

Photoionization/Flame-Ionization Detection of Atmospheric Hydrocarbons after Capillary Gas Chromatography

Winai Nutmagul and Dagmar R. Cronn*

Laboratory for Atmospheric Research, College of Engineering, Washington State University, Pullman, Washington 99164-2730

Herbert H. Hill, Jr.

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

A "gastight, low-volume" photoionization detector has been constructed for the purpose of detecting trace hydrocarbons in atmospheric samples. This modified PID, in tandem with an FID, was tested by use of a standard gaseous mixture of aromatics, alkenes, and alkanes. The average minimum detectable amounts for the PID were found to be 1.2 pg for aromatics, 2.0 pg for alkenes, and 8.6 pg for alkanes. When the detector was operated in tandem with a standard flame ionization detector, PID/FID response ratios normalized to toluene produced values that could be used to classify hydrocarbons according to their degree of saturation. Normalized PID/FID ratios for alkanes were found to range from 0 to 43, alkenes from 44 to 88, and aromatics from 75 to 158. Using this ratio criteria an ambient air sample was determined to contain 52% alkanes, 14% alkenes, and 34% aromatics by weight excluding C₂ hydrocarbons.

Hydrocarbon compounds, especially unsaturated hydrocarbons, play a significant role in atmospheric chemistry and their concentrations in remote environments, i.e., background or "clean" air environments, are important for understanding atmospheric chemical processes. Modelers require concentrations of various hydrocarbon classifications such as alkanes, alkenes, and aromatics as input data to validate their models and to predict secondary air pollutants such as ozone and PAN (peroxyacyl nitrate).

One analytical technique generally used for hydrocarbon measurements in the atmosphere is gas chromatography with flame ionization detection. However, the sensitivity of the flame ionization detector (FID) is only marginally sufficient for background atmospheric hydrocarbon measurements even with preconcentration of 1- or 2-L sample aliquots using cryogenic liquid (oxygen) to trap hydrocarbons from the air sample (1). Moreover, the FID is a universal detector for hydrocarbons and cannot be used to distinguish between unsaturated and saturated compounds. Normally retention times are used to identify components in the sample by comparison with those of known compounds. Also, gas chromatography/mass spectrometry can be used for accurate qualitative identification. GC/MS methods are, however, usually less sensitive, more costly, and less mobile than FID methods. In both methods, information on total concentrations of saturated hydrocarbons vs. unsaturated hydrocarbons must be obtained by summing the concentrations of the appropriate identified individual compounds. A simpler approach for the determination of these important hydrocarbon fractions in air would save both time and money.

Photoionization detection coupled with flame ionization detection has been demonstrated to have the potential to classify hydrocarbons into saturated and unsaturated groups.

However, this method has not been widely used in the classification of hydrocarbons in atmospheric samples.

The response of a photoionization detector (PID) is dependent on several parameters such as the column and make-up gas flow rate (2, 3), lamp intensity (4), type of carrier gas (5), and the physical and chemical properties of the compound being detected (6-9). The major factor that governs PID response has been reported to be the ionization potential (IP) of the ionizable molecule (8, 9) or the combination between the IP and the number of carbon-carbon π -bonding electrons (3). Thus photoionization has shown promise for the selective detection of unsaturated hydrocarbons (8, 10, 11). Moreover, it has been found to be more sensitive for many hydrocarbons than the standard FID.

By use of a normalized PID/FID ratio (using any alkane as a normalizing compound), alkanes have been reported to have values in the <2 range, alkenes in the 2-4 range, and aromatics in the 5-10 range (10). Normalized PID/FID ratios using toluene as a normalizing compound also have been reported (4). Although similar results have been confirmed by other investigators (8), the validity of using the normalized PID/FID ratios as an index to identify hydrocarbon classes has been questioned (3).

One method for obtaining PID/FID data is to operate the two detectors in parallel with the aid of a postcolumn splitter (4). The drawback to this approach for the analysis of real atmospheric samples on a routine basis is in the loss of sensitivity due to the sample split and in the uncertainty of the split ratio over long periods of time. Sequential injections into both the PID and FID have also been reported (8) but, for complex samples such as organics in air, time becomes a major consideration as well as the matching of the chromatographic separation.

Since the PID is virtually nondestructive (the ionization efficiency is about 0.1%), it is possible to connect the PID in series with other GC detectors. The connection of a PID in series with a FID has been used for the detection of aromatics in a light hydrocarbon feedstock for a synthetic natural gas plant and for samples from a coal gasification pilot plant (10, 12). In the latter study by Kapila and Vogt (12) problems due to large dead volumes inside the detector and gas leaks in the PID were discussed and a "gastight low-volume" detector was constructed.

In this study the PID designed by Kapila and Vogt was constructed and modified for the sensitive detection of hydrocarbons in air. The use of this detector in series with a commercial FID for the classification of hydrocarbons in real air samples is evaluated.

EXPERIMENTAL SECTION

Instrumentation. The photoionization detector used in this study is shown in Figure 1 and was patterned after the "gastight, low-volume" design of Kapila and Vogt (12) but with two con-

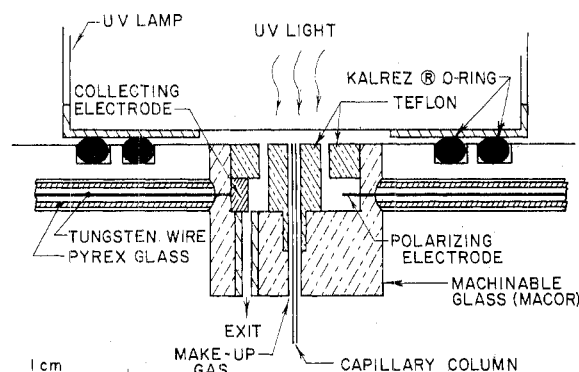


Figure 1. Schematic diagram of the final form of modifications made to the photoionization detector. (Actual position of polarizing electrode is at right angles to collecting electrode and behind drawing rather than as shown for clarity.)

struction modifications. First, the electrode configuration has been changed to permit total shielding of both electrodes from the UV radiation and the detector body has been constructed from Macor machinable glass rather than boron nitride. The light source for this detector was a standard HNU 10.2-eV hydrogen lamp with power supply. An HNU electrometer used in commercial HNU PID's was used to amplify the signal from the collecting electrode. Potential for the polarizing electrode was also supplied from HNU electronics.

This detector was mounted in series with a commercial Hewlett-Packard Model 18710A flame ionization detector and maintained at 200 °C. The transfer line connecting the two detectors was a 0.3 m × 0.8 mm i.d. stainless steel tube which was wrapped with heating tape and maintained at 200 °C. Gas flows for the FID were normally 30 mL/min of hydrogen, 260 mL/min of air, and 12 mL/min of helium carrier gas (make-up gas included) through the PID detector with a column flow rate of 1 mL/min.

The gas chromatograph used in this study was a Hewlett-Packard 5700A with a SE-30 fused silica capillary column purchased from J & W Scientific, Inc., Sacramento, CA. A six-port gas sampling valve (Model 5518, Carle Instruments, Inc., Anaheim, CA) was used to load gas samples into a sample trap loop and then to inject samples into the GC. Samples were injected into the sample trap loop with a Pressure-Lok 5-mL syringe (Precision Sampling Corp., Baton Rouge, LA) or a 100-mL syringe (B-D Yale Becton, Dickinson & Co., Rutherford, NJ). The sample trap loop was filled with glass beads and cooled to -183 °C in a liquid oxygen bath. Samples were transferred from the loop to the GC column by switching the six-port valve and immersing the loop in a hot water bath. After injection of a sample onto the column the column oven was temperature programmed from -50 °C to +80 °C at 4 °C/min and held isothermally at 80 °C for 10 min. A Hewlett-Packard Model 3352A laboratory data system integrated peaks for both chromatograms of the PID/FID system whereas strip chart recorders (Hewlett-Packard model 7127A) provided chromatograms.

Hydrocarbon Standards. Hydrocarbon compounds used for evaluation of the PID were as follows: (alkanes) *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-dodecane; (alkenes) 1-hexene, 2-heptene, 1-octene, 1-nonene, and 1-decene; (aromatics) benzene, toluene, ethylbenzene, *o*-xylene, and isopropylbenzene. All of these standards except *n*-nonane, 1-nonene, and 1-decene were obtained from Chem Service, Inc., West Chester, PA. *n*-Nonane was purchased from Polyscience Corp., Niles, IL, 1-nonene from Aldrich Chemical Co., Inc., Milwaukee, WI, and 1-decene from Alfa Products, Danvers, MA. A standard gaseous mixture of 0.204 ppm 2,2-dimethylbutane (certified to be within ±2%) and C₂-hydrocarbons from Scott Specialty Gases, San Bernardino, CA, was used as a primary standard for coinjection with the gaseous hydrocarbon mixtures.

Three hydrocarbon mixtures, one of *n*-alkanes, one of alkenes, and one of aromatics, were prepared by injecting 1 μL of each of the five representative compounds in each group into a 1-mL vial sealed with a crimp-on Teflon-lined septum filled with 0.5 mL of *n*-dodecane as a solvent. One microliter of each hydrocarbon mixture was withdrawn and injected into an evacuated

6-L stainless steel canister (D & S Instrument Ltd, Pullman, WA). The inside surfaces of the stainless steel container had been electropolished and had been demonstrated to be clean and inert with respect to the standard hydrocarbons used in this study. Canisters were pressurized to 270 kPa by a pure air generator (Model 737, AADCO, Inc., Rockville, MD) and allowed to mix at least 3 h before use.

The standard hydrocarbon mixture was calibrated by injecting 70-mL aliquots of the mixture with 20 mL of the 0.204 ppm 2,2-dimethylbutane primary standard into the GC/PID-FID system. To determine detection limits of the PID for hydrocarbons, the standard gaseous hydrocarbon mixture was diluted by a factor of 124 by withdrawing 100 mL from the standard gaseous hydrocarbon mixture and injecting this aliquot into another evacuated 6-L stainless steel canister. This canister was then pressurized to 200 kPa by using the pure air generator. Seventy-milliliter or 10-mL aliquots of the second standard gaseous hydrocarbon mixture with 10 mL of the 0.204 ppm 2,2-dimethylbutane primary standard were injected into the GC/PID-FID system. The peak height of each hydrocarbon compound was used in the calculation of its detection limit (signal/noise = 2).

Air Samples. Whole-air samples were collected in pressurized (~150 kPa) 6-L stainless steel canisters from a small parking lot during heaviest traffic periods with a Metal Bellows MB 41 pump (Metal Bellows Co., Sharon, MA). The sampling transfer-lines and pump were flushed with sample air for about 10 min before sampling commenced.

RESULTS AND DISCUSSION

To successfully use the PID and FID in series for the detection of atmospheric organic vapors after capillary gas chromatography, the PID must be leak tight in order to accurately reflect true PID/FID response ratios. Also, residence time of the sample in the PID cell and the associated transfer line should be as low as possible in order to maintain the integrity of the chromatographic separation.

Figure 1 provides a schematic of the PID design used in this study. While the total cell volume of this detector is 150 μL, the effective cell volume (that volume in which the chromatographic effluents are exposed to UV radiation) is much less (about 1 μL) since gases exit radially from the chromatographic column, about 1 mm from the UV window, and flow in the narrow space between the window and the Teflon column support. Residence time in this ionization region is only about 5 ms. Even when the total cell volume and transfer line is considered, residence time between detectors is only about 1.4 s. There is no observable increased peak broadening or peak tailing in the FID chromatograms and loss of resolution between the two detectors is insignificant. The upper temperature limit of the cell is about 200–210 °C unless the Teflon parts are replaced by another insulating material such as machinable glass.

As with the previously described (12) design, our PID was leak tight. The flow rates measured at the column exit and at the exhaust port of the PID were the same. With the transfer line connected to the FID, no leaks were detected at the connection between the PID and the FID or around the PID itself using a helium leak detector.

Two important design modifications were found to be necessary in order to gain the high sensitivity required for atmospheric vapor detection. First, the collecting and polarizing electrodes must be recessed and well shielded so that the UV radiation does not impinge upon their metal surfaces. The work functions of most metals are sufficiently below the energy level of the ionizing photons and, if the light strikes the electrodes, an unacceptable high background current is produced that ranges from 10 to 15 nA due to the production of free electrons from the metal surfaces. When this occurs, noise is increased and anomalous peaks can be observed when electrophilic compounds pass through the detector. When

Table I. PID/FID Relative Responses and Normalized PID/FID Responses of Hydrocarbon Compounds for Electrode Geometry 1

compound	PID/FID	PID/FID normalized to <i>n</i> -octane	PID/FID normalized to toluene ($\times 100$)	min detection limit (pg) for the PID
<i>n</i> -hexane	0.19 ± 0.03	0.42	2	14.7
<i>n</i> -heptane	0.58 ± 0.03	1.29	7	9.0
<i>n</i> -octane	0.45 ± 0.01	1.00	5	7.5
<i>n</i> -nonane	0.72 ± 0.02	1.60	8	6.7
<i>n</i> -decane	0.90 ± 0.02	2.00	10	5.1
1-hexene	6.48 ± 0.12	14.4	74	1.6
2-heptene	7.68 ± 0.16	17.1	88	1.3
1-octene	4.73 ± 0.14	10.5	54	2.1
1-nonene	4.30 ± 0.09	9.6	49	2.7
1-decene	3.99 ± 0.21	8.9	46	2.1
benzene	11.94 ± 0.27	26.5	137	0.6
toluene	8.71 ± 0.22	19.4	100	0.8
ethylbenzene	7.91 ± 0.17	17.6	91	1.3
<i>o</i> -xylene	7.52 ± 0.10	16.7	86	1.3
isopropylbenzene	6.03 ± 0.46	13.4	69	1.8

the electrodes were positioned within the sensing volume such that they were removed from direct UV light, the background current decreased to a level in the 5–20 pA range. This is about the same as that observed with commercial PI detectors.

The second modification of our system, compared to the Kapila-Vogt design, was to construct the detector housing from a machinable glass rather than from boron nitride. When boron nitride was used for fabrication, the base line of the PID chromatogram consistently drifted upward at the beginning of a temperature programmed run and dropped abruptly back to the original value when the oven temperature reached about 34 °C. At temperatures higher than 34 °C, chromatographic peaks were broader and exhibited pronounced tailing. Although the explanation of these observations is unclear, the use of machinable glass for construction of the detector body produced a stable base line and good peak shape throughout the chromatographic run.

The optimum electrode shape for maximum sensitivity was empirically selected by determining the relative sensitivities for five different electrode geometries. In the first electrode configuration, the polarizing electrode constituted a point electrode and was constructed by simply inserting a tungsten wire through an insulator in the electrode shield arm. The collecting electrode consisted of a 7.4 mm i.d. stainless steel tubing with a 30° sector removed to provide the space for the polarizing electrode. The second electrode configuration consisted of two stainless steel arcs of 142.5°. Designs three and four were point electrodes opposing 142.5° arc electrodes. In the third design the point electrode was the polarizing electrode and in the fourth design it was the collecting electrode. The fifth design was the same as the first except that the polarizing and collecting functions were interchanged. Each geometry was evaluated by injecting a gaseous mixture of 15 hydrocarbons three times and calculating the relative response between the PID and the FID using the average areas of each compound.

The PID/FID ratios obtained for the five aromatic compounds for each of the five electrode geometries are given in Figure 2 and are arranged in order of the most sensitive (design 1) to the least sensitive configuration (design 5). The order of sensitivity followed that of the surface areas of the collecting electrode with the collecting electrode containing the largest surface area being the most sensitive. PID/FID ratios obtained for each geometry for alkanes (*n*-C₆ to *n*-C₁₀) and alkenes (1-hexene, 2-heptene, 1-octene, 1-nonene, and 1-decene) also showed the same sensitivity pattern as obtained for the aromatics, i.e., geometry 1 was greater than geometry 2, etc.

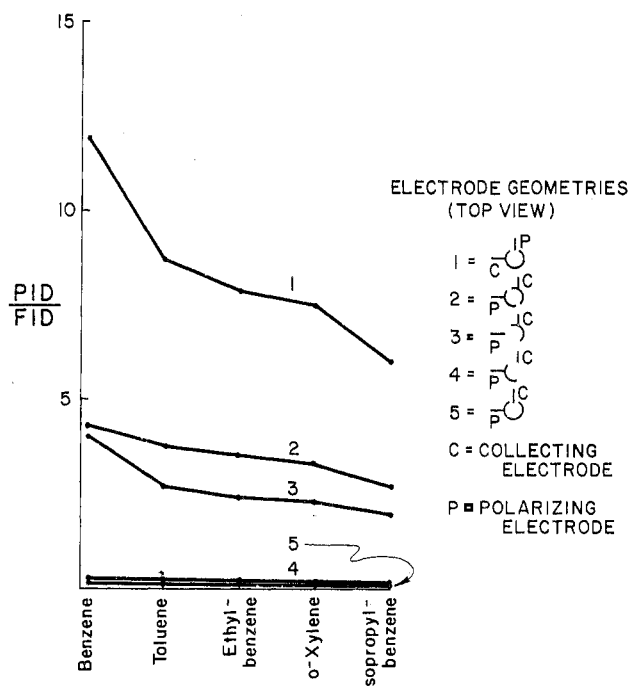


Figure 2. Relative (PID/FID) response for five aromatic compounds for different electrode geometries.

For a given geometry, ratios for aromatics were generally higher than those obtained for alkenes, which were generally higher than for alkanes (Figure 3). From these studies, geometry 1 was selected as the optimum electrode configuration for this detector. By use of electrode geometry 1, minimum detectable amounts (MDA's), based on peak height and defined as signal/noise ratio equal to 2, are reported in Table I. MDA's were determined to range from 0.6 to 1.8 pg for the aromatic test compounds, from 1.3 to 2.7 pg for the alkenes, and from 5 to 15 pg for the alkanes. These values for aromatics are lower than those of 2 pg for benzene (2) and 25 pg for anthracene (12) which have been reported in the literature and are lower than those typically found with the FID.

Again with electrode geometry 1, normalized PID/FID ratios were obtained for each of the test compounds. First, these ratios were normalized to the PID/FID response ratio for the alkane *n*-octane. As expected, the normalized response ratios for the alkanes were equal to or less than 2 for all five of the alkanes investigated. However, the normalized

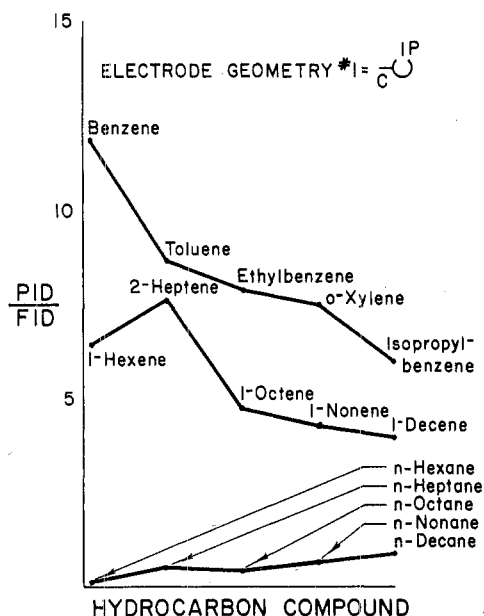


Figure 3. Relative (PID/FID) response for 15 hydrocarbons (five alkanes, five alkenes, and five aromatics) for electrode geometry 1.

PID/FID ratios for alkenes and aromatics were higher than the expected values of 2–4 for alkenes and 5–10 for aromatics (8, 10). With this PID design alkenes had a response ratio between 9 and 17 while the aromatic compounds exhibited alkane-normalized response ratios between 13 and 27. Table I lists the individual response ratios for these test compounds.

When the response ratio of toluene rather than *n*-octane is used to normalize the data, normalized response ratios compared favorable with literature values (4). Both the values obtained in this study and those obtained from ref 4 for the same hydrocarbons ranged from 0.02 to 0.16 for alkanes and from 0.69 to 1.37 for aromatics. Toluene-normalized response ratios for alkenes, however, ranged in this work from 0.46 to 0.88, which was somewhat higher than the 0.36 to 0.59 range found in the study reported in ref 4.

It should be noted that the wider disparity in normalized response ratios reported in this paper cannot specifically be attributed to the electrode geometry. All five geometries which were investigated in this work gave the same normalized response ratios; only the overall sensitivity of the detector was affected by the various designs. Perhaps the basic design of the detector with its recessed and shielded electrodes is important but this was not systematically investigated. Nevertheless, the larger differences in response ratios enable this PID/FID detector combination to more easily distinguish between saturated and unsaturated hydrocarbons than those of standard commercial designs.

To further investigate the ability of this detector to distinguish between saturated and unsaturated hydrocarbons, an air sample was collected in a small parking lot on February 4, 1983, at 1700 LT (local time) and evaluated with this dual detection system. Chromatograms from the two detectors are shown in Figure 4. The offset in retention time between the PID and the FID traces was between 1 and 2 s. There was no observable increase in peak broadening or peak tailing in the FID chromatogram relative to the PID chromatogram; thus the loss of resolution during the transfer between detectors was insignificant.

With toluene as the normalizing compound, normalized PID/FID response ratios multiplied by 100 were used to identify the sample components as alkanes, alkenes, or aromatics. Twenty-three of the components of this air sample were identified via retention time data and are listed along with their normalized response ratios in Table II. The range

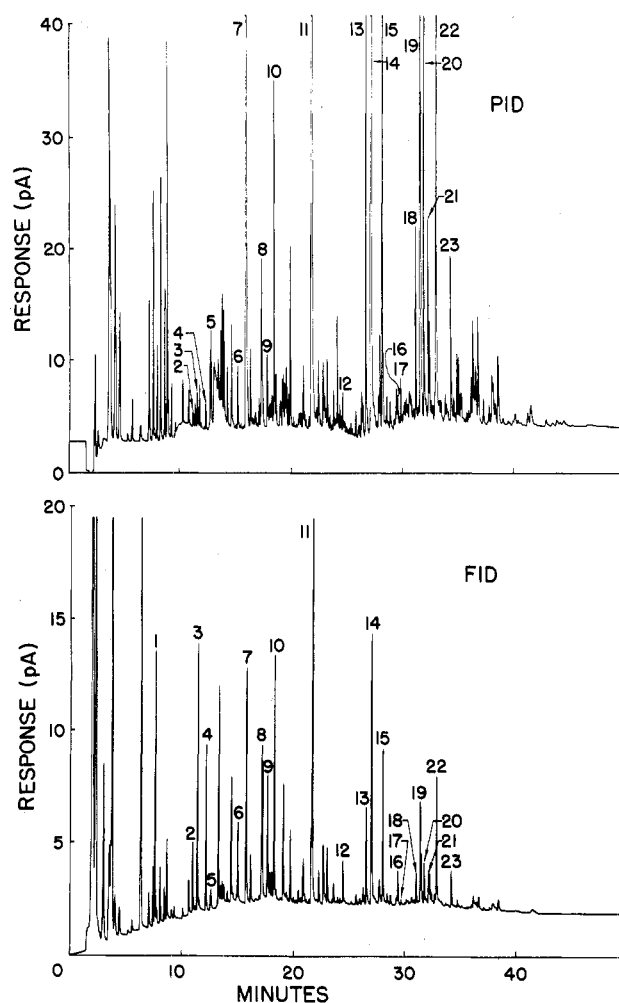


Figure 4. PID (top) and FID (bottom) chromatograms of a real air sample collected at 1700 LT in a small parking lot on 2/4/83. The sample aliquot size was 500 mL of air and the UV lamp intensity for the PID was 70% full scale.

Table II. Hydrocarbon Compounds Determined in the Real Air Sample of Figure 4 Including the Observed PID/FID Ratios Normalized to Toluene

peak no.	compound	PID/FID normalized to toluene (×100)
1	<i>n</i> -butane	
2	2,3-dimethylbutane	4
3	2-methylpentane	3
4	3-methylpentane	3
5	1-hexene	75
6	2,4-dimethylpentane	15
7	benzene	129
8	2,3-dimethylpentane	40
9	3-methylhexane	12
10	2,2,4-trimethylpentane	28
11	toluene	100
12	<i>n</i> -octane	22
13	ethylbenzene	84
14	<i>p</i> - and <i>m</i> -xylene	116
15	<i>o</i> -xylene	82
16	<i>n</i> -nonane	25
17	isopropylbenzene	134
18	<i>n</i> -propylbenzene	103
19	<i>p</i> -ethyltoluene	76
20	1,3,5-trimethylbenzene	158
21	<i>o</i> -ethyltoluene	105
22	1,2,4-trimethylbenzene	123
23	1,2,3-trimethylbenzene	95

of normalized PID/FID ratios for all peaks in the real air sample was found to be from 0 to 43 for alkanes, from 44 to

88 for alkenes, and from 75 to 158 for aromatics.

The normalized ratios for *n*-octane, *n*-nonane, and isopropylbenzene varied somewhat from the values obtained with the standards due to the fact that their areas (in the FID chromatogram for isopropylbenzene and in the PID chromatogram for *n*-octane and *n*-nonane) were too small to measure accurately. Nevertheless, the normalized response ratios fell into the appropriate identifiable range so that these compounds could be correctly classified.

When the normalized PID/FID ratio fell in the overlap region between the alkenes and aromatics, assignments were made based on comparison of the ratio of the unknown and the response ratio of the nearest known alkene. The normalized response ratios for alkenes have a tendency to decrease as the molecular weight increases and the compound takes on more alkane character (4). Thus the response ratios of aromatics and alkenes seldom overlap for compounds eluting from the chromatograph at approximately the same time.

In this study, the distribution of hydrocarbons in the real air sample (excluding C₂ hydrocarbons) was found to be 52% alkanes, 14% alkenes, and 34% aromatics by weight. The percentage of aromatics (34%) was comparable to the approximately 30% aromatics found in typical urban area samples (13). The percentage of alkenes (14%) identified in this sample was higher than the average of about 6% (excluding ethylene) for typical urban air samples (13). However, the amount of alkenes in diluted automobile exhaust is reported to be significantly higher than in urban air samples (14). The ratio (by weight) of alkenes to alkanes for C₃ to C₇ hydrocarbons as calculated by use of data obtained from ref 14 was 0.56:1, which is higher than the ratio of 0.27:1 from the parking lot sample reported here. Since the parking lot sample was collected during peak traffic periods, one might expect higher levels of alkenes than those usually found from more aged urban air samples. It should be noted also that the sum of alkanes and alkenes (69%) in the parking lot sample was comparable to the sum in typical urban area samples (13).

In conclusion, this modified PID is a highly sensitive, low dead-volume, low-background photoionization detector, which when used in conjunction with a standard FID can provide reliable information on the various alkane, alkene, and aromatic fractions of atmospheric samples.

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Registry No. *n*-Hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; *n*-decane, 124-18-5; 1-hexene, 592-41-6; 2-heptene, 592-77-8; 1-octene, 111-66-0; 1-nonene, 124-11-8; 1-decene, 872-05-9; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6; isopropylbenzene, 98-82-8; *n*-butane, 106-97-8; 2,3-dimethylbutane, 79-29-8; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,4-dimethylpentane, 108-08-7; 2,3-dimethylpentane, 565-59-3; 3-methylhexane, 589-34-4; 2,2,4-trimethylpentane, 540-84-1; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *n*-propylbenzene, 103-65-1; *p*-ethyltoluene, 622-96-8; 1,3,5-trimethylbenzene, 108-67-8; *o*-ethyltoluene, 611-14-3; 1,2,4-trimethylbenzene, 95-63-6; 1,2,3-trimethylbenzene, 526-73-8.

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