THE PHOTOIONIZATION DETECTOR

THEORY, PERFORMANCE AND APPLICATION AS A LOW-LEVEL MONITOR OF OIL VAPOUR

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SUMMARY

The photoionization detector (PID) is being developed for the detection of low concentrations of oil in the carbon dioxide coolant of gas-cooled reactors. In this paper the theoretical response of the PID is derived and compared with its practical response and with that of the flame ionization detector (FID). The PID response is shown to depend primarily upon ionization potential and molar concentration unlike FID response which depends upon carbon number. The dependence of PID response upon the carrier gas used is discussed and the criterion of detection using the PID to measure oil vapour in carbon dioxide was found to be 2 ppb*.

INTRODUCTION

A new gas chromatography (GC) detector based on the principle of photo-ionization has recently become commercially available[1]. This detector (PID) contains a lamp which produces monochromatic radiation in the ultraviolet (UV) region and molecules which have an ionization potential (IP) less than the energy of the UV radiation are ionized on passing through the beam. The ions formed are driven to a collector electrode by an electric field and the current measured. In practice, compounds with ionization potentials just above the photon energy may also give a signal due to a proportion of the molecules being in excited vibrational states. The energy difference between the ground state of the ion and the excited state of the molecule can be up to 0.4 eV less than the IP.
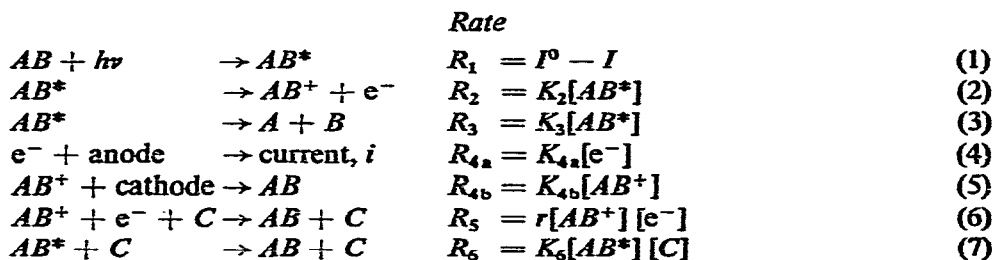
The performance of the detector has been studied by Driscoll and co-workers[2-4] of HNU Systems (Newton, Mass., U.S.A.), the manufacturers; however there has been little attempt to evaluate PID performance against that expected from theoretical considerations. The work reported here attempts to cover these deficiencies, and is part of a programme to investigate the performance of the PID as a low-level monitor of circulator oil in the carbon dioxide coolant of the advanced gas-

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* Throughout this article, the American billion (10^9) is meant.

cooled nuclear reactor (AGR). (Oil ingress is a cause of carbon deposition on fuel elements which affects heat transfer efficiency[5]). A flame ionization detector (FID) would not be suitable as a monitor since it responds to the methane normally present in the coolant as an inhibitor of radiolytic graphitic corrosion. Since the IP of methane is above the lamp energy there is no PID response.

THEORY

Sevcik and Krysl[6] have derived an expression for the factors which affect the ion current in the PID based on the kinetic scheme shown below. The treatment given here is slightly different to theirs and gives a simpler expression for the ion current.

$$Rate$$

$AB + h\nu$	$\rightarrow AB^*$	$R_1 = I^0 - I$	(1)
AB^*	$\rightarrow AB^+ + e^-$	$R_2 = K_2[AB^*]$	(2)
AB^*	$\rightarrow A + B$	$R_3 = K_3[AB^*]$	(3)
$e^- + anode$	$\rightarrow current, i$	$R_{4a} = K_{4a}[e^-]$	(4)
$AB^+ + cathode$	$\rightarrow AB$	$R_{4b} = K_{4b}[AB^+]$	(5)
$AB^+ + e^- + C$	$\rightarrow AB + C$	$R_5 = r[AB^+][e^-]$	(6)
$AB^* + C$	$\rightarrow AB + C$	$R_6 = K_6[AB^*][C]$	(7)

where AB is an ionizable substance with concentration $[AB]$ and C the carrier gas with concentration $[C]$. The initial photon flux is I^0 and the number of photons absorbed per second $= I^0 - I$. This is equivalent to the number of moles of AB^* produced per second since one photon excites one molecule. Eqn. 2 expresses the pre-ionization and eqn. 3 the pre-dissociation process. r is the recombination coefficient.

When oxygen is present the following reactions can also occur[2]:

$$e^- + O_2 \rightarrow O_2^- \tag{8}$$

$$O_2^- + AB^+ \rightarrow AB + O_2 \tag{9}$$

The probability that a photon will be absorbed (eqn. 1) depends upon the absorption cross-section of the substance, σ. This can be defined by the Beer–Lambert law

$$I = I^0 \exp(-\sigma N[AB]L) \tag{10}$$

where N is Avogadro's number and L is the path length. The probability that the excited state will ionize (eqn. 2) depends upon the photoionization efficiency, η, where

$$\eta = \frac{K_2}{K_2 + K_3 + K_6} \tag{11}$$

Assuming a steady state the rate of formation of AB^* will equal its rate of removal, *i.e.*

$$I^0 - I = K_2[AB^*] + K_3[AB^*] + K_6[AB^*][C]$$

$[C] \approx 1$, therefore $I^0 - I = [AB^*][K_2 + K_3 + K_6]$ (12)

The recombination reaction (eqn. 6) can be suppressed with a sufficiently high voltage[6], therefore the rate of ion formation which equals the rate of ion collection can be expressed as:

$$K_4[AB^+] = K_2[AB^*]$$ (13)

Substituting in eqn. 12 gives:

$$I^0 - I = K_4[AB^+] \frac{K_2 + K_3 + K_6}{K_2} = K_4[AB^+] \frac{1}{\eta}$$ (14)

thus

$$I^0 - I = i/F \cdot 1/\eta$$ (15)

where i is the ion current which is amplified to give the PID signal and F is the Faraday. From eqns. 10 and 15

$$I^0 - I = I^0 \left[1 - \exp(-\sigma NL[AB])\right] = \frac{i}{F\eta}$$ (16)

Expanding the function as a Taylor series and neglecting all terms with exponents greater than unity, (which is justified since $[AB]$ is small) gives:

$$i = I^0 F \eta \sigma NL[AB]$$ (17)

Thus, for a particular detector and lamp, the PID signal is proportional to ionization yield, absorption cross section and molar concentration. The product $\sigma\eta$ is the photoionization cross section, σ_i, which expresses both the probability that a molecule will absorb a photon and the probability that the excited state will ionize. Attempts have been made by several workers to calculate photoionization cross sections for various molecules[7]. These calculations are complex and beyond the scope of this paper, however, it is worth noting that Schweig and Thiel[7] state that there is "a direct dependence of the photoionization cross sections on the photon energy and the ionization potential". This dependence is complex, however it might be expected that the PID signal will be related to ionization potential through the photoionization cross section.

The FID is one of the most popular GC detectors for organic compounds. Since Driscoll[2] has suggested that the PID has many advantages over the FID, and more recently[4] has proposed a dual FID–PID detection system for the identification of aromatics in complex mixtures, it is instructive to compare its response to that expected from the PID. In the PID a molecular ion is formed which gives rise to the ion current. In the FID it is generally accepted[8] that CHO^+ ions are formed which give rise to the FID signal. The response is proportional to the number of carbon

atoms in a hydrocarbon molecule since an H-atom cracking reaction produces single carbon atom species which are ultimately oxidized to CHO^+. The response of non-hydrocarbon compounds is smaller, depending on the type and percentage of hetero-atoms in the molecule. Sternberg *et al.*[10] set up a table of contributions to the effective carbon number for various hetero-atoms. It is clear from the above discussion that the relative molar response of hydrocarbons on a FID should be proportional to the carbon content of the molecule, but, there are no reasons why this should be so for the PID, where the IP of the compound in question is likely to be a major factor.

EXPERIMENTAL

The HNU Systems Model PI51 PID fitted with a 10.2-eV lamp was used for this work. Although other lamps are available, the 10.2-eV lamp was chosen as it is the only one suitable for use with carbon dioxide which has a high UV absorption at the other available frequencies[11]. This is important since the work reported here is associated with the development of the PID as a low level monitor of oil in the carbon dioxide coolant of gas-cooled reactors.

The PID was connected by a trace heated line to the column outlet of a Perkin Elmer Model F11 gas chromatograph fitted with a 3 m × 3.25 mm O.D. stainless-steel column packed with 10% SE-30 on 80–100 mesh Chromosorb P. The column oven temperature was increased from 40 to 200° at 10°/min. A helium carrier gas flow-rate of 36 ml/min was used. The signal from the PID amplifier was recorded on a chart recorder and the peak areas were measured using an Infotronics 204 integrator.

The relative molar responses (RMR) of the following groups of hydrocarbons were determined:
  (1) C_6 to C_{10} normal alkanes
  (2) C_6 to C_{10} 1-alkenes
  (3) Benzene, toluene, xylene, mesitylene
  (4) Styrene
  (5) Cyclohexane, methyl cyclohexane, dimethyl cyclohexane
  (6) Cyclohexene, methyl cyclohexene.
Solutions containing up to five of the above compounds in *n*-pentane were prepared at a concentration of 1% of each by liquid volume. *n*-Pentane was used as the solvent because it has a low PID response (IP = 10.33 eV); it is rapidly eluted from the GC column and it dissolves all the compounds of interest. The relatively high solute concentration was used to overcome problems of column bleed and interference from solvent impurities. The components of each solution used were chosen so that the RMR values of all the compounds of interest could be compared on the same scale. A 5-μl volume of each solution was injected into the gas chromatograph. About six injections were made with each solution and retention times and peak areas recorded. In each case the peak areas for an individual run were normalized to one component (to overcome errors due to syringe injection and deposits on the PID lamp window) and mean relative areas were calculated. These values were then multiplied by molecular weight/density and re-normalized to give the RMR.

The effect of using carbon dioxide rather than helium as the carrier gas was investigated using a solution of 1% cyclohexane, toluene, 1-nonene and *n*-decane in

n-pentane. These compounds were chosen so that any differences due to the type of compound could be noted. A series of injections was made with the solution using CO_2 as the carrier gas, followed by a similar series of injections using helium. The flow-rate was kept constant. Further series of injections were then made using alternatively CO_2 and helium as the carrier gas. Mean areas were calculated for each series of injections and the ratios of these areas for successive runs using CO_2 and He determined. Finally a mean ratio for each compound was calculated.

The experimental arrangements to determine the RMR on the FID were as described above except the PID was replaced by an FID. Six injections of 5 μl of the solution used in the previous experiment were made and the average peak areas for each compound calculated. These were then converted to areas/mol and areas/g for comparison with the mean peak areas obtained using the PID with helium carrier gas determined in the previous experiment.

The response of the PID to oil vapour in carbon dioxide was determined using the apparatus shown in Fig. 1. By bubbling carbon dioxide through the oil in a thermostatic bath a range of oil concentrations up to 1 ppm could be achieved by changing the bath temperature between ambient and 100°. Baseblend circulator oil, free of additives, was used since earlier work with the normal oil had shown that an antioxidant present was preferentially stripped out by the carbon dioxide in the bubbler.
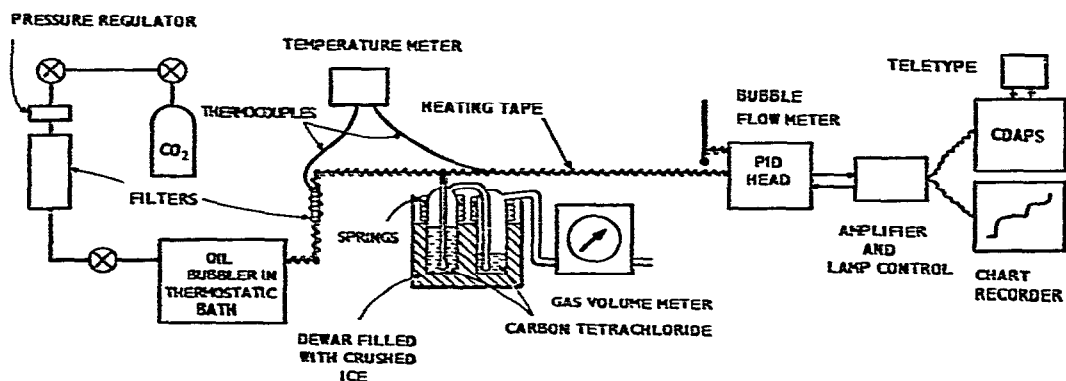

Fig. 1. PID calibration apparatus.

The output signal from the PID was monitored on a chart recorder and logged at one minute intervals using a central data acquisition and processing system[12] which collects data from rigs throughout the laboratory site, processes them in real time and prints them out on a teletype at the rig. At a particular setting of the bath temperature, bubblers containing carbon tetrachloride (Fig. 1) were connected to the line while a known volume of gas, usually 90–100 l, was allowed to bubble through. The ambient pressure and temperature were recorded at the beginning and end of each run to allow conversion of the gas volume to NTP. The first bubbler contained 25 ml of BDH (Poole, Great Britain) spectroscopy grade carbon tetrachloride. The second bubbler contained only 10 ml to avoid any possibility of plasticizer being leached from the plastic tube connecting the bubblers to the wet gas volume meter.

At the end of the run the amount of oil in the carbon tetrachloride was deter-

mined by measuring the infrared absorption at the C–H stretching frequency of 2930 cm^{-1} (3.41 μm). A simple computer program was used to give the oil in gas concentration and the mean and standard deviation of the PID signal. The oil concentration and the corresponding mean and standard deviation of the PID signal were determined several times at each of a range of bath temperatures and the results plotted as signal against concentration.

The PID response to oil vapour in air and helium was also determined by measuring the PID signal at a range of bath temperatures while air, carbon dioxide and helium were successively used as the bulk gas.

RESULTS AND DISCUSSION

Table I shows the relative molar responses obtained for the compounds studied. They are plotted against carbon number for each series in Fig. 2. Fig. 3 shows the RMR values plotted against IP for all those compounds whose IP (as determined by photoionization) is known. The linear regression line (shown) has a correlation coefficient of -0.93. Fig. 4 shows RMR plotted against IP and carbon number for the aromatic series. This is the only series for which IP values are known for all members. It was stated above that the RMR for substances on the PID would depend, in part, on IP. This can be clearly seen in Figs. 3 and 4. The correlation coefficient of -0.93 for RMR against IP is particularly good when it is recalled that such factors as the molecular geometry for some quite different molecular shapes have not been included.

When a single homologous series is considered the influence of molecular

TABLE I

RELATIVE MOLAR RESPONSE OF HYDROCARBONS

| Compound	Formula	B.p. (°C)	Mol.wt.	Density	IP	RMR	Retention time (min)
Benzene	C_6H_6	79.1	78	0.8787	9.24	40.34	4.6
Cyclohexene	C_6H_{10}	83	82	0.8110	8.945	16.8	4.3
Cyclohexane	C_6H_{12}	81	84	0.7780	9.88	6.17	3.6
Hexene	C_6H_{12}	64	84	0.6845	9.46	14.37	2.8
Hexane	C_6H_{14}	69	86	0.65937	10.18	1.00	2.8
Toluene	C_7H_8	110	92	0.8669	8.82	41.95	5.6
Methyl cyclohexene	C_7H_{12}	110.5	96	0.8130	—	16.44	5.4
Methyl cyclohexane	C_7H_{14}	101	98	0.7700	9.85	12.97	4.7
Heptene	C_7H_{14}	94	98	0.6970	—	18.83	4.3
Heptane	C_7H_{16}	98	100	0.68376	10.08	1.98	4.0
Styrene	C_8H_8	50.5	104	0.9050	8.47	48.42	8.0
Xylene	C_8H_{11}	144	106	0.8630	8.5	48.81	8.2
Octene	C_8H_{16}	126	112	0.7149	—	20.43	6.3
Dimethyl cyclohexane	C_8H_{16}	124	124	0.7780	—	30.06	6.8
Octane	C_8H_{18}	122.5	114	0.7025	9.86	3.71	6.4
Mesitylene	C_9H_{14}	163	120	0.8640	8.39	54.86	10.2
Nonene	C_9H_{18}	146	126	0.7433	—	22.05	8.4
Nonane	C_9H_{20}	151	128	0.7176	—	5.37	8.5
Decene	$C_{10}H_{20}$	181	140	0.7408	—	23.49	9.9
Decane	$C_{10}H_{22}$	174	142	0.7300	—	9.02	10.5
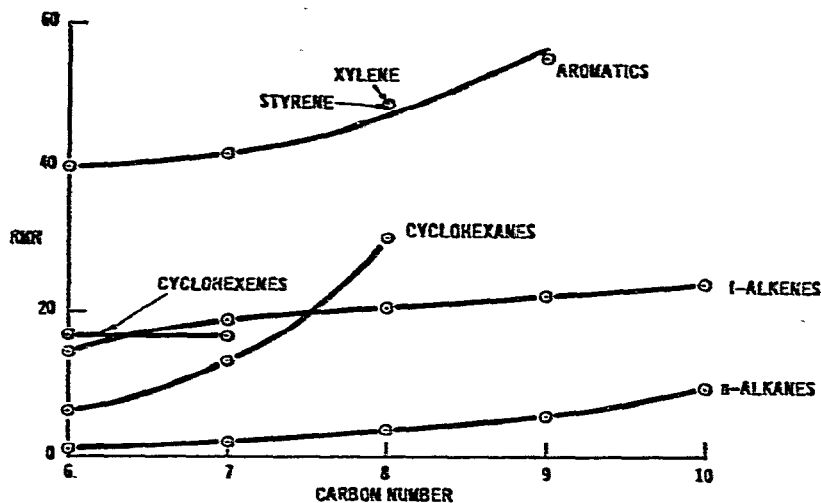
Fig. 2. Relative molar responses on PID.

geometry changes is smaller. The smooth curve obtained in the RMR against IP plot for the aromatic series shown in Fig. 4 further confirms the close relationship between these two parameters. It seems likely that within an homologous series the main reason for the increase in RMR with carbon number (Fig. 2) is the corresponding decrease in IP with carbon number. Vilesov[13] shows a smooth plot of IP against number of benzene hydrogen atoms replaced by methyl groups. He explains that the contribution of successive methyl groups to the stabilization energy of the molecule is smaller by a factor of three or four than for the corresponding ion. Con-
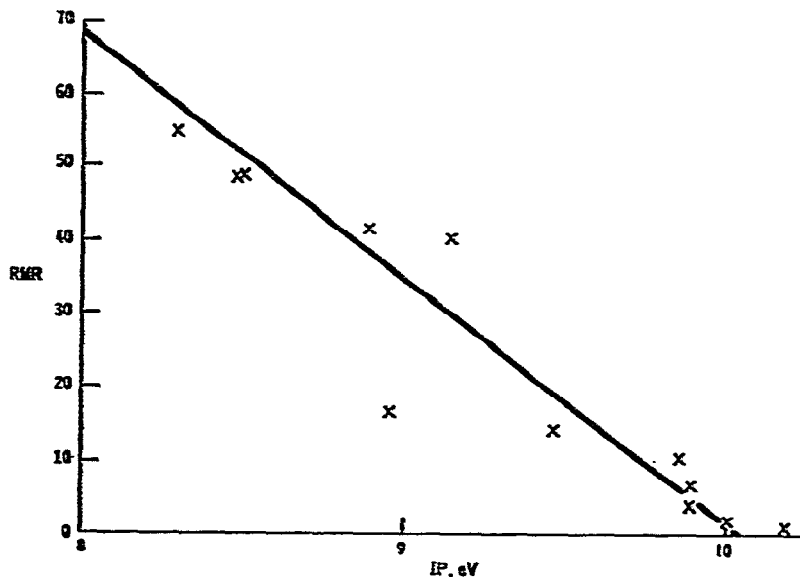

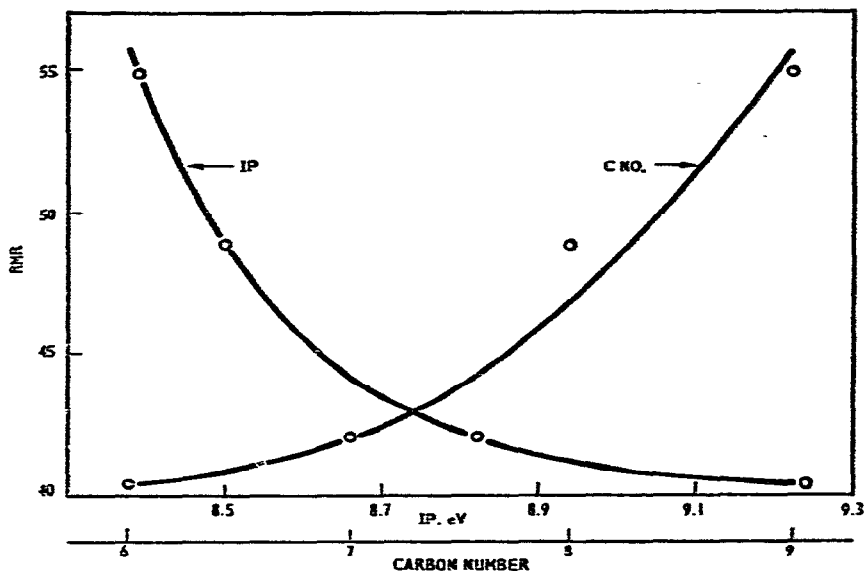Fig. 3. Response against ionization potential.

Fig. 4. RMR against IP and carbon number for aromatic series.

sequently the energy difference between the molecule and ion, the IP, decreases with each substitution.

Driscoll[2] determined the relative sensitivities of a wide range of compounds using a similar PID. He concluded that "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". This conclusion was repeated in a later paper[4]. It is a surprising conclusion since it contradicts the theoretical responses of the two detectors which are quite different (see above). In addition it is doubtful whether Driscoll's data are consistent with this conclusion. They were derived from a least squares linear regression of PID response against carbon number for some of the compounds studied. The low correlation coefficient of 0.67 which was obtained indicates that PID response is not a direct function of carbon number. Even within an homologous series where the RMR does increase smoothly with carbon number, the relationship is by no means linear (Fig. 2).

The results of this work in which PID and FID response were compared for cyclohexane, toluene, 1-nonene and *n*-decane are shown in Table II. The variation in PID response is almost certainly due to IP differences. Unfortunately only the photo-ionization IP values for cyclohexane (9.88 eV) and toluene (8.82 eV) are known. Values of *ca.* 9.35 eV for 1-nonene and *ca.* 10 eV for *n*-decane can be estimated from electron impact data given by Vilesov[13]. A linear regression using RMR (from Table II) and these IP figures has a correlation coefficient of −0.99. In contrast, a linear regression of RMR against carbon number has a correlation coefficient of −0.12. A linear regression of RMR of these compounds on the FID against carbon number gives a correlation coefficient of 0.996.

Driscoll[4] has reported normalized PID/FID relative response ratios (alkane = 1.0) for some hydrocarbons and concluded that, on this basis, aromatics have a ratio

TABLE II

COMPARISON OF PID AND FID RESPONSE

Compound	Area/g (cyclohexane = 1.00)		Area/mol (cyclohexane=6.00)		$\dfrac{Area\ PID}{Area\ FID}$	$\dfrac{Area\ PID}{Area\ FID}$ (n-decane = 1.0)	IP (eV)
	PID	FID	PID	FID			
Cyclohexane	1.00	1.00	6.00	6.00	20	1.4	9.88
Toluene	5.59	1.05	36.73	6.88	108	7.7	8.82
1-Nonene	2.65	1.06	23.89	9.53	50	3.6	(9.35)*
n-Decane	0.76	1.10	7.75	11.14	14	1.0	(10.00)*
Correlation coeff. area/mol against carbon number			−0.117	0.996			

* Estimated values.

between 5 and 10, alkenes between 2 and 4 and alkanes less than 2. The data reported here are consistent with these ranges (Table II). The degree of improvement in response of the PID over the FID depends primarily on IP (Table II). A linear regression of PID/FID relative response against IP gives a correlation coefficient of −0.98.

If the response of the PID depends upon sample concentration (eqn. 17), rather than on carbon number, the response to a discrete sample should be flow-rate dependent since at a faster flow-rate the sample is effectively diluted in a greater volume of carrier gas than at lower flow-rates giving a smaller response. This effect has been confirmed by Driscoll[2]. The flow-rate for a gas containing a constant concentration of sample i.e., using the PID as a direct detector rather than a chromatographic one, should not affect response. Studies of PID response to 1 ppm oil vapour in carbon dioxide in which the gas flow-rate was varied between 60 and 120 ml/min confirmed that this was the case. It might be expected that carrier gas flow-rate would not affect FID response to a discrete sample. In practice, however, there is a complex relationship between response and the carrier, air and hydrogen flow-rates. This has been studied by Grant and Clarke[14] who show a series of humped curves for FID response against carrier gas flow-rates depending on the particular air and hydrogen flow-rates fixed for the experiment.

The ratios of PID response using helium as the carrier gas to PID response using carbon dioxide are shown in Table III.

The UV transmission (T) at 10.2 eV can be calculated from the expression $T = 100\,e^{-aL}\%$. Using a value of 200 m^{-1} for the absorption coefficient a derived

TABLE III

PID RESPONSE IMPROVEMENT USING HELIUM AS CARRIER GAS COMPARED TO CARBON DIOXIDE

Compound	PID response improvement
Cyclohexane	4.9
Toluene	5.4
1-Nonene	5.2
n-Decane	5.5
Oil	5.2

from the results of Nakata *et al.*[11], and $L = 2$ mm, $T = 67\%$. Since there is no absorption in helium the response in helium should be $1/0.67 = 1.5$ times greater than in carbon dioxide. The difference between this figure and those in Table III can be explained by reference to eqn. 7 above. Carbon dioxide is much more efficient than helium at deactivating the excited state by collision. Helium atoms only have translational energy states in which to absorb the excited state energy of the sample whereas carbon dioxide has rotational and vibrational states as well.

The ratio of the response in helium to that in air for oil was 3.3. The lower response in air is a consequence of the oxygen quenching effect (eqns. 8 and 9) in which the sample ion is neutralised before it reaches the cathode.

Studies of the PID response to oil vapour in carbon dioxide using linear regression analysis gave a sensitivity of 34 ppb/mV with a correlation coefficient of 0.952. The criterion of detection, which is the smallest signal which can be distinguished with 95% confidence from the background noise, is calculated as 2.326 σ_B[15] where σ_B is the standard deviation of the blank. This expression assumes that the errors have a Gaussian distribution. Thus by determining the standard deviation of the blank, in this case the signal at an ambient bath temperature, and by multiplying it by 2.326 and by the sensitivity a figure for the smallest concentration which can be detected above the background noise is obtained. In this work $\sigma_B = 0.0253$ mV therefore the criterion of detection is $2.326 \times 0.0253 \times 34 = 2$ ppb oil in carbon dioxide.

CONCLUSIONS

(1) The response of the PID depends upon the absorption cross section, ionization efficiency and molar concentration of the compound in question.

(2) Since the photoionization cross section (the product of ionization efficiency and absorption cross section) is related to the IP it might be expected that PID response would depend on IP. This has been shown to be the case.

(3) Within an homologous series where IP is related to carbon number there is also a relationship between PID response and carbon number.

(4) The PID response for different compounds with the same carbon number can vary considerably depending primarily upon IP. There is therefore no overall relationship between PID response and carbon number.

(5) The degree of improvement in response of the PID over the FID depends primarily on IP.

(6) PID response to a gas containing a constant concentration of sample is not affected by flow-rate.

(7) PID response to samples in helium is around five times greater than the response to the same sample in carbon dioxide, and 3.3 times greater than to the same sample in air.

(8) The criterion of detection using the PID for oil vapour in carbon dioxide is 2 ppb.

ACKNOWLEDGEMENTS

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