Translated from *Uspekhi Khimii* **58** 1354–1383 (1989) U.D.C. 543.544.25

Photoionisation detection in gas chromatography

V L Budovich, A F Shlyakhov
All-Union Research and Design Institute of Chromatography, Moscow

ABSTRACT. Problems of the design and application in gas chromatography or photoionisation detectors with separated and non-separated ionisation and detection compartments are examined. The characteristics of the detectors of both types are described and specific problems of their construction are discussed. The mechanism of the signal generation and the factors determining the magnitude of the response are examined.

Extensive experimental data concerning the use of photoionisation detectors with separated detection and ionisation compartments in gas-chromatographic analysis are presented. The application of such detectors in multi-detector schemes in combination with flame-ionisation, electron-capture, and other detectors is discussed. The employment of such combinations of detectors for the purposes of identification is analysed.

The bibliography includes 151 references.

Contents

I. Introduction 778
II. Signal generation in the photoionisation detector 778
III. Detectors with non-separated emission and detection compartments 779
IV. Detectors with separated emission and detection compartments 782
V. The response of the photoionisation detector 783
VI. The application of the photoionisation detector in the gas-chromatographic analysis of mixtures of organic and inorganic compounds 787
VII. Multidetector systems 789

I. Introduction

Among the numerous detection methods used in gas chromatography, ionisation methods based on the use of a non-independent discharge have come to be widely used. Depending on the type of the external source of ionisation in the measuring compartment, it is possible to distinguish radioionisation and photoionisation detection. Both methods have been used successfully for the solution of various analytical problems. They possess advantages such as high sensitivity and a virtually non-disruptive character of their effect on the compounds analysed.

Photoionisation detection is technically more complex than radioionisation detection because it requires the use of a stable source of emission of vacuum UV radiation. The development of the technique of photoionisation detection is determined to a large extent by the improvement of the emission sources. Therefore, despite the fact that the first photoionisation detector (PID) was described as early as 1960,[1] the industrial production of chromatographs with PID did not begin until the end of the 1970s when it became possible to incorporate adequate sources of UV radiation.

The use as ionisation sources of resonance UV lamps working stably over long periods of time made it possible to simplify significantly the design of the apparatus. In particular, there is no need for an auxiliary gas, the open flame is eliminated, and there is no need for the use of radioisotopes. It becomes possible to employ air as the carrier gas. These properties combined with high sensitivity, selectivity, and the large linear range promoted the use of PID in laboratory and portable chromatographs.[2–5]

The use of PID in the gas-chromatographic analysis has led to the appearance of a whole series of studies devoted to the design, operating conditions, and practical use of this detector (see, for example, Refs. 6–8). The available literature data (for the last 15 years) concerning the design, characteristics, and analytical applications of the photoionisation detector are analysed in the present review.

II. Signal generation in the photoionisation detector

The essential feature of the operation of the PID is that a flux of photons emitted by the source in the far ultraviolet ionises the substance to be analysed. The motion of the charges produced in the ionisation chamber generates a current signal characterising the concentration of the substance analysed.

The ionisation of the molecules AB can occur as a result of direct ionisation with formation of an ion and an electron:

$$AB + h\nu \rightarrow AB^+ + e + \text{energy},$$

direct ionisation with formation of an ion pair:

$$AB + h\nu \rightarrow A^+ + B^- ,$$

or with preionisation:

$$AB + h\nu \rightarrow AB^* \rightarrow AB^+ + e .$$

The contribution of each of these processes to the formation of charged species is determined both by the characteristics of the radiation (its spectrum and its monochromatic nature) and by the characteristics of the substance irradiated (the distribution of molecules with respect to energies in the ground state, the distribution of the energy level density in the excited state, and the distribution of the probability of ionisation transitions).

In the range of energies close to the ionisation threshold, the direct ionisation processes predominate. With increase in the energy of photons, the contribution of the preionisation processes rises. Preionisation can occur with appearance of fragment ions, formed

from excited molecular ions. The fraction of fragment ions increases for energies exceeding the second ionisation potentials of the molecules.[9]

Apart from the processes mentioned, molecular excitation and dissociation processes are also important when molecular gases are acted upon by UV light.[10]

The overall cross-section of the processes enumerated determines the overall absorption cross-section. The photoionisation cross-section is only a fraction of the absorption cross-section, which depends on the radiation energy.

The absorption of photons in the ionisation chamber of the detector obeys the Beer–Lambert–Bouguer law:

$$I = I_0 \exp\left(-\sigma N_A c l \frac{P}{760}\frac{273}{T}\right), \quad (1)$$

where I_0 and I are the intensities of the entering and emerging light fluxes respectively, σ is the overall absorption cross-section, N_A the Loschmidt number, c the concentration of the test substance, l the length of the absorption path, and P and T are respectively the pressure and temperature in the ionisation chamber.

The absolute photoionisation quantum yield is

$$\eta = i/(I_0 - I), \quad (2)$$

where i is the ion current.

The dependence of the current on the concentration of the ionised component is determined from Eqns. (1) and (2). If the exponent in Eqn. (1) is less than unity, then we have, for P = 760 mmHg and T = 273 °C,

$$\eta = i/(I_0 \sigma N_A c l). \quad (3)$$

Multiplication of the right- and left-hand sides of Eqn. (3) by σ yields the expression

$$i = I_0 N_A c l \sigma_i, \quad (4)$$

where $\sigma_i = \eta\sigma$ is the effective photoionisation cross-section. It has been noted[11] that equations of type (4) are valid for low pressures of the test substance and for a short length of the ionisation chamber. When applied to the PID under gas-chromatographic conditions, this expression holds at normal pressure P owing to the low value of c.

For a cross-sectional area of the ionisation chamber S and a light flux density $j_0 = I_0/S$, the current is given by

$$i = j_0 N_A c V \sigma_i, \quad (5)$$

where V is the volume of the chamber.

Thus the current in the ionisation chamber is proportional to the concentration of the substance analysed and the sensitivity of the PID is proportional to the volume of the ionisation chamber.†

The ion current is also linearly related to σ_i but the latter quantity itself depends as a rule on the wavelength of the radiation in a complex manner. Since mainly non-monochromatic sources are used currently for photoionisation detection several emitted lines of different intensity are involved in signal generation. In many cases fragment ions with different masses are produced in the ionisation chamber together with molecular ions under these conditions. The fraction of particular ions in the overall ion current depends on the characteristics of the source of the UV radiation.

† The mechanisms of the current limitation, inducing deviations from linearity, are not discussed here.

Fig. 1 presents curves for the efficiency of the photoionisation (the ratio of the current of ions with the selected mass to the photon flux) of a methanethiol with formation of the molecular ions CH_3SH^+ and the fragment ions CH_3S^+.[12] The most intense lines in the argon, krypton, and xenon line spectra are also indicated. Fig. 1 shows that, when the argon emission is used for ionisation, the photoionisation efficiency can increase as a result of the appearance of fragments ions, while part of the xenon line spectrum makes no contribution at all to the current flowing in the ionisation chamber.

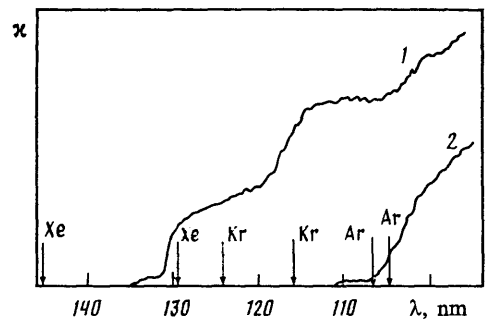


Figure 1. Photoionisation efficiency curves for methanethiol: *1*, the CH_3SH^+ molecules ion; *2*, the CH_3S^+ fragment ion.

III. Detectors with non-separated emission and detection compartments

Vigorous investigations of detectors with non-separated emission and detection compartments began in the middle 1960s. In these detectors, the radiation emitted by the electric discharge in an inert gas or hydrogen is introduced via a light conducting channel into the ionisation chamber. The chamber is not then separated from the emitter by any partition preventing the movement of the gas from one compartment to the other. The gas pressures in the source of radiation and in the ionisation chamber are the same. Eqn. (4) quoted above is not suitable for this detector, because some of the charged and metastable species from the radiation source also enter the ionisation chamber.

Such detectors make it possible to detect both organic and inorganic substances depending on the working medium in the radiation sources—the gas involved in the discharge. The use of helium, for example, makes the detector universal because of the presence in the spectrum of this gas of an intense continuum up to 50 nm (photon energy 24.3 eV). A d.c. discharge[1,13–20] and HF and UHF discharges[21–24] are used to excite the emission. There is a possibility of devices of two types: detectors in which the gas is present at low[1,15–17,21] and high (not more than atmospheric) pressures.[13,14,18–20] Table 1 shows that the characteristics of the different detectors in general agree with one another.

Despite the high sensitivity and universality of detectors of this type, they have not found applications in commercial instruments, since, firstly, detectors operating at reduced pressures require a vacuum system and, secondly, the spectroscopic characteristics of the radiation, influencing the sensitivity, vary as a function of the

Table 1. The working characteristics of PID with non-separated emission and detection compartments.

Carrier gas	Discharge gas	Type of discharge	Pressure, mmHg	Ionisation efficiency	Background current, nA	Detection limit and substance determined	Linear dynamic range	Refs.
Ar	Ar	Glow	<760	10^{-4}	0.1		10^4	[1]
He	He	»	760	—	0.1—1	2.8×10^{-11} g ml^{-1} (O_2)	10^3	[14]
						6.8×10^{-11} g ml^{-1} (C_3H_8)	10^3	[14]
Ar, He, N_2	Ar, He, N_2	»	<120	$6\cdot10^{-5}$	0.5	2×10^{-10} g (C_3H_8)	10^5	[16]
H_2, N_2, Ar	H_2, N_2, Ar	»	<100	10^{-3}	0.2	5×10^{-13} g s^{-1} (C_3H_8)	10^5	[17]
He	He	UHF	<25	$3\cdot10^{-3}$	6	1.3×10^{-11} g ml^{-1} (Ar)		
						4×10^{-10} g ml^{-1} (O_2)	10^4	[21]
He	He	Glow	760	$0.14\cdot10^{-3}$ (O_2)	0.5	4.9×10^{-11} g ml^{-1} (O_2)	10^4	[19]
				$1.1\cdot10^{-3}$ (Ar)		9×10^{-13} g ml^{-1} (Ar)		
Ar	Ar	UHF	760	—	—	7.7×10^{-11} g s^{-1} (C_6H_6)	10^5	[23]

pressure in the detector. Although the detectors operating at atmospheric pressure are in fact incorporated at the outlet from the chromatographic column without auxiliary devices, nevertheless they too suffer currently from a series of disadvantages retarding their application. In the first place one must include among such disadvantages the increased noise level caused by the instability of the discharge and the transfer of charged species from the emitting to the detecting compartment.

In order to ensure the stability of a d.c. discharge with $i < 1$ A, it is desirable to use a gas with a high thermal conductivity—hydrogen or helium.[25] In practice, helium is used, since the short-wavelength part of its spectrum makes it possible to determine inorganic gases. Since the presence of impurities in helium affects the emission spectrum, it is essential to use pure gas and to take special precautions to reduce the erosion of the electrodes and to prevent the diffusion of the substances analysed into the emitting compartment.

In order to increase the stability of the discharge in detectors with a d.c. discharge, measures are taken to optimise the electrode system. As a result, it has been possible to reduce the noise from 10^{-12} A [26] to 10^{-13} A and below.[15] It has been noted[15] that an increase in the discharge current increases the noise and does not always reduce the detection threshold. The detector described by Roesler[15] has been used[27] to analyse organic and inorganic compounds.

The employment of an electrodeless discharge makes it possible to solve the problem of erosion and to increase the power injected and the sensitivity of the detector. Thus the sensitivity of a PID in a UHF discharge amounting to 1.57 K g^{-1} has been reported,[22] which is probably the maximum value at the present time (the power injected into the discharge was 20 W).

For the wide-scale practical use of the PID considered, the maximum working temperature must be increased. The question of the stability of the temperature (owing to its influence on the discharge current) is also important in this respect.[15] The maximum working temperature of PID with non-separated emission and detection compartments is at present 200 °C.[21]

IV. Detectors with separated emission and detection compartments

The difficulties in the practical use of PID with a reduced pressure in the detection compartment stimulated not only the development of sources operating stably at atmospheric pressure but also the appearance of photoionisation detectors of a new type, with separated emission and detection compartments. The first suggestion to separate these compartments was made in Ref. 28 and was then additionally justified by Locke and Meloan.[16] The first descriptions of the design of PID with an optical window between the source of vacuum UV radiation (VUV) and the ionisation chamber soon appeared.[29–31] The window is normally part of the design of the hermetically sealed UV source in which the pressure does not exceed tens of millimetres of mercury. This technical solution proved extremely promising and the manufacture of chromatographs with built in PID was initiated.[32] This was promoted by the development and manufacture of stable sources emitting vacuum UV radiation.

Metal halides and certain oxides can be used as materials for the transmission of the radiation. The dependence of the transmittances of some of these compounds on wavelength in the VUV is illustrated in Fig. 2.[33] Thin SiO films fixed on a metallic grid also have a satisfactory transmittance in the range 60–90 nm (20–70%). However, their mechanical strength is inadequate. A SiO window 100 nm thick and 10 mm in diameter can withstand a pressure difference not greater than 1000 N m^{-2}.[33]

In terms of the combination of optical and mechanical properties, lithium and magnesium fluorides are the most acceptable materials. However, lithium fluoride, which has the lowest transmittance limit (106 nm) among all the halides, has not come to be used as widely as magnesium fluoride because of its high hygroscopicity which alters the emission spectrum. The transmittance of lithium fluoride is also impaired on VUV irradiation owing to the formation of colour centres.[34] Magnesium fluoride has a fairly low short-wavelength limit (113 nm), which makes it able to transmit photons with the energy required for the ionisation of the majority of organic

substances. Some decrease in the transparency of magnesium fluoride is observed when it is heated to 200–400 °C with simultaneous exposure to the VUV radiation.[35] The decrease in the transmittance of magnesium fluoride windows can be associated with the absorption by the film (including the substance to be analysed) present on the surface of the crystal.[36,37] Organic films can be removed from the surface by employing VUV radiation in the presence of oxygen.[38] In chromatographic practice, the transparency of windows is restored mechanically (by wiping).[4]

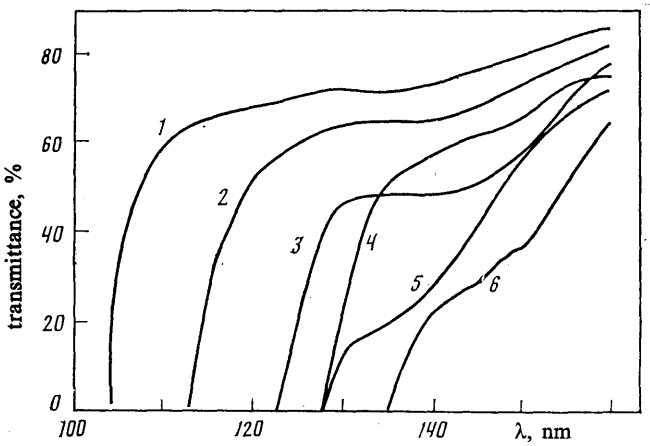


Figure 2. The transmittances of certain metal halides as a function of wavelength in the VUV region: *1*, LiF; *2*, MgF_2; *3*, CaF_2; *4*, NaF; *5*, SrF_2; *6*, BaF_2.

The characteristics of the materials which can be used to transmit VUV radiation have been specified in detail.[39]

Sources, with a line spectrum, capable of operating for a long time under continuous conditions,‡ have come to be most widely used for the generation of the VUV radiation in photoionisation detectors. For a discharge in a rarefied gas, there are lines at 104.82 (11.8 eV) and 106.67 nm (11.6 eV) in the argon spectrum, at 116.49 nm (10.64 eV) and 123.58 nm (10.03 eV) in the krypton spectrum, and at 129.55 nm (9.57 eV) and 146.96 nm (8.44 eV) in the xenon spectrum (the energy is indicated in brackets).[41]

Fairly reliable resonance lamps, filled with different substances and working in glow or arc discharge regimes, are currently widely used in PID designs. Inert gas (krypton and xenon) resonance lamps each emit virtually two resonance lines, the intensity of the long-wavelength lines being higher by 1–2 orders of magnitude than that of the short-wavelength lines.[42] The emission quantum yield for such sources is $10^{14}-10^{16}$ quanta s^{-1} behind the window of the lamp. He–Kr on He–Xe gas mixtures at a Kr or Xe pressure of 0.12–0.06 mmHg are used in such lamps, which makes it possible to obtain non-self-reversed Kr and Xe resonance lines, in the presence of which He is not excited.[43] Modern modifications of the krypton and xenon resonance lamps, developed in the USSR, have been described.[44] The power required by such lamps does not exceed 1–2 W.

Resonance lamps manufactured by the HNU Systems Company filled with krypton, xenon, and argon are used in chromatographs produced by a series of foreign manufacturers and fitted with photo-ionisation detectors. These lamps differ in the values of so called nominal energy. The nominal energies do not determine the energy of the photons emitted by the lamp but represent a conventional designation defining the type of the lamp. Lamps with nominal energies of 8.3, 9.5, 10.0, 10.2, 10.9, and 11.7 eV are known. Detectors with the corresponding lamps are designated by PID-8.3, PID-10.0, etc. The distribution of the emission energy in the line spectra of lamps with nominal energies of 8.3, 9.5, 10.2, and 11.7 eV, obtained using a vacuum UV spectrometer, has been published.[45] Only the lamp with a nominal energy of 8.3 eV produces monochromatic radiation. The remaining lamps emit not less than two lines. The intensity of the emitted lines in the range of the working currents is independent of the current in the lamp. The lamp with a nominal energy of 11.7 eV has a lithium fluoride optical window. Its operating life is several hundreds of hours.[46]

It has been suggested[47] that electrodeless UHF discharge lamps be used as radiation sources in PID. A portable chromatograph, fitted with a PID incorporating a UHF discharge lamp was later constructed.[48,49]

In the development of PID ionisation chambers, serious specific problems frequently arise. They are associated with the hermetic seal in the chamber, the reduction of the influence of the photoeffect, the elimination of the contamination of the window, etc. The question of the volume of the detector in a capillary chromatograph is of fundamental importance. The first, commercially produced PID had an ionisation chamber with a volume of 50 μl [32] (Fig. 3). The volume of the modified detector of the same series was 175 μl.[50] Such a volume is not optimal when used in conjunction with capillary columns, although it does make it possible to ensure a high sensitivity of detection.

Studies designed to reduce the detector volume are being prosecuted both to reduce the physical (total) volume and to reduce the effective volume responsible for the signal generation.

The decrease in the physical volumes of the ionisation chamber involves difficulties arising from the need to ensure a hermetic seal and a high sensitivity, but such reduction makes it possible to operate at lower potentials on the polarising electrode and with low flow rates of the make-up gas. The latter is important because the PID is a concentration detector.

A detector with a physical volume of 50 μl operating with a make-up gas flow rate of 2–3 ml min^{-1} has been reported.[51] There are data concerning the operation of PID altogether without a make-up gas flow. Thus the experimental results of a study of the influence of the volume of the photoionisation detector on the spreading of the chromatographic peaks of acetone have been published.[52] Fig. 4 reproduces these data,[52] obtained for detectors with volumes of 225, 150, and 50 μl and also for a flame-ionisation detector (FID). The figure shows that spreading could not be eliminated completely even in the detector with a volume of 50 μl.

The efficiency of the chromatographic system in which a PID with a volume§ of 50 μl and a FID were connected in series has been estimated. The loss of efficiency compared with the direct inclusion

‡ It is essential to note that the use of laser multistep ionisation, ensuring a high selectivity, is undoubtedly promising.[40]

§ The 50 μl volume was referred to as effective in the relevant study although a make-up gas was not supplied to the detector.

of the FID at the outlet from the chromatographic system after recalculation in terms of the number of theoretical plates is less than 10%.[53] A detector with a volume of 37 μl not requiring a make-up gas has also been reported.[45] In one of the variants of fluid chromatography, the designs of PID with volumes of 70 and 7 μl were investigated.[54]

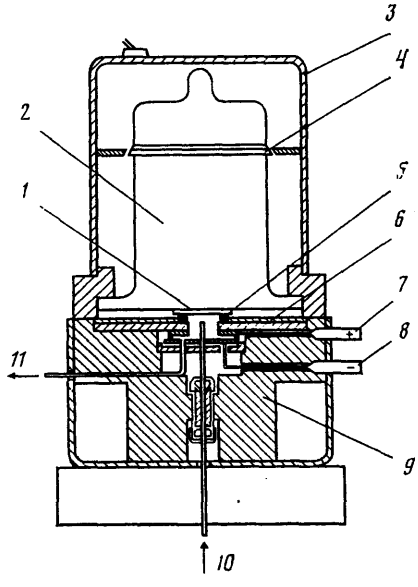


Figure 3. The design of the photoionisation detector based on the system of the HNU Systems Company: *1*, window for the transmission of radiation; *2*, vacuum UV lamp; *3*, lamp shell; *4*, electrode; *5*, Kalrez seal; *6*, graphite seal; *7*, measuring electrode; *8*, polarising electrode; *9*, heating block; *10*, gas inlet; *11*, gas outlet.

A decrease in the effective detector volume is achieved by reducing the irradiated region and by organising a "shielding" gas flow. The effective detector volumes were 1 and 10 μl respectively in the studies of Nutmagul et al.[55] and in Ref. 56. In the study of Gmür et al.,[54] the make-up gas flow rate was maintained at the level of 8–10 ml min^{-1}, which is close to the make-up flow rates of 10–15 ml min^{-1} used in a commercial detector with a volume of 150 μl.[57,58]

The shell of the ionisation chamber is made of a material with the highest possible specific resistance and the lowest porosity: PTFE,[47,59] boron nitride,[53] and a special glass.[55] In order to ensure a background current at the level of 10^{-11} A at a detector supply potential of ~100 V, the specific resistance of the insulators must be of the order of 10^{13} Ω cm. At temperatures up to 200 °C, PTFE is suitable. Ceramics are more heat resistant, but their electrical resistances fall significantly on raising the temperature to 300–400 °C, which increases the background current and the noise level and hence impairs the characteristics of the detector. The specific resistances ρ_V of several types of ceramics at 20° and 500 °C have been published in a monograph.[60] The ceramic based on Al_2O_3, which also has a low porosity, is the most suitable (Table 2).

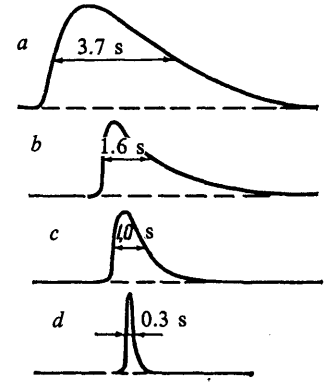


Figure 4. Chromatographic peaks of acetone obtained with PID having a chamber with different volumes (μl): *a*, 225; *b*, 150; *c*, 50; *d*, obtained with a FID.

Table 2. Specific resistances of various types of ceramics.[60]

Type of ceramic	ρ_V, Ω cm	
	20° C	500° C
Al_2O_3	10^{14}	10^{12}
$2MgO \cdot SiO_2$	10^{14}	10^{10}
$MgO \cdot Al_2O_3$	10^{14}	10^{11}
MgO	10^{14}	10^{12}
BeO	10^{14}	10^{12}

When the PID is series-connected to other detectors, the problem of its hermetic seal becomes important. It is solved mainly in the traditional manner using the seal between the ionisation chamber and the lamp. The limiting temperature for this design using perfluorinated rubber is 300 °C.[45] It has been suggested[61] that an additional window, glued to the shell of the ionisation chamber, be introduced into the PID design to ensure a hermetic seal. A disadvantage of this design is the weakening of the radiation flux in the chamber and also the impossibility of cleaning the additional window. It has likewise been suggested that the MgF_2 window be sealed to the chamber with the aid of a conical sealing arrangement.[62] A hermetically sealed junction between the shell and the window and also between the ceramic shell and the electrode can be achieved with the aid of diffusionally hardening solders.[63] In order to increase the maximum working temperature of the detector, it has been suggested[64] that the hermetic seal in the ionisation chamber be abandoned so that the release of gas through the gap between the detector shell and the optical window can be ensured.

A coaxial electrode system is most often employed in the ionisation chamber of the PID. In this system, the central electrode is generally subjected to VUV radiation, which increases the background current. The shielding of the electrode from the direct effect of the radiation made it possible to reduce the background current by three orders of magnitude.[53]

The optimum configuration of the electrodes for which the highest signal is attained has been sought.[55] The possibility of achieving such a configuration may be associated with the fact that the chamber operates under conditions far from saturation. Optimisation implies the attainment of maximum sensitivity for low detector supply potentials when the gas-induced intensification processes are absent and the leakage through the insulator is small.

It is shown below how the nature of the carrier gas affects the sensitivity of the PID with a 10.2 eV lamp in the detection of benzene:[65]

Carrier gas	Air	Ar	CO_2	N_2	CF_4	He	CO
Response, rel. units	0.542	1.401	0.285	1.00	1.01	0.987	1.07

It has been suggested that the following processes are responsible for the decrease in the response of the PID; the capture by the carrier gas of the electrons formed as a result of photoionisation; the absorption of the UV radiation by the carrier gas; the de-excitation of the components analysed on their collision with the molecules of the carrier gas having vibrational and rotational levels. The fact that the response of the PID is greatest when argon is used has been explained[65] by the high rate of drift of the electrons (v_e) in this gas, which lowers the losses in recombination compared with He or N_2. However, in argon v_e is greater than in He or N_2 only for $E/P < 10^{-2}$ V cm^{-1} (mmHg)$^{-1}$ (E is the strength of the electric field between the electrodes of the ionisation chamber).[66] Under real conditions, where $E/P > 10^{-1}$ V cm^{-1} (mmHg)$^{-1}$, the quantity v_e in argon is smaller than in He or N_2. The increased values of v_e in argon may be caused by its greater sensitivity to molecular impurities.[66] The presence of the latter (including ionisable impurities) diminishes the electron temperature and increases v_e.

Table 3. Characteristics of PID with separated emission and detection compartments.

Gas filling the lamp	Background current $10^{11}I_b$, A	Noise $10^{14}I_m$, A	Detection limit w.r.t. benzene	Maximum working temperature, °C	Detector volume, μl	Linear dynamic range	Refs.
H_2, Ar, Kr, Xe	1.4	4	2×10^{-12} g	300	175 50	10^7	[50]
H_2	2	—	0.6×10^{-12} g	200	1	—	[55]
H_2	—	2	0.5×10^{-12} g	220	10	10^5	[56]
H_2	2	5	0.67×10^{-14} g s^{-1}	300	—	10^6	[68]

The fluctuation noise in PID constitutes a serious problem. The nature of the noise is determined mainly by the variation of the photocurrent with the composition of the gas in the detector and by the contamination of the insulating elements, causing leakage.[45,67] The increased level of PID noise (compared with FID) precludes the full utilisation of its greatest advantage—its high sensitivity.[67]

Certain characteristics of PID with separated emission and detection compartments are presented in Table 3. It follows from Table 3 that, in terms of their characteristics, the detectors are similar. The PID produced by the HNU Systems Company is outstanding as regards its long linear range. The detection threshold and the linear range of the PID are illustrated in Fig. 5, which includes for comparison the analogous data for FID and the electron capture (ECD), flame-photometric (FPD), and ultraviolet (UVD) detectors.

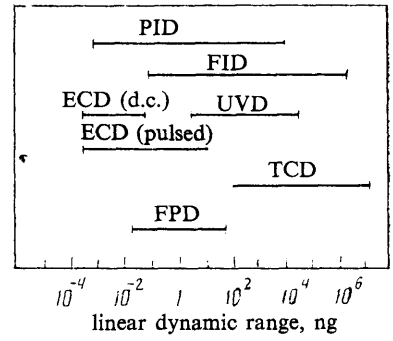


Figure 5. The linear dynamic range for certain detection methods[7] [TCD = thermal conductivity detection (Ed. of Translation)].

V. The response of the photoionisation detector

The magnitude of the response of the PID depends on the effective photoionisation cross-section σ_i, which is determined by the energy of the photoionising photons and by the characteristics of the substance analysed. The dependence of σ_i on the energy of the ionising photons E_{ph} is complex. It can be estimated using the photoionisation efficiency curves (PEC) $\eta(E_{ph})$, obtained, for example, with the aid of photoionisation mass spectrometry.[9] These relations have been resorted to in order to explain qualitatively the influence of the energy of the photons on the response.[69] However, the PID responses cannot be estimated quantitatively with the aid of the PEC because of the different intensities of the lamps and the non-monochromatic nature of the radiation.

The PID response can be estimated to a first approximation with the aid of the quantity $E_{ph} - E_i$, where E_i is the ionisation energy of the test substance. For non-monochromatic lamps, one must take into account not only the most intense line but also other lines. If the quantity $E_{ph} - E_i$ is fairly large (1–2 eV and more), ionisation occurs along the PEC section remote from the threshold value, where the $\eta(E_{ph})$ relation has a plateau for many substances. The response is then independent of E_i.[69] On the other hand, if the difference $E_{ph} - E_i$ is small (a fraction of an electron-volt), then ionisation occurs in the pre-threshold region on the PEC, and the response therefore also depends on the closeness of the E_i to the photoionisation threshold or, for a given E_{ph}, on E_i. A greater difference $E_{ph} - E_i$ obtains when a lamp with a nominal energy of 11.7 eV is used, 71.1% of its radiation corresponding to photons

with an energy of 11.62 eV. The PID responses to alkanes, alkenes, and aromatic hydrocarbons are in this case approximately the same. A small difference $E_{ph} - E_i$ is characteristic of a large number of compounds of different classes when a lamp with a nominal energy of 10.2 eV is used (the spectrum contains photons with energies of 10.03 and 10.64 eV). It is essential to note that, when $(E_{ph} - E_i) < 0$, a signal due to the removal of electrons from vibrationally excited molecules may be observed and may increase with increasing temperature in proportion to $\exp[-(E_{ph} - E_i)/kT]$, where k is the Boltzmann constant. An attempt has been made[70] to relate the PID response to the number of electrons participating in the formation of multiple carbon–carbon bonds, but the conclusions reached[70] were subjected to serious criticism.[37]

Table 4. The relative sensitivities of the PID-10.2 to organic compounds.[71]

Substance	$K_{i,M}$	Substance	$K_{i,M}$
n-Alkanes		Ketones	
Heptane	0.032	Acetone	0.35
Octane	0.080	2-Butanone	0.40
Nonane	0.14	2-Pentanone	0.45
Decane	0.23	3-Pentanone	0.54
Undecane	0.30	2-Hexanone	0.52
Dodecane	0.37	2-Heptanone	0.59
Tridecane	0.46	3-Heptanone	0.68
Tetradecane	0.53	4-Heptanone	0.70
Pentadecane	0.59	2-Octanone	0.71
Hexadecane	0.71	3-Octanone	0.73
Heptadecane	0.72	2-Nonanone	0.78
Octadecane	0.79	5-Nonanone	0.82
Nonadecane	0.86	3-Methyl-2-butanone	0.58
Eicosane	0.93	3-Methyl-2-pentanone	0.60
Heneicosane	1.03	2-Methyl-3-pentanone	0.62
Docosane	1.13	4-Methyl-2-hexanone	0.62
Isoalkanes and Cycloalkanes		5-Methyl-2-hexanone	0.65
2,2-Dimethylbutane	0.037	3-Methyl-2-heptanone	0.72
2,3-Dimethylbutane	0.032	5-Methyl-3-heptanone	0.75
2-Methylpentane	0.011	3,3-Dimethyl-2-butanone	0.65
3-Methylpentane	0.027	2,4-Dimethyl-3-pentanone	0.70
2,4-Dimethylpentane	0.080	2,6-Dimethyl-4-heptanone	0.81
2,3-Dimethylpentane	0.10	Cyclopentanone	0.57
3-Methylhexane	0.075	Cyclohexanone	0.62
2,4- and 2,5-Dimethylhexane	0.15	2-Methylcyclohexanone	0.66
2,2,4-Trimethylpentane	0.21	3-Methylcyclohexanone	0.66
2,3,4-Trimethylpentane	0.22	4-Methylcyclohexanone	0.63
3-Methylheptane	0.13	Butane-2,3-dione	0.45
2,2,5-Trimethylhexane	0.26	Aldehydes	
Cyclohexane	0.18	Butanal	0.30
Methylcyclohexane	0.28	Pentanal	0.36
Decahydronaphthalene	1.04	Hexanal	0.41
Alkenes, Dienes, and Alkynes		Heptanal	0.45
3-Methylbut-1-ene	0.52	Octanal	0.49
n-Hept-1-ene	0.54	Nonanal	0.53
n-Hept-2-ene	0.51	Alcohols	
n-Hept-3-ene	0.58	1-Butanol	0.023
n-Oct-1-ene	0.55	1-Pentanol	0.053
n-Non-1-ene	0.58	1-Hexanol	0.086
n-Dec-1-ene	0.67	1-Heptanol	0.12
n-Undec-1-ene	0.70	1-Octanol	0.16
n-Dodec-1-ene	0.73	1-Nonanol	0.20
n-Tridec-1-ene	0.81	1-Decanol	0.25
n-Tetradec-1-ene	0.87	1-Undecanol	0.29
n-Pentadec-1-ene	0.92	1-Dodecanol	0.36
n-Hexadec-1-ene	0.99	Isobutyl alcohol	0.029
n-Heptadec-1-ene	1.06	Isopentyl alcohol	0.057
n-Octadec-1-ene	1.10	t-Pentyl alcohol	0.054
n-Nonadec-1-ene	1.17	Hex-3-en-1-ol	0.46
Deca-1,9-diene	1.07	Butane-1,4-diol	0.10
n-Oct-2-yne	2.75	Esters	
Halogeno-derivatives of aliphatic hydrocarbons		Methyl propionate	0.010
1-Bromobutane	0.066	Methyl butanoate	0.039
1-Iodobutane	1.93	Methyl pentanoate	0.082
1,2-Dibromobutane	0.081	Methyl hexanoate	0.096
Hexachlorocycloyhexane	0.027	Methyl heptanoate	0.14
Hexachlorocyclopentadiene	0.88	Methyl octanoate	0.15
Hexachlorobuta-1,3-diene	1.34	Methyl nonanoate	0.26
		Methyl decanoate	0.33
		Methyl dodecanoate	0.48
		Methyl tetradecanoate	0.66
		Methyl hexadecanoate	0.82

Table 4 cont'd.

Substance	$K_{i,M}$	Substance	$K_{i,M}$
Esters		Polychlorobiphenyls	
Ethyl acetate	0.020	3,3',4,4'-Tetrachlorobiphenyl	2.96
Ethyl butanoate	0.15	2,2',4,5,5'-Pentachlorobiphenyl	2.45
Ethyl hexanoate	0.24	2,2',3,4,5'-Pentavchlorobiphenyl	2.80
Ethyl octanoate	0.32	2,2',3,4,5,6'-Hexachlorob iphenyl	2.55
Ethyl decanoate	0.51	2,2',4,4',5,5'-Hexachlorobiphenyl	2.60
Ethyl dodecanoate	0.70	Phthalates	
Propyl acetate	0.025	Dimethyl phthalate	0.56
Propyl butanoate	0.21	Diethyl phthalate	0.87
Butyl acetate	0.044	Di-n-butyl phthalate	1.06
Aromatic hydrocarbons		Di-(2-ethylhexyl) phthalate	1.78
Benzene	1.00	Benzyl butyl phthalate	1.78
Toluene	1.09	Phenols	
o-Xylene	1.14	Phenol	1.05
m-Xylene	1.15	*p*-Cresol	1.07
p-Xylene	1.20	2,4-Dimethylphenol	1.10
Cumene	1.22	2-Chlorophenol	1.19
p-Cymene	1.27	3-Chlorophenol	1.32
Mesitylene	1.27	4-Chlorophenol	1.30
Ethylbenzene	1.16	2,3-Dichlorophenol	1.34
n-Propylbenzene	1.21	2,4-Dichlorophenol	1.34
n-Butylbenzene	1.27	2,5-Dichlorophenol	1.34
n-Hexylbenzene	1.29	2,6-Dichlorophenol	1.33
n-Octylbenzene	1.52	3,4-Dichlorophenol	1.37
n-Decylbenzene	1.69	3,5-Dichlorophenol	1.35
Naphthalene	1.97	2,3,4-Trichlorophenol	1.28
Biphenyl	1.88	2,3,5-Trichlorophenol	1.28
Anthracene	2.44	2,3,6-Trichlorophenol	1.47
Phenanthrene	2.50	2,4,5-Trichlorophenol	1.32
1,2-Benzoanthracene	2.46	2,4,6-Trichlorophenol	1.30
p-Terphenyl	2.20	3,4,5-Trichlorophenol	1.20
Pyrene	3.02	2,3,4,5-Tetrachlorophenol	1.14
Chrysene	2.96	2,3,4,6-Tetrachlorophenol	1.43
Triphenylene	3.08	2,3,5,6-Tetrachlorophenol	1.38
Fluorene	2.08	Pentachlorophenol	1.18
Fluoranthene	2.85	2-Chloro-5-hydroxytoluene	1.20
Acenaphthene	3.06	Organic compounds with different functional groups	
Halogenobenzenes		Nitrobenzene	0.29
Chlorobenzene	1.30	4-Nitrophenol	0.29
1,3-Dichlorobenzene	1.42	1-Fluoro-4-nitrobenzene	0.15
1,4-Dichlorobenzene	1.39	2,4-Dinitrophenol	0.094
1,2-Dichlorobenzene	1.30	2,4-Dinitrotoluene	0.062
1,3,5-Trichlorobenzene	1.26	Aniline	1.13
1,2,4-Trichorobenzene	1.20	Pyridine	0.50
1,2,3-Trichlorobenzene	1.44	Benzoic acid	0.50
1,2,4,5-Tetrachlorobenzene	1.28	Benzaldehyde	0.96
1,2,3,4-Tetrachlorobenzene	1.40	Mesityl oxide	0.61
Pentachlorobenzene	1.32	Acetophenone	0.94
Hexachlorobenzene	1.25	1,2-Dimethoxybenzene	1.19
Bromobenzene	1.82	Diphenyl ether	2.10
Iodobenzene	2.50	Dibenzofuran	0.86
1-Chloro-2-fluorobenzene	0.98	Dibenzo-*p*-dioxin	0.93
Polychlorobiphenyls		Dibenzothiophen	1.31
2,3-Dichlorobiphenyl	2.18	2-Bromophenyl phenyl ether	3.30
4,4'-Dichlorobiphenyl	2.47	2-Chloronaphthalene	2.04
2',3,4-Trichlorobiphenyl	2.40	Tetrahydrofuran	0.39
2,2',5,5'-Tetrachlorobiphenyl	2.43	Diethyl ether	0.36
2,3',4',5-Tetrachlorobiphenyl	2.39		

It has been established experimentally that PID is highly sensitive to aromatic hydrocarbons with low ionisation potentials. In practice, it is convenient to determine the absolute sensitivity and the PID detection limit with respect to benzene (Tables 4 and 5). The molecular sensitivity coefficients $K_{i,M}$ have been measured[71] for a large number of organic compounds relative to benzene (Table 4):

$$K_{i,M} = (S_i/S_{st})(c_{st}/c_i),$$

where S_i and S_{st} are the peak area of the ith substance and benzene and c_i and c_{st} are the concentrations (in nmol ml^{-1}) of the ith substance and benzene in the model mixture respectively. A model P1-51-02 PID from the HNU Systems Company, fitted with a UV lamp having a nominal energy of 10.2 eV, was used for the measurements.

Table 4 shows that the molar sensitivity of the PID increases with increasing number of carbon atoms in the molecule within the limits of the homologous series. The linear equation

$$K_{i,M}=0.715n-0.475.$$

is valid for n-alkanes. The following sequence in the variation of the $K_{i,M}$ is characteristic of normal aliphatic compounds with different functional groups and having the same numbers of carbon atoms: alkanes < alcohols < methyl ethers < ethyl ethers < aldehydes < 2-ketones < 3-ketones. Branches in the carbon chain of the molecule and the presence in the latter of saturated rings or double bonds tend to increase the PID response, whilst the presence of nitro-groups tends to decrease it.

Table 5. Detection limits of the PID.

Compound	Detection limit		Lamp energy, eV	Type of column*	Company manufacturing the PID**	Refs.
	pg	fmol				
1	2	3	4	5	6	7
Propane	200	$4.5\cdot10^3$	11.7	P	«HNU Systems»	[46]
n-Butane	260	$4.5\cdot10^3$	10.2	C	»	[76]
	181	$3.1\cdot10^3$	10.2	MP	»	[74]
	26	446	11.7	MP	»	[74]
n-Pentane	161	$2.2\cdot10^3$	10.2	C	»	[76]
n-Hexane	15	171	10.2	C	—	[55]
n-Heptane	9.0	90	10.2	C	—	[55]
n-Octane	7.5	66	10.2	C	—	[55]
	458	$4.0\cdot10^3$	10.2	C	«HNU Systems»	[76]
n-Nonane	6.7	52	10.2	C	—	[55]
n-Decane	5.1	36	10.2	C	—	[55]
Propene	5.6	134	10.2	MP	«HNU Systems»	[74]
	37	839	11.7	MP	»	[74]
	22	536	10.2	C	»	[76]
Butene	30	536	10.2	C	»	[76]
Hex-1-ene	1.6	19	10.2	C	—	[55]
Hept-2-ene	1.3	13	10.2	C	—	[55]
Oct-1-ene	2.1	19	10.2	C	—	[55]
Non-1-ene	2.7	21	10.2	C	—	[55]
Dec-1-ene	2.1	15	10.2	C	—	[55]
Butadiene	1.7	31	10.2	MP	«HNU Systems»	[74]
	12	224	11.7	MP	»	[74]
Methyl bromide	10	105	10.9	P	«Photovac Jnc.»	[77]
Methyl chloride	11	224	11.7	MP	«HNU Systems»	[74]
Methylene chloride	190	$2.2\cdot10^3$	10.2	C	»	[76]
1,1,1-Trichloroethane	60	446	11.7	MP	»	[74]
Trichloroethylene	18	137	10.2	MP	»	[74]
	90	685	11.7	MP	»	[74]
	30	228	10.2	C	»	[76]
Vinyl chloride	4	64	10.2	P	»	[31]
	50	800	10.2	P	»	[77]
Tetrachloroethylene	37	223	10.2	C	»	[76]
Formaldehyde	300	$1\cdot10^3$	11.7	P	»	[46]
Methanethiol	20	417	10.2	P	»	[7]
Ethanethiol	20	323	10.2	P	»	[78]
Propanethiol	20	263	10.2	P	»	[78]
t-Butanethiol	20	222	10.2	P	»	[78]
s-Butanethiol	20	222	10.2	P	»	[78]
n-Butanethiol	60	667	10.2	P	»	[78]
Dimethyl sulphide	20	323	10.2	P	»	[7]
Dimethyl sulphide	22	234	10.2	P	»	[7]
Methylamine	5	161	10.2	P	»	[31]
Dimethylnitrosoamine	100	$1.3\cdot10^3$	10.2	C	»	[79]
Ethylbutynylnitrosoamine	100	769	10.2	C	»	[79]
Nitrosopyrrolidinone	50	500	10.2	C	»	[79]
Nitropentane	$>10^6$	$>8.5\cdot10^6$	10.2	P	»	[80]
Nitrocyclohexane	$>10^6$	$>7.8\cdot10^6$	10.2	P	»	[80]
Benzene	5	64	10.2	P	—	[81—82]
	0.6	7.7	10.2	C	—	[55]
	0.8	10	10.9	P	«Photovac Jnc»	[83]
	20	256	10.9	C	»	[84]
	0.7	9.0	10.2	MP	«HNU Systems»	[74]
	1.1	14	10.2	P	»	[85]
	2.0	26	10.2	P	»	[31]
	2.0	26	10.2	P	»	[73]
	7.0	90	11.7	MP	»	[74]
	18	225	10.2	C	»	[76]
Toluene	1.2	13	10.2	P	»	[85]
	1.2	13	10.9	P	«Photovac Jnc.»	[83]
	0.8	8.7	10.2	C	—	[55]
Ethylbenzene	1.3	12	10.2	C	—	[55]
	4.2	40	10.9	P	«Photovac Jnc.»	[83]
o-Xylene	4.2	40	10.9	P	»	[83]

Table 5 cont'd.

Compound	Detection limit		Lamp energy, eV	Type of column*	Company manufacturing the PID**	Refs.
	pg	fmol				
1	2	3	4	5	6	7
o-Xylene	1.3	12	10.2	C	—	[55]
m-Xylene	4.3	41	10.9	P	«Photovac Jnc.»	[83]
p-Xylene	4.3	41	10.9	P	»	[83]
	2.8	26	10.2	P	«HNU Systems»	[85]
Isopropylbenzene	1.8	15	10.2	C	—	[55]
Anthracene	25	140	10.2	C	—	[53]
Naphthalene	10	78	10.2	P	«HNU Systems»	[86]
C_{10}–C_{15} poloyarenes and their monochloro-derivatives	50—100		10.2	P	»	[36]
C_{10}–C_{18} polyarenes	$(0.2—1)\cdot10^3$		10.2	MP	»	[87]
Phenol	80	851	10.2	P	»	[88]
Aniline	900	$9.7\cdot10^3$	10.2	C	»	[89]
	700	$7.5\cdot10^3$	9.5	C	»	[89]
2-Chloroaniline	100	787	10.2	C	»	[89]
	600	$4.7\cdot10^3$	9.5	C	»	[89]
4-Bromoaniline	600	$3.5\cdot10^3$	10.2	C	»	[89]
	$1.4\cdot10^3$	$8.1\cdot10^3$	9.5	C	»	[89]
2,4,5-Trichloroaniline	200	$1\cdot10^3$	10.2	C	»	[89]
	800	$4.1\cdot10^3$	9.5	C	»	[89]
2-Nitroaniline	900	$6.5\cdot10^3$	10.2	C	»	[89]
	$1.3\cdot10^3$	$9.4\cdot10^3$	9.5	C	»	[89]
3-Nitroaniline	$2\cdot10^3$	$1.4\cdot10^4$	10.2	C	»	[89]
	$1\cdot10^4$	$7.2\cdot10^4$	9.5	P	»	[89]
o-Nitrotoluene	400	$2.9\cdot10^3$	10.2	P	»	[80]
2,6-Dinitrotoluene	$2.8\cdot10^3$	$1.5\cdot10^4$	10.2	C	»	[80]
2,4-Dinitroaniline	$2.1\cdot10^4$	$1.1\cdot10^5$	10.2	C	»	[89]
	$1\cdot10^5$	$5.5\cdot10^5$	9.5	C	»	[89]
Androsterone	33	114	10.2	C	»	[90]
Testosterone	55	191	10.2	C	»	[90]
Oestrone	62	228	10.2	C	»	[90]
Oestradiol	69	253	10.2	P	»	[90]
Barbital	150	815	10.2	P	»	[91]
Secobarbital	400	$1.7\cdot10^3$	10.2	P	»	[91]
Hexobarbital	200	847	10.2	P	»	[91]
Phenobarbital	950	$4.1\cdot10^3$	10.2	P	»	[91]
Butethal	500	$2.4\cdot10^3$	10.2	P	»	[91]
Pentobarbital	450	$2\cdot10^3$	10.2	P	»	[91]
Tetraethyllead	150	464	10.2	P	»	[32]
Hydrogen sulphide	15	442	10.2	P	»	[31]
	15	442	10.2	P	»	[7]
Phosphine	25	735	10.2	P	»	[31]
	20	588	10.2	P	»	[91]
Ammonia	200	$1.2\cdot10^4$	10.2	P	»	[31]
	200	$1.2\cdot10^4$	10.2	P	»	[91]
Arsine	25	321	10.2	P	»	[91]
Nitrogen oxide	52	$1.7\cdot10^3$	10.2	P	»	[91]
Iodine	25	98	10.2	P	«HNU Systems»	[91]
Chlorine	$1\cdot10^4$	$1.4\cdot10^5$	11.7	P	»	[46]
Carbon disulphide	3.4	45	10.2	MP	»	[74]
	6.8	89	11.7	MP	»	[74]
	30	395	10.2	P	»	[7]

* The following abbreviations have been adopted: P = packed column; C = capillary column; MP = micropacked column.
** The dash denotes the author's own design.

The high sensitivity of the PID with respect to the characteristic features of the carbon skeleton of organic compounds is very important for the practical purposes of group identification. It is noteworthy that, since the PID selectivity varies with the quantity $E_{ph} - E_i$, it can be regulated by using UV lamps with different nominal energies.

For example, when a lamp with a nominal energy of the 11.7 eV was used, the molar sensitivity coefficients for benzene, cyclohexane, and cyclohexene were approximately the same[72] and, when a 10.2 eV lamp was employed, the PID responses to cyclohexane and cyclohexene were respectively 15 and 30% of the response to benzene.[57] According to the results of Locke and Meloan,[16] the signal of the PID with an 11.7 eV lamp in response to arenes exceeded on average by 30% the signal in response to alkanes. When a 10.2 eV lamp was used, the sensitivity of the PID to arenes was found to be higher by a factor of 5.[73]

The non-monochromatic radiation from certain lamps, the probable change in the distribution of the emission energy as the temperature of the PID is varied, and the marked difference between the emission intensities of lamps having different nominal energies have an interfering effect on detailed studied of the relation between $E_{ph} - E_i$ and the relative sensitivity coefficients and on the development of methods for the determination of the required compound against the background of large amounts of other substances. An idea may be obtained about the last interfering factor by comparing the sensitivities of PID with 8.3, 9.5, 10.2, and 11.7 eV lamps of polyalkylated arenes and benzenes, which are in the proportions 1 : (10–20) : (100–400) : 20 respectively.[51,57] The high intensity of the emission proved to be decisive in reducing the benzene, butadiene, carbon disulphide, and trichloroethylene detection limits in a PID with a 10.2 eV lamp compared with one fitted with an 11.7 eV lamp. The sensitivity of the PID to n-butane depends mainly on the quantity $E_{ph} - E_i$ and it is therefore seven times greater for the PID with an 11.7 eV lamp.[74] One should also bear in mind the influence of the change in the emission intensity of the same lamp on the relative sensitivity coefficients of the PID. It has been found[75] that an increase in the emission intensity of 10.2 eV lamp by a factor of 1.6 led to an increase in the ratios of the responses to C_4-C_5 alkenes to the response to toluene by 30–40%. For alkanes and alkylbenzenes, these changes are significantly smaller.

The threshold sensitivity of the detector or the detection limit (DL) is important for the determination of microimpurities. In practice, the threshold sensitivity of the detector is usually expressed in terms of the amount of the substance (in grams or moles) generating a detector signal (the height of the chromatographic peak) greater by a factor of 2–5 than the noise of the zero line. Although this quantity is determined by the characteristics of the entire chromatographic system and the analytical conditions (namely the volume of the chromatographic peak at the outlet from the column, the rate of its passage through the detector, the make-up gas flow rate, etc.), nevertheless the data in Table 5 contain useful information about the real results obtained with PID in the analysis of trace amounts of substances. To facilitate the comparison of the data in Tables 5 and 4, the detection limits in Table 5 are expressed in grams and moles. Table 5 shows that the DL has been reached at the level of picograms for light aromatic hydrocarbons, alkenes, and amines and at the level of tens of picograms for mercaptans, sulphides, chloroalkanes and chloroalkenes, nitrosoamines, steroids, certain polyarenes, and inorganic gases. For barbiturates and aniline derivatives, with the exception of nitroanilines, the DL can apparently be reduced by improving the efficiency of the gas-chromatographic separation.

The choice of the lamp with a specific nominal energy depends on the sample composition and the purposes and conditions of the analysis. For example, in the determination of substances with comparatively short retention times in mixtures with a large amount of a polar solvent (methanol, Freon 11, methylene chloride, acetonitrile), it is useful to employ a PID with a 10.2 eV lamp, which is only slightly sensitive to solvents of this type. As a result the solvent tail is diminished and the accuracy of the determination of the substances eluted in the vicinity of the solvent peak is increased.

The photoionisation detector can be used under conditions where the useful signal is generated as a result of electron capture[92,93] or the absorption of radiation.[94] A specific feature of experiment under these conditions is that a large background current ($10^{-8}-10^{-9}$ A) is generated by virtue of the ionisation of the make-up gas introduced into the ionisation chamber and ionised by the radiation from the lamp. The useful signal is generated at the expense of the decrease in the background current.

Table 6. Characteristics of the analytical methods using PID.

Object of analysis and sample size	Compounds determined, detection limits (DL), PID efficiency	Preparation of sample	Column characteristics	Temperature regime in separation	Carrier gas, flow rate	PID characteristics	Refs.
1	2	3	4	5	6	7	8
Air (20 litres)	Benzene, C_7–C_9 alkylbenzenes, halogenobenzenes; DL 5 μg m^{-3}	Enrichment on a tube with Poropak N, desorption with methanol	2.7 m × 2 mm packed column, 15% SF-96 + 6% OV-225 on Chromosorb WAW DMCS; 100/120 mesh	Heating from 65° to 80 °C (10 min) at a rate of 3 K min^{-1}	N_2, 30 ml min^{-1}	"HNU Systems", model P-101, 250 °C	[96]
Air (1 litre)	Benzene, n-butane and trichloroethylene; DL 2×10^{-1}, 7×10^{-9}, and 3×10^{-10}% respectively (for the 10.2 eV lamp) and 2×10^{-10}, 1×10^{-9}, and 1.5×10^{-9}% respectively (for the 11.7 eV lamp). Other hydrocarbons and halogenohydrocarbons	Cryogenic concentration in a tube with glass beads at –173 °C	9 m × 0.2 mm micropacked column, Duropak n-C_8/Porasil-C; 100/120 mesh	Heating from –103 ° to 47 °C at a rate of 25 K min^{-1} and then to 127 °C at a rate of 2 K min^{-1}		"HNU Systems", model PI 52, 10.2 eV 187 °C lamp. 11.7 eV 87 °C lamp; N_2 make-up gas flow at a rate of 13 ml min^{-1}	[74]
Air	Benzene and chlorobenzene; DL 6.5×10^{-8}% and 2.5×10^{-7}% respectively. Chloroalkenes	Enrichment in passive traps with activated charcoal, desorption with 5% CS_2 solutions in methanol	2.4 m × 3 mm packed column, 1% SP 1000 on Carbopack B	Heating from 100° (10 min) to 180 °C at a rate of 4 K min^{-1}	N_2, 30 ml min^{-1}	"HNU Systems", 10.2 eV lamp	[97, 98]
Air	Mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes: DL $(0.7–1.2)\times10^{-7}$%	Enrichment on a tube with Amberlite XAD-2; desorption with CCl_4	3 m × 3 mm packed column; 0.5% PEG 20 M + 5% Synerg C on Chromosorb WAW; 80/100 mesh	Heat6ing from 50° (3 min) to 200 °C (6 min) at a rate of 10 K min^{-1}	N_2, 18 ml min^{-1}	"HNU Systems" 10.2 eV, 250 °C	[99]
Air (1 ml)	Benzene, toluene, ethylbenzene, and xylenes: DL 2.5×10^{-8} 3.2×10^{-8}, 9.4×10^{-8}, and 9.7×10^{-8}% respectively	Without enrichment	1.5 m × 3.1 mm packed column, 5% SE-30 on Chromosorb G; 100/120 mesh	Room temperature	Air, 15 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp, room temperature	[83]
Air (1 ml)	Dibromoethylene and epoxyethane: DL 5×10^{-7} and 1×10^{-3}% respectively	Without enrichment	Packed column	Room temperature	Air	"Photovac" 10A10, 10.9 eV lamp, room temperature	[100]

Table 6 cont'd.

Object of analysis and sample size	Compounds determined detection limits (DL), PID efficiency	Preparation of sample	Column characteristics	Temperature regime in separation	Carrier gas, flow rate	PID characteristics	Refs.
1	2	3	4	5	6	7	8
Air	Methyl bromide (the sensitivity of its determination with a FID is ~100 times higher than with a PID)	ditto	2 m × 3 mm packed column, Carbopack; 40/60 mesh	32 °C	Air, 10 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp	[101]
Air	Formaldehyde (the sensitivity of its determination with a FID is 33 times higher than with a PID)	"	1.2 m × 3 mm packed column, Carbopack BHT	25 °C	Air, 12 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp	[102]
Air (5 ml)	Ethane-, t-butane-, propane-, and s-butanethiols: DL 4 μg m^{-2} (12 μg m^{-3} for butanethiol)	"	Packed column 2.7 m long 15% SF-96 + 6% OV-225 on Chromosorb WAW DMCS	60 °C	N_2, 30 ml min^{-1}	"HNU Systems", 10.2 eV lamp, 200 °C	[78]
Air (10 litres)	Carbon disulphide: DL 1×10^{-5}%	Enrichment on a tube with activated charcoal, desorption with acetonitrile	0.75 m × 2.1 mm packed column, Chromosorb 108; 80/100 mesh	105 °C	N_2, 30 ml min^{-1}	"HNU Systems", 210 °C	[103]
Water	Benzene, toluene, xylene, and vinyl chloride: DL 1 μg $litre^{-1}$	Gas extraction from 100 ml of H_2O at 45 °C, enrichment on a tube with Porapak N, desorption with methanol	For arenes: 2 m × 2 mm packed column, 20% SE-30 on Gas Chrom Q; for vinyl chloride: 2 m × 2 mm packed column, Porapak T; 80/100 mesh	Heating from 40° to 60 °C at a rate of 3 K min^{-1}; 90 °C for vinyl chloride	He, 30 ml min^{-1}	"HNU Systems", 200 °C	[104]
Water	Vinyl chloride: DL 0.01 μg $litre^{-1}$	Analysis of 5 ml from 60 ml of equilibrium vapour over 100 ml of water at 56 °C	0.9 m × 2 mm packed column, Chromosorb 104	90 °C	He, 20 ml min^{-1}	"HNU Systems", model PI-52-02, 10.2 eV lamp, 250 °C	[77]
Water (18 litres)	Bicyclic and tricyclic arenes and their chloroderivatives: DL at the level of ng $litre^{-1}$ and mg $litre^{-1}$	Concentration by the HPLC method on a column with C_{18}-Corasil II with elution of fractions by a mixture of H_2O and acetonitrile	2.4 m × 2 mm packed column, 1.5% SP 2250 + 1.95% SP 2401 on Supelcort; 100/120 mesh	182 °C	N_2, 23 ml min^{-1}	"HNU Systems", model PI 51, 250 °C; N_2 make-up gas flow at a rate of 10–75 ml min^{-1}	[36]
Sewage water (1 litre)	Aniline and halogeno-, halogenonitro-, nitro-, and dinitro-anilines [the quantitative analysis is difficult owing to the complexity of the chromatogram. The (N/P)-detector is recommended]	Extraction with CH_2Cl_2, purification by the LC method on a column with Florisil	30 m × 0.25 mm glass capillary column, SE-52	Heating from 80° to 230 °C at a rate of 4 K min^{-1}	He, 30 cm s^{-1}	"HNU Systems", model PI 50, 10.2 and 9.5 eV lamps, He make-up gas flow	[89]
Blood serum (10 ml)	Barbiturates and other medicinal drugs (the sensitivity of the determination with a FID is 8–16 times higher than with a PID	Extraction with CCl_4, distillation of solvent, dissolution of residue in acetonitrile	1.8 m × 2 mm packed column, 3% OV-17 on Gas Chrom Q deactivated with H_3PO_4	Heating from 200° to 285 °C at a rate of 12 K min^{-1}	N_2, 19 ml min^{-1}	"HNU Systems", model PI 52-02, 10.2 eV lamp	[105]
Blood (5 g) and urine (20 g)	Mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes: DL 3–19 ng g^{-1} in blood and 0.7–4.9 ng g^{-1} in urine	Extraction with CCl_4, purification by the LC method on a column with silica gel	1.8 m × 3 mm packed column, 0.2% PEG 40 M + 0.5% synerg C on Chromosorb WAW	Heating from 60° (2 min) to 180 °C at a rate of 12 K min^{-1}	N_2, 18 ml min^{-1}	"HNU Systems", 10.2 eV lamp, 250 °C	[99]
Deposit (15 g)	Benzene, alkylbenzenes, chloroalkenes, and halogenobenzenes: DL 7 ng g^{-1}	Gas extraction at 120 °C with concentration on a tube with Porapak N, desorption with methanol	60 m × 0.25 mm quartz capillary column, DV-5	Heating from 50° to 170 °C (156 min) at a rate of 4 K min^{-1}	He, 60 cm s^{-1}	"HNU Systems", 10.2 eV lamp, 220 °C, He make-up gas flow at a rate of 8 ml min^{-1}	[106]
Atmospheric dust (9.8 mg)	Tri-, tetra-, and pentacyclic arenes (the more selective FID with an 8.3 eV lamp is recommended)	Vacuum sublimation at 260 °C with cryogenic concentration in a trap	30 m × 0.32 mm quartz capillary column, DV-5	Heating from 55° (10 min) to 225 °C (30 min) at a rate of 10 K min^{-1}	He, 6 ml min^{-1}	"HNU Systems", model PI 52-02, 9.5 eV lamp, 230 °C, He make-up gas flow	[107]
Meat products	Nitrosoamines (owing to the complexity of the chromatogram, the determination of low concentrations is difficult)	Extraction, purification by the LC method on a column with silica gel	50 m × 0.32 mm glass capillary column, Triton X-305	Rapid heating from room temperature (4 min) to 60 °C followed by heating to 160 °C at a rate of 5 K min^{-1}	He	"HNU Systems", 9.5 and 10.2 eV lamps, 250 °C, He make-up gas flow	[79]

In the operation of the PID under electron conditions, a threshold level of detection of heptachlorodicyclopentadiene (heptachlor) of 10^{-12} g was attained.[93]

Light hydrocarbons, having large absorption coefficients *in vacuo* in the UV region of the spectrum, have been determined with the aid of PID.[94] The detection limit with respect to methane was 8×10^{-7}%.

The operation of the detector under conditions corresponding to the generation of a negative signal by the diminution of the background current improves the selectivity and extends the scope of the photoionisation detection method, since it makes it possible, for example, to detect certain substances whose ionisation energies exceed significantly the energy of the emitted photons.

VI. The application of the photoionisation detector in the gas-chromatographic analysis of mixtures of organic and inorganic compounds

The high sensitivity and selectivity of the PID promoted its application primarily for the determination of impurities in complex multicomponent systems. The PID is particularly promising in the

analysis of substances in the environment: air, natural and waste water, soils, marine and lake deposits, etc.

Table 6 presents the characteristics of certain practical methods employing PID. It shows that the main components of air and water determined with the aid of PID are benzene, C_7-C_9 alkylbenzenes, halogeno-derivatives of these compounds, halogenoalkenes, and polycyclic aromatic hydrocarbons. The lowest detection limit of benzene in air using cryogenic concentration is 2×10^{-11}% (HNU Systems Detector with a 10.2 eV lamp),[74] while without concentration it amounts to 2.5×10^{-8}% (Photovac detector with a 10.9 eV lamp).[83] These figures are satisfactorily correlated, since the volume of the sample in the former case was 1 litre, while in the latter case it was 1 ml. The employment of high performance capillary columns and PID in which the volume of the working chamber was 30–40 μl for a minimal make-up gas flow rate or even in its absence made it possible to reduce still further the DL. The use of PID for the determination in air and aqueous media of alkylbenzenes, chloroalkenes, chlorobenzenes, mercaptans, carbon disulphide, and formaldehyde as microimpurities is effective. A DL of 10^{-8}% has been attained for formaldehyde on a HNU Systems microprocessor gas chromatograph 301D fitted with a PID having an 11.7 eV lamp.[95]

At the same time, the increased sensitivity of the PID to compounds of certain classes sometimes does not compensate for the non-clear-cut gas-chromatographic separation. Thus the use of PID with a 9.5 eV lamp for the determination of polyarenes in atmospheric dust without preliminary fractionation of the sample components gives rise to difficulties. The background due to alkanes, cycloalkanes, ethers, etc. is too large to analyse reliably trace elements of polyarenes.[107] The authors recommend a more selective PID with an 8.3 eV lamp. An analogous result has been obtained in a study of synthetic fuel using a 10.2 eV lamp.[108] The employment of 9.5 and 8.3 eV lamps made it possible to ensure a higher selectivity in relation to polyalkylated arenes, napthalene, and *N*-heterocyclic compounds, but the absolute sensitivity was significantly lower than that obtained with a 10.2 eV lamp. The insufficient selectivity of the PID-10.2 to aromatic amines and their halogeno- and nitro-derivatives and the insufficient sensitivity of the PID-9.5 to nitro- and dinitro-amines precluded the determination of the admixture of these compounds in a complex mixture of subtances.[89] For this purpose, it was necessary to employ columns with a greater separating capacity or to fractionate more fully the sample before the gas-chromatographic analysis.

In order to increase the sensitivity of PID to steroids and alcohols, it has been suggested that they be converted with the aid of flophemesyl chloride (pentafluorophenyldimethylsilyl chloride) into the corresponding derivatives.[90,109] The DL of the initial substances and their derivatives, obtained on a capillary column (15 m × 0.33 mm) with SP 2100 at 275 °C and a PID at 300 °C, are compared in Table 7.

The possibilities for the quantitative determination of more than 40 chlorine-, sulphur-, phosphorus-, and nitrogen-containing pesticides and for the recognition of their structures using PID with two lamps (9.5 and 10.2 eV) have been investigated.[110,111] A highly sensitive method has been developed for the determination of methadone in blood plasma. When a PID and a capillary column (25 m × 0.2 mm) with VR-5 was used, the DL was 10 fg.[112] Significant advantages of PID with a 10.2 eV lamp compared with FID have been discovered in the analysis of the methyl esters of saturated and unsaturated $C_{16}-C_{18}$ essential acids. In terms of sensitivity, the PID was superior to the FID by a factor of five and in addition to experiments with the PID the molar response was found to vary linearly with the number of double bonds in the acid molecule.[91] It has been suggested that the PID be used for the continuous monitoring of the content of epoxyethane in air[113] and for the determination of PH_3,[114] amines,[115] light hydrocarbons, arsine, phosphine, hydrogen sulphide, carbon disulphide, dimethyl sulphoxide, and chlorofluorohydrocarbons.[116] A portable Photovac 10A10 chromatograph, fitted with (0.25–4) m × 2.5 mm Teflon columns with SE-30 or CSP-20M, deposited on Chromosorb GAWDMCS, was used in the last case. The separation was carried out at room temperature. The detection limit for chlorofluorohydrocarbons was 10^{-8}%. In PID, new chemically bound stationary phases were tested for DB-624 capillary columns[117] and for HNU-permabond packed columns.[118] The phases proved to be extremely effective for the determination of polyarenes and chlorophenols[118]—the principal contaminants of the environment.[117] The piezoelectric detector was tested with the aid of the PID.[119]

Table 7. Detection limits of steroids and their derivatives.

Compound	Detection limit, pg	
	initial compounds	derivatives
Androsterons	33.3	6.2
Testosterone	55.4	13.9
Cholesterol	ND*	21.2
Ergosterol	ND*	39.5
Oesterone	61.6	8.1
Oestradiol	69.0	10.1
Etisterone	ND*	29.9

*ND – not detected.

The PID has come to be widely used in specialised gas chromatographs and systems. A method has been described[120] for the identification of 40 solvents ranging from n-pentane to 1,1,2,2-tetrachloroethane, including aliphatic hydrocarbons, arenes, alcohols, ketones, etc., on a Nordion/HNU Micromat two-channel chromatograph. The sample was separated on two parallel quartz capillary columns 25 m long, with SE-54 and Yukon 50. A PID with a 10.2 eV lamp was used. The identification was based on a retention index data bank.

Two PID with a non-separated emission and detection compartments[19] were built into a 4-channel multidimensional chromatograph.[27] The PID detected permanent gases and C_1-C_2 hydrocarbons after their separation on a micropacked column (2 m × 0.53 mm) with Porapak N or on a capillary column of the PLOT type (10 m × 0.32 mm) with 5 Å molecular sieves. Heavier hydrocarbons were determined on capillary columns with chemically bound stationary phases connected to two FID. The combination of FID and PID in a multidimensional chromatograph has been used to determine volatile impurities (including oxygen-containing compounds) in air.[121,122] Through a three-way connector, 6% of the gas stream emerging from the first packed column with 1,2,3-tri(2-cyanoethoxy)propane was directed into the PID and benzene and toluene were determined quantitatively, the formation of the required fraction being monitored at the same time, i.e. the

instant of its being directed to the cryogenic trap was determined. The trapped fraction was analysed in detail on a quartz capillary column (50 m × 0.3 mm) with OV-101 connected to the FID.

Attempts were made to use the PID-10.2 in hypercritical fluid chromatography.[54] A design for a PID with a hermetic seal, withstanding high pressures of the carrier gas, has been described. Tests of the PID showed that the sensitivity of the detector, determined with respect to benzene, falls sharply with increase in the CO_2 pressure: it is 4×10^{-4} C g^{-1} at a 1 atm pressure and 5×10^{-8} C g^{-1} at 100 atm. There is a corresponding increase in the DL—from 2×10^{-9} to 1.8×10^{-5} g s^{-1}. The authors explained the reduced sensitivity of the PID by the quenching effect:

$$M + h\nu \rightarrow M^+ + \bar{e}, \quad CO_2 + \bar{e} \rightarrow CO_2^-,$$
$$CO_2^- + M^+ \rightarrow CO_2 + M.$$

It has been concluded that the PID cannot compete with the FID in liquid chromatography.

Investigators,[87] who tested the PID (model 52-02 from the HNU Systems Company) with a 10.2 eV lamp at atmospheric CO_2 pressure, arrived at the opposite view. A pneumoresistance, heated to 400 °C, was mounted at the outlet from a micropacked column, while the outlet from the PID freely communicated with the atmosphere. Comparison of the PID with the FID in the determination of polyarenes, up to coronene, showed that the DL with the PID (0.2–1 ng) is significantly lower than with the FID. Furthermore, owing to the instability of the flame, particularly at a high CO_2 flow rate (20–70 ml min^{-1}), sharp deviations and a shift of the zero line were observed when the FID was used. An experiment involving the use of a PID in high performance liquid chromatography (HPLC) for the analysis of traces of organic compounds has also been described.[123,124]

VII. Multidetector systems

Different variants of multidimensional chromatography with several selective detectors have undergone a new development recently.[125] The substances emerging from the column pass simultaneously to several detectors connected in series or in parallel. The simplified chromatograms thus recorded reflect mainly the presence of substances to which a particular selective detector is sensitive. The case where virtually all the substances are detected by the detectors but the signal from each detector for the same substance is different is also important. Since in the series connection of the detectors the amount of the substance entering into each detector is the same while in the parallel connection it is possible to measure and take into account the ratio of the separated fluxes, the ratio of the signals due to the same substance from two detectors A and B is the ratio of the sensitivity coefficients. For stable characteristics of the detectors and for linearity of their response, this ratio is independent of the concentration of the substances being determined and is a constant suitable for identification. In order to increase the stability of the constants, the responses are normalised with respect to a selected standard:

$$K_i^{A/B} = (R_i^A/R_{st}^A)/(R_i^B/R_{st}^B),$$

where $K_i^{A/B}$ is the ratio of the normalised responses of the detectors A and B with respect to the ith substance, R_i^A and R_{st}^A are the responses (the peak area or height) of the detector A with respect to the ith substance and the standard respectvely, and R_i^B and R_{st}^B are the responses of the detector B.

As will be shown below, the values of $K_i^{A/B}$ differ appreciably for substances of different classes of chemical compounds and significantly less so for substances within a single class. The quantities $K_i^{A/B}$ are therefore used mainly for group identification. A universal analytical system has been developed in which the sensitivity ratios for the two detectors are used together with universal retention indices.[126]

Table 8. The values of $K_i^{PID/FID}$ for organic compounds.[75]

Compound	$100\ K_i^{PID/FID}$	Compound	$100\ K_i^{PID/FID}$
n-Pentene	2	Hept-3-ene	51
n-Hexane	4	Hept-2-ene	57
n-Heptane	7	2-Ethylhex-1-ene	57
n-Octane	8	α-Pinene	75
n-Nonane	14	β-Pinene	65
n-Decane	16	Vinyl chloride	53
n-Undecane	15	1,1-Dichloroethylene	190
2,3-Dimethylbutane	7	Trichloroethylene	300
2,3-Dimethylpentane	10	Tetrachloroethylene	290
2,2,4-Trimethylpentane	18	*cis*-1,3-Dichloropropene	124
3-Methylheptane	7	Acetone	160
2,2,5-Trimethylhexane	21	Butanone	153
Cyclohexane	25	2-Pentanone	105
Methylcyclohexane	36	3-Pentanone	141
But-1-ene	65	Propionaldehyde	84
Pent-1-ene	64	Butyraldehyde	60
Hex-1-ene	59	Isobutyraldehyde	67
Hept-1-ene	49	Isovaleraldehyde	66
Oct-1-ene	44	Valeraldehyde	56
Non-1-ene	52	Methanethiol	650
Dec-1-ene	36	Ethanethiol	350
Undec-1-ene	35	Butanethiol	133
Tetrahydrothiophen	185	n-Butylbenzene	66
Benzene	112	p-Diethylkbenzene	75
Toluene	100	Indan	80
m-Xylene	95	Naphthalene	123
o-Xylene	77	Chlorobenzene	150
p-Xylene	105	*m*-Chlorotoluene	135
Ethylbenzene	87	*o*-Chlorotoluene	124
n-Propylbenzene	79	*p*-Chlorotoluene	130
p-Ethyltoluene	79	*m*-Dichlorobenzene	154
1,3,5-Trimethylbenzene	117	*o*-Dichlorobenzene	137
1,2,4-Trimethylbenzene	81	*p*-Dichlorobenzene	155

Note. A 10.0 eV lamp was used; the standard was toluene

1. The photoionisation detector/flame inisation detector combination

The flame-ionisation detector (FID) is a universal detector with a high sensitivity and a wide linear dynamic range. One of the first two-detector combinations developed abroad[127] and in our country[128] and designed for identification incorporated a FID. The properties of PID and FID have been compared.[129] Table 8 presents the values of $K_i^{PID/FID}$ for oganic compounds. The PID/FID combination was first tested for the group identification of hydrocarbons and pesticides.[69] The values of $K_i^{PID/FID}$, normalised for C_5–C_8 alkanes, alkenes, and arenes, differ appreciably: <2, 2–4, and 5–10 respectively. For the sulphur- and chlorine-containing pesticides having aromatic and aliphatic carbon skeletons, the values of $K_i^{PID/FID}$ differ by a factor of 12–16, while pesticides with alkene structures have intermediate values of $K_i^{PID/FID}$. The possibility of the group identification of hydrocarbons has been investigated in numerous studies. Polotnyuk et al.[130,131] successfully used the PID-10.2/FID combination to assign the components of petrol [gasoline] to alkenes and cycloalkanes (K_i = 0.02–0.45), alkenes and cycloalkenes (0.4–0.65), and dienes and arenes

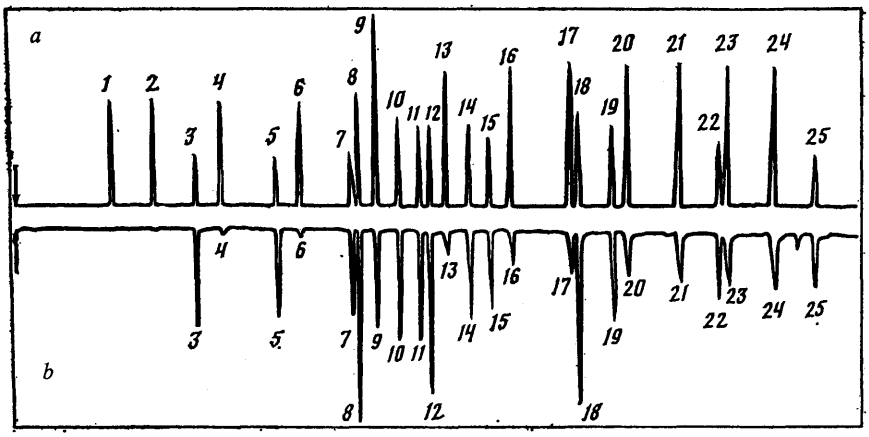


Figure 6. Chromatograms of a model mixture of hydrocarbons obtained with a FID (*a*) (8×10^{-9} A scale) and a PID-10.2 (*b*) (32×10^{-9} A scale).[57] 24 m × 0.5 mm × 1.1 μm glass capillary column with SE-54; carrier gas N_2; flow rate 1.6 ml min^{-1}; the stream of nitrogen from the column is divided between the detectors in proportions of 1 : 1; flow rate of the N_2 make-up gas for FID and PID 30 and 14 ml min^{-1} respectively; column temperature rise programmed between 40° and 270 °C at a rate of 6 K min^{-1}; temperature of detectors 270 °C; 0.12 μl sample injected directly into the column; *1*, n-C_5; *2*, n-C_6; *3*, benzene; *4*, n-C_7; *5*, toluene; *6*, n-C_8; *7*, ethylbenzene; *8*, *m*-xylene + *p*-xylene; *9*, n-C_9 + *o*-xylene; *10*, cumene; *11*, n-propylbenzene; *12*, mesitylene; *13*, n-C_{12}; *14*, *p*-cymene; *15*, n-butylbenzene; *16*, n-C_{11}; *17*, n-C_{12}; *18*, naphthalene; *19*, n-hexylbenzene; *20*, n-C_{13}; *21*, n-C_{14}; *22*, n-octylbenzene; *23* n-C_{15}; *24*, n-C_{16}; *25*, n-decylbenene.

(0.65 – 1.00) and demonstrated the effectiveness of this procedure for the refinement of the gas-chromatographic identification. According to the authors,[132,133,138] the ratios of the sensitivities of the PID and the FID combined with the retention indices ensure a reliable identification of the peaks. An experiment involving the group identification of alkanes (0 – 43), alkenes (44 – 48), and arenes (75 – 158) in $C_6 - C_9$ hydrocarbons present in air has been described.[55] Measurements have been made[57] of the quantities $K_i^{PID/FID}$ using PID-10.2 for methyl ethers and aldehydes (< 1) and alkanes, isoalkanes, naphthenes, and alcohols (1 – 6), alkenes (12 – 17), alkylbenzenes (6 – 17), and *N*-heterocyclic compounds (5 – 40). It was shown that, with increase in the molecular weight of the substances, the overlap of the $K_i^{PID/FID}$ ranges for different groups increases (Fig. 6). The photoionisation detector with a 9.5 eV lamp is more selective but its sensitivity is appreciably lower. The reliability of the group identification could be increased by employing two groups of tabulated values of $K_i^{PID/FID}$,[75] which assigned the test substances to halogenoalkanes, alkanes, cycloalkanes, trimethylalkanes, alkynes, alkenes, aldehydes, ketones, arenes, halogenoarenes, and sulphur-containing hydrocarbons. The substances emerging from the column during the first 17 min were identified in terms of one group of values, while those eluted after 17 min were identified in terms of the second group. The values of $K_i^{PID/FID}$ for these substances are listed in Table 8.

The same workers used a parallel PID/FID combination for the determination of $C_1 - C_{10}$ hydrocarbons in air.[134] The impurities were concentrated from air in a cryogenic trap and were separated on a capillary column 60 m long with SE-30. Alkanes, alkenes, and arenes were differentiated.

2. The photoionistion detector/electron capture detector combination

The high sensitivity of the ECD to organic halogeno-compounds makes it irreplaceable in the determination of halogenohydrocarbons in the environment. It has been acknowledged that the PID/ECD combination is promising for the determination of chlorine-containing compounds in atmospheric waste.[133]

In the study of Jaramillo et al.,[133] as in those of Polotnyuk et al.[131] and Towns et al.,[132] the values of $K_i^{PID/FID}$ served as an additional factor for the identification of the individual compounds. The combination of PID with ECD makes it possible to differentiate chlorobenzenes in terms of the number of chlorine atoms in the molecule.[135] The difference is based on weak dependence of the sensitivity of the PID-10.02 on the chlorine content (Table 4) and on the appreciable increase in the ECD signal on passing from chlorobenzene to dichlorobenzene and further to hexachlorobenzene. Accordingly, the PID/ECD signal ratio varies from 4.0 and 0.03. The values of $K_i^{PID/FID}$ are also used to identify hydrocarbons and their nitro-derivatives.[80,135] In this case, the sensitivities of the detectors change in the opposite direction. The values of $K_i^{PID/FID}$ are 25 – 78 for polyarenes, 0.3 – 0.6 for nitropolyarenes, 1 – 1.5 for nitrotoluenes, and 0.004 – 0.020 for dinitrotoluenes. Thus the identification of arenes and their nitro- and dinitro-derivatives is extremely reliable.

3. Combination of the photoionisation detector with electrical conductivity detector

Chlorine-containing compounds are detected selectively by the Hall or Coulson electrical conductivity detector (ECD). This feature of the ECD has been used to determine halogenohydrocarbons in

water, while light arenes were detected with a PID-10.2 connected in series with an ECD.[136] Three columns were used to separate halogenohydrocarbons and alkylbenzenes—the main column and the two special columns. The employment of selective detectors simplifies the chromatogram. Out of the 42 substances detected in the sample, the PID failed to detect 18 halogenohydrocarbons, while the ECD failed to detect nine alkylbenzenes. A similar problem was solved using the halogen variant of the ECD and a PID-9.5.[137] In a sample of soil water (volume 5 ml), it is possible to determine with the aid of the ECD chlorinated hydrocarbons at concentrations up to 0.6–4.0 μg litre^{-1}, while with the aid of the PID it is possible to determine C_6-C_8 arenes at concentrations up to 1.0–1.1 μg litre^{-1}.

Methods have been developed for the determination of volatile organic compounds in drinking water using gas extraction and concentration[138] and also in sewage on quartz capillary columns.[139] The influence of experimental parameters on the duration of analysis and the reproducibility of the determination of 36 chlorohydrocarbons and arenes in natural water using a series-connected combination of a PID and an ECD in capillary columns 0.32 and 0.53 mm in diameter has been investigated in detail.[140] It has been shown that the PID/ECD combination makes it possible to reduce the analytical time and the cost of analysis as a result of the high selective sensitivity of the PID to hydrocarbons and of the ECD to nitrogen-, sulphur-, and halogen-containing compounds.[141] The PID/ECD combination has been used successfully to determine DDT and DDE impurities (10 p.p.m.) in the presence of 1000 p.p.m. of toxaphene.[125] The use of a PID with a 9.5 eV lamp permitted the selective detection of *p,p'*-DDT and *p,p'*-DDE, which have aromatic rings in their structure, while the employment of the ECD permitted the detection of all the halogen-containing substances.

4. The combination of the photoionisation detector with other detectors

The series connection of PID with 10.2 and 8.3 eV lamps and of a thermionic detector tuned to determine nitrogen-containing compounds has been used for the structural identification of aromatic and aliphatic amines.[142] Fig. 7 shows that the combination of the PID-10.2 with a (N/P)-detector makes it possible to differentiate reliably hydrocarbons from amines, while the combination of the PID-8.3 with a (N/P)-detector makes it possible to differentiate primary amines from secondary and tertiary amines. The ratio of the PID signal to the signal of the (N/P)-detector is appreciably greater for tertiary amines compared with secondary amines (Table 9).

The development of an improved UV-detector based on the absorption of light in the far UV region and having a working chamber with a volume of 40 μl increased significantly the possibilities for its combination with PID fitted with 10.2 and 11.7 eV lamps.[143] The UV-detector detects certain Freons, methane, and water to which the PID-11.7 is almost insensitive. It is recommended that the PID/UV detector response ratio be used to identify low-molecular-weight hydrocarbons, aldehydes, alcohols, and sulphur-containing compounds.[86]

Combinations of PID fitted with lamps having different energies have been used to identify hydrocarbons. The PID-11.7/PID-10.2 response ratios proved suitable for the differentiation of alkanes, alkenes, cycloalkanes, and arenes.[72] The combination of PID fitted with 9.5 and 8.3 eV lamps is sensitive to the structure of polyarenes and can be used to differentiate isomers. For example, the PID-9.5/PID-8.3 response ratio is 13 for anthracene and 43 for phenanthrene.[144]

5. Combination of three detectors

The combination of PID with two detectors has been used to analyse organic impurities in air and different gases. The PID/FID/ECD combination has been used.[74,76,145,146] In this combination, the universal FID is designed to detect hydrocarbons, PID is designed to detect alkenes and arenes, and ECD is designed to detect halogenohydrocarbons, i.e. the entire set of the principal low-boiling compounds usually present in air.

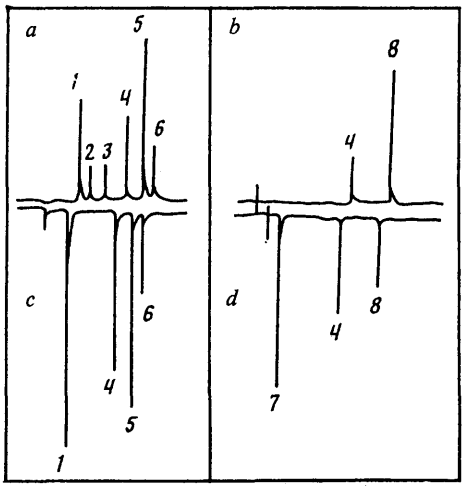


Figure 7. Chromatograms of amines obtained with a PID-10.2 (*a*), a PID-8.3 (*b*), and a (N/P)-detector (*c* and *d*); column 1.8 m long with Synerg C-AP at temperatures programmed from 80° to 190 °C at a rate of 15 K min^{-1} and with a helium carrier gas flow rate of 30 ml min^{-1}; *1*, n-heptylamine; *2*, n-dodecane; *3*, n-tridecane; *4*, di-n-hexylamine; *5*, dicyclohexylamine; *6*, dodecylamine; *7*, n-hexylamine; *8*, tri-n-hexylamine.[142]

Table 9. The ratio of the PID and (N/P)-detector signals for certain amines.

Compound	Signal ratio	
	PID-10.2 signal: (N/P)-detector signal	PID-8.3 signal: (N/P)-dector signal
Di-n-hexylamine	2.3	0.01
Tri-n-hexylamine	4.0	0.04
Dibenzylamine	6.4	0.004
Tribenzylamine	9.8	0.3

The stream of carrier gas emerging from the capillary column 60 m long and containing Al_2O_3/KCl was divided in proportions of 1 : 5 between ECD and PID + FID.[76] The impurities from one litre of air were concentrated in a cryogenic accumulator and C_1-C_2 halogenohydrocarbons were determined by the ECD with a DL in the range $1 \times 10^{-10}-9 \times 10^{-9}$%; benzene, C_3-C_8 alkenes and

alkanes, and C_1-C_3 chloroalkenes were determined by the PID-10.2 with a DL in the range $5 \times 10^{-12}-1 \times 10^{-8}$%, and C_2-C_8 aliphatic hydrocarbons and benzene were determined by the FID and a DL of $(1.2-5) \times 10^{-9}$%. A trap cooled to −173 °C was also used by Rudolph and Jepsen.[74] The detectors were connected in series. For an air sample volume of one litre, the DL for the detection of C_1-C_2 halogenohydrocarbons and CS_2 by the ECD was $2 \times 10^{-11}-3 \times 10^{-10}$%, the DL for C_3-C_6 hydrocarbons and certain chloroalkanes detected by the FID was $5 \times 10^{-10}-5 \times 10^{-11}$%, the DL for C_3-C_6 hydrocarbons and halogenohydrocarbons detected by the PID-11.7 was $2 \times 10^{-10}-2 \times 10^{-9}$%, and the DL for propene, butadiene, benzene, trichloroethylene, and CS_2 detected by the PID-10.2 was $2 \times 10^{-11}-3 \times 10^{-10}$%. The three detectors indicated made it possible to identify twenty organic compounds out of the 150 found in air.[146] The identification was based on the retention times and the detector response ratios. The advantages of the series connection of a UV-detector, a PID, and an FID have been examined.[147] The detector system has been recommended for the analysis of industrial gaseous waste and smoke and exhaust gases. It has been suggested that a combination of a PID, an ECD, and an ultrasonic detector be used for the determination of impurities comprising inert, corrosive, and combustible substances (at the level of p. p. m.) in different gases.[148] The characteristics of the detection of nitrogen, argon, hydrogen, oxygen, methane, ammonia, silanes, phosphine, arsine, etc. by the ultrasonic detector have been examined.

6. Devices for multidimensional detection

The combinations examined represent mechanical combinations of standard detecting devices. Multidimensional detectors, in which there are one or several detection zones combined in a single shell while the output signals reflect different properties of the detected molecules, have been developed vigorously recently. A design has been proposed for a detector with two chambers separated by a LiF or MgF_2 window in which the ionisation current and non-absorbed photons are recorded.[149] An example of a multidimensional detector, in which photoionisation is used and there is one detection zone, is provided by a device where the principal element is an evacuated chamber and a laser beam is used to ionise the compounds emerging from the column and entering the chamber and to excited their fluorescence.[150] The total electron current is measured with the aid of an electrode placed in the chamber. The fluorescence emitted is detected by a photomultiplier. Positive ions enter a time-of-flight mass spectrometer tuned to a specific mass. Thus the device ensures the detection of three different angles. Its operation was tested on a model mixture of 64 compounds. The sensor measuring the total electron current detected 24 compounds, predominantly of an aromatic character, with a detection limit of 6−500 pg. The mass detector had a significantly greater sensitivity: the detection limit varied from 1 to 63 pg. The fluorescence signal arose from 15 substances. The use of a controllable vacuum UV laser is in general extremely promising for photoionsation detection, because it increases the spectral selectivity and ionisation efficiency, reduces the detection volume, and creates the possibility of measuring the ionic mobilities. The PID constructed on the basis of these principles make it possible to detect polycyclic arenes with the detection limit of 0.3−50 pg.[151]

---o0o---

Photoionisation sensors are some of the principal detectors in gas chromatographs together with FID, ECD, (N/P)-detectors, and the katharometer. The high sensitivity to many organic and inorganic compounds (the sensitivity is in fact highest to certain classes of compounds) together with a pronounced selectivity and a wide linear dynamic range constitute the advantages of the use of PID in gas-chromatographic analysis. Important features of PID are the possibility of the specific regulation of the selectivity by employing UV lamps with different emission energies and also an increased sensitivity to the structure of the carbon skeleton of the molecule. The use of new materials, the improvement of the design, and an increase in the operating life of the lamps are the principal ways of improving the operating characterisics of PID and of securing reproducible detector signals. The development of detectors based on laser multiphoton ionisation is also promising.

References

1. S E Lovelock *Nature*, 1960, **186** 401
2. *Series HNO 300 Chromatographs.* Publicity leaflet from the HNU Systems Company, 1988
3. *The Varian 3600 Chromatograph.* Publicity leaflet from the Varian Company, 1988
4. *The DI-200 Chromatograph.* Publicity leaflet from the Delsi Company, 1988
5. *The Model 421 Chromatograph.* Publicity leaflet from the AID Company, 1987
6. L Ya Gavrilova, V I Zheivot, O A Emel'yanova *Usp. Khim.*, 1984, **53**(12) 2078 [English translation in *Russ. Chem. Rev.*, 1984(12)]
7. P Verner *J. Chromatogr.*, 1984, **300** 249
8. J N Driscoll *J. Chromatogr. Sci.*, 1985, **23** 488
9. M E Akopyan *Fizika Vakuumnogo Ul'trafioletovogo Izucheniya* (The Physics of Vacuum Ultraviolet Radiation), Izd. Naukova Dumka, Kiev, 1974, p. 113
10. G V Marr *Photoionisation Process in Gases*, Acad. Press, New York, 1968, 268 pp
11. F I Vilesov *Usp. Fiz. Nauk*, 1963, **81** 669
12. M E Akopyan, Yu L Sergeev, F I Vilesov *Khim. Vys. Energii*, 1970, **4** 305
13. M Yamane *J. Chromatogr.*, 1963, **11** 158
14. M Yamane *J. Chromatogr.*, 1964, **14** 355
15. S Roesler *Anal. Chem.*, 1964, **36** 1900
16. D C Locke, Y E Meloan *Anal. Chem.*, 1965, **37** 389
17. Y C W Price, D C Fenimor, P G Simmonds, A Zlatkis *Anal. Chem.*, 1968, **40** 541
18. J Rosiek, W Gucowski, S Lasa *Chem. Anal.*, 1976, **21** 1251
19. K Kawazoe, T Kamo, Y Takata, N Shikama *Bunseki Kagaku*, 1985, **34** 309
20. N A Spivak *Zh. Anal. Khim.*, 1982, **37** 759
21. R R Freeman, W E Wentwork *Anal. Chem.*, 1971, **43** 1987
22. Europe. P. 0 184 912.
23. Q Jin, G Yang, Z Guo, J Lio *J. Microchem.*, 1987, **35** 281
24. R C Leveson, N Y Barker *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 238
25. J Meek, J Craggs *Electrical Breakdown in Gases* (Translated into Russian), Inostr. Lit., Moscow, 1960, 605 pp
26. US P. 4 266 196

27. H Tani, M Furumo *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1986, **9** 712
28. USSR P. 160 032; *Byull. Izobret.*, 1964, (2)
29. J Sevčic, S Krysl *Chromatographia*, 1973, **6** 375
30. N Ostojic, Z Sternberg *Chromatographia*, 1974, **7** 3
31. J N Driscoll, J B Clarici *Chromatographia*, 1976, **9** 567
32. J N Driscoll, S Ford, L Jaramillo, et al. *Am. Lab.*, 1978, **10** 137
33. J F Rabek *Experimental Methods in Photochemistry and Photophysics* (Translated into Russian), Izd. Mir, Moscow, 1986, 608 pp
34. P Marneck *J. Opt. Soc. Am.*, 1965, **55** 921
35. L P Shishatskaya, P A Tsiryul'nik, V M Reiterov, et al. *Optiko-Mekhanicheskaya Promyshlennost'*, 1972, No. 10, p. 69
36. A R Oyler, D L Bodenner, K J Welch, et al. *Anal. Chem.*, 1978, **50** 837
37. A N Freedman *J. Chromatogr.*, 1982, **236** 11
38. B I Khrushch, Yu A Ershov, A M Lyulichev, et al. *Khim. Vys. Energii*, 1977, **11** 332
39. I V Smushkov, L M Soifer, M I Shakhnovich *Kristallicheskie Opticheskie Materialy dlya Vakuumnoi Ul'trafioletovoi Oblasti* (Crystalline Optical Materials for the Vacuum Ultraviolet Region), Izd. Nauka, Leningrad, 1986, 59 pp
40. V S Letokhov *Lazernaya Fotoionizatsionnaya Spektroskopiya* (Laser Photoionisation Spectroscopy) Izd. Nauka, Moscow, 1987, 308 pp
41. A I Zaidel', E Ya Shpaider *Vakuumnaya Spektroskopiya i Ee Primenenie* (Vacuum Spectroscopy and Its Applications), Izd. Nauka, Leningrad, 1967, 431 pp
42. S A Yakovlev *Optiko-Mekhanicheskaya Promyshlennost'*, 1978, (4) 52
43. L P Shishatskaya *Optiko-Mekhanicheskaya Promyshlennost'*, 1984, (9) 54
44. S A Yakovlev, I A Nevyazhskaya *Fotometriya i Ee Metrologicheskoe Obespechenie. Trudy 5-i Vsesoyuznoi Nauchno-Tekhnicheskoi Konferentsii* (Photometry and Its Metrological Basis. Transactions of the 5th All-Union Science and Engineering Conference), Izd. Nauka, Moscow, 1984, p. 209
45. Y N Davenport, E R Adlard *J. Chromatogr.*, 1984, **290** 13
46. B D Towns, J N Driscoll, D Conron *Abstracts of the Pittsburgh Conference and Expositions on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 419
47. US P. 4 398 152
48. US P. 4 413 185
49. R C Leveson, N Y Barker *Anal. Instrument.*, 1981, **19** 7
50. *The Model PI 52-02A Photoionisation Detector.* Publicity leaflet from the HNU Systems Company, 1988
51. J N Driscoll *Am. Lab.*, 1986, **18** 95
52. R Yoder, R Sacks *J. Chromatogr. Sci.*, 1987, **25** 21
53. S Kapila, C R Vogt *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1981, **4** 233
54. W Gmür, J O Bosset, E Plattner *Chromatographia*, 1987, **23** 199
55. W Nutmagul, D R Cronn, H H Hill *Anal. Chem.*, 1983, **55** 2160
56. *The Photoionisation Detector for the MGC 4000 Laboratory Gas Chromatograph.* Publicity Leaflet from the Chromatron Factory, Academy of Sciences of the German Democratic Republic, 1988
57. J A Yancey *Adv. Instrument. Proc. USA Intern. Conf. and Exbit., Philadelphia, 1982*, No. 37. Pt. 2, p. 547
58. L F Jaramillo, J N Driscool *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1979, **2** 536
59. USSR P 968 751; *Byull. Izobret.*, 1982, (39)
60. K Okazaki *Technology of Ceramic Dielectrics* (Translated into Russian), Izd. Energiya, Moscow, 1976, 336 pp
61. S S Vashchun, L I Voitenko, A A Melik'yan, et al. *Zavod. Lab.*, 1986, (11) 5
62. DDR P. 232 992
63. USSR P. 1 430 862; *Byull. Izobret.*, 1988, (38)
64. USSR P. 1 444 659; *Byull. Izobret.*, 1988, (46)
65. J G Senum *J. Chromatogr.*, 1981, **205** 413
66. E W McDaniel *Collision Phenomena in Ionised Gases* (Translated into Russian), Izd. Mir, Moscow, 1967, 832 pp
67. P A Rodriguez, C L Eddy, C R Culberton *J. Chromatogr.*, 1985, **330** 365
68. *The PID-13 Photoionisation Detector.* Publicity leaflet from the Design Bureau of the Academy of Sciences of the Estonian SSR, 1986
69. J N Driscoll, J Ford, L F Jaramillo, et al. *J. Chromatogr.*, 1978, **158** 171
70. M E Casida, K C Casida *J. Chromatogr.*, 1980, **200** 35
71. M L Langhorst *J. Chromatogr. Sci.*, 1981, **19** 98
72. J N Driscoll *J. Chromatogr. Sci.*, 1982, **20** 91
73. J N Driscoll *J. Chromatogr.*, 1977, **134** 49
74. J Rudolph, C Jebsen *J. Environment. Anal. Chem.*, 1983, **13** 129
75. R D Cox, R F Earp *Anal. Chem.*, 1982, **54** 2265
76. F J Reineke, K Bächmann *J. Chromatogr.*, 1985, **323** 323
77. V B Stein, R S Narang *Bull. Environmen. Contam. Toxicol.*, 1981, **27** 583
78. V B Stein, R S Narang *Anal. Chem.*, 1982, **54** 991
79. J Meili, P Bronniman, B Brechbühler, et al. *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1979, **2** 475
80. I S Krull, M Swartz, R Hilliard, et al. *J. Chromatogr.*, 1983, **260** 347
81. A Korus, J Lasa *Rap. Inst. Fiz. Techn. Jadr. AGH*, 1986, **1**(199) 53
82. A Korus, J Lasa *EUROANALYSIS; 5: 5th European Conference on Analytical Chemistry, Cracow, 26–31 Aug., 1984*; Abstracts, Cracow, 1984, p. 69
83. A J Clark, A E McIntyre, J N Lester, et al. *Intern. J. Environment. Anal. Chem.*, 1984, **17** 315
84. J Yerpe, A Davis *J. Chromatogr. Sci.*, 1987, **25** 154
85. N E Hester, R A Meyer *Environment. Sci. Technol.*, 1979, **13** 107
86. J N Driscoll, B J Grimes, G F Hewitt *Kem. Kemi*, 1983, **10** 978
87. P G Sim, C M Elson, M A Quilliam *J. Chromatogr.*, 1988, **445** 239
88. P A Mulawa, S H Cadle *Anal. Lett.*, 1981, **14** 671
89. R M Riggin, T F Cole, S Billets *Anal. Chem.*, 1983, **55** 1862
90. I S Krull, M Swartz, J N Driscoll *Anal. Lett*, 1985, **18** 2619
91. *A Photoionisation Detector.* Publicity leaflet from the HNU Systems Company, 1978
92. W E Wentworth, A Tishbee, C F Batten, A Zlatkis *J. Chromatogr.*, 1975, **112** 229
93. S Kapila, D J Borhop, S E Manahan, G L Nichell *J. Chromatogr.*, 1983, **259** 205
94. I V Bondarenko, V L Budovich, M Ya Bykhovskii *Zavod. Lab.*, 1989, (1) 11

95. J H Becker, D Renaud, K Walsh, et al. *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J, 1986*, No. 194
96. S van Tassel, N Amalfitano, R S Narang *Anal. Chem.*, 1981, **53** 2130
97. R G Lewis, J D Mulio, R W Coutant, et al. *Anal. Chem.*, 1985, **57** 214
98. R W Coutant *Environ. Sci. Technol.*, 1982, **16** 410
99. N Langhorst, T Y Nestrick *Anal. Chem.*, 1979, **51** 2018
100. M Collins, N J Barker *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., 1983*, No. 619
101. T Dumas, E J Bond *J. Agric. Food. Chem.*, 1985, **33** 276
102. T Dumas *J. Chromatogr.*, 1982, **247** 289
103. D B Smith, L A Krause *Amer. Ind. Hyg. Assoc. J.*, 1974, **29** 709
104. N S Narang, B Bush *Anal. Chem.*, 1980, **52** 2076
105. L F Jaramillo, J N Driscoll *J. Chromatogr.*, 1979, **186** 637
106. T A Amin, R S Narang *Anal. Chem.*, 1985, **57** 648
107. S L Kopczynski *Anal. Lett.*, 1984, **17** 97
108. J A Yancey *Instr. Technol.*, 1983, **30**(4) 65
109. I Krull, M Swartz, J N Driscoll *Anal. Lett.*, 1984, **17** 2369
110. J N Driscoll, J Ford *29th Pittsburgh Conference on the State of the Art in Analytical Chemistry and Applied Spectroscopy. Cleveland, Ohio; Abstracts, Monroeville, 1978*, No. 6.
111. J N Driscoll, L F Jaramillo, R G Hanisch, S D Soileaux *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1980*, No. 410
112. B Norlander, B Carlsson, A Bertler *J. Chromatogr. Biomed. Appl.*, 1986, **375** 313
113. J N Driscoll, E S Atwood, J Hayhurst *Int. Labmate*, 1988, **13** LG98
114. A Verstuyft *Rev. Am. Hyg. Assoc. J.*, 1978, **39** 431
115. G O Woods, J W Nicols *Los Angeles Alamos Sci. Lab. Project R-059, NJOSH-JA-77-12*, 1977
116. Y Kaneko *Nenryo Oyo bi Nensho; Fuel Combust.*, 1981, **48** 829
117. R R Freeman, R M A Lautano *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1986*, No. 1000
118. L F Jaramillo, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1980*, No. 413
119. M H Ho, G G Suilbault *Anal. Chem.*, 1983, **55** 1830
120. A Kiviranta, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1987*, No. 774
121. S Berg, A Jonsson *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1984, **7** 687
122. A Jonsson, S Berg *J. Chromatogr.*, 1983, **279** 307
123. D C Locke, B S Dhingra, A D Baker *Anal. Chem.*, 1982, **54** 447
124. J N Driscoll, D W Conron, P Ferioli, et al. *J. Chromatogr.*, 1984, **302** 43
125. I S Krull, M Swartz, J N Driscoll *Adv. Chromatogr.*, 1984, **24** 247
126. N F Belyaev, M S Vigdergauz *Zh. Anal. Khim.*, 1986, **41** 1882
127. A B Littlewood *J. Chromatogr.*, 1965, **3** 111
128. D N Sokolov, L K Golubova *Zavod. Lab.*, 1969, **35** (2)
129. H H Hill, M A Baim *Trends Anal. Chem.*, 1982, **1**(9) 206
130. V O Polotnyuk, I A Revel'skii, S A Leont'eva, A A Grinberg *Zh. Anal. Khim.*, 1984, **39** 529
131. V O Polotnyuk, I A Revel'skii, A A Grinberg, S A Leont'eva *Zh. Anal. Khim.*, 1985, **40** 511
132. B D Downs, J N Driscoll, E S Atwood, D Conron, R Hogan *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 477
133. L F Jaramillo, J N Driscoll, D Conron *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1981*, No. 864
134. R D Cox, K W Lee, R F Earp *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 782
135. M Swartz, Xie Kuang-Hua, R Hilliard, et al. *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 421
136. B Kingsley, C Inin, D Coulson, et al. *Ann. Arbor. Sci.*, 1981, **4** 132
137. T F Cole, R M Riggin, M P Miller *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 209
138. B B Bernard, R C Hall *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1988*, No. 767
139. J Butler, T Wilks *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1985*, No. 374
140. M Duffy, J N Driscoll, S Pappas, W Sanford *J. Chromatogr.*, 1988, **441** 73
141. W A McKinley, R Anderson, P W Thide *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 473
142. B D Towns, J N Driscoll *Am. Lab.*, 1982, **14** 59
143. J N Driscoll, M Duffy, S Pappas *J. Chromatogr.*, 1988, **441** 63
144. D W Conron, J N Driscoll, B D Towns *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 618
145. J N Driscoll, J K Marshall, L F Jaramillo, et al. *Am. Lab.*, 1980, **12** 84
146. J W Bonelli, B Kebbekus, J Kemp *179th ACS Nat. Meet. Houston, Texas, 1980. Abstr. Pap., Washington, 1980*, No. 58
147. P Ferioli, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1985*, No. 725
148. J Butler *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1986*, No. 110
149. Czech. P. 162 220
150. R L Dobson, A P D'Silva, S J Weeks, et al. *Anal. Chem.*, 1986, **58** 2129
151. C M Klimčak, J E Wessel *Anal. Chem.*, 1980, **52** 1239