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# Determination of percent composition of a mixture analyzed by gas chromatography Comparison of a helium pulsed-discharge photoionization detector with a flame ionization detector

Julie G. Dojahn<sup>a</sup>, W.E. Wentworth<sup>a,\*</sup>, Stanley N. Deming<sup>a</sup>, Stanley D. Stearns<sup>b</sup>

<sup>a</sup>University of Houston, Department of Chemistry, 4800 Calhoun Road, Houston, TX 77024-5641, USA

<sup>b</sup>Valco Instruments Co, Inc., P.O. Box 55603, Houston, TX 77255, USA

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## Abstract

We present the results of a study of percent composition for a mixture which has been separated by gas chromatography and analyzed using helium pulsed-discharge photoionization detection (He-PDPID) and flame ionization detection (FID). FID has long been the means by which the percent composition of a hydrocarbon mixture has been determined since it has been previously established as a “carbon counting device”. However, in this study we present results which show that He-PDPID is more accurate in determining the percent composition of a hydrocarbon mixture and, because it is a universal detection method and can detect compounds that FID cannot, it is also more effective for determining the percent composition of mixtures containing organic compounds with a variety of other functional groups. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Since its introduction in the late 1950s, flame ionization detection (FID) has been the subject of numerous quantitative investigations, mainly with respect to straight-chain hydrocarbons. The theory of using the ionization principle as a means of detection

in gas chromatography was first suggested by Harley and Pretorius [1] and Ryce and Bryce [2]. McWilliam [3–5] have provided an excellent historical review of the development and characteristics of this detector and is credited, along with Dewar [3], with being the first to apply for its patent in 1957.

FID has long been favored by chromatographers because of its high sensitivity, small detector volume, and quantitative proportional output. The linearity of FID has been determined in a number of studies including those by Oster and Oppermann [6],

\*Corresponding author. Tel.: +1-713-7432-727; fax: +1-713-7432-709.

E-mail address: waynewent@aol.com (W.E. Wentworth).

Bromly and Roga [7], Marshall and Crowe [8], and Colson [9]. As a result of these investigations, the flame ionization detector has been found to exhibit a linearity over seven orders of magnitude although this can be affected by detector construction. As a result of their experiments, Bromly and Roga [7] have reported a nonlinear region for hydrocarbons beyond elution rates of 2  $\mu\text{g/s}$  and just prior to detector overload.

There have been many determinations of FID response factors for organic compounds and many studies of factors affecting detector response [10–24]. The flame ionization detector is considered a carbon counting device because its response to hydrocarbons is proportional to the rate of introduction of carbon into the flame [25]. However, it has been shown that molecular structure affects the response; hence, the response factor for each compound is reported as a molar response or as an “effective carbon number”. FID is not universally responsive to all carbon-containing compounds. Notable examples are no response to CO, CO<sub>2</sub>, CH<sub>2</sub>O, and a very weak response to perhalogenated alkanes.

The mechanism by which FID ionizes the sample molecules is still not completely understood. Sternberg et al. [26] gave a detailed analysis of the mechanism of flame ionization detectors, summarizing the earlier work of Calcote [27] who reported that chemi-ionization, rather than thermal ionization, is the means by which the mechanism occurs. Other notable mechanistic studies have been performed by Bulewicz [28] and Blades [29,30]. A more recent study by Holm and Madsen [31] has shown that all hydrocarbons are quantitatively converted to methane in the cooler inner cone region of the flame prior to the combustion process in the outer portion of the flame. Unsaturated hydrocarbons are hydrogenated prior to the splitting of C–C bonds and thus the hydrocarbons go through this methanation prior to combustion. Holm and Madsen claim that this quantitative formation of methane explains the equal response per carbon observed for the hydrocarbons. However, carbon atoms bonded to O or N atoms do not undergo quantitative conversion to methane and molecules containing O or N do not give a response proportional to the number of C atoms.

The mechanism of pulsed discharge photoionization detection (PDPID) is reasonably well under-

stood and has been described in detail [32]. Helium pulsed-discharge photoionization detection (He-PDPID) is capable of ionizing all compounds which have ionization potentials lower than 17.5 eV and, unlike FID, it appears to have a universal response with the one known exception of Ne. The molar response of PDPID can be approximated by the number of electrons whose ionization energies are less than the photoionization energy emanating from the pulsed discharge [32]. Gill and Hartmann [33] have previously summarized the characteristics of several types of ionization detectors currently used in gas chromatography at that time and have made an in-depth comparison among them.

The idea of using two gas chromatographic detectors together in series or parallel is not new. The flame ionization detector and photoionization detector have been coupled by Driscoll et al. [34], by Cox and Earp [35], and by Bengård and Colmsjö [36]. Driscoll [37] has reported that PID can also be used as a carbon counter and notes that PID shows a greater sensitivity than FID for both aromatics and alkanes.

The agreement/disagreement of the calculated percent composition with the known composition will be a measure of the constancy of the mass dependent response factors. The objective of this present study is to compare the constancy of the mass dependent response factors of FID and He-PDPID. The detectors are connected in series so the same sample passes through both detectors. He-PDPID is essentially non-destructive and the added He discharge gas (~24 ml/min) matches the N<sub>2</sub> conventionally added prior to FID to eliminate dead volume in the detector. Furthermore, because FID is mass sensitive and not concentration sensitive, the He make-up gas from the PDPID system does not affect FID sensitivity.

Conventionally the FID response is used to determine the percent composition of a mixture by measuring the area under each of the peaks and assuming the percent area for a peak is the percent composition based upon mass. The basic assumption inherent in this calculation is that the mass dependent response factors are equal for all compounds in the mixture. In this study we have carried out these percent composition calculations with both FID and He-PDPID. The mean peak areas for compounds in

eight different mixtures are compared with the calculated values of the percent composition by mass for those compounds.

## 2. Experimental

The separations were carried out with a Hewlett-Packard (HP) 5880A gas chromatograph connected to a 5880 Series A gas chromatograph terminal. The FID system was a 0.18 in. I.D. jet and the He-PDPID system was built at the University of Houston and constructed as shown in Fig. 1 (1 in.=2.54 cm). The basic design of the He-PDPID system uses a concentric arrangement of alternate insulators and electrodes in the ionization region. The internal diameter of the He-PDPID system used in this study is 2 mm vs. 3 mm in the commercial detector.

The discharge region of the He-PDPID system was constructed from a 1/8 in. stainless steel “T”. Through the top fitting, a 0.25 mm O.D. molybdenum wire, which serves as the ground, was held in place using a PTFE ferrule. The high voltage discharge electrode consisted of 0.25 mm O.D. molybdenum wire sealed inside a hollow quartz tube using a polyimide sealing resin. Molybdenum was chosen as the wire for the electrode and ground since it has been found to be virtually unreactive towards helium and other inert gases. The high voltage discharge electrode was connected to a 12 V E-30

ignition coil (Borg-Warner) and its ancillary power supply as well as to the pulse generator.

The hollow quartz tube containing the molybdenum wire was inserted through the bottom port in the “T” assembly and held in place by a PTFE ferrule. The distance from the end of the ground electrode to the end of the high voltage electrode was approximately 2 mm which is equivalent to the inside diameter of the ionization region. A small solid glass rod held by a PTFE ferrule was inserted through the side opening in the “T” and served as the viewing port as well as to seal the chamber. The “T” assembly was sealed to a quartz spacer by a gold “O” ring which was set into a groove scored into the assembly. The distance from the ionization region to the bias electrode was 2.3 cm.

The body of the He-PDPID system was housed in the cavity of a stainless steel heating block which was maintained within a temperature range of 114 to 120°C to prevent sample condensation. The bias and collector electrodes were separated by quartz insulators and were sealed to those insulators by gold “O” rings. Selectro type connectors were inserted through holes drilled into the heating block so that they could make contact with the electrodes.

The pulsed discharge was generated using electronic components designed and built by the electronics shop at the University of Houston. The discharge parameters were set at a 220  $\mu$ s pulse spacing and a 28  $\mu$ s pulse width during which the d.c. current was applied. The d.c. potential is variable with a maximum value of 20 V and was adjusted to make the discharge the most stable. A 280 V negative bias potential was applied to the coil to direct the photoinduced current towards the collector electrode.

The electric current in the cell was measured at the collector electrode with a custom designed electrometer (Valco Instruments, Houston, TX, USA) which provides a fixed gain of  $2 \cdot 10^8$ . The electrometer collection circuit consists of a DT-2770 (Data Translation, Marlboro, MA, USA) interfaced to a DT-2802-4 A/D Intel 486 motherboard. The A/D interface board was set to a digital resolution of 19 bits and a sampling frequency of 20 Hz [38]. Data analysis was performed using EZ Chrom, Version 5.2 (Scientific Software).

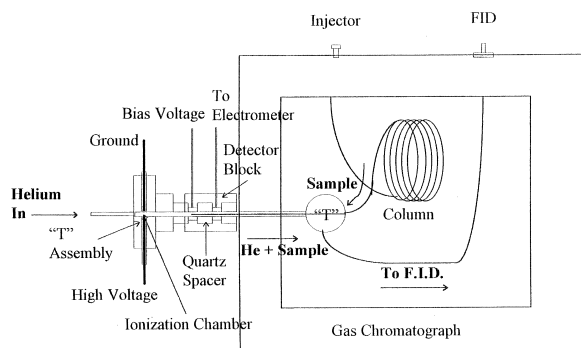


Fig. 1. Block diagram of gas chromatographic system using He-PDPID and FID connected in series (not drawn to scale). Column is 60 m  $\times$  0.25 mm with a poly(dimethylsiloxane) bonded phase of 1  $\mu$ m thickness.

For all of the analyses, the samples were injected via a liquid injection port which was maintained at 200°C and was split using a split injection valve at a ratio of 88:1. The samples passed through a poly(dimethylsiloxane) column (Supelco, Bellefonte, PA, USA) which was 60 m×0.25 mm I.D. and had a bonded phase of 1 µm thickness. The carrier gas used was 99.999% UHP grade Helium (Air Liquide, Houston, TX, USA) which was further purified by passing it through a gas purifier (Valco Instruments) operated in the “bake-out” mode at 400°C. The helium flowed through the column at a rate of 0.856 ml/min. The end of the column was positioned close to the bias electrode so that eluents from the column, flowing counter to the helium flow from the discharge zone of the PDPID system, were ionized by the high energy photons from the helium discharge [38]. The bias electrode repelled the resulting electrons towards the collector electrode.

The helium entering the He-PDPID system was 99.999% UHP grade (Air Liquide) which was further purified by passing it through two gas purifiers (Valco Instruments) connected in series and operated as described above. The helium flowed through the discharge region of the PDPID system at approximately 24 ml/min.

The helium carried the sample compounds out of the PDPID system and directly into the FID system via a 1/16 in. O.D.×0.02 in. I.D. stainless steel tubing and 0.32 mm fused-silica transfer lines. Since He-PDPID is non-destructive, this served not only to provide sample to the flame ionization detector but also to provide a make-up gas and combust the compounds. This type of series arrangement was first described by Bengård and Colmsjö in 1992 [36].

FID was operated at 200°C with a hydrogen flow-rate of 50 ml/min and an air/make-up gas flow-rate of 320 ml/min. These flows were previously determined to provide the optimum sensitivity for this detector under the conditions specified [38,39].

Initially, each of the compounds used in these analyses was chromatographed separately to determine its purity. A reproducibility study was also performed using five different solutions of mixture 1 which consisted of benzene, toluene, 1-octyne, chlorobenzene, *m*-xylene, *o*-xylene, cumene, bromobenzene, and 1,2-dichlorobenzene. Each solution was

chromatographed five times. This was done to determine the error in the analysis caused by variations in making up the solution.

The eight mixtures analyzed were composed of approximately equal molar amounts of each compound and were made using volumetric glassware. Each mixture contained seven to 10 compounds which represented a variety of organic functional groups and was made up in 25 ml amounts and except for mixtures 7 and 8, the make-up compound was *n*-dodecane. For mixture 7 diethyl ether was used as the make-up compound because of difficulties with the solubility of some of the compounds in that mixture. The make-up compound for mixture 8 was *n*-pentane because *n*-dodecane was one of the compounds of interest. Each mixture was made fresh on the day it was to be chromatographed and was placed into a 2.5-ml vial which was then sealed using a rubber septum. Injection amounts varied with mixtures 1, 2, 3, 4, and 5 being injected in 0.4-µl quantities while mixtures 6, 7, and 8 were injected at a volume of 0.2 µl. The number of nanograms detected for each component ranged between 15.5 and 269.3. Each mixture was chromatographed a total of five times.

The gas chromatograph oven was temperature programmed (if necessary) for complete separation of each mixture. Table 1 gives a summary of the temperature programs used.

Confirming analyses were performed on mixtures 1 and 6 at the Dow Chemical Company's research facility in Freeport, TX, USA. For these analyses, a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard 7673 GC/SFC autoinjector was used. The column was a Supelco 50 m×0.32 mm, 1 µm DB-1. The inlet pressure was set at 16 p.s.i., the split ratio at 88:1 and the column flow at 1.3 ml/min (1 p.s.i.=6894.76 Pa). The linear velocity through the column was determined to be 26 cm/s. Detector and injector temperatures were set at 200°C with the make-up gas to the FID system being 99.999% UHP helium. A 0.2-µl injection was used for both mixtures, with mixture 1 being chromatographed isothermally at 125°C while the temperature program for mixture 6 was set as previously described. The data were collected and interpreted using HP ChemStation software.

Table 1  
GC temperature programs for compound mixtures

Mixture	Initial temperature (°C)	Time at initial temperature (min)	Ramp (°C/min)	Final temperature (°C)	Time at final temperature (min)
1	135	15	0	135	0
2	135	12	0	135	0
3	110	8	10	135	25
4	110	10	10	150	20
5	110	10	10	150	17
6	110	7	15	180	23
7	110	7	15	190	35
8	75	10	15	200	35

### 3. Results and discussion

A linearity study was performed for this detector using the compounds which are contained in mixture 1 and described previously. The detector was found to be linear for these compounds over a range of five orders of magnitude. To evaluate the ability of FID and He-PDPID to quantitatively determine the percent composition of a mixture, we must calculate the standard deviation for the determination of each component in the mixture, which in turn, will be used to calculate the error in the chromatographic analysis. The error in the solution preparation is also determined. Mixture 1 was used for this analysis and

five separate solutions were prepared. Each solution was injected five times to evaluate the error in the chromatographic analysis which also includes the variance in the two detectors. The data were collected for each solution and recorded in tables such as Table 2. The percent area was evaluated using the software for each chromatogram. The mean of the percent area for the five chromatograms is shown in Table 2 using FID and He-PDPID. These will be compared to the actual percent composition later in the paper. The standard deviation (SD) of the mean percent area for the five chromatograms is shown for each of the detectors. Note that the standard deviations range from ~0.04 to 0.46 which are small

Table 2  
Repeatability of area% versus % (w/w) composition for mixture 1

Compound	Purity	Mass (ng)	% Composition in mixture	FID			He-PDPID		
				Mean %area	SD	RSD (%)	Mean %area	SD	RSD (%)
Benzene	0.998	20.652	8.031	11.49	0.458	3.990	9.15	0.377	4.116
Toluene	0.987	23.251	9.042	11.92	0.137	1.151	10.32	0.159	1.545
1-Octyne	0.951	28.279	10.997	13.25	0.052	0.390	13.81	0.136	0.986
Chlorobenzene	0.965	28.997	11.276	9.72	0.044	0.453	10.04	0.042	0.417
<i>m</i> -Xylene	0.983	26.932	10.473	12.59	0.081	0.643	11.73	0.070	0.597
<i>o</i> -Xylene	0.946	25.644	9.972	12.15	0.096	0.787	11.33	0.076	0.670
Cumene	0.985	30.757	11.960	12.29	0.120	0.978	11.88	0.099	0.835
Bromobenzene	0.966	39.244	15.261	8.46	0.107	1.259	9.64	0.122	1.267
1,2-Dichlorobenzene	1.000	37.820	12.987	8.13	0.194	2.389	12.10	0.364	3.005
Total			99.999						
Mean RSD (%)						1.338			1.344

compared to area percents of around 10%. The relative percent standard deviation of the mean percent area is given in the next column for each of the detectors and these range from 0.3 to about 4%. This is the kind of reproducibility expected from a gas chromatographic analysis. Note that the mean percent standard deviation using He-PDPID and FID are coincidentally both 1.34%. In general the precisions of the detectors are comparable with an average mean relative standard deviation (RSD) of less than 1.4%. As will be noted later, analysis of other mixtures also gives comparable precision for FID and He-PDPID with the error in He-PDPID slightly less than that for FID.

Table 3 presents a summary of the results for the five different solutions. The chromatographic error for each component in solution of mixture 1 was determined from Eq. (1):

$$SD_c = \left[ \frac{\sum_{j=1}^m \sum_{i=1}^n (X_{ij} - \bar{X}_j)^2}{m(n-1)} \right]^{0.5} \quad (1)$$

where  $n$  = the number of chromatographic runs for each solution and  $m$  = the number of solutions. The subscript  $i$  references a single injection within a solution while the subscript  $j$  references the solution number. Therefore,  $X_{ij}$  represents the peak area percent for a compound in solution  $j$  for one injection  $i$  and  $\bar{X}_j$  represents the mean peak area percent for that compound in solution  $j$ . In the denominator,  $m(n-1)$  refers to the number of degrees of freedom and for these experiments,  $m=5$  and  $n=5$ . Since one degree of freedom is lost for the mean of each of the five solutions, the total degrees of freedom are 20.

This error,  $SD_c$ , results from detector variation and

Table 3  
Reproducibility: comparison of five different solutions of mixture 1

Compound	He-PDPID						Chromatographic error ( $SD_c$ )	$SD_{xj}$	Solution error ( $SD_{sol}$ )
	He mean <sub>1</sub> %area	He mean <sub>2</sub> %area	He mean <sub>3</sub> %area	He mean <sub>4</sub> %area	He mean <sub>5</sub> %area	He mean of means			
Benzene	8.851	8.857	9.008	8.790	9.127	8.930	0.310	0.138	0.095
Toluene	10.123	10.110	10.201	10.247	10.306	10.191	0.136	0.084	0.058
1-Octyne	13.693	13.728	13.437	13.700	13.774	13.666	0.115	0.154	0.145
Chlorobenzene	10.091	10.188	10.084	9.979	10.036	10.055	0.081	0.088	0.041
<i>m</i> -Xylene	11.736	11.915	11.701	11.767	11.709	11.770	0.050	0.094	0.082
<i>o</i> -Xylene	11.489	11.360	11.382	11.445	11.326	11.408	0.052	0.066	0.045
Cumene	11.936	11.819	11.883	11.987	11.880	11.918	0.086	0.064	0.051
Bromobenzene	9.680	9.740	9.740	9.745	9.663	9.711	0.113	0.042	0.000
1,2-Dichlorobenzene	12.402	12.564	12.564	12.339	12.179	12.351	0.264	0.169	0.127
Mean error							$\overline{SD_c} = 0.134$	$\overline{SD_{xj}} = 0.100$	$\overline{SD_{sol}} = 0.072$
	FID						Chromatographic error ( $SD_c$ )	$SD_{xj}$	Solution error ( $SD_{sol}$ )
	FID mean <sub>1</sub> %area	FID mean <sub>2</sub> %area	FID mean <sub>3</sub> %area	FID mean <sub>4</sub> %area	FID mean <sub>5</sub> %area	FID mean of means			
Benzene	11.111	11.237	11.382	11.070	11.489	11.242	0.354	0.180	0.086
Toluene	11.753	11.800	11.877	11.924	11.921	11.837	0.120	0.077	0.055
1-Octyne	13.192	13.139	12.987	13.208	13.251	13.144	0.077	0.115	0.110
Chlorobenzene	9.791	9.845	9.760	9.686	9.721	9.744	0.063	0.063	0.056
<i>m</i> -Xylene	12.655	12.787	12.594	12.670	12.590	12.651	0.067	0.081	0.075
<i>o</i> -Xylene	12.364	12.285	12.246	12.322	12.155	12.276	0.080	0.080	0.072
Cumene	12.383	12.218	12.311	12.424	12.285	12.344	0.099	0.084	0.071
Bromobenzene	8.468	8.497	8.513	8.500	8.456	8.496	0.088	0.027	0.000
1,2-Dichlorobenzene	8.283	8.191	8.327	8.194	8.132	8.264	0.139	0.089	0.064
Mean error							$\overline{SD_c} = 0.121$	$\overline{SD_{xj}} = 0.088$	$SD_{sol} = 0.065$

the interpretation variations of the software. The estimated overall chromatographic error or  $SD_c$ , for all compounds in the solution is given by Eq. (2):

$$\overline{SD}_c = \left[ \frac{\sum SD_c^2}{n} \right]^{0.5} \quad (2)$$

where  $n$  = the number of compounds in the mixture. As can be seen from Table 3, the mean repeatability error for all compounds is 0.134 for He-PDPID and 0.121 for FID, again indicating comparable precision using these detection methods.

In order to evaluate if there was a significant error in making up the solutions, the variation of the mean  $\bar{X}_j$  for each component in the solution was evaluated, as shown in Eq. (3):

$$(\overline{SD}_{xj}) = \left[ \frac{\sum (\bar{X}_j - \bar{X})^2}{m - 1} \right] \quad (3)$$

Values for  $\overline{SD}_{xj}$  are shown in Table 3. A mean of five chromatographic runs were used for each solution in order to minimize the contribution from the chromatographic error,  $SD_c$ . The contribution of the chromatographic error to  $\bar{X}_j$  will be:

$$\frac{(SD_c)^2}{5} \quad (4)$$

since there are five chromatographic measurements for each  $\bar{X}_j$ . In addition, there is the possible contribution of the error in making up the solution,  $SD_{sol}$ , and its variance must be included in  $(\overline{SD}_{xj})^2$ . The equation for the variance  $(\overline{SD}_{xj})^2$  is thus given by Eq. (5):

$$(\overline{SD}_{xj})^2 = \frac{\sum (X_j - X)^2}{m - 1} = \frac{(SD_c)^2}{5} + (SD_{sol})^2 \quad (5)$$

Using the values of  $\overline{SD}_{xj}$  and  $SD_c$  for each compound in mixture 1, values of  $SD_{sol}$  were calculated using Eq. (5) and are shown in Table 3. For both detectors the solution error ( $SD_{sol}$ ) is generally less than the chromatographic error ( $SD_c$ ) with the exceptions of 1-octyne and *m*-xylene where the  $SD_{sol}$  is slightly in excess of  $SD_c$ . For both detectors the  $SD_{sol}$  calculated from Eq. (5) for bromobenzene gives the square root of a slightly negative number and is therefore assigned a value of zero. The contribution of the chromatographic error

and the solution error is assessed best by comparison of the average values of these quantities for all components in the solution. For He-PDPID  $SD_{sol}$  is only 0.072 compared to  $SD_c$  of 0.134, and for FID  $SD_{sol}$  is only 0.065 compared to  $SD_c$  of 0.121. Generally the  $SD_c$  quantity is larger than  $SD_{sol}$  and only in the cases when  $SD_c$  is exceptionally small is the  $SD_{sol}$  comparable to  $SD_c$ .

To evaluate the responses of both FID and He-PDPID to different organic compounds, each of eight different mixtures was chromatographed five times and only the peaks of interest were integrated. From this, the peak area percents were determined for each compound. If the response of a particular compound was low, the relative peak area percents for each of the other compounds increased accordingly, since the sum of the percent compositions is 100%.

The absolute difference between the percent composition of the component in the mixture and the experimentally determined mean peak area percent for a given compound in a mixture,  $\Delta_{comp}$ , is defined by Eq. (6):

$$\Delta_{comp} = X_c - X_{sol} \quad (6)$$

where  $X_c$  represents the experimentally determined mean peak area percent and  $X_{sol}$  represents the percent composition in the mixture. The standard deviation for  $\Delta_{comp}$ , and  $SD_{\Delta_{comp}}$  is obtained from the propagation of errors from  $X_c$  and  $X_{sol}$ . The result is:

$$SD_{\Delta_{comp}} = [SD_c^2 + SD_{sol}^2]^{0.5} \quad (7)$$

The error in the  $X_{sol}$  value has previously been determined as  $SD_{sol}$  and the error in  $X_c$  has been identified as  $SD_c$ .

The  $\Delta_{comp}$  values and their associated errors calculated by Eq. (7), are shown in Table 4 for mixture 1. Comparing the  $SD_{\Delta_{comp}}$  values in Table 4 with the  $SD_c$  values in Table 3, one can see that the  $SD_{\Delta_{comp}}$  are only slightly in excess of the  $SD_c$  and, therefore, the  $SD_c$  makes the major contribution to the  $SD_{\Delta_{comp}}$ . For the remainder of the data presented in this paper we will use  $SD_c$  as the expected error in  $SD_{\Delta_{comp}}$ . Most importantly, one should note in Table 4 for mixture 1 that the errors in  $\Delta_{comp}$  and  $SD_{\Delta_{comp}}$  are generally only 5–10% of the  $\Delta_{comp}$  value. Thus we conclude that the  $\Delta_{comp}$  values obtained for the

Table 4  
Deviations of %area from %composition for mixtures 1–4

Compound	%	FID		He-PDPID	
		%Area	$\Delta_{\text{comp}} \pm \text{SD}_{\text{comp}}$	%Area	$\Delta_{\text{comp}} \pm \text{SD}_{\text{comp}}$
<i>Mixture 1</i>					
Benzene	8.03	11.49	3.46±0.45	9.15	1.12±0.38
Toluene	9.04	11.92	2.88±0.14	10.32	1.28±0.16
1-Octyne	11.00	13.25	2.25±0.05	13.81	2.81±0.14
Chlorobenzene	11.28	9.72	1.56±0.04	10.04	-1.24±0.04
<i>m</i> -Xylene	10.47	12.59	2.12±0.08	11.73	1.26±0.07
<i>o</i> -Xylene	9.97	12.15	2.18±0.08	11.33	1.36±0.08
Cumene	11.96	12.29	0.33±0.12	11.88	-0.08±0.10
Bromobenzene	15.26	8.46	-6.80±0.11	9.64	-5.62±0.12
1,2-Dichlorobenzene	12.99	8.13	-4.86±0.19	12.10	-0.89±0.29
			$\Delta_{\text{mean}} = 2.94 \pm 0.21$		$\Delta_{\text{mean}} = 1.74 \pm 0.23$
<i>Mixture 2</i>					
2-Propanol	5.85	9.25	3.40±0.04	9.55	3.70±0.29
Carbon disulfide	4.20	0.00	-4.20±0.00	3.69	-0.51±0.12
3-Pentanone	8.52	11.43	2.91±0.16	9.60	1.08±0.12
<i>n</i> -Heptane	10.01	19.75	9.74±0.21	13.58	3.57±0.41
<i>n</i> -Butyl acetate	11.68	13.00	1.32±0.31	11.57	-0.11±0.65
1,2-Dibromoethane	18.25	5.36	-12.89±0.25	11.43	-6.82±0.30
Tetrachloroethylene	17.19	6.48	-10.71±0.08	16.00	-1.19±0.38
Propyl butyrate	12.43	15.35	2.92±0.26	13.42	0.99±0.40
Cumene	11.87	19.39	7.52±0.34	11.17	-0.71±0.31
			$\Delta_{\text{mean}} = 6.18 \pm 0.24$		$\Delta_{\text{mean}} = 2.08 \pm 0.40$
<i>Mixture 3</i>					
Chloroform	10.87	9.26	-1.61±0.12	8.91	-1.96±0.14
2-Methyl-2-propanethiol	8.40	1.84	-6.56±0.02	10.87	2.47±0.15
<i>tert</i> -Amyl alcohol	8.42	11.51	3.09±0.16	10.42	2.00±0.15
4-Methyl-2-pentanone	9.37	11.96	2.59±0.12	10.22	0.85±0.11
<i>n</i> -Octane	10.48	18.75	8.27±0.41	13.79	3.31±0.24
1-Bromohexane	14.88	11.96	-2.92±0.11	10.25	-4.62±0.11
Hexanenitrile	9.00	13.00	4.00±0.13	12.99	3.99±0.13
Diethyl methyl malonate	15.69	9.85	-5.84±0.21	13.22	-2.47±0.24
Methyl benzoate	12.89	11.86	-1.03±0.27	9.33	-3.56±0.24
			$\Delta_{\text{mean}} = 3.99 \pm 0.23$		$\Delta_{\text{mean}} = 2.80 \pm 0.20$
<i>Mixture 4</i>					
2-Methylbutane	7.68	12.98	5.30±0.63	9.18	1.50±0.25
Dichloromethane	9.68	2.77	-6.91±0.06	7.25	-2.43±0.15
Isopropyl mercaptan	7.95	8.43	0.48±0.17	8.48	0.53±0.21
Propyl formate	9.40	8.60	-0.80±0.17	8.45	-0.95±0.16
Dibromomethane	17.15	10.37	-0.42±0.21	7.63	-9.52±0.11
Butyronitrile	7.53	2.88	-4.65±0.05	10.15	2.62±0.21
2-Methylcyclohexanon	11.66	17.66	6.00±0.20	14.43	2.77±0.20
Methyl enanthate	15.46	17.67	2.21±0.34	17.14	1.68±0.39
1-Octanol	13.50	18.64	5.14±0.53	17.29	3.79±0.47
			$\Delta_{\text{mean}} = 4.25 \pm 0.35$		$\Delta_{\text{mean}} = 2.86 \pm 0.29$



various mixtures are significant, their magnitude being much larger than the associated error.

Fig. 2a and b represent typical chromatograms for mixture 2 which consists of 2-propanol, carbon disulfide, 3-pentanone, *n*-heptane, *n*-butyl acetate, 1,2-dibromoethane, tetrachloroethylene, propyl butyrate, and cumene. The chromatogram presented in Fig. 2a shows the responses for the compounds of interest as detected by FID while Fig. 2b gives the responses for the same compounds using He-PDPID.

One of the most significant differences between the two chromatograms is the lack of a carbon disulfide peak in Fig. 2a. The percent composition of carbon disulfide in the mixture is 4.199%. Experimentally, it is determined by He-PDPID as 3.69%. This is an absolute difference or  $\Delta_{\text{comp}}$  of only 0.513%, indicating that He-PDPID is an excel-

lent means for detecting carbon disulfide. Two other notable differences between the two chromatograms occurs for 1,2-dibromoethane and tetrachloroethylene. A comparison between Fig. 2a and b reveals that He-PDPID gives a larger response to these compounds than does FID. The calculated percent composition for 1,2-dibromoethane in the mixture is 18.250%. He-PDPID produces a chromatographic peak which has a mean area percent of 11.43%, while FID gives a mean area percent of 5.36% for the same peak. This gives a  $\Delta_{\text{comp}}$  value of 6.821% for He-PDPID and 12.89% for FID. While neither value is exceptional, He-PDPID does provide a response which is closer to the actual percent composition. In the case of the tetrachloroethylene, the percent composition in the mixture is 17.19%. The mean area percent for that compound as de-

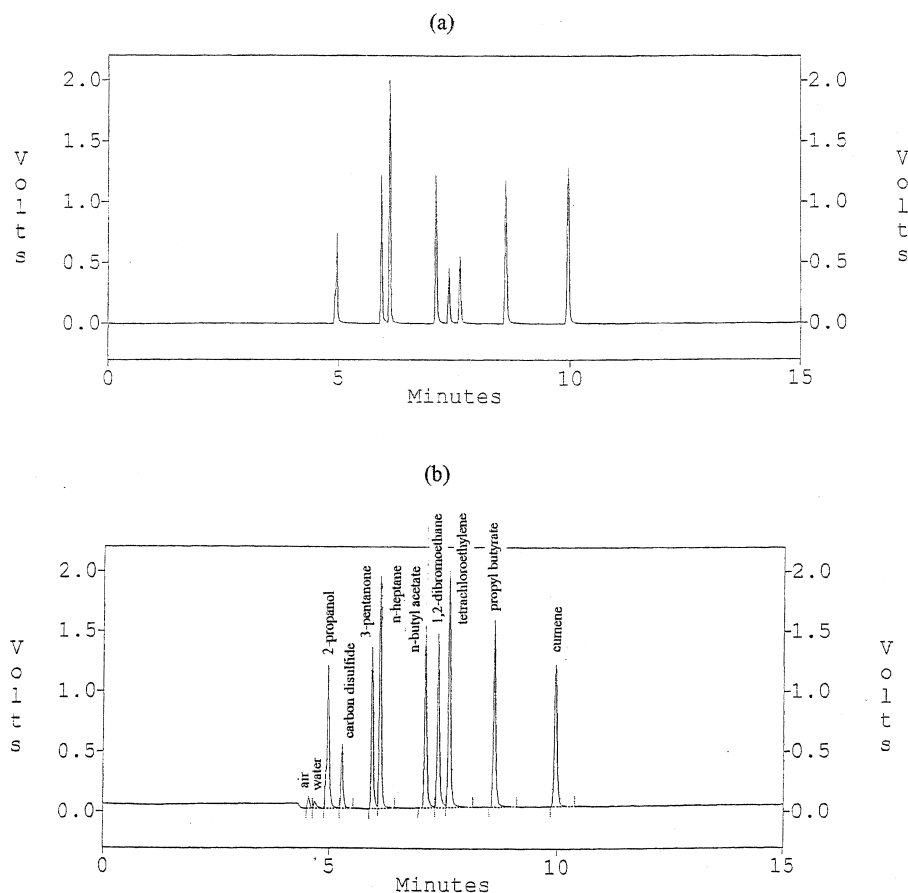


Fig. 2. Gas chromatograms of mixture 2 using (a) FID and (b) He-PDPID. Column as in Fig. 1.

terminated by He-PDPID is 16.00% while that for FID is 6.48%. This gives  $\Delta_{\text{comp}}$  values of 1.19% and 10.71%, respectively. Clearly in this case He-PDPID provides a better means of quantitation.

A graph of %area versus %composition shows explicitly the agreements/disagreements for the different components using FID and He-PDPID. Such graphs are shown in Fig. 3a and b for mixture 1. If there were perfect agreement between the area% and the % (w/w) composition, the data would fall on the straight line passing through the origin with a slope of 1.0. The deviations of the data points from this straight line represent the extent of discrepancy of the area% as determined by FID (Fig. 3a) and He-PDPID (Fig. 3b) from the actual % (w/w). One should note that the chloro- and bromo-substituted compounds fall below the line for the FID response, as expected, since the detector does not respond to the Cl and Br substituents. The response/gram from He-PDPID for the Cl and Br containing compounds are also less than that for the hydrocarbons, but the discrepancies are not as great as they are with FID. This is readily apparent from the graph of area% versus % (w/w) composition as shown in Fig. 3b. Since the discrepancy is lower for the Cl and Br containing compounds, this also makes the discrepancy of the hydrocarbons lower. A measure of the deviations from the straight lines in Fig. 3a and b can be obtained from the mean of the absolute  $\Delta_{\text{comp}}$  values which we designate as  $\Delta_{\text{mean}}$ . This is shown in Table 4 for mixture 1 as  $\Delta_{\text{mean}} = 2.94$  for the FID results and  $\Delta_{\text{mean}} = 1.74$  for the He-PDPID results. As we will see shortly, the  $\Delta_{\text{mean}}$  from the He-PDPID results is generally less than the  $\Delta_{\text{mean}}$  from the FID results for the other mixtures examined in this study.

It has been shown in previous studies [32,40] that to a good approximation the He-PDPID response on a molar basis is a function of the number of ionizable electrons. In order for an electron to be ionizable, it must occupy a molecular orbital whose energy is less than the Hopfield emission in the region 13.5–17.5 eV. In order to evaluate how many such molecular orbitals are available in a molecule, it is necessary to carry out a quantum mechanical calculation of the energies of the molecular orbitals. If the molecule contains only C and H atoms, these calculations can be performed with satisfactory accuracy. However,

when the molecule contains heteroatoms such as Cl, Br, I, S, and O, the calculations are much more difficult and the results are less satisfactory.

Even though we cannot perform the quantum mechanical calculations accurately for molecules containing especially high atomic number heteroatoms, we can anticipate the effect on the He-PDPID response. In the quantum mechanical calculations involving carbon atoms, only the 2s and 2p electrons are considered. The two 1s electrons of carbon are so tightly held by the strong attraction to the positively charged nucleus, their ionization potentials are much greater than the photoionization energy from the He discharge (13.5–17.5 eV). When there is a heavier heteroatom in the molecule such as Cl and Br, only the outer shell electrons will have sufficiently low energy that they will be involved in the molecular orbital calculations. In the case of Cl these would be the 3s and 3p electrons and the 1s, 2s, and 2p electrons would be tightly attracted to the highly charged positive nucleus, resulting in molecular orbital energies greater than the photoionization energy from the He discharge. Recall that the nuclear charge for the heavier heteroatoms is much greater than that for carbon, which further enhances the attraction between the positively charged nucleus and the inner electrons. For example, in the case of Cl the nuclear charge would be +17 compared to the +6 for C. Since there are more electrons in Cl that are not ionizable (10) compared to C (2), the response/gram will be less for Cl compared to C. Consequently, we would expect the calculated %composition for Cl-containing compounds to be less than that for only C-containing compounds. Since Br has a greater atomic number than Cl, there will be an even greater number of inner shell electrons (18) from the 1s, 2s, 2p, 3s, and 3p orbitals that would not be ionizable. Consequently, we would expect the calculated %composition for Br-containing compounds to show an even greater discrepancy from C-containing compounds. This fact is readily apparent from the results shown in Fig. 3b. Note that the peak area% calculated for bromobenzene shows a greater negative deviation from the straight line than chlorobenzene and 1,2-dichlorobenzene. As a consequence of the lower response for the Cl- and Br-containing compounds, on a relative basis the response for the hydrocarbons must necessarily be

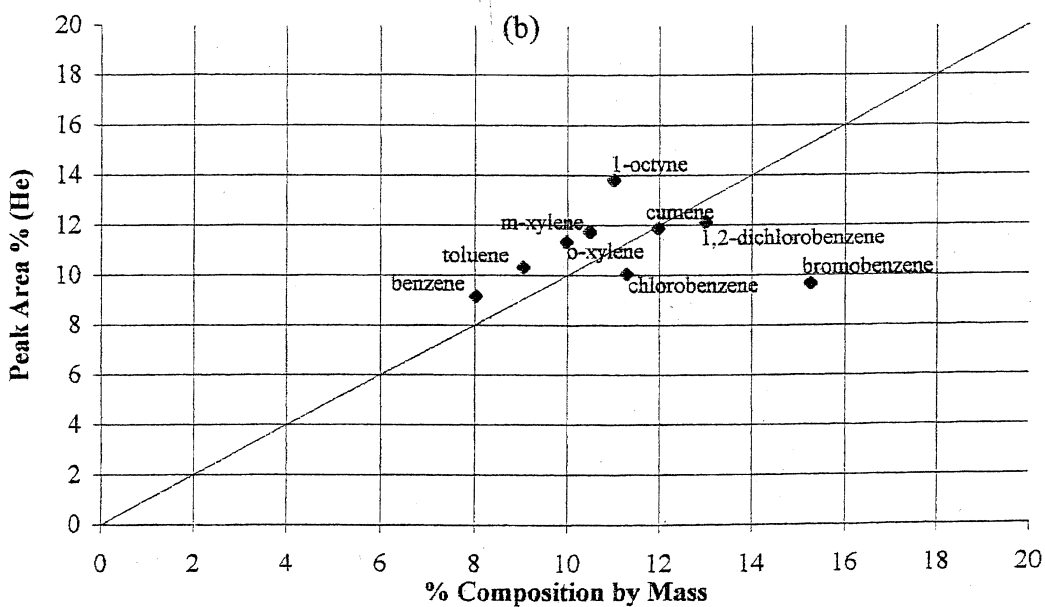
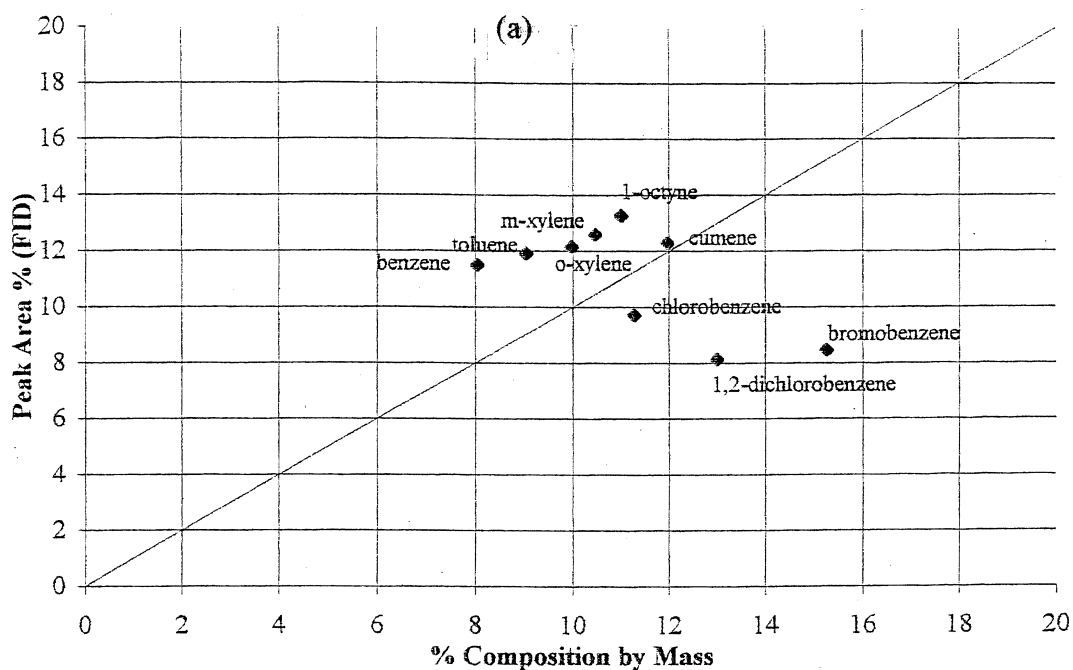


Fig. 3. Plot of area% versus % (w/w) composition for mixture 1 using (a) FID and (b) He-PDPID.

greater and they have positive deviations from the straight lines in Fig. 3a and b. Since the Cl- and Br-containing compounds have smaller negative deviations from the He-PDPID results compared to the FID results, the hydrocarbons necessarily show smaller positive deviations from the straight line in Fig. 3b compared to the FID results shown in Fig. 3a.

In this study we have examined eight mixtures which were made from a variety of compounds available in our laboratory. There was no thought in regards to the selection of the compounds for a mixture except that they would separate on the column chosen for the study, elute within a reasonable time, and that the peaks were reasonably well-shaped so that the integration could be carried out with sufficient accuracy. The evaluation of the analysis for any mixture is best shown on graphs similar to those for mixture 1 in Fig. 3a and b. However, these figures occupy considerable space and in order to decrease the length of the paper, we have presented the results in the form of that for mixture 1 in Table 4. In order to conserve space, mixtures 2, 3, and 4 are also shown in Table 4, mixtures 5, 6, 7, 8A and 8B are in Table 5. These tables give a summary of only the results required to evaluate the performance of the two detectors. Details in regard to purities of the compounds and chromatographic data have not been included so that the results can be more readily evaluated.

The deviation of the area% from the straight lines in Fig. 3a and b are shown as  $\Delta_{\text{comp}}$  as defined in Eq. (6). We have shown the sign of the deviation of the  $\Delta_{\text{comp}}$  so that positive deviations can be distinguished from negative deviations. In order to obtain some measure of goodness of fit of the area% to the % (w/w) composition, we have calculated the average of the absolute values of  $\Delta_{\text{comp}}$  which we designate as  $\Delta_{\text{mean}}$ . The use of the absolute deviations is necessary, since the average of the actual values would necessarily be zero; i.e., the sum of the positive deviations must equal the sum of the negative deviations. The  $\Delta_{\text{mean}}$  values obtained by using each of the detectors for each mixture are shown at the bottom of the column of  $\Delta_{\text{comp}}$ :

$$\Delta_{\text{mean}} = \frac{\sum |\Delta_{\text{comp}}|}{n} \quad (8)$$

As mentioned previously, the error in  $\Delta_{\text{comp}}$  is principally the chromatograph error:

$$SD_{\Delta_{\text{comp}}} \sim SD_c \quad (9)$$

and the overall chromatographic error  $SD_c$  for all compounds in the mixture is given by Eq. (2). The  $SD_{\Delta_{\text{comp}}}$  is shown in Tables 4 and 5 at the bottom of the column alongside the  $\Delta_{\text{mean}}$  values. Generally the  $SD_{\Delta_{\text{comp}}}$  is an order of magnitude smaller than the  $|\Delta_{\text{comp}}|$  so the difference between the  $|\Delta_{\text{comp}}|$  for FID and He-PDPID are significant. The  $SD_{\text{comp}}$  is calculated by a formula similar to Eq. (2) except that  $n$  would now represent the number of components in the mixture.

The results for mixture 2 are summarized in Table 4. From our previous discussion the negative deviations for 1,2-dibromoethane and tetrachloroethylene are quite understandable for the He-PDPID response. As mentioned earlier, negative deviations for these compounds with He-PDPID are considerably less than for FID. In summary, the  $\Delta_{\text{mean}} = 2.08$  with He-PDPID is considerably less than the  $\Delta_{\text{mean}} = 6.18$  with FID.

The results for mixture 3, also shown in Table 4, give a comparison between compounds with a single heteroatom and compounds with multiple heteroatoms or a heavier heteroatom, Br. The presence of a single O, S, or N atom does not lower the He-PDPID response significantly compared to the compounds with two O atoms, three Cl atoms, or Br. Consequently, in the mixture the compounds with a single heteroatom have positive deviations ( $\Delta_{\text{comp}} > 0$ ) and the compounds with more or heavier heteroatoms show a negative deviation ( $\Delta_{\text{comp}} < 0$ ). Again the  $\Delta_{\text{mean}} = 2.80$  with He-PDPID is less than the  $\Delta_{\text{mean}} = 3.99$  with FID.

Mixture 4 results, which are summarized in Table 4, show a single heteroatom and compounds with multiple/heavier heteroatoms. The dichloromethane and dibromomethane show the greatest negative deviations for both FID and He-PDPID. However, in this case the dibromomethane shows a greater negative deviation with He-PDPID than with FID. This would not be anticipated based upon our previous discussion and we do not have any explanation for this result. Despite the large negative deviation for dibromomethane with He-PDPID, the  $\Delta_{\text{mean}} = 2.86$

Table 5  
Deviation of %area from %composition for mixtures 5–8B

Compound	%	FID		He-PDPID	
		%Area	$\Delta_{\text{comp}} \pm \text{SD}_{\text{comp}}$	%Area	$\Delta_{\text{comp}} \pm \text{SD}_{\text{comp}}$
<i>Mixture 5</i>					
Ethanol	5.07	12.98	5.30±0.63	9.18	4.11±0.25
1-Chlorobutane	10.14	2.77	-7.37±0.06	7.25	-2.89±0.15
Cyclohexane	8.30	8.43	0.13±0.17	8.48	0.18±0.21
sec.-Butylmercaptan	8.94	8.60	-0.34±0.17	8.45	-0.49±0.16
Propyl acetate	10.79	10.37	-0.42±0.21	7.63	-3.16±0.11
2-Methyl-3-hexanone	12.11	2.88	-9.23±0.05	10.15	-1.96±0.21
Isoamyl acetate	13.61	17.66	4.05±0.20	14.43	0.82±0.20
1,3-Dibromopropane	20.22	17.67	-2.55±0.34	17.14	-3.08±0.39
Benzonitrile	10.81	18.64	7.83±0.54	17.29	6.48±0.47
			$\Delta_{\text{mean}} = 4.42 \pm 0.35$		$\Delta_{\text{mean}} = 2.57 \pm 0.29$
<i>Mixture 6</i>					
2-Bromopropane	9.46	8.31	-1.15±0.22	10.35	0.89±0.23
tert.-Butanol	10.78	10.62	-0.16±0.26	10.67	-0.11±0.26
2-Pentanone	14.15	14.46	0.31±0.35	13.11	-1.04±0.31
Cyclopentyl chloride	15.14	15.06	-0.08±0.21	15.30	0.16±0.22
Propyl sulfide	15.49	14.19	-1.30±0.11	15.24	-0.25±0.12
n-Decane	16.22	17.28	1.06±0.11	15.83	-0.39±0.06
1-Heptanol	18.75	20.08	1.33±0.86	19.50	0.75±0.91
			$\Delta_{\text{mean}} = 0.77 \pm 0.42$		$\Delta_{\text{mean}} = 0.51 \pm 0.44$
<i>Mixture 7</i>					
1,1,2-Trichloro-1,2,2-trifluoroethane	11.84	8.16	-3.68±0.12	9.28	-2.56±0.20
4-Chloro-3-iodobenzotrifluoride	15.20	6.76	-8.44±0.14	13.62	-1.58±0.51
Hexadecafluoroheptane	17.43	9.06	-8.37±0.15	10.33	-7.10±0.11
1-Iodobutane	8.97	11.13	2.16±0.17	6.43	-2.54±0.15
1-Bromo-4-fluorobenzene	8.94	14.24	5.30±0.19	9.99	1.05±0.27
1-Iododecane	9.41	18.28	8.87±0.35	15.89	6.48±0.36
1-Fluoro-4-methoxybenzene	5.79	12.12	6.33±0.41	13.79	8.00±0.40
Iodobenzene	12.15	7.90	-4.25±0.16	8.45	-3.70±0.26
Iodoctane	10.27	12.35	2.08±0.45	12.21	1.94±0.24
			$\Delta_{\text{mean}} = 5.50 \pm 0.29$		$\Delta_{\text{mean}} = 3.88 \pm 0.35$
<i>Mixture 8A</i>					
n-Hexane	6.17	7.37	1.20±0.31	6.24	0.07±0.25
n-Heptane	7.74	8.70	0.96±0.39	7.51	-0.23±0.33
n-Octane	8.17	9.20	1.03±0.32	8.58	0.41±0.24
n-Nonane	10.21	10.69	0.48±0.23	10.50	0.28±0.14
n-Decane	8.10	8.05	-0.05±0.14	8.39	0.29±0.14
n-Undecane	11.08	11.39	0.31±0.11	11.54	0.46±0.25
n-Dodecane	12.54	12.32	-0.22±0.31	12.76	0.22±0.27
n-Tridecane	11.80	11.16	-0.64±0.33	11.64	-0.16±0.29
n-Tetradecane	11.51	10.87	-0.64±0.23	11.40	-0.11±0.26
n-Hexadecane	12.68	10.24	-2.44±0.64	11.44	-1.24±0.46
			$\Delta_{\text{mean}} = 0.796 \pm 0.38$		$\Delta_{\text{mean}} = 0.347 \pm 0.30$
<i>Mixture 8B</i>					
n-Hexane	2.36	9.23	0.57±0.06	2.69	0.33±0.08
n-Heptane	0.23	0.40	0.18±0.06	0.39	0.16±0.07
n-Octane	8.22	8.83	0.61±0.07	8.52	0.30±0.09
n-Undecane	17.28	17.49	0.21±0.10	17.44	0.16±0.14
n-Dodecane	12.33	12.34	0.01±0.04	13.00	0.67±0.03
n-Tridecane	34.52	32.23	-2.28±0.08	31.23	-3.29±0.21
n-Tetradecane	20.19	19.83	-0.36±0.13	20.39	0.20±0.20
			$\Delta_{\text{mean}} = 0.66 \pm 0.11$		$\Delta_{\text{mean}} = 0.82 \pm 0.16$

for the He-PDPID analysis is less than the  $\Delta_{\text{mean}} = 4.25$  for FID analysis.

The results for mixture 5, given in Table 5, seem to be in line when using He-PDPID. The compounds containing the heavier heteroatoms show the greatest negative deviations. However, the response for benzonitrile seems to be exceptionally large giving a positive deviation of 6.48%. The results using FID give some deviations that are greater than expected. For example, the FID response to 2-methyl-3-hexanone is exceptionally low to give a negative deviation of 9.23% and the FID response to benzonitrile is exceptionally high to give a positive deviation of 7.83%. The overall performance of He-PDPID with a  $\Delta_{\text{mean}} = 2.57\%$  is better than FID with a  $\Delta_{\text{mean}} = 4.42\%$ .

Mixture 6 consists of one hydrocarbon and six compounds containing a variety of heteroatoms: Br, O, Cl, and S. Surprisingly the analyses, given in Table 5, are amazingly good using both He-PDPID and FID. The heteroatom compounds each contains a single heteroatom and one would expect the effect to be minimized. Evidence for a good fit between the experimentally determined area% and the % (w/w) composition is the low values for the  $\Delta_{\text{mean}} = 0.77\%$  for FID and the  $\Delta_{\text{mean}} = 0.51\%$  for He-PDPID. Both values being less than 1% is exceptionally good and both are just above the estimated error of  $\sim 0.4\%$ .

Mixture 7 on the other hand consists of nine compounds all of which contain heavy substitution of heteroatoms of F, Cl, Br, and I, the results for which are in Table 5. Because of the multitude of heteroatoms one would expect great deviations from the linear relationship between area% and % (w/w) composition. Indeed this is the case with values of  $\Delta_{\text{mean}} = 5.5\%$  using FID and  $\Delta_{\text{mean}} = 3.88\%$  using He-PDPID. With such large ranges of heteroatom substitution it is difficult to impossible to rationalize the results. However, we can conclude that He-PDPID gives a better estimate than FID in the calculation of % (w/w) composition, but the discrepancies can be large when one has extensive heteroatom substituents.

Mixture 8A consists of *n*-alkanes  $C_6 - C_{16}$ . Since there are no heteroatoms in these compounds, one would expect the FID response/gram to be similar for all saturated hydrocarbons. The results for mixture 8A are in Table 5 and indeed the response/gram

using FID must be approximately constant since the  $\Delta_{\text{comp}}$  values are small. However, there tends to be a trend in the  $\Delta_{\text{comp}}$  values from positive to negative in going from the shorter chain to the longer chain hydrocarbons. This would suggest that the response/gram is decreasing slightly as the chain length increases. Surprisingly, the  $\Delta_{\text{comp}}$  values obtained using He-PDPID are even smaller than with FID, suggesting that the response/gram with He-PDPID is even more constant than with FID. There is also a slight trend from positive to negative  $\Delta_{\text{comp}}$  values with He-PDPID as the chain length is increased, but the change is much less than with FID. The  $\Delta_{\text{mean}}$  value with He-PDPID is only 0.35 which is just in excess of the average error of  $\pm 0.30$ . In other words, the response/gram using He-PDPID is as constant as can be expected with the precision carried out in this experimental procedure.

In the previous mixtures each of the components was present at a relatively high concentration so that the gas chromatographic peaks could be measured with greater accuracy. A reviewer of the initial phase of this work questioned how the results would vary if the components were present over a greater range of concentrations. For this reason we selected the  $C_6 - C_{14}$  aliphatic hydrocarbons used in mixture 8A and varied the composition from 0.2 to 34% (w/w). We have labeled this mixture 8B and the results are somewhat different from mixture 8A but not dramatically. Tridecane showed a significant negative deviation in both the FID and He-PDPID analyses, suggesting that this could be due to the purity of the sample or sample preparation error. In this analysis the  $\Delta_{\text{mean}}$  using FID is slightly less than with He-PDPID.

Table 6 presents a summary of the  $\Delta_{\text{mean}}$  values and their errors for each of the mixtures analyzed. From Table 6, it can be seen for all mixtures, with the exception of mixture 8B, that the  $\Delta_{\text{mean}}$  values for He-PDPID are less than those of FID. For mixtures 6, 8A, and 8B, the  $\Delta_{\text{mean}}$  values for the two detectors are within the experimental error of one another. The ratios of the  $\Delta_{\text{mean}}$  values are also included in this table and will be discussed later.

In order to make a comparison between the organic functional groups tested and each detector, Table 7 was compiled using the data obtained for each of the compounds in their original mixtures.

Table 6  
Summary of  $\Delta_{\text{mean}}$  values with errors for all mixtures

Mixture	FID: $\Delta_{\text{mean}} \pm \text{SD}_{\Delta\text{comp}}$	He-PDPID: $\Delta_{\text{mean}} \pm \text{SD}_{\Delta\text{comp}}$	$\Delta_{\text{mean}}$ ratio: FID/He-PDPID
1	2.94±0.21	1.74±0.23	1.69
2	6.18±0.24	2.08±0.40	2.98
3	3.99±0.23	2.80±0.20	1.42
4	4.25±0.35	2.86±0.29	1.48
5	4.42±0.35	2.57±0.29	1.72
6	0.771±0.42	0.514±0.44	1.50
7	5.50±0.29	3.88±0.35	1.42
8A	0.796±0.38	0.347±0.30	2.29
8B	0.660±0.11	0.821±0.16	0.803

Table 7  
Mean absolute difference according to organic functional group

Functional group	FID: $\Delta_{\text{mean}} \pm \text{SD}_{\Delta\text{comp}}$	He-PDPID: $\Delta_{\text{mean}} \pm \text{SD}_{\Delta\text{comp}}$	<i>n</i>
Alcohols	3.504±0.550	2.410±0.508	6
Aromatics	3.081±0.282	0.967±0.251	6
Esters	2.324±0.278	1.716±0.373	8
Aliphatic halogenated compounds	4.979±0.233	3.463±0.266	16
Aromatic halogenated compounds	5.997±0.254	3.471±0.382	6
Aliphatic hydrocarbons	2.170±0.362	0.952±0.284	16
Ketones	4.207±0.236	1.539±0.241	5
Nitriles	5.493±0.398	4.365±0.382	3
Sulfides/mercaptans	2.575±0.151	0.854±0.192	5

The  $\Delta_{\text{mean}}$  values categorized by organic functional group are shown for both FID and He-PDPID, along with the errors. As can be seen, for all functional groups tested, the He-PDPID mean peak area percents differed less from the calculated percent composition than did those for FID.

Confirming analyses were performed at Dow Chemical Company's Research and Development Center in Freeport, TX, USA. For the purposes of these analyses, mixtures 1 and 6 were chosen to be tested. Table 8 presents a summary of these data and are compared with those obtained previously at the University of Houston (UH).

The confirming analyses show that the  $\Delta_{\text{mean}}$  values for mixtures 1 and 6 do not differ significantly between Dow FID and FID used to perform the experiments at the University of Houston. Further, the  $\Delta_{\text{mean}}$  values as determined by both flame ionization detectors for mixture 6 agree, within experimental error, with the  $\Delta_{\text{mean}}$  value obtained with He-PDPID. For mixture 1, the He-PDPID  $\Delta_{\text{mean}}$  value is slightly less than that of both FIDs, within experimental error. Therefore, it can be concluded that there is no significant difference between the two FIDs.

One might argue that since the total percent

Table 8  
Results of confirming analyses for mixtures 1 and 6

Mixture	Mean absolute difference – Dow FID	Mean absolute difference – UH FID	Mean absolute difference – UH He-PDPID
1	1.900±0.5074	2.351±0.2314	1.357±0.1991
6	1.727±0.7125	1.232±0.2641	1.008±0.2398

composition must add up to 100% in each mixture, the results are unfairly biased. To eliminate these concerns, the data for the 69 compounds were analyzed by a second method. This method is based on Eq. (10):

$$R_i = Pk'_i m_i \quad (10)$$

where  $R_i$  is the integrated response for a given compound,  $P$  is the power to the detector,  $k'_i$  is a factor or constant for that compound, and  $m_i$  is the mass of the compound being detected. Assuming the power to the detector remains constant, which it should during a single chromatogram, then Eq. (10) can be rearranged to give Eq. (11):

$$k_i = Pk'_i = \frac{R_i}{m_i} \quad (11)$$

$k_i$  is a constant, called the response factor, which varies somewhat from compound to compound. In this study, we are examining the  $k_i$  for different compounds to see how much variation there is for both He-PDPID and FID. Table 9 presents these data for the five runs of mixture 1.

The means of the mean  $k_i$ , standard deviation (SD), and RSD were determined for each detector in each of the eight mixtures described previously. The relative average absolute residuals (rel. avg. abs. res.) were determined from Eq. (12):

$$\text{Rel. avg. abs. res.} = \left[ \frac{\sum |k_i - \bar{k}_i|}{\bar{k}_i n} \right] \quad (12)$$

Table 10 presents a comparison of the results for FID and He-PDPID as calculated using Eqs. (11) and (12) for the eight mixtures previously discussed.

Table 11 compares the relative average absolute residual ratios from Table 10 with the  $\Delta_{\text{mean}}$  ratios from Table 6. As can be seen by comparing the two ratios, there is little difference between them indicating that the method of directly comparing percent composition with peak area percent gives very good results.

#### 4. Conclusions

We have presented the results of a series of analyses which compares the mean peak area percents for compounds in different organic mixtures as determined by FID and He-PDPID with their percent compositions by mass. These data have further been categorized by organic functional group. In each case, He-PDPID produced mean peak area percents which differ less from the percent composition of the compounds in the mixtures.

For the  $n$ -alkanes, the difference between the mean peak area percents of the compounds as

Table 9  
 $k_i$  calculations for mixture 1

Compound	Mass (ng)	FID					Mean	He-PDPID					Mean
		$k_{i\text{run}1}$	$k_{i\text{run}2}$	$k_{i\text{run}3}$	$k_{i\text{run}4}$	$k_{i\text{run}5}$		$k_{i\text{run}1}$	$k_{i\text{run}2}$	$k_{i\text{run}3}$	$k_{i\text{run}4}$	$k_{i\text{run}5}$	
Benzene	8.03	73 939	82 523	85 009	84 775	87 335	60 733.9	81 485.8	90 987.6	92 497.6	90 489.0	94 078.7	
Toluene	9.04	70 261	74 332	77 648	75 672	83 425	17 766.0	83 955.8	88 743.6	92 332.1	87 939.4	97 588.5	
1-Octyne	11.00	64 381	67 541	70 545	68 703	77 492	14 082.3	92 870.1	97 213.0	100 807.0	96 284.4	108 816.4	
Chlorobenzene	11.28	46 112	48 291	50 447	48 825	55 807	15 206.7	65 507.2	68 972.3	71 450.1	67 819.1	78 025.2	
<i>m</i> -Xylene	10.47	64 223	67 292	70 214	67 946	78 275	17 766.0	82 618.9	86 400.5	89 767.3	85 242.8	98 630.9	
<i>o</i> -Xylene	9.97	65 237	68 230	71 209	68 685	79 425	14 082.3	83 567.4	87 936.2	90 715.3	86 232.2	100 677.0	
Cumene	11.96	54 782	57 470	59 961	57 820	67 327	15 206.7	72 603.3	77 314.1	79 410.3	74 939.1	88 266.8	
Bromobenzene	15.26	29 616	30 918	32 345	31 094	36 453	17 766.0	45 931.0	48 695.1	50 808.4	47 675.6	56 724.8	
1,2-Dichlorobenzene	12.99	32 843	34 997	36 482	34 997	42 126	14 082.3	66 480.9	71 475.6	74 633.7	70 113.0	86 214.4	
Mean $k_i$		55 710.5	59 065.9	61 539.7	59 835.2	67 518.3	60 733.9	75 002.3	79 748.7	82 491.3	78 526.1	89 891.4	81 132
SD		16 121.4	17 667.0	18 254.7	18 247.5	18 539.4	17 766.0	14 082.3	14 909.4	15 206.7	15 006.7	15 348.5	14 911
RSD (%)		28.94	29.91	29.66	30.50	27.46	29.29	18.78	18.70	18.43	19.11	17.07	18.42
Rel. av. abs. res.		0.237	0.243	0.242	0.247	0.225	0.239	0.147	0.146	0.145	0.152	0.124	0.143



Table 10  
Summary of  $k_i$  calculations by mixture

Mixture	FID				He-PDPID				Rel. av. abs. res. ratio FID/He-PDPID
	Mean $k_i$	SD $_{k_i}$	RSD $_{k_i}$ (%)	Rel. av. abs. res.	Mean $k_i$	SD $_{k_i}$	RSD $_{k_i}$ (%)	Rel. av. abs. res.	
1	60 734	17 766	29.29	0.239	81 132	14 911	18.42	0.143	1.67
2	16 006	11 136	69.57	0.526	31 491	9678	30.77	0.199	2.64
3	21 104	9778	46.38	0.375	36 782	10 015	27.26	0.239	1.57
4	23 305	11 572	49.76	0.401	43 096	12 178	28.20	0.218	1.84
5	20 719	7709	37.21	0.259	41 348	7570	18.33	0.140	1.85
6	31 296	2412	7.58	0.343	66 715	3873	5.70	0.327	1.05
7	18 170	9793	53.90	0.445	48 946	25 426	52.05	0.381	1.17
8A	59 171	5205	8.55	0.0702	81 628	2931	3.65	0.0267	2.63
8B	72 535	17 796	24.04	0.260	98 829	22 617	22.42	0.250	1.04

compared to the actual percent composition in the mixture as determined by FID and He-PDPID is very close to being within experimental error. Therefore it can be concluded that there is no significant difference between the responses for these compounds with the two detectors.

On the other hand, the aromatic hydrocarbons, esters, halogenated compounds, ketones, nitriles, and sulfides/mercaptans all showed better agreement between the actual percent composition and the He-PDPID mean peak area percents than did the FID mean peak area percents. For the alcohols, the absolute difference is close to being within experimental error.

In order to eliminate any questions about bias in the data analysis, the data from these experiments were analyzed by two different methods. Both of these methods produced results from which the same conclusion can be drawn – He-PDPID is an excellent quantitative tool.

Table 11  
Comparison of relative average absolute residual ratios with  $\Delta_{\text{mean}}$  ratios

Mixture	Rel. av. abs. res. ratio FID/He-PDPID	$\Delta_{\text{mean}}$ ratio FID/He-PDPID
1	1.67	1.69
2	2.64	2.98
3	1.57	1.42
4	1.84	1.48
5	1.85	1.72
6	1.05	1.5
7	1.17	1.42
8A	2.63	2.29
8B	1.04	0.803

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