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By J.N. Driscoll and M. Duffy
Reprinted from Chromatography
Volume 2, Number 4
May 1987

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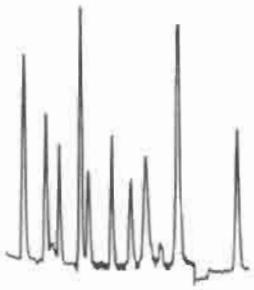

Photoionization Detector: A Versatile Tool for Environmental Analysis

by J.N. Driscoll* and M. Duffy

ABSTRACT

The principles behind photoionization detection are explored and the various types of PIDs described. Comparison is made to the FID, outlining the reasons why the PID is often the better choice for certain applications. Routine EPA methods calling for the use of the PID, especially in series with other detectors, are discussed and projected into the future. Combinations with universal and other selective detectors to provide structural identification and differentiation also are summarized.

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BY THE LATE 1950s, the detection principles for nearly all the modern detectors for gas chromatography, including the photoionization detector (PID), were established (1). Lovelock published a review of ionization techniques in 1961 (2) which described the flame ionization detector (FID), the argon ionization detector, the photoionization detector, the cross-section ionization detector, and electron capture detector (ECD).

In a very short period of time, the FID had become the most popular of the group as a result of its wide dynamic range, its universal response to organics, and its simplicity of construction.

It is interesting to note that the FID and ECD, mentioned above, have been available commercially for more than 30 years, with a significant improvement in performance for the ECD over this period (1). The PID, on the other hand, has only been commercially available as a GC detector for slightly more than a decade (3). Some review articles on the history of the detector and applications have been published recently (4-6).

During the 1960s, developmental work on the photoionization detector continued (3), but by the early 1970s, most researchers believed that photoionization was not a viable analytical technique for GC. In the 1973-74 period, however, a major advance in photoionization technology occurred: separation of the lamp from the ion chamber (7-9). Thus, after a period of obscurity, photoionization detection was once again under consideration.

The new GC detector (11) was utilized first because of its dramatic improvement in sensitivity (approximately 50 times) over the FID for the detection of aromatic hydrocarbons such as benzene (12). This led to the development of many methods for the analysis of environmental contaminants where measurements of trace quantities were essential.

In fact, the detector was used along with the mass spectrometer for the analysis of many samples from one of the most publicized hazardous waste sites in the world, Love Canal in upper New York state.

A PID system for HPLC initially was reported in 1975 by Schermund and Locke (13), followed by Driscoll *et al* several years later (14). Although this approach showed considerable promise, no commercial instrument is yet available.

GC detectors are selected for a particular application depending on whether the response needed is universal, specific, or selective. The PID generally falls into the latter category, with the majority of its applications (except for some high-sensitivity work) focused on this aspect of its capabilities.

One of the more-important environmental applications for the PID has been the analysis of organics in industrial discharge water using EPA method 602, or in drinking water using EPA method 503.1 (15). Here, the choice of the PID over the FID was the better selectivity.

It is interesting to note that in contrast to the selectivity feature of the PID for GC, the PID in HPLC is most often chosen for its nearly universal response, as the UV detector only responds to the narrow range of compounds that possess suitable spectral properties.

Another application for the PID is the use of the differential response between two detectors as a means of identifying the structure of various compounds (16). Here, the important feature of the PID is its nondestructive character which allows a second detector to be run in series.

In the following sections, we will discuss briefly the principles of detector operation, detector design, optimization of sensitivity, GC applications of response selectivity and structural sensitivity of the PID, and some brief information on the HPLC PID.

Principles of detector operation/design. Photoionization is initiated by the absorption of a photon ($h\nu$) by a molecule (R). If the energy of the photon is greater than the ionization potential (IP) of species R, then some portion of the energy is utilized in ionization as follows:

$$\begin{aligned} R + h\nu &\rightarrow R^+ + e^- \quad (k_1) \\ &\rightarrow R^* \quad (k_2) \\ C + h\nu &\rightarrow C^* \quad (k_3) \\ C^* + R^+ &\rightarrow R^+ + C \quad (k_4) \end{aligned}$$

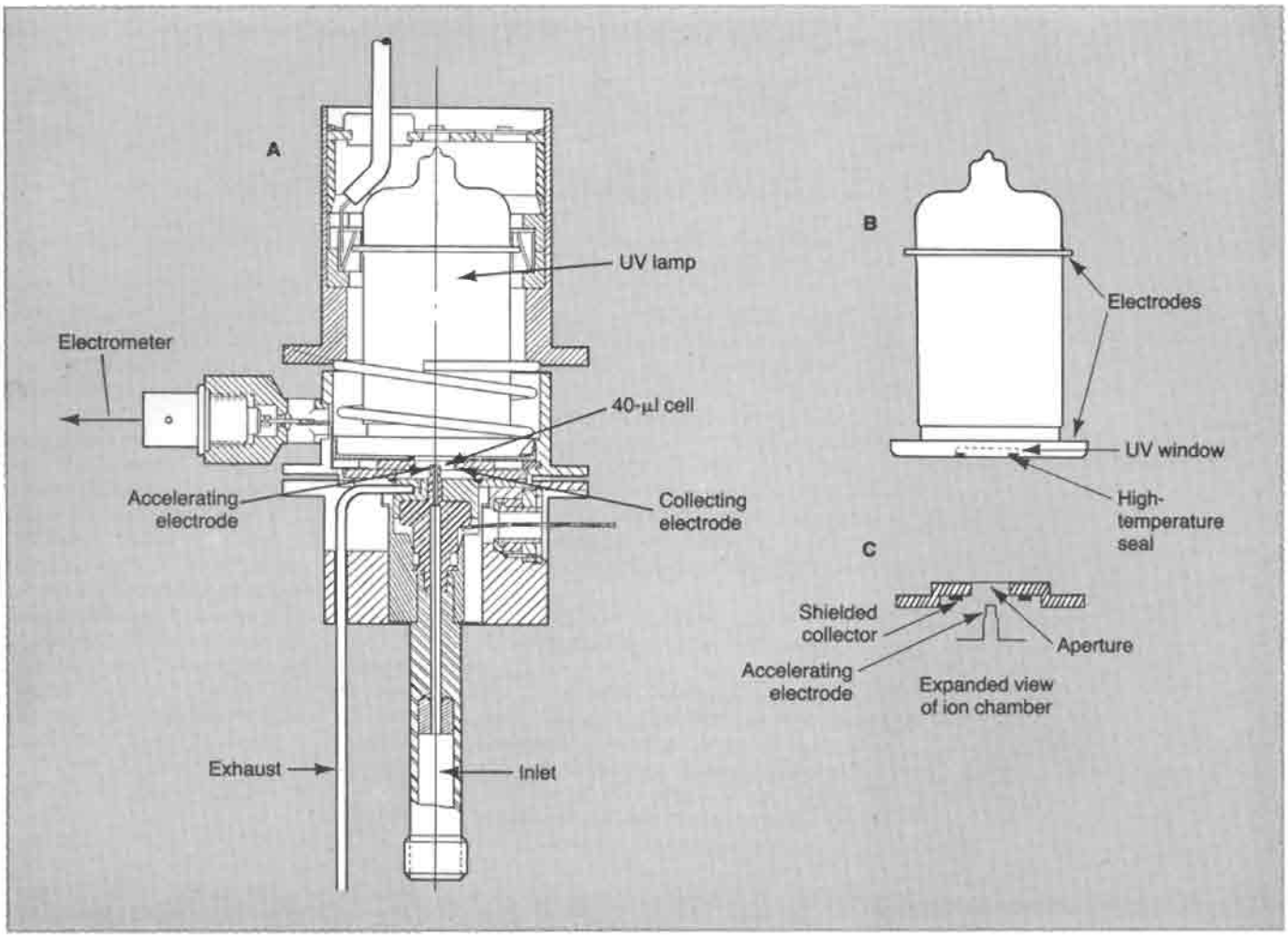


Figure 1. Typical photoionization detector. **A:** Schematic. **B:** Detail of the UV source. **C:** Expanded view of ionization chamber.

where C represents the carrier gas.

Since typical ionization efficiencies for photoionization are on the order of 0.001% (3), other processes such as neutralization or relaxation predominate, resulting in a reduction of the ion concentration as follows:

$$R^+ + e^- \rightarrow R \quad (k_5)$$
$$e^- + C \rightarrow C^- \quad (k_6)$$
$$R^+ + C^- \rightarrow R + C \quad (k_7)$$
$$R^* \rightarrow R + h\nu \quad (k_8)$$
$$R^+(\text{sum}) = (k_1 + k_4) - (k_5 + k_7)/(k_2 + k_3) - k_8$$

The photoionization yield is then given by (R^+(sum)/number of photons absorbed) × 100. From this equation, it is clear that the number of ions produced (R^+) is proportional to the absorption coefficient and the intensity of the lamp.

A typical PID (Figure 1A) has two functional parts. The first is the lamp (Figure 1B) which is filled with a gas at low pressure. The lamp produces an emission line or lines in the far or vacuum UV when excited by an electrical or RF discharge. Gases used could be argon, hydrogen, krypton, or others, depending on the emission lines required (8 to 11.7 eV) for a particular application.

The lamps can utilize a variety of different metal fluoride windows since few other materials transmit in this region. The short wavelength cutoff for these windows are as follows: lithium fluoride, 105 nm; magnesium fluoride, 112 nm; calcium fluoride, 122 nm; strontium fluoride, 128 nm; etc.

Lithium fluoride, used for the 11.7-eV lamp, has a serious problem with solarization (color center formation) which limits its lifetime to about 500 hours.

Another problem is the shift in short wavelength cutoff (to longer wavelengths) as the window becomes heated. Since the argon emission lines for the 11.7-eV lamp already are close to the cutoff at ambient temperatures, heating reduces the photon flux and increases the solarization at the same time.

What does this mean for use as a GC detector? For reasonable lifetimes, the upper temperature limit should be about 100°C. Is this useful for chromatography?

As indicated in previous publications (17,18), the 11.7-eV lamp is useful for low-molecular-weight (<150 AMU) compounds such as CCl_4, $CHCl_3$, C_2H_6, C_2H_2, etc., which have more-tightly bound electrons and, hence, higher ionization potentials.

Note the difference in response for the 10.2- and 11.7-eV lamps for some typical environmental samples such as hazardous waste samples (Figure 2). The 10.2-eV PID does not detect the chloroalkanes which are present in most samples of this type.

Another useful application is the detection of formaldehyde at low-nanogram levels (19). These levels generally are not feasible with any other GC detector.

The most popular detector lamp is the 10.2-eV source which has the highest photon flux and, therefore, the greatest sensitivity. This lamp uses a magnesium fluoride window.

Figure 3 compares the relative sensitivity of different UV lamps used for the PID to the FID. For an aromatic hydrocarbon, such as benzene, the 11.7-eV and 9.5-eV lamps have equivalent sensitivities, while the 10.2-eV lamp is 40 times more sensitive, and the 8.3-eV

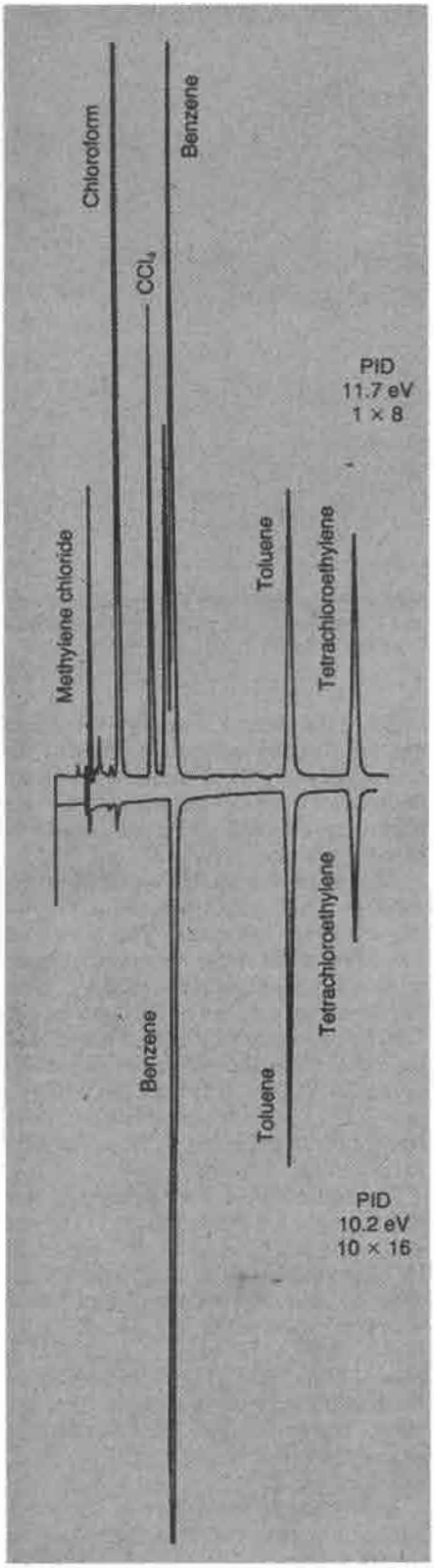


Figure 2. Chromatogram of a typical hazardous waste sample by capillary GC with in-series PIDs (10.2 and 11.7 eV). Column: Quadrex "Halomatics" bonded fused-silica capillary column, 25 m × 0.32 mm ID, 0.5-μm film thickness. Sample: 300 μl, gas-sampling valve, 10-ppm gas mixture. Temperature: oven 60°C; det/inj, 100°C. GC: HNU Model 321. Carrier: helium, 2 ml/min.; 15 ml/min. makeup flow. Analysis time: 7.5 min.

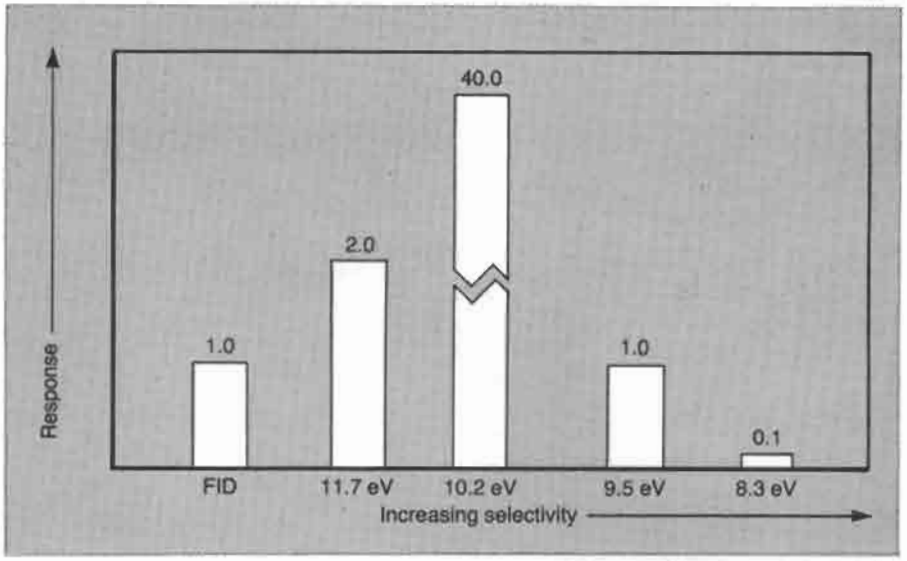


Figure 3. Comparison of the response and selectivity of the FID and various lamps in the PID for benzene or biphenyl detection.

lamp has a tenth the sensitivity.

The 11.7-eV lamp has similar response factors to the FID's for many hydrocarbons, but it lacks the methane response. Here, the PID also responds to a number of inorganic compounds, such as chlorine, phosphine, etc., whereas the FID detects only carbon-containing species.

As noted above, when the lamp energy is lowered from 11.7 to 8.3 eV, the selectivity is increased dramatically. The 11.7-eV lamp makes an excellent alternative to the FID, especially where a nondestructive detection is required.

Another important feature is that no detector support gases (hydrogen or air) are required for the PID. The latter lamp also will respond well to polyaromatic hydrocarbons, amines, and sulfur compounds such as mercaptans and disulfides.

The second integral part of the PID is the ion chamber (Figure 1C), where the ions (formed through absorption of the UV radiation) are collected. There are two functional parts of the ion chamber: the accelerating electrode and the collection electrode. A potential of 100 to 200 V is applied to the accelerating electrode to push the ions to the collection electrode where the current (proportional to concentration) is measured.

The most effective design of an ion chamber is a coaxial configuration, with the electric field given by:

$$E = V/2.3\ r \log(a/b)$$

where V is the applied voltage between the collector of radius a and the accelerating electrode of radius b, while E is the electric field at any point in distance r from the center of the accelerating electrode. Thus, the field increases rapidly as $r \rightarrow b$.

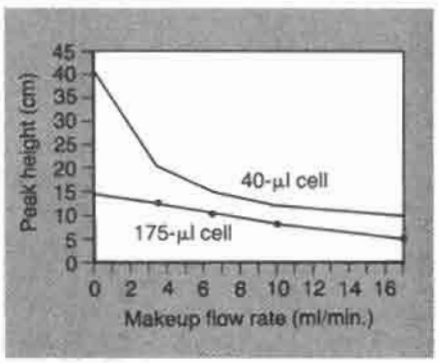


Figure 4. Comparison of the peak height *vs* makeup flow rate for the 40- and 175-μl cells.

If the collection electrode is placed in the UV beam, the background current will be increased by one to two orders of magnitude. On the other hand, placing the accelerating electrode in the UV beam has little effect on the background current.

The HNU ion chamber (10) was novel due to shielding the collection electrode, resulting in the lowest background possible. This design allowed high field strength and shielding of the collector. For the first time there was a detector with a low background current, high sensitivity, and an overall improvement of two to three orders of magnitude in linear range (3).

Optimization of sensitivity. The PID is a concentration-sensitive detector with response that is inversely proportional to the carrier gas flow rate:

$$C \approx 1/F$$

where C is the solute concentration and F is the carrier gas flow rate.

A third-generation PID was intro-

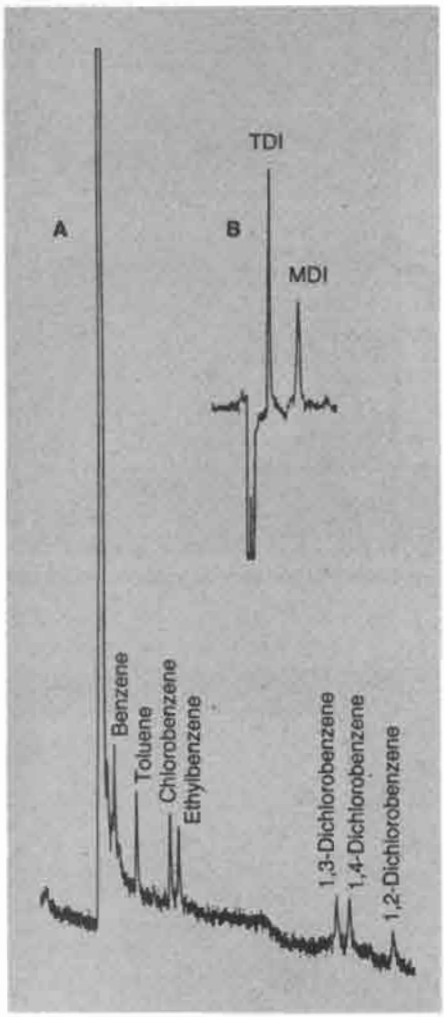


Figure 5A. Detection of aromatic hydrocarbons at 0.5-pg level with the 40-µl cell in the PID. Column: Nordion, fused silica, 25 m × 0.32 mm ID, 0.25-µm film, SE-54. Sample: EPA method 602 standard, 0.1 µl of a 1-ppm mixture, split ratio, 100:1. Temperature: 70°C. GC: HNU Model 331, equipped with low-volume (40 µl) PID. Carrier: 3 ml/min. helium, no makeup gas. Attenuation: 1 × 1, 5-pA FSD. **5B.** Detection of ppb levels of TDI and MDI with the 175-µl cell in PID. Column: Quadrex, bonded fused silica, 10 m × 0.53 mm ID, 1.0-µm film, methyl silicone. Sample: 1-ml gas sampling valve. Temperature: 125°C. GC: HNU Model 301 (PID). Carrier: 15 ml/min. N_2.

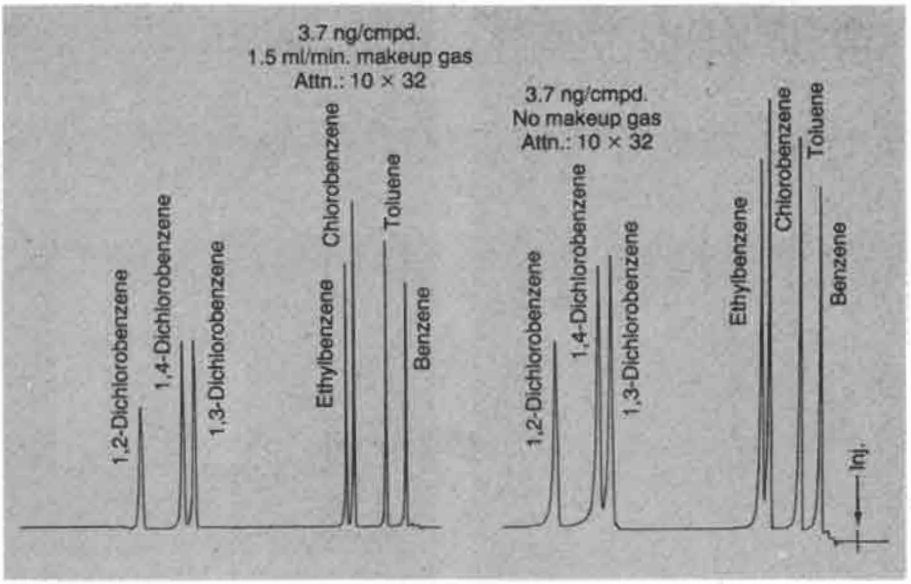


Figure 6. Detection of low-nanogram levels of EPA 602 compounds with the low-volume PID. Column: as in Figure 5A. Sample: 0.5 µl injection of a 100-ppm EPA standard mixture, split ratio 13.5:1. Temperature: oven 70°C, inj/det 175°C. GC: as in Figure 5A.

duced recently (5,6). Some preliminary work has been done on a low-dead-volume design where volume of the original cell (225 µl) was reduced to 175 µl. In this section, we will describe a comparison of the two ionization cells for packed and capillary columns.

We investigated two different cells (40- and 175-µl volumes) for the PID with both packed and capillary columns and found that the former cell performs best only with capillary columns, while the latter can be used with both packed and capillary. For the purpose of this study, we will direct ourselves to capillary columns of 320 µm ID or smaller.

The low-dead-volume cell exhibits a threefold reduction in sensitivity for a packed column at 30 ml/min. when compared to the 175-µl PID cell. How can this be explained?

The sensitivity (S) of a concentration sensitive detector is given as:

$$S = \text{peak area} \times \text{flow rate} / \text{sample weight}$$

with the peak area expressed in mV • sec and the flow rate in ml/min.

With the low-dead-volume cell, the residence time is shorter, and the subsequent peak area is proportionately lower, even at the same flow rate and sample size. Another difference is that the 40-µl cell has a lower photon flux due to a smaller aperture.

In terms of sensitivity, the 175-µl cell is considerably better for packed-column work. However, if 15 ml/min. of a makeup gas is used, the 175-µl cell will perform satisfactorily with the capillary column; this can be important because a 175-µl cell would be the preferred choice for analytical tasks favoring a combination of paired and capillary columns.

If a total flow rate of 2 to 3 ml/min. is used for the carrier gas on a capillary column (no makeup gas), the low-volume detector (40 µl) will be about three to five times more sensitive than the larger (175 µl) cell due the lower cell volume, resulting in sharper peaks.

Peak height *vs* makeup flow rate for the two cells (40 and 175 µl, respectively), is plotted in Figure 4. In terms of sensitivity, the 40-µl cell is shown to be better by a factor of three to five, due to the lower flow rates. Hence, if applications predominantly require the use of capillary columns of <320 µm ID, the low-volume PID will provide optimum results.

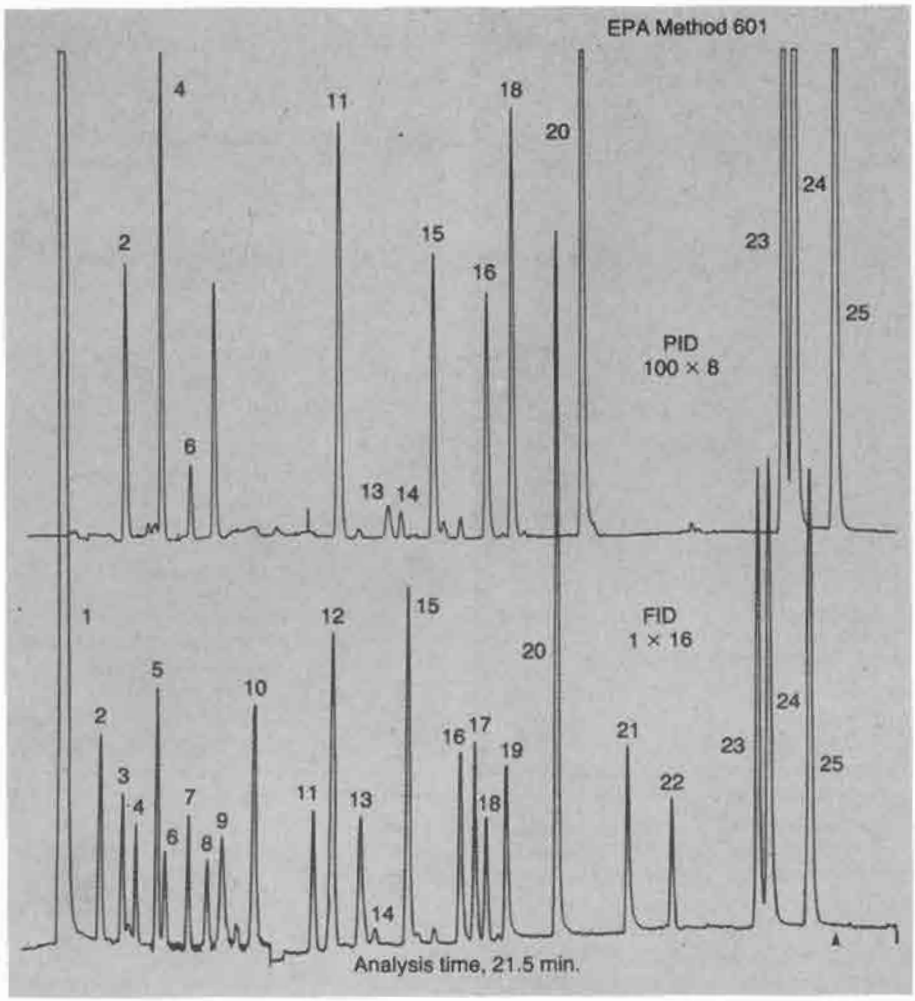
Since the nature of analysis is different for the two column types and the complexity involved makes it difficult to change between the two cells, the analyst must decide which cell would be best for his use.

Figure 5A demonstrates an improvement in sensitivity for the 40-µl cell using capillary columns. The detection limit for benzene on a packed column with a 1-pA amplifier was 2 pg. With the capillary column and a 5-pA amplifier, the detection limit was about 0.25 pg. Since the cell used for the chromatogram in Figure 5A was particularly noisy, the noise level and the detection limit can be expected to improve with an improved version.

In Figure 5B, a chromatogram containing toluene diisocyanate (TDI) and 4,4′-diphenylmethane diisocyanate (MDI) at the levels of 2 ppb and 0.6 ppb demonstrates the sensitivity and peak characteristics of the 175-µl cell, utilizing a 530-µm-ID column and a flow rate of 15 ml/min. The detection limits for these compounds with such a column, under the specified conditions, are on the order of 1 to 2 pg (1 pA FSD), as expected.

In Figure 6, the value of the 40-µl PID cell is demonstrated for the detection of nanogram quantities of EPA 602 compounds. Some tailing is observed with no makeup gas, resulting in an incomplete resolution between chlorobenzene and ethylbenzene.

Note that the total flow through this detector was a mere 1.5 ml/min. When 1.5 ml/min. of makeup gas was added to compensate, virtually all tailing was eliminated and a baseline resolution attained between the chlorobenzene and ethylbenzene peaks.



Peak No.	Compound
1.	Methanol (solvent)
2.	1,1-Dichloroethene
3.	Methylene chloride
4.	*trans* 1,2-Dichloroethene
5.	1,1-Dichloroethane
6.	*cis* 1,2-Dichloroethene
7.	Chloroform
8.	1,1,1-Trichloroethane
9.	Carbon tetrachloride
10.	1,2-Dichloroethane
11.	Trichloroethene
12.	1,2-Dichloropropane
13.	Bromodichloromethane
14.	2-Chloroethylvinylether
15.	*trans* 1,3-Dichloropropene
16.	*cis* 1,3-Dichloropropene
17.	1,1,2-Trichloroethane
18.	Tetrachloroethene
19.	Dibromochloromethane
20.	Chlorobenzene
21.	Bromoform
22.	1,1,2,2-Tetrachloroethane
23.	1,3-Dichlorobenzene
24.	1,4-Dichlorobenzene
25.	1,2-Dichlorobenzene

Figure 7. Comparison of selectivity of the PID *vs* FID for EPA method 601. Column: Quadrex "Halomatics (624)" bonded fused-silica capillary column, 30 m × 0.53 mm ID, 3.0-μm film. Sample: 10-ppb EPA 601 compounds, 5-ml sample sparger. Carrier: 15 ml/min. desorb and carrier gas flow rate, N_2. Temperature: 35°C, hold for 7 min., 35°C to 120°C at 8°C/min., hold at 120°C for 15 min. GC: HNU Model 421, with column attached directly to the heated transfer line. P and T conditions: as specified in EPA method 601.

However, this slightly higher flow rate through the detector somewhat decreased the sensitivity. Hence, one can optimize either sensitivity or resolution when utilizing capillary columns with this low-volume detector.

GC applications. Development of methodology for the analysis of 111 priority pollutants in water was mandated by the Clean Water Act. These methods are designated by the U.S. government as 601-613 (and the corresponding 500 series methods for drinking water), 624, 625, 1624, and 1625. A full description is available in the Federal Register (20).

Twelve of the proposed analytical methods involve GC or HPLC, while three proposed alternative methods involve GC-MS. In the present paper, we will be concerned with EPA methods 601 (29 compounds; purgeable halocarbons) and 602 (7 compounds; purgeable aromatics).

The Federal Register (15) specified the HNU PID for EPA method 602 as well as for the drinking water method EPA 503.1. The methodology in the 600 series is based on packed columns; however, with the recent significant advantages of capillary column technology, a considerable effort is under way to convert the methods to capillary techniques (21).

As noted earlier, the combination of a selective and a universal detector, or even two selective detectors, can yield considerable structural information (16,17). It is even possible to convert a selective detector, such as the PID, to an element-specific detector for P, S, or N, using a combustion furnace at high temperatures in a hydrogen stream (22).

⇒ RESPONSE SELECTIVITY. The EPA 601 and 602 procedures involve concentrating the water sample via the purge-and-trap technique, where the volatile organics are sparged from water and collected on a Tenax GC or other solid sorbent trapping material, which subsequently is heated to release the concentrated sample. The sample then is transferred to a gas chromatograph where it becomes separated on a packed column (15) and is detected by an electrolytic conductivity (601) or PID (10.2) detector (602).

As noted earlier, the PID was chosen for the 602 application because of its increased selectivity compared to the FID. An example of this is shown in Figure 7 where method 601 was employed with a PID and FID in series.

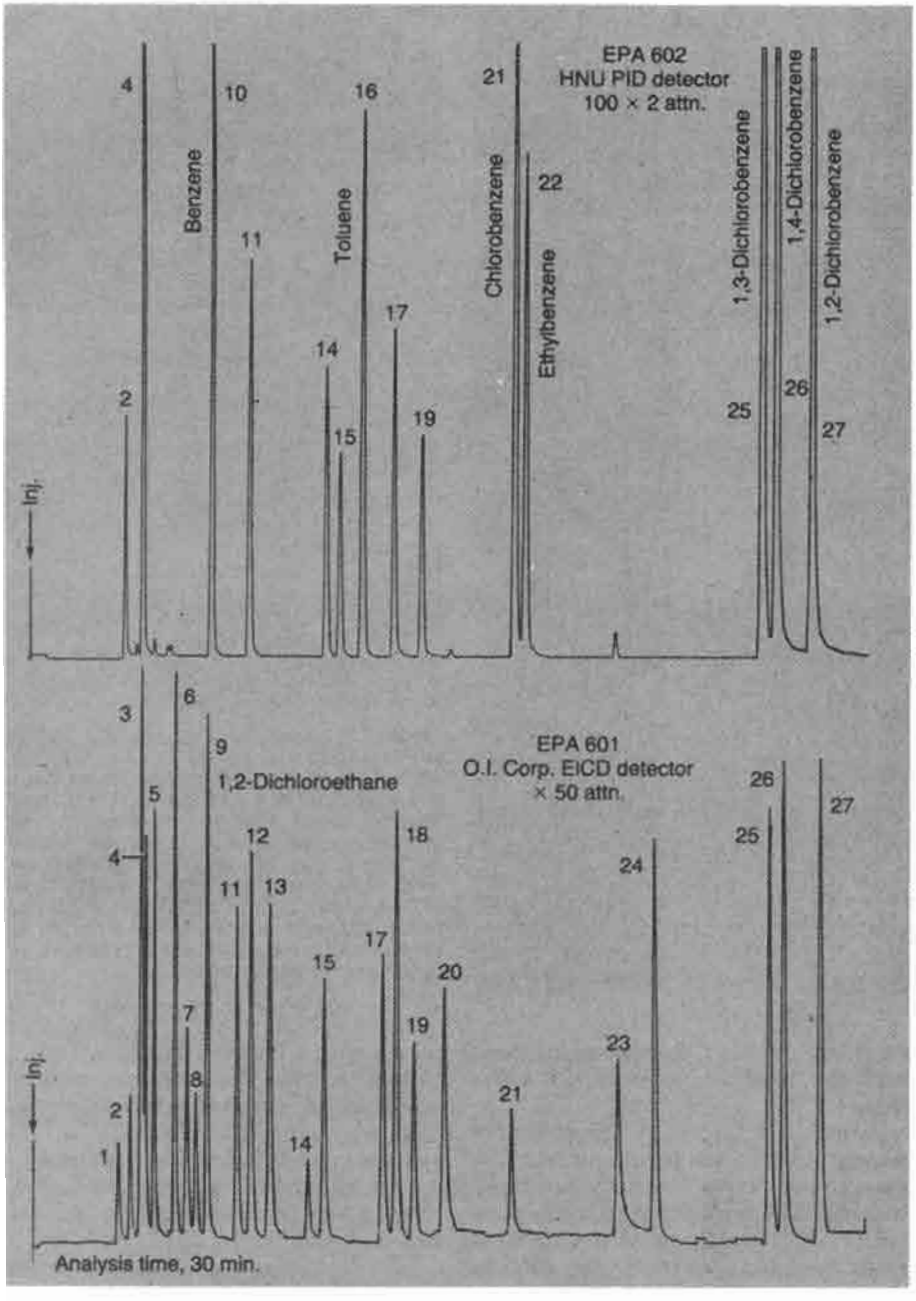
Note that the FID responds to every solute in the mixture (chloroalkanes, chloroalkenes, and aromatics). The PID responds only to chloroalkenes and aromatics. Chloroalkanes have IPs higher than 10.5 eV and, consequently, are not detected.

With capillary columns, analysis time is reduced to less than 22 min. from the approximate 45 min. on packed columns, and component resolution is improved dramatically. Thus, the selective nature of the PID yields a more simplified chromatogram, which is easier to visualize.

Due to the nondestructive nature of the PID, the use of a second detector such as the electrolytic conductivity detector (ElCD), run in series with the PID, is possible.

With the superior resolution of capillary columns and the selectivity of the PID, both methods (601 and 602) can be extracted from a single chromatographic run, as shown in Figure 8. This type of system is described in the proposed EPA method 502.2 for the analysis of drinking water and can lead to a considerable reduction in analysis and QC time for these methods.

⇒ STRUCTURAL SELECTIVITY. A tech-



Peak No.	Compound
1.	Bromomethane
2.	1,1-Dichloroethene
3.	Methylene chloride
4.	*trans* 1,2-Dichloroethene
5.	1,1-Dichloroethane
6.	Chloroform
7.	1,1,1-Trichloroethane
8.	Carbon tetrachloride
9.	1,2-Dichloroethane
10.	Benzene
11.	Trichloroethene
12.	1,2-Dichloropropane
13.	Bromodichloromethane
14.	2-Chloroethylvinylether
15.	*trans* 1,3-Dichloropropane
16.	Toluene
17.	*cis* 1,3-Dichloropropene
18.	1,1,2-Trichloroethane
19.	Tetrachloroethene
20.	Dibromochloromethane
21.	Chlorobenzene
22.	Ethylbenzene
23.	Bromoform
24.	1,1,2,2-Tetrachloroethane
25.	1,3-Dichlorobenzene
26.	1,4-Dichlorobenzene
27.	1,2-Dichlorobenzene

Figure 8. Capillary chromatogram of EPA methods 601 and 602 run in series and simultaneously in 30 min. Column: 60-m Supelco "Vocol" column. Sample: 10 ppb of a mixture of 601 and 602 standard test mixes, 5-ml sample sparger. Carrier: as in Figure 7. Temperature: 35°C, hold for 8 min., 35°C to 165°C at 8°C/min., hold at 165°C for 15 min. Equipment: HNU Model 331 GC, PID; O.I. Corp. ElCD (Model 4420) and purge and trap system (Model 4460). Utilized O.I. Corp. low-dead-volume interface. P and T conditions: as specified in EPA method 602.

nique was reported nine years ago (16) which utilized the unique response ratio of two detectors to identify hydrocarbon structures. The selective response of PID (10.2) was found to be a function of a compound's electronic structure, since pi electrons were ionized by UV more efficiently than were sigma electrons.

In comparison, the FID responds mainly to the number of carbon atoms, and less to their environment, such as the sigma or pi electrons present, giving a more universal response.

The PID is also a "carbon counter" for a homologous series, as demonstrated by Langhorst (23). This technique was used first by Driscoll *et al* (16) to identify aromatic, olefinic, and aliphatic hydrocarbons in a synthetic natural gas feedstock.

Driscoll (17) developed a method for identification of hydrocarbons using three lamps (9.5, 10.2, and 11.7 eV) for the PID. Alkanes, olefins, aromatics, and polyaromatics could be characterized at the nanogram level by determining the response ratios with the various lamps. Hence, the PID was found to be capable of determining aromatic hydrocarbons in complex aliphatic species.

Cox *et al* (24) evaluated capillary GC/PID-FID for the detection and identification of volatile organic hydrocarbons (VOC) in wastewater treatment facilities. Using the PID-FID technique, they were able to classify all sample components into compound groups with some degree of confidence. They could obtain greater than 80% species-identification on 76% of the air samples and 29% of the water samples.

Data by Cox *et al* clearly indicated the tremendous potential of this technique since it was easier to use as well as less expensive than GC-MS. Of course, a PID-ECD may have been a better choice for the water samples because of the preponderance of chlorinated hydrocarbons.

Towns and Driscoll (25) detected and identified amines using a combination of a PID with the nitrogen-phosphorus detector (NPD). The use of the NPD would provide qualitatively all peaks containing nitrogen.

Structural differences between di- or triamines and aliphatic or aromatic amines can be distinguished by their PID-NPD detector response ratios. The PID (8.3)- or PID (10.2)-NPD response ratios have been utilized to differenti-

ate between these primary, secondary, and tertiary amines.

Krull *et al* (26) combined PID and ECD detectors as a means for differentiating between polycyclic aromatic hydrocarbons and their analogs containing nitro groups. A similar technique also was used by Krull *et al* (27) for the identification of organic nitro compounds and explosives.

HPLC applications. One of the more interesting detectors for HPLC still awaits commercial development. Driscoll *et al* (28) described an HPLC PID which had detection limits in the low nanogram range. Here, the sample is thermally vaporized after separation by the column.

Aromatic hydrocarbons substituted with electronegative groups had detection limits which were two orders of magnitude lower than benzene. Although the actual mechanism remains obscure, it appears that the dipole induced by the electronegative group prevents quenching of the ionized species prior to collection. This would result in increased sensitivity.

Classes of compounds most suitable for HPLC PID appear to be those with electron-absorbing groups such as –OH, –Cl, –Br, $–NR_2$, etc. The PID (10.2) appears to be useful for reversed-phase HPLC since all of the solvents used have IPs >10.5 eV and would not be ionized. There should be no major problem with peak broadening, and detection limits in the low nanogram levels can be attained.

The problem of solvent vaporization reducing the sensitivity (quenching effect) still remains to be solved.

Conclusions. The photoionization detector, although a useful, selective, and sensitive detector for GC, still is in its infancy compared to other GC detectors such as the FID and ECD. Nevertheless, recent developments have led to an improved and optimized detector for use with capillary columns.

Many of the applications for the PID have been in the environmental area as a result of the PID selectivity. Some notable methods include EPA 602, 502, and 503.1 for the analysis of industrial effluents and drinking water.

The use of the PID for structural selectivity data has grown dramatically over the past eight to nine years. The PID has also some applications to the analysis of HPLC effluents, but a commercial detector is not available at this time. Further developments may change this situation in the near future.

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