

# Analysis of Hydrocarbons in a Hydrogen Atmosphere by Gas Chromatography with Flame Ionization

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The ionization response of hydrocarbons in a hydrogen-atmosphere flame was compared to that of a normal flame ionization detector used in gas chromatography. Absolute response in the hydrogen-atmosphere flame ionization detector (HAFID) was found to be two orders of magnitude less than that of the normal FID. This reduced response is attributed both to oxidation of hydrocarbons in the precombustion zone of the flame and to differences in collecting electrode positions in the two detectors. Relative responses for hydrocarbons in the two flames were found to be similar. Both systems responded to hydrocarbons in a manner proportional to the number of carbon atoms in a test compound. These results do not support the postulate that H-atom cracking in the precombustion zone of a flame is the initial mechanism for the origin of single carbon units in the FID. Relative response similarities did not extend to aromatic or hetero compounds.

Since the introduction of the flame ionization detector (FID) by McWilliams and Dewar in 1958 (1, 2), flame ionization has been the major detection method for hydrocarbons in gas chromatography (GC). The FID enjoys a widespread popularity for a variety of reasons such as durability, low cost, high sensitivity, and a predictable relative response. For hydrocarbons, response is proportional to the number of unoxidized carbon atoms in a molecule (3-9).

The origin of this proportional carbon response is one of the most interesting facets of the FID mechanism. Though it is generally accepted that preionization reactions which reduce hydrocarbons to single carbon units in the precombustion zone of the flame are the origin of this response, it is not at all clear what reactions these might be. Sternberg et al. (5) suggested that single carbon units are produced near the outer boundary of the oxygen free precombustion zone by partial pyrolysis followed by Rice-Herzfeld cracking processes (10) that are initiated by back-diffusion of hydrogen atoms from the main reaction zone. On the other hand, Peeters, Lambert, Hertoghe, and Van Tiggelen (11) have proposed oxidative degradation while, more recently, Blades (12) has argued for H-atom cracking.

Blades claimed evidence for H-atom cracking based on a comparison of four flames in which reaction gases were introduced in a variety of ways: an  $H_2$ -in-air diffusion flame with the hydrocarbons in air, an  $O_2$ - $N_2$  diffusion flame in  $H_2$  with hydrocarbons in  $O_2$ - $N_2$ , a premixed  $H_2$ - $O_2$ - $N_2$ -hydrocarbon flame and a normal FID with hydrocarbons in  $H_2$ . Only when hydrocarbons were placed in a hydrogen-rich precombustion environment did he observe response proportional to the number of carbon atoms.

The hydrogen atmosphere flame ionization detector (HAFID), which has been developed as a GC selective detector for organometallics and silicon containing compounds (13-16), offers a convenient method by which to explore further the effects on ionization when hydrocarbons are introduced into a flame from an oxygen-rich environment. This paper serves to investigate analytical aspects of hydrocarbon response in

Table I. Conditions for Heteroatom Hydrocarbons

test compounds	column temperature, °C	amount injected, g	
		FID	HAFID
fluorobenzene	30	$5 \times 10^{-7}$	$5 \times 10^{-7}$
dipropylsulfide	40	$5 \times 10^{-7}$	$5 \times 10^{-7}$
ethyl benzene	50	$5 \times 10^{-7}$	$5 \times 10^{-7}$
tetraethylsilane	50	$5 \times 10^{-7}$	$5 \times 10^{-7}$
pyridine	65	$5 \times 10^{-7}$	$5 \times 10^{-7}$
chlorobenzene	65	$5 \times 10^{-7}$	$5 \times 10^{-7}$
amyl ether	80	$5 \times 10^{-7}$	$5 \times 10^{-7}$
dodecane	90	$5 \times 10^{-7}$	$5 \times 10^{-7}$
tetraethyllead	90	$5 \times 10^{-7}$	$5 \times 10^{-8}$
ferrocene	120	$5 \times 10^{-7}$	$5 \times 10^{-11}$
nitrobenzene	120	$5 \times 10^{-7}$	$5 \times 10^{-7}$
tetrabutylgermane	140	$5 \times 10^{-7}$	$5 \times 10^{-8}$
tetrabutyltin	165	$5 \times 10^{-7}$	$5 \times 10^{-9}$
aniline	125	$5 \times 10^{-7}$	$5 \times 10^{-7}$
triphenylantimony	250	$5 \times 10^{-7}$	$5 \times 10^{-7}$
triphenylarsine	250	$5 \times 10^{-7}$	$5 \times 10^{-7}$

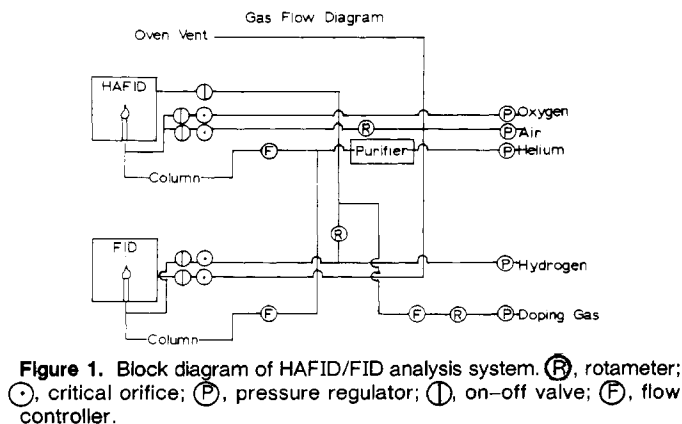
an HAFID and to relate and discuss these results in terms of "equal per carbon" response which is common to normal FID operation.

## EXPERIMENTAL

**Instrumentation.** The rear detector of a Hewlett-Packard 5830-A dual FID gas chromatograph was converted to an HAFID by reversing the hydrogen and oxygen flows so that oxygen flowed through the jet with the column effluent and hydrogen flowed directly into the detector housing. Thus an oxygen-fed flame burned in a hydrogen atmosphere. The detector's collecting electrode, positioned 50 mm above the jet tip, was polarized negatively with a 90-V battery whose positive terminal was connected to a Keithley 417 picoammeter. Signals from the picoammeter were channeled via a Hewlett-Packard Model 18871A A/D converter to a Hewlett-Packard 18850A terminal for printout and peak integration. A more detailed description of the detector can be found in Ref. 14. The FID was operated in the normal mode using conditions recommended in the instrument manual. A 6 ft  $\times$  1/4 in. o.d. (2-mm i.d.) borosilicate column packed with Ultrabond 20 M 80/100 mesh (RFR Corp., Hope, R.I.) was used throughout this study by interchanging it between the two detectors.

**Procedure.** A homologous series of seven *n*-alkanes (Sigma Chemical Co., St. Louis, Mo. 63178) from undecane to heptadecane was chosen as the primary test mixture because the components could be chromatographed and separated easily within the temperature range of the analytical column and because relative responses of alkanes in such a series have been well documented for the FID. Three independent mixtures of these alkanes were prepared in hexane by standard weighing and dilution techniques so the final concentration was approximately 2  $\mu$ g of each alkane in 1  $\mu$ L of solvent. Exact concentrations of each component were employed in the calculations. Three repetitive injections of 1  $\mu$ L of each mixture were used to evaluate the relative response of each detector. A calibration curve for each detector was established with tetradecane. Other test compounds which were employed to evaluate detector response were injected as individual standards and are listed in Table I.

**Operating Conditions.** Both the FID and HAFID were operated at 225 °C while the injection port was held at a constant 200 °C. For the *n*-alkane series with the FID, the oven tem-



perature was programmed to hold an initial temperature of 80 °C for 1 min and then to increase at a rate of 10°/min to a maximum of 155 °C. With the HAFID, it was programmed to hold an initial temperature of 85 °C for 0.5 min and then to increase at a rate of 10°/min to a maximum of 175 °C. For the tetradecane calibration curves, the column was operated isothermally at 100 °C. Individual isothermal operating temperatures for other test compounds are reported in Table I.

Detector gas flows for the FID were 240 mL/min of air and 30 mL/min of hydrogen. For the HAFID they were 120 mL/min of air, 150 mL/min of oxygen, and 1600 mL/min of hydrogen which was doped with approximately 25 ppm of silane. For both detector studies, helium was used as the carrier gas at a flow rate of 20 mL/min. A block diagram of the gas flow design is given in Figure 1.

**Calculations.** Effective carbon numbers (ECN) were determined using the following relation

$$ECN = N_s \frac{R_x W_s M_x}{R_s W_x M_s} \quad (1)$$

where  $N_s$  is number of carbon atoms in the standard,  $R_s$  and  $R_x$  are the area responses of the standard compound and the test compound, respectively,  $W_s$  and  $W_x$  equal the amount of standard and test compound injected, and  $M_s$  and  $M_x$  are the molecular weights of the two compounds. For the alkane mixtures, a series of ECN calculations was made using each of the components in turn as an internal standard. For the individual injections of the other test compounds, dodecane was chosen as an external standard.

The effective carbon number contribution (ECNC) is simply

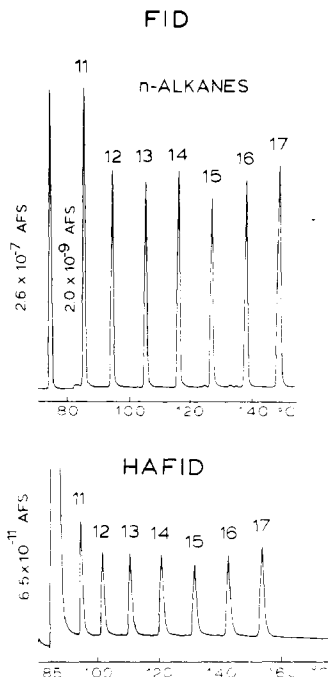
$$ECNC = ECN/N_x \quad (2)$$

where ECN is the value calculated from above and  $N_x$  is the number of carbon atoms contained in the test compound.

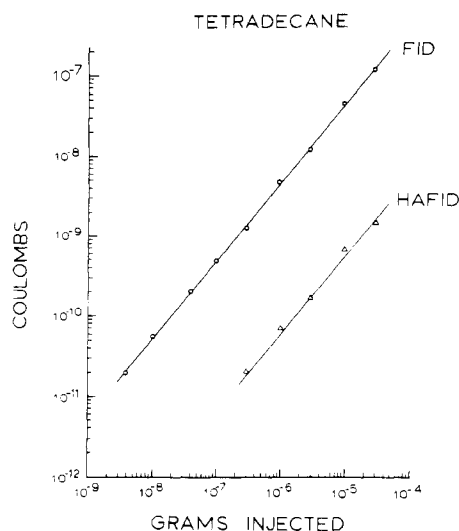
## RESULTS AND DISCUSSION

Figure 2 contains two typical chromatograms of a test mixture of *n*-alkanes, one obtained with a flame ionization detector and the other with a hydrogen atmosphere flame ionization detector. From simple visual inspection, two conclusions which are quantified in this paper become qualitatively obvious. First, the HAFID is less sensitive than the FID to hydrocarbons since the response in amperes is noticeably lower in the HAFID chromatogram than in the FID chromatogram. Second, the pattern in both chromatograms is similar, indicating that relative response for hydrocarbons is similar. The remaining figure and tables simply illustrate these two observations in more detail.

Figure 3 represents calibration curves for tetradecane in both detectors. As was expected, the FID response was linear over several orders of magnitude with a minimum detectable limit below the nanogram range and a sensitivity of 0.90 C/mol. This is a reasonable value, although not as large as is often reported, since no effort was made to optimize the FID response. The HAFID on the other hand exhibited a reduced sensitivity of 0.013 C/mol with a minimum detectable



**Figure 2.** Typical temperature programmed chromatograms of *n*-alkane mixture with FID and HAFID detection



**Figure 3.** HAFID and FID calibration graphs for tetradecane

limit in the microgram region and a linear calibration curve of only two orders of magnitude.

Reduced HAFID hydrocarbon sensitivity, which is desirable because of the selective nature of the detector, can be attributed to both the position and potential of the collecting electrode relative to that in the FID and to the presence of oxygen in the precombustion zone of the flame. In the FID the electrode height and potential have been optimized to collect a maximum amount of ions from the detector, thus the collector consists of a cylinder whose orifice is placed close to the flame with a potential of +400 V relative to the jet tip. The HAFID, on the other hand, utilizes a low surface area pin-head electrode placed 5 cm above the jet tip with a potential of only -90 V. Negative potential attracts slower moving positive ions (presumably  $H_3O^+$ ) with a reduced potential gradient allowing more opportunity for ions to neutralize by interaction with negative ions and electrons or by diffusion to the walls of the detector. Since oxygen is mixed with the column effluent, the ionization efficiency of hydrocarbons in the HAFID is further reduced with respect to the

Table II. Effective Carbon Numbers for *n*-Alkanes from FID

compound	standard used							av. of six
	11	12	13	14	15	16	17	
undecane	11.00	10.61	10.91	10.48	11.10	10.77	10.50	10.73
dodecane	12.45	12.00	12.34	11.85	12.56	12.18	11.87	12.21
tridecane	13.14	12.68	13.00	12.51	13.26	12.86	12.53	12.83
tetradecane	14.71	14.19	14.58	14.00	14.85	14.39	14.02	14.46
pentadecane	14.87	14.34	14.74	14.16	15.00	14.55	14.19	14.47
hexadecane	16.35	15.77	16.21	15.57	16.50	16.00	15.59	16.00
heptadecane	17.84	17.20	17.68	16.97	18.00	17.45	17.00	17.52
av. dev.	2.56	2.05	2.13	2.60	3.24	1.88	2.49	2.20

Table III. Effective Carbon Numbers for *n*-Alkanes from HAFID

compound	standard used							av. of six
	11	12	13	14	15	16	17	
undecane	11.00	10.63	10.99	10.59	11.26	10.75	10.54	10.79
dodecane	12.42	12.00	12.41	11.95	12.71	12.14	11.89	12.25
tridecane	13.03	12.60	13.00	12.54	13.34	12.75	12.49	12.79
tetradecane	14.56	14.07	14.55	14.00	14.90	14.23	13.94	14.37
pentadecane	14.67	14.18	14.66	14.12	15.00	14.34	14.06	14.34
hexadecane	16.37	15.82	16.36	15.75	16.75	16.00	15.68	16.12
heptadecane	17.76	17.16	17.75	17.08	18.18	17.35	17.00	17.55
av. dev.	2.40	2.06	2.34	2.23	4.13	1.92	2.54	2.38

FID because of oxidation of carbon in the precombustion zone of the flame. Precombustion oxidation has been observed in the FID when hydrogen which is normally mixed with column effluents prior to combustion is doped with small amounts of oxygen (5).

The amount of hydrocarbon required for detection in the HAFID is not only a function of reduced sensitivity but also increased background ionization. The ability to detect small amounts of hydrocarbons by the FID can be attributed in part to low background ionization which in turn leads to low noise. Background ionization of a FID is commonly on the order of  $1 \times 10^{-14}$  A and even that is often attributed to hydrocarbon impurities in the flame gases. The HAFID on the other hand has a background ionization of  $1 \times 10^{-9}$  A, depending on the configuration of the detector. This rise in background current concomitantly increases noise, requiring a larger quantity of compound for minimum detection.

In the past when "equal per carbon" response has been demonstrated in the FID, test compounds with less than 10 carbon atoms have been used primarily and *n*-heptane was often the standard. A homologous series of *n*-alkanes from C-5 to C-10 would commonly result in an average per cent deviation from theoretical "equal per carbon" response of about 2%. When hexadecane was used as a standard in the studies reported in this paper, a homologous series of *n*-alkanes from C-11 to C-17 yielded an average per cent deviation from theoretical "equal per carbon" response in the FID of 1.88%. However, the per cent deviation varied with respect to the standard chosen with pentadecane producing a value of 3.24%. Table II shows the results of this homologous series when each of the components of the series was used in turn as the standard. The column headed "Average of Six" gives the average ECN values for each of the test compounds using all of the components as standards except the one being reported. The average per cent deviation from theoretical for this column was 2.2%.

Table III gives HAFID response values for the test mixture in which undecane yields an average ECN of 10.79; dodecane, 12.25; tridecane, 12.79; tetradecane, 14.37; pentadecane, 14.34; hexadecane, 16.12; and heptadecane, 17.55. The average per cent deviation for this series was 2.38%. These results indicate that the HAFID exhibits an "equal per carbon" response

Table IV. Effective Carbon Number Contribution Values for *n*-Alkanes

compounds	HAFID	FID	HAFID/FID
undecane	0.98	0.98	1.00
dodecane	1.02	1.02	1.00
tridecane	0.98	0.99	0.99
tetradecane	1.03	1.03	1.00
pentadecane	0.96	0.96	1.00
hexadecane	1.01	1.00	1.01
heptadecane	1.03	1.04	0.99

similar to that seen in the FID.

This similarity between the FID and the HAFID is more dramatically demonstrated in Table IV. ECNC values are calculated from each of the average ECN values in Tables II and III. All ECNC values are approximately 1.00 ranging from a low of 0.96 for pentadecane to a high of 1.04 for heptadecane. Moreover, when an ECNC value appears low in the FID, it also appears low in the HAFID, while high values in the FID are matched by high values in the HAFID. Ratios of HAFID to FID ECNC values in each case equal  $1.00 \pm 0.01$ . Such precision between the two detection methods indicates that the major fraction of deviation from theoretical "equal per carbon" response occurs during sample and standard preparation processes and is not a function of variations in flame response nor in variations of injection procedure.

The similarity observed here in the relative responses of hydrocarbons within each of the detectors is important because in the precombustion region of the flame where "equal per carbon" response is thought to originate the flame systems are considerably different. In the FID, this region consists primarily of hydrogen plus nitrogen while in the HAFID it is made up of oxygen and nitrogen. To date, the only experimental evidence that is often cited (17-22) to support a theory of hydrogen-atom cracking of hydrocarbons as the initial mechanism responsible for producing single carbon units prior to ionization in the FID is that of Blades (12) where he does not observe carbon proportional responses in an "O<sub>2</sub>-N<sub>2</sub> diffusion flame in H<sub>2</sub>".

An explanation unifying the experimental results reported in this study and in the Blades study remains unclear and will not be attempted in this paper. Perhaps parameter settings

Table V. HAFID/FID Effective Carbon Number Contribution Ratios for Heteroatom Hydrocarbons

compound	
dodecane (standard)	1.00
amyl ether	0.96
tetraethylsilane	1.14
chlorobenzene	2.47
ethyl benzene	2.50
aniline	2.77
triphenylarsine	3.43
nitrobenzene	4.02
fluorobenzene	5.80
dipropylsulfide	6.35
pyridine	8.94
triphenylantimony	$2.37 \times 10^1$
tributylphosphate	$2.89 \times 10^1$
tetrabutylgermane	$2.90 \times 10^1$
tetrabutyltin	$5.09 \times 10^2$
tetraethyllead	$9.78 \times 10^2$
ferrocene	$4.71 \times 10^4$

were considerably different when Blades compared responses of low molecular weight (C-1 to C-4) hydrocarbons. This study however, does demonstrate that "equal per carbon" response can be observed when the precombustion region of the flame is oxygen rich, reducing the credibility of H-atom cracking as the initial mechanism for the origin of single carbon units in the FID. It should be noted that hydrogen may still be available in the precombustion zone of the HAFID from entrainment or diffusion processes.

Nonalkane hydrocarbon test compounds complicate comparisons between the FID and HAFID. Table V provides HAFID/FID ratios of effective carbon number contributions for a variety of nonalkane compounds with many compounds demonstrating a dissimilar behavior between the two detectors when dodecane is used as the standard. Amyl ether and tetraethylsilane produced the most similar response. The amyl ether response appears reasonable when compared to results obtained with *n*-alkanes since it contains only singly bonded C, H, and O. Tetraethylsilane response may be explained by assuming that silane doping in the HAFID saturates any mechanism in which Si contributes to ionization. For aromatic compounds, response is enhanced in the HAFID relative to that in the FID. Introduction of heteroatoms to hydrocarbons further increases the relative response in the HAFID while such compounds are known to exhibit decreased relative re-

sponses in the FID. The most striking increase in relative response in the HAFID compared to the FID is, of course, observed for organometallics.

Results of this study compare absolute and relative responses between a carbon sensitive FID and a metal sensitive HAFID. Alkanes were shown to have a decreased absolute response while exhibiting a similar relative response in the HAFID. If only one general mechanism is to be proposed for the origin of the "equal per carbon" response in flames, the fact that response in an HAFID is also proportional to the number of carbon atoms contained in an alkane requires that such a mechanism must be possible in both a hydrogen-rich and an oxygen-rich environment in the precombustion zone of the flame. Since relative response similarity does not extend to heterohydrocarbons, a systematic study of these compounds with homologous series and multiple heteroatoms must be undertaken before a better understanding of the decomposition reactions which occur in the precombustion zone of such analytical flames can be attained.

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