CHROMSYMP. 257

PHOTOIONIZATION DETECTORS FOR GAS CHROMATOGRAPHY

J. N. DAVENPORT and E. R. ADLARD*

Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH (U.K.)

SUMMARY

The principles of photoionization detectors for gas chromatography and the potential advantages of these detectors are described. Experience with a commercially available detector shows that it has a high sensitivity and selectivity for certain classes of compounds such as olefins and aromatics. Improvements in the commercial design have been made at Thornton Research Centre to make the detector more compatible with capillary columns. These improvements are discussed and an outline is given of possible future developments.

INTRODUCTION

The role of the detector in gas chromatography (GC) is to monitor changes in the composition of the gas eluted from the column and to give an electrical signal related to these changes. Bulk properties such as thermal conductivity have been used successfully, but a detector is likely to have a higher sensitivity if it measures a physical or chemical property of the compounds of interest and gives little or no response for the carrier gas itself.

In many analyses the most useful detector is one that gives an equal and high response for all compounds. The flame ionization detector when used for the analysis of hydrocarbon mixtures approximates to this ideal. However, the analysis of complex mixtures may require the use of a selective detector such as the electron capture detector for halogenated compounds and the flame photometric detector for sulphur and phosphorus compounds. Selective detectors of this sort are often used in conjunction with a non-selective detector.

The photoionization detector first appeared commercially as a portable trace gas analyser for compounds such as vinyl chloride, benzene and ammonia. In 1978 a modified version became available as a GC detector which was claimed to have higher sensitivity than the flame ionization detector and selectivity towards olefins and aromatics. However, interest has been slow to develop in spite of a number of papers which have appeared describing the detector and its applications[1-33]; one reason for this is that the photoionization detector has to be calibrated for every compound of interest.

The photoionization detector is selective in that its response can be greater or less than that of the flame ionization detector and the selectivity can be altered by changing the photon source. This paper describes some investigations into the behaviour of the HNu model PI 52-02 photoionization detector, with experimental data

obtained with both the 10.2-eV and 9.5-eV lamps. The spectral distributions of these and other lamps have been determined. Current theory of the photoionization process is covered in some detail and is compared with recently published empirical theories of detector response. Modifications to improve the performance of the commercial detector are also described.

THE PHOTOIONIZATION PROCESS

Photoionization is one of the processes by which an atom or molecule can absorb energy. It is the result of an electron transition from one of the discrete, low energy levels (usually the ground state) to the higher energy continuum of the ion, and the energy required is about 5–20 eV. For photon excitation this corresponds to the far ultraviolet region of the spectrum.

Absorption cross-section

In many cases the absorption of light by a substance follows the Beer–Lambert Law, *i.e.* $I = I_0 \exp(-\alpha x)$, where I_0 and I are the intensities (photons/sec) of incident and transmitted light, x is the path length (m) and α is the absorption coefficient (m^{-1}). For many purposes it is more useful to use σ, the absorption per atom or molecule per unit volume. Thus, for an ideal gas

$$\sigma = \frac{\alpha}{n} \tag{1}$$

where α is the absorption coefficient (m^{-1}), σ is the absorption cross-section (m^2), n is the Loschmidt's number $= \dfrac{6.023 \times 10^{26}}{22.4} = 2.69 \times 10^{25}$ mol/m^3 at STP. Hence

$$I = I_0 \exp(-\sigma n x) \tag{2}$$

Under conditions other than STP (273°K, 760 mmHg) the absorption equation can be written

$$I = I_0 \exp\left(-\sigma n \frac{P}{760} \cdot \frac{273}{T} \cdot x\right) \tag{3}$$

where P is the pressure (mmHg) and T is the absolute temperature.

Typical values of absorption cross-section are in the range $1 \cdot 10^{-22}$–$100 \cdot 10^{-22}$ m^2. (In older texts it is common to encounter absorption cross-section expressed in megabarns, where 1 Mb $\equiv 10^{-22}$ m^2.)

Photoionization cross-section

The photoionization cross-section σ_i is defined as the absorption cross-section multiplied by the photoionization yield or efficiency, hence

$$\sigma_i = \eta \sigma \tag{4}$$

The photoionization yield (η) is the probability that absorption of a photon will result in ionization, and is often unity for atoms, but considerably less for molecules.

Photon–atom interactions

The lowest energy state that an atom can adopt is that in which the electrons are in their ground states. Each of the electrons has a set of discrete higher energy states which converge on a limit at which point the electron is no longer bound to the atom and ionization takes place. Energy states beyond the ionization limit are continuous rather than quantized because any excess energy can be removed as kinetic energy by the electron (and to a much smaller extent by the ion). Thus

$$hv = (V_2 - V_1)e \qquad \text{below the series limit} \tag{5}$$

and

$$hv = (V_i + K^2)e \qquad \text{above the series limit} \tag{6}$$

where h is the Planck's constant, v is the frequency, V_1, V_2 are the potentials of electron state, V_i is the ionization potential, K^2 is the kinetic energy contribution and e is the electronic charge.

It is now assumed that the photon energy is greater than the ionization energy of the atom.

If absorption of the photon energy results in the transition of the outermost electron then direct photoionization takes place. However, if an inner electron is excited to below its series limit, but above the ionic state, then the result is an atom in a superexcited state, *i.e.* its energy is greater than that of the ion in its ground state. If these two states have the same angular momentum there is the possibility of a radiationless transition to ion plus electron (plus kinetic energy). This process is known as autoionization and is illustrated in Fig. 1. Autoionization manifests itself as a series of lines superimposed on the absorption and photoionization continua, and is readily observed for argon[34].

Another form of excitation is for the photon energy to cause the transition of an inner electron to beyond its series limit, producing an excited ion which subsequently decays emitting radiation, or an Auger electron. However, photon energies for this process are greater than those being considered here, and this effect may be disregarded.

The events which can take place when a photon of sufficient energy interacts with an atom are thus: (a) direct photoionization $hv + X \rightarrow X^+ + e^- + \text{K.E.}$; (b) autoionization $hv + X \rightarrow X^*$; $X^* \rightarrow X^+ + e^- + \text{K.E.}$; (c) no ionization $hv + X \rightarrow X^*$. The overall photoionization yield for atoms is usually close to unity because the probability of forming stable superexcited states is low.

Photon–molecule interactions

The interaction of a photon with a molecule is very much more complex than that with an atom because there are far more degrees of freedom. Electronic transitions within the energy range under consideration are vibronic, *i.e.* transitions between rotational levels of different electronic and vibrational states. If the transition is to a level of high vibrational energy then dissociation into neutral fragments may
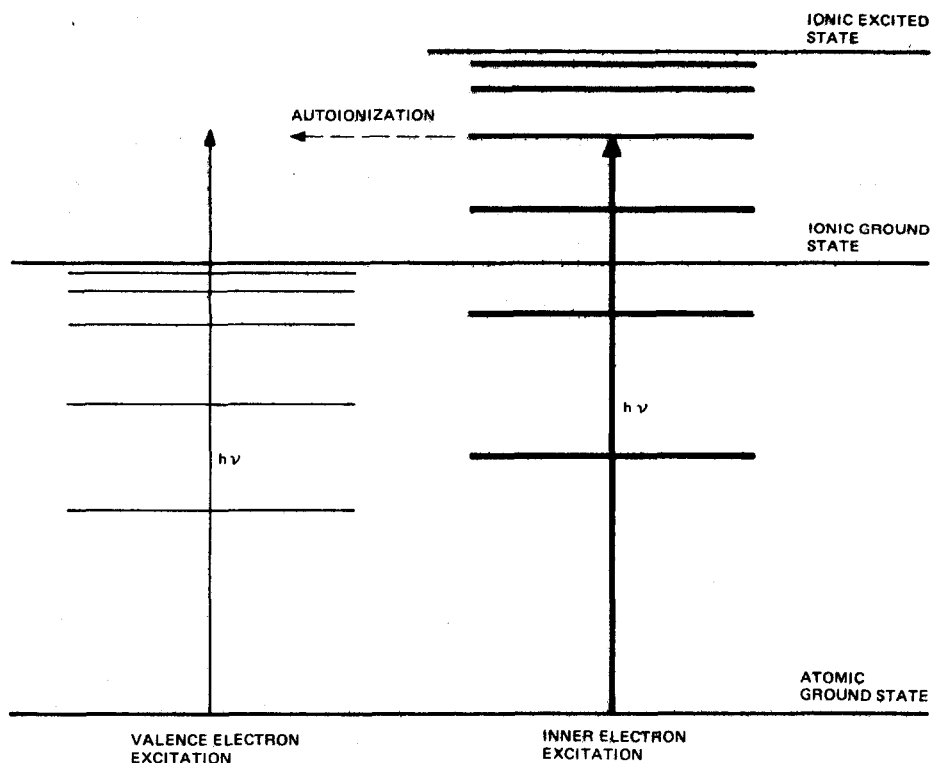
Fig. 1. Direct photoionization and autoionization.

take place, whereas transition to an excited electronic state can result in an ion pair. However, if the energy of the final state exceeds the lowest energy level of the molecular ion ground state then photoionization may occur. As for an atom, any excess energy can be removed by kinetic energy of the electron, but the removal may be only partial, in which case the molecular ion is left in an excited state.

Another possibility, subject to selection rules, is the formation of a superexcited molecule, analogous to the superexcited atom, in which the overall energy is greater than that of the molecular ion. This species can break down via autoionization to form a molecular ion plus kinetic energy (known by some authors as preionization), but the formation of neutral fragments —predissociation— can also occur. Evidence for the autoionization process (and hence molecular superexcitation) in organic molecules comes from the observation of isotope effects in photoionization yields. It has been argued[35] that if predissociation and autoionization are competing processes, i.e. occurring at similar rates, then substitution of a heavier isotope should decrease predissociation and thereby increase autoionization, giving a higher photoionization yield. Such an effect has since been demonstrated, using deuterated compounds, for methanol[36], benzene[37] and many other species.

Of the many processes which can occur when a photon interacts with a molecule, the ones which have been discussed here are as follows: (a) photoionization $hv + AB \rightarrow AB^+ + e^-$; (b) dissociation $hv + AB \rightarrow A + B$; (c) ion pair formation

$hv + AB \rightarrow A^+ + B^-$; (d) predissociation $hv + AB \rightarrow AB^*$, $AB^* \rightarrow A + B$; (e) autoionization $hv + AB \rightarrow AB^*$, $AB^* \rightarrow AB^+ + e^-$.

In view of all these possible processes (as well as re-radiation and rapid recombination for example) it is hardly surprising that photoionization yields rarely exceed 50%. Furthermore, photoionization cross-sections as a function of photon energy are often much more complicated than might at first be expected, and their prediction from first principles is very difficult. As an example, Fig. 2 shows the photoionization cross-section of methyl bromide taken from ref. 36.
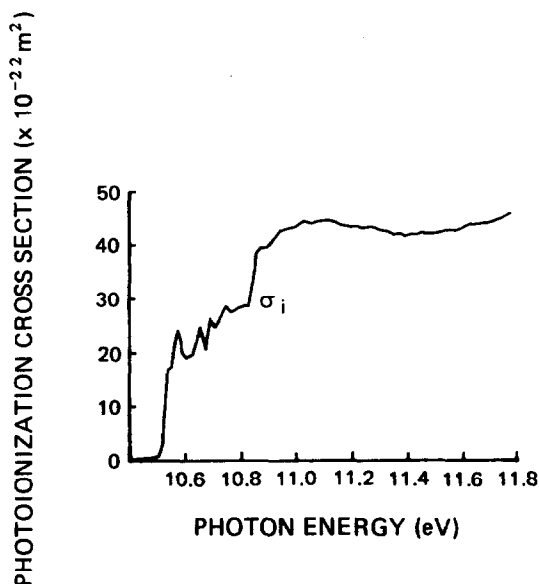

Fig. 2. Photoionization cross section of methyl bromide[36].

Photoionization as a detection process for gas chromatography

The photoionization process has many features which make it suitable as the detection mechanism for gas chromatography. One of the most important is that detection is dependent on concentration, rather than on mass-flow. This is of considerable advantage because capillary columns can be used with no loss of detector sensitivity.

As mentioned above, the sensitivity of a detector in a gas chromatograph will be higher if the carrier gas gives no response. Photoionization will not generally occur unless the incident photon energy is greater than the ionization potential of the species concerned, and fortunately the ionization potentials of the common carrier gases are higher than those of nearly all organic compounds (*e.g.* helium 24.6 eV; argon 15.8 eV; nitrogen 15.6 eV; hydrogen 15.4 eV). Thus ionization of the carrier gas will not take place unless the photon energy is greater than about 15 eV. This cannot occur in the HNu detector because the photon sources have windows, and the limit of transparency for suitable materials is about 12 eV.

The composition of the gas coming out of a photoionization detector will be

virtually the same as that going in, thereby allowing a second detector (*e.g.* another photoionization detector or a flame-ionization detector) to be placed in series. This is because the photoionization process is rather inefficient; typically 0.001 to 0.1% (while this sounds very low it is better than that of the flame ionization process). The cleanliness of a photoionization detector is helped by the fact that additional gases are not required, although for a capillary column it may be necessary to add a small amount of make-up gas (see Experimental).

It is clear from the discussion in the *Photon–molecule interactions* section that a photoionization detector will be selective, *i.e.* its response will differ from compound to compound. The narrower the energy spread of the incident photons the greater the selectivity, until for monochromatic photons the detector response can be zero (*i.e.* when the photon energy is less than the ionization potential), or appreciable and virtually any value (depending on the absorption cross-section and photoionization yield at that energy). While this selectivity can be advantageous, for example in simplifying a complex chromatogram, it can also be a serious disadvantage when quantitative analysis is required.

THE HNu PHOTOIONIZATION DETECTOR

Detector construction

The construction of the HNu photoionization detector (Model PI 52-02) is shown in Fig. 3. The ultraviolet source, which is easily removed, is of sealed construction with a ring cathods and a disk-shaped anode at the base. The photons, which are collimated by an internal capillary, emerge through a window sealed into the anode. The detection cell is formed by the source window, the collecting electrode and various seals, and has a volume of about 150 μl. A polarizing voltage of about -400 V applied to the other electrode within the cell produces a potential gradient which drives any electrons to the collector and thence to the amplifier. The detection cell is surrounded by a heater block which can be maintained at temperatures up to a maximum of 300°C.

Associated electronics

The detector is supplied with all the required electronics, *i.e.* the power supply, the lamp control, the electrometer and the temperature control. The power supply has two outputs, the lamp high voltage supply, which can deliver up to 1400 V d.c., and the polarizing voltage, which also has a maximium of 1400 V d.c. The supply is arranged in such a manner that both outputs are off or both on. In order to measure the spectral output of the sources (see *Spectral distribution of the HNu sources*) current has to be drawn from the polarizing supply (this was done through a 10-MΩ resistance to ground). The outputs appear to be unregulated as zero current drain gives maximum voltage. In normal use typical voltages are 400 V for both outputs.

The lamp control is a 5-MΩ logarithmic, single turn rheostat which changes the source voltage and hence the current and detector sensitivity. As Fig. 4 shows, the current drawn by a 10.2-eV source can be altered from 0.2 to 1.6 mA. In view of the importance of using repeatable source currents in the evaluation of the detector a digital milliammeter has been installed in the supply.

The electrometer supplied by HNu is fairly conventional except that the backing-off current is somewhat larger than usual.
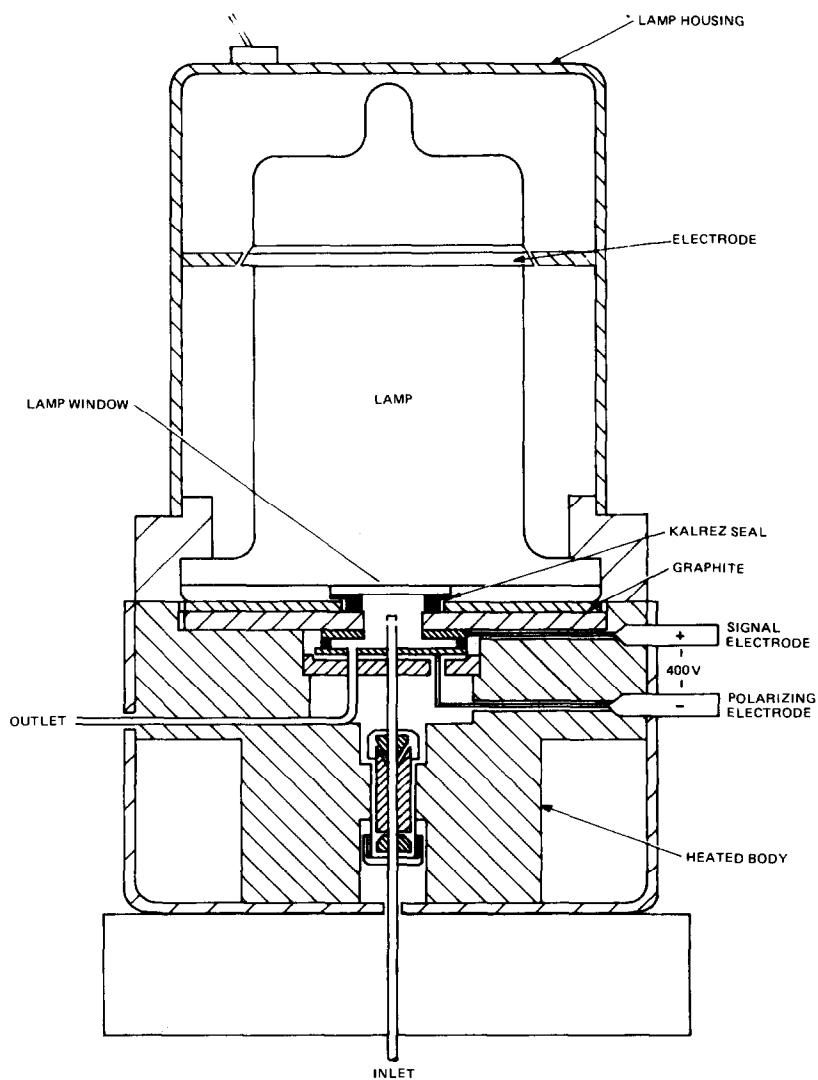
Fig. 3. Construction of the HNu photoionization detector.

The temperature of the cell is controlled by a variable resistor, but this has been found to be unsatisfactory and a separate power supply with a Honeywell proportional controller has been installed to give better temperature stability[38].

Electrical characteristics of a 10.2-eV source
The voltage-current characteristics of one of the 10.2-eV sources (which are typical for discharge lamps in general) are shown in Fig. 5.

Spectral distribution of the HNu sources
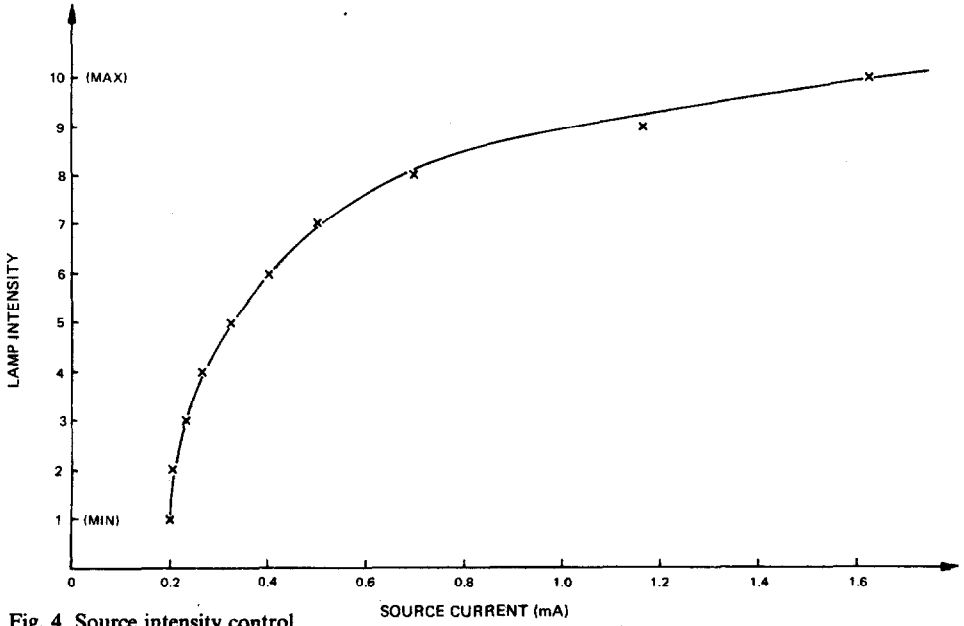The sources available from HNu have nominal energies of 8.3, 9.5, 10.0, 10.2,
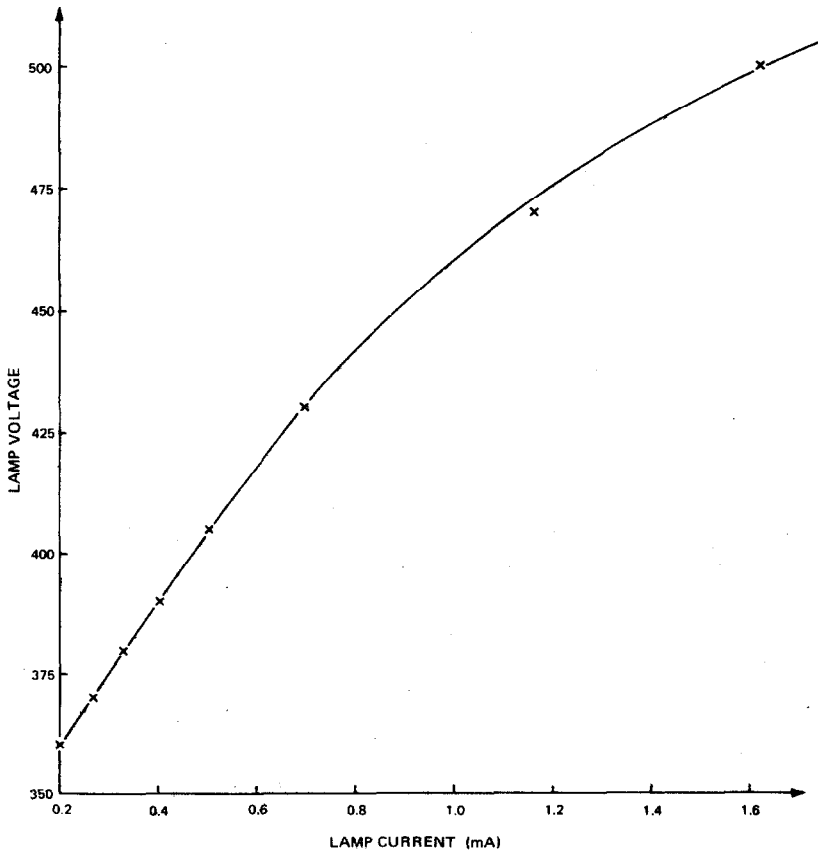
Fig. 4. Source intensity control.

Fig. 5. Voltage-current characteristics of a 10.2-eV source.

10.9 and 11.7 eV. The spectral outputs of the sources, with the exception of the 10.0 and 10.9 eV, have been examined using a McPherson Model 241 vacuum ultraviolet spectrometer. This apparatus, which is housed in the Chemistry Department at the University of Dundee, has a 3-m focal length and a 1200 line/mm grating to give a dispersion of 0.278 nm/mm. An entrance slit of 10 μm was used, and spectra were obtained over the range 100–180 nm (12.4–6.9 eV) at a scanning speed of 2.5 nm/min, while individual peak heights were scanned at 0.25 nm/min. For each source all measurements were made at minimum and maximum intensities (*i.e.* lamp currents of 0.2 and 1.6 mA). The detection system consisted of a Centronics Type Q4249 BA photomultiplier and pulse height analysis equipment. The dark signal was of the order of 20 photons/sec compared with typical count rates on an emission line of 10,000 photons/sec. The very high quality of the spectra obtained using the instrument can be seen in Fig. 6, which shows the energy distribution of the output from a 10.2-eV source.
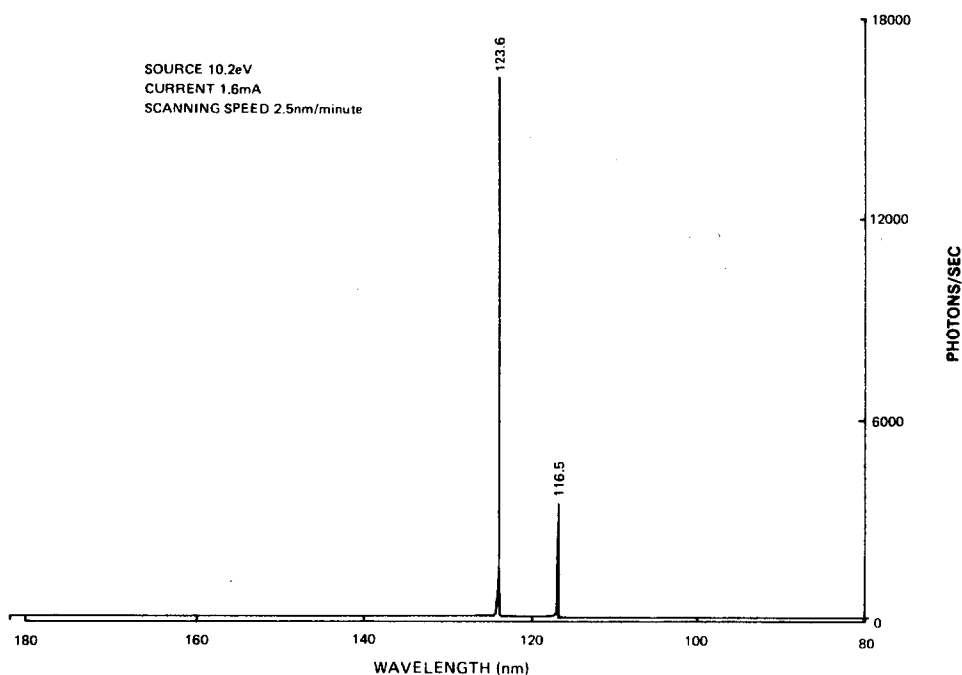

Fig. 6. Far ultraviolet spectrum.

The characteristic lines of the various sources are listed in Table I. Several important points may be made: (1) Of the four different sources investigated only the 8.3 eV lamp is monochromatic within the range examined. However, the energy of this line is 8.44 eV, not 8.3 eV. (2) The 9.5-eV source is the worst as nearly all the light emitted is at 8.4 eV. Of the remaining lines the most intense is at 9.57 eV, but others are present up to 10.88 eV. (3) The 10.2-eV source has two sharp lines at 10.03 eV (83%) and 10.64 eV (17%). This is of considerable importance as the 10.2-eV source is the one most commonly used (see *Theories of detector response*). (4) The 11.7-eV source again has two sharp lines (11.62 and 11.82 eV), but as they are closer

TABLE I

CHARACTERISTIC LINES FOUND IN VACUUM UV OUTPUT OF HNu LAMPS

Lamp designation (eV)	Wavelength (nm)	Energy (eV)	Output (%)	Lamp type
8.3	147.0	8.44	100	Xenon
9.5	114.0	10.88	0.03	Xenon
	117.2	10.58	0.01	
	119.3	10.40	0.18	
	125.0	9.92	0.05	
	129.6	9.57	2.1	
	147.0	8.44	97.6	
10.2	116.6	10.64	17.1	Krypton
	123.6	10.03	82.9	
11.7	104.9	11.82	26.2	Argon
	106.6	11.62	71.8	
	121.6	10.20	2.0	

together than those of the 10.2-eV source they do not create as much of a problem when interpreting detector responses. (5) The output of the lamps does not include an emission continuum, implying that the gases are at low pressure. (6) The gases used are very pure. (7) The importance of the lamp window material can be seen in the spectra of the 8.3- and 9.5-eV sources —both are filled with xenon, but the 8.3-eV source uses a window of material which cuts off completely above about 8.5 eV. (8) Although not shown in Table I, three of the 9.5-eV and two of the 10.2-eV sources were in fact examined. The relative peak heights of the lines were identical for all lamps of the same type. (9) The peak heights of the characteristic lines of the 9.5-, 10.2- and 11.7-eV sources were measured at lamp currents of 0.2 and 1.6 mA; the spectral distribution was found to be independent of current. (10) It was not possible to compare the outputs of the sources because there was no means of aligning the source with the entrance slit of the spectrometer to obtain absolute measurements of light intensity.

Theories of detector response

        In the last two years some workers[22,23,28] have presented theories regarding the response to various organic compounds of the HNu photoionization detector with the 10.2-eV source. The data used to support the theories have been selected mainly from the compilation of relative responses made by Langhorst[26]. Casida and Casida[23] sought to show that detector response is proportional to the number of π-bonding electrons in the compound, but as pointed out by Freedman[28] if this were true the alkanes, which contain no such electrons, would give no response at all. In fact the response to *n*-octane and higher alkanes is quite large (see Fig. 7). Freedman[28] postulated a direct relationship between photoionization detector response and ionization potential and concluded that "ionization potential is the most important single factor determining photoionization detector response".
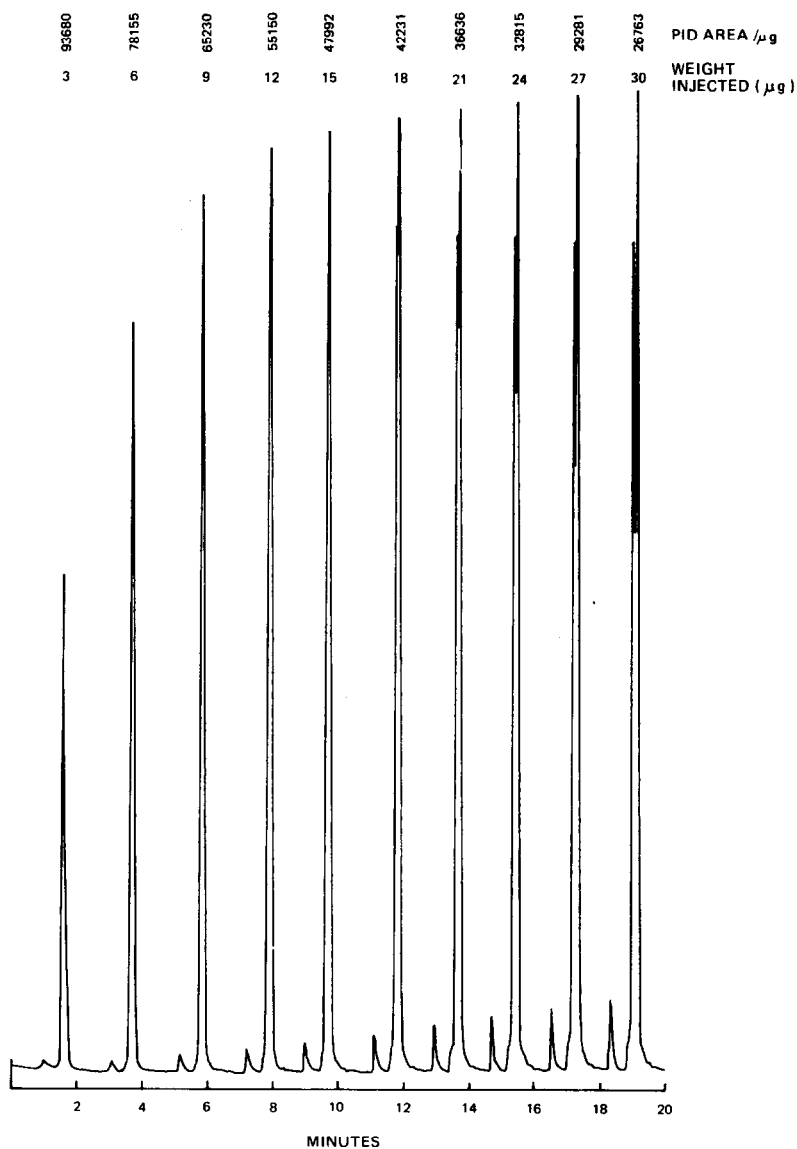
Fig. 7. Chromatograms of photoionization detector response for *n*-octane.

While each author was able to present data supporting his particular theory it is easy to find results which do not fit (see Results). Indeed, from a practical viewpoint the merit of such theories is doubtful because it is difficult to predict the response of a known compound and impossible to identify an unknown from its detector response alone.

It is not surprising that the theories fit experimental results so poorly. The 10.2-eV source is not monochromatic, and the dependence of ionization cross-section on incident photon energy is very complex. It is interesting to note that Schoen[39]

found the maximum value of ionization cross-section (at about 16 eV) for the low alkanes to be roughly proportional to the number of bonding electrons. It must be emphasised, however, that this does not apply at lower energies because the shapes of the ionization cross-section/energy curves differ markedly.

EXPERIMENTAL

Experiments were carried out with the HNu detector to measure the upper limit of response, the upper limit of linearity, the baseline stability and noise level and the selectivity and sensitivity for a range of compounds.

The detector was mounted originally with the source in a horizontal position, on the side of a Perkin-Elmer F17 gas chromatograph with the detector inlet and outlet pipes passing through holes drilled in the GC oven. The reason for mounting the detector horizontally was to minimize the length of transfer line. However, this configuration proved very inconvenient when changing sources as it was very difficult to locate the gas seals correctly (see Fig. 3), and the detector was subsequently mounted vertically. The transfer lines were heated with a low voltage winding and the outlet of the photoionization detector was connected to one of the flame ionization detectors of the GC.

Initial work was carried out using a 2 m × 1/8 in. O.D. stainless-steel column packed with 5% OV 101 on Chromosorb G with a column flow-rate of about 20 ml/min of helium. The capillary column used for most of the subsequent work was 50 m × 0.3 mm O.D. fused-silica wall coated with SP 2100, with a 50:1 inlet splitter to give a column flow-rate of about 0.3 ml/min helium. Because of the relatively large volume of the photoionization cell (150 μl) helium make-up gas was added at 10 ml/min to improve chromatographic resolution (this also improves the detector performance). Fig. 8 shows the flow system used with the capillary column.

The initial performance of the detector was poor because of leaks and consequent loss of sensitivity. This was overcome by using Kalrez (perfluorinated butyl rubber) seals in the detection cell.
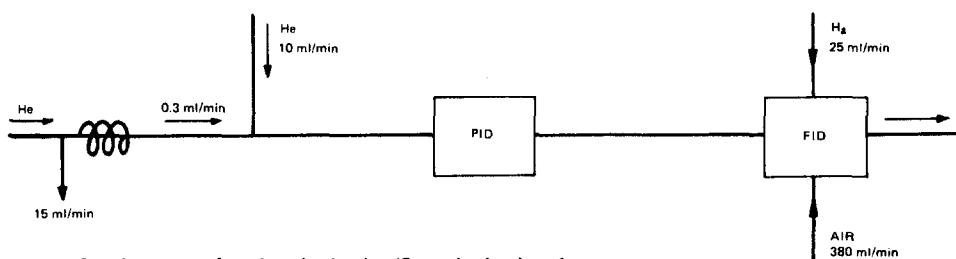

Fig. 8. Gas flow-rates for photoionization/flame ionization detectors.

RESULTS AND DISCUSSION

Upper limit of detection and detector linearity

The upper limit of response for the 10.2-eV source was determined by the injection of *n*-octane (3% w/w in pentadecane) into a packed column. Chromatograms of injections covering the range 3–30 μg nC$_8$, together with figures for peak

area per μg are shown in Fig. 7. The upper limit of response to *n*-octane is 9 μg; greater sample sizes produce a double peak, an effect which has been attributed[24] to the recombination of ions above a critical concentration. It is possible that this effect would be delayed by the use of a higher field strength within the detection cell.

The upper limit of linear response for *n*-octane is around 1 μg (not shown in figure). This corresponds to a maximum concentration of 0.1% of the analyte in a 1-μl injection. This is a lower concentration than that frequently encountered and for analysis using packed columns it means that dilution of the sample is required. Alternatively the injection could be split. From this point of view and from the concentration-dependent response of a photoionization detector it is clear that this type of detector is far better suited to use with capillary than with packed columns.

Linearity of the detector response over a wide range of sample weights has not yet been investigated. There is a small impurity peak in the chromatograms in Fig. 7, however, whose photoionization response is linear over one order of magnitude at least. Using peak areas from a flame ionization detector and assuming equal response factors for the unknown and for *n*-octane the impurity weights would be in the range 5–50 ng. The photoionization detection area *versus* weight injected for this unknown compound is shown in Fig. 9.
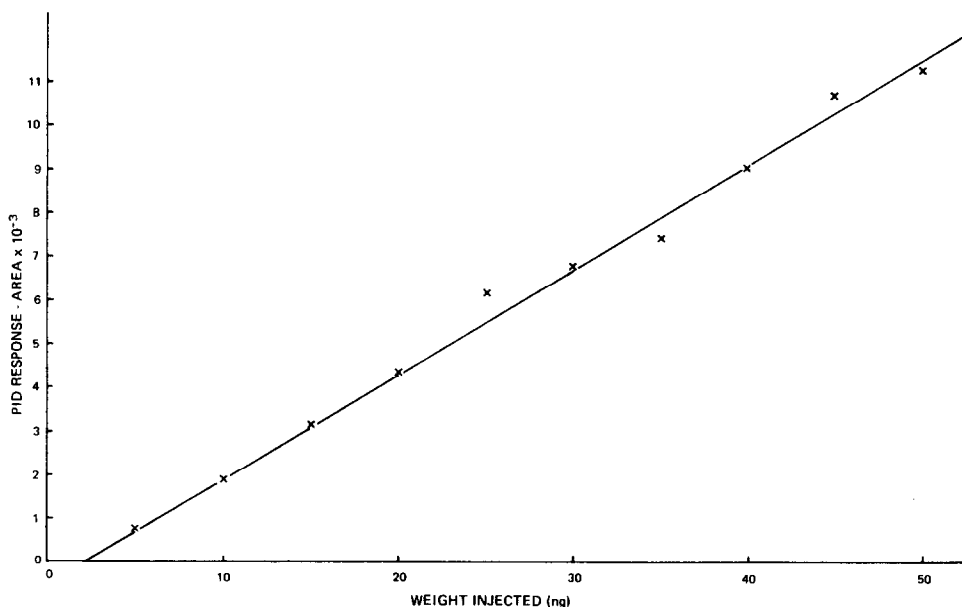

Fig. 9. Photoionization detector response for unknown contaminant.

Lower limit of detection

The manufacturer claims a lower limit of detection of 2 pg for benzene with a 10.2-eV source and although we have not verified the manufacturer's figure accurately it is approximately correct.

Baseline stability and noise

The poor baseline stability and high noise level of the detector have been

serious problems. Several causes of the baseline drift have been identified and the situation is now greatly improved. The biggest single cause of the drift was poor temperature stability of the detection cell, as this affected the background photoelectric current from the metal electrodes (although HNu use beryllium for the collector in order to reduce the photoelectric yield, they use a gold polarizing electrode). Temperature stability of the cell was improved by using a Honeywell proportional controller.

It has been found recently that the sporadic high noise level is due to contamination of the insulating material in the cell, which leads to a variable polarizing voltage and occasional arcing, but although various parts of the detector have been replaced this problem remains and is unlikely to be cured completely without redesigning the cell.

Detector sensitivity

While Langhorst[26] reports molar sensitivities relative to that of benzene, it is more useful when employing a flame ionization detector in series with the photoionization device to report photoionization sensitivity of a compound relative to the flame ionization sensitivity (although this ratio will be strongly dependent on the gas flow-rate). Relative sensitivities have been determined for a variety of compounds,

TABLE II

RELATIVE RESPONSES (PHOTOIONIZATION/FLAME IONIZATION)

Compound	9.5-eV source		10.2-eV source		Ionization potential (eV)
	Minimum	Maximum	Minimum	Maximum	
Heptane	1.4	7.8	0.4	3.2	10.0
Cycloheptane	1.8	9.2	1.8	11.2	
Methylcyclohexane	1.4	7.8	6.2	39.1	9.85
Toluene	7.9	32.7	19.5	123	8.82
1-Heptene	3.3	14.7	12.4	74.7	9.44
2-Methyl-1-hexene			13.4	79.5	9.04
3-Methyl-1-hexane	3.1	13.2	10.6	66.9	
2-Methyl-2-hexene			14.2	88.0	8.62
2,3-Dimethyl-2-pentene			12.0	76.1	8.21
Cycloheptene	4.2	13.6	9.8	59.8	8.87
3-Methylcyclohexene	4.9	17.9	9.4	61.2	8.94
2,3-Dimethyl-2-butene			13.8	81.5	8.30
2-Methyl-2-butene			16.9	92.8	8.68
1-Butene			21.0	126	9.58
2-Butene (cis)			22.5	166	9.13
2-Butene (trans)			25.0	154	9.13
1,3-Butadiene			29.0	181	9.06
2-Methylpropene			27.5	175	9.23
Propene			20.1	143	9.73

mostly alkenes, using the 10.2- and 9.5-eV sources with a flow-rate (including make-up gas) of 10 ml/min. The results are given in Table II together with ionization potentials taken from the literature[40,41]. Several points emerge from the results: (1) For many of the compounds chosen the photoionization detector is far more sensitive than the flame ionization detector. (2) In general the 10.2-eV source is six times more sensitive at maximum intensity than at minimum intensity, while the 9.5-eV source is about four times as sensitive at the higher source current. (3) The results for *n*-heptane and methyl cyclohexane with the 9.5 eV source show its non-monochromatic nature, as the ionization potentials are 10.0 and 9.9 eV respectively. (4) In general a decrease in ionization energy (*i.e.* a larger difference between it and the photon energy) results in a decrease in detector sensitivity. However, this is only true for molecules which are structurally very closely related. Indeed, even in the small amount of data presented here it is easy to find compounds with similar ionization potentials but different structures and widely differing detector sensitivities (*e.g.* toluene and cycloheptene). These effects are seen more clearly in Fig. 10. The theories of detector response are not in agreement with the results presented here. (5) The fact that the sources are not monochromatic makes interpretation of some of the results very difficult (*e.g. n*-heptane gives a higher response with the 9.5-eV source than with the 10.2-eV source, yet its ionization potential is 10.0 eV).
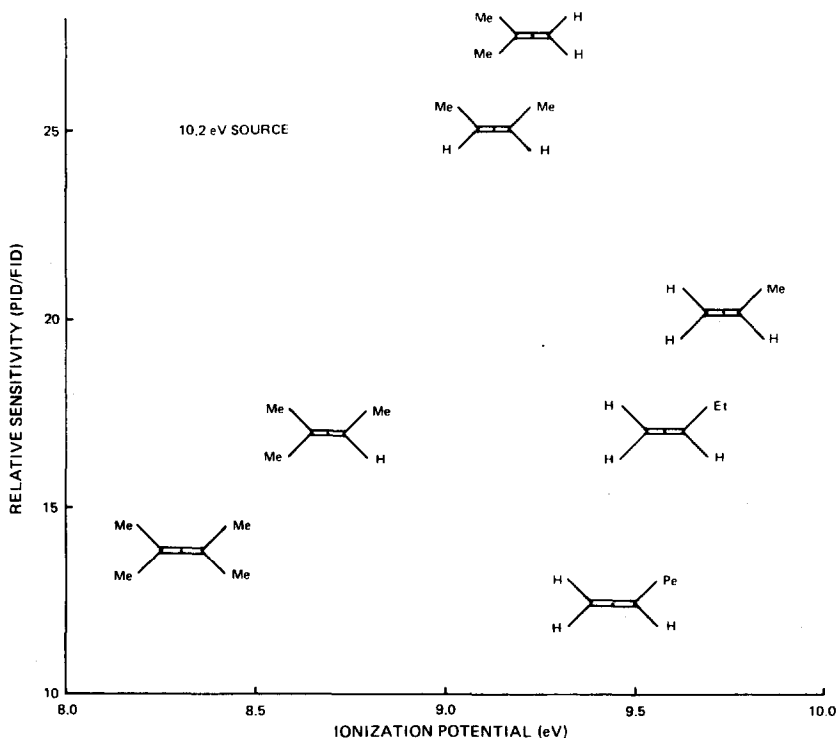

Fig. 10. Relative sensitivities (photoionization/flame ionization) *vs.* ionization potential.

TABLE III

SELECTIVITY OF THE PHOTOIONIZATION DETECTOR

Compound	9.5-eV source		10.2-eV source	
	Minimum	Maximum	Minimum	Maximum
1-Heptene (9.44)*/heptane (10.0)	2.3	1.9	33	25
Toluene (8.82)/methylcyclohexane (9.85)	5.7	4.2	3.2	3.2
3-Methylcyclohexene (8.94)/ methylcyclohexane (9.85)	3.6	2.3	1.5	1.6
Cycloheptene (8.87)/cycloheptane (–)	2.3	1.5	5.3	5.3

  * Figures in parenthesis are ionization potentials.

Detector selectivity

A measure of the selectivity of the detector towards unsaturated and aromatic species can be obtained from ratios of relative molar response. Some of these ratios have been calculated from the data in Table II, and are shown in Table III.

10.2-eV source

For the compounds listed in Table III the selectivity is independent of source intensity as might be expected (the sensitivity towards *n*-heptane at minimum intensity is very low and because of this the 1-heptene/*n*-heptane ratio is subject to larger errors). There is no advantage in using the 10.2-eV source at minimum intensity with compounds such as these, since the sensitivity at maximum source output is about six times higher.

9.5-eV source

The selectivity towards unsaturates appears to be dependent on source current. Careful measurement of the spectral distribution of this source has shown that the relative intensities of the various lines are not a function of current, and another reason for the varying selectivity must be sought. It is possible that recombination is taking place to some extent, but it is not known why similar effects are apparently absent when using the 10.2-eV source. Whatever the cause, the increased selectivity with the 9.5-eV source at minimum intensity has to be balanced against the lower sensitivity.

Photoionization versus flame-ionization for a gasoline

Chromatograms produced using photoionization (9.5 eV) and flame ionization detectors with a gasoline sample are shown in Fig. 11. The high sensitivity of the photoionization detector towards aromatics and olefins and its low sensitivity towards saturated compounds produce a chromatogram which is easy to interpret in terms of hydrocarbon type, but the widely ranging sensitivities within each type (see Fig. 10) make quantitative analysis difficult. Rather than using the photoionization detector alone it seems far better to use it for identification only, and to use the signal from a flame ionization detector for quantitative information, since the response factors of the flame ionization detector are all close to unity for hydrocarbons.
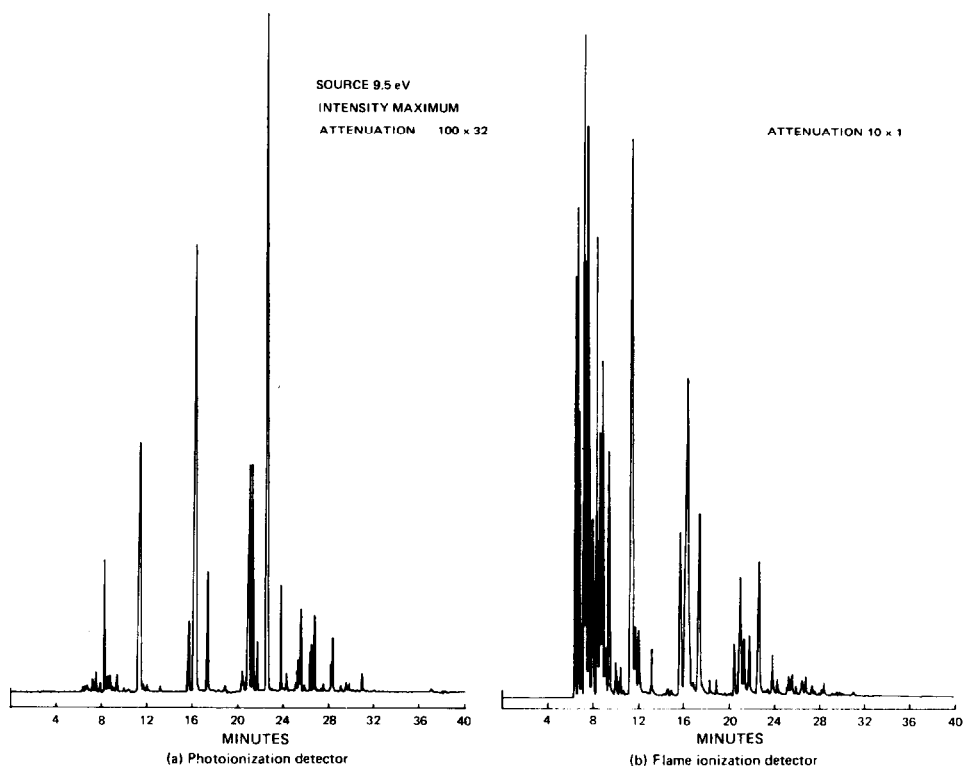
Fig. 11. Chromatograms of gasoline.

Advantages of the photoionization detector

(1) Knowing the spectral output of the sources it is easy to pick a solvent that will give little or no response, *e.g.* for a 10.2-eV source possible solvents would be dichloromethane (IP 11.3), methanol (10.9), Freon 11 (11.8), acetonitrile (12.2), etc.

(2) The response towards alkenes and aromatics with the 10.2-eV source is 10–100 times greater than that of the flame-ionization detector.

(3) The selectivity of the photoionization detector towards olefins and aromatics assists rapid identification of these species in a complex mixture. Although the response factors of the photoionization detector are all different, quantitative results can be obtained from the output of a flame ionization detector in series with the photoionization detector.

(4) The photoionization detector gives better performance with a capillary column than with a packed one.

Modifications to the HNu detector

As has been pointed out the photoionization detector is a concentration dependent device and as such is well suited for use with capillary columns. The HNu detector has an undesirably large dead volume for capillary column work and modifications to reduce this have been published by Kapila and Vogt[27]. An outline draw-
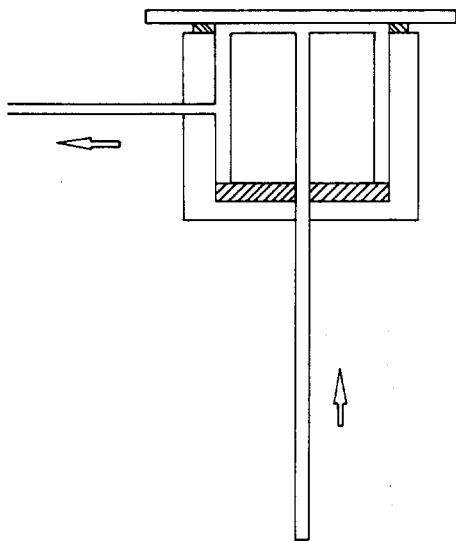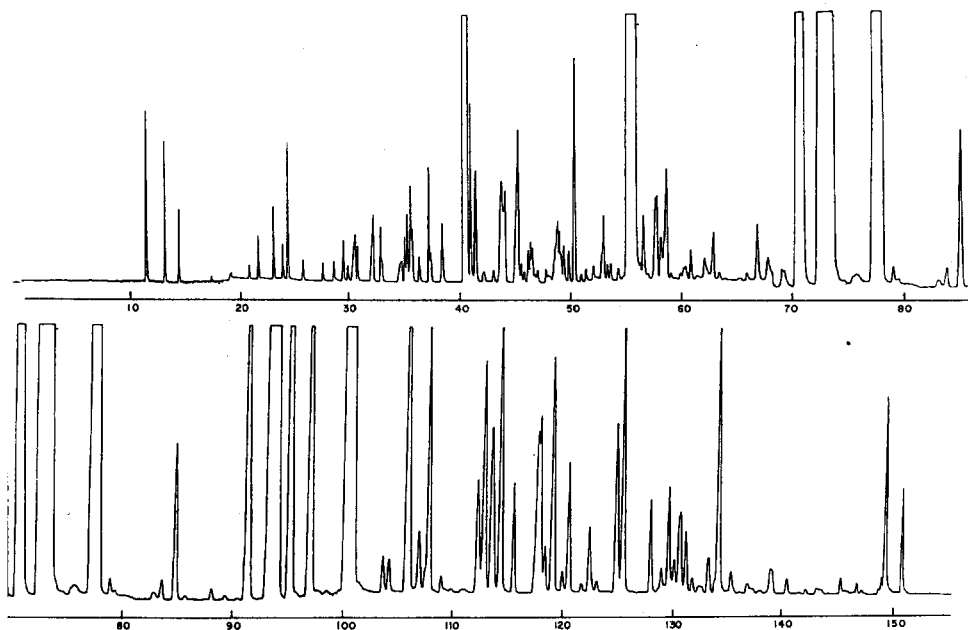
Fig. 12. Modified HNu detector.

Fig. 13. Gasoline chromatogram obtained from modified HNu detector. Conditions: sample, 0.5 μl gasoline, 50:1 split; column, 50 m × 0.25 mm silica coated with methyl silicone; carrier gas, helium as 30 p.s.i.g.; temperature programme, −80°C to 150°C at 2°/min; source, 10.2-eV lamp, 1.6 mA, −30 V; attenuation, 100 × 4.

ing of a cell modified by us to reduce the dead volume to about 35 μl is shown in Fig. 12. Essentially the dead volume has been reduced by inserting an electrically insulated stainless steel cylinder with an annular gap of 0.3 mm to leave a small volume cell at the top. The chromatogram of a gasoline obtained with this modified cell is shown in Fig. 13. Further modifications to reduce contamination problems and photoelectric emission are under consideration but the ultimate limitations of this design lie in the limitations of the available UV lamps. We have for example, shown that the use of the 8.3-eV lamp gives a high selectivity for naphthalene but since the intensity of this lamp is relatively low the signal obtained is small and there is little practical advantage.

CONCLUSIONS

Photoionization holds great promise as a detection mechanism in gas chromatography since it offers high sensitivity and novel selectivity. The concentration dependence of the photoionization process and the possibility of a small detection cell allow the use of this type of detector with high resolution fused-silica capillary columns, and it will unquestionably find application in the identification of unsaturated and aromatic compounds in complex mixtures. While the HNu detector suffers from some design weaknesses it is not difficult to overcome most of these and obtain satisfactory performance.

REFERENCES

1 R. R. Freeman and W. E. Wentworth, *Anal. Chem.*, 43 (1971) 1987.
2 J. Sevcik and S. Krysl, *Chromatographia*, 6 (1973) 375.
3 N. Ostojic and V. Z. Sternberg, *Chromatographia*, 7 (1974) 3.
4 T. B. Aliev, *Protsessy Khromatogr. Kolonkakh*, 17 (1972) 64.
5 J. N. Driscoll and F. F. Spaziani, *Res. Develop. Ind.*, 27 (1976) 50, 54.
6 J. N. Driscoll, *Amer. Lab.*, 8 (1976) 1071.
7 J. N. Driscoll, *J. Chromatogr.*, 134 (1977) 49.
8 J. N. Driscoll and J. B. Clarici, *GIT Fachz. Lab.*, 21 (1977) 199.
9 J. N. Driscoll and J. B. Clarici, *Chromatographia*, 9 (1976) 567.
10 J. N. Driscoll, *Nat. Bur. Stand. (U.S.) Spec. Publ.*, 464 (1977) 415.
11 J. N. Driscoll, J. Ford, L. Jaramillo, J. H. Becker, G. Hewitt, J. K. Marshall and F. Onishuk, *Amer. Lab.*, 10 (1978) 137, 143.
12 L. F. Jaramillo and J. N. Driscoll, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 536.
13 J. N. Driscoll, J. K. Marshall, L. F. Jaramillo, G. Hewitt and V. Alongi, *Amer. Lab.*, 12 (1980) 84, 86, 89, 92.
14 L. F. Jaramillo and J. N. Driscoll, *J. Chromatogr.*, 186 (1979) 637.
15 R. Zepeck, *Chem. Tech. (Heidelberg)*, 9 (1980) 177.
16 R. C. Leveson and N. J. Baker, *Anal. Instr.*, 19 (1981) 7.
17 W. G. Jennings, S. G. Wyllie and S. Alves, *Chromatographia*, 10 (1977) 426.
18 F. Matthys, A. Christophe, R. Geers and G. Verdonk, in A. Frigerio and L. Renoz (Editors), *Recent Developments in Chromatography and Electrophoresis, Chromatography Symposium Series, Vol. 1*, Elsevier, Amsterdam, Oxford, New York, 1979, p. 135.
19 M. L. Langhorst and T. J. Nestrick, *Anal. Chem.*, 51 (1979) 201.
20 J. Meili, P. Broennimann, B. Brechbeuhler and H. J. Heiz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 475.
21 W. G. Jennings and S. Alves, *Chem. Mikrobiol. Technol. Lebensm.*, 6 (1980) 124.
22 A. N. Freedman, *J. Chromatogr.*, 190 (1980) 263.
23 M. E. Casida and K. C. Casida, *J. Chromatogr.*, 200 (1980) 35.

24 G. I. Senum, *J. Chromatogr.*, 205 (1981) 413.
25 C. H. Hsueh and P. H. Cho, *Fen Hsi Hua Hsueh*, 8 (1980) 288.
26 M. L. Langhorst, *J. Chromatogr. Sci.*, 19 (1981) 98.
27 S. Kapila and .C. R. Vogt, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 233.
28 A. N. Freedman, *J. Chromatogr.*, 236 (1982) 11.
29 A. R. Oyler, D. L. Bodenner, K. J. Welch, R. J. Liukkonen, R. M. Carlson, H. L. Kopperman and R. Caple, *Anal. Chem.*, 50 (1978) 837.
30 J. N. Driscoll, J. Ford, L. F. Jaramillo and E. T. Grubber, *J. Chromatogr.*, 158 (1978) 171.
31 N. H. Hester and R. A. Meyer, *Environ. Sci. Technol.*, 13 (1979) 107.
32 S. Kapila, D. J. Bornhop, S. E. Manahan and G. L. Nickell, *J. Chromatogr.*, 259 (1983) 205.
33 I. S. Krull, M. Swartz, R. Hilliard, K-H. Xie and J. N. Driscoll, *J. Chromatogr.*, 260 (1983) 347.
34 J. A. R. Samson, *J. Opt. Soc. Amer.*, 54 (1964) 420.
35 W. P. Jesse and R. L. Platzmann, *Nature (London)*, 195 (1962) 790.
36 J. C. Person and P. P. Nicole, *J. Chem. Phys.*, 55 (1971) 3390.
37 J. C. Person, *J. Chem. Phys.*, 43 (1965) 2553.
38 E. R. Cole, Shell Research Ltd., Sittingbourne Research Centre, personal communication.
39 R. I. Schoen, *J. Chem. Phys.*, 37 (1962) 2032.
40 Rosenstock *et al.*, *J. Chem. Ref. Data*, 6 Supplement 1 (1977).
41 J. L. Holmes, M. Fingas and F. P. Lossing, *Can. J. Chem.*, 59 (1981) 80.