vapor samples collected in the Houston area by the Radian Corporation of Austin, Texas. Three different types of samplers were used: high volume (hi-vol) and dichotomous samplers were employed to collect particulates, and resin-trap samplers (developed at the Illinois Institute of Technology Research Institute and known as IITRI samplers) were employed to collect vapor-phase organic samples. Filters and sorbent resins were shipped to RTI following field sampling. A total of 23 samples were analyzed: 12 filter and adsorbent trap samples, 5 dichotomous samples, and 6 hi-vol samples.

Hi-vol samples were extracted and solvent-partitioned prior to analysis by glass capillary gas chromatography/mass spectrometry (GC/MS). Dichotomous filters were extracted and the concentrated extracts analyzed directly by GC/MS. Vapors were analyzed by thermal desorption from the resin bed followed by GC/MS.

Analyses showed the presence of many saturated and unsaturated materials in all samples. The extracts from hi-vol filters contained small quantities of organics, and their analysis was complicated by the presence

of background contaminants tentatively identified as siloxanes. Results from the dichotomous samples indicated insufficient collection of material for comprehensive air analysis. Vapor-phase organics collected in IITRI samples consisted predominantly of hydrocarbons, alkylated benzenes, and some chlorinated compounds. Quantitative analysis was carried out for selected components from each sample type.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The 1977 Clean Air Act Amendments called for EPA research studies in the Gulf Coast area. Priority was given to the problems of aerosol pollutants, and Houston, Texas, was chosen as the initial study site. The EPA issued a procurement request to obtain gas chromatography/mass spectrometry (GC/MS) evidence on the identity of the organic particulate pollutants present in the atmosphere above Houston and surrounding areas. The evidence obtained was intended to guide studies of health effects from ambient aerosols and to determine sources and causes of aerosol pollution in the Houston area.

Sampling

The major sampling effort for the Houston air study was provided by Radian Corporation, Austin, Texas, under a separate contract. All samples analyzed by RTI were collected by Radian during September and October 1978 using filter and adsorbent trap, dichotomous, or hi-vol samplers.

Filter and Adsorbent Trap (IITRI) Sampler

The filter and adsorbent trap sampler consisted of a conventional high-volume sampler modified to allow for sampling of vapor-phase material downstream of the aerosol filter. The vapors were collected by passing a portion of the post-filter airstream through cartridges containing a trapping medium consisting of polymeric sorbents. Two sorbent-containing cartridges were connected in series, and four such cartridge pairs comprised the vapor sampling unit. This sampler was designed and constructed by researchers at the Illinois Institute of Technology Research Institute (IITRI) and is referred to in this report as the IITRI sampler. A total of three IITRI samplers (12 cartridge pairs) was used for this program.

The sorbent selected for use in the samplers was Tenax® GC, a phenylene

oxide polymer with well-tested vapor trapping properties.

All sorbed organic species had to be removed from the Tenax® GC before it was released for field use. These materials were removed by thermal desorption, after which the levels of background materials remaining were assessed by glass capillary gas chromatography/flame ionization detection (GC/FID) of the desorbed vapors.

Once the cartridge pairs were cleaned by thermal desorption, all U-tubes were reassembled and each sealed sampler was shipped to Houston. The samplers were designated by number (samplers 1, 2, and 3), and each of the four cartridge pairs for each sampler was numbered 1 through 4. In addition, the individual sorbent beds were labeled as either upstream (U) or downstream (D). Thus, each sample could be described by a single designation preceded by "IT" for IITRI. For example, the upstream Tenax® GC sample from U-tube 3, sampler 1, was referred to as IT1-3U.

All sampling information was recorded on data sheets supplied by RTI to Radian and returned with each sampler. This information is detailed in Table 1. One cartridge pair for each sampler was utilized as a field blank. The blank was never exposed to the sampling stream, but experienced the same shipment, storage, and handling conditions as the sample cartridges.

Dichotomous Sampler

The dichotomous sampling effort for the Houston study was carried out by the EPA (Inorganic Pollutant Analysis Branch, Atmospheric Chemistry and Physics Division). A portion of the many dichotomous filters used for aerosol collection was shipped to RTI as specified in the sampling protocol. Five "fine" filters were designated for extraction and analysis by RTI. The sampling information for the dichotomous samples is shown in Table 2.

Hi-Vol Sampler

The high-volume samples were collected on quartz fiber filters (Gelman Micro Quartz). Prior to field studies, investigations were conducted to determine the extent of background organics contained in the quartz fiber filters (QFF). Each filter was subjected to solvent washing experiments to determine the results of such clean-up procedures and the best wash medium if clean-up was shown to be effective. Filter extracts and solvent washes were analyzed using packed column GC/FID. Results showed that both methanol/chloroform and diethyl ether removed significant amounts of contaminants but that methanol/chloroform was more efficacious than ether. A variation in contaminant levels for filters from the

Table 1. Sampling Data—IITRI Samples

IITRI Sample No.	Houston Site	Sampling Data	Sampling Rate (L/min)	Sampling Time (min)	Sample Volume (L)
IT1-1 (blank)	—	—	—	—	—
IT1-2	#21-Alief	10-08-78 (day)	2.84	710	2,016
IT1-3	#23-Stude Park	10-06-78 (day)	2.84	720	2,045
IT1-4	#23-Stude Park	10-06-78 (night)	2.84	595	1,690
IT2-1 (blank)	—	—	—	—	—
IT2-2	#23-Stude Park-Central	10-11-78 (day)	2.84	585	1,661
IT2-3	#23-Stude Park-Central	10-11-78 (night)	2.84	720	2,045
IT2-4	#21-Alief-West	10-10-78 (day)	2.84	720	2,045
IT3-1	#22-Baytown Area-North	10-10-78 (day)	2.84	690	1,960
IT3-2	#22-Baytown Area-North	10-11-78 (night)	2.84	660	1,874
IT3-3	#22-Baytown Area-North	10-11-78 (day)	2.84	720	2,045
IT3-4 (blank)	—	—	—	—	—

Table 2. Sampling Data—Dichotomous Samples.

Dichotomous Filter No.	Houston Site	Sampling Date	Sampling Rate (l/min)	Sampling Time (hr)	Sampling Volume (m ³)
4F-011	#19	9-27-78 (night)	16.7	12.0	12.0
4F-012	#19	9-28-78 (day)	16.7	12.0	12.0
4F-018	#17	10-6-78 (day)	16.7	11.8	11.8
4F-021	#21	10-9-78 (day)	16.7	12.0	12.0
4F-022	#21	10-10-78 (day)	16.7	12.0	12.0

same lot was noted, and these results were conveyed to Radian prior to field sampling.

Data sheets were supplied to Radian for recording pertinent sampling information and were returned to RTI.

Sample Analysis

To minimize problems associated with sample decomposition, all analytical work was carried out in a laboratory fitted with yellow lights (transmission ≥ 500 nm); samples and sample extracts were never allowed to exceed 50°C, and were stored under conditions of refrigeration and darkness.

IITRI Samples

The Tenax® GC was removed from the IITRI samplers, and a measured portion of the resin was transferred to clean glass cartridges. The cartridge contents were then analyzed by glass capillary GC/MS. The whole sample was introduced to the analytical system by thermal desorption into a cryogenic capillary trap and then rapidly swept onto the chromatographic column. Each cartridge was loaded with a known amount of perfluorobenzene and perfluorotoluene for use in quantitation. Qualitative data interpretation was done by visual inspection of the spectra and comparison with standard reference spectra. Quantitation was achieved by determining the peak intensity of a characteristic mass for a compound from the chromatographic peak. The amount of compound in the sample was then calculated using the relative molar response (RMR) factor and the integrated area for a standard. The concentration

in ambient air was calculated using the volume sampled.

Dichotomous Samples

Preliminary Experiments

The dichotomous sampler was designed to collect aerosols for size fractionation, mass determination, and compositional characterization. The sample rate (16.7 l/min) is low compared to the commonly used hi-vol sampler (~600 l/min), and thus the amount of aerosol collected is smaller. Since organics typically comprise 5 to 15 percent of the total mass of air aerosols, and since only a limited fraction of a sample extract can be introduced into the GC/MS system, experiments were undertaken prior to field sample analysis to optimize the organics recovery procedure. Efforts were directed toward reducing the extracts to the smallest practical volume, since the maximum aliquot that could be removed for GC/MS injection was fixed at approximately 1 μ l. Given the small amounts of organics likely to be present and the size of the containers available for use, concentrations of an extract to low μ l volumes without concomitant, significant losses of sample components presented some difficulty.

Information obtained from EPA led to examination of Schenk-Bauer sedimentation tubes as appropriate containers for sample concentration. Recoveries were tested using ¹⁴C-7, 12-dimethylbenz(a)anthracene, a compound presumably representative of an important class of aerosol organics. The tests succeeded in concentrating a significant amount of material in a small volume of solvent, from which aliquots could then be removed for GC/MS analysis. Varia-

tions in the precise extent of recovery could be compensated through the use of internally added standards.

Analysis of Field Samples

Based on the preceding study, final concentration of dichotomous filter extracts was achieved using Schenk-Bauer sedimentation tubes. Each dichotomous filter was extracted using a custom-made Teflon® extraction block provided by EPA. Two extractions were carried out with approximately 4 ml of chloroform and sonication in a water bath. The extracts were combined and the internal standard (anthracene-d₁₀) added. The extract was then transferred in portions to the sedimentation tubes for solvent removal. Just prior to GC/MS analysis, the dried extracts were reconstituted in 10 μ l of chloroform. Approximately 1 μ l was removed for injection onto the GC column.

Hi-Vol Samples

Extraction/Partition

Hi-vol filters (QFF) were extracted overnight with methanol using a Soxhlet apparatus. Following solvent removal, the residue was fractionated. The individual fractions were then concentrated for GC/MS/COMP analysis.

The efficacy of the scheme was assessed by subjecting a mixture containing known amounts of compounds to the partition procedure. The mixture consisted of benzoic acid, phenol, quinoline, hexadecane, phenanthrene, and ethylene glycol. These compounds were chosen to represent the five classes of materials produced by the partition scheme (all these materials have been found in air particulate samples except ethylene glycol). No information on the composition of the polar neutral fraction was available; therefore, ethylene glycol was included as a likely component of this fraction based on its known chemical properties. The experiment was conducted using both large and small mass samples. Recoveries were determined gravimetrically.

As a further check on the procedure, thin-layer chromatography (TLC) scans were conducted on each fraction to ascertain the extent, if any, of compound spillover into other fractions. No such spillover was detected.

GC/MS/COMP Analysis

Samples were analyzed using an LKB 2091 GC/MS with a dedicated PDP-11/34 data system. The samples were chromatographed on an OV-101 capillary column (25 m, WCOT, obtained from LKB). The column was held at 100°C for 2 minutes after injection, and then heated to 265°C at a rate of 8°/min. Carrier gas flow rate was 1.8 ml/min. Injector temperature was 245°C. Mass spectral scans were taken every 3 sec, scanning from 5 to 492 amu. The ion source temperature was 210°; electron energy, 70 eV; trap current, 50 μ A; accelerating voltage, 3500 V; and multiplier setting, 400-500. Total ion current and mass spectra plots were generated for interpretation.

Data were interpreted by comparison of the unknown spectra with standard reference collections. Where no reference spectrum was available, or where spectral quality was not sufficient for positive identification, the compounds were labeled "tentative." Further validation of equivocal identification was made by consultation with other chemists and spectroscopists experienced in similar research. This mass spectral interpretation protocol was established to extract the maximum information from the data and to guard against misidentification. The specific compound identification criteria are as follows: (1) computer interpretation, (2) manual interpretation, (3) manual interpretation plus retention time/boiling point of compound, (4) manual interpretation plus retention time of authentic compounds, and (5) criterion number (4) plus independent confirmation techniques.

Results

Within the limits of the GC/MS technique, complete identifications of the organics isolated from each sampler medium were made. Of the compounds identified, certain components were selected for quantitation. The selection was based on relative abundance and the known hazard potential of each compound, and was made after consultation with the project officer. The results for each of the three sample types are discussed individually in the following sections.

IITRI Samples

Five quartz fiber filters were returned for analysis of aerosol organics (a blank

filter was subsequently made available for analysis), and 12 sorbent-containing cartridge pairs (9 samples, 3 blanks) were returned for analysis of volatiles.

Volatiles—Qualitative Analysis

The 12 IITRI cartridge tubes contained an upstream and a downstream Tenax® GC bed (~2.5 g Tenax® GC/cartridge) thus providing 24 samples for analysis. Analyses of both the upstream and downstream cartridges for all blanks and for two sample cartridges were carried out. For all these samples it was evident that the analysis of the downstream cartridge represented a duplication of effort since a large number of compounds (>50) were found on both the upstream and downstream cartridge, the same compounds were found on the downstream as the upstream cartridge, and no useful information was obtained by virtue of analysis of the downstream cartridge. Therefore, only the upstream cartridge was analyzed for the bulk of the volatile samples. A summary of those samples analyzed is provided in Table 3. For each sample a gas chromatogram, in the form of a total ion

current (TIC) plot (TIC versus mass spectral scan number) was obtained. Each peak of the TIC plot was numbered and the identification of all compounds corresponding to each peak was tabulated.

A large number of compounds was identified for each cartridge. With one exception, from 104 to 174 compounds were characterized for each upstream cartridge, with approximately two-thirds of these components detected on the corresponding downstream cartridge. The appearance of relatively large numbers of components on the downstream cartridge indicates significant breakthrough from the upstream cartridge. In view of the volume of air sampled (Table 1), and the known breakthrough volumes for similar components using Tenax® GC under similar conditions, these findings are not surprising. The vast bulk of volatile species (~80 to 85 percent) was identified as saturated/monounsaturated hydrocarbons and alkylated aromatic hydrocarbons. For the amount of Tenax® GC used and the temperatures at which sampling was carried out, the breakthrough volumes for these compound types are on the

Table 3. Summary of Analysis of IITRI Volatiles

IITRI Sample No. *	Qualitative Analysis by GC/MS	Number of Components Identified
IT1-1U (Blank)	+	82
IT1-1D (Blank)	+	46
IT1-2U	+	174
IT1-2D	+	112
IT1-3U	+	147
IT1-3D	+	104
IT1-4U	+	167
IT1-4D	-	-
IT2-1U (Blank)	+	89
IT2-2D (Blank)	+	69
IT2-2U	+	165
IT2-2D	-	-
IT2-3U	+	153
IT2-3D	-	-
IT2-4U	+	149
IT2-4D	-	-
IT3-1U	+	68
IT3-1D	-	-
IT3-2U	+	104
IT3-2D	-	-
IT3-3U	+	107
IT3-3D	-	-
IT3-4U (Blank)	+	81
IT3-4D (Blank)	+	70

*Sample Code: IT3-4U refers to IITRI Sampler #3, cartridge pair #4, upstream cartridge.

+Indicates analysis performed.

-Indicates analysis not performed.

order of 0 to 100 l and 100 to 1,000 l, respectively. The amount of air sampled for the IITRI cartridges averages about 2,000 l.

The qualitative data from the IITRI cartridge analysis shows a considerable number and amount (from TIC) of compounds associated with the blank cartridges. These cartridges were never intentionally exposed to ambient air, and thus should have produced gas chromatographic patterns similar to those for components desorbed from the IITRI cartridges. The intensity of the chromatographic pattern obtained for the blanks indicates exposure of these cartridges to ambient air. This was presumably due to leakage through either the toggle valves controlling air flow to the IITRI U-tubes or the Swage-lock fittings.

The qualitative profile of the volatile components collected by the IITRI samplers is very similar to results obtained by other workers at various urban sites. Approximately 150 compounds were identified from each cartridge. Of these about 60 percent were saturated/monounsaturated hydrocarbons, about

20 to 25 percent were aromatics, about 5 percent were halogenated hydrocarbons, and the remaining components (~10 to 15 percent) consisted of oxygenated compounds (aldehydes, ketones, ethers).

Sampling for vapor phase material was carried out at three sites representing a suburban community, a downtown area, and a heavily industrialized site. Based solely on the qualitative results, no major trends or characteristics regarding site specificity were noted. Although similar volumes of air were sampled at each site, the average number of compounds identified from the industrialized site was less (93) than the average number identified from the suburban site (162) or the downtown area (158). While this observation may seem noteworthy, the limited number of samples analyzed from each site and the excessive volume of air sampled for the amount of Tenax® GC used detract from its significance.

No significant differences were noted between results obtained for samples collected during the day and those collected at night.

Volatiles—Quantitative Analysis

The selection of compounds for quantitative determination was based on considerations of relative abundance and toxicity. These criteria were adopted following consultation with the project officer. Toxicity information was obtained from the "Handbook of Environmental Data on Organic Chemicals."

Using the method of relative molar response (RMR) factors, reference quantitation standards were obtained and their GC/MS response relative to an internal standard was determined under the same conditions as were used for the analysis of field samples. In some cases, duplication of effort was avoided by the determination of RMRs for several similar species using a single, representative standard. It is known from past experience that structurally similar compounds generally produce similar response factors.

A total mass of each species was divided by the volume of air sampled to provide ambient air concentrations. These quantitation results are shown in Table 4. In one case, methylene chloride, the large amount of material introduced

Table 4. Quantitation Results from IITRI Volatiles Analysis

Compound	Concentration (ng/m ³)								
	IT1-2U	IT1-3U	IT1-4U	IT2-2U	IT2-3U	IT2-4U	IT3-1U	IT3-2U	IT3-3U
<i>n</i> -Hexane					5920		998	4115	788
methylcyclohexane							126		
<i>n</i> -heptane					1582				
<i>n</i> -octane	1059								
<i>n</i> -nonane	1086		4211	4561	1052				
<i>n</i> -decane	1418	1796	6049	9631	1209			203	
<i>n</i> -undecane	2495	2478	4285	9201	1963	2476			
<i>n</i> -dodecane	880	811		33454					
<i>n</i> -tridecane				3112					
benzene	6636						158	3393	1169
toluene	2860	10443	11214	23698	14197		1319	6242	
ethylbenzene			8126			5336		1458	99
xylene isomer	3835		8064	21841	8239	20124		2475	47
xylene isomer	1659	1362		7763	1725	4781		643	5
1,2,3-trimethylbenzene		333	1151			337			22
1,2,4-trimethylbenzene	234	233	1383	2240	371	4107			
1,3,5-trimethylbenzene		473	1253			766			
ethyltoluene isomer		181	1650	756		208	429		
styrene		165	8971	4078	1480	677	104	721	64
naphthalene		7169							22
chloroform							685		236
carbon tetrachloride							388	1922	
methylene chloride	4142	3624	27817	79281	13451	169982	149526	284218	15200
1,2-dichloroethane							219		
trichloroethylene				3172	6786	2543	1967	1414	
1,1,1-trichloroethane					179	79	216		
dichlorobenzene									15

Table 5. Summary of Qualitative Results from Dichotomous Filter Extracts

Filter No.	Total Peaks Identified	Background Components	Real Components	Composition of Real Components				
				Sat'd Hydrocarbons	Unsat'd Hydrocarbons	Alkyl Phenols	Unknowns	
4F-011	25	10	15	8	2	1	4	
4F-012	41	16	25	13	5	1	6	
4F-018	42	16	26	11	8	2	5	
4F-021	28	13	15	6	3	1	5	
4F-022	25	8	17	12	1	1	3	

to the GC/MS produced analyzer saturation. For this compound a minimum concentration is therefore reported. However, as noted previously, the relatively large volume of air sampled exceeded the known breakthrough volumes (BTVs) for most components. Thus *all* quantitative results must be interpreted as *minimum* concentrations.

Nonvolatiles

Since each IITRI sampler was used in conjunction with a hi-vol sampler, a quartz fiber filter (QFF) corresponding to each of the IITRI cartridge pairs was used at each sampling period. Five such filters were returned to the RTI for aerosol organics analysis.

The analytical protocol for nonvolatile, aerosol organics involved Soxhlet extraction followed by fractionation of the extracted organics into five major fractions. These fractions were individually analyzed using GC/MS. Earlier results obtained for the analysis of the hi-vol filters not used in conjunction with the IITRI samplers showed very low levels of organics in each of the five fractions. Consequently, for all but one of the hi-vol filters used with the IITRI samplers, the fractionation scheme was not employed, and the GFF extract was analyzed directly by GC/MS. Diminished peak intensities from the TIC plots and the relatively few compounds identified even from the nonfractionated extracts seem to indicate that the levels of nonvolatile aerosol organics from these samples are quite low. The other obvious result of these analyses is the presence of substantial levels of background components, principally phthalate esters and siloxanes.

Dichotomous Samples

Preliminary Studies

Prior to complete analysis of aerosol organics from the five dichotomous

filters, the levels of background contaminants and their sources were determined. Control runs were carried out to allow for the contribution of background components from the extraction solvent, from the dichotomous filter, and from the extraction device utilized in the scheme. All operations for the control runs were identical to those used for the analysis of field samples.

The results of these control runs indicated that the number of contaminants was acceptably low. Not unexpectedly, phthalate esters are present in the solvent; the only other major contaminant is an unsaturated hydrocarbon (octadecene) extracted from the extraction block. The relative retention time and mass spectral fragmentation patterns of all background compounds were noted for subsequent use during qualitative analysis of the field samples.

Qualitative Analysis

The number of components identified from each extract ranged from 25 to 43, of which a substantial portion was background contaminants. Phthalate esters and siloxanes were the major contaminants. Of those compounds identified as non-background materials, saturated and unsaturated hydrocarbons accounted for nearly all species. An alkylated phenol (C₉ and/or C₁₀) was also identified in each extract, presumably indicating a motor vehicle exhaust source for this compound. A summary of these results is presented in Table 5.

Quantitative Analysis

The amount of aerosol collected on each dichotomous filter is quite low (approximately 100 to 2,000 μg) compared to aerosol collection devices more commonly used for nonvolatile organics analysis. Thus, low-level components were not present in quantities sufficient for full qualitative/quantitative treatment.

Of the materials characterized from the dichotomous filter extracts, roughly half were identified as non-background components. Of these, 5 to 6 were present at levels that permitted quantitation. These compounds, all higher molecular weight long chain hydrocarbons plus nonylphenol, are shown in Table 6.

The variation both qualitatively and quantitatively between extracts is small, and no trends were noted regarding sampling site or time of sampling. The levels of saturated hydrocarbons (C₁₅ - C₁₈) were comparable to levels from other urban sites and slightly higher than levels found from nonurban sites.

Hi-Vol Samples

The quartz fiber filters designated for analysis under this program were received approximately 3 months after field collection. They were stored and shipped by Radian Corporation per protocol and were stored at -20°C in our laboratories until analysis was initiated. Although it had been anticipated that a gravimetric determination of total collected aerosols would be made, tearing and loss of small but significant portions of the QFF during unpacking precluded such determinations. Following extraction, the total mass of aerosol organics was determined; the results are shown in Table 7. The organic loads ranged from low to average in comparison with expected levels from urban aerosols.

In contrast to the amount of aerosol collected by the dichotomous sampler, the hi-vol sampler is capable of efficiently trapping approximately 200 to 500 times as much aerosol for a 24-hour sampling period. It is known from a large body of work that a wide variety of organic compounds are adsorbed to the air particulate. As the direct analysis of

Table 6. Quantitative Results from Dichotomous Filter Extracts

Compound	Filter			
	4F-001	4F-012	4F-018	4F-021
<i>C</i> ₉ -alkyl phenol isomer	60 ng (5.0 ng/m ³)	20 ng (1.7 ng/m ³)	20 ng (1.4 ng/m ³)	20 ng (1.7 ng/m ³)
<i>n</i> -pentadecane	70 ng (5.8 ng/m ³)	50 ng (4.2 ng/m ³)	50 ng (3.6 ng/m ³)	35 ng (2.9 ng/m ³)
<i>n</i> -hexadecane	90 ng (7.5 ng/m ³)	50 ng (4.2 ng/m ³)	100 ng (7.2 ng/m ³)	30 ng (2.5 ng/m ³)
<i>n</i> -heptadecane	100 ng (8.3 ng/m ³)	60 ng (5.0 ng/m ³)	100 ng (7.2 ng/m ³)	70 ng (5.8 ng/m ³)
<i>n</i> -octadecane	260 ng (21.7 ng/m ³)	80 ng (6.7 ng/m ³)		130 ng (10.8 ng/m ³)
octadecene & isomers		6620 ng (551.7 ng/m ³)		620 ng (51.6 ng/m ³)

Table 7. Total Organics Extracted from Hi-vol Filters

Filter Number	Weight of Organics Extracted (mg)
12	8.5
13	5.2
14	7.3
15	14.1
65	23.1
66	24.3
91 (blank)	3.4

such a mixture is not practical owing to the large number of species present and the generally unfavorable GC behavior of some classes (e.g., acids, bases), a sample fractionation procedure was proposed for the organic extracts obtained from the hi-vol filters used in this study

Qualitative Analysis

Analysis by glass capillary GC/MS was accomplished for each fraction from each QFF extract. Firm characterization proved difficult for all fractions because of the unexpected presence of large numbers and amounts of interfering substances. Coelution of the interfering species with the compounds of interest produced complicated MS fragmentation patterns, obscured sample components in some cases, and effectively raised sensitivity limits. The problem was noted for virtually all hi-vol samples (no such interferences were seen for the ITRI or dichotomous samples), and investigations into the precise nature of the substances were made.

The identification of the components from the sample filters indicated the presence of a disproportionate number of phthalate esters and siloxanes of indeterminate structure. Both classes of compounds possess single ions that are characteristic of each compound type. It is recognized that GC column bleed from columns employing silicone-based

phases consists predominantly of siloxanes. This process is characterized by a relatively slow increase in GC baseline and by the continuous presence throughout a long series of recorded mass spectra of background levels of siloxane fragment ions. The siloxanes found associated with the hi-vol samples were identified as discrete and, for the most part, intense peaks, possessing mass spectra with fragment ion intensities much greater than is normally observed for column bleed. Thus, in addition to TIC chromatograms of the filter blank fractions, single ion plots (*m/z* 73,149) were also obtained. When compared with similar chromatograms obtained from the GC/MS analysis of a solvent control, where minimal *m/z* 73,149 responses were noted, it would appear that the background components are associated with the filters utilized for sample collection. Although each QFF was cleaned prior to field use, as noted earlier, a great deal of variation in background contamination levels was observed, even for filters from the same lot. Further, the filter clean-up procedures as carried out in our laboratories showed that different solvent systems can be more effective than others for removing some contaminants. It is possible that the ether washing procedure used for the hi-vol filters in the Houston study was not fully efficacious.

Other sources of background contamination were considered, including the

GC septa and silanized glass surface. Most septa are composed predominantly of silicone-based polymers. High temperature, exposure to solvent vapor clouds, and repeated piercing by syringe needles are among those processes that could conceivably lead to the production of siloxanes. Silanized glass surfaces are commonly used in trace organic analysis systems, and are therefore also a likely source of siloxanes. Both materials were examined and ruled out as siloxane sources.

From the evidence obtained, within the limits of funding and effort provided for this program, the background components, principally siloxanes and phthalate esters, appear to be associated with the QFF used in this study.

Quantitative Analysis

The analysis of extracts from the hi-vol filters showed generally low levels of organics, except for the above-mentioned phthalate esters and siloxanes. At the direction of the project officer, quantitation was carried out only for saturated hydrocarbons. Based on the GC/MS behavior of C₁₅ - C₁₈ hydrocarbon standards, the relative molar responses (RMRs) of these compounds were shown to be very similar for *m/z* 71, 99, and 113 (these ions are present in all saturated hydrocarbons). Thus average RMRs for each ion could be used for the quantitative determination of each compound possessing these chromatographic ions. Although any of the three ions would suffice for quantitation, calculations based on all three ions were made, where possible, to detect interference from other compounds, and as a check on the overall method. To calculate amounts of the individual compounds, determinations based on all three ions were averaged. If one determination was clearly deviant (i.e., if it differed by more than a factor of 2 from the other values), it was not used

in the calculation of the average. It is recognized that the use of average RMRs for all hydrocarbons produces some uncertainty in final tabulations, and the figures obtained are best viewed as approximate. The paucity of material for filters 0014 and 0065, in part because of the lower volume of air samples (approximately 850 m³ as compared to about 1,050 m³ for filter 0012), allowed for the quantitation of only five compounds.

For purposes of comparison, concentrations of selected aliphatic hydrocarbons were obtained from two sources, one representing results of "clean" air and the other representing results obtained from urban air. Average hydrocarbon concentrations (for the alkanes chosen) from Houston aerosols are comparable to other urban levels, and are significantly higher than values obtained for "clean" air. It must be noted that the Houston data presented here are somewhat suspect because of the background contamination problem, the limited number of filters examined, and the method of estimation utilized. More rigorous methods of quantitation are clearly desirable.

Conclusions and Recommendations

Overall results indicate that the organic component of Houston ambient air aerosol is predominantly saturated hydrocarbons, with lesser but significant amounts of alkyl aromatics and lower molecular weight (C₁ - C₂) halogenated hydrocarbons. The levels of these materials are comparable to those found in other urban atmospheres and are significantly higher than those found in nonurban "clean" air. No clear relationship was observed between levels or number of components found, and time or location of sampling site.

The results of this study indicate several areas where further investigations could provide useful results. Specific recommendations include:

- 1) Modification of the IITRI sampler. Leakage through fittings and valves was evident from cartridge analysis; redesign should include vacuum tight valves and fittings. The ease of handling of the sampler could be improved by construction of an all-glass or glass/stainless steel unit.

- 2) Further research into the use of the dichotomous sampler for collection and subsequent analysis of aerosol organics. The automated nature of this sampler, its high collection efficiency, sizing capability, and use of standard Teflon® filters for collection are attractive features that could well be taken advantage of for aerosol organics analysis. Research should be directed toward improving analytical sensitivity to a point that is compatible with the amount of aerosol collected by the dichotomous sampler.
- 3) Investigation of the source and nature of glass or quartz fiber filter (GFF and QFF, respectively) background contamination. The development of suitable clean-up procedures and a determination of the precise nature of the contaminants associated with such filters would allow for greater confidence in analytical results obtained from samples collected via GFF or QFF.
- 4) Development of methodology for accurate nonmethane hydrocarbon determinations. Software development (GC/MS) could provide for the group quantitation of paraffinic hydrocarbons as obtained from the routine analysis of GFF extracts by glass capillary GC/MS/COMP. Such data could thus be available in a reliable and relatively rapid fashion as an adjunct to comprehensive qualitative results from ambient air aerosol analysis.

This Project Summary was authored by Catherine H. Skintik of WAPORA, Inc., Cincinnati, OH 45233.

Kenneth Krost is the EPA Project Officer (see below).

The complete report, entitled "GC/MS Analysis of Ambient Aerosols in the Houston, Texas, Area," was authored by Charles M. Sparacino of Research Triangle Institute, Research Triangle Park, NC 27709.

The above report (Order No. PB 81-126 377; Cost: \$20.00, subject to change) will be available only from:

*National Technical Information Service
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*The EPA Project Officer can be contacted at:
Environmental Sciences Research Laboratory
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