O·I·Analytical

A New Photoionization/Flame-Ionization Series Detector for Gas Chromatography

Application Note 00541095

Keywords
Gasoline
Hydrocarbon
Kerosene
Natural Gas Well
PID/FID

Introduction

Class determination of hydrocarbon species is of interest since structure plays an important role in reactivity in photochemical reactions (1). Saturated, low molecular weight hydrocarbons (e.g., methane and ethane) are not photochemically reactive. Branched alkanes, alkenes, and aromatics, however, tend to be very reactive in atmospheric photochemical reactions that form irritating oxidants (such as ozone), PAHs, and smog.

A GC detection method has been developed that is based on analyzing the effluent from a chromatographic column with two detectors and then comparing the relative responses for each analyte. The technique of evaluating response ratios was introduced over 30 years ago by Grant (2) and first applied to PID/FID applications by Driscoll (3). The relative response of the FID is similar for many types of carbon compounds (e.g., aromatics, alkenes, and alkanes); therefore, it is used to measure the relative levels of a particular hydrocarbon regardless of the degree of saturation. In contrast, the PID's relative response differs greatly depending on a compound's degree of saturation. The PID has low sensitivity for alkanes but is very sensitive for aromatics.

A tandem detector has been developed that takes advantage of the sensitivity differences between the PID and FID. The detector set presented here takes advantage of a unique design that allows the FID to interface directly to the PID without a transfer line; previous PID/FID detector systems have required splitters and/or transfer lines (4, 5) between the detectors to achieve an interface. The design used in this study eliminates the need for nonstandard fittings and the possibility of dead volumes associated with those fittings. It also eliminates cold spots associated with non-heated transfer lines. Series operation is possible since the PID is a nondestructive detector.

Determine hydrocarbon class by evaluating the normalized response ratio obtained by dividing the PID response by the FID response, then normalize to an internal reference compound.

Experimental

A cross section of the dual detector set used, a Model 4450 PID/FID (OI Analytical, College Station, TX), is shown in Figure 1. The PID was equipped with a standard 10.0 eV lamp. In this series detector, the sample stream flows through the PID's ionization chamber where it is continuously irradiated with high energy ultraviolet light. As compounds enter this chamber, those that have a lower ionization potential than that of the irradiation energy (10 eV) are ionized. The ions formed are in an electric field and are accelerated to a collector, producing an ion current proportional to the amount of analyte. This current is then amplified and output by the chromatograph's electrometer. The sample stream then flows out of the PID through the FID jet. At the exit of the jet, the sample is ionized in a hydrogen/air flame. Few ions are formed until an organic compound elutes into the flame. At that point, a large increase in ions occurs. These ions are also formed in an electric field and accelerated to a collector, again producing an ion current proportional to the amount of analyte present and then amplified.

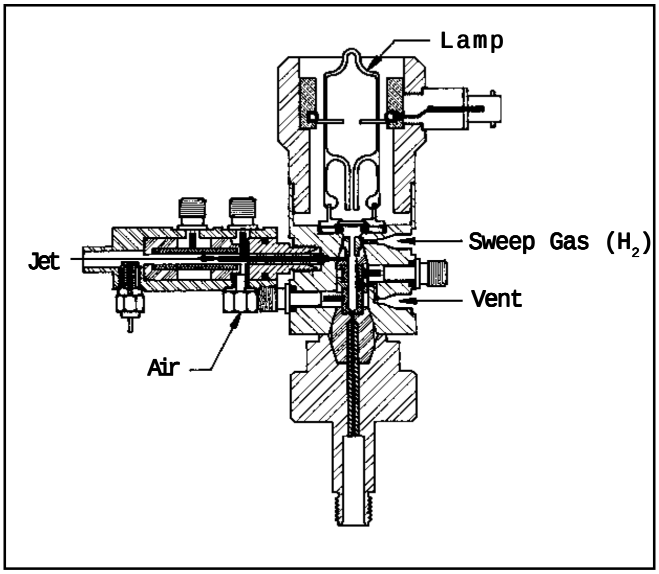

Figure 1. Cross Section of the OI Model 4450 Dual Detector Set

The hydrocarbon samples were injected into a split/splitless injector operating with a 100:1 slit, and then separated with an Rt_x-5 (30 m x 0.25 mm x 0.25 µm) (Restek Corp., Bellefonte, PA) operated at an initial temperature of 30°C for 5 minutes and then temperature programmed to 200°C at a rate of 2°C/min. The carrier was zero grade helium at a rate of approximately 1 mL/min (35 cm/min). The GC used was an HP 5890 Series II (Hewlett-Packard, Avondale, PA). The detector set was operated with 20 mL/min helium as makeup gas (also zero grade). With the unique detector- set design, the hydrogen for the FID fuel was introduced into the PID as the sweep gas at a flow of 35 mL/min. The sweep gas prevented compounds from condensing on the PID lamp window. Breathing air was used at a rate of 180 mL/min in the FID.

Result and Discussion

As mentioned earlier, the response of the PID relative to the FID depends upon the class of the compound of interest. Figure 2 illustrates these differences with a simple hydrocarbon mixture containing alkanes, branched alkanes, alkenes, and aromatics. The response ratios were evaluated for each pair of peaks and then normalized to an internal reference compound, in this case, toluene. The following equation was used for this procedure:

$$\frac{U_{PID}}{U_{FID}} \times \left(\frac{R_{PID}}{R_{FID}} \right)^{-1} \times 10 \qquad (1)$$

where U_{PID} and U_{FID} are the PID and FID responses for the compound of interest, respectively, and R_{PID} and R_{FID} are the PID and FID responses for the reference compound, respectively. The factor of 10 is used to set the response ratio of the reference compound, toluene, to 10. By normalizing the response ratios, individual detector performance is eliminated. Therefore, any PID coupled with any FID will yield similar results when the response ratios are normalized. The normalized response ratios (NRR) for the compounds in Figure 2

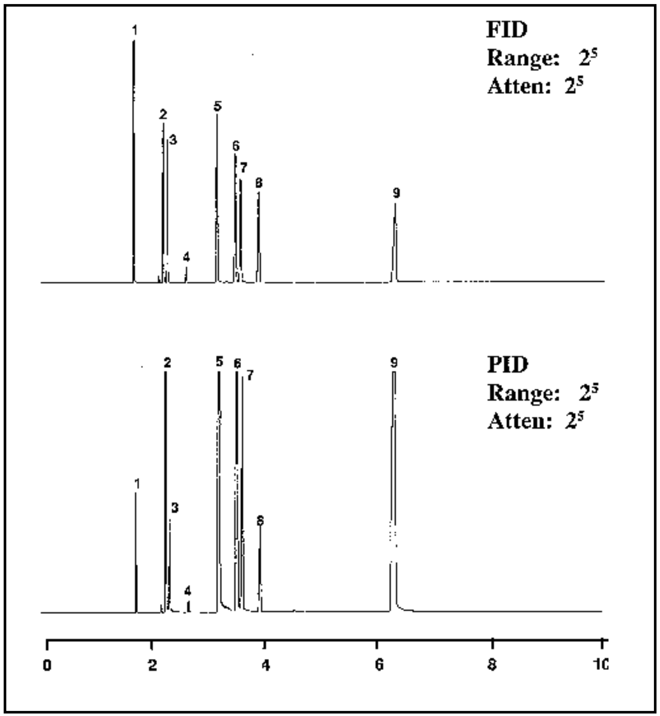

Figure 2. Analysis of Hydrocarbon Mixture Using Tandem PID/FID Detectors

are presented in Table 1. As seen, the NRR for alkanes are around 1; branched alkanes are from 2 to 3; alkenes are from 4 to 6; and aromatics are from 8 to 11.

Using this technique, 121 compounds were evaluated. The NRRs are given in Table 2. The compound classes included alkane, alkene, aromatic, alcohol, aldehyde, ketone, ester, and ether. Some of the compounds evaluated here have been investigated before (4), and the numbers presented here are in agreement. The remainder of the compounds have not been previously reported in the literature. There are several possible observations; the NRR for alkanes increases with increasing carbon chain length. This may be due to a decrease in FID ionization efficiency, thus causing the NRR to increase, or it may be due to an increase in PID ionization efficiency, or both. Also, the NRR does not seem to change when a chlorine atom is substituted for a hydrogen atom. The NRRs for the aromatics tend to be around 10, but are dependent on the character of the functional group(s). If there is a large degree of "aliphatic character," then the total "aromatic character" of the molecule is reduced, as is the PID ionization efficiency. For example, benzene is completely aromatic and has an NRR of 10.66, while propyl benzene has a degree of aliphatic character a lower NRR of 8.64. The system efficiency was evaluated by calculating the number of theoretical plates (N_{TH}) obtained using

Ref. No.	R.T	NRR	Compound
1	1.762	0.35	Pentane
2	2.285	6.08	1-Hexene
3	2.355	0.81	Hexane
4	2.684	0.80	Unknown (3-Methyl Pentane)
5	3.228	10.54	Benzene
6	3.548	5.60	Cyclohexene
7	3.643	2.58	i-Octane
8	3.954	1.06	Heptane
9	6.333	10.00	Toluene

Table 1. Normalized Response Ratios for the Hydrocarbon Mixture

***n*-Alkanes**	
Butane	0.06
Pentane	0.42
Hexane	0.85
Heptane	1.13
Octane	1.36
Nonane	1.97
Decane	2.32
Undecane	3.26
Dodecane	3.32
Tridecane	3.73
Tetradecane	3.98
Pentadecane	4.32
Hexadecane	4.61
Octadecane	5.22
Nonadecane	5.25
Heneicosane	7.08
Docosane	8.72
Cyclopentane	1.00
Cyclohexane	2.73
Chlorinated Alkanes	
1-Chloropentane	0.55
1-Chlorohexane	0.84
1-Chloroheptane	1.10
1-Chlorooctane	1.32
1-Chlorononane	1.58
1-Chlorodecane	1.84
Branched Alkanes	
2-Methyl Propane	0.06
2-Methyl Butane	0.50
2-Methyl Pentane	1.16
2,2,4-Trimethyl Pentane (iso-octane)	2.69
Dimethyl hexane	2.26
2,2,5-Trimethyl hexane	3.31
1-Alkenes	
1-Pentene	8.04
1-Hexene	6.58
1-Heptene	5.98
1-Octene	5.96
1-Nonene	5.92
1-Decene	5.90
1-Undecene	5.86
1-Dodecene	5.87
1-Tridecene	5.95
1-Tetradecene	6.03
Cyclohexene	5.60
Aromatics	
Benzene	10.66
Toluene	10.00
Ethyl Benzene	9.23
o-Xylene	9.10
m-Xylene	10.71
p-Xylene	10.64
p-Cymene	7.69
Isopropyl Benzene	7.62
n-Propyl Benzene	8.64
1,3,5-Trimethyl Benzene	12.63
s-Butyl Benzene	7.66
n-Butyl Benzene	8.40
Naphthalene	13.20
***n*-Alcohols**	
Methanol	.0042
Ethanol	1.15
Propanol	1.38
Butanol	1.39
Pentanol	1.52
Hexanol	1.84
Heptanol	2.21
Branched Alcohols	
Isopropanol	1.69
2-Methyl-1-Propanol	1.63
2-Methyl-2-Propanol	2.01
2-Butanol	2.25
2-Ethyl-1-Butanol	2.94
4-Methyl-2-Pentanol	3.23
3-Methyl-3-Pentanol	5.51
Cyclohexanol	5.49
***n*-Ketones**	
2-Propanone (Acetone)	14.19
3-Pentanone	13.19
2-Heptanone	7.98
4-Heptanone	8.80
Branched Ketones	
4-Methyl-2-Pentanone	8.21
5-Methyl-2-Hexanone	8.08
5-Methyl-3-Heptanone	8.64
2,6-Dimethyl-4-Heptanone	7.43
***n*-Aldehydes**	
Propanal	7.68
Butanal	8.88
Pentanal	6.68
Hexanal	5.47
Heptanal	5.15
Octanal	4.99
Nonanal	4.96
Decanal	5.27
Hendecanal	5.19
Dodecanal	5.38
Tridecanal	5.89
Tetradecanal	5.94
Branched Aldehydes	
2-Methyl Propanal	7.22
3-Methyl Butanal	6.04
Benzaldehyde	11.45
Esters	
Methyl Decanoate	3.57
Methyl Dodecanoate	4.24
Methyl Tetradecanoate	5.21
Methyl Hexadecanoate	7.35
Methyl Octadecanoate	11.84
Ethyl Acetate	2.14
Ethyl Propionate	3.12
Ethyl Butyrate	3.25
Ethyl Valerate	3.44
Ethyl Caproate	3.51
Propyl Acetate	1.97
Propyl Propionate	3.15
Propyl Butyrate	3.33
Propyl Valerate	3.54
Propyl Caproate	3.68
Butyl Propionate	3.22
Butyl Valerate	3.66
Butyl Caproate	3.77
Butyl Heptanoate	3.94
Ethers	
Ethyl Ether	8.81
Propyl Ether	6.10
Butyl Ether	5.46
Pentyl Ether	5.23
Methyl t-Butyl Ether	9.05
Ethyl t-Butyl Ether	8.01
Ethyl Butyl Ether	6.40
Isobutyl Ether	5.44
Isopentyl Ether	5.57

Table 2. Normal Response Ratios for 121 Hydrocarbons

the PID/FID combination detector and comparing it to a stand alone FID (HP, Avondale, PA). Three compounds were used to calculate N_{TH} for each detector. They were heptane, methyl i-butyl ketone (MIBK), and toluene. N_{TH} was calculated using the following equation:

$$N_{TH} = 5.54 \left(\frac{t_r}{W_{1/2}}\right)^2 \qquad (2)$$

Where t_r is the retention time of the peak and $W_{1/2}$ is the width of the peak at half height, the results are in Table 3.

N_{TH} is the same, within experimental error, for each compound on each detector. It is concluded that there is no loss in chromatographic efficiency when using the direct interface between the PID and the FID.

The PID/FID NRR technique has been applied to several practical applications. The first is presented in Figure 3, which shows a set of chromatograms for super-unleaded gasoline (91 octane). Table 4 gives the NRRs for many of the compounds. The table lists several unknowns. By knowing the relative retention times and the NRRs of the unknowns, a likely identification may be made. The peaks at 2.653 and 3.387 have NRRs of 1.27 and 1.59, respectively, so they are methyl alkanes, most likely a methyl hexane and a methyl heptane. The peak at 3.261 has an NRR of 2.41, indicating a branched alkane, and is probably a dimethyl hexane. The NRRs for peaks at 5.449 and 5.608 indicate branched alkanes and are likely to be dimethyl or trimethyl heptanes. The remaining unknowns at 18.875, 18.944, 20.195, 23.437, and 43.735 all have NRRs near 10 and can therefore be identified as aromatics. In fact, the peak at 43.735 is probably 2-methyl naphthalene.

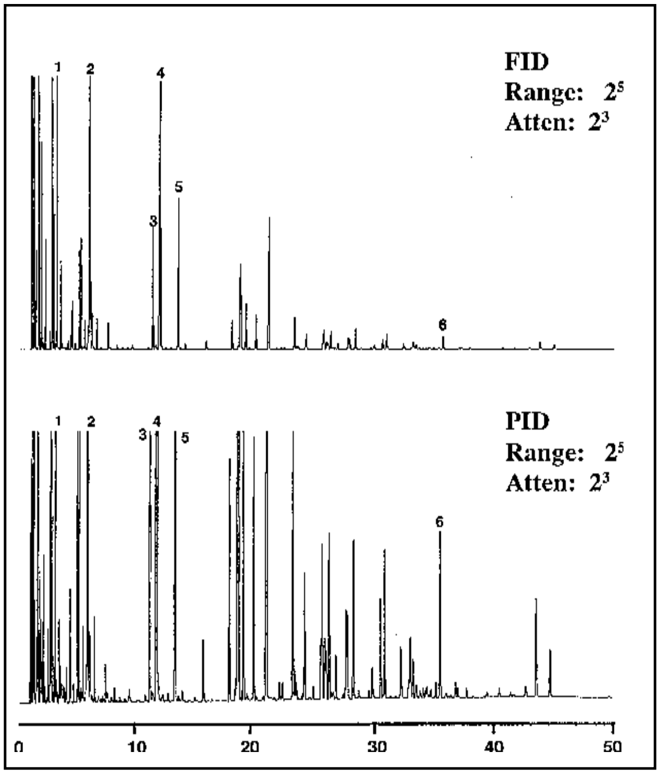

Figure 3. Analysis of Super-Unleaded Gasoline Using PID/FID Series Detector. The Normalized Response Ratios are Presented in Table 4

	PID	FID	FID (Stand-Alone)
Heptane	134310	135565	133860
MIBK	137412	134028	140634
Toluene	145499	146237	143370

Table 3. Number of Theoretical Plates (N_{TH}) for PID/FID and Stand-Alone FID

Ref.#	R.T.	NRR	Compound
	1.539	0.19	Unknown (Butane or i-Butane)
	1.678	0.48	i-Pentane
	1.757	0.71	Pentane
	2.095	0.86	Cyclopentane
	2.124	9.28	MTBE
	2.201	1.12	i-Hexane
	2.346	0.71	Hexane
	2.653	1.27	Unknown (Methyl Alkane)
1	3.215	7.99	Benzene & Cyclohexane
	3.261	2.41	Unknown (Branched Alkane)
	3.387	1.59	Unknown (Methyl Alkane)
	3.624	2.48	Unknown (Branched Alkane)
	3.927	1.06	Heptane
	5.449	3.83	Unknown (Branched Alkane)
	5.608	4.15	Unknown (Branched Alkane)
2	6.336	10.00	Toluene
3	11.544	9.32	Ethyl Benzene
4	12.135	10.90	m,p-Xylene
5	13.678	9.29	o-Xylene
	18.875	9.36	Unknown (Aromatic)
	18.944	9.04	Unknown (Aromatic)
	19.343	13.05	1,3,5-Trimethyl Benzene
	20.195	8.23	Unknown (Aromatic)
	21.283	10.10	1,2,4-Trimethyl Benzene
	23.437	9.35	Unknown (Aromatic)
6	35.720	13.70	Naphthalene

Table 4. Normalized Response Ratios for Super-Unleaded Gasoline Analysis

Another application of this technique is shown in the analysis of low lead aviation gasoline (100 octane) as shown in Figure 4. Table 5 gives the NRRs and peak identification. Benzene and cyclohexane coelute at a retention time of around 3.20 with the column and oven program used for this study. As seen in the table, there is a peak at 3.287 with an NRR of 2.38. Because the NRR matches that of cyclohexane (2.73) and not benzene (10.66), the peak can be confidently identified as cyclohexane. The unknowns at times 2.672 and 3.409 are probably a methyl hexane and a methyl heptane, respectively. The peaks at times 2.749, 3.702, and 4.864 are probably dimethyl hexanes, while the peaks at times 4.924, 5.963, and 6.946 are probably dimethyl heptanes. The peaks at times 5.554, 5.729, and 8.605 are most likely trimethyl heptanes.

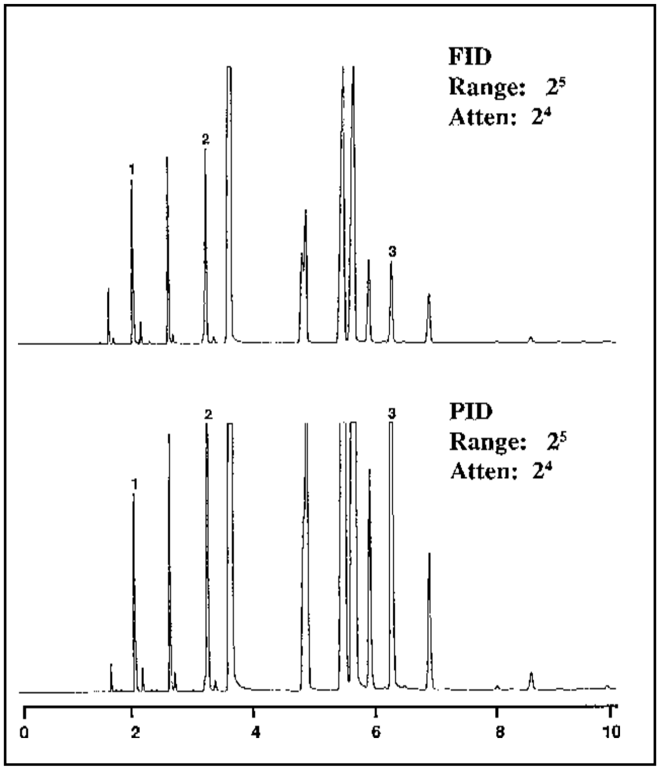

Figure 4. Analysis of Low Lead Aviation Gasoline Using PID/FID Series Detector. The Normalized Response Ratios are Presented in Table 5

Ref. #	R.T	NRR	Compound
	1.691	0.60	i-Pentane
1	2.085	1.34	Cylcopentane
	2.216	1.24	i-Hexane
	2.672	1.63	Unknown (Methyl Alkane)
	2.749	2.44	Unknown (Branched Alkane)
2	3.287	2.38	Cyclohexane
	3.409	1.82	Unknown (Methyl Alkane)
	3.702	2.64	Unknown (Branched Alkane)
	4.864	2.14	Unknown (Branched Alkane)
	4.924	3.15	Unknown (Branched Alkane)
	5.554	4.03	Unknown (Branched Alkane or Alkene)
	5.729	4.37	Unknown (Branched Alkane or Alkene)
	5.963	3.20	Unknown (Branched Alkane)
3	6.333	10.00	Toluene
	6.946	3.29	Unknown (Branched Alkane)
	8.605	4.16	Unknown (Branched Alkane or Alkene)

Table 5. Normalized Response Ratios for Low Lead Aviation Gasoline Analysis

The liquid fraction of a natural gas well has also been evaluated using this technique and is shown in Figure 5, with the NRRs presented in Table 6. There is a peak at retention time 2.698, which is very close to one in Figure 4 at 2.749. But since the NRRs are different, it was concluded that they were two different compounds. In Figure 5 the peak is probably dimethyl butane or 3-methyl pentane. The NRRs for the peaks at 3.194 and 3.247 were used to identify cyclohexane, which elutes at around 3.20 minutes and has an NRR of 2.73. The peak at 3.194 most closely fits this value. The other peak is probably a dimethyl hexane. The peaks at times 3.413, 3.586, 3.651, and 3.710 are methyl hexanes and methyl heptanes. The unknown at retention time 4.593 is probably a dimethyl heptane.

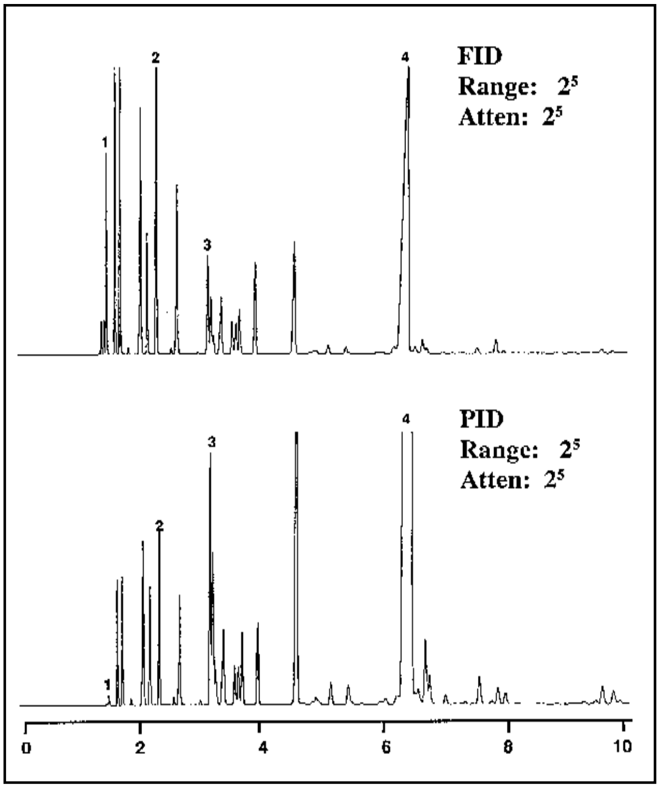

Figure 5. Analysis of the Liquid Fraction of a Natural Gas Well Using the PID/FID Series Detector - Toluene was Added as an Internal Standard for Normalization Purposes

Ref. #	**R.T.**	**NRR**	**Compound**
1	1.554	0.06	Butane
	1.693	0.49	i-Pentane
	1.772	0.35	Pentane
	2.113	0.77	Cyclopentane
	2.220	1.08	i-Hexane
2	2.368	0.66	Hexane
	2.698	0.79	Unknown (Methyl Alkane)
3	3.194	2.91	Cyclohexane
	3.247	3.29	Unknown (Branched Alkane)
	3.413	1.56	Unknown (Methyl Alkane)
	3.586	1.38	Unknown (Methyl Alkane)
	3.651	1.41	Unknown (Methyl Alkane)
	3.710	1.84	Unknown (Methyl Alkane)
	3.964	1.02	Heptane
	4.593	3.93	Unknown (Branched Alkane)
4	6.457	10.00	Toluene (Internal Reference)

Table 6. Normalized Response Ratios for the Liquid Fraction of a Natural Gas Well

A final application is given in Figure 6. It is the determination of jet kerosene. Notice in the FID chromatogram that the primary components are n-alkanes but that most of the smaller peaks are branched alkanes and alkenes. Table 7 gives the NRRs and identification for several of the compounds present. Some possible identifications are made for unknowns in this table.

Conclusion

By combining the PID with the FID in series, compound identification may be made and confirmed in a single GC run. With the direct interface between the PID and FID, the problems of nonstandard fittings and transfer lines are eliminated. It is expected that this technique will be useful for a variety of applications where detection and differentiation of hydrocarbon class are necessary.

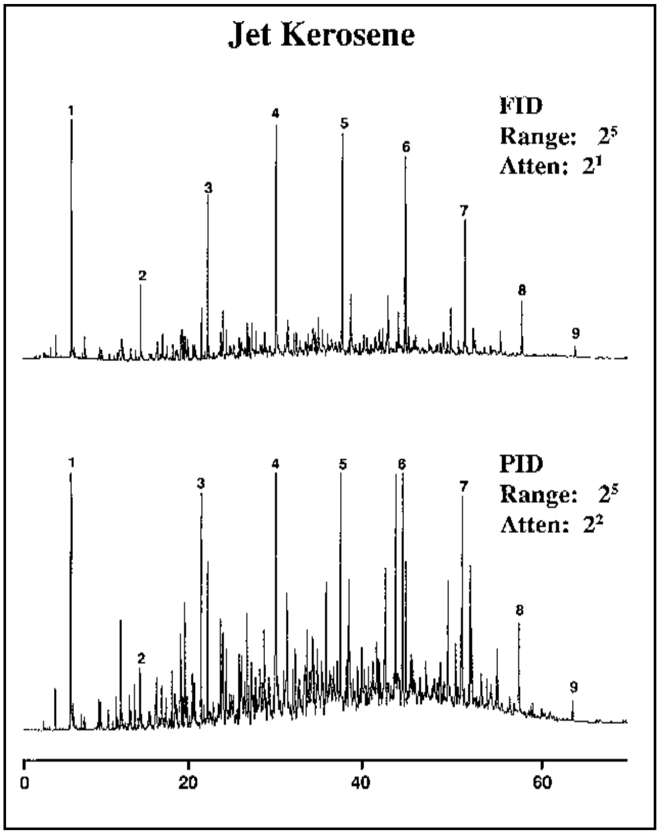

Figure 6. Analysis of Jet Kerosene Using PID/FID Series Detector - Toluene was Added as an Internal Standard for Normalization Purposes

Ref. #	**R.T.**	**NRR**	**Compound**
1	6.337	10.00	Toluene (Internal Reference)
2	14.262	2.04	Nonane
	21.217	9.77	Unknown (t-Butyl Benzene)
3	21.953	2.40	Decane
	23.692	5.61	Unknown (Branched Alkane or Alkene)
	24.064	6.08	Unknown (Branched Alkane or Alkene)
	26.456	8.25	Unknown (C11 Alkene)
4	29.831	3.58	Undecane
	31.130	8.86	Unknown (Alkene or Aromatic)
	34.053	7.37	Unknown (Alkene)
	34.648	4.86	Unknown (Branched Alkane)
5	37.413	3.50	Dodecane
	38.376	5.35	Unknown (Branched Alkane or Alkene)
	42.601	6.62	Unknown (Branched Alkane or Alkene)
	43.753	16.75	Unknown (PAH)
6	44.591	4.00	Tridecane
	49.728	8.63	Unknown (C14 Alkene)
7	51.365	5.59	Tetradecane
	55.317	6.81	Unknown (Branched Alkane or Alkene)
8	57.755	4.03	Pentadecane

Table 7. Normal Response Ratios for Jet Kerosene Analysis

References

(1) Leighton, P. A. *Photochemistry of Air Poll*ution 1960, Academic Press, New York.

(2) Grant, D. W. in Desty (ed). *Gas Chromatog*raphy 1958, Academic Press, New York.

(3) Driscoll, J. N., Ford, J., Jaramillo, L. F., and Gruber, E. T. “Gas Chromatographic Detection and Identification of Aromatic and Aliphatic Hydrocarbons in Complex Mixtures by Coupling Photoionization and Flame-ionization Detectors.” *J. Chromatogr.* 1978, 158: 171–180.

(4) Cox, R. D. and Earp, R. F. “Determination of Trace-Level Organics in Ambient Air by High-Resolution Gas Chromatography with Simultaneous Photoionization and Flame-ionization Detection.” *Anal. Chem.* 1982, 54: 2265–2270.

(5) Kapila, S. and Vogt, C. R. “A gas-tight low-volume photoionization detector for capillary gas chromatography. HRCC CC. J. High Resolut. Chromatogr. Commun. 1979, 2: 536.

OI Analytical's Model 4450 PID/FID is protected under U.S. Patent #4,804,846.

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