

Determination of Trace Level Organics in Ambient Air by High-Resolution Gas Chromatography with Simultaneous Photoionization and Flame Ionization Detection

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Chromatographic separation of C_2 - C_{10} hydrocarbons was obtained in a single analysis using a 60-m SE-30 fused silica capillary column and subambient temperature programming. The column effluent was split to a PID and a FID detector, which were operated simultaneously. The effects of varying PID and splitter operating parameters on PID/FID response ratios and PID sensitivity are discussed. Retention time and normalized response data are presented for 143 compounds including alkanes, alkenes, aromatics, aldehydes, ketones, and chlorine- and sulfur-containing hydrocarbons. Averaged normalized response data can be used to estimate chemical classes of organic compounds in ambient air.

Volatile organic compounds present in the atmosphere are of interest since some of these are known toxins or irritants. Also, certain classes of organic compounds participate in photochemical reactions resulting in the formation of irritating atmospheric oxidants (ozone, PAN) and smog. Current regulatory policies are attempting to control atmospheric oxidants by decreasing emissions of oxidant precursors, particularly hydrocarbons and oxides of nitrogen. Information on hydrocarbon species present in ambient air is important to help pinpoint sources of emissions, as well as to provide data necessary for photochemical modeling studies. In addition, with the recent increase in awareness of the problems associated with hazardous waste disposal, there is a need for techniques to monitor emissions in the air around disposal sites.

The determination of hydrocarbon species in ambient air has routinely been accomplished by cryogenic concentration, followed by gas chromatography using flame ionization detection. However, the compounds normally of interest for photochemical modeling (C_2 - C_{10}) have boiling points ranging from -102 °C to $+190$ °C. For this boiling point range, two or three different chromatographic analyses have been required (1, 2). Furthermore, the use of flame ionization detection does not always provide sufficient differentiation of hydrocarbon species within different classes. This is very important since different hydrocarbon classes (alkanes, alkenes, aromatics, aldehydes) display varying degrees of photochemical reactivity (3). Subtractive techniques have been used to provide additional class information (4). However, this approach adds additional chromatographic analyses. Mass spectrometric detection provides sufficient information for qualitative identification of many organic compounds present in the atmosphere. However, it is often difficult to differentiate between various aliphatic hydrocarbon species by mass spectrometry, and quantitation of C_2 and C_3 species is difficult. Because of these reasons, and the expense involved, GC/MS techniques are not routinely used to analyze ambient air for C_2 - C_{10} hydrocarbon species.

In this paper, a method is discussed which provides quantitative evaluation of the C_2 - C_{10} organic content in ambient

air in a single chromatographic analysis. This was accomplished through high-resolution chromatography and subambient temperature programming. To provide additional capabilities for species identification, a photoionization detector and a flame ionization detector were used simultaneously. The flame ionization detector responds to compounds on the basis of carbon content; hence, it serves as a universal detector for hydrocarbons and is good for quantitative purposes. The photoionization detector responds to compounds based on their ionization potentials, which in turn is dependent on the degree of unsaturation in the molecule. A study of the PID response as a function of molecular structure has been performed (5). By calculating a ratio of the response between the two detectors, it was possible to estimate the degree of unsaturation (and chemical class) for a compound producing a given chromatographic peak. The chemical class information provided by the dual detector technique proved to be a valuable tool when used in conjunction with GC retention time data for species identification.

The initial application of PID and FID detectors to hydrocarbon analysis in a gas mixture was published by Driscoll et al. (6). Although this early work did not involve simultaneous use of the detectors and was only applied to a C_6 - C_8 hydrocarbon gas mixture, the potential utility of the technique was demonstrated. In-series operation of a FID and a PID has been described and applied to the analysis of tars (7). In this case, the commercially available PID was not sufficient and a special low volume cell was designed and constructed. The combination of ECD and FID detectors has also been described (8). For the present work, a variety of organic compounds which may be of interest in the atmosphere were studied. Chromatographic retention time data and normalized PID/FID responses will be presented for alkanes, alkenes and dienes, alkynes, aromatics, aldehydes, ketones, saturated and unsaturated chlorinated hydrocarbons, and sulfur-containing hydrocarbons.

EXPERIMENTAL SECTION

A schematic diagram of the analytical system which was used in this work is presented in Figure 1. The system was designed to accept air samples collected in pressurized canisters, in polymeric bags, or on solid sorbents (via thermal desorption). The first step of the analysis involved removal of moisture. This was accomplished with a 24-in. single tube Perma Pure Drier (Perma Pure Inc., Farmingdale, NJ). Typical sample flow rates through the drier were 100 mL/min and purge rates were maintained at 1000 mL/min of UHP air. The drier was heated to 60 °C and purged for 10-15 min between analyses. After the removal of moisture, organic compounds were separated from the ambient air matrix and concentrated on a 6 in. by $1/8$ in. o.d. nickel tube packed with 80/100 mesh glass beads and cooled in liquid oxygen (-183 °C). The design of the valving associated with the traps, and the efficiency of hydrocarbon collection have previously been described (9). One modification of the design for this work was replacing the high-precision pressure gauge with a high-precision vacuum gauge (Wallace and Tiernan Model 61C-1A-0015) and evacuating the gas reservoir. The volume of gas passed through

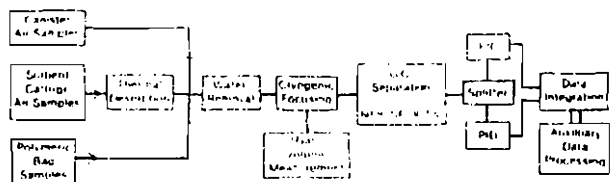


Figure 1. Schematic diagram of the cryogenic GC/PID/FID analysis of ambient air.

the cryogenic trap was calculated by monitoring the pressure differential of the evacuated gas reservoir. Samples containing parts per million levels organic content were analyzed by direct injection to the cryogenic trap with a 5-mL gastight syringe. Trap loading and injection flows were controlled by a two-position eight-port valve (Valco No. V-8-HTa). The valve and associated stainless steel connecting tubing were heated to 60 °C to avoid sample condensation. Organic species were rapidly desorbed by immersing the trap in boiling water until the temperature of the trap reached 90 °C. At that time (approximately 20 s), the water bath was removed and the trap was heated to 180 °C with a 750-W heating cartridge (Watlow No. J4A198). Trap temperatures were controlled with an Omega Model 4201 RTD temperature controller. Desorbed compounds were swept from the trap to the chromatographic column by He carrier gas. The transfer lines to the column were heat traced (60 °C) $1/16$ in. o.d. stainless steel tubing.

Separation of organic species was achieved on a 60-m SE-30 wide bore, thin-film fused silica capillary column (J & W Scientific). The column was operated at an initial temperature of -50 °C for 2 min and then temperature programmed to +100 °C at a rate of 6 °C/min. The carrier gas was UHP grade helium at a rate of approximately 2 mL/min and a column head pressure of approximately 19 psi. The output of the capillary column was split to a PID and a FID detector. The splitter (Scientific Glass Engineering, Austin, TX) consisted of a short piece of 0.4 mm i.d. glass-lined stainless steel tubing which was silver soldered into a low dead volume union. Two lengths of 0.22 mm i.d. fused silica tubing were cemented into a two-hole graphitized-vespel ferrule which butted against one end of the glass-lined tubing. The analytical column (0.35 mm i.d.) was inserted through the glass-lined tubing and butted against the two-hole ferrule. The ratio of flow to each detector was controlled by adjusting the lengths of splitter tubing. The basis of the splitter function is the pressure drop across each of the splitter tubes. It is important that the splitter tubing is of a smaller internal diameter than that of the GC column. However, if the splitter tubing is too small, a significant pressure drop and decrease in the carrier gas flow rate will result. Several different sizes of splitter tubing were evaluated, and it was found that 0.22 mm i.d. provided the best results with a 0.35 mm i.d. GC column. As a general rule in selecting splitter tubing for other size capillary columns, the combined internal areas of the splitter tubing should be approximately 70% to 80% of the internal area of the capillary column. Once this criteria has been satisfied, the lengths of splitter tubing should be as short as possible to minimize the overall pressure drop.

The gas chromatograph used in this work was a Varian 3700 GC with subambient temperature programming capabilities. The detectors used were a Varian FID and an HNU Model 52 high-temperature PID. Both detectors were operated with UHP nitrogen makeup gas at 30 mL/min. Two lamps were evaluated for use with the PID. A general purpose 10.2-eV lamp was obtained from HNU (Newton, MA) and a 10.0-eV lamp was obtained from Scientific Services (Rocky Hill, NJ).

Chromatographic data were processed with a Varian 401 chromatography data system. This served primarily as an integrator and transferred integrated data to an Apple II Plus microcomputer which was used for quantitative and qualitative peak identification and calculation of PID/FID response ratios.

RESULTS AND DISCUSSION

To achieve sub-part-per-billion level detection limits, organic compounds must be separated from the ambient air matrix and concentrated. The efficiency of the cryogenic glass

bead traps for collection and recovery of light hydrocarbon species has been discussed in a previous paper (9). Some losses of ethylene were observed when trapping more than 400 mL of air using 4 in. long traps, so 6 in. traps were used in this work. Although moisture does not interfere with the cryogenic trapping of hydrocarbons, it can cause extinguishing of the FID flame or a disruption of carrier gas flow since the analytical column was operated at subfreezing temperatures (-50 °C) when the glass bead traps were desorbed. Two methods were investigated for removal of moisture. Passing air samples through a 1-g bed of potassium carbonate served to remove the moisture and provided good recoveries of aliphatic hydrocarbons, benzene, and toluene. However, significant losses of heavier aromatic compounds were observed. A 24-in. single-tube Perma Pure drier also functioned well in the removal of water and, in addition, provided good recoveries of all aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, and aldehydes which were tested. Low recoveries of alcohols and variable recoveries of ketones were obtained with the Perma Pure drier. Specific results of the drier comparison will be presented in a subsequent paper. With the use of the Perma Pure drier, up to 2 L of ambient air could be concentrated without significant disturbances to detectors or column flow.

Simultaneous use of the PID and FID detectors with capillary chromatography required operating the two detectors in a manner which would not sacrifice chromatographic resolution or detector sensitivity. The PID ionizes only a small percentage of the sample and can be considered a nondestructive detector, thus allowing in-series operation of the PID prior to the FID. However, since the PID is located outside the GC oven, this would require running a heat-traced line back into the GC oven and to the FID. Furthermore, both detectors require makeup gas for optimal resolution (using the commercially available PID). Addition of makeup gas at the inlet of the PID could result in a loss of resolution and sensitivity by the time the sample reached the FID, if the detectors were operated in series. Since the PID was more sensitive than the FID, it was feasible to split a small portion of the chromatographic column effluent to the PID, without a significant sacrifice in FID sensitivity. The splitter which was described was very simple to install and provided the option of varying split ratios. No discernible loss in resolution was observed for the FID when using the splitter. Optimization of the PID for capillary chromatography has been described (10). Resolution for the PID was a function of the makeup gas flow. As the makeup gas flow was increased, peak widths decreased, but the detector sensitivity also decreased. When using a makeup flow of 30 mL/min, peak half-widths for both detectors were very similar (2-3 s).

Example chromatograms from the cryogenic capillary system and the two detectors for a 38-component hydrocarbon mixture are presented in Figure 2. To facilitate labeling, alkenes and aromatics are labeled on the PID (upper) chromatogram and alkanes are labeled on the FID (lower) chromatogram. The mixture contained ethane, ethylene, and acetylene, which coeluted and were detected only by the FID. Propane and propylene also coeluted. However, the PID responded only to propylene. Good separation was obtained between the C₂ and C₃ hydrocarbons. Separation was obtained for all C₄ hydrocarbons, with the exception of 1-butene and isobutene which coeluted (only 1-butene is in the mix in Figure 2). Aromatic hydrocarbons began eluting at 17 and 21 min (benzene and toluene), while the compound of lowest volatility in the mixture, 1,2,4-trimethylbenzene eluted at 29 min. The FID chromatogram demonstrates that quantitative evaluation of hydrocarbon species in the C₂-C₁₀ range can be achieved in a single chromatographic analysis.

Table I. Effect of PID and Splitter Conditions on PID/FID Response Ratios

conditions	1		2		3		4		5	
splitter FID/PID	1/1		1/1		3/1		3/1		3/1	
lamp setting	5		8		5		5		5	
PID makeup flow (mL/min)	30		30		30		20		30	
light source (eV)	10.2		10.2		10.2		10.2		10.0	
compound	TNR ^a	(P/F) ^b	TNR	(P/F)	TNR	(P/F)	TNR	(P/F)	TNR	(P/F)
isopentane	1.3	(0.04)	2.0	(0.11)	1.8	(0.10)	2.0	(0.03)	2.0	(0.07)
<i>n</i> -hexane	3.6	(0.01)	2.7	(0.14)	1.7	(0.02)	2.0	(0.03)	5.0	(0.16)
3-methylhexane	7.5	(0.22)	7.4	(0.39)	7.7	(0.09)	8.2	(0.14)	12.0	(0.43)
<i>n</i> -nonane	14.7	(0.43)	15.8	(0.84)	14.1	(0.15)	16.5	(0.28)	15.6	(0.55)
all alkanes (16) ^c	7.2	(0.21)	7.1	(0.38)	7.0	(0.08)	7.7	(0.13)	8.7	(0.32)
1-butene	63.5	(1.9)	85.4	(4.5)	77.4	(0.86)	73.8	(1.3)	65.0	(2.3)
1-pentene	62.4	(1.8)	80.6	(4.3)	68.6	(0.76)	67.3	(1.2)	64.3	(2.8)
<i>trans</i> -2-pentene	77.2	(2.3)	107.0	(5.7)	83.5	(0.92)	81.8	(1.4)	77.0	(2.5)
cyclopentene	65.3	(1.9)	67.0	(3.6)	69.4	(0.77)	69.7	(1.2)	63.7	(2.3)
all alkenes (8) ^c	73	(2.2)	95	(5.0)	79	(0.9)	78	(1.3)	70	(2.5)
benzene	106.0	(3.1)	106.0	(5.7)	110.7	(1.2)	109.4	(1.9)	112.3	(4.1)
ethylbenzene	91.2	(2.7)	87.8	(4.7)	89.8	(1.0)	81.7	(1.4)	86.5	(3.1)
<i>p</i> -ethyltoluene	85.5	(2.5)	83.1	(4.4)	81.9	(0.91)	81.6	(1.4)	79.0	(2.8)
1,3,5-trimethylbenzene	124.2	(3.6)	122.3	(6.5)	117.3	(1.3)	118.8	(2.0)	116.5	(4.1)
all aromatics (9) ^c	98	(2.9)	97	(5.1)	96	(1.1)	94	(1.6)	97	(3.3)

^a Toluene normalized response. ^b PID/FID compound response. ^c Total number of compounds tested within each class.

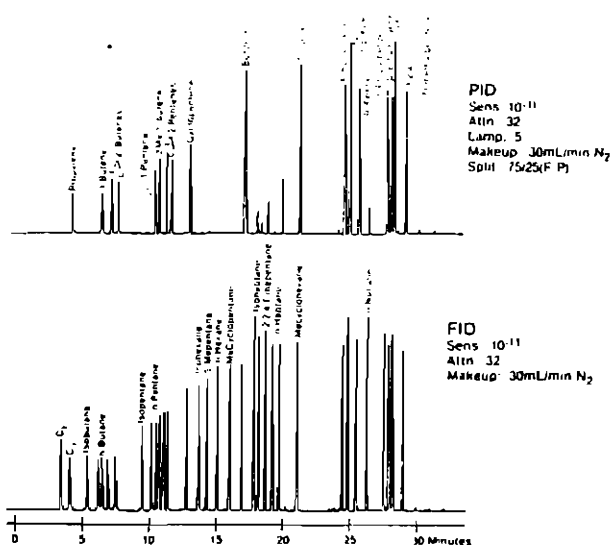


Figure 2. Analysis of a 38-component hydrocarbon mixture by the cryogenic GC/PID/FID.

The advantage of simultaneously using PID and FID detectors can be observed in Figure 2. Little response was observed on the PID for C₂-C₆ alkane species. A slightly higher response was observed for some of the branched C₇-C₈ hydrocarbons, while good responses were obtained for alkenes and aromatic species in the mixture. Since the FID responds to molecules based on the number of carbon atoms and the PID response is roughly based on the degree of unsaturation, the ratio between the two detectors can be used as a tool in identifying chromatographic peaks. It is possible to obtain relative detector responses for organic species by simply ratioing results between the two detectors. However, values obtained in this manner would be very sensitive to response fluctuations in either detector. For relative response data which can be used over a long period of time, effects of detector fluctuations can be minimized by normalizing all response ratios to the response ratio for a single compound. Toluene was chosen as the normalizing compound since it gave a good response on both detectors, and a review of the literature indicated that toluene was normally present in ambient air. In this laboratory, toluene has been used as a

retention time marker for GC/FID analyses, since this compound is easy to identify in the chromatogram and has routinely been observed above 1 ppbv-C (part per billion volume of carbon). Toluene normalized responses (TNR) for the PID and FID detectors were calculated by using the following equation:

$$\text{TNR} = \frac{\text{PR}_x \cdot \text{FR}_T}{\text{FR}_x \cdot \text{PR}_T} \times 100$$

where PR_x and PR_T are PID responses for organic species x and toluene, respectively, and FR_x and FR_T are FID responses for species x and toluene, respectively. By definition, toluene will always have a value of 100.

Several parameters were varied to optimize the PID selectivity and sensitivity. Optimum selectivity would be no response for alkanes (TNR = 0), a high response for aromatics (≥100), and a medium response for alkenes (TNR = 50). Parameters which were studied include the splitter ratio, PID lamp intensity setting, PID makeup flow, and a 10.0-eV lamp as opposed to a 10.2-eV lamp. The results of this study are presented in Table I. Results are presented for four representative compounds within each class and class averages. Results are expressed as toluene normalized responses (TNR). Direct PID/FID (P/F) responses are presented in parentheses. TNR values reflect the PID selectivity, while P/F values reflect the effect of changing conditions on the PID sensitivity and of the detector split ratio. The first two sets of test conditions demonstrate the effect of PID lamp intensity. With an increase of the lamp current setting from 5 to 8 (arbitrary units), the PID response was roughly doubled with respect to the FID response. However, very little effect was observed in the normalized responses for alkanes and aromatics. At the higher lamp intensity the average response obtained for alkenes was nearly equivalent to that for aromatics.

The effect of the split ratio can be observed by comparing columns 1 and 3 in Table I. The 1/1 split was obtained with equal lengths of 0.22 mm i.d. splitter tubing to each detector. The 3/1 split was obtained by decreasing the length of tubing to the FID so that it was one-third the length of tubing to the PID. The P/F ratio for the 3/1 split (column 3) decreased to approximately one-third of the P/F ratios for the even split (column 1), demonstrating correct splitter operation. The utility of using normalized response ratios is also demonstrated

Table II. Retention Times and Normalized PID/FID Responses for Hydrocarbon Species

compound	retention time, min	TNR ^a	compound	retention time, min	TNR ^a
Alkanes					
ethane	3.30	0	cyclohexane	17.35	25
propane	4.02	0	isoheptane	17.94	8
isobutane	5.38	0	2,3-dimethylpentane	17.94	10
<i>n</i> -butane	6.50	0	3-methylhexane	18.26	8
neopentane	7.14	2	2,2,4-trimethylpentane	18.72	18
isopentane	9.55	2	<i>n</i> -heptane	19.25	7
<i>n</i> -pentane	10.76	2	methylcyclohexane	19.78	36
neohexane	12.21	4	2,5-dimethylhexane	20.44	16
cyclopentane	13.30	2	2,3,4-trimethylpentane	21.03	33
2,3-dimethylbutane	13.55	7	3-methylheptane	21.96	17
isohexane	13.82	5	2,2,5-trimethylhexane	22.36	21
3-methylpentane	14.39	5	<i>n</i> -octane	22.93	8
<i>n</i> -hexane	15.15	4	<i>n</i> -nonane	26.35	14
methylcyclopentane	16.08	4	<i>n</i> -decane	29.80	16
2,4-dimethylpentane	16.39	9	<i>n</i> -undecane	34.38	15
Alkenes, Dienes, and Alkynes					
ethylene	3.30	0	2-ethyl-1-butene	15.11	65
acetylene	3.30	0	<i>trans</i> -2-hexene	15.43	67
propylene	4.02	72	<i>cis</i> -2-hexene	15.76	69
propyne	4.60	2	<i>cis</i> -3-methyl-2-pentene	16.00	70
1-butene	6.24	65	methylcyclopentene	17.07	73
isobutene	6.24	79	cyclohexene	17.98	58
1,3-butadiene	6.36	104	1-heptene	18.81	49
<i>trans</i> -2-butene	6.95	78	3-heptene	19.19	51
1-butyne	7.27	7	2-heptene	19.27	57
<i>cis</i> -2-butene	7.50	70	2,4,4-trimethyl-1-pentene	19.57	55
3-methyl-1-butene	8.73	65	2,4,4-trimethyl-2-pentene	20.27	50
1-pentene	10.26	64	1-methylcyclohexene	21.51	60
2-butyne	10.31		3,5,5-trimethyl-1-hexene	21.70	57
2-methyl-1-butene	10.61	73	2-ethyl-1-hexene	22.44	57
isoprene	10.85	89	1-octene	22.57	44
<i>trans</i> -2-pentene	11.18	77	<i>trans</i> -2-octene	23.06	61
<i>cis</i> -2-pentene	11.45	71	<i>cis</i> -2-octene	23.31	54
2-methyl-2-butene	11.72	76	1-nonene	25.95	52
cyclopentene	12.88	75	4-nonene	26.19	47
4-methyl-1-pentene	13.20	59	α -pinene	27.30	75
<i>cis</i> -4-methyl-2-pentene	13.80	53	β -pinene	28.65	65
<i>trans</i> -4-methyl-1-pentene	13.95	62	1-decene	29.35	36
2-methyl-1-pentene	14.64	65	limonene	30.60	63
1-hexene	14.70	59	1-undecene	33.75	35
Aromatics					
benzene	17.02	112	1,3,5-trimethylbenzene	28.17	117
toluene	21.13	100	<i>tert</i> -butylbenzene	28.95	61
ethylbenzene	24.51	87	1,2,4-trimethylbenzene	29.04	81
<i>p</i> -xylene	24.83	105	isobutylbenzene	29.67	66
<i>m</i> -xylene	24.87	95	1,2,3-trimethylbenzene	30.09	83
styrene	25.38	111	indan	30.47	80
<i>o</i> -xylene	25.54	77	<i>p</i> -isopropyltoluene	30.22	80
isopropylbenzene	26.65	79	<i>m</i> -diethylbenzene	31.15	73
<i>n</i> -propylbenzene	27.61	79	<i>n</i> -butylbenzene	31.53	66
<i>m</i> -ethyltoluene	27.87		<i>p</i> -diethylbenzene	31.61	75
<i>p</i> -ethyltoluene	27.98	79	naphthalene	38.21	123
Aldehydes					
acetaldehyde	5.84	2	butyraldehyde	14.15	60
propionaldehyde	9.87	84	isovaleraldehyde	16.70	66
isobutyraldehyde	12.78	67	valeraldehyde	18.35	56
Ketones					
acetone	10.05	160	2-pentanone	18.09	105
butanone	14.70	153	3-pentanone	18.47	141
Halogenated Alkanes					
chloromethane	4.80	0	1,2-dichloroethane	16.42	0
bromomethane	6.97	0	tetrachloromethane	17.22	0
chloroethane	7.73	0	bromodichloromethane	18.55	0
trichlorofluoromethane	9.93	0	1,2-dichloropropane	18.19	0
dichloromethane	11.71	0	1,1,2-trichloroethane	20.82	0
1,1-dichloroethane	13.46	0	dibromochloromethane	21.68	0
trichloromethane	15.30	0	1,1,2,2-tetrachloroethane	25.53	3
1,1,1-trichloroethane	16.14	0			

Table II (Continued)

compound	retention time, min	TNR ^a	compound	retention time, min	TNR ^a
Chlorinated Alkenes and Aromatics					
vinyl chloride	5.71	53	chlorobenzene	23.77	150
1,1-dichloroethylene	11.12	190	<i>o</i> -chlorotoluene	27.32	124
<i>trans</i> -1,2-dichloroethylene	13.29	410	<i>m</i> -chlorotoluene	27.43	135
trichloroethylene	18.58	300	<i>p</i> -chlorotoluene	27.50	130
<i>cis</i> -1,3-dichloropropene	19.86	124	<i>m</i> -dichlorobenzene	29.14	154
<i>trans</i> -1,3-dichloropropene	20.09	129	<i>p</i> -dichlorobenzene	29.35	155
tetrachloroethylene	22.76	290	<i>o</i> -dichlorobenzene	30.18	137
Sulfur Hydrocarbons					
methyl mercaptan	6.64	650	butyl mercaptan	19.06	133
ethyl mercaptan	10.23	350	tetrahydrothiophene	22.27	185

^a Toluene normalized response.

with these data. Although the chromatographic column flow to each detector was changed by 50%, with a corresponding change in sensitivity, TNR values remained essentially constant for individual compounds and compound classes.

The effect of makeup gas flow rate on PID sensitivity is demonstrated in data columns 3 and 4 of Table I. With a reduction in the makeup gas flow rate, the PID sensitivity was increased by approximately 50%. Once again, no significant change in the normalized compound or class response was observed.

The PID response to an individual compound is determined by the ionization potential of that compound and the excitation energy of the light source. Data presented thus far were obtained with a 10.2-eV source which was obtained from HNU. Since ionization potentials of most alkenes are higher than those for aromatics, the possibility of increasing the selectivity between these classes of compounds was investigated by using a lower energy light source. Data presented in column 5 were obtained with a 10.0-eV light source. This source appeared to provide the PID with increased sensitivity by approximately a factor of 3. This can be observed by comparing the P/F ratios in columns 3 and 5. Normalized responses for alkenes increased slightly using the 10.0-eV lamp, those for alkenes decreased by 11%, and those for aromatics remained essentially constant. With the exception of C₃ and C₄ alkenes, TNR values for individual compounds did not vary considerably with the different sources. The average TNR value for C₃ and C₄ alkenes decreased by 16% with the 10.0-eV lamp. These compounds have higher ionization potentials than other alkenes and should be the most affected by the lower energy lamp. It is possible to use a 9.5-eV lamp with the PID. However, at this energy, some alkenes would give very low responses. Furthermore, it has been demonstrated that the PID sensitivity when using a 9.5-eV lamp was significantly less than that achieved by using a 10.2-eV lamp (11). Because of its better sensitivity and selectivity, the 10.0-eV lamp was chosen for routine operation.

Gas chromatographic retention times and TNR values for 143 compounds are presented in Table II. TNR data were obtained by using the 10.0-eV lamp because of its higher sensitivity. TNR values for most species were reproducible to within 5–10%. Compounds and classes presented in Table II are those which have been reported in, or are of specific interest in, ambient air. Toluene, which is normally present in ambient air above 1 ppbv-C, was used as a GC retention time marker. The carrier gas flow rate was not routinely monitored. Instead, the column head pressure was adjusted to provide a constant elution time for toluene. By use of this technique, relative retention times for individual compounds varied by less than 1%. Gas chromatographic identifications were based on relative retention times (RRT) to toluene. Even

with high-resolution chromatography, the large numbers of compounds which can be present in ambient air made peak identification using only retention time data very difficult. The additional qualitative information provided by the PID/FID system became very important when analyzing complex air samples. Species data presented in Table II demonstrate that many closely eluting compounds can be differentiated with the PID/FID technique, whereas identification using only retention time data could be questionable. Spurious results can be obtained with the PID/FID technique when coeluting species of different chemical classes are both present in a sample, since the resulting TNR would represent a weighted response of the coeluting species.

An additional goal of this work was to achieve the capability to identify chemical classes of sample components for which species identifications could not be established. This capability would be very useful since photochemical reactivities vary significantly for different chemical classes and most atmospheric models group species according to chemical classes or other reactivity schemes. To compare relative detector responses for different classes, TNR data were averaged for all species eluting before and after 17 min. This time was chosen because all aromatics eluted later and because TNR values for alkenes decreased as the carbon number (and retention time) of the compound increased. Average TNR data for hydrocarbon classes are presented in Table III. For species eluting before 17 min, it was very easy to differentiate between alkenes and alkanes, which are the predominant hydrocarbon classes present in ambient air in this volatility range. Alkynes and chlorinated alkenes must be differentiated from alkenes chromatographically. Aldehydes, with the exception of acetaldehyde, gave TNR values similar to alkenes and must also be differentiated by chromatographic means. Only two ketones eluted in the early range, and both gave TNR values higher than those for alkenes. Chlorinated alkenes gave TNR values significantly above the TNR values for their nonchlorinated analogues, presumably due to the decreased FID response for these compounds. TNR values for chlorinated alkenes which contained a nonchlorinated carbon atom were considerably lower than TNR values for compounds which did not (i.e., 1,1-dichloroethylene as opposed to 1,2-dichloroethylene). Mercaptans eluting in this range gave the highest TNR values. TNR values for dienes were averaged with those for alkenes. However, the two diene species tested, 1,3-butadiene and isoprene, both gave higher TNR values than alkenes which eluted near them.

Identification of C₆–C₁₀ hydrocarbon species in ambient air is difficult, due to the extremely large number of compounds in this range. The majority of hydrocarbon content in the C₆–C₁₀ range which has been identified in ambient air was aromatic (12). Data presented in Table III demonstrate that

Table III. Hydrocarbon Class PID/FID Normalized Responses

class	retention times <17 min		retention times >17 min	
	species tested	TNR (mean \pm std dev)	species tested	TNR (mean \pm std dev)
halogenated alkanes	9	0 \pm 0	6	1 \pm 1
simple alkanes	13	3 \pm 3	10	12 \pm 4
cycloalkanes + trimethylalkanes	2	3 \pm 1	5	27 \pm 8
alkynes	3	3 \pm 3	0	
alkenes	23	70 ^a \pm 11	20	55 \pm 10
aldehydes	4	69 ^b \pm 10	1	56
ketones	2	157 \pm 5	2	123 \pm 25
aromatics	0	---	21	87 \pm 18
chlorinated aromatics	0	---	7	141 \pm 12
chlorinated alkenes	3	218 \pm 180	4	211 \pm 97
sulfur hydrocarbons	2	500 \pm 210	2	129 \pm 37

^a Does not include ethylene. ^b Does not include acetaldehyde.

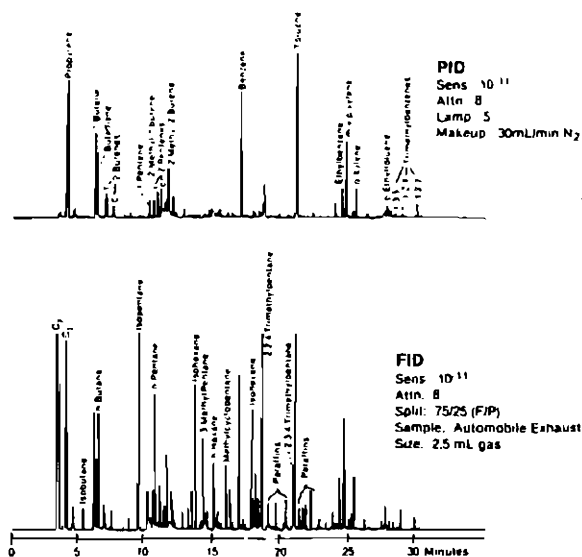


Figure 3. Analysis of automobile exhaust—1981 American model using unleaded gasoline.

TNR values can be used to estimate chemical classes for this volatility range. Chlorinated alkanes eluting in this range gave no PID response, whereas all alkanes eluting in this range did. Simple alkanes (*n*-alkanes, methyl and dimethyl alkanes) gave less than half the response of cyclic and highly branched alkanes providing some qualitative information within this class. Differentiation of alkenes from alkanes and aromatics is possible within a confidence interval of one standard deviation. Some complex alkenes such as limonene and pinenes gave TNR values as high as some aromatics. The aldehyde species which were tested gave TNR values similar to alkenes, while the average TNR for ketones was above that of the aromatics. Species within these classes which may be expected in ambient air eluted between benzene and toluene and were easy to identify as a result. Unsaturated chlorinated hydrocarbons in this range gave TNR values considerably higher than those for most other hydrocarbons. Different chlorinated aromatic hydrocarbons gave similar TNR results, whereas the chlorinated alkenes tested varied considerably.

As an example of the application of this technique to a complex sample, an analysis of automobile exhaust (1981 model, unleaded gasoline) is presented in Figure 3. Some of the major components in the sample are labeled. The major alkenes observed in the sample were in the C₃–C₅ range. Good separation of the C₄ compounds provided identification of 1,3-butadiene, which is very photochemically reactive. The identification of this compound was confirmed by the PID/FID response. Alkanes were observed over a considerable

boiling range. These were not observed on the PID chromatogram, with the exception of a low response for 2,2,4-trimethylpentane. The PID chromatogram also shows the ease of identification of aromatics as compared to the FID chromatogram.

CONCLUSIONS

The combination of high-resolution chromatography and simultaneous PID/FID detection offers a degree of identification for organics in ambient air which previously has not been possible. It is possible to estimate chemical classes for sample components using only normalized PID/FID data. This can be very helpful in providing data for atmospheric modeling studies. However, when possible PID/FID data should be used in conjunction with chromatographic identification. This technique can provide tentative identification for a number of aldehydes, ketones, and chlorine- and sulfur-containing hydrocarbons, in addition to alkane, alkene, and aromatic identifications. The ability to screen for volatile compounds within these various classes makes this technique ideal for screening complex samples, such as air above hazardous waste disposal sites.

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