

## Note

### Quenching or enhancement of the response of the photoionization detector

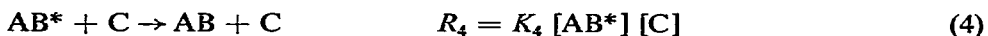
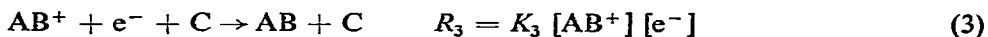
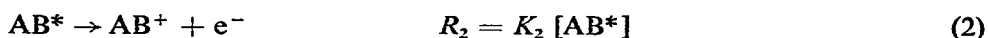
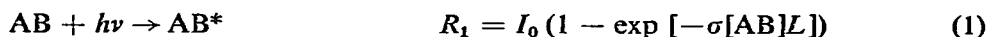
G. I. SENUM

*Environmental Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973 (U.S.A.)*

(First received September 18th, 1980; revised manuscript received October 7th, 1980)

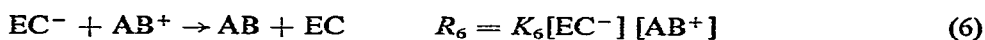
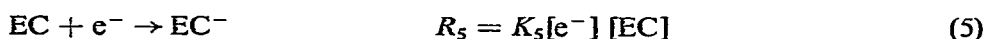
The photoionization detector (PID) is finding an increased use as a gas chromatographic (GC) detector<sup>1-5</sup> especially since the PID has an enhanced response for aromatic compounds when compared to the flame ionization detector (FID)<sup>2,4,5</sup>. In almost all instances, a solvent is used to inject the compounds of interest into the GC column for subsequent separation. A selection criterion for an appropriate solvent is that it has ideally, a negligible PID response, which has generally been interpreted to mean that the solvent ionization potential (IP) be less than the energy of the PID excitation. A similar selection criterion is implicit in the choice of carrier gas. However, as will be illustrated in this note, there are other factors which influence the choice of a carrier gas and/or solvent in order to optimize the PID.

A proposed mechanism for the PID response has been detailed by Freedman<sup>4</sup> and is given as follows



in which AB is a photoionizable compound, C is the carrier gas,  $I_0$  is the initial photon flux,  $\sigma$  is the absorption cross section, and  $L$  is the pathlength. Eqns. 1 and 2 detail the steps leading to the formation of the ions which are collected in the PID, with the consequent current being proportional to the concentration of the photoionizable compound. Likewise eqns. 3 and 4 detail the removal processes responsible for a reduction or quenching of the photoion concentration. Any increase in these removal rates or the appearance of new removal mechanisms will consequently lead to increased quenching of the PID response for photoionizable compounds, *i.e.*, a smaller percentage of collectable photoions being formed. Similarly, any decrease in these removal rates will enhance the PID response. Consequently, for ultimate sensitivity, the removal rates should be minimized.

An alternate removal mechanism has been illustrated by Driscoll<sup>4</sup>, namely quenching via electron capture. This is detailed as follows,



in which EC is a compound which is able to attach an electron. At high concentrations of EC, the rate of eqn. 6,  $R_6$ , can become significantly larger than  $R_3$  and consequently this leads to increased quenching of the PID response. This was illustrated by Driscoll<sup>1</sup> by the appearance of a negative PID response peak for oxygen which is a result of the reduction in the PID background current due to increased quenching by oxygen via electron capture. A chromatogram reproducing this is shown in Figure 1a. The background current (*ca.*  $2-3 \cdot 10^{-12}$  A) results from photoionizable compounds apparently outgassing in the PID cell. Additional current can originate from column bleed, carrier gas impurities, etc. Nonetheless, the presence of oxygen will quench the PID response and consequently oxygen or air should never be used as a PID carrier gas. Other gases which are similarly electron capturing, for example, nitrous oxide ( $N_2O$ ), and to a lesser extent<sup>6</sup> carbon dioxide ( $CO_2$ ), exhibit a similar negative PID response as illustrated in Figs. 1b and 1c, respectively. However, for  $N_2O$ , there are additional quenching processes as will be detailed later.

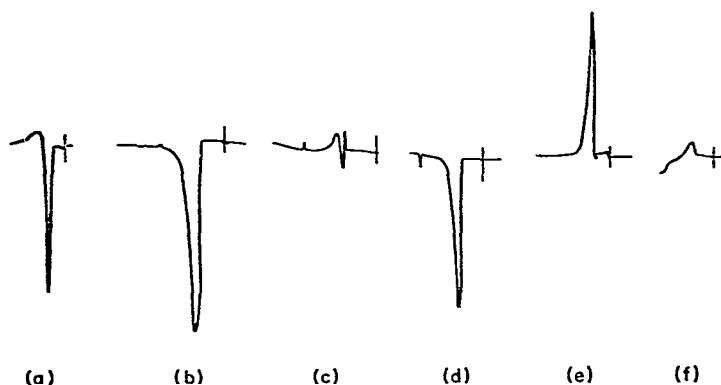


Fig. 1. Photoionization detector response to a 0.25-ml injection of various gases. (a) Oxygen; (b), nitrous oxide; (c), carbon dioxide; (d), methane-nitrogen (10:90); (e), carbon tetrafluoride; (f), carbon monoxide. The carrier gas was nitrogen at 15 ml/min. The PID was at 200°C. The vertical line indicates the point of injection.

The effect of using  $CO_2$  as a PID carrier gas was examined by Freedman<sup>4</sup> and indeed a slight quenching of PID response was observed when compared to a He carrier gas. Freedman ascribed *ca.* 30% of this  $CO_2$  PID response quenching to a reduction in the initial photon flux,  $I_0$ , by  $CO_2$  absorption at 10.2 eV (1215.7 Å) and the other 70% to an increase in a removal rate (eqn. 4) by noting that  $CO_2$  is much more efficient than He in deactivating excited state  $AB^*$  by collisions. However, it is more likely that the quenching observed by Freedman was due to quenching via electron capture (eqns. 5 and 6). This can be inferred from the apparent lack of quenching of the PID baseline response when injecting CO and  $CF_4$ . Carbon monoxide has a slightly larger absorption coefficient<sup>7</sup>,  $3 \text{ cm}^{-1}$ , compared to  $CO_2$  ( $2 \text{ cm}^{-1}$ ) at 10.2 eV, yet there is no negative peak with CO as displayed in Fig. 1f. Similarly, carbon tetrafluoride which has a negligible electron-capture rate constant<sup>8,9</sup>, a negligible absorption coefficient at 10.2 eV (ref. 10), and is expected to be a more efficient quench-

er than  $\text{CO}_2$  since it has more internal degrees of freedom, has no observable PID quenching as would be evidenced by a negative peak (Fig. 1e). Thus quenching via electron capture (eqns. 5 and 6) is more predominant than Freedman's quenching mechanism (eqn. 4) when gases with a high electron affinity such as  $\text{CO}_2$  and  $\text{O}_2$  are used as carrier gases.

Freedman did, however, note the importance of carrier gas absorption at the PID excitation energy, and this may be regarded as another PID quenching mechanism. This is responsible for the observed negative peaks by  $\text{N}_2\text{O}$  and  $\text{CH}_4$  as is shown in Figs. 1b and 1d. The absorption coefficients at 10.2 eV of these and other potential PID carrier gases are given in Table I. The absorption coefficients for  $\text{CH}_4$  ( $400 \text{ cm}^{-1}$ ) and  $\text{N}_2\text{O}$  ( $100 \text{ cm}^{-1}$ ) are quite large and consequently this precludes the use of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  as PID carrier gases. The unsuitability of  $\text{CH}_4$  as a PID carrier gas precludes the use of the dual detection system, PID and an electron-capture detector (ECD), with argon-methane mixtures used as a carrier gas. However, nitrogen is suitable as a carrier gas for a dual PID and ECD detection system.

TABLE I

IONIZATION POTENTIALS AND ABSORPTION COEFFICIENTS FOR VARIOUS PID CARRIER GASES

Carrier gas	Ionization potential (eV)	Absorption coefficient at 10.2 eV ( $\text{cm}^{-1}$ )
Oxygen	12.063*	0.27 <sup>§</sup>
Nitrous oxide	12.894*	100 <sup>§</sup>
Carbon dioxide	13.769*	2 <sup>§</sup>
Methane	12.6*	400 <sup>§</sup>
Carbon tetrafluoride	15.67**	Negligible <sup>§§</sup>
Carbon monoxide	14.013*	3 <sup>§§§</sup>
Argon	15.67***	Negligible <sup>§</sup>
Helium	24.58***	Negligible <sup>§</sup>

\* Ref. 11.

\*\* Ref. 12.

\*\*\* Ref. 13.

§ Ref. 14.

§§ Ref. 10.

§§§ Ref. 7.

In order to quantify the aforementioned effects, the PID response for five test compounds, benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene were measured with seven different carrier gases with the results given in Table II. The chromatography was done on an 8 ft.  $\times$  1/8 in. stainless-steel column of 10% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 100-120 mesh Chromosorb P AW in a Varian 3700 chromatograph. The PID was a Hnu Model PI-51 with a 10.2 eV source and operated at 200°C. The output of the PID was amplified by the Varian 3700 electrometer and the areas were integrated by a Varian CDS-111 computing integrator. The carrier gases were all maintained at 15 ml/min as measured by a bubble flowmeter since the PID is a concentration-dependent detector. The PID responses, *i.e.* the measured areas, for the five test compounds were normalized to the response for nitrogen carrier gas so as to allow

TABLE II  
RELATIVE PID RESPONSES

Carrier gas at 15 ml/min	Normalized response $\pm$ S.D.				
	Benzene	Toluene	p-Xylene	m-Xylene	o-Xylene
Argon	1.401 $\pm$ 0.07	1.44 $\pm$ 0.08	1.49 $\pm$ 0.12	1.40 $\pm$ 0.08	1.42 $\pm$ 0.09
Carbon monoxide	1.03 $\pm$ 0.02	1.02 $\pm$ 0.01	1.03 $\pm$ 0.01	1.00 $\pm$ 0.02	1.00 $\pm$ 0.03
Carbon tetrafluoride	1.010 $\pm$ 0.005	0.998 $\pm$ 0.017	0.848 $\pm$ 0.025	1.098 $\pm$ 0.029	1.27 $\pm$ 0.57
Nitrogen	1.00 $\pm$ 0.08	1.00 $\pm$ 0.003	1.00 $\pm$ 0.10	1.00 $\pm$ 0.09	1.00 $\pm$ 0.10
Helium	0.987 $\pm$ 0.023	0.987 $\pm$ 0.026	1.126 $\pm$ 0.025	0.970 $\pm$ 0.033	0.982 $\pm$ 0.016
Air	0.542 $\pm$ 0.028	0.525 $\pm$ 0.030	0.487 $\pm$ 0.024	0.456 $\pm$ 0.037	0.433 $\pm$ 0.038
Carbon dioxide	0.285 $\pm$ 0.004	0.269 $\pm$ 0.030	0.278 $\pm$ 0.09	0.249 $\pm$ 0.016	0.179

a more direct comparison of the results. As is seen in Table II, the PID response as measured for the five compounds is comparable when a nitrogen, helium, carbon monoxide, or carbon tetrafluoride carrier gas is used. As discussed earlier, this is expected since none of these four carrier gases have any appreciable absorption cross-sections at 10.2 eV nor any appreciable electron capture cross-section. The PID response for the five test compounds are quenched when carbon dioxide or air is used as a carrier gas, *i.e.*, by factors of 4 and 2 respectively, which is due to the appreciable electron-capture cross-section of oxygen and carbon dioxide, allowing the additional removal processes 5 and 6 to occur.

In contrast, the PID response as measured for the five test compounds is enhanced with the use of argon as a carrier gas, by at least 40% when compared to a nitrogen or a helium carrier gas. This is apparently due to the increased drift velocity of the electrons in argon as compared to nitrogen<sup>15</sup>. This increased electron drift velocity enhances the collection of the electrons by the PID and also minimizes the mutual recombination of the photo ions and electrons (eqn. 3) due to a decreased electron concentration which is a consequence of the increased electron collection efficiency. Consequently, for a fixed electron collection potential as is available in commercial PID units, it is advisable to use an argon carrier gas since it offers the greatest relative PID response. The use of an argon carrier gas is also advantageous since it requires a relatively low carrier gas flow-rate for maximum chromatographic column efficiency, which in turn increases the PID response, since the PID is a concentration-dependent detector<sup>1,2</sup>.

Two other gases, methane and nitrous oxide, were used as PID carrier gases, in order to examine their effect on the PID response of the five test compounds. As expected, the PID response was severely quenched due to the high absorption coefficient of these two gases at 10.2 eV.

The quenching of the PID response by absorption of the excitation energy is also apparent when solvent peaks are eluted into the PID. When the solvent has an ionization potential greater than the PID excitation, then in some instances the solvent will give an apparent negative PID response, *i.e.*, the solvent has quenched the PID via absorption of the excitation energy by the solvent. In some instances, when the solvent has a large electron-capture cross-section, *e.g.*, CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, etc., PID quenching via electron capture may also contribute to the observed negative peak. When the solvent has an appreciable PID response, *i.e.*, ionization potential less than

the excitation energy, PID quenching via excitation absorption, may still quench the solvent peak, after a certain threshold concentration, so as to give the appearance of two peaks. An illustration of this is shown in Fig. 2, where the PID response for benzene is quenched after a certain threshold concentration, when the excitation absorption rate becomes greater than the other PID removal rates, *e.g.*, eqns. 3–6, and consequently, this gives the solvent peak the appearance of being two peaks. Thus caution must be used in identifying peaks which are due to the response of the PID to solvents.

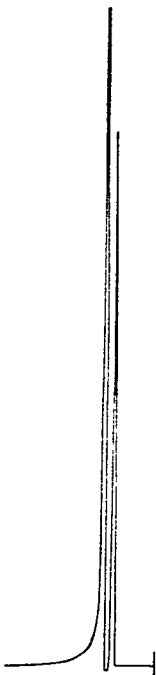


Fig. 2. Photoionization detector response to a 1- $\mu$ l injection of benzene onto a 8 ft.  $\times$  1/8 in. stainless-steel 10% TCEP on 100–120 mesh Chromosorb P AW column at 70°C with a nitrogen carrier gas at 15 ml/min and the PID at 200°C.

In conclusion, the optimal use of a PID requires that the ion-formation mechanisms be maximized, *i.e.*, the compounds being detected have a large photoionization cross-section, and that the removal processes be minimized, *i.e.*, a negligible excitation absorption and electron capture rate exerted by the carrier gas. Argon is preferable as a PID carrier gas since it minimizes the PID ion removal processes; consequently an argon carrier gas provides at least a 40% PID response enhancement when compared to a nitrogen or helium carrier gas.

#### ACKNOWLEDGEMENTS

I wish to thank Dr. Russell N. Dietz for his helpful discussions.

This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH00016.

## REFERENCES

- 1 J. N. Driscoll, *J. Chromatogr.*, 134 (1977) 49.
- 2 J. N. Driscoll, J. Ford, L. F. Jaramillo and E. T. Gruber, *J. Chromatogr.*, 158 (1978) 171.
- 3 M. L. Langhorst and T. J. Nestruck, *Anal. Chem.*, 51 (1979) 2018.
- 4 A. N. Freedman, *J. Chromatogr.*, 190 (1980) 263.
- 5 A. R. Oyler, D. L. Bodener, K. J. Welch, R. J. Liukkonen, R. M. Carlsen, H. L. Kopperman and R. Caple, *Anal. Chem.*, 50 (1978) 837.
- 6 P. G. Simmonds, *J. Chromatogr.*, 166 (1978) 593.
- 7 J. A. Meyers and J. A. R. Samson, *J. Chem. Phys.*, 52 (1970) 266.
- 8 R. W. Fessenden and K. M. Bansal, *J. Chem. Phys.*, 53 (1970) 3468.
- 9 R. Schumacher, H. R. Sprünken, A. A. Chistodoulides and R. N. Schindler, *J. Phys. Chem.*, 82 (1978) 2248.
- 10 G. Belanger, P. Sauvageau and G. Sandorfy, *Chem. Phys. Lett.*, 3 (1969) 649.
- 11 J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, *Ionization Potentials, Appearance Potentials and Heats of Formation of Positive Ions*, National Standard Reference Data System, National Bureau of Standards No. 26, Washington, DC, 1968.
- 12 W. E. Bull, B. P. Pullen, F. A. Grimm, W. E. Moddeman, G. K. Schweitzer and T. A. Carlson, *Inorg. Chem.*, 9 (1974) 2474.
- 13 C. E. Moore, *Atomic Energy Levels*, Vol. 1, National Bureau of Standards Circular 467, Washington, DC, 1949.
- 14 A. N. Zaidel' and E. Ya. Shreider, *Vacuum Ultraviolet Spectroscopy*, Ann Arbor-Humphrey Sc. Publ., Ann Arbor, MI, 1970.
- 15 G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants*, Wiley, New York, 1959.