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## Multiple detector responses for gas chromatography peak identification

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### Abstract

Four detectors have been employed in this study to assist in gas chromatography peak identification along with the relative retention time. These four detectors are based upon different principles and their responses appear to be independent. The detectors are the classical flame ionization detector and three photoionization detectors using the photon emission from He, Ar, and Kr. Relative detector responses, including an internal standard, have been used to eliminate concentration terms and account for long-term drifts in the electronic equipment. A total of 127 compounds, containing numerous functional groups, varying structures, and degrees of unsaturation, were included in the study. The relative detector responses, in conjunction with the relative retention time, gave a set of four values that were unique to each of the 127 compounds. © 1998 Elsevier Science B.V.

**Keywords:** Detection, GC; Photoionization detection; Flame ionization detection; Relative retention times

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### 1. Introduction

Almost since the inception of gas chromatography (GC) there has been a need for peak identification. The retention time of a peak can be used but it is well accepted that more than one compound can have the same or similar retention time. For the most part GC peak identification is carried out by mass spectrometry coupled to the end of the GC column. The use of multiple detector responses has also been suggested for peak identification in that two compounds with the same retention time probably would have different responses to two different detectors,

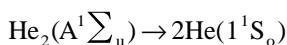
providing the detectors are based upon different physical properties. The use of various pairs of the following detectors have been proposed for the use of GC peak identification: flame ionization detector (FID), photoionization detector (PID), Hall electrolytic conductivity detector in the halogen mode (HECD-X), and in the sulfur mode (HECD-S) [1]. The major drawback to the use of these detectors for this purpose is that none of these is universal to all compounds and the PID and HECD have very specific responses to certain classes of compounds or elemental composition. In this paper we present the use of four detector responses in conjunction with the retention time that can be used to identify a GC peak. In many cases this technique can be used in place of mass spectrometry, and possibly in some

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cases it may be superior to mass spectrometry in peak identification.

The use of the pulsed discharge source in a PID has been described in two publications [2,3]. The photon emission arises from the discharge and is dependent upon the composition of the make-up gas passing through the discharge. When pure helium is used as the make-up gas the emission arises from the transition [4]



The emission spectra from this transition is broad, extending from ~13.5 to 17.5 eV. This emission is of sufficient energy to ionize significantly all compounds and elements with the exception of neon, which is only slightly ionized. For the most part this photoionization source produces the most extensive ionization since the high energy photons can potentially ionize electrons from numerous occupied molecular orbitals (MO) [5]. Since the helium emission is used we refer to this as the helium pulsed discharge PID (He-PDPID).

If the make-up gas passing through the discharge region is doped with argon or krypton, the emission spectra consists principally of the resonance lines from argon or krypton. A concentration of 1–3% argon or krypton is sufficient to produce the atomic resonance line emissions [2]. As the concentration of dopant is increased, an emission from Ar<sub>2</sub> or Kr<sub>2</sub> is observed. These occur at a lower energy and are less effective in ionization than the atomic resonance lines. In an earlier study [3] two different argon concentrations were used, anticipating that the additional emission from Ar<sub>2</sub> would make the response from the detector at a higher argon concentration different from that at a lower concentration. However, the responses from the detectors at two different concentrations were proportional for most compounds and with a few exceptions the additional emission from Ar<sub>2</sub> did not effectively change the nature of the response. In this study we use only a single concentration of argon and krypton in the make-up gas. Since the emission spectra arises from argon and krypton, we refer to these detectors as the argon pulsed discharge PID (Ar-PDPID) and the krypton pulsed discharge PID (Kr-PDPID).

The use of the various PDPID can be accom-

plished by using a single detector whereby the composition of the make-up gas is varied by a stream selection valve [2]. The stream selection valve should be one in which the individual gas streams are continuous so that the gas purifier will have a continuous gas flow. This also allows for rapid switching between the pure helium, argon-doped helium, and krypton-doped helium streams. In order to observe the varied response from the three PDPID, the chromatograms must be repeated with each of the three gas streams. Accurate comparison of relative peak heights will be dependent upon the reproducibility of the gas chromatograms.

An alternative procedure for observing the three PDPID responses is to split the column effluent into three independent PDPID, each employing a different make-up gas composition. This procedure is being continued in the present study where the responses to the three PDPID are fed to a computer through precise A/D conversions (19 bits). As mentioned previously, in this study only a single concentration of argon was used so there are only the three PDPID. In this study we have added a conventional FID as the fourth detector. The FID should have comparable sensitivity to the PDPID, but its basis for response is quite different and, consequently, should be complementary to the PDPID responses. The objective of this work remains the same as in the previous study [2]: to identify GC peaks by the multiple responses of the detectors in addition to conventional use of retention times. As will be described later, the relative detector responses and retention times are reference to an internal standard so that long-term variations can be taken into account.

## 2. Experimental

### 2.1. PDPID

The three detectors (PDPID) used throughout this work (Fig. 1) were designed and built in our laboratories. The detector sections are constructed of quartz. The detector is divided into two zones: the discharge zone and the ionization zone. The two end flanges and all electrodes (bias, collector and discharge) were made of stainless steel. The discharge

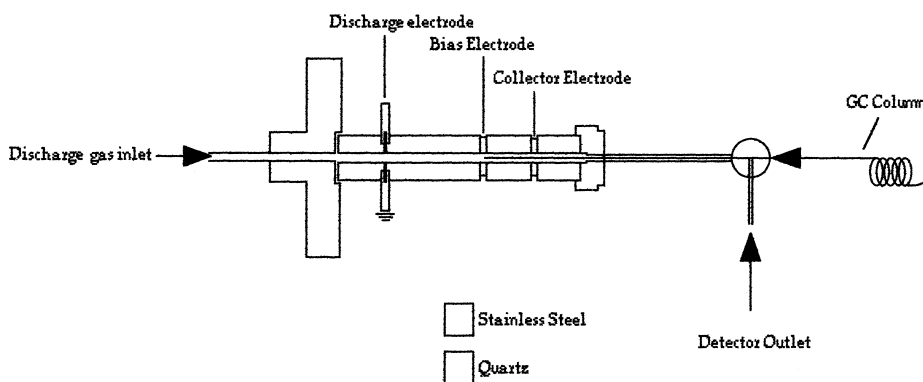


Fig. 1. Schematic diagram of the PDPID.

region has the same I.D. as the ionization region. The discharge electrodes were platinum tipped and cemented with polyimide resin into the discharge section. Both flanges had stainless steel tubing (1/16 in. O.D.  $\times$  0.03 in. I.D.; 1 in. = 2.54 cm) silver soldered to the center. The discharge gas mixture was brought into the detector through the 1/16 in. tubing attached to the flange on the discharge side. The 1/16 in. tubing attached to the flange on the outlet side was connected to a 1/16 in. tee with a large bore so that the GC column could be inserted into the detector as shown in Fig. 1. The outlet of the detector was through a 20 cm length of 1/16 in. tubing (0.02 in. I.D.) which was also connected to the 1/16 in. tee. The purpose of this long outlet tubing was to prevent back diffusion of the ambient air into the detector. The various sections of the detector were sealed using gold O-rings. Spring washers were used to maintain the compression on the gold seals as the detector underwent expansion during heating. The ionization zone was between the bias electrode and the collector electrode. Note that the end of the GC column is near the bias electrode.

The platinum tipped electrodes appeared to function satisfactorily throughout most of this work which was carried out over a period of several months. However, for the Kr-PDPID there appeared to be a dark film formed on the inside of the quartz section which held the electrodes. A similar effect was observed with the Ar-PDPID but to a much lesser effect. There was no darkening associated with the He-PDPID at any time. Near the end of the study

the Kr-PDPID was unable to give good results and for five compounds there are no reported values for the Kr-PDPID response. At the conclusion of the study the film was analyzed by electron spectroscopic chemical analysis (ESCA) and found to be platinum. Apparently the excited or ionized krypton, and to a lesser extent argon, are reactive towards platinum, forming a volatile compound which is unstable upon contact with the quartz wall. In a subsequent study the platinum has been replaced with molybdenum and there has been no indication of a reaction for a period of 3–4 months.

The detectors were housed in a stainless steel block, which was maintained at  $\sim 105^\circ\text{C}$  to prevent condensation of the compounds being eluted from the GC column. This heating block held Selectro type connectors that made contact with the bias and collector electrodes. One of the discharge electrodes was grounded and the other was connected to the pulsed high voltage source. The electronic circuit used to generate the pulsed high voltage contained a E-30 Borg Warner coil, 20 V power supply, and a pulse generator set at 28  $\mu\text{s}$  pulse width and 220  $\mu\text{s}$  pulse interval. The voltage supplied to the coil was variable and was adjusted to make the discharge stable, generally around 15–20 V. A schematic diagram of the components is shown in Fig. 2. The stainless steel block was constructed to house four pulsed discharge detectors but only three were used in this study. The fourth port could be used for a xenon-doped pulsed discharge detector if this were desired in future studies. A negative potential of 300

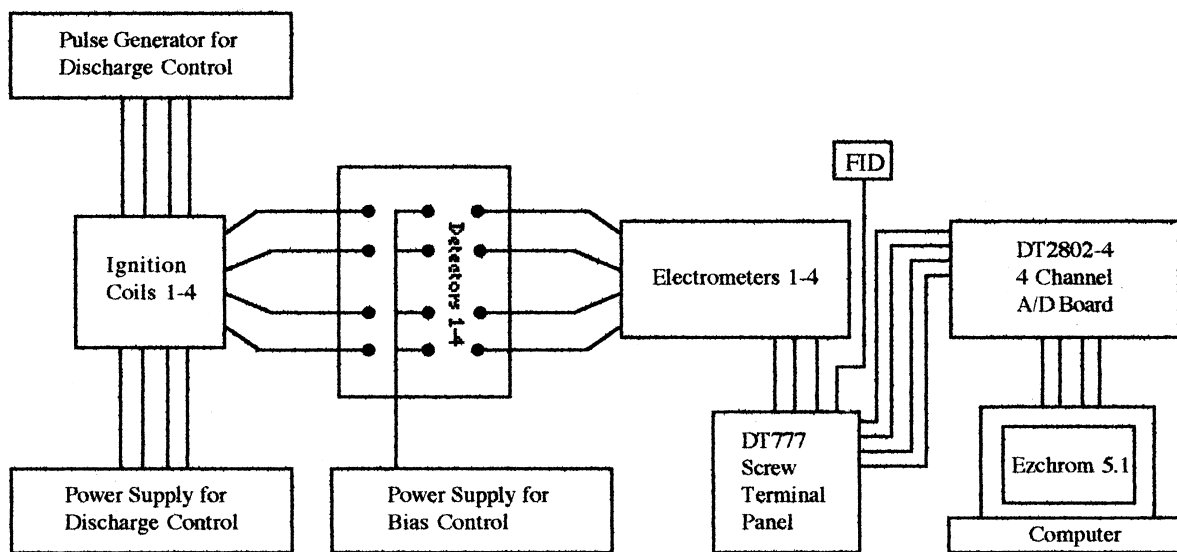


Fig. 2. Schematic diagram of the electronic components.

V was applied to the bias electrode to repel the electrons to the collector electrode. The current was measured with an electrometer providing a fixed gain of  $2 \cdot 10^8$ . The electrometer collection circuitry consisted of a DT-2770 interfaced to a DT-2802-4 A/D Intel 486 motherboard. The three PDPID and the FID electrometer outputs were input to the DT-2770 as shown in Fig. 2. All data were acquired using EZCHROM 5.1 (Scientific Software, San Ramon, CA, USA) chromatographic acquisition software. The A/D board was set to a digital resolution of 19 bits and sampling frequency of 20 Hz.

The discharge gas of helium or doped helium was introduced through the flange nearest to the discharge with a flow-rate of  $\sim 30$  ml/min (cf. Fig. 1). Sample is introduced from the end of the GC column, positioned in the vicinity of the bias electrode. Eluents from the column, flowing counter to the flow of the discharge gas, are ionized by the high energy photons from the helium discharge. Ionization occurs within the region between the bias electrode and the collector electrode. With this flow configuration only pure helium or argon-, krypton-doped helium passes through the pulsed discharge. Capillary column flow-rates are very low compared to the flow-rate of the discharge gas and there is little chance for contamination of the electrodes by the GC eluents.

## 2.2. Chromatographic system

A schematic diagram of the entire set up is shown in Fig. 3. All gases for these experiments were 99.999% purity (five nines) from Trigas (Houston, TX, USA) and were additionally purified by passing them through inert gas purifiers (Valco Instruments, Houston, TX, USA) operated in the "bakeout" position ( $400^\circ\text{C}$ ) in order to remove nitrogen. The helium must be free of impurities above  $\sim 1$  ppm in order for the He-PDPID to attain its sensitivity. The pressure regulated helium flow was split using a cross and three fixed restrictors. Dopant gas (argon or krypton) concentrations were achieved by adding pressure regulated gases through fixed restrictors prior to a mixing tee downstream of the above described helium restrictors. All gases were transferred through portions of this system using 1/16 in. stainless steel tubing (0.03 mm I.D.).

The carrier gas was also five nines helium purified by the inert gas purifier in the same manner as the discharge gases. The chromatograms were obtained using a  $30 \text{ m} \times 0.25 \text{ mm}$  I.D.,  $0.25 \mu\text{m}$  Rtx-5 column from Restek (Bellefonte, PA, USA). The effluent is split using a four way manifold. The transfer lines from this manifold to the individual detectors is made from  $0.33 \text{ m} \times 0.05 \text{ mm}$  I.D.,  $0.05 \mu\text{m}$  DB-5 column. These lines were precisely cut to the same

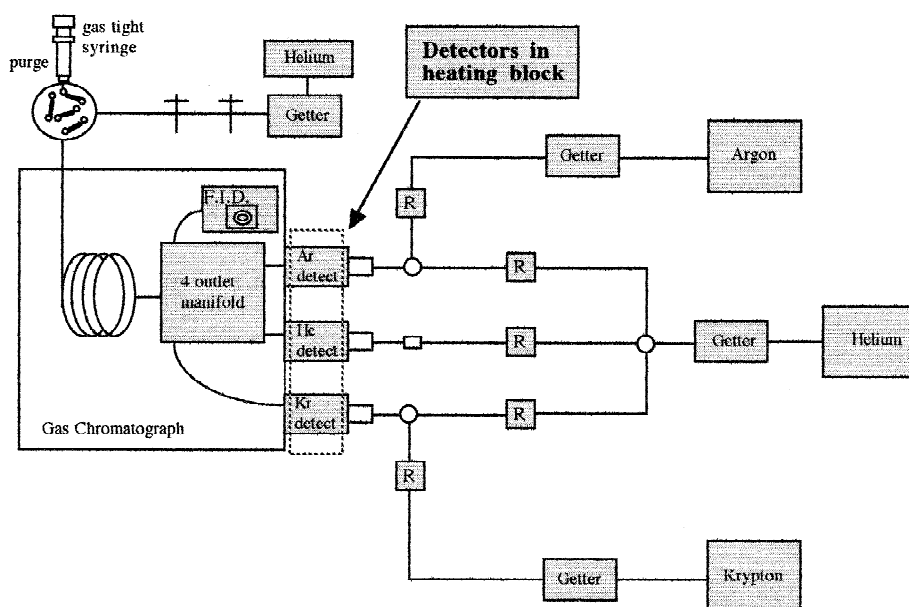


Fig. 3. Schematic flow diagram of the gas chromatographic–detector system.

length so that there is equal flow to each of the detectors. The carrier gas flow was 3.9 ml/min. The split GC effluent was directed to each of the three pulsed discharge detectors and to a conventional FID which was present in the HP 5880 gas chromatograph.

The chemicals were purchased in 99% purity and used as received. The samples were prepared by using a 10  $\mu\text{l}$  syringe to inject 1–10 compounds and an internal standard into a 100  $\mu\text{l}$  gas tight syringe filled with either air or helium. The samples were allowed to evaporate completely. Helium was used instead of air when an early eluting solute was difficult to separate from the air. The loaded syringe was then fitted to a 6-port gas sampling valve with a 5  $\mu\text{l}$  loop. Sample injections were performed in the stream of carrier gas before a GC column. Multiple chromatograms (minimum of five) of the same sample were run in order to give statistical data for the analysis.

### 2.3. Emission spectra measurements

The spectral distributions of the krypton and argon emissions were measured at their respective concentrations; i.e.  $\sim 1.5\%$  Kr and  $\sim 3\%$  Ar. The emis-

sion spectra from the discharge were recorded using an Acton 502 monochromator (Acton Research Corp., Acton, MA, USA). The monochromator contains a holographic grating which is capable of making spectral measurements in the range 50–550 nm. However, the efficiency of the grating is poor below 100 nm and above 200 nm. Since the emission spectra from helium is below 100 nm the actual emission spectra will be more intense than that which is recorded. Normally the monochromator is evacuated in order to be transparent below 200 nm. However, evacuation of the monochromator requires windows to seal the entrance and exit slits to prevent air from entering the monochromator. Unfortunately, there are no windows that transmit radiation with wavelengths below 110 nm. For this reason we have purged the monochromator with pure helium which is transparent down to  $\sim 60$  nm. Below 60 nm the helium begins to absorb primarily through the resonance line at 58.44 nm.

The recorded spectra from the three PIDs is shown in Fig. 4. The sharp lines commonly observed in the helium emission spectrum are due to trace impurities of nitrogen and water. The emission spectrum for the  $\text{He}_2$  is actually much more intense than the impurity emissions, but because of the low efficiency of the

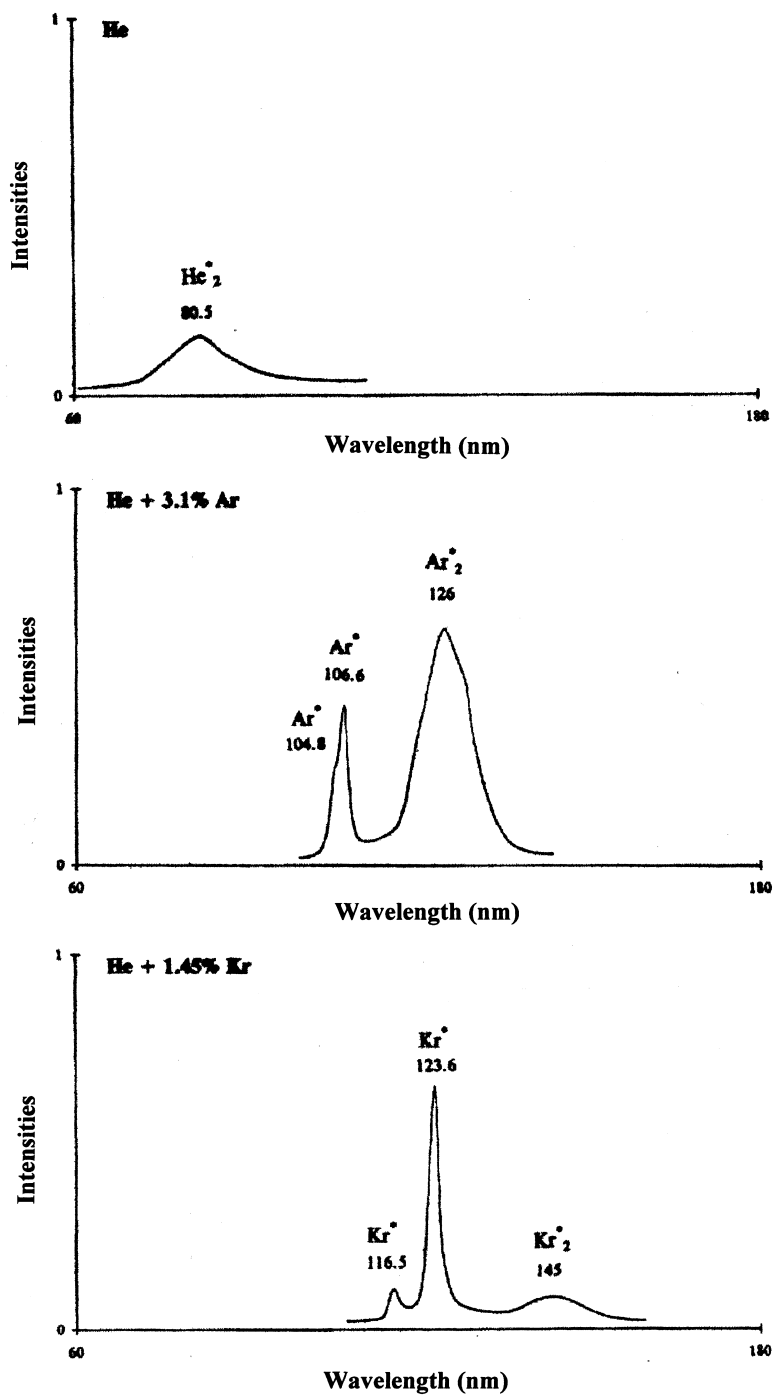


Fig. 4. Emission spectra of the photoionization sources.

grating in this region the recorded spectra appears to be less intense. In Fig. 4 we have removed the N, H, and O emission lines in order to avoid confusion with the helium, argon, and krypton emission spectra.

#### *2.4. Dependence of emission spectra on argon and krypton concentration*

Previously there was a study of the dependence of the PDPID spectra upon the amount of argon or krypton added to the discharge gas [3]. The percent argon was varied from 0.0–5.5% and the krypton from 0.0–0.85%. In both argon and krypton the intensity of the atomic resonance emission increased until a concentration of ~0.5% was reached, at which time the intensity remained approximately constant. At higher concentrations of both argon and krypton the emission intensity from the excited diatomic species increased with increasing concentration. Also in this study [3] it was noted that the relative response of the Ar-PDPID was about the same for numerous compounds when the Ar-PDPID was operated at two different argon concentrations. In another study [2] the sensitivities of the Ar-PDPID and the Kr-PDPID to several compounds was studied as a function of the concentrations of argon and krypton, respectively. At low concentrations of argon or krypton the sensitivity changed with increasing concentration of dopant, but then later levelled off to a reasonably constant value. Since we would like to obtain the maximum stability in the PDPID, we would prefer to work at concentrations where the dependence on the dopant concentration was a minimum; i.e., higher concentrations of dopant. Other factors to consider in the choice of concentration of dopant are the cost of the dopant and the effect of the dopant on the thermal conductivity of the gas and the associated cooling of the discharge electrodes. Since krypton is somewhat expensive, the lowest concentration at which the response became constant was selected, ~1.5%. Since argon is less expensive, a slightly higher concentration of ~3% Ar was chosen for this study. In both cases the sensitivities of the detectors should be somewhat insensitive to slight variations in the concentration of dopant.

#### *2.5. Calculation procedures*

The procedure for the calculation of the relative photoionization cross section (RePIX) values has been given in a previous publication [3]. We will repeat this discussion so that we can point out how the variation of several experimental variables are accounted for by the internal standard. If the spectral distribution for each detector remains constant, the RePIX value should be characteristic of the compound, independent of other factors. In order to obtain this RePIX value, it is necessary to take into account three experimental variables: (1) the concentration distribution of the gas chromatographic peak, (2) the variation in the split of the column effluent to the four detectors and (3) the power applied to the three PDPIDs.

The first of the three variables could be taken into account by integrating over the GC peak. However, integration can introduce errors when the GC peak is broad or tails badly. We find the peak height is more reproducible. Since the effluent is split approximately equally, the concentration distribution should be the same in all four detectors. Therefore the concentration of the compounds at the peak maximum should be the same in all detectors, except for the slight difference in the split ratios which is taken into account in a different manner. If we take the ratios of the peak heights from two detectors, the concentration terms should cancel, except for the difference in split ratios. In this study we assume that these GC peaks have the same distribution in all four detectors and we use the peak heights in the calculation of the RePIX values. The alternative would be to use peak areas and for relatively sharp peaks, this would be equally satisfactory.

The split ratio is subject to greater variation due to the possibility of contamination over long periods of time. However, over the time of one chromatogram, this should stay approximately constant. The third variable, the power to the detectors is also critical since the magnitude of the response will vary directly with the power applied to the detector. This could occur by operator movement of the pulse settings or gradual change due to the deterioration of the electronic components. In the following calculations, we will assume that the split ratios and the detector sensitivities remain constant throughout a

chromatogram. With these assumptions, the long-term variations in the split ratio and the detector sensitivities can be taken into account by using an internal standard to calculate RePIX values. In this work, we use benzene as the internal standard since it is easily detected by all four detectors because of its low ionization potential. Other internal standards could be used for this scale provided the relative value to the other standard were known accurately relative to benzene.

The responses for the He-PDPID and Kr-PDPID can be expressed as follows:

$$R_{\text{He},X} = k_{\text{He},X} f_{\text{He}} P_{\text{He}} C_X \quad (1)$$

$$R_{\text{He,Std}} = k_{\text{He,Std}} f_{\text{He}} P_{\text{He}} C_{\text{Std}} \quad (2)$$

$$R_{\text{Kr},X} = k_{\text{Kr},X} f_{\text{Kr}} P_{\text{Kr}} C_X \quad (3)$$

$$R_{\text{Kr,Std}} = k_{\text{Kr,Std}} f_{\text{Kr}} P_{\text{Kr}} C_{\text{Std}} \quad (4)$$

where the  $R$ 's are the response, the  $k$ 's are the linear response factors and are proportional to the photoionization cross sections, the  $f$ -values are the split ratios, the  $P$ -values are the power supplied to the respective detectors,  $C_X$  is the concentration of the analyte while  $C_{\text{Std}}$  is the concentration of the internal standard. Similar expressions can be given for the Ar-PDPID.

By taking the responses relative to the standard, the variation of the split ratio between the detectors and the differences in power supplied to the detector are cancelled; i.e., dividing Eq. (1) by Eq. (2) and Eq. (3) by Eq. (4) will give:

$$\frac{R_{\text{He},X}}{R_{\text{He,Std}}} = \frac{k_{\text{He},X}}{k_{\text{He,Std}}} \frac{C_X}{C_{\text{Std}}} \quad (5)$$

$$\frac{R_{\text{Kr},X}}{R_{\text{Kr,Std}}} = \frac{k_{\text{Kr},X}}{k_{\text{Kr,Std}}} \frac{C_X}{C_{\text{Std}}} \quad (6)$$

The following ratio of the relative responses, the RePIX, eliminates the concentration terms; i.e., dividing Eq. (6) by Eq. (5)

$$\text{RePIX} = \frac{\frac{R_{\text{Kr},X}}{R_{\text{Kr,Std}}}}{\frac{R_{\text{He},X}}{R_{\text{He,Std}}}} = \frac{\frac{k_{\text{Kr},X}}{k_{\text{He},X}}}{\frac{k_{\text{Kr,Std}}}{k_{\text{He,Std}}}} \quad (7)$$

Since the denominator in Eq. (7) is the same for all unknowns, X, the RePIX values are true measures of the relative photoionization cross sections.

The relationship is applicable to any detectors where the single column effluent is split between parallel detectors, including the FID and the Ar-PDPID which were used in this study. Since some other detectors, such as the FID, are not dependent on PIX, it would be appropriate to rename the acronym to reflect this difference; e.g., ReFID for relative FID response. However, for consistency we will use the acronym FID-RePIX.

## 2.6. MO calculations

According to the basic principles of photoelectron spectroscopy [7], any electron in a molecule with an orbital energy less than the energy of the absorbed photon can be removed via photoionization. Consequently, the probability of photoionization occurring should be directly related to the number of electrons in the molecule that have sufficiently low orbital energies that they may be photoionized by the absorbed radiation. The response of a PID should be directly proportional to the probability of photoionization and thus to the number of potentially photoionizable electrons in the molecule.

In order to determine the number of ionizable electrons in a molecule, we use a program called Hyperchem. Hyperchem is a commercially available software program from Hypercube (Waterloo, Canada) which calculates self consistent molecular orbitals (SCF-MO) for molecules using various Hamiltonians and parameter sets. The AM1 (Austin Model 1) version has been used to calculate the number of ionizable electrons of different classes of molecules using the  $\text{He}_2^*$  continuum and the resonance lines of argon and krypton [5,6].

## 3. Results and discussion

Before looking at the specific results and their significance, let us consider the five different parameters being measured and the rationale for the magnitude of each parameter. The first is the retention time and of course this is a measure of the absorption of the compounds being separated on the stationary phase. Of course the stationary phase can



range from a nonpolar, methylsilicone type group, to a highly polar phase. In general, nonpolar compounds will be more strongly adsorbed on nonpolar stationary phases and polar compounds will be more strongly adsorbed onto polar stationary phases. In this manner one can be selective in choosing a phase which is best suited for most of the components in the mixture. However, once a phase has been selected, the compounds in a homologous series for the most part will elute according to the chain length. This is caused by the additional Van der Waals attractive forces resulting from the additional carbon chain length. Consequently, the compounds with the same functional group will be separated to a greater or lesser degree extent by the attached carbon chain or chains. Of course isomers with the same carbon number may elute at similar times and the only separating property is due to branching of the carbon chains. Generally for an efficient capillary column, these isomers can be separated and in general we do not expect two overlapping peaks with the same functional group. However, coincidentally compounds with different functional groups could overlap and it is compounds with different functional groups that we must distinguish by the use of the four detector responses.

The FID completely consumes the compound by oxidation in a  $H_2$ /air flame. It is thought that the ionization is the result of the formation of an excited species  $CHO^*$  during the oxidation process and the flame ionization is the result of the following chemical ionization step



If a percentage of the carbons pass through this excited  $CHO^*$  state, the FID response will be proportional to the number of carbon atoms in the molecule. There are exceptions to this, but we will assume to a first approximation that the FID response is proportional to the number of carbon atoms contained in the molecule. Of course the presence of any hetero atoms, such as O, N, F, Cl, Br, S, and I will decrease the FID response since they add mass to the sample but will not undergo any ionization in the flame.

Analysis of the PDPID responses is not so obvious but easily understood in terms of basic principles. The emission spectra from the pulsed discharge has

been well documented [3,5] and was shown in detail in Fig. 4. The emission from the pulsed discharge in pure helium consists of a broad distribution with the widths at halfheight ranging from  $\sim 13.5$  to  $17.5$  eV. When the helium is doped with argon in the range 1–5%, the emission consists of the two argon resonance transitions at 11.6 and 11.8 eV, followed by the  $Ar_2$  emission at 9.3 to 10.2 eV. When the helium is doped with 1–5% Kr the emission consists of the two resonance transitions at 10.1 eV and 10.6 eV followed by the  $Kr_2$  emission at 8.1 to 8.8 eV. Normally atomic resonance transitions give very sharp emission lines and consequently there would be a very narrow spread in the photon energy. However, for what reason we are not sure, the argon and krypton resonance lines are quite broad. This may be due to the high helium background pressure in the discharge or possibly to the mode of excitation through the  $He_2$  metastables. In any event, the resonance lines are reasonably broad with halfwidths of  $\sim 0.2$  to  $0.3$  eV. The emission spectra are shown in Fig. 5 along the vertical axis.

It has been shown that to a first approximation the response of a PID is proportional to the number of electrons in the molecule with energies less than the photoionization energies coming from the discharge [5,6]. In Fig. 5 we show the Hyperchem AM1 MO calculations for six  $C_6$  hydrocarbons with varying degrees of unsaturation. Note that in hexane the highest energy occupied MO falls below the resonance emission lines for krypton. Consequently, we anticipate that hexane should give little or no response to the Kr-PDPID. As we will see later, experimentally we observe very little response for hexane with the Kr-PDPID. On the other hand, there are occupied MOs for hexane that fall above or in the vicinity of the argon resonance lines and we would expect a good response to hexane using the Ar-PDPID. Again this is borne out experimentally as we will see later. Obviously, from the broad emission spectra from  $He_2(a^1\Sigma_u)$  there are numerous occupied energy levels in hexane with energies above or within this energy distribution that can be ionized and again we expect a high response for hexane using the He-PDPID. In fact one can readily understand why the He-PDPID gives a universal response since all atomic and molecular species have energies above or within this broad emission band.

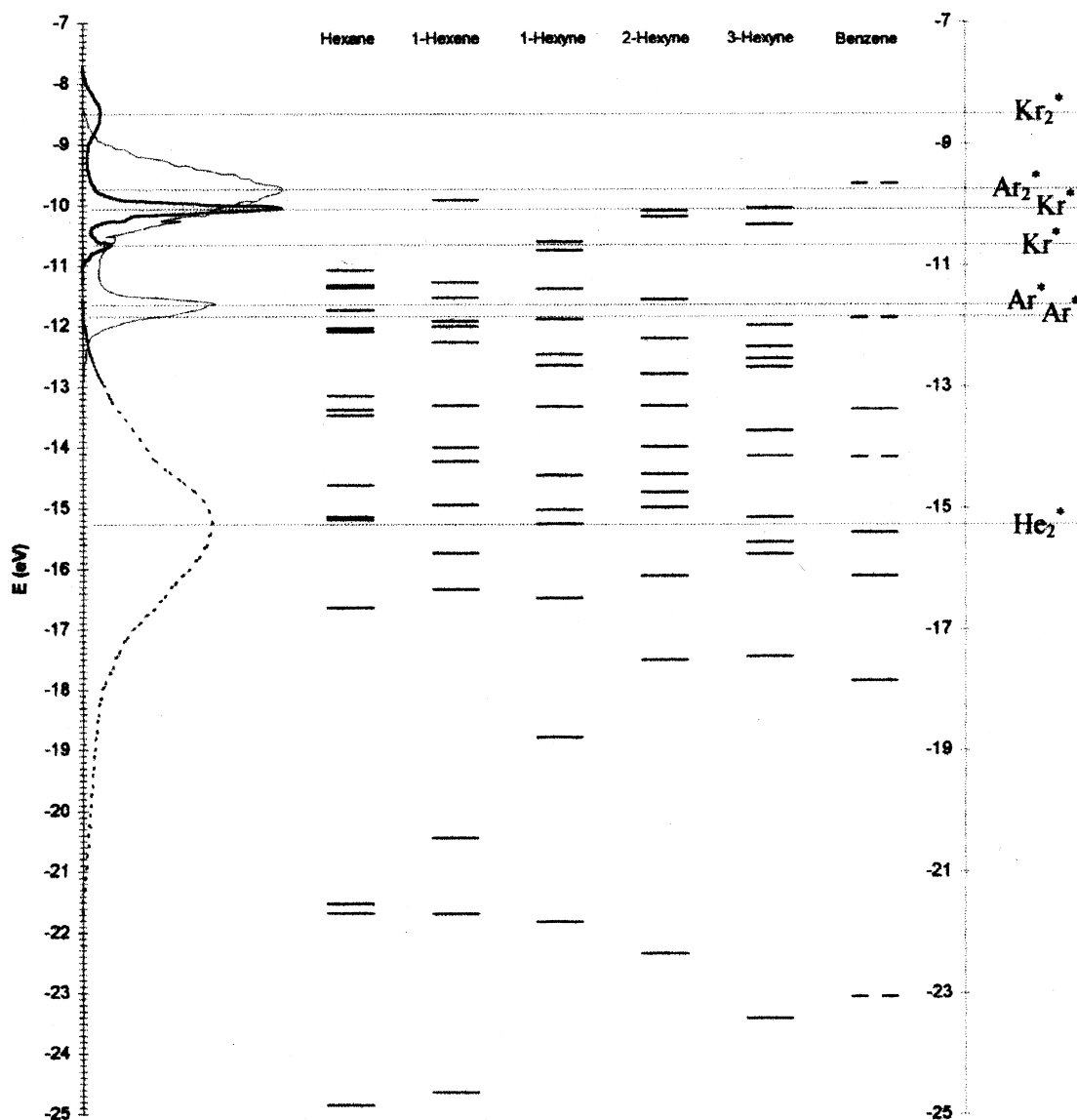


Fig. 5. Molecular orbital energy diagram for some C<sub>6</sub> hydrocarbons. Photon energy distributions for the PDPID are given on the energy axis.

In Fig. 5 we can see the effect that unsaturation has upon the energy of the occupied MOs and one can anticipate the effect this has on the response of this compound to the various PDPID's. For example, the highest occupied MO in 1-hexene falls above the krypton resonance line at 10.1 eV and the response to the Kr-PDPID should be reasonably high, as we observe experimentally. The response of 1-hexene to the Ar- and He-PDPID's should also be high since

again there are numerous occupied orbitals which lie above the corresponding photo emission energies for argon and He<sub>2</sub>.

The highest occupied MO for the hexynes varies according to the position of the triple bond. For 1-hexyne it falls at -10.6 eV, in the vicinity of the 10.6 eV resonance line for krypton but below the more intense line at 10.1 eV. On the other hand, the highest occupied MO for 2-hexyne and 3-hexyne

falls above the more intense krypton resonance line at 10.1 eV. Consequently, the response of 2- and 3-hexyne to the Kr-PDPID should be considerably higher than that for 1-hexyne, and, as we will see later, this is borne out experimentally.

For benzene there are two occupied MOs with energies above 10.0 eV and one would anticipate an even greater response for benzene to the Kr-PDPID than the hexenes. This result is also observed experimentally. Since benzene would give a good response to all three PDPID, it is a logical choice for an internal standard.

As a result of this discussion, one can readily understand how molecules can have different responses to the three PDPID. However, without the MO calculations one would have difficulty in predicting the relative responses to these PDPID.

### 3.1. Correlation between relative measurements

From our discussion of the nature of the various measurements which we will use to characterize a GC peak, it would appear that the measurements are for the most part uncorrelated. This is essential if the set of numbers are to be unique for a given compound. In order to test if two measurements are correlated, we have made several graphs relating the relative parameters. As discussed previously, ratios of the detector responses must be used in order to eliminate the concentration dependence of the response. Furthermore, benzene has been chosen as an internal standard so that variations in sensitivity of the detectors over long periods of time can be taken into account by the internal standard.

In Figs. 6–8 we show graphs of the three relative detector responses versus the retention time relative to benzene. In all three graphs there appears to be little or no correlation between the relative detector responses and the relative retention time. Consequently, the relative retention time should make an independent contribution towards the identification of a GC peak.

In Fig. 9 we show a graph of the Ar-RePIX versus the FID-RePIX values. One might anticipate that these detector responses are correlated since both detector responses should increase with carbon number. However, since the FID does not respond to hetero atoms whereas the Ar-PDPID would respond

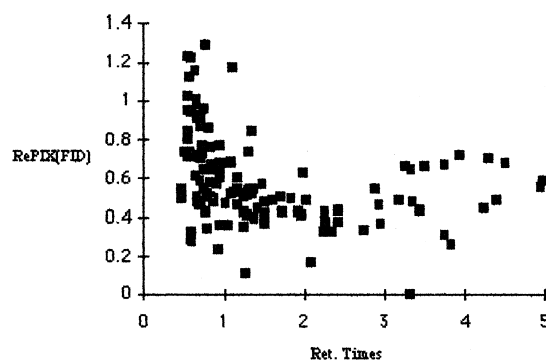


Fig. 6. FID-RePIX versus retention time.

at least partially to the hetero atoms, the two responses should not be correlated in general. In Fig. 9 we see no apparent correlation between the relative detector responses.

Finally in Fig. 10 we graph the Kr-RePIX versus the Ar-RePIX values. Again there is no apparent correlation between these relative detector responses. In some cases the Kr-PDPID response is essentially zero and in these cases this value is only partially useful in making a qualitative identification. However, it could be useful in eliminating the possibility of certain functional groups which characteristically would give a high Kr-PDPID response. In summary it would appear that the three relative detector responses in addition to the relative retention times are uncorrelated and that all four values would contribute towards the qualitative identification of a GC peak.

### 3.2. Qualitative analysis of GC peaks

In Table 1 we give results for 127 compounds in terms of relative retention times and relative ratios of detector responses to the He-PDPID. These compounds include 13 classes in terms of functional groups; e.g., alcohols, ethers, etc. To the right of each value is the standard deviation (S.D.) of the mean of five chromatograms. As mentioned earlier, all values are relative to benzene, the internal standard, hence the values of 1.000 for all values of benzene. The precision in the relative retention times is very high for the more volatile compounds which eluted before the temperature program was started. In these situations the standard error is  $\approx 0.01$ –

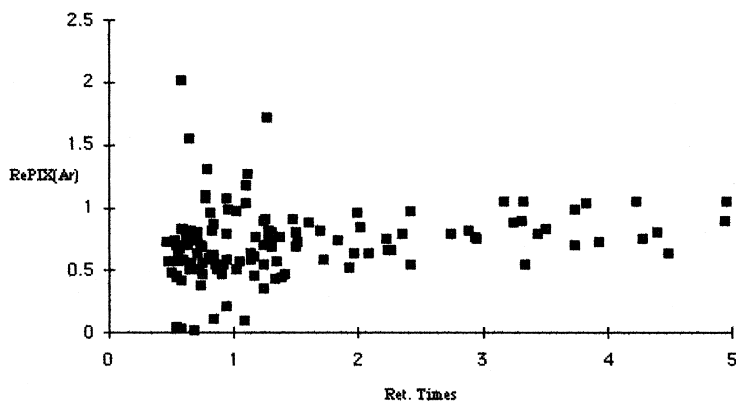


Fig. 7. Ar-RePIX versus retention time.

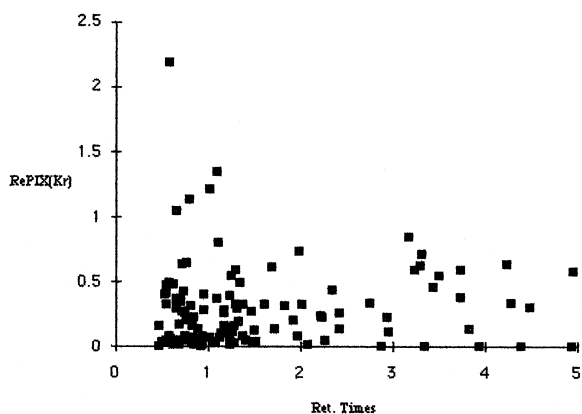


Fig. 8. Kr-RePIX versus retention time

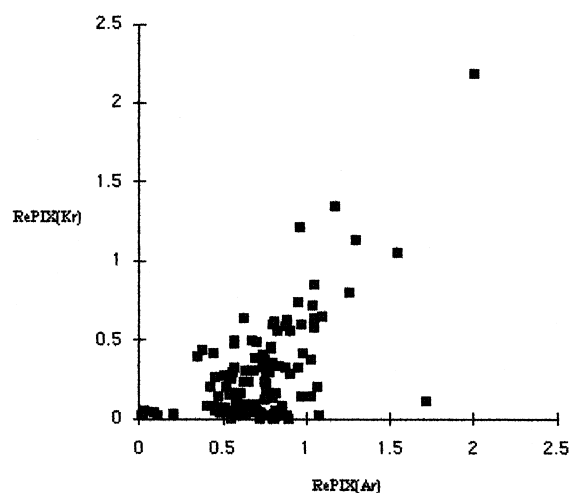


Fig. 10. Kr-RePIX versus Ar-RePIX.

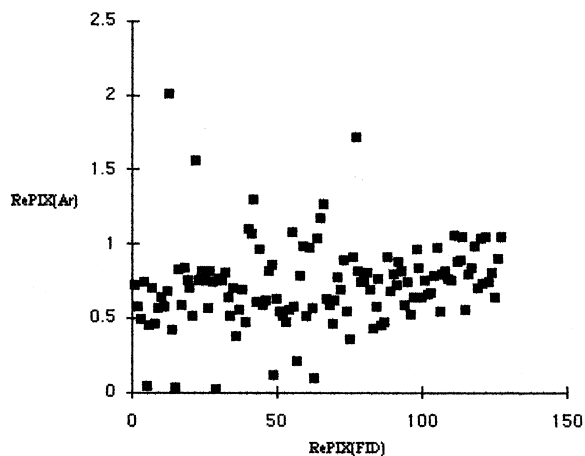


Fig. 9. Ar-RePIX versus FID-RePIX.

0.08%. For the less volatile compounds, which eluted during the temperature program, the standard error is of the order of 0.2–0.5%. The larger error associated with retention times affected by the temperature program could very likely be reduced considerably if a newer gas chromatograph were used. As mentioned earlier in the Section 2, the Kr-PDPID could not be used for five compounds at the end of the study due to deterioration of the platinum electrodes. In Table 1 the Kr-PDPID values for these compounds are designated by xxxxxx.

The data have been ordered by the relative retention times, which would be our initial quantity for qualitative analysis. Since the relative retention times are so precise ( $\sim 0.01$ – $0.02\%$ ), many of the com-

Table 1  
Relative photoionization cross section (RePIX) sorted by relative retention time

Compounds	He DET <sup>a</sup>	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz) Mean	RT/RT(Bz) S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.
Methanol	0.47417	0.00015	0.49412	0.01817	0.72398	0.02823	0.0075	0.00264
Acetaldehyde	0.47937	0.00094	0.548	0.00351	0.57236	0.0034	0.1539	0.01133
Ethanol	0.51152	0.0001	0.73425	0.00684	0.48529	0.00721	0.0406	0.0072
1-Pentene	0.53924	0.00011	1.2267	0.00859	0.74068	0.00925	0.3986	0.00511
Acetonitrile	0.54394	0.00034	0.94727	0.00832	0.03544	0.02608	0.045	0.01429
Acetone	0.54597	0.00075	0.84618	0.00575	0.44658	0.00794	0.4157	0.05802
Pentane	0.54977	0.0006	1.02318	0.00803	0.70226	0.0062	0.0404	0.00947
Isopropanol (2-propanol)	0.55048	0.00017	0.71188	0.00282	0.45641	0.00482	0.0453	0.0035
Propionaldehyde	0.55134	0.00075	0.72717	0.0075	0.56616	0.0094	0.4715	0.02572
2-Chloropropane	0.55653	0.00029	0.80584	0.00807	0.63089	0.01069	0.0254	0.00339
Diethyl ether	0.55925	0.00008	0.74075	0.01262	0.57438	0.00642	0.3231	0.0049
2-Methylbutene-2	0.57619	0.00012	1.12593	0.0096	0.67439	0.00713	0.4911	0.01233
Idomethane (T.P.)	0.58033	0.00178	0.32337	0.00381	2.00935	0.02766	2.1856	0.01311
2-Methyl-2-propanol	0.58518	0.00012	0.94403	0.01549	0.41114	0.00591	0.0804	0.01505
Freon-113	0.58777	0.00022	0.28147	0.00148	0.02731	0.00182	0.0232	0.00547
Acrylonitrile	0.58842	0.00025	1.22002	0.01305	0.82595	0.00747	0.0334	0.01052
2,2-Dimethylbutane	0.59413	0.00021	0.93579	0.00331	0.58076	0.01082	0.0621	0.00408
CH <sub>2</sub> Cl <sub>2</sub>	0.60014	0.00014	0.27785	0.00512	0.8297	0.00637	0.0262	0.00411
1-Chloropropane	0.62231	0.0006	0.72418	0.00559	0.74839	0.01377	0.0184	0.00369
Cyclopentene	0.63715	0.00006	1.15275	0.00459	0.70006	0.00399	0.4803	0.00401
1-Propanol	0.6508	0.00012	0.61434	0.00796	0.50862	0.004	0.0396	0.00209
<i>trans</i> -CHCl = CHCl	0.65533	0.0001	0.50408	0.00747	1.55098	0.02507	1.0475	0.02455
<i>cis</i> -4-Methylpentene-2	0.65641	0.00015	0.98218	0.01328	0.7529	0.00864	0.353	0.0162
Cyclopentane	0.65678	0.00065	1.00622	0.00479	0.81092	0.00764	0.0278	0.00338
<i>trans</i> -4-Methylpentene-2	0.66347	0.00017	0.91673	0.0161	0.7532	0.01157	0.3659	0.00406
Methyl <i>tert.</i> -butyl ether	0.66475	0.00013	0.71149	0.00409	0.5626	0.00384	0.2879	0.00514
Nitromethane	0.66696	0.0002	0.47479	0.00273	0.81689	0.00435	0.0514	0.01326
CHCl <sub>2</sub> -CH <sub>3</sub>	0.68753	0.00019	0.45688	0.00634	0.73669	0.00231	0.0126	0.00571
Propionitrile (T.P.)	0.69434	0.00086	0.71583	0.102	0.0163	0.00234	0.0111	0.00376
2-Bromopropane	0.69512	0.00007	0.5898	0.0023	0.76242	0.00261	0.173	0.01453
2-Methyl-1-pentene	0.70973	0.00014	0.87357	0.00801	0.74947	0.02317	0.3627	0.00663
1-Hexene	0.71234	0.00011	0.9204	0.00248	0.80252	0.00296	0.3477	0.01678
2,3-Butanedione	0.71872	0.00066	0.47429	0.00571	0.63212	0.00671	0.6379	0.01069
Butyraldehyde	0.72813	0.0004	0.7009	0.00914	0.51021	0.01011	0.2665	0.02908
Hexane	0.73627	0.00041	0.76891	0.00277	0.70304	0.00213	0.045	0.00419
MEK (2-butanone)	0.74134	0.00053	0.72977	0.00369	0.37512	0.00273	0.4287	0.01596
Diisopropyl ether	0.75393	0.00016	0.64785	0.00341	0.55617	0.00537	0.2534	0.00448
Methacrylonitrile	0.75483	0.00017	0.95266	0.00289	0.68321	0.0061	0.0773	0.01035
<i>sec.</i> -Butanol (2-butanol)	0.75646	0.00022	0.54494	0.01306	0.47118	0.00164	0.044	0.00715
<i>cis</i> -CHCl = CHCl	0.77317	0	0.42965	0.00398	1.0928	0.01277	0.6477	0.01255
Hexafluorobenzene (T.P.)	0.77622	0.00076	1.2935	0.01234	1.06673	0.02261	0.2015	0.00649
Ethyl iodide	0.79388	0.00012	0.34656	0.0016	1.29889	0.02568	1.1322	0.10807
Ethyl acetate	0.80265	0.00039	0.5175	0.00459	0.59955	0.00669	0.0637	0.00436
1-Hexyne	0.81763	0.00027	0.86421	0.00905	0.95821	0.06774	0.319	0.0218
Propyl formate	0.82932	0.00045	0.58089	0.00711	0.58226	0.01337	0.0298	0.00905
2,4-Dimethylpentane (T.P.)	0.83262	0.00056	0.64582	0.0034	0.61485	0.00524	0.066	0.0023
1-Bromopropane	0.83578	0.00022	0.50282	0.01004	0.81485	0.01565	0.1599	0.00975

<sup>a</sup> DET = detector.

(Cont.)

Table 1. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Methylcyclopentane	0.83789	0.00014	0.75887	0.01144	0.85939	0.00952	0.0719	0.02084
Isobutyronitrile	0.84409	0.00011	0.6682	0.01375	0.1082	0.00534	0.0192	0.0052
THF	0.84769	0.00038	0.65018	0.00551	0.62713	0.00451	0.2283	0.00562
2-Methyl-1-propanol	0.86178	0.00014	0.47514	0.0026	0.54194	0.00188	0.0447	0.0008
Methyl propionate	0.86651	0.00032	0.4959	0.00341	0.50944	0.00339	0.063	0.01021
2-Methyl-2-butanol	0.90186	0.00032	0.57206	0.01266	0.47168	0.00496	0.1393	0.02223
CCl <sub>3</sub> CH <sub>3</sub>	0.91911	0.00016	0.23497	0.00152	0.54969	0.00532	0.0084	0.00149
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.94232	0.0001	0.35996	0.0026	1.07522	0.00991	0.0129	0.00329
3,3-Dimethylpentane	0.9475	0.00012	0.60126	0.00157	0.57665	0.00264	0.0826	0.00474
Trimethylacetone	0.94798	0.00019	0.65429	0.00644	0.20552	0.00773	0.0305	0.00687
3-Ethyl-1-pentene	0.95216	0.0002	0.68094	0.00301	0.78263	0.00618	0.2856	0.00653
Crotonaldehyde	0.95435	0.00048	0.76779	0.00375	0.9855	0.00575	0.4468	0.04005
Isopropyl acetate	1.02429	0.00039	0.47201	0.00546	0.50676	0.01694	0.065	0.02763
3-Hexyne	1.02474	0.00013	0.67688	0.00702	0.96744	0.0344	1.2091	0.03339
1-Butanol	1.05617	0.0003	0.35865	0.00136	0.56738	0.0018	0.0406	0.00177
Butyronitrile	1.08918	0.00027	0.52033	0.00152	0.09628	0.0053	0.0342	0.00643
Cyclohexene	1.10435	0.00014	0.68871	0.00321	1.03156	0.0059	0.3668	0.00805
2-Hexyne	1.1062	0.00015	0.68025	0.00939	1.16919	0.01729	1.3453	0.0412
1,4-Difluorobenzene	1.11527	0.00011	1.16899	0.00556	1.25982	0.01114	0.7967	0.04005
3-Ethylpentane	1.13585	0.00012	0.53162	0.00051	0.62841	0.00187	0.0727	0.00364
2,2,4-Trimethylpentane	1.14032	0.00025	0.5287	0.00107	0.5879	0.00443	0.1013	0.00416
2-Pentanone	1.16896	0.00067	0.54499	0.00461	0.45733	0.00324	0.2632	0.01131
Propyl ether	1.17109	0.00011	0.4637	0.00271	0.6098	0.00364	0.1625	0.00443
1-Heptene	1.17707	0.00041	0.6013	0.00531	0.76676	0.02381	0.2845	0.01933
Heptane	1.23928	0.0002	0.51124	0.00433	0.69205	0.01078	0.082	0.00657
CH <sub>2</sub> Cl-CHCl-CH <sub>3</sub>	1.24057	0.00013	0.35476	0.00254	0.88731	0.00985	0.0115	0.0081
Valeraldehyde	1.24349	0.00074	0.51661	0.00526	0.53953	0.0182	0.1443	0.00719
3-Pentanone	1.24441	0.0009	0.50071	0.00296	0.34982	0.00151	0.3908	0.012
Ethyl sulfide (T.P.)	1.25715	0.0013	0.4244	0.00223	0.90585	0.01781	0.55	0.01795
Dibromomethane	1.26684	0.00006	0.10869	0.00137	1.71767	0.0121	0.1116	0.0097
Allyl acetate	1.28076	0.00119	0.50818	0.00154	0.8102	0.00572	0.159	0.02665
2-Nitropropane	1.28144	0.00077	0.41406	0.00169	0.73565	0.01	0.0306	0.01322
<i>trans</i> -2-Heptene	1.3048	0.00017	0.53957	0.00505	0.75169	0.01154	0.325	0.0065
Bicyclo[2,2,1]hepta-2,5-diene	1.30506	0.00025	0.73496	0.00402	0.79927	0.00623	0.5923	0.01631
3-Ethyl-2-pentene	1.31511	0.00031	0.54619	0.02512	0.6857	0.01133	0.2971	0.01064
3,3-Dimethyl-2-butanone	1.3367	0.00054	0.52002	0.00708	0.42765	0.00424	0.1962	0.01773
a,a,a-Trifluorotoluene	1.35256	0.00015	0.84229	0.0047	0.56811	0.00738	0.4893	0.02567
<i>cis</i> -Heptene-2	1.37652	0.00014	0.54521	0.00468	0.75738	0.00919	0.3198	0.01419
Ethyl propionate	1.38307	0.00163	0.3946	0.00151	0.44621	0.00555	0.0784	0.01266
Propyl acetate	1.41143	0.0008	0.44489	0.00252	0.46437	0.01019	0.0436	0.01036
1-Heptyne	1.47095	0.00088	0.5702	0.00632	0.90958	0.03598	0.2744	0.00658
Butyl formate	1.50438	0.00178	0.41584	0.00137	0.67954	0.00277	0.0344	0.00454
1-Bromobutane	1.50937	0.00023	0.36473	0.00377	0.79748	0.017	0.1299	0.000836
Cyclopropylcyanide	1.51938	0.00055	0.48144	0.00347	0.72398	0.00964	0.0375	0.0082
4-Methylcyclohexene	1.60847	0.00112	0.48699	0.00497	0.87269	0.00814	0.32	0.02012
<i>trans</i> -2-Methyl-2-butenal	1.69613	0.00236	0.50345	0.00591	0.81221	0.00451	0.6109	0.01184
2,3,4-Trimethylpentane	1.72484	0.00062	0.42701	0.00465	0.5786	0.00863	0.1315	0.00519
1-Ethylclopentene	1.83476	0.00148	0.49664	0.00576	0.73853	0.01647	0.3162	0.01731

Table 1. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
2-Ethylbutylaldehyde	1.92889	0.00208	0.42612	0.00605	0.52125	0.01034	0.1976	0.01018
2-Methyheptane	1.96599	0.00186	0.40725	0.01033	0.63739	0.01247	0.0832	0.00949
Toluene (T.P.)	1.99181	0.0067	0.62429	0.00856	0.95692	0.0044	0.7304	0.00746
1-Methylcyclohexene	2.01593	0.00204	0.48681	0.00307	0.83811	0.00522	0.3257	0.01066
CHCl <sub>2</sub> -CH <sub>2</sub> Cl	2.08984	0.00081	0.16595	0.00055	0.63513	0.00652	0.0118	0.00307
2-Bromopentane (T.P.)	2.22391	0.00271	0.32587	0.00252	0.75069	0.0146	0.2336	0.01822
1,1-Dimethylcyclohexane (T.P.)	2.24501	0.00139	0.42921	0.00454	0.65543	0.01364	0.2239	0.02946
Cyclopentylchloride (T.P.)	2.272	0.00917	0.3788	0.00687	0.66435	0.00438	0.0427	0.00687
3-Bromopentane	2.35268	0.00253	0.32324	0.0036	0.78678	0.06548	0.4363	0.10967
Cycloheptane	2.42153	0.00017	0.43796	0.00653	0.9715	0.01185	0.1398	0.01638
2-Hexanone	2.42682	0.00553	0.37873	0.01164	0.53809	0.004	0.2584	0.02057
1-Pentanethiol (T.P.)	2.75093	0.01561	0.33338	0.00673	0.79458	0.02979	0.3357	0.03269
1-Octyne (T.P.)	2.88345	0.00483	0.54124	0.00938	0.8146	0.01371	xxxxxx	xxxxxx
Ethylcyclohexane (T.P.)	2.93536	0.00674	0.45746	0.00562	0.75985	0.0051	0.2215	0.02136
1-Bromopentane (T.P.)	2.95019	0.00726	0.36898	0.00464	0.75576	0.02498	0.1134	0.00544
Allylsulfide (T.P.)	3.17447	0.02195	0.48274	0.01047	1.05077	0.02795	0.8419	0.0134
Ethylbenzene (T.P.)	3.24631	0.0094	0.65953	0.00694	0.88007	0.01902	0.586	0.07822
<i>m</i> -Xylene (T.P.)	3.30813	0.00962	0.93714	0.01022	0.88578	0.02768	0.624	0.05773
<i>p</i> -Xylene (T.P.)	3.32435	0.01001	0.6483	0.01195	1.04334	0.01845	0.7115	0.08044
3,3-Diethylpentane (T.P.)	3.34264	0.0094	0.47862	0.00901	0.54946	0.00832	xxxxxx	xxxxxx
Propylsulfide (T.P.)	3.44289	0.02558	0.4344	0.01178	0.78849	0.02016	0.4555	0.00519
<i>o</i> -Xylene (T.P.)	3.50361	0.01086	0.6646	0.00901	0.83249	0.02551	0.5486	0.04039
Ethyl disulfide (T.P.)	3.73955	0.01293	0.31059	0.00207	0.97631	0.01975	0.59	0.10218
Cumene (T.P.)	3.74044	0.01214	0.67083	0.00829	0.69707	0.01968	0.3784	0.029
1,3-Dibromopropane (0.4 μl) (T.P.)	3.83051	0.03022	0.2577	0.0101	1.02997	0.04837	0.1352	0.00455
Propylbenzene (T.P.)	3.93691	0.01402	0.71998	0.01001	0.72797	0.0176	xxxxxx	xxxxxx
1,3-Dichlorobenzene (T.P.)	4.23624	0.01416	0.44702	0.01898	1.04631	0.04437	0.6376	0.03139
<i>sec.</i> -Butylbenzene (T.P.)	4.28667	0.01643	0.70137	0.00951	0.74486	0.02266	0.3314	0.07167
1,2-Dichlorobenzene (0.5 μl) (T.P.)	4.39759	0.01781	0.48324	0.01465	0.79921	0.02477	xxxxxx	xxxxxxx
<i>n</i> -Butylbenzene (0.5 μl) (T.P.)	4.49655	0.01563	0.67621	0.02301	0.63614	0.02428	0.2983	0.0233
4-Bromo- <i>m</i> -xylene (T.P.)	4.94333	0.02167	0.55626	0.00485	0.89546	0.01983	xxxxxx	xxxxxx
2-Bromo- <i>p</i> -xylene (T.P.)	4.95617	0.01952	0.58727	0.00913	1.04512	0.02502	0.5755	0.0603

pounds can be distinguished simply by relative retention time. However, many times the sole use of retention times is somewhat tenuous and confirmation by additional characterization is welcome and this is where the relative ratios of detector responses come into play. Close examination of the tabular data will reveal that all 127 compounds can be readily distinguished by this set of four values, which supports the primary objective of this study: qualitative analysis of GC peaks. In most cases all four numbers differ sufficiently from adjacent entries in the table and positive identification is unequivocal.

In order to demonstrate the variation in the relative detector responses more visually, we have represented the RePIX values for each of the compounds

in a bar graph. The same bar pattern is used for each compound representing the four relative values from left to right in the same order as in Table 1: RT/RT(Bz), FID-RePIX, Ar-RePIX, Kr-RePIX. These are shown in Fig. 11 for the first 8 compounds in Table 1. Since all values are relative to that for benzene, both the magnitude of the bars as well as the pattern define the set of values for each compound. Note in Fig. 11 the variety of bar structures and how well each compound is defined by the bar graph. In Fig. 12 we show similar bar graphs for the sequence of compounds at the end of Table 1. The relative retention times are not shown since their values are of much larger magnitude than the RePIX values. In this graph only three bars representing the

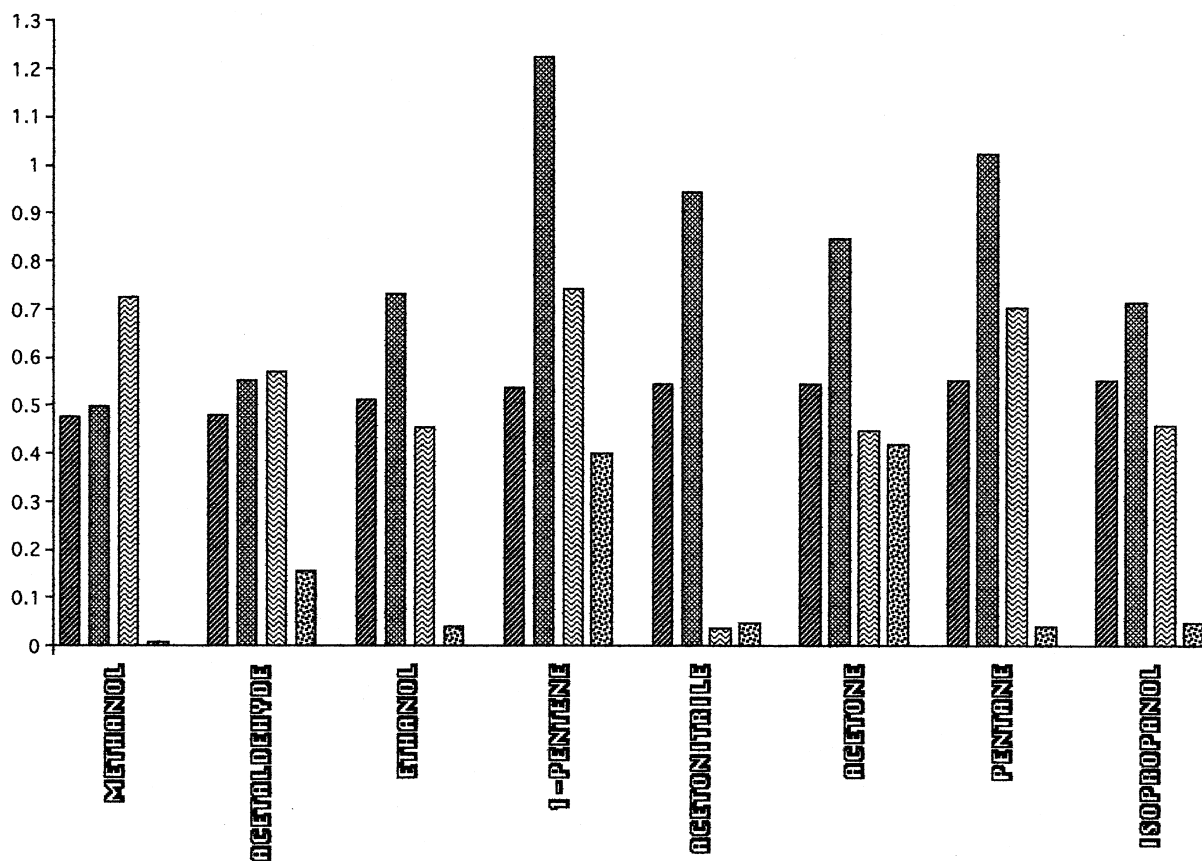


Fig. 11. Bar graph of RePIX values for first 8 compounds from Table 1.

RePIX values are used to identify a compound. In some cases the Kr-RePIX is missing because of an experimental problem which was discussed previously. Even in these cases the remaining two bars representing the FID-RePIX and Ar-RePIX values can be used to identify a compound.

In order to test if two numbers are different, considering their individual standard deviations, a two-sided  $t$ -test can be performed. In applying the two-sided  $t$ -test, one must first decide on the confidence level that is desired. Commonly a 95% confidence level is used and  $\alpha = 1 - 95/100 = 0.05$ . The values in Table 1 are the average of five chromatographic runs so for each relative retention time or relative detector response the number of observations is  $n = 5$  and the degrees of freedom =  $n - 1 = 4$ . In applying the two-sided  $t$ -test for the comparison of two means,  $\bar{X}_A$  and  $\bar{X}_B$ , one looks up

in the  $t$ -test table the value of  $t_{1-\alpha/2}$  for  $\nu = n_A + n_B - 2 = \text{total degrees of freedom}$  for the two values. For the values in Table 1  $n_A = n_B = 5$ ,  $\nu = 8$  and the value of  $t_{1-\alpha/2} = 2.306$ . In applying the two-sided  $t$ -test one also needs the variance ( $\sigma^2$ ) in each of the values being compared. A value of  $u$  is then evaluated from

$$u = (t_{1-\alpha/2}) \sqrt{\left( \frac{(n_A - 1)\sigma_A^2 + (n_B - 1)\sigma_B^2}{n_A + n_B - 2} \right)} \sqrt{\frac{n_A + n_B}{n_A n_B}} \quad (8)$$

For  $n_A = n_B = 5$  and  $t_{1-\alpha/2} = 2.306$ ,  $u$  becomes

$$u = 1.03 \sqrt{\sigma_A^2 + \sigma_B^2} \quad (9)$$

The application of the two-sided  $t$ -test is then simply a comparison of



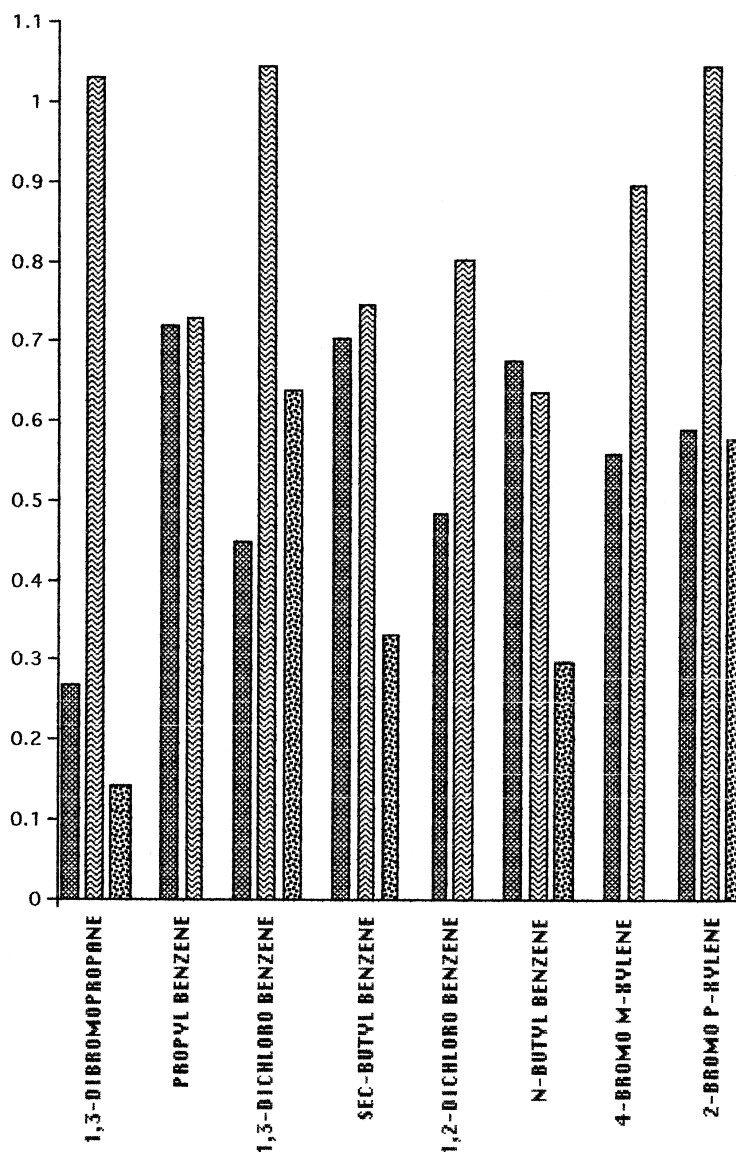


Fig. 12. Bar graph of RePIX values for last 8 compounds from Table 1.

$$|\bar{X}_A - \bar{X}_B| \cong u \quad (10)$$

If the absolute value of the difference in the means,  $|\bar{X}_A - \bar{X}_B|$ , is greater than  $u$ , then the values are considered different at the 95% confidence level. Obviously if  $|\bar{X}_A - \bar{X}_B|$  is less than  $u$ , then the  $\bar{X}_A$  and  $\bar{X}_B$  are not distinguishable.

Application of Eqs. (9) and (10) to the data in Table 1 is quite straight forward. For most cases the

relative retention times are sufficiently different compared to their standard deviations that they can be distinguished. For example, if the error in  $\sigma_A$  and  $\sigma_B$  are of the order of 0.0003, typical of compounds eluted before the temperature program was initiated, the difference in relative retention times must be

$$|\bar{t}_A - \bar{t}_B| > 0.00042$$

This criterion is generally satisfied. For the com-

pounds which elute after the temperature program is initiated the  $\sigma_A$  and  $\sigma_B$  are of the order of 0.02 and

$$|\bar{t}_A - \bar{t}_B| > 0.028$$

will be the criterion for distinguishability. For the later eluting compounds the difference in relative retention times is generally greater than those eluting earlier. In more complex mixtures the possibility that two relative retention times cannot be distinguished is more likely and in these cases the relative detector responses must be used to qualitatively identify the compounds.

Earlier it was mentioned that compounds with a given functional group would be separated on a GC column on the basis of the attached carbon chains. In order to illustrate this we have selected the alcohols and ordered them according to their relative retention times, as shown in Table 2. The standard deviations have been placed beneath the value so that it can be readily compared to the value. Note that the relative retention times can be easily distinguished compared to the standard deviations in these values. The closest values differ by 0.04 but the errors are generally  $\pm 0.0002$ , less than 1% of the difference. Examination of the relative detector ratios (RePIX values) reveals some interesting variations and constancies. Note the variation in the FID-RePIX values

which range from 0.94 for 2-methyl-2-propanol to 0.35 for 1-butanol. Obviously these values depend on the attached carbon chain to the OH. On the other hand, the Ar-RePIX and the Kr-RePIX values remain more constant and are obviously dependent mainly upon the OH functional group. Note the low values for the Kr-RePIX which results from the vertical ionization potential being greater than the 10.6 eV resonance line of krypton. Except for  $\text{CH}_3\text{OH}$ , the Ar-RePIX values range only from 0.41 to 0.56. Similar analyses of the data can be made for other functional groups such as ethers, ketones, esters, etc. For some functional groups there can be a significant variation in the RePIX values and these are useful in making the qualitative analysis.

All of the detector RePIX values make a contribution towards the identification of a GC peak. However, the FID and Ar-RePIX values are more universally valuable compared to Kr-RePIX values since the Kr-RePIX values are very small for some functional groups. The relative value of the individual RePIX values can be assessed better by observing the RePIX value in ascending order. In Table 3 we have sorted the compounds in the order of ascending FID-RePIX values. Note the large and gradual change from 0.1 to 1.3. Because of this wide distribution there is a better chance that the value is characteristic of a compound. It is also interesting to

Table 2  
Relative retention and RePIX values for aliphatic alcohols

Compound	RT/RT(Bz)	FID-RePIX	Ar-RePIX	Kr-RePIX
Methanol	0.47417 $\pm 0.00015$	0.494 $\pm 0.018$	0.724 $\pm 0.028$	0.0075 $\pm 0.0026$
Ethanol	0.511552 $\pm 0.0001$	0.7343 $\pm 0.0068$	0.4853 $\pm 0.0072$	0.0406 $\pm 0.0072$
2-Propanol	0.55048 $\pm 0.00017$	0.7119 $\pm 0.0028$	0.4564 $\pm 0.0048$	0.0453 $\pm 0.0035$
2-Methyl-2-propanol	0.58518 $\pm 0.00012$	0.944 $\pm 0.015$	0.4111 $\pm 0.0059$	0.080 $\pm 0.015$
1-Propanol	0.65080 $\pm 0.00012$	0.6143 $\pm 0.0080$	0.5086 $\pm 0.0040$	0.0396 $\pm 0.0021$
2-Butanol	0.75646 $\pm 0.00022$	0.545 $\pm 0.013$	0.4712 $\pm 0.0016$	0.0440 $\pm 0.0072$
2-Methyl-1-propanol	0.86178 $\pm 0.00014$	0.4751 $\pm 0.0026$	0.5419 $\pm 0.0019$	0.0447 $\pm 0.022$
2-Methyl-2-butanol	0.90186 $\pm 0.00032$	0.572 $\pm 0.013$	0.4717 $\pm 0.0050$	0.139 $\pm 0.022$
1-Butanol	1.05607 $\pm 0.00030$	0.3586 $\pm 0.0014$	0.5674 $\pm 0.0018$	0.0406 $\pm 0.018$

Table 3  
Relative photoionization cross section (RePIX) sorted by FID

Compounds	He DET <sup>a</sup>	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Dibromomethane	1.26684	0.00006	0.1087	0.00137	1.71767	0.0121	0.1116	0.0097
CHCl <sub>2</sub> CH <sub>2</sub> Cl	2.08984	0.00081	0.166	0.00055	0.63513	0.00652	0.0118	0.00307
CCl <sub>3</sub> -CH <sub>3</sub>	0.91911	0.00016	0.235	0.00152	0.54969	0.00532	0.0084	0.00149
1,3-Dibromopropane (0.4 μl) (T.P.)	3.83051	0.03022	0.2577	0.0101	1.02997	0.04837	0.1352	0.00455
CH <sub>2</sub> Cl <sub>2</sub>	0.60014	0.00014	0.2779	0.00512	0.8297	0.00637	0.0262	0.00411
Freon-113	0.58777	0.00022	0.2815	0.00148	0.02731	0.00182	0.0232	0.00547
Ethyl disulfide (T.P.)	3.73955	0.01293	0.3106	0.00207	0.97631	0.01975	0.59	0.10218
3-Bromopentane	2.35268	0.00253	0.3232	0.0036	0.78678	0.06548	0.4363	0.10967
Idomethane (T.P.)	0.58033	0.00178	0.3234	0.00381	2.00935	0.02766	2.1856	0.01311
2-Bromopentane (T.P.)	2.22391	0.00271	0.3259	0.00252	0.75069	0.0146	0.2336	0.01822
1-Pentanethiol (T.P.)	2.75093	0.01561	0.3334	0.00673	0.79458	0.02979	0.3357	0.03269
Ethyl iodide	0.79388	0.00012	0.3466	0.0016	1.29889	0.02568	1.1322	0.10807
CH <sub>2</sub> Cl-CHCl-CH <sub>3</sub>	1.24057	0.00013	0.3548	0.00254	0.88731	0.00985	0.0115	0.0081
1-Butanol	1.05617	0.0003	0.3587	0.00136	0.56738	0.0018	0.0406	0.00177
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.94232	0.0001	0.36	0.0026	1.07522	0.00991	0.0129	0.00329
1-Bromobutane	1.50937	0.00023	0.3647	0.00377	0.79748	0.017	0.1299	0.00836
1-Bromopentane (T.P.)	2.95019	0.00726	0.369	0.00464	0.75576	0.02498	0.1134	0.00544
2-Hexanone	2.42682	0.00553	0.3787	0.01164	6.53809	0.004	0.2584	0.02057
Cyclopentylchloride (T.P.)	2.272	0.00917	0.3788	0.00687	0.66435	0.00438	0.0427	0.00687
Ethyl propionate	1.38307	0.00163	0.3946	0.00151	0.44621	0.00555	0.0784	0.01266
2-Methylheptane	1.96599	0.00186	0.4073	0.01033	0.63739	0.01247	0.0832	0.00949
2-Nitropropane	1.28144	0.00077	0.4141	0.00169	0.73565	0.01	0.0306	0.01322
Butyl formate	1.50438	0.00178	0.4158	0.00137	0.67954	0.00277	0.0344	0.00454
Ethyl sulfide (T.P.)	1.25715	0.0013	0.4244	0.00223	0.90585	0.01781	0.55	0.01795
2-Ethylbutyraldehyde	1.92889	0.00208	0.4261	0.00605	0.52125	0.01034	0.1976	0.01018
2,3,4-Trimethylpentane	1.72484	0.00062	0.427	0.00465	0.5786	0.00863	0.1315	0.00519
1,1-Dimethylcyclohexane (T.P.)	2.24501	0.00139	0.4292	0.00454	0.65543	0.01364	0.2239	0.02946
cis-CHCl=CHCl	0.77317	0	0.4297	0.00398	1.0928	0.01277	0.6477	0.01255
Propylsulfide (T.P.)	3.44289	0.02558	0.4344	0.01178	0.78849	0.02016	0.4555	0.00519
Cycloheptane	2.42153	0.00017	0.438	0.00653	0.9715	0.01185	0.1398	0.01638
Propyl acetate	1.41143	0.0008	0.4449	0.00252	0.46437	0.01019	0.0436	0.01036
1,3-Dichlorobenzene (T.P.)	4.23624	0.01416	0.447	0.01898	1.04631	0.04437	0.6376	0.03139
CHCl <sub>2</sub> -CH <sub>3</sub>	0.68753	0.00019	0.4569	0.00634	0.73669	0.00231	0.0126	0.00571
Ethylcyclohexane (T.P.)	2.93536	0.00674	0.4575	0.00562	0.75985	0.0051	0.2215	0.02136
Dipropyl ether	1.17109	0.00011	0.4637	0.00271	0.6098	0.00364	0.1625	0.00443
Isopropyl acetate	1.02429	0.00039	0.472	0.00546	0.50676	0.01694	0.065	0.02763
2,3-Butanedione	0.71872	0.00066	0.4743	0.00571	0.63212	0.00671	0.6379	0.01069
Nitromethane	0.66696	0.0002	0.4748	0.00273	0.81689	0.00435	0.0514	0.01326
2-Methyl-1-propanol	0.86178	0.00014	0.4751	0.0026	0.54194	0.00188	0.0447	0.0008
3,3-Diethylpentane (T.P.)	3.34264	0.0094	0.4786	0.00901	0.54946	0.00832	xxxxxx	xxxxxx
Cyclopropylcyanide	1.51938	0.00055	0.4814	0.00347	0.72398	0.00964	0.0375	0.0082
Allylsulfide (T.P.)	3.17447	0.02195	0.4827	0.01047	1.05077	0.02795	0.8419	0.0134
1,2-Dichlorobenzene (0.5 μl) (T.P.)	4.39759	0.01781	0.4832	0.01465	0.79921	0.02477	xxxxxx	xxxxxx
1-Methylcyclohexene	2.01593	0.00204	0.4868	0.00307	0.83811	0.00522	0.3257	0.01066
4-Methylcyclohexene	1.60847	0.00112	0.487	0.00497	0.87269	0.00814	0.32	0.02012
Methanol	0.47417	0.00015	0.4941	0.01817	0.72398	0.02823	0.0075	0.00264
Methyl propionate	0.86651	0.00032	0.4959	0.00341	0.50944	0.00339	0.063	0.01021

<sup>a</sup> DET = detector.

(Cont.)

Table 3. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
1-Ethylcyclopentene	1.83476	0.00148	0.4966	0.00576	0.73853	0.01647	0.3162	0.01731
3-Pentanone	1.24441	0.0009	0.5007	0.00296	0.34982	0.00151	0.3908	0.012
1-Bromopropane	0.83578	0.00022	0.5028	0.01004	0.81485	0.01565	0.1599	0.00975
<i>trans</i> -2-Methyl 2-butenal	1.69613	0.00236	0.5035	0.00591	0.81221	0.00451	0.6109	0.01184
<i>trans</i> -CHCl = CHCl	0.65533	0.0001	0.5041	0.00747	1.55098	0.02507	1.0475	0.02455
Allyl acetate	1.28076	0.00119	0.5082	0.00154	0.8102	0.00572	0.159	0.02665
Heptane	1.23928	0.0002	0.5112	0.00433	0.69205	0.01078	0.082	0.00657
Valeraldehyde	1.24349	0.00074	0.5166	0.00526	0.53953	0.0182	0.1443	0.00719
Ethyl acelate	0.80265	0.00039	0.5175	0.00459	0.59955	0.00669	0.0637	1.00436
3,3-Dimethyl-2-butanone	1.3367	0.00054	0.52	0.00708	0.42765	0.00424	0.1962	0.01773
Butyronitrile	1.08918	0.00027	0.5203	0.00152	0.09628	0.0053	0.0342	0.00643
2,2,4-Trimethylpentane	1.14032	0.00025	0.5287	0.00107	0.5879	0.00443	0.1013	0.00416
3-Ethylpentane	1.13585	0.00012	0.5316	0.00051	0.62841	0.00187	0.0727	0.00364
<i>trans</i> -2-Heptene	1.3048	0.00017	0.5396	0.00505	0.75169	0.01154	0.325	0.0065
1-Octyne (T.P.)	2.88345	0.00483	0.5412	0.00938	0.8146	0.01371	xxxxxx	xxxxxx
<i>sec</i> .-Butanol (2-butanol)	0.75646	0.00022	0.5449	0.01306	0.47118	0.00164	0.044	0.00715
2-Pentanone	1.16896	0.00067	0.545	0.00461	0.45733	0.00324	0.2632	0.01131
<i>cis</i> -Heptene-2	1.37652	0.00014	0.5452	0.00468	0.75738	0.00919	0.3198	0.01419
3-Ethyl-2-pentene	1.31511	0.00031	0.5462	0.02512	6.6857	0.01133	0.2971	0.01064
Acetaldehyde	0.47937	0.00094	0.548	0.00351	0.57236	0.0034	0.1539	0.01133
4-Bromo- <i>m</i> -xylene (T.P.)	4.94333	0.02167	0.5563	0.00485	0.89546	0.01983	xxxxxx	xxxxxx
1-Heptyne	1.47095	0.00088	0.5702	0.00632	0.90958	0.03598	0.2744	0.00658
2-Methyl-2-butanol	0.90186	0.00032	0.5721	0.01266	0.47168	0.00496	0.1393	0.02223
Propyl formate	0.82932	0.00045	0.5809	0.00771	0.58226	0.01337	0.0298	0.00905
2-Bromo- <i>p</i> -xylene (T.P.)	4.95617	0.01952	0.5873	0.00913	1.04512	0.02502	0.5755	0.0603
2-Bromopropane	0.69512	0.00007	0.5898	0.0023	0.76242	0.00261	0.173	0.01453
3,3-Dimethylpentane	0.9475	0.00012	0.6013	0.00157	0.57665	0.00264	0.0826	0.00474
1-Heptene	1.17707	0.00041	0.6013	0.00531	0.76676	0.02381	0.2845	0.01933
1-Propanol	0.6508	0.00012	0.6143	0.00796	0.50862	0.004	0.0396	0.00209
Toluene (T.P.)	1.99181	0.0067	0.6243	0.00856	0.95692	0.0044	0.7304	0.00746
2,4-Dimethylpentane (T.P.)	0.83262	0.00056	0.6458	0.0034	0.61485	0.00524	0.066	0.0023
Diisopropyl ether	0.75393	0.00016	0.6479	0.00341	0.55617	0.00537	0.2534	0.00448
<i>p</i> -Xylene (T.P.)	3.32435	0.01001	0.6483	0.01195	1.04334	0.01845	0.7115	0.08044
THF	0.84769	0.00038	0.6502	0.00551	0.62713	0.00451	0.2283	0.00562
Trimethylacetone	0.94798	0.00019	0.6543	0.00644	0.20552	0.00773	0.0305	0.00687
Ethylbenzene (T.P.)	3.24631	0.0094	0.6595	0.00694	0.88007	0.01902	0.586	0.07822
<i>o</i> -Xylene (T.P.)	3.50361	0.01086	0.6646	0.00901	0.83249	0.02551	0.5486	0.04039
Isobutyronitrile	0.84409	0.00011	0.6668	0.01375	0.1082	0.00534	0.0192	0.0052
Cumene (T.P.)	3.74044	0.01214	0.6708	0.00829	0.69707	0.01968	0.3784	0.029
<i>n</i> -Butylbenzene (0.5 µl) (T.P.)	4.49655	0.01563	0.6762	0.02301	0.63614	0.02428	0.2983	0.0233
3-Hexyne	1.02474	0.00013	0.6769	0.00702	0.96744	0.0344	1.2091	0.03339
2-Hexyne	1.1062	0.00015	0.6803	0.00939	1.16919	0.01729	1.3453	0.0412
3-Ethyl-1-pentene	0.95216	0.0002	0.6809	0.00301	0.78263	0.00618	0.2856	0.00653
Cyclohexene	1.10435	0.00014	0.6887	0.00321	1.03156	0.0059	0.3668	0.00805
Butyraldehyde	0.72813	0.0004	0.7009	0.00914	0.51021	0.01011	0.2665	0.02908
<i>sec</i> .-Butylbenzene (T.P.)	4.28667	0.01643	0.7014	0.00951	0.74486	0.02266	0.3314	0.07167
Methyl <i>tert</i> .-butyl ether	0.66475	0.00013	0.7115	0.00409	0.5626	0.00384	0.2879	0.001514
Isopropanol (2-propanol)	0.55048	0.00017	0.7119	0.00282	0.45641	0.00482	0.0453	0.0035

Table 3. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Propionitrile (T.P.)	0.69434	0.00086	0.7158	0.102	0.0163	0.00234	0.0111	0.00376
Propylbenzene (T.P.)	3.93691	0.01402	0.72	0.01001	0.72797	0.0176	xxxxxx	xxxxxx
1-Chloropropane	0.62231	0.0006	0.7242	0.00559	0.74839	0.01377	0.0184	0.00369
Propionaldehyde	0.55134	0.00075	0.7272	0.0075	0.56616	0.0094	0.4715	0.02572
MEK (2-butanone)	0.74134	0.00053	0.7298	0.00369	0.37512	0.00273	0.4287	0.01596
Ethanol	0.51152	0.0001	0.7343	0.00684	0.48529	0.00721	0.0406	0.0072
Bicyclo[2,2,1]hepta-2,5-diene	1.30506	0.00025	0.735	0.00402	0.79927	0.00623	0.5923	0.01631
Diethyl ether	0.55925	0.00008	0.7408	0.01262	0.57438	0.00642	0.3231	0.0049
Methylcyclopentane	0.83789	0.00014	0.7589	0.01144	0.85939	0.00952	0.0719	0.02084
Crotonaldehyde	0.95435	0.00048	0.7678	0.00375	0.9855	0.00575	0.4068	0.04005
Hexane	0.73627	0.00041	0.7689	0.00277	0.70304	0.00213	0.045	0.00419
2-Chloropropane	0.55653	0.00029	0.8058	0.00807	0.63089	0.01069	0.0254	0.00339
a,a,a-Trifluorotoluene	1.35256	0.00015	0.8423	0.0047	0.56811	0.00738	0.4893	0.02567
Acetone	0.54597	0.00075	0.8462	0.00575	0.44658	0.00794	0.4157	0.05802
1-Hexyne	0.81763	0.00027	0.8642	0.00905	0.95821	0.06774	0.319	0.0218
2-Methyl-1-pentene	0.70973	0.00014	0.8736	0.00801	0.74947	0.02317	0.3627	0.00663
<i>trans</i> -4-Methyl-pentene-2	0.66347	0.00017	0.9167	0.0161	0.7532	0.01157	0.3659	0.00406
1-Hexene	0.71234	0.00011	0.9204	0.00248	0.80252	0.00296	0.3477	0.01678
2,2-Dimethylbutane	0.59413	0.00021	0.9358	0.00331	0.58076	0.01082	0.0621	0.00408
<i>m</i> -Xylene (T.P.)	3.30813	0.00962	0.9371	0.01022	0.88578	0.02768	0.624	0.05773
2-Methyl-2-propanol	0.58518	0.00012	0.944	0.01549	0.41114	0.00591	0.0804	0.01505
Acetonitrile	0.54394	0.00034	0.9473	0.00832	0.03544	0.02608	0.045	0.01429
Methacrylonitrile	0.75483	0.00017	0.9527	0.00289	0.68321	0.0061	0.0773	0.01035
<i>cis</i> -4-Methylpentene-2	0.65641	0.00015	0.9822	0.01328	0.7529	0.00864	0.353	0.0162
Cyclopentane	0.65678	0.00065	1.0062	0.00479	0.81092	0.00764	0.0278	0.00338
Pentane	0.54977	0.0006	1.0232	0.00803	0.70226	0.0062	0.0404	0.00947
2-Methylbutene-2	0.57619	0.00012	1.1259	0.0096	6.67439	0.00713	0.4911	0.01233
Cyclopentene	0.63715	0.00006	1.1528	0.00459	0.70006	0.00399	0.4803	0.00401
1,4-Difluorobenzene	1.11527	0.00011	1.169	0.00556	1.25982	0.01114	0.7967	0.04005
Acrylonitrile	0.58842	0.00025	1.22	0.01305	0.82595	0.00747	0.0334	0.01052
1-Pentene	0.53924	0.00011	1.2267	0.00859	0.74068	0.00925	0.3986	0.00511
Hexafluorobenzene (T.P.)	0.77622	0.00076	1.2935	0.01234	1.06673	0.02261	0.2015	0.0649

note in this sequence of FID-RePIX values that the lower values are obtained for compounds which are highly substituted with hetero atoms, such as the halogens. It is probably because of this fact that there is such a large range of FID-RePIX values.

Ordering of the compounds by ascending Ar-RePIX values is shown in Table 4. Again we see a large range of values from 0.02 to 2.0. The reasons for this range of values is completely different from the reason for the range of FID-RePIX values. Consequently, the RePIX from the FID and argon will be complimentary and individually will contribute to the identification of a compound. The order of Ar-RePIX values is dependent upon the number of ionizable electrons and this is especially critical if

the vertical ionization potential is high. Note the very low values for the nitriles which have exceptionally high ionization potentials compared to other functional groups.

In Table 5 we have the compounds listed in ascending order of the Kr-RePIX values. This listing is quite different from the FID- and Ar-RePIX values in that the variation is *not* gradual. Note that about half the compounds have values <0.1. This is obviously the result of few or no electrons which can be ionized by the krypton 10.6 eV line. We then see a gradual increase to 0.5 where the vertical ionization potential drops below even the more intense krypton 10.1 eV line. The values in this region are very helpful in distinguishing subtle changes in the energy

Table 4  
Relative photoionization cross section (RePIX) sorted by Ar-RePIX

Compounds	He DET <sup>a</sup>	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz) Mean	RT/RT(Bz) S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.
Propionitrile (T.P.)	0.69434	0.00086	0.7158	0.102	0.0163	0.00234	0.0111	0.00376
Freon-113	0.58777	0.00022	0.2815	0.00148	0.02731	0.00182	0.0232	0.00547
Acetonitrile	0.54394	0.00034	0.9473	0.00832	0.03544	0.02608	0.045	0.01429
Butyronitrile	1.08918	0.00027	0.5203	0.00152	0.09628	0.0053	0.0342	0.00643
Isobutyronitrile	0.84409	0.00011	0.6668	0.01375	0.1082	0.00534	0.0192	0.0052
Trimethylacetonitrile	0.94798	0.00019	0.6543	0.00644	0.20552	0.00773	0.0305	0.00687
3-Pentanone	1.24441	0.0009	0.5007	0.00296	0.34982	0.00151	0.3908	0.012
MEK (2-butanone)	0.74134	0.00053	0.7298	0.00369	0.37512	0.00273	0.4287	0.01596
2-Methyl-2-propanol	0.58518	0.00012	0.944	0.01549	0.41114	0.00591	0.0804	0.01505
3,3-Dimethyl-2-butanone	1.3367	0.00054	0.52	0.00708	0.42765	0.00424	0.1962	0.01773
Ethyl propionate	1.38307	0.00163	0.3946	0.00151	0.44621	0.00555	0.0784	0.01266
Acetone	0.54597	0.00075	0.8462	0.00575	0.44658	0.00794	0.4157	0.05802
Isopropanol (2-propanol)	0.55048	0.00017	0.7119	0.00282	0.45641	0.00482	0.0453	0.0035
2-Pentanone	1.16896	0.00067	0.545	0.00461	0.45733	0.00324	0.2632	0.01131
Propyl acetate	1.41143	0.0008	0.4449	0.00252	0.46437	0.01019	0.0436	0.01036
sec.-Butanol (2-butanol)	0.75646	0.00022	0.5449	0.01306	0.47118	0.00164	0.044	0.00715
2-Methyl-2-butanol	0.90186	0.00032	0.5721	0.01266	0.47168	0.00496	0.1393	0.02223
Ethanol	0.51152	0.0001	0.7343	0.00684	0.48529	0.00721	0.0406	0.0072
Isopropyl acetate	1.02429	0.00039	0.472	0.00546	0.50676	0.01694	0.065	0.02763
1-Propanol	0.6508	0.00012	0.6143	0.00796	0.50862	0.004	0.0396	0.00209
Methyl propionate	0.86651	0.00032	0.4959	0.00341	0.50944	0.00339	0.063	0.01021
Butyraldehyde	0.72813	0.0004	0.7009	0.00914	0.51021	0.01011	0.2665	0.02908
2-Ethylbutyraldehyde	1.92889	0.00208	0.4261	0.00605	0.52125	0.01034	0.1976	0.01018
2-Hexanone	2.42682	0.00553	0.3787	0.01164	0.53809	0.004	0.2584	0.02057
Valeraldehyde	1.24349	0.00074	0.5166	0.00526	0.53953	0.0182	0.1443	0.00719
2-Methyl-1-propanol	0.86178	0.00014	0.4751	0.0026	0.54194	0.00188	0.0447	0.0008
3,3-Diethylpentane (T.P.)	3.34264	0.0094	0.4786	0.00901	0.54946	0.00832	xxxxx	xxxxxxx
CCl <sub>3</sub> CH <sub>3</sub>	0.91911	0.00016	0.235	0.00152	0.54969	0.00532	0.0084	0.00149
Diisopropyl ether	0.75393	0.00016	0.6479	0.00341	0.55617	0.00537	0.2534	0.00448
Methyl tert.-butyl ether	0.66475	0.00013	0.7115	0.00409	0.5626	0.00384	0.2879	0.00514
Propionaldehyde	0.55134	0.00075	0.7272	0.0075	0.56616	0.0094	0.4715	0.02572
1-Butanol	1.05617	0.0003	0.3587	0.00136	0.56738	0.0018	0.0406	0.00177
a.a.a-Trifluorotoluene	1.35256	0.00015	0.8423	0.0047	0.56811	0.00738	0.4893	0.02567
Acetaldehyde	0.47937	0.00094	0.548	0.00351	0.57236	0.0034	0.1539	0.01133
Diethyl ether	0.55925	0.00008	0.7408	0.01262	0.57438	0.00642	0.3231	0.0049
3,3-Dimethylpentane	0.9475	0.00012	0.6013	0.00157	0.57665	0.00264	0.0826	0.00474
2,3,4-Trimethylpentane	1.72484	0.00062	0.427	0.00465	0.5786	0.00863	0.1315	0.00519
2,2-Dimethylbutane	0.59413	0.00021	0.9358	0.00331	0.58076	0.01082	0.0621	0.00408
Propyl formate	0.82932	0.00045	0.5809	0.00771	0.58226	0.01337	0.0298	0.00905
2,2,4-Trimethylpentane	1.14032	0.00025	0.5287	0.00107	0.5879	0.00443	0.1013	0.00416
Ethyl acetate	0.80265	0.00039	0.5175	0.00459	0.59955	0.00669	0.0637	0.00436
Dipropyl ether	1.17109	0.00011	0.4637	0.00271	0.6098	0.00364	0.1625	0.00443
2,4-Dimethylpentane (T.P.)	0.83262	0.00056	0.6458	0.0034	0.61485	0.00524	0.066	0.0023
THF	0.84769	0.00038	0.6502	0.00551	0.62713	0.00451	0.2283	0.00562
3-Ethylpentane	1.13585	0.00012	0.5316	0.00051	0.62841	0.00187	0.0727	0.00364
2-Chloropropane	0.55653	0.00029	0.8058	0.00807	0.63089	0.01069	0.0254	0.00339
2,3-Butanedione	0.71872	0.00066	0.4743	0.00571	0.63212	0.00671	0.6379	0.01069
CHCl <sub>2</sub> -CH <sub>2</sub> Cl	2.08984	0.00081	0.166	0.00055	0.63513	0.00652	0.0118	0.00307

<sup>a</sup> DET = detector.

Table 4. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
<i>n</i> -Butylbenzene (0.5 µl) (T.P.)	4.49655	0.01563	0.6762	0.02301	0.63614	0.02428	0.2983	0.0233
2-Methylheptane	1.96599	0.00186	0.4073	0.01033	0.63739	0.01247	0.0832	0.00949
1,1-Dimethylcyclohexane (T.P.)	2.24501	0.00139	0.4292	0.00454	0.65543	0.01364	0.2239	0.02946
Cyclopentylchloride (T.P.)	2.272	0.00917	0.3788	0.00687	0.66435	0.00438	0.0427	0.00687
2-Methylbutene-2	0.57619	0.00012	1.1259	0.0096	0.67439	0.00713	0.4911	0.01233
Butyl formate	1.50438	0.00178	0.4158	0.00137	0.67954	0.00277	0.0344	0.00454
Methacrylonitrile	0.75483	0.00017	0.9527	0.00289	0.68321	0.0061	0.0773	0.01035
3-Ethyl-2-pentene	1.31511	0.00031	0.5462	0.02512	0.6857	0.01133	0.2971	0.01064
Heptane	1.23928	0.0002	0.5112	0.00433	0.69205	0.01078	0.082	0.00657
Cumene (T.P.)	3.74044	0.01214	0.6708	0.00829	0.69707	0.01968	0.3784	0.029
Cyclopentene	0.63715	0.00006	1.1528	0.00459	0.70006	0.00399	0.4803	0.00401
Pentane	0.54977	0.0006	1.0232	0.00803	0.70226	0.0062	0.0404	0.00947
Hexane	0.73627	0.00041	0.7689	0.00277	0.70304	0.00213	0.045	0.00419
Cyclopropylcyanide	1.51938	0.00055	0.4814	0.00347	0.72398	0.00964	0.0375	0.0082
Methanol	0.47417	0.00015	0.4941	0.01817	0.72398	0.02823	0.0075	0.00264
Propylbenzene (T.P.)	3.93691	0.01402	0.72	0.01001	0.72797	0.0176	xxxxxx	xxxxxx
2-Nitropropane	1.28144	0.00077	0.4141	0.00169	0.73565	0.01	0.0306	0.01322
CHCl <sub>2</sub> -CH <sub>3</sub>	0.68753	0.00019	0.4569	0.00634	0.73669	0.00231	0.0126	0.00571
1-Ethylcyclopentene	1.83476	0.00148	0.4966	0.00576	0.73853	0.01647	0.3162	0.01731
1-Pentene	0.53924	0.00011	1.2267	0.00859	0.74068	0.00925	0.3986	0.00511
<i>sec.</i> -Butylbenzene (T.P.)	4.28667	0.01643	0.7014	0.00951	0.74486	0.02266	0.3314	0.07167
1-Chloropropane	0.62231	0.0006	0.7242	0.00559	0.74839	0.01377	0.0184	0.00369
2-Methyl-1-pentene	0.70973	0.00014	0.8736	0.00801	0.74947	0.02317	0.3627	0.00663
2-Bromopentane (T.P.)	2.22391	0.00271	0.3259	0.00252	0.75069	0.0146	0.2336	0.01822
<i>trans</i> -2-Heptene	1.3048	0.00017	0.5396	0.00505	0.75169	0.01154	0.325	0.0065
<i>cis</i> -4-Methylpentene-2	0.65641	0.00015	0.9822	0.01328	0.7529	0.00864	0.353	0.0162
<i>trans</i> -4-Methylpentene-2	0.66347	0.00017	0.9167	0.0161	0.7532	0.01157	0.3659	0.00406
1-Bromopentane (T.P.)	2.95019	0.00726	0.369	0.00464	0.75576	0.02498	0.1134	0.00544
<i>cis</i> -Heptene-2	1.37652	0.00014	0.5452	0.00468	0.75738	0.00919	0.3198	0.01419
Ethylcyclohexane (T.P.)	2.93536	0.00674	0.4575	0.00562	0.75985	0.0051	0.2215	0.02136
2-Bromopropane	0.69512	0.00007	0.5898	0.0023	0.76242	0.00261	0.173	0.01453
1-Heptene	1.17707	0.00041	0.6013	0.00531	0.76676	0.02381	0.2845	0.01933
3-Ethyl-1-pentene	0.95216	0.0002	0.6809	0.00301	0.78263	0.00618	0.2856	0.00653
3-Bromopentane	2.35268	0.00253	0.3232	0.0036	0.78678	0.06548	0.4363	0.10967
Propylsulfide (T.P.)	3.44289	0.02558	0.4344	0.01178	0.78849	0.02016	0.4555	0.00519
1-Pentanethiol (T.P.)	2.75093	0.01561	0.3334	0.00673	0.79458	0.02979	0.3357	0.03269
1-Bromobutane	1.50937	0.00023	0.3647	0.00377	0.79748	0.017	0.1299	0.000836
1,2-Dichlorobenzene (0.5 µl) (T.P.)	4.39759	0.01781	0.4832	0.01465	0.79921	0.02477	xxxxxx	xxxxxx
Bicyclo[2,2,1]hepta-2,5-diene	1.30506	0.00025	0.735	0.00402	0.79927	0.00623	0.5923	0.01631
1-Hexene	0.71234	0.00011	0.9204	0.00248	0.80252	0.00296	0.3477	0.01678
Allyl acetate	1.28076	0.00119	0.5082	0.00154	0.8102	0.00572	0.159	0.02665
Cyclopentane	0.65678	0.00065	1.0062	0.00479	0.81092	0.00764	0.0278	0.00338
<i>trans</i> -2-Methyl-2-butenal	1.69613	0.00236	0.5035	0.00591	0.81221	0.00451	0.6109	0.01184
1-Octyne (T.P.)	2.88345	0.00483	0.5412	0.00938	0.8146	0.01371	xxxxxx	xxxxxx
1-Bromopropane	0.83578	0.00022	0.5028	0.01004	0.81485	0.01565	0.1599	0.00975
Nitromethane	0.66696	0.0002	0.4748	0.00273	0.81689	0.00435	0.0514	0.01326
Acrylonitrile	0.58842	0.00025	1.22	0.01305	0.82595	0.00747	0.0334	0.01052
CH <sub>2</sub> Cl <sub>2</sub>	0.60014	0.00014	0.2779	0.00512	0.8297	0.00637	0.0262	0.00411
<i>o</i> -Xylene (T.P.)	3.50361	0.01086	0.6646	0.00901	0.83249	0.02551	0.5486	0.04039

(Cont.)

Table 4. Continued

Compounds	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	RT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
1-Methylcyclohexene	2.01593	0.00204	0.4868	0.00307	0.83811	0.00522	0.3257	0.01066
Methylcyclopentane	0.83789	0.00014	0.7589	0.01144	0.85939	0.00952	0.0719	0.02084
4-Methylcyclohexene	1.60847	0.00112	0.487	0.00497	0.87269	0.00814	0.32	0.02012
Ethylbenzene (T.P.)	3.24631	0.0094	0.6595	0.00694	0.88007	0.01902	0.586	0.07822
<i>m</i> -Xylene (T.P.)	3.30813	0.00962	0.9371	0.01022	0.88578	0.02768	0.624	0.05773
CH <sub>2</sub> Cl-CHCl-CH <sub>3</sub>	1.24057	0.00013	0.3548	0.00254	0.88731	0.00985	0.0115	0.0081
4-Bromo- <i>m</i> -xylene (T.P.)	4.94333	0.02167	0.5563	0.00485	0.89546	0.01983	xxxxxx	xxxxxx
Ethyl sulfide (T.P.)	1.25715	0.0013	0.4244	0.00223	0.90585	0.01781	0.55	0.01795
1-Heptyne	1.47095	0.00088	0.5702	0.00632	0.90958	0.03598	0.2744	0.00658
Toluene (T.P.)	1.99181	0.0067	0.6243	0.00856	0.95692	0.0044	0.7304	0.00746
1-Hexyne	0.81763	0.00027	0.8642	0.00905	0.95821	0.06774	0.319	0.0218
3-Hexyne	1.02474	0.00013	0.6769	0.00702	0.96744	0.0344	1.2091	0.03339
Cycloheptane	2.42153	0.00017	0.438	0.00653	0.9715	0.01185	0.1398	0.01638
Ethyl disulfide (T.P.)	3.73955	0.01293	0.3106	0.00207	0.97631	0.01975	0.59	0.10218
Crotonaldehyde	0.95435	0.00048	0.7678	0.00375	0.9855	0.00575	0.4068	0.04005
1,3-Diromopropane (0.4 μl) (T.P.)	3.83051	0.03022	0.2577	0.0101	1.02997	0.04837	0.1352	0.00455
Cyclohexene	1.10435	0.00014	0.6887	0.00321	1.03156	0.0059	0.3668	0.00805
<i>p</i> -Xylene (T.P.)	3.32435	0.01001	0.6483	0.01195	1.04334	0.01845	0.7115	0.08044
2-Bromo- <i>p</i> -xylene (T.P.)	4.95617	0.01952	0.5873	0.00913	1.04512	0.02502	0.5755	0.0603
1,3-Dichlorobenzene (T.P.)	4.23624	0.01416	0.447	0.01898	1.04631	0.04437	0.6376	0.03139
Allylsulfide (T.P.)	3.17447	0.02195	0.4827	0.01047	1.05077	0.02795	0.8419	0.0134
Hexafluorobenzene (T.P.)	0.77622	0.00076	1.2935	0.01234	1.06673	0.02261	0.2015	0.00649
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.94232	0.0001	0.36	0.0026	1.07522	0.00991	0.0129	0.00329
<i>cis</i> -CHCl=CHCl	0.77317	0	0.4297	0.00398	1.0928	0.01277	0.6477	0.01255
2-Hexyne	1.1062	0.00015	0.6803	0.00939	1.16919	0.01729	1.3453	0.0412
1,4-Difluorobenzene	1.11527	0.00011	1.169	0.00556	1.25982	0.01114	0.7967	0.04005
Ethyl iodide	0.79388	0.00012	0.3466	0.0016	1.29889	0.02568	1.1322	0.10807
<i>trans</i> -CHCl=CHCl	0.65533	0.0001	0.5041	0.00747	1.55098	0.02507	1.0475	0.02455
Dibromomethane	1.26684	0.00006	0.1087	0.00137	1.71767	0.0121	0.1116	0.0097
Iodomethane (T.P.)	0.58033	0.00178	0.3234	0.00381	2.00935	0.02766	2.1856	0.01311

levels with structure, as will be discussed shortly. The lower portion of Table 5, where the values approach 1.0, are aromatics or compounds with two double bonds and ionization potentials less than the krypton resonance lines. These values are extremely useful in characterizing certain classes of compounds and for specific qualitative identification.

### 3.3. Rationale for Kr-RePIX values based upon MO calculations

Previously in Fig. 5 the calculated MOs for some C<sub>6</sub> compounds were given. At this time we want to look at the experimental results for these compounds and rationalize their values based upon the MO calculations. As noted previously, hexene has a pair of electrons in a low energy MO which is generally

associated with the unsaturation and the single  $\pi$  orbital. Other alkenes which contain a single double bond and the associated  $\pi$  orbital have been included in this study and these can be found in Table 5. For convenience we have put the results for the alkenes with a single double bond in Table 6 in ascending order of their RePIX values. As noted previously, the calculated low energy MO in 1-hexene lies just above the 10.1 eV line of krypton. Consequently almost all of the photons from krypton have sufficient energy to ionize these two electrons and we would expect a reasonably high response with the Kr-PDPID. The Kr-RePIX value for 1-hexene is 0.348. Since the RePIX values are relative to benzene we must also consider the benzene response to the Kr-PDPID. As noted before, benzene has two low energy MO which are of even lower energy than



Table 5  
Relative photoionization cross section (RePIX), sorted by Kr-RePIX

Compound	He DET <sup>a</sup>	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz) Mean	KT/RT(Bz) S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.	RePIX Mean	RePIX S.D.
Methanol	0.47417	0.00015	0.4941	0.01817	0.72398	0.02823	0.0075	0.00264
CCl <sub>3</sub> CH <sub>3</sub>	0.91911	0.00016	0.235	0.00152	0.54969	0.00532	0.0084	0.00149
Propionitrile (T.P.)	0.69434	0.00086	0.7158	0.102	0.0163	0.00234	0.0111	0.00376
CH <sub>2</sub> Cl-CHCl-CH <sub>3</sub>	1.24057	0.00013	0.3548	0.00254	0.88731	0.00985	0.0115	0.0081
CHCl <sub>2</sub> -CH <sub>2</sub> Cl	2.08984	0.00081	0.166	0.00055	0.63513	0.00652	0.0118	0.00307
CHCl <sub>2</sub> -CH <sub>3</sub>	0.68753	0.00019	0.4569	0.00634	0.73669	0.00231	0.0126	0.00571
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	0.94232	0.0001	0.36	0.0026	1.07522	0.00991	0.0129	0.00329
1-Chloropropane	0.62231	0.0006	0.7242	0.00559	0.74839	0.01377	0.0184	0.00369
Isobutyronitrile	0.84409	0.00011	0.6668	0.01375	0.1082	0.00534	0.0192	0.0052
Freon-113	0.58777	0.00022	0.2815	0.00148	0.02731	0.00182	0.0232	0.00547
2-Chloropropane	0.55653	0.00029	0.8058	0.00807	0.63089	0.01069	0.0254	0.00339
CH <sub>2</sub> Cl <sub>2</sub>	0.60014	0.00014	0.2779	0.00512	0.8297	0.00637	0.0262	0.00411
Cyclopentane	0.65678	0.00065	1.0062	0.00479	0.81092	0.00764	0.0278	0.00338
Propyl formate	0.82932	0.00045	0.5809	0.00771	0.58226	0.01337	0.0298	0.00905
Trimethylacetone	0.94798	0.00019	0.6543	0.00644	0.20552	0.00773	0.0305	0.00687
2-Nitropropane	1.28144	0.00077	0.4141	0.00169	0.73565	0.01	0.0306	0.01322
Acrylonitrile	0.58842	0.00025	1.22	0.01305	0.82595	0.00747	0.0334	0.01052
Butyronitrile	1.08918	0.00027	0.5203	0.00152	0.09628	0.0053	0.0342	0.00643
Butyl formate	1.50438	0.00178	0.4158	0.00137	0.67954	0.00277	0.0344	0.00454
Cyclopropylcyanide	1.51938	0.00055	0.4814	0.00347	0.72398	0.00964	0.0375	0.0082
1-Propanol	0.6508	0.00012	0.6143	0.00796	0.50862	0.004	0.0396	0.00209
Pentane	0.54977	0.0006	1.0232	0.00803	0.70226	0.0062	0.0404	0.00947
Ethanol	0.51152	0.0001	0.7343	0.00684	0.48529	0.00721	0.0406	0.0072
1-Butanol	1.05617	0.0003	0.3587	0.00136	0.56738	0.0018	0.0406	0.00177
Cyclopentylchloride (T.P.)	2.272	0.00917	0.3788	0.00687	0.66435	0.00438	0.0427	0.00687
Propyl acetate	1.41143	0.0008	0.4449	0.00252	0.46437	0.01019	0.0436	0.01036
sec.-Butanol (2-butanol)	0.75646	0.00022	0.5449	0.01306	0.47118	0.00164	0.044	0.00715
2-Methyl-1-propanol	0.86178	0.00014	0.4751	0.0026	0.54194	0.00188	0.0447	0.0008
Hexane	0.73627	0.00041	0.7689	0.00277	0.70304	0.00213	0.045	0.00419
Acetonitrile	0.54394	0.00034	0.9473	0.00832	0.03544	0.02608	0.045	0.01429
Isopropanol (2-propanol)	0.55048	0.00017	0.7119	0.00282	0.45641	0.00482	0.0453	0.0035
Nitromethane	0.66696	0.0002	0.4748	0.00273	0.81689	0.00435	0.0514	0.01326
2,2-Dimethylbutane	0.59413	0.00021	0.9358	0.00331	0.58076	0.01082	0.0621	0.00408
Methyl propionate	0.86651	0.00032	0.4959	0.00341	0.50944	0.00339	0.063	0.01021
Ethyl acetate	0.80265	0.00039	0.5175	0.00459	0.59955	0.00669	0.0637	0.00436
Isopropyl acetate	1.02429	0.00039	0.472	0.00546	0.50676	0.01694	0.065	0.02763
2,4-Dimethylpentane (T.P.)	0.83262	0.00056	0.6458	0.0034	0.61485	0.00524	0.066	0.0023
Methylcyclopentane	0.83789	0.00014	0.7589	0.01144	0.85939	0.00952	0.0719	0.02084
3-Ethylpentane	1.13585	0.00012	0.5316	0.00051	0.62841	0.00187	0.0727	0.00364
Methacrylonitrile	0.75483	0.00017	0.9527	0.00289	0.68321	0.0061	0.0773	0.01035
Ethyl propionate	1.38307	0.00163	0.3946	0.00151	0.44621	0.00555	0.0784	0.01266
2-Methy-2-propanol	0.58518	0.00012	0.944	0.01549	0.41114	0.00591	0.0804	0.01505
Heptane	1.23928	0.0002	0.5112	0.00433	0.69205	0.01078	0.082	0.00657
3,3-Dimethylpentane	0.9475	0.00012	0.6013	0.00157	0.57665	0.00264	0.0826	0.00474
2-Methylheptane	1.96599	0.00186	0.4073	0.01033	0.63739	0.01247	0.0832	0.00949
2,2,4-Trimethylpentane	1.14032	0.00025	0.5287	0.00107	0.5879	0.00443	0.1013	0.00416
Dibromomethane	1.26684	0.00006	0.1087	0.00137	1.71767	0.0121	0.1116	0.0097
1-Bromopentane (T.P.)	2.95019	0.00726	0.369	0.00464	0.75576	0.02498	0.1134	0.00544

<sup>a</sup> DET = detector.

(Cont.)

Table 5. Continued

Compound	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	KT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
1-Bromobutane	1.50937	0.00023	0.3647	0.00377	0.79748	0.017	0.1299	0.00836
2,3,4-Trimethylpentane	1.72484	0.00062	0.427	0.00465	0.5786	0.00863	0.1315	0.00519
1,3-Dibromopropane (0.4 µl) (T.P.)	3.83051	0.03022	0.2577	0.0101	1.02997	0.04837	0.1352	0.00455
2-Methy-2-butanol	0.90186	0.00032	0.5721	0.01266	0.47168	0.00496	0.1393	0.02223
Cycloheptane	2.42153	0.00017	0.438	0.00653	0.9715	0.01185	0.1398	0.01638
Valeraldehyde	1.24349	0.00074	0.5166	0.00526	0.53953	0.0182	0.1443	0.00719
Acetaldehyde	0.47937	0.00094	0.548	0.00351	0.57236	0.0034	0.1539	0.01133
Allyl acetate	1.28076	0.00119	0.5082	0.00154	0.8102	0.00572	0.159	0.02665
1-Bromopropane	0.83578	0.00022	0.5028	0.01004	0.81485	0.01565	0.1599	0.00975
Dipropyl ether	1.17109	0.00011	0.4637	0.00271	0.6098	0.00364	0.1625	0.00443
2-Bromopropane	0.69512	0.00007	0.5898	0.0023	0.76242	0.00261	0.173	0.01453
3,3-Dimethyl-2-butanone	1.3367	0.00054	0.52	0.00708	0.42765	0.00424	0.1962	0.01773
2-Ethylbutyraldehyde	1.92889	0.00208	0.4261	0.00605	0.52125	0.01034	0.1976	0.01018
Hexafluorobenzene (T.P.)	0.77622	0.00076	1.2935	0.01234	1.06673	0.02261	0.2015	0.00649
Ethylcyclohexane (T.P.)	2.93536	0.00674	0.4575	0.00562	0.75985	0.0051	0.2215	0.02136
1,1-Dimethylcyclohexane (T.P.)	2.24501	0.00139	0.4292	0.00454	0.65543	0.01364	0.2239	0.02946
THF	0.84769	0.00038	0.6502	0.00551	0.62713	0.00451	0.2283	0.00562
2-Bromopentane (T.P.)	2.22391	0.00271	0.3259	0.00252	0.75069	0.0146	0.2336	0.01822
Diisopropyl ether	0.75393	0.00016	0.6479	0.00341	0.55617	0.00537	0.2534	0.00448
2-Hexanone	2.42682	0.00553	0.3787	0.01164	0.53809	0.004	0.2584	0.02057
2-Pentanone	1.16896	0.00067	0.545	0.00461	0.45733	0.00324	0.2632	0.01131
Butyraldehyde	0.72813	0.0004	0.7009	0.00914	0.51021	0.01011	0.2665	0.02908
1-Heptyne	1.47095	0.00088	0.5702	0.00632	0.90958	0.03598	0.2744	0.00658
1-Heptene	1.17707	0.00041	0.6013	0.00531	0.76676	0.02381	0.2845	0.01933
3-Ethyl-1-pentene	0.95216	0.0002	0.6809	0.00301	0.78263	0.00618	0.2856	0.00653
Methyl <i>tert.</i> -butyl ether	0.66475	0.00013	0.7115	0.00409	0.5626	0.00384	0.2879	0.00514
3-Ethyl-2-pentene	1.31511	0.00031	0.5462	0.02512	0.6857	0.01133	0.2971	0.01064
<i>n</i> -Butylbenzene (0.5 µl) (T.P.)	4.49655	0.01563	0.6762	0.02301	0.63614	0.02428	0.2983	0.0233
1-Ethylcyclopentene	1.83476	0.00148	0.4966	0.00576	0.73853	0.01647	0.3162	0.01731
1-Hexyne	0.81763	0.00027	0.8642	0.00905	0.95821	0.06774	0.319	0.0218
<i>cis</i> -Heptene-2	1.37652	0.00014	0.5452	0.00468	0.75738	0.00919	0.3198	0.01419
4-Methylcyclohexene	1.60847	0.00112	0.487	0.00497	0.87269	0.00814	0.32	0.02012
Diethyl ether	0.55925	0.00008	0.1408	0.01262	0.57438	0.00642	0.3231	0.0049
<i>trans</i> -2-Heptene	1.3048	0.00017	0.5396	0.00505	0.75169	0.01154	0.325	0.0065
1-Methylcyclohexene	2.01593	0.00204	0.4868	0.00307	0.83811	0.00522	0.3257	0.01066
<i>sec.</i> -Butylbenzene (T.P.)	4.28667	0.01643	0.7014	0.00951	0.74486	0.02266	0.3314	0.07167
1-Pentanethiol (T.P.)	2.75093	0.01561	0.3334	0.00673	0.79458	0.02979	0.3357	0.03269
1 Hexene	0.71234	0.00011	0.9204	0.00248	0.80252	0.00296	0.3477	0.01678
<i>cis</i> -4-Methylpentene-2	0.65641	0.00015	0.9822	0.01328	0.7529	0.00864	0.353	0.0162
2-Methyl-1-pentene	0.70973	0.00014	0.8736	0.00801	0.74947	0.02317	0.3627	0.00663
<i>trans</i> -4-Methyl-pentene-2	0.66347	0.00017	0.9167	0.0161	0.7532	0.01157	0.3659	0.00406
Cyclohexene	1.10435	0.00014	0.6887	0.00321	1.03156	0.0059	0.3668	0.00805
Cumene (T.P.)	3.74044	0.01214	0.6708	0.00829	0.69707	0.01968	0.3784	0.029
3-Pentanone	1.24441	0.0009	0.5007	0.00296	0.34982	0.00151	0.3908	0.012
1-Pentene	0.53924	0.00011	1.2267	0.00859	0.74068	0.00925	0.3986	0.00511
Crotonaldehyde	0.95435	0.00048	0.7678	0.00375	0.9855	0.00575	0.4068	0.04005
Acetone	0.54597	0.00075	0.8462	0.00575	0.44658	0.00794	0.4157	0.05802
MEK (2-butanone)	0.74134	0.00053	0.7298	0.00369	0.37512	0.00273	0.4287	0.01596

Table 5. Continued

Compound	He DET	He DET	FID	FID	Ar DET	Ar DET	Kr DET	Kr DET
	RT/RT(Bz)	KT/RT(Bz)	RePIX	RePIX	RePIX	RePIX	RePIX	RePIX
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
3-Bromopentane	2.35268	0.00253	0.3232	0.0036	0.78678	0.06548	0.4363	0.10967
Propylsulfide (T.P.)	3.44289	0.02558	0.4344	0.01178	0.78849	0.02016	0.4555	0.00519
Propionaldehyde	0.55134	0.00075	0.7272	0.0075	0.56616	0.0094	0.4715	0.02572
Cyclopentene	0.63715	0.00006	1.1528	0.00459	0.70006	0.00399	0.4803	0.00401
a,a,a-Trifluorotoluene	1.35256	0.00015	0.8423	0.0047	0.56811	0.00738	0.4893	0.02567
2-Methylbutene-2	0.57619	0.00012	1.1259	0.0096	0.67439	0.00713	0.4911	0.01233
<i>o</i> -Xylene (T.P.)	3.50361	0.01086	0.6646	0.00901	0.83249	0.02551	0.5486	0.04039
Ethyl sulfide (T.P.)	1.25715	0.0013	0.4244	0.00223	0.90585	0.01781	0.55	0.01795
2-Bromo- <i>p</i> -xylene (T.P.)	4.95617	0.01952	0.5873	0.00913	1.04512	0.02502	0.5755	0.0603
Ethyl benzene (T.P.)	3.24631	0.0094	0.6595	0.00694	0.88007	0.01902	0.586	0.07822
Ethyl disulfide (T.P.)	3.73955	0.01293	0.3106	0.00207	0.97631	0.01975	0.59	0.10218
Bicyclo[2,2,1]hepta-2,5-diene	1.30506	0.00025	0.735	0.00402	0.79927	0.00623	0.5923	0.01631
<i>trans</i> -2-Methyl 2-butenal	1.69613	0.00236	0.5035	0.00591	0.81221	0.00451	0.6109	0.01184
<i>m</i> -Xylene (T.P.)	3.30813	0.00962	0.9371	0.01022	0.88578	0.02768	0.624	0.05773
1,3-Dichlorobenzene (T.P.)	4.23624	0.01416	0.447	0.01898	1.04631	0.04437	0.6376	0.03139
2,3-Butanedione	0.71872	0.00066	0.4743	0.00571	0.63212	0.00671	0.6379	0.01069
<i>cis</i> -CHCl = CHCl	0.77317	0	0.4297	0.00398	1.0928	0.01277	0.6477	0.01255
<i>p</i> -Xylene (T.P.)	3.32435	0.01001	0.6483	0.01195	1.04334	0.01845	0.7115	0.08044
Toluene (T.P.)	1.99181	0.0067	0.6243	0.00856	0.95692	0.0044	0.7304	0.00746
1,4-Difluorobenzene	1.11527	0.00011	1.169	0.00556	1.25982	0.01114	0.7967	0.04005
Allylsulfide (T.P.)	3.17447	0.02195	0.4827	0.01047	1.05077	0.02795	0.8419	0.0134
<i>trans</i> -CHCl = CHCl	0.65533	0.0001	0.5041	0.00747	1.55098	0.02507	1.0475	0.02455
Ethyl iodide	0.79388	0.00012	0.3466	0.0016	1.29889	0.02568	1.1322	0.10807
3-Hexyne	1.02474	0.00013	0.6769	0.00702	0.96744	0.0344	1.2091	0.03339
2-Hexyne	1.1062	0.00015	0.6803	0.00939	1.16919	0.01729	1.3453	0.0412
Iodomethane (T.P.)	0.58033	0.00178	0.3234	0.00381	2.00935	0.02766	2.1856	0.01311
3,3-Diethylpentane (T.P.)	3.34264	0.01194	0.4786	0.00901	0.54946	0.00832	xxxxxx	xxxxxx
Propylbenzene (T.P.)	3.93691	0.01402	0.72	0.01001	0.72797	0.0176	xxxxxx	xxxxxx
1,2-Dichlorobenzene (0.5 $\mu$ l) (T.P.)	4.39759	0.01781	0.4832	0.01465	0.79921	0.02477	xxxxxx	xxxxxx
1-Octyne (T.P.)	2.88345	0.00483	0.5412	0.00938	0.8146	0.01371	xxxxxx	xxxxxx
4-Bromo- <i>m</i> -xylene (T.P.)	4.94333	0.02167	0.5563	0.00485	0.89546	0.01983	xxxxxx	xxxxxx

the single MO in 1-hexene. Since benzene contains four electrons in the two low energy MOs, one would expect its response to the Kr-PDPID to be twice that of 1-hexene. In addition, since virtually all of the krypton photons are capable of ionizing the four electrons in benzene, we would expect the Kr-PDPID response to benzene to be more than double that for 1-hexene. Indeed that is what we observe in that the Kr-RePIX value for 1-hexene is 0.348. A more precise analysis would also take into account the responses to the He-PDPID, since all responses are made relative to the He-PDPID in order to eliminate the concentration term. In looking at the orbital diagram in Fig. 5, it would appear that benzene may have a slightly lower He-PDPID response than 1-hexene since it has slightly fewer

number of ionizable electrons. This would make the Kr-RePIX for 1-hexene even smaller, so a value 0.348 is quite reasonable.

This being the case, one might expect other alkenes containing a single  $\pi$  bond to have a comparable Kr-RePIX value. This is reasonably correct in that the values in Table 6 range from 0.284 for 1-heptene to 0.491 for 2-methyl-2-butene. From our past experience in making these MO calculations, the chain length and chain branching can alter the calculated MO energy and this would have a bearing on the Kr-RePIX value. In particular if the energy of the lowest energy MO falls lower than in 1-hexene, in the vicinity of the krypton 10.6 eV line, then the fraction of photons capable of ionizing these electrons will be reduced and one would expect the

Table 6  
RePIX values for C<sub>5</sub>–C<sub>7</sub> alkenes and alkynes

Compound	FID-RePIX	Ar-RePIX	Kr-RePIX
1-Heptene	0.601	0.767	0.284
3-Ethyl-1-pentene	0.681	0.783	0.286
3-Ethyl-2-pentene	0.546	0.686	0.297
1-Ethylcyclopentene	0.497	0.739	0.316
<i>cis</i> -2-Heptene	0.545	0.757	0.320
4-Methylcyclohexene	0.487	0.873	0.320
<i>trans</i> -2-Heptene	0.540	0.752	0.325
1-Hexene	0.920	0.803	0.348
<i>cis</i> -4-Methyl-2-pentene	0.982	0.753	0.353
2-Methyl-1-pentene	0.874	0.749	0.363
<i>trans</i> -4-Methyl-2-pentene	0.917	0.753	0.363
Cyclohexene	0.689	1.036	0.367
1-Pentene	1.227	0.741	0.399
Cyclopentene	1.153	0.700	0.480
2-Methyl-2-butene	1.126	0.674	0.491
1-Hexyne	0.497	0.739	0.361
3-Hexyne	0.677	0.967	1.209
2-Hexyne	0.680	1.11699	1.345

Kr-PDPID response to decrease. For this reason there is some variation in the Kr-RePIX values for the single unsaturated alkenes and in this case the Kr-RePIX value can be helpful in identifying the analyte. One should note the rather large change in going from 1-heptene to 2-heptene (*cis* or *trans*) and an even greater change in going from 1-heptene to 1-hexene to 1-pentene. Many of these variations can be rationalized on the basis of the MO calculations, and this will be the subject of a later paper.

Finally in Table 6 we give the experimental Kr-RePIX values for the three hexynes. The MO calculations for all three hexynes are given in Fig. 5. Since the hexynes have two low energy  $\pi$  orbitals, as shown in Fig. 5, one might expect the Kr-PDPID response for the hexynes to be comparable to that for benzene. However, according to the MO calculations given in Fig. 5, the energy of the two lowest MOs for 1-hexyne are considerably lower (more stable) than those for 2-hexyne and 3-hexyne. In fact the energy for the two lowest MOs for 1-hexyne are well below the 10.1 eV krypton line and would only be ionized by the less intense 10.6 eV krypton line. Thus one can rationalize for the big difference in Kr-RePIX values between 1-hexyne (0.361) and 2-hexyne (1.209) and 3-hexyne (1.345). This is similar to the experimentally observed difference in Kr-RePIX values for 1-hexene and 2-hexene. However,

the large values for the hexynes in general is very noticeable. From the MO diagram in Fig. 5 one would expect the Kr-PDPID for benzene to be greater than that for the 2- and 3-hexynes, since the MOs for benzene are higher than those for 2- and 3-hexyne. However, experimentally we observe quite the opposite in that the 2- and 3-hexyne Kr-RePIX values are greater than those for benzene. Apparently the triple bond has an extraordinarily high cross section for photoionization. Other triple bonded compounds will be investigated in the future.

Future studies will include element specific detectors which will be used in conjunction with more universal detectors. For example, a Cl-specific detector could be combined with a He-PDPID, FID, and Kr-PDPID. Combination of these detector responses would not only identify Cl-containing compounds, but also allow specific identification of the compound. For example, the Kr-PDPID response would readily differentiate between a saturated and an unsaturated Cl-containing compound.

#### 4. Conclusions

Four detectors have been used in this study for the qualitative analysis of GC peaks. The response of each detectors has a different basis and, consequently, the responses are independent. In order to eliminate the concentration dependence of the responses, the detector responses are made relative to the He-PDPID, which is a universal response. In addition these relative detector responses are made relative to an internal standard in order to account for long-term drifts in the electronic equipment. The relative detector responses, combined with the relative retention time, give four values which are unique to each of the 127 compounds included in this study. The compounds covered 13 classes of compounds containing various functional groups.

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