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EVALUATION OF A NEW PHOTOIONIZATION DETECTOR FOR ORGANIC COMPOUNDS

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SUMMARY

A photoionization detector (PID) which employs a very stable sealed ultraviolet (10.2 eV) lamp adjacent to an ionization chamber is described. This new design when compared to previous PID's provides improved sensitivity, extended temperature range, and a 100-fold increase in the linear dynamic range. The dynamic range of $>10^7$ ($>10^8$ with dilution) is larger than that observed for any other gas chromatography detector. The PID was compared to a flame ionization detector (FID) and found to have approximately the same noise and background level although the sensitivity was improved 30-fold, *e.g.*, 0.3 C/g compared to 0.01 C/g for the FID. The detection limit was found to be less than 2 pg for benzene. The PID response to carbon compounds was proportional to the carbon number in a manner similar to an FID. The PID is a non-destructive detector which is sensitive to the concentration of the sample. Thus, maximum sensitivity is obtained at low flow-rates. Although the PID appears to complement the FID in many respects, it should be considered a new sensitive detector in its own right.

INTRODUCTION

The flame ionization detector (FID) is the most frequently used detector for trace analysis today because of its sensitivity, wide dynamic range, and selective response to carbon-containing compounds. In spite of its wide usage, the detector has numerous problems, which include the requirement for air and hydrogen in addition to carrier gas, long initial warmup time (approx. 1 h) and occasional instability, *i.e.*, the flame becomes unstable or blows out when orifices get plugged. In many laboratories, the requirement for hydrogen and the open flame is a real detriment to the use of this detector. Since the FID is a destructive detector, stream splitting is required for sample collection or running in series with another detector.

Flame ionization and photoionization are both ionization methods which differ in the mechanism of ion generation but are similar in ion-collection techniques. Photoionization detectors (PIDs) described in the early sixties[1–7] were reported to be more sensitive (approx. 10×) than FIDs, however, stability was a serious problem. These detectors were maintained at low pressures with a vacuum pump, were prone to coating problems from column bleed, and were very complex to operate. As a result, none of these PIDs employing flowing gas discharges achieved commercial viability.

PIDs with sealed UV lamps[8–10] have been shown to eliminate the deficiencies of the windowless PIDs by allowing the ionization chamber to be run at atmospheric pressure. This new design[8] improves the sensitivity, simplifies the operation of the detector, and extends the temperature range considerably over previous PIDs with sealed lamps[9,10]. This PID was evaluated previously for benzene[8] and found to be 30–40 times as sensitive as a FID with approximately the same noise and background characteristics. The current paper considerably extends that work by comparing the PID and FID sensitivities for a number of carbon compounds.

EXPERIMENTAL

The photograph of the photoionization detector shown in Fig. 1 contains two modules, *viz.* the detector and the power supply interconnected by a multiconductor cable. The power supply module provides high voltage for both firing the UV lamp and accelerating ions to the collection electrode in the ionization chamber. This module also contains a rheostat for varying the power to the detector heater and a pyrometer for reading the detector temperature.

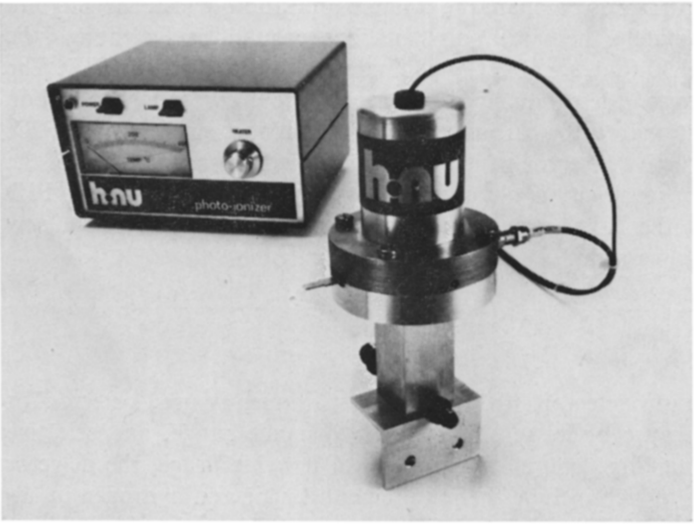


Fig. 1. Photoionization detector for gas chromatography.

The detector module shown in Fig. 1 consists of a sealed UV lamp which emits the lyman α line of hydrogen at 121.6 nm (10.2 eV) through a magnesium fluoride window into the ionization chamber. The process of photoionization is initiated by absorption of a 10.2-eV photon by a molecule. If the molecule has an ionization potential equal to or less than 10.2 eV, the following process occurs

$$R + h\nu \rightarrow R^+ + e^-$$

where $h\nu$ is a photon with an energy $\geqslant$ 10.2 eV.

The ions resulting from photoionization are collected in the ionization chamber by applying a positive potential to one of the electrodes and thereby pushing the ions to the collector electrode where the current (proportional to concentration) is measured with the FID electrometer in the Tracor Model 550 gas chromatograph.

The PID was mounted on a bracket adjacent to the FIDs. The two detectors (PID and FID) were run in parallel with a selector valve at the column exit. Comparative results were obtained by repeated injections of a particular compound onto the column and switching the effluent between the detectors. The temperature of the PID equilibrated about 30 min after the power had been turned on. If the detector was at temperature, the lamp could be turned on and the signal would equilibrate in several minutes. The PID was maintained at a temperature at least 20° above the temperature of the column oven. The columns used in this study (6 ft. × 1/4 in. O.D.) contained Porapak P and Q as well as 3% OV-1 on an 80–100 mesh diatomaceous earth type solid support.

Relative sensitivities, compared to benzene, were obtained by direct injection of 0.1–0.2 μl of liquid into the chromatograph. Dilution gas (helium) was added through one side of the tee in the PID to ensure that the 100–200 μg of sample injected did not saturate the detector. The dilution ratio employed was approximately 10:1. Lower levels of gases were prepared using permeation tubes or by dilution of 10- and 100-ppm gas mixtures. For intermediate levels, known volumes of liquid were injected into a 1-l cylinder and allowed to evaporate.

RESULTS AND DISCUSSION

The PID with a 10.2-eV UV source does not respond to permanent gases because of their high (> 12 eV) ionization potentials. There is also no response from C_1–C_4 aliphatic hydrocarbons (ionization potentials 12.98–10.6 eV) but C_5 and above do respond. Note the relatively low ionization potentials for most organics in Table I and also that the larger the molecule, the lower the ionization potential, so that the possibility of response to high-molecular-weight organics is excellent.

The typical chromatogram shown in Fig. 2 was obtained by injecting an 0.5-ml sample containing 1 ppm of benzene in air. The negative peak in Fig. 2 is apparently the result of a reduction in background current due to oxygen quenching. The positive ions produced by photoionization can be neutralized much more efficiently by O_2^- than by e^-, *i.e.*

$$e^- + O_2 \xrightarrow{k_1} O_2^-$$

$$e^- + R^+ \xrightarrow{k_2} R$$

$$O_2^- + R^+ \xrightarrow{k_3} R$$

where $k_3 \gg k_2$ and both reduce the measured ion current. At flow-rates of 40 ml/min, peak widths for the PID and FID were nearly identical.

The specifications for the PID and FID shown in Table II indicate approximately the same noise and background characteristics but considerably wider dynamic range and more sensitivity for the PID: it is over 30 times more sensitive than the

TABLE I

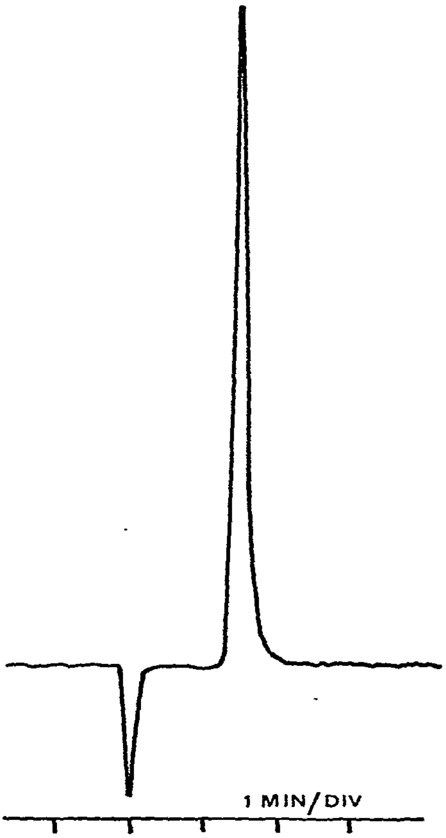
IONIZATION POTENTIALS FOR SELECTED MOLECULES

Compound	*I.P. (eV)*
Diethyl sulfide	8.43
m-Xylene	8.56
Dimethyl sulfide	8.68
Toluene	8.82
Cyclohexene	8.94
1,3-Butadiene	9.07
Benzene	9.25
Pyridine	9.32
Trichloroethylene	9.45
Allyl alcohol	9.67
Acetone	9.69
Methyl ethyl ketone	9.53
Tetrahydrofuran	9.54
Cyclohexane	9.88
Vinyl chloride	9.95
Carbon disulfide	10.08
Acrolein	10.10
Hexane	10.17
Ethyl alcohol	10.48
Ethylene	10.51
Oxygen	12.07
Water	12.59
Carbon dioxide	12.80
Methane	12.98
Carbon monoxide	14.01
Nitrogen	15.55

FID. The temperature range of the present PID is more restricted, however, because of PTFE in the current construction of the detector.

There are some differences between the PID and FID with regard to the sample. The PID is a non-destructive detector which measures concentration whereas the FID is a consumptive detector that is sensitive to the mass flow-rate, *i.e.*, higher sample flow-rates give a stronger response. The PID area increases at a lower flow-rate because the concentration per unit time in the detector increases as the flow-rate is decreased. An example of area *versus* flow-rate is shown in Fig. 3[8]. Note the increased area at low flow-rates.

The relative sensitivities of the PID and FID are compared in Table III. The FID tests were run on the Tracor Model 550 instrument at the same time and with the same columns as used for the PID tests. Note the low PID response for hexane, ethylene, and ethanol. These species have ionization potentials which are between 10.3–10.5 eV and the photons from the UV lamp have an energy of 10.2 eV, hence their sensitivities are lower. The cyclic compounds (cyclohexane and cyclohexene) have lower sensitivities than expected on the basis of their ionization potentials. All the other compounds evaluated have sensitivities which varied in proportion to the number of carbon atoms in the molecule. This mode of operation is similar to that used for a FID. Note the considerably higher sensitivities when the PID is compared to the FID. The aromatics and chlorinated compounds have a similar ratio on the



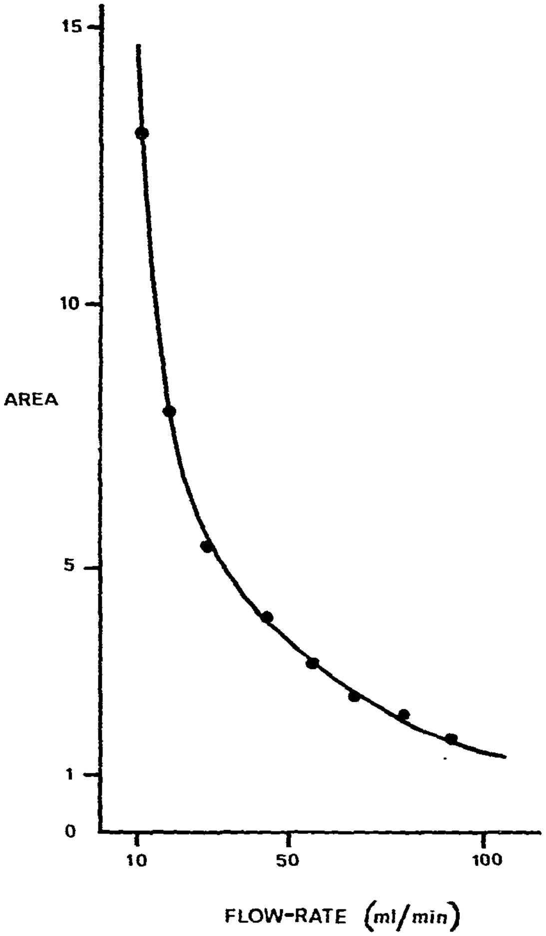


Fig. 2. Typical chromatogram obtained with the PID. Column temperature, 90°; detector temperature, 128°; sample, 0.5 ml containing 1 ppm of benzene in air; attenuation, 32 × 10.

Fig. 3. Effect of PID response as a function of flow-rate. ●, Measured values.

TABLE II

COMPARISON OF SPECIFICATIONS OF PID AND FID

	PID	*FID*
Linearity	$>10^{7*}$	approx. 10^6
Noise, A	4×10^{-14}	5×10^{-14}
Background current, A	1.5×10^{-11}	2×10^{-11}
Minimum detectable level** (as benzene)	2 pg	30 pg
Sensitivity, C/g	0.3	0.01
Carrier flow-rate, ml/min	10–100, normal even 1–10	10–100
Operating temperature, °C	to 250°	to 400°

* $>10^8$ with dilution.

** Injection of sample in air; flow-rate, 30 ml/min.

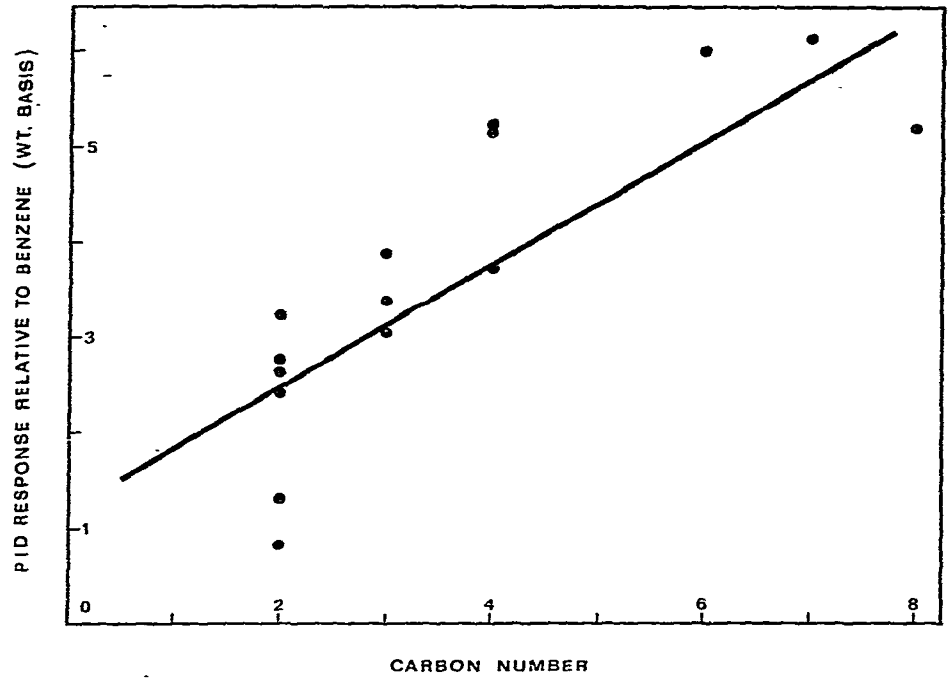


Fig. 4. Variation of PID response with carbon number. $y = 1.169 + 0.67x$; $r^2 = 0.67$.

TABLE III

COMPARISON OF THE RELATIVE SENSITIVITIES OF THE PHOTOIONIZATION AND FLAME IONIZATION DETECTORS

Conditions: flow-rates, 30 ml/min; carrier gas, helium; column temperature, 110°; PID temperature, 140°.

Compound	*PID response*	*FID response*	*Ratio PID/FID*
Toluene	6.10	0.18	34
Benzene	6.00*	0.16	38
1,3-Butadiene	5.20	—	
Diethyl sulfide	5.20	—	
p-Xylene	5.03	0.15	34
Carbon disulfide	4.20	0	
Propylene	3.90	—	
Methyl ethyl ketone	3.72	—	
Allyl alcohol	3.40	—	
Dimethyl sulfide	3.25	—	
Acetone	3.04	0.06	51
Cyclohexene	2.44	—	
Acrolein	2.70	—	
Trichloroethylene	2.76	0.08	35
Vinyl chloride	2.44	0.06	41
Tetrahydrofuran	1.86	—	
Pyridine	1.78	—	
Ethylene	1.34	0.07	19
Hexane	1.23	0.15	8.2
Cyclohexane	0.90		
Ethanol	0.81		

* All values (PID and FID) were normalized to benzene = 6.0 on PID.

FID and PID. For hexane, which has a low efficiency (ionization potential approx. 10.3 eV), the PID is still nearly an order of magnitude more sensitive than a FID but the PID/FID response ratio of hexane relative to aromatics is low. The carbonyl compounds appear to have a PID sensitivity nearly twice that of the FID when compared to the work of Dietz[11]. Some other differences between the PID and FID are noted when one compares the excellent sensitivity of the PID to CS_2 to the lack of sensitivity on a FID.

A plot of the PID response *versus* carbon number is shown in Fig. 4. Hexane was eliminated on a statistical basis and the cyclic compounds did not fit well either but all the additional data from Table III are plotted. Although there is considerable scatter in the data, there is a statistically significant relationship between these two variables. The regression equation obtained is $y = 1.169 + 0.67x$ and the correlation coefficient (r^2) is 0.67. When one considers that these data include the relative responses of aromatics, olefins, chlorinated compounds and carbonyl and sulfur compounds, the fit is very good indeed.

CONCLUSIONS

The PID has been shown to respond to carbon-containing compounds in a manner similar to a FID, *i.e.*, it is a carbon counter. The PID should even be more useful for trace analysis than the FID because of its 30-fold increase in sensitivity. Since the dynamic range of the PID is $> 10^7$, it will also be useful at high levels. The non-destructive aspect of the PID should extend its usefulness when coupled in series with element-selective detectors for S, N and P[12]. Although the PID complements the FID in many respects, the PID should be considered as a new sensitive detector in its own right which has response to many organic and some inorganic[12] species.

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