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## Experimental and theoretical relative response factors for a pulsed discharge krypton photoionization detector

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### Abstract

The relative photoionization cross sections (RePIX) have been determined for a series of compounds normalized to benzene. The detectors are doped (5.01% Kr) Kr-PDPID and pure helium (He-PDPID) pulsed discharge helium photoionization detectors. The pure helium detector is used to reference the responses. The magnitudes for the Kr-PDPID varied from about 0.0 to 0.95. In order to understand the relative responses of these compounds in the Kr-PDPID, the SCF-MO energy levels were calculated for these compounds using HyperChem. Calculated vertical ionization potentials are compared with experimental adiabatic ionization potentials.

**Keywords:** Detection, GC; Photoionization detection; Krypton; Benzene

### 1. Introduction

In the preceding publication [1], the absolute response of a universal He photoionization detector was measured. This was correlated to the number of ionizable electrons calculated using a SCF-MO procedure and the distribution of the He emission. The use of argon and krypton doped helium as the discharge gas provides a selective detector. The energy of the discharge is deposited in different excited states in helium and transferred to argon or krypton. The emission then arises from the resonance lines of the elements and the diatomic species Ar<sub>2</sub> and Kr<sub>2</sub>. These detectors are called pulsed discharge photoionization detectors (PDPID) with a dopant as

a prefix, such as Kr-PDPID. The PDPID then could also be called a He-PDPID.

The simultaneous measurement of the responses from both a Kr-PDPID and a He-PDPID leads to relative photoionization cross sections, normalized to a reference compound, specifically, benzene. This is characteristic of the compound and has been designated as the RePIX. The He-PDPID provides a simultaneous measurement of the relative concentrations. We have presented data for representative compounds and have shown that the doped detectors are selective [2]. In this paper, we present additional values of the Kr-RePIX values using a higher concentration of Kr (5% versus 0.5%).

The Kr-RePIX values cover a range of values. Because of the high energy of the photons, there were no compounds with low responses. In the case

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of the Kr-PDPID, this is not true. For example, there is no response to water, acetonitrile and several chlorinated hydrocarbons and a low response to methanol. In the preceding paper [1] it was found that the absolute molar response of the He-PDPID is related to the number of ionizable electrons obtained from SCF-MO calculations. Therefore we have chosen to determine the *RePIX* values for a series of alkanes, alkenes, chlorinated compounds and oxygen containing compounds. By calculating the SCF-MO values for these same compounds, this hypothesis can be tested.

HyperChem is a commercial software program from Hypercube (Waterloo, Canada), which calculates SCF-MO molecular orbitals for molecules using various Hamiltonians and parameter sets. The AM1 (Austin Model 1) variation has been used to calculate absolute electron affinities and ionization potentials [3] of the purines and pyrimidines in good agreement with experimental values. This was used to calculate the number of electrons of different classes of molecules that are ionizable by the  $\text{He}_2^*$  continuum [1] in the PDPID.

It was found that the calculated energy of the HOMO for oxygenated compounds did not overlap the photon energy for the Krypton emission using the default AM1 parameters. Also the calculated vertical ionization potentials were much higher than the experimental values. Therefore, three variations of one parameter for oxygen were made to obtain a better correlation for the oxygen containing compounds. With these modifications, it is possible to estimate *RePIX* values from the SCF-MO calculations.

## 2. Experimental and calculation procedures

The experimental apparatus and experimental procedures used in a previous study were applied to these compounds with a few modifications [2]. In the previous study, two Ar-PDPID were used, one at a low concentration of dopant (<1%) and the other at a high concentration of dopant (~5%). It was noted that the responses of these two Ar-PDPID were highly correlated and little was gained in using both of these for qualitative identification of the analyte.

The flame ionization detector of the HP 5880 gas

chromatograph was substituted for the 1% Ar-PDPID detector. The analog output from the HP5880 is input to the previously described collection circuitry. The krypton source is replaced by a premixed cylinder of 5.01% Kr/He, research grade minimum purity 99.999%, from Alphagaz, Morrisville PA, USA. The total gas flow-rates for the PDPID are 20.0 ml/min. In this study, the outlet from the capillary column was split approximately equally into four streams going to the four detectors: He-PDPID, 5% Ar-PDPID, 5% Kr-PDPID and the FID. A schematic diagram of the modified experimental set up is shown in Fig. 1.

The procedure for the calculation of the *RePIX* values from the actual chromatographic ratios has been given. For clarity, this presentation will be expanded. The quantity that we are seeking is the relative photoionization cross sections, thus the abbreviation *RePIX*, of a certain compound measured using a certain doped PDPID to that of the He-PDPID. If the spectral distribution for each detector remains constant, this *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.

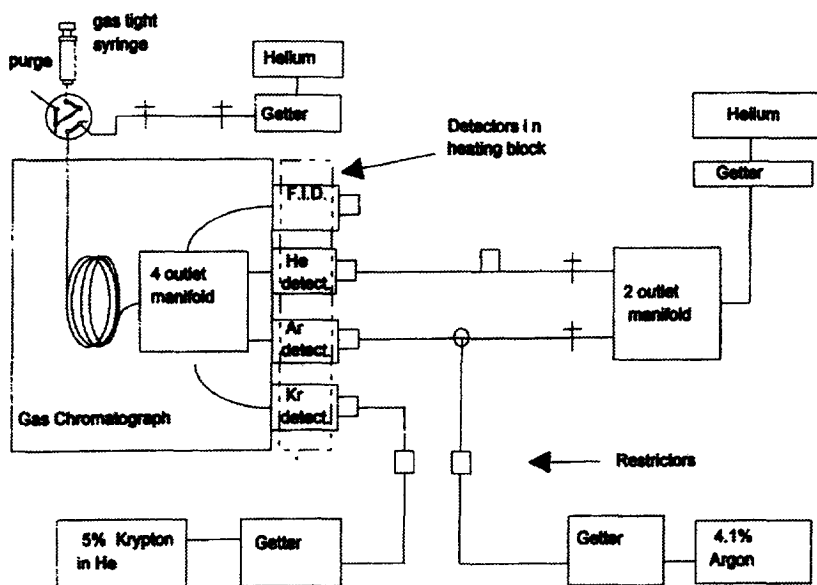


Fig. 1. Schematic diagram of experimental apparatus.

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 setting 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. Differential or multiple internal standards could be used providing the *RePIX* values are known relative to one another. In this study, we use benzene as the internal standard since it has a large response in all four detectors

The responses can be expressed as follows

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

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

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

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

where the  $R$  is the response, the  $k$  is 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 and  $C_x$  is the concentration of the analyte while  $C_{\text{std}}$  is the concentration of the internal standard.

By taking the ratios of the responses for the compounds  $X$ , and the internal standard, and assuming that the concentrations at the maximum are at the same time for the Kr-PDPID and the He-PDPID, i.e., the concentration distribution is the same in the two detectors, the concentration terms can be eliminated. That is dividing Eq. (1) by Eq. (3) and Eq. (2) by Eq. (4) will give

$$\frac{R_{\text{He},X}}{R_{\text{Kr},X}} = \frac{k_{\text{He},X} f_{\text{He}} P_{\text{He}}}{k_{\text{Kr},X} f_{\text{Kr}} P_{\text{Kr}}} \quad (5)$$

$$\frac{R_{\text{He},\text{std}}}{R_{\text{Kr},\text{std}}} = \frac{k_{\text{He},\text{std}} f_{\text{He}} P_{\text{He}}}{k_{\text{Kr},\text{std}} f_{\text{Kr}} P_{\text{Kr}}} \quad (6)$$

The following ratio of the relative responses called the relative photoionization cross section (*RePIX*) eliminates the variation of the split ratio between the detectors and the differences in power supplied to the

detector. This assumes that the split ratio and the power supplied to the detector is the same for the standard and the sample

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

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 which was used in this study. Since some other detectors will not be dependent on photoionization cross sections, it would be appropriate to rename the acronym to reflect this difference, for example ReFIX for relative flame ionization detector response. The complete results of this study will be reported at a later date. In this paper we will only use the data from the He-PDPID and the Kr-PDPID.

The calculation of the theoretical *RePIX* values are based on the determination of the number of ionizable electrons by the radiation in the discharge. This is defined as

$$RePIX(\text{calc}) = \frac{\{\text{Electrons}_{Kr,X}/\text{Electrons}_{Kr,Std}\}}{\{\text{Electrons}_{He,X}/\text{Electrons}_{He,Std}\}} \quad (8)$$

where the number of electrons are determined as in the previous paper for the Helium ionization and for the Krypton ionization using the spectrum from a 3% Kr in Helium discharge.

### 3. Results and discussion

In a previous publication [4], the relative photoionization cross sections for heptane, 3,3-dimethylpropane, 1-hexene, 1-bromopropane and 2-butanone were measured as a function of argon and krypton concentrations in a doped PDPID. The argon concentration was varied from 0.5% to 5%. At low argon concentrations (<3%) there was a slight decrease in the responses relative to benzene which was used as an internal standard. Between 3% and 5%, the relative responses were essentially constant. Since argon is relatively inexpensive, a concentration of 5% was used in the previous study.

The relative values were measured for krypton concentrations in the range of 0.3% to 1.9%. The relative values appeared to level off at higher concentrations. Since krypton is considerably more expensive than argon, the study was not continued to higher concentrations. A concentration of 1.4% was used in the previous study.

Since the pre-mixed 5% krypton concentration was used in the Kr-PDPID in the present study, we have extended the measurement of relative photoionization cross sections from 3% to 5% for acetone, 1-hexene, methyl *tert.*-butyl ether, 2-butanol, isopropanol, and benzene. Indeed, we do see a leveling off of the relative values, becoming essentially constant in this region. The only exception to this is a slight decrease in the relative values for the alcohols. The response for the alcohols is weak and shows an apparently greater percent variation since the value is lower.

In this paper, we will use the *RePIX* values obtained using 5% krypton. The spectral distribution of the Kr emission was measured up to 3% Kr due to the experimental limitations. However, since there is essentially no change in the *RePIX* values in the range of 3%–5%, the 3% Kr distribution can be used to estimate *RePIX* values at 5%. The slight variations in the alcohol values have been taken into consideration.

In Table 1, the Kr-*RePIX* values are given. The results for those compounds reported in a previous study using 0.5% Kr are quite similar [2]. There are some variations over this large of concentration range. Table 1 also lists the calculated *RePIX* values in groups in the order of decreasing ionization potentials. The groups are chlorinated hydrocarbons, hydrocarbons, esters, ketones, ethers, alcohols, and aldehydes. Also shown are the calculated vertical ionization potentials and the experimental adiabatic ionization potentials.

The Kr-*RePIX* values correspond to the lowest energy photons examined thus far. Many compounds do not respond because of their high ionization potentials. Less than 5% of the emission is above 11.0 eV. This should represent a threshold for ionization and indeed, all compounds with experimental ionization potentials greater than 10.3 eV have *RePIX* values below 0.03. The chloroalkanes have little or no response and the response to

Table 1  
Experimental and calculated ionization potentials and *RePIX* values

Compound	<i>IE</i> (eV)		<i>RePIX</i>	
	Experimental	Calculated	Experimental	Calculated
Dichloromethane	11.32	11.39	0.008	0.005
1,1-Dichloroethane	11.06	11.45	0.000	0.003
1,2-Dichloroethane	11.04	11.38	0.000	0.010
1,1,1-Trichloroethane	11.00	11.99	0.000	0.000
1,1,2-Trichloroethane	11.00	11.57	0.000	0.006
1,2-Dichloropropane	10.87	11.29	0.0025	0.016
<i>cis</i> -1,2-Dichloroethene	9.66	9.97	0.549	0.650
Pentane	10.35	11.12	0.036	0.016
Hexane	10.13	11.06	0.051	0.017
2,2-Dimethylbutane	10.02	11.19	0.070	0.014
Heptane	9.92	11.01	0.080	0.019
3-Ethylpentane	9.90	10.98	0.117	0.045
3,3-Dimethylpentane	9.90	11.00	0.117	0.024
Methylcyclopentane	9.85	10.97	0.076	0.033
2,2,3-Trimethylpentane	9.80	10.99	0.121	0.055
2,3,3-Trimethyl-1-butene	9.80	9.68	0.305	0.345
1-Pentene	9.52	9.92	0.363	0.435
1-Hexene	9.45	9.93	0.355	0.365
2-Methyl-1-pentene	9.44	9.70	0.325	0.383
Cyclopentene	9.01	9.83	0.579	0.501
<i>cis</i> -4-Methylpentene-2	8.98	9.61	0.374	0.311
Cyclohexene	8.94	9.49	0.419	0.437
4-Methylcyclohexene	8.91	9.47	0.438	0.380
2-Methylbutene-2	8.68	9.23	0.469	0.469
1-Methylcyclohexene	8.67	9.21	0.437	0.377
Bicyclo(2.2.1)hepta-1-diene	8.67	8.67	0.675	0.562
1-Ethylcyclopentene	8.53	9.19	0.409	0.375
<i>cis</i> -Heptene 2	8.44	9.54	0.371	0.303
Propyl formate	10.52	10.81	0.019	0.036
Butyl formate	10.50	10.95	0.028	0.024
Methyl propionate	10.15	10.52	0.101	0.107
Ethyl acetate	10.04	10.63	0.105	0.079
Propyl acetate	10.01	10.64	0.107	0.096
Ethyl propionate	10.00	10.57	0.111	0.148
Isopropyl acetate	9.99	10.70	0.140	0.059
Allyl acetate	9.40	10.18	0.293	0.364
Acetone	9.70	9.91	0.656	0.549
Methyl ethyl ketone	9.51	9.83	0.557	0.589
2-Pentanone	9.38	9.72	0.479	0.407
3-Pentanone	9.31	9.73	0.418	0.418
2,3-Butanedione	9.20	9.30	0.648	0.445
3,3-Dimethyl-2-butanone	9.11	9.70	0.367	0.323
Diethyl ether	9.51	10.07	0.307	0.329
Tetrahydrofuran	9.41	9.88	0.416	0.361
Dipropyl ether	9.27	10.06	0.238	0.245
Methyl <i>tert.</i> -butyl ether	9.24	10.11	0.317	0.286
Diisopropyl ether	9.20	10.14	0.308	0.351
Methanol	10.85	11.13	0.004	0.016
Ethanol	10.47	10.88	0.063	0.046

(Continued on p. 154)

Table 1 (continued)

Compound	IE (eV)		<i>RePIX</i>	
	Experimental	Calculated	Experimental	Calculated
1-Propanol	10.22	10.65	0.105	0.110
Isopropanol	10.12	10.55	0.109	0.140
Isobutyl alcohol	10.12	10.48	0.129	0.091
1-Butanol	10.06	10.48	0.121	0.112
<i>tert.</i> -Butyl alcohol	9.94	10.62	0.116	0.062
<i>sec.</i> -Butanol	9.88	10.52	0.149	0.096
2-Methyl-2-butanol	9.80	10.59	0.173	0.086
Acetaldehyde	10.23	10.21	0.329	0.420
Propionaldehyde	9.95	10.11	0.446	0.346
Butyraldehyde	9.84	10.07	0.378	0.387
Valeraldehyde	9.74	10.07	0.384	0.325
Crotonaldehyde	9.73	10.10	0.941	1.036
<i>trans.</i> -2,2-Methyl butenal	9.60	9.45	0.956	0.971
2-Ethylbutyraldehyde	9.54	9.97	0.415	0.305

methanol and ethanol is low. The values for the saturated hydrocarbons are low while those for the olefins intermediate and those for the olefins are close to that of benzene. This relationship between saturated and unsaturated compounds is also reflected in the other groups. For example, allyl acetate has the highest value of all the esters while the unsaturated aldehydes have the largest response among the aldehydes. In each group, there is a general tendency for the *RePIX* values to become greater than zero at a threshold ionization potential and increase with decreasing ionization potential.

However, there does not seem to be a simple correlation between the *RePIX* values and the ionization potentials. For example, the aldehydes have an unusually large response for a given ionization potential while the formates give an unusually low response for a specific ionization potential. In order to provide a quantitative technique for estimating *RePIX* values, SCF-MO calculations were carried out for those molecules investigated in this study. In the cases where the default values provided reliable estimates of the *RePIX* values, they were used. These included the formates, methanol, and the hydrocarbons and chlorinated hydrocarbons. In the case of high molecular weight alcohols, branched alcohols, ketones, aldehydes, and esters, three modifications in the default parameter were made. The default value of the one center electron repulsion integral,  $G_{pp} = (pp|p'p')$  was 12.98 while it was adjusted to 13.25 for the linear alcohols and esters; 13.5 for the

aldehydes, ethers, and branched alcohols, and 14.0 for ketones. These data are shown in Table 1. In Fig. 2, the calculated *RePIX* values are plotted against the experimental *RePIX* values. The line that is shown is drawn with a fixed unit slope. The least squares fit has a slope of approximately 1.03. Thus, including the three modifications of the SCF-MO parameter, there are three parameters used to generate the line.

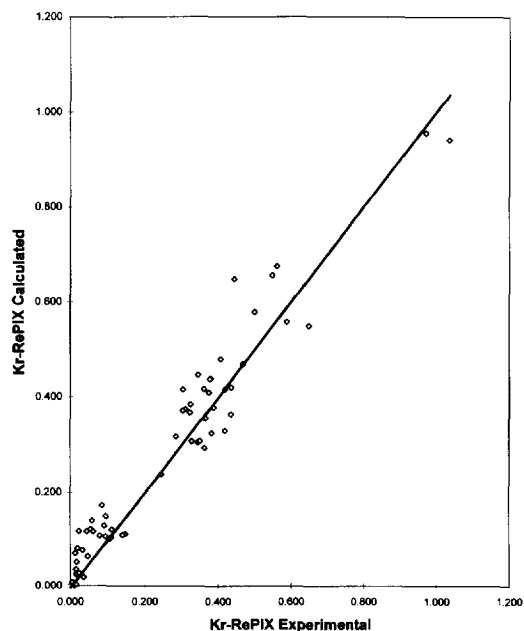


Fig. 2. Calculated vertical ionization potentials versus experimental ionization potentials.

The calculated ionization potentials can be compared to the experimental ones. The calculated values are all higher than the experimental ones but this can be explained by the differences in the adiabatic and vertical ionization potentials. The experimental values are generally adiabatic ones where the energy difference is between the most stable forms of the neutral and the ions respectively. The calculated values are vertical ionization potentials in which the geometry of the neutral and the positive ion is the same. This is generally referred to as the value of the Highest Occupied Molecular Orbital (HOMO). The difference is about 1 eV for the saturated hydrocarbons. For all of the compounds, the average difference is about 0.5 eV. The calculations for the oxygenated compounds have been obtained with the three changes in the default parameter mentioned above. The experimental values are plotted against the calculated ones in Fig. 3.

The use of experimental values of ionization potentials to validate the parameters used to calculate the ionization potential is important. For example,

the largest Kr-*RePIX* measured in the earlier study was 1.43 for ethyl iodide. The calculated ionization potential is greater than 10.43 eV that would predict a Kr-*RePIX* value of less than 0.1. However, the experimental ionization potential is 9.35 eV that would predict a Kr-*RePIX* of greater than 1. Obviously, the parameters could be adjusted to fit the experimental ionization potential.

#### 4. Conclusions

The Kr-*RePIX* values are correlated to the number of ionizable electrons and can be approximated from SCF-MO calculations. However the default values for oxygen given in the HyperChem 4.0 program must be adjusted. This is also indicated by the values of the vertical ionization potentials as compared to the experimental ones. The vertical ionization potentials calculated using SCF-MO procedures are correlated to the experimental values.

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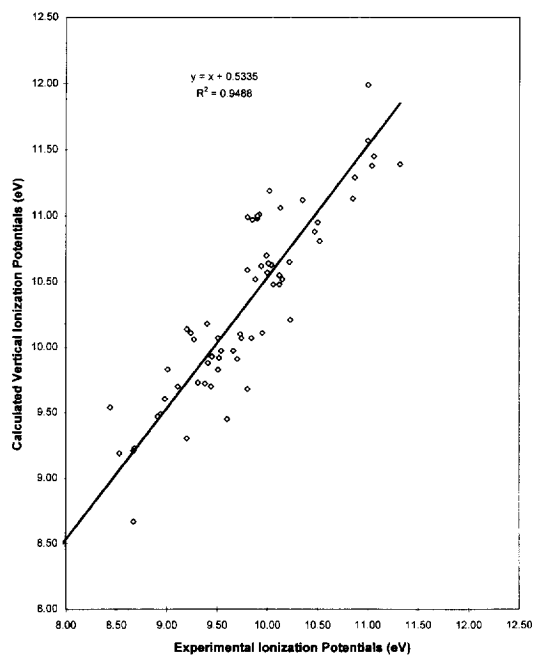


Fig. 3. Experimental *RePIX* values versus calculated *RePIX* values.