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GAS CHROMATOGRAPHIC DETECTION AND IDENTIFICATION OF AROMATIC AND ALIPHATIC HYDROCARBONS IN COMPLEX MIXTURES BY COUPLING PHOTOIONIZATION AND FLAME-IONIZATION DETECTORS

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SUMMARY

A technique has been developed that is based on analyzing the effluent from a gas chromatograph with both photoionization (PID, with 10.2-eV lamp) and flame-ionization (FID) detectors. The relative molar response per mole of carbon (RMR) for the FID is similar for many types of carbon atoms, *e.g.*, aromatic and aliphatic and therefore the FID is used to measure the relative levels of a particular hydrocarbon regardless of the degree of saturation. The RMR for the PID, however, increases with unsaturation. A ten-fold difference is observed between aromatics and alkanes, and the alkene response on the PID is midway between these two classes of compounds. When the PID and FID responses (*i.e.*, peak areas) are normalized to any alkene (*e.g.*, *n*-hexane) and are compared, those compounds with a normalized PID/FID ratio of 2-4 are alkenes, those with a ratio of 5-10 are aromatics and those with similar ratios (<2) are alkanes. Preliminary work on this technique was started with simple hydrocarbon mixtures, then extended to high-molecular-weight heteroatom molecules such as chlorinated and sulfur-based pesticides. Finally, a practical application of this approach was demonstrated with the successful analysis of aromatics in a light hydrocarbon feedstock for a synthetic natural gas plant. This technique should prove useful for analyses (nanogram levels) and for the identification of complex hydrocarbon mixtures.

INTRODUCTION

The differentiation of classes of hydrocarbons has been of concern to many analytical chemists. In air pollution there are significant differences in atmospheric photochemical reactivities with hydrocarbon structure¹. Low-molecular-weight saturated hydrocarbons such as methane and ethane are not photochemically reactive, whereas branched-chain aliphatics (trimethylpentane), olefins and aromatics, in

general, tend to be very active in atmospheric photochemical smog formation.

The aromatic content of fuel is of importance as aromatic hydrocarbons have low heats of combustion and have been associated with aircraft engine maintenance problems related to inefficient combustion. In synthetic natural gas plants, the presence of residual aromatics is an indication that more hydrogen has to be added to the feedstock to complete the processing to methane.

These and similar analyses have, in the past, been accomplished by gas chromatography (GC) using subtractive techniques, whereby one class or group of hydrocarbons have been selectively retained on columns or in traps²⁻⁵. These approaches make chromatographic methods very complex and may lead to problems in reproducibility as column or trapping efficiencies change. It appears that a better, simpler approach would involve the development of a selective detection technique for the classes of compounds. A technique was developed by Grant⁶ about 20 years ago in which a flame-emissivity detector (FED) with a katharometer was used to differentiate between aromatic and aliphatic hydrocarbons. This FED was not commercially available and the technique, unfortunately, has not seen wide usage.

The past decade has seen the development and routine usage of many new element-selective detectors (S, N and P) for GC. The flame-ionization detector (FID), while responding selectively to carbon over other elements, does not differentiate between aliphatic and aromatic carbon linkages. This can make the identification of individual types of hydrocarbons in complex mixtures difficult if S, P, N or halogens are not present to permit identification of a particular hydrocarbon via an element-selective detector.

The photoionization detector (PID) was reported⁷ to be a carbon counter like the FID, with a 35-fold greater sensitivity for aromatics than the FID and a 7-fold greater sensitivity for alkanes such as *n*-hexane. We have observed that with the PID (10.2-eV lamp), this 5-10-fold increase in sensitivity for aromatic over alkane structures was seen even for complex heteroatoms with high molecular weights (300-400 a.m.u.) such as pesticides. As the FID has the same relative molar response per mole of carbon (RMR) for both aliphatic and aromatic carbons⁸ and the PID (10.2-eV source) shows a 5-10-fold difference in sensitivity between aromatics and alkanes, a comparison of the RMRs for a group of hydrocarbons on these two detectors should permit the identification of both the aromatic and aliphatic constituents.

In this paper, we report the results obtained for a series of simple and complex hydrocarbons and a practical application for determining aromatic hydrocarbons in synthetic natural gas feeds by using the PID and FID jointly to identify and quantify classes of hydrocarbons.

EXPERIMENTAL

The results were obtained with the new HNU Systems high-temperature, glass-lined photoionization detector (Model P152-02-HT) with an HNU Systems electrometer. The pesticides were separated on 2 m × 4 mm I.D. glass columns packed with 3% OV-101 on Chromosorb W HP (100-120 mesh) in a Tracor Model 560 gas chromatograph. The aromatic and aliphatic hydrocarbon samples were separated on a 1 m × 4 mm I.D. column packed with 4.5% Carbowax 20M on 80-100-mesh Chromosorb G in an F & M Model 810 gas chromatograph. The chromatograms

were recorded on a Linear Instruments Model 261 recorder. Quantitation was effected with a Shimadzu Model E1A integrator.

The carrier gas was high-purity helium from Matheson Gas Products (East Rutherford, N.J., U.S.A.). Flow-rates were 30 ml/min. A charcoal/molecular sieve trap was incorporated in the carrier gas line to remove hydrocarbon impurities and to keep backgrounds low. This also prevents build-up of hydrocarbons in the flow regulators.

The light hydrocarbon feedstock was analyzed by injecting the sample (0.5 μ l) via a Valco high-pressure sampling valve into a Hewlett-Packard Model 5710 chromatograph. The separation was effected on 3 ft. \times 1/8 in. O.D. Porapak Q. The FID detector on the HP 5710 was run *versus* an HNU Model PI51-01-08 photo-ionization detector. The areas and retention times were taken from a Hewlett-Packard data system.

The sulfur-based pesticides were a gift from the Food and Drug Administration. Stock solutions of sulfur-based pesticides were prepared in *n*-hexane and stored in a refrigerator at -15° to prevent decomposition. For the working solutions, the *n*-hexane was evaporated and the residue dissolved in acetonitrile. The chlorinated pesticides were obtained from Polyscience (Niles, Ill., U.S.A.). The hydrocarbon samples were obtained from Fisher Scientific (Pittsburgh, Pa., U.S.A.).

Solvents were either spectrograde methanol from Aldrich (Milwaukee, Wisc., U.S.A.) or acetonitrile (Resi-Analyzed from J. T. Baker, Phillipsburgh, N.J., U.S.A.). The pesticide samples were prepared in volumetric flasks and transferred to screw-type culture tubes with Teflon-lined caps. The samples (1 μ l) were injected with Hamilton Model 701 syringes using the solvent flush injection technique⁹. This technique was found to provide the most-reproducible results on either the PID or FID with high-molecular-weight compounds.

RESULTS AND DISCUSSION

Many of the earlier workers utilized helium (20.2 eV) or argon (11.7 eV) as the discharge gases for the PID¹⁰⁻¹². When a helium discharge was used, the emphasis placed was on the development of a sensitive detector with a universal response, *i.e.*, to organic (RMR for aromatics = RMR for aliphatics), inorganic and permanent gases. A PID with an *argon discharge was investigated as a detector that had some selectivity for organics over inorganics (permanent gases did not respond)*. With this argon-discharge (11.7-eV) lamp, the RMR response for aromatics was about 30% higher than for alkanes^{11,12}. The lower energy of the 10.2-eV lamp, however, produced an RMR for aromatics that was five times greater than that for an alkane such as *n*-hexane⁷. A plot of the RMR as a function of photon energy for an alkane and an aromatic hydrocarbon (*n*-hexane *versus* benzene) is shown in Fig. 1. These data were calculated from the relative sensitivities and cross-sections in the literature^{7,10,12-15}. As the photon energy was decreased, the RMR for the aromatic hydrocarbon remained constant, while the RMR for the alkane dropped sharply below 11.0 eV. Note that in the 10-eV region, we are at the ionization threshold for alkanes (Table I), but still well above the ionization threshold for aromatics.

Watanabe and co-workers^{16,17} and Chupka and Berkowitz¹⁸ found, in their studies of ionization potentials and efficiencies, that alkanes have very low photo-

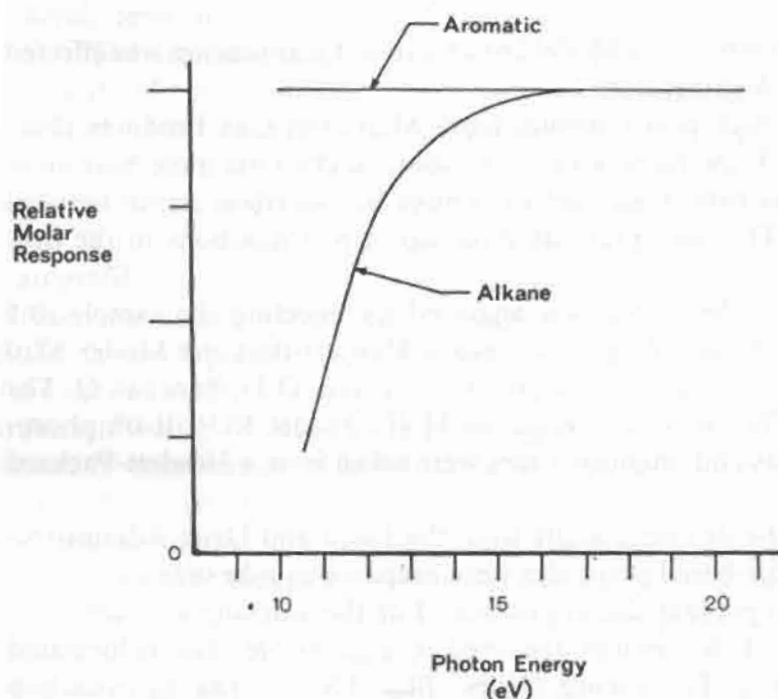


Fig. 1. Relative molar response for an alkane and an aromatic hydrocarbon as a function of photon energy.

ionization yields near their ionization threshold (*ca.* 10 eV for *n*-hexane). Structureless yield curves were found to be typical for alkanes. Watanabe and co-workers^{16,17} attributed these features to the non-localization of the most loosely bound sigma-electron.

The ionization efficiency curves as a function of photon energy for an aromatic (benzene) and an aliphatic hydrocarbon (*n*-hexane) are given in Fig. 2 (ref. 16, 17 and 19). Note that the low RMR for the alkane at 10.2-eV photon energy in Fig. 1 can be directly attributed to the low photoionization efficiency (Fig. 2) for the alkane at 10.2 eV. Similarly, the high RMR for the aromatic hydrocarbon is a result of the high ionization efficiency attained at about 10 eV.

TABLE I
IONIZATION POTENTIALS FOR DIFFERENT CLASSES OF HYDROCARBONS

Class	Compound	Ionization potential (eV)
Alkanes	Isopentane	10.32
	Hexane	10.18
	Cyclohexane	9.88
	Heptane	10.08
Aromatics	Benzene	9.24
	Toluene	8.82
	Xylene	8.45
Alkenes	Propylene	9.73
	Butadiene	9.07
	Cyclohexene	8.90

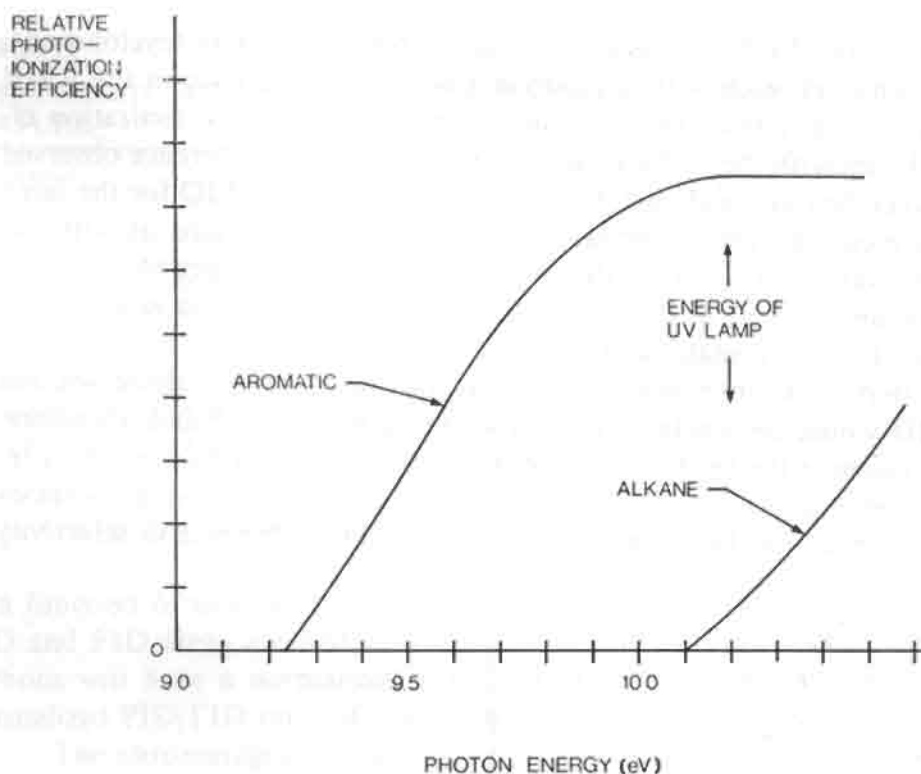


Fig. 2. Photoionization efficiency curves as a function of photon energy for an aromatic hydrocarbon and an alkane.

These photoionization yield curves for benzene, alkylbenzenes, alkenes and cyclic alkenes were all reported to be very similar in that they rose rapidly to maximum values close to the ionization potentials¹⁶. This type of curve was reported¹⁶ to be typical of photoionization involving a pi-electron.

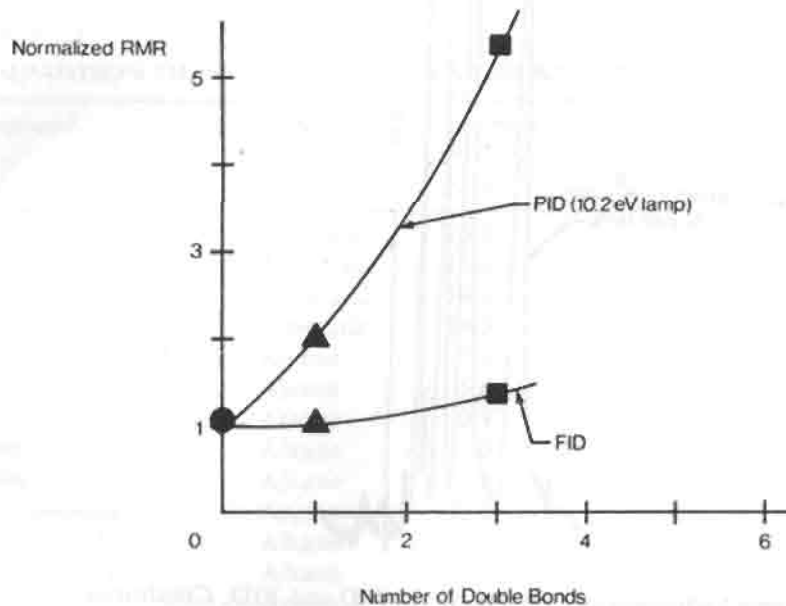


Fig. 3. Comparison of the responses of the PID and FID as a function of the degree of unsaturation. ■ = Benzene; ▲ = cyclohexene; ● = cyclohexane.

The RMR of the PID was determined for three compounds (cyclohexane, cyclohexene and benzene), each with six carbon atoms. The difference in the RMR for these compounds was considerable, as shown in Fig. 3. The low ionization efficiency for the alkanes with the 10.2-eV lamp produces the large difference observed in the RMR between benzene and cyclohexane. The RMR for the FID for the same three compounds measured under similar chromatographic conditions as with the PID showed a relatively flat response with no dependence on the degree of unsaturation. This was not unexpected, as the data given by Dietz⁸ indicate an equal RMR response with the FID for aromatic and aliphatic carbon atoms.

It follows that if an unknown sample were run on these two detectors, the RMR for the FID would be similar for all types of carbon atoms⁸ and, therefore, could be used to estimate the relative concentration of a particular hydrocarbon regardless of its degree of unsaturation. The RMR for the PID is different. It increases with the degree of unsaturation, as indicated in Fig. 3. The difference in selectivity

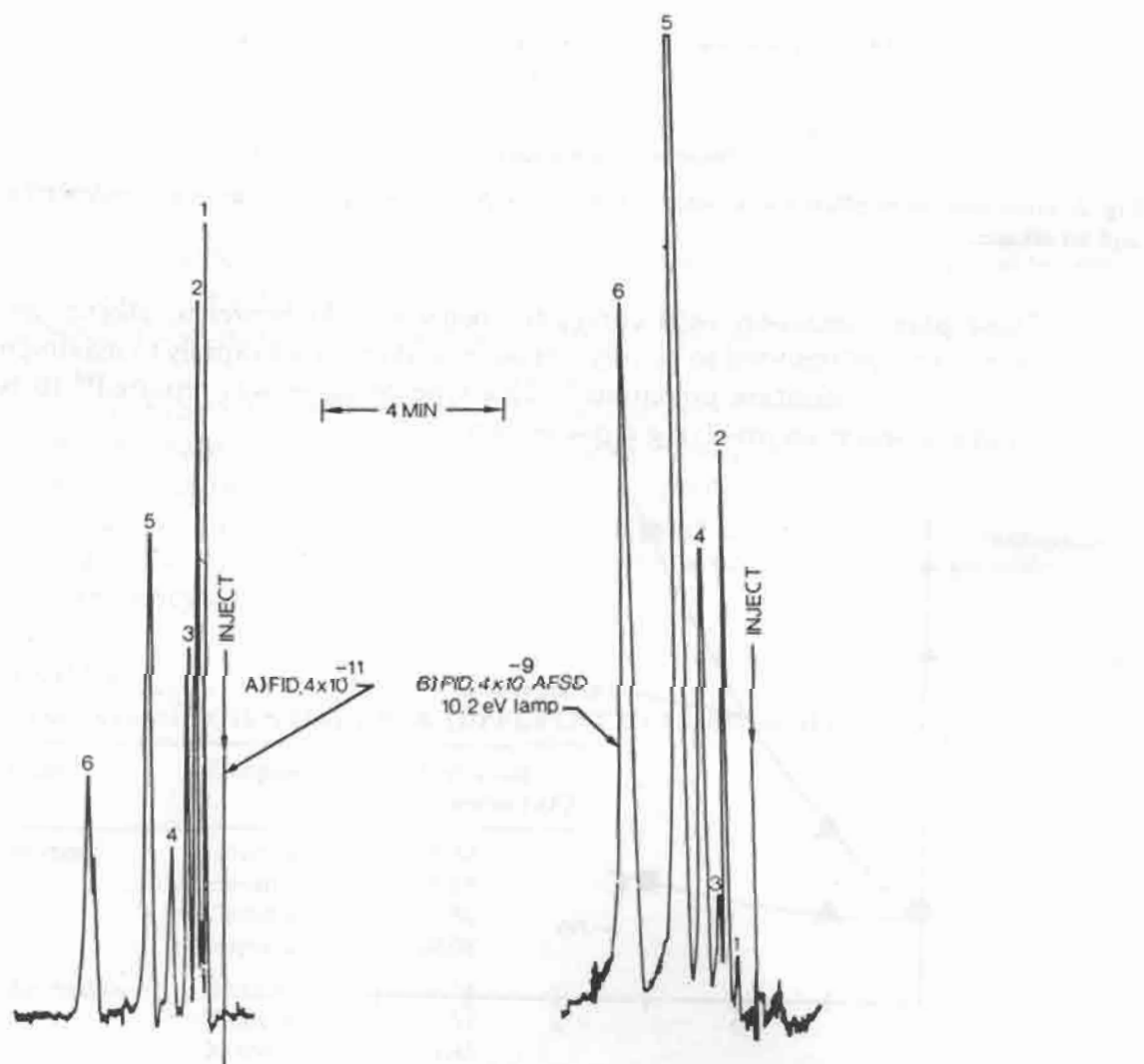


Fig. 4. Chromatograms of simple hydrocarbon mixtures on the PID and FID. Conditions: 1 m \times 4 mm I.D., 4.5% Carbowax on 80-100 mesh Chromosorb G; N₂ flow-rate 45 ml/min; temperature 80°. Hydrocarbon samples: 1 = *n*-hexane; 2 = cyclohexane; 3 = *n*-octane; 4 = *cis*-2-octene; 5 = benzene; 6 = toluene.

TABLE II

NORMALIZED* RELATIVE RESPONSE RATIOS FOR THE SIMPLE HYDROCARBON MIXTURE

Compound	Normalized PID/FID ratio
Hexane	0.25**
Cyclohexane	2.1
Octane	1.0
<i>cis</i> -2-Octene	5.2
Benzene	8.4
Toluene	9.8

* Normalized to octane; 400–600 ng of sample injected.

** This low response for hexane in the PID could not be duplicated.

as a function of unsaturation can then be used as a means of identification. If the PID and FID areas are first normalized to the area of an alkane, aromatic hydrocarbons will have a normalized PID/FID ratio of *ca.* 10 and alkanes will have a normalized PID/FID ratio of approximately 1 (by definition).

The chromatographic separation of a simple hydrocarbon mixture detected with a PID and FID and shown in Fig. 4 illustrates the difference in RMR for these two detectors. The large difference in electrometer attenuation for these two detectors should also be noted. The PID response (10.2-eV lamp) for both alkanes and aromatic hydrocarbons will always be greater than with the FID. The reduced data are given in Table II. The alkanes had normalized PID/FID ratios of <2 and the normalized PID-FID ratio for aromatic hydrocarbons was *ca.* 10. *n*-Hexane showed a considerably lower PID sensitivity than that observed previously⁷, and therefore the results were normalized to *n*-octane. The normalized PID-FID ratio for *cis*-2-octene was

TABLE III

COMPARISON OF NORMALIZED PID/FID RATIOS FOR PESTICIDES

Compound	Type of structure	Normalized PID/FID ratio
<i>p,p'</i> -DDT	Aromatic	16.7
<i>o,p'</i> -DDD	Aromatic	16.6
<i>o,p'</i> -DDT	Aromatic	16.3
<i>p,p'</i> -DDE	Aromatic	14.2
Heptachlor epoxide	Alkene	5.6
Aldrin	Alkene	5.6
α -BHC	Alkane	0.9
β -BHC*	Alkane	1.0
γ -BHC	Alkane	1.3
Chlorobenside	Aromatic	12.0
Endosulfan I**	Alkane	1.0
Endosulfan II	Alkane	2.0
Tetrasul	Aromatic	14.4

* Chlorinated pesticides response normalized to β -BHC.

** Sulfur pesticide response normalized to Endosulfan I.

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<i>p,p'</i> -DDE	Aromatic	14.2
Heptachlor epoxide	Alkene	5.6
Aldrin	Alkene	5.6
α -BHC	Alkane	0.9
β -BHC*	Alkane	1.0
γ -BHC	Alkane	1.3
Chlorobenside	Aromatic	12.0
Endosulfan I**	Alkane	1.0
Endosulfan II	Alkane	2.0
Tetrasul	Aromatic	14.4

* Chlorinated pesticides response normalized to β -BHC.

** Sulfur pesticide response normalized to Endosulfan I.

found to be *ca.* 5, *i.e.*, between the PID/FID ratios for the aromatic and aliphatic hydrocarbons. A similar result was observed for cyclohexene (Fig. 3).

A group of sulfur-based and chlorinated pesticides were investigated in order to determine whether this 10:1 aromatic to aliphatic hydrocarbon selectivity ratio for the PID extended to high-molecular-weight carbon compounds with extensive substitution. The data for the pesticides are given in Table III. The normalized PID/FID ratio for aromatic sulfur-based and chlorinated pesticides varied between 12 and 16, whereas the aliphatic pesticides had normalized PID/FID ratios of 2 or less. Again, the pesticides with double bonds (alkene structures), heptachlor epoxide and aldrin, had normalized PID/FID ratios between the PID/FID ratios for the pesticides with aromatic and alkane structures.

A practical application of this technique as applied to natural gas liquid feed-

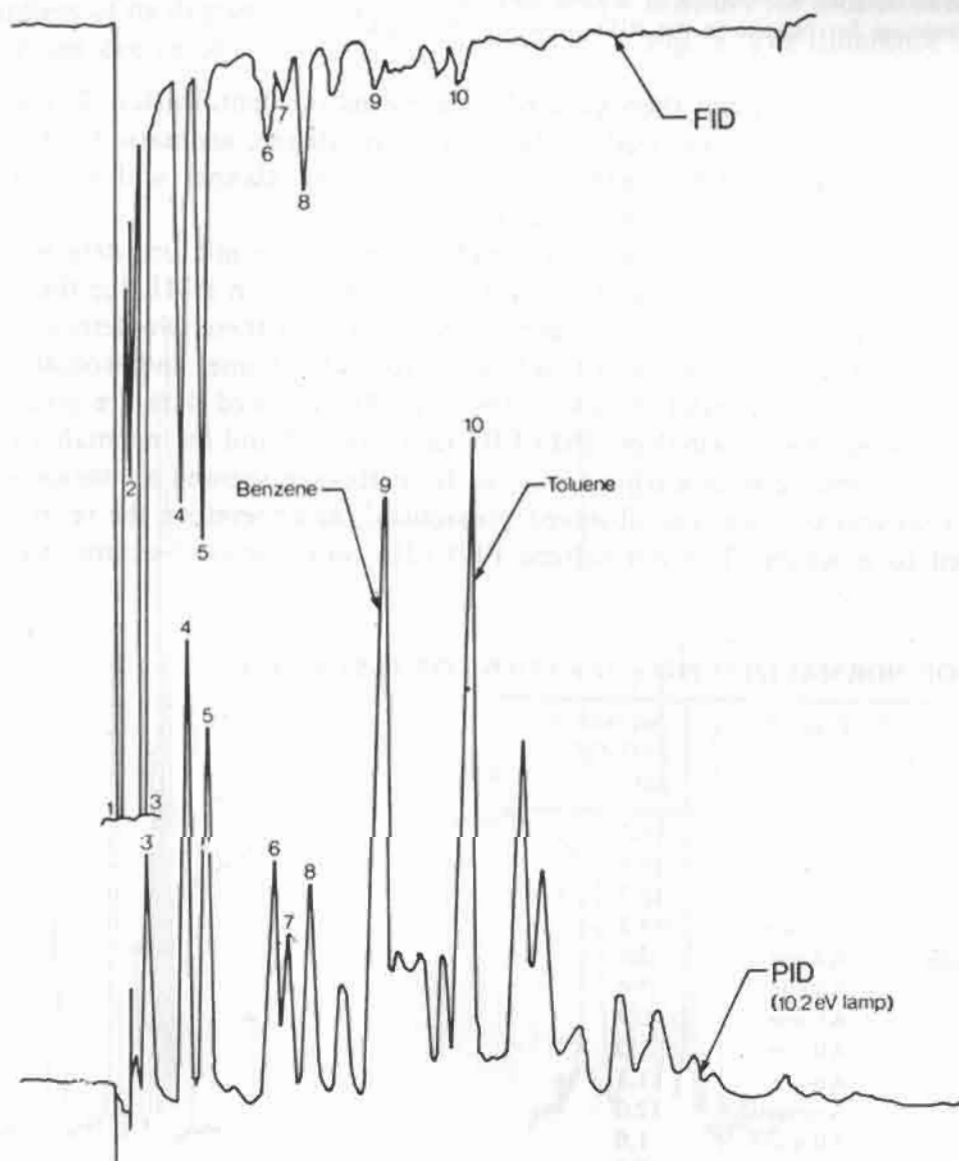


Fig. 5. Comparison of chromatograms of the PID and FID for a light hydrocarbon synthetic natural gas feedstock. Conditions: 3 ft. \times 1/8 in. I.D. Porapak Q column, temperature programmed from 0 to 190° at 8°/min; N₂ flow-rate 36 ml/min, 0.5 ml of liquid petroleum gas injected with high-pressure valve.

stocks is shown in Fig. 5. Note that the low-molecular-weight C_1 - C_3 alkanes are not detected with the PID but aromatics such as benzene and toluene on the PID (peaks 9 and 10) have 20 times their respective areas on the FID. Table IV gives the peak identity and PID/FID ratios for the hydrocarbon peaks. All of the alkanes had normalized PID/FID ratios of *ca.* 2 or less, in good agreement with the data above. The unknowns between peaks 9 and 10 are an aromatic (ratio 10.05) and alkene, respectively, on the basis of their PID/FID ratios. A similar series of aromatic and alkene compounds was observed after the toluene peak.

TABLE IV
LIGHT HYDROCARBON NATURAL GAS FEEDSTOCK ANALYSIS

Peak No.	Compound	Normalized PID/FID ratio	Retention time (min)
4	Isopentane	0.66	1.33
5	<i>n</i> -Pentane	0.54	1.68
	Neohexane	2.22	2.17
6	2-Methylpentane	1.15	2.28
7	3-Methylpentane	1.67	3.06
8	<i>n</i> -Hexane	1.00	3.38
	Methylcyclopentane + 2,2'-dimethylpentane	1.22	3.86
9	Benzene	12.40	4.56
	Unknown	10.05	4.81
	Unknown	3.65	5.58
10	Toluene	8.40	5.92
	Unknown	8.20	7.24
	Unknow	5.60	7.75

CONCLUSIONS

By coupling the PID and FID, subnanogram amounts of aromatic compounds and at least nanogram amounts of alkanes can be detected and the class of compound can be identified. The results reported here were run with three different PIDs on three different chromatographs with different FID designs. All of the data appear to be independent of the PID or FID used for analysis. The versatility and selectivity of this technique has been demonstrated with simple and complex hydrocarbon mixtures and pesticides. We expect it to be generally applicable to many areas of analytical and environmental chemistry where the detection and differentiation of hydrocarbon classes is necessary.

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