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PHOTOIONIZATION DETECTION AND ITS APPLICATION IN GAS CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

Since the beginning of the development and application of gas chromatography as an analytical and preparative technique, much attention has been paid to the detection aspects of the chromatographic system: optimization of detectors and the development of more suitable detection methods. This development resulted in a series of commercially available detectors, mostly based on ionization techniques [flame-ionization detection (FID), thermionic detection (TID), alkali flame-ionization detection (AFID), electron-capture detection (ECD) and helium detection (HeD) etc.]. More complex, more expensive but in some applications irreplacable are combinations such as of gas chromatography with mass spectrometry (GC–MS) or absorbance measurement on samples in the infrared region (GC–IR), possibly completed with signal processing by Fourier transformation (GC–FT-IR).

Further detectors have also been developed using other well known but underestimated detection methods or by modifying already applied principles. In so-called ion trap detection (ITD)[1], ionization is by electron impact (EI), common in mass spectrometry, with subsequent emission of ions from the ionization chamber into the detector (multiplier) according to the increasing ratio of molecular mass to charge (m/e); the more complex mass selective detector uses the same ionization technique but a more complex quadruple analyzer[2]. Non-radioactive ECD using a thermionic emitter as the source of electrons[3] or photoionization of an added doping agent[4] is

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a modification of ECD. One of the newest detectors is the FUV detector, using absorption of substances in the far UV region[5].

Photoionization detection (PID) belongs to those detection techniques using ionization by light radiation. This ionization principle was described by Lossing and Tanaka[6] in 1955; the practical application of this principle was subjected to extensive development before the first detectors of this type for commercial applications were designed.

The photoionization detector was mentioned in Lovelock's survey of ionization detectors in 1961[7] and the first detectors were constructed by Lovelock[8], Roesler[9], Lock and Meloan[10], Price *et al.*[11] and other workers[12–16]. In these detectors, an electric discharge in argon or helium was used as a photon source. The tube where the discharge took place was not separated from the compartment with the carrier gas flow, so that a reduced pressure had to be maintained in the overall detector space. Disadvantages of these detectors were also instability of the radiation source and hence of the detector response, the necessity for a constant supply of very pure gas into the discharge region, problems with clogging of this space with impurities and mechanical and operational complexity.

In the 1970s, photoionization detectors were designed for the first time with a UV source separated from the ionization chamber by an LiF, MgF_2 or other window by Ševčík and Krýsl[17] and, later, by other workers[18–21]. In contrast to the first types of photoionization detector, this detector was so improved within a short time that it could be used commercially and is now offered by several manufacturers.

The development of photoionization detectors is continuing. Kapila *et al.*[4] suggested a combination PID–ECD using a common ionization chamber and ionizing radiation. On switching, this detector can operate as in either the normal PID or ECD mode, where a doping agent ionized by UV radiation is used as a source of electrons. Such a detector possesses a high response, wide linear dynamic range and similar selectivity in comparison with ECD.

2. PRINCIPLE OF PHOTOIONIZATION DETECTION

Molecules of substances eluted by the carrier gas from the chromatographic column pass through the ionization chamber of the detector between a pair of electrodes. On the wall of the chamber is the window of the UV lamp. Vapours of ions arising in the ionization chamber are diverted to the electrodes and an ionization current is generated between them.

Ionization of compounds in the ionization chamber of the detector takes place owing to absorption of energy of photons emitted by the UV lamp:

$$AB + h\nu \rightarrow AB^* \quad (1)$$

$$AB^* \rightarrow AB^+ + e^- \quad (2)$$

and also by reaction with the excited molecules of the carrier gas:

$$N_2 + h\nu \rightarrow N_2^* \quad (3)$$

$$N_2^* + AB \rightarrow N_2 + AB^* \quad (4)$$

with subsequent reaction 2. Here the photon energy necessary for the ionization of a substance must be higher than its ionization potential. Ostojič and Šternberg[18] gave the following relationship for the number of ion pairs formed in unit time:

$$\frac{dN_i}{dt} = 2\,\sigma_i\,\varphi\{1 - \exp\,[-\sigma_t N(t)]\,l\}$$

where

σ_t = $\sigma_i + \sigma_e$;
σ_i = absorption coefficient for photoionization;
σ_e = absorption coefficient for processes other than photoionization;
φ = number of photons entering the ionization chamber of the detector in unit time;
l = optical path (length of the ionization chamber);
$N(t)$ = number of sample molecules in unit volume.

The above equation is an exponential relationship between the sample concentration in the carrier gas and the number of ion pairs that arise. If $\sigma_t N(t)\,l \ll 1$, which is the usual case, the exponential relationship is transformed into a linear one.

Ševčík and Krýsl[17] derived the following expression for the dependence of the current between the collecting and the reference electrodes of the photoionization detector:

$$i = \frac{I_v^0 p_v L l V_c\,[\mathrm{AB}]}{\frac{1}{\eta_v} + \frac{k_6}{k_2}\,[\mathrm{C}]}$$

where

[AB] = concentration of the ionizable substance (mol/l);
[C] = concentration of the carrier gas (mol/l);
p_v = area of ionization chamber (cm^2);
I_v^0 = intensity of light radiation (mol/sec);
L = Loschmidt constant ($2.69 \cdot 10^9$ atoms/cm^3);
l = thickness of the absorbing layer;
V_c = volume of 1 mole of the carrier gas under normal conditions (l/mole),

$$\eta_v = \frac{v_2}{v_2 + v_5};$$

v_2, v_5 = velocity of reactions 2 and 5 (see below);
k_2, k_6 = velocity constants of reactions 2 and 6 (see below).

They also found that the current (i) is a linear function of the concentration of AB at a sufficiently high voltage on the collecting electrode, a low concentration of AB in the carrier gas and at constant values of I_v^0, k_2, k_6 and C.

Reaction 6 is one of the reactions causing "quenching" of the excited molecules of AB or recombination of the ionized molecules:

$$AB^* \rightarrow A' + B' \quad (5)$$
$$AB^* + C \rightarrow AB' + C' \quad (6)$$
$$AB^+ + C + e^- \rightarrow AB' + C' \quad (7)$$

$$O_2 + e^- \rightarrow O_2^- \quad (8)$$
$$O_2^- + AB^+ \rightarrow AB' + O_2' \quad (9)$$

Quenching and recombination of molecules according to reactions 5–9 reduce the detector response for AB, the most efficient process being reaction 9. In the same manner, the presence of oxygen molecules reduces the detector response for flow-rates of vapours of some solvents and gases with ionization potentials higher than the energy of the radiation used. This typically results in reduction of the background current of the detector, which is the response of the detector to bleeding of the chromatographic column and traces of impurities in the carrier gas, during the passage of a solvent with a high ionization potential, leading to the formation of a negative peak at the beginning of the chromatogram (Fig. 1).

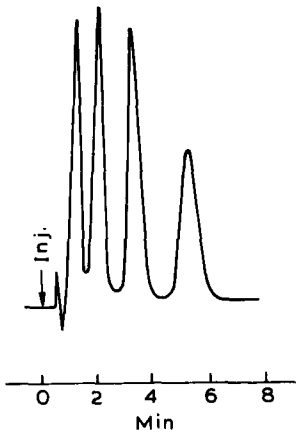

Fig. 1. Chromatogram of a mixture of C_{11} C_{14} hydrocarbons. Column, 80 × 0.2 cm I.D., Nickel 200, 3% Dexsil 410 on Gas-Chrom Q (120–140 mesh); carrier gas, nitrogen; column temperature, 150°C; photoionization detector (HNU 52-02), 10.2 eV lamp, temperature 250°C.

3. CHARACTERISTICS OF THE DETECTOR

3.1. Selectivity

As only substances with ionization potentials lower than or equal to the energy of the radiation used are ionized, the choice of the source giving radiation in a limited range of wavelengths permits a certain selectivity of detection.

Hydrogen-, helium- or argon-filled tubes are mostly used as radiation source in photoionization detectors. A hydrogen-filled discharge tube emitting a hydrogen

TABLE 1

SOME MATERIALS USED IN THE CONSTRUCTION OF UV-LAMP WINDOWS

Material	*Permeability limit*	
	nm	*eV*
LiF	1040	11.9
MgF_2	1120	11.1
CaF_2	1220	10.3
NaF	1320	9.4
BaF_2	1340	9.2
Sapphire	1425	8.7

band spectrum with the most intensive Lyman α-line of 121.6 nm with an energy of 10.2 eV is the most used. A source of energy 10.2 eV gives the most intense radiation; this is advantageous in trace analysis as the detector response increases with increasing intensity of the ionizing radiation. The choice of the material for the source window separating the discharge region from the ionization region enables the energy of the radiation entering the ionization chamber to be defined (Table 1). Using various materials, lamps with radiation energy up to 9.5, 10.0, 10.2, 10.9 and 11.7 eV have been manufactured. The choice of a suitable lamp determines the detection selectivity and permits the selection of a solvent that does not respond at the given energy of light radiation (Table 2). The term "that does not respond" is not, however, completely exact in this instance, as the typical negative peak mentioned occurs during elution of the solvent on decreasing the background current of the detector. This "negative response" is substantially lower than the detector response for ionized compounds and a return to the zero line is much faster; this can be preferably used for the detection of trace amounts of substances with short retention times, which can be separated from the tailing peak of the solvent only with difficulty when using other detectors.

TABLE 2

IONIZATION POTENTIALS OF SOME SOLVENTS

Solvent	*Ionization potential (eV)*
Toluene	8.80
Cyclohexane	9.01
Benzene	9.24
Trichloroethylene	9.45
Acetone	9.69
n-Hexane	10.17
Ethanol	10.48
Methanol	10.85
Methyl chloride	11.28
Chloroform	11.42
Acetonitrile	12.22
Water	12.59

TABLE 3

COMPARISON OF PID RESPONSES FOR VARIOUS COMPOUNDS

The response values were normalized to benzene = 6.0. Detection conditions: flow-rate, 30 ml/min of helium; column temperature, 110°C; PID temperature, 140°C; lamp, 10.2 eV. From Driscoll and Clarici[20].

Compound	*PID response*	*Compound*	*PID response*
Toluene	6.10	Acetone	3.04
Benzene	6.00	Cyclohexane	2.44
1,3-Butadiene	5.20	Acrolein	2.70
Diethyl sulphide	5.20	Trichloroethylene	2.76
p-Xylene	5.03	Vinyl chloride	2.44
Carbon disulphide	4.20	Tetrahydrofuran	1.86
Propylene	3.90	Pyridine	1.78
Methyl ethyl ketone	3.72	Ethylene	1.34
Allyl alcohol	3.40	*n*-Hexane	1.23
Dimethyl sulphide	3.25	Cyclohexane	0.90
		Ethanol	0.81

3.2. Sensitivity, linearity

According to literature data, the sensitivity of photoionization detection is approximately 10–50 times higher than that of flame-ionization detection. This high sensitivity of PID is due to the fact that ionization by light radiation proceeds in the absence of oxygen molecules, which limits the relatively efficient quenching by O_2^- ions and hence increases the efficiency of ionization. Simultaneously, the sensitivity of PID is different for various groups of substances (Table 3). For benzene the sensitivity of PID was reported to be 0.3 C/g, compared with 0.01 C/g for FID[22]. Several factors play important roles in establishing the sensitivity of photoionization detection in practice, as follows.

(a) Ionization potential of the substance. It has been found that the ionization efficiency increases with increasing radiation energy up to a certain limiting value when using ionizing radiation of various energies exceeding the ionization potential. When using a source with a certain radiation energy, substances with substantially lower ionization potentials give larger relative molar responses than substances with ionization potentials approaching to the energy of the radiation used.

(b) Number of carbon atoms in the sample molecule. Although this dependence is not as marked as with FID, the PID response increases with the increasing carbon number for various compounds. However, numerous compounds do not show this dependence (*n*-hexane, cyclic hydrocarbons, etc.).

(c) Carrier gas flow-rate. The response of the photoionization detector as a non-destructive detector is proportional to the concentration of the substance in the carrier gas and, therefore, it increases with decreasing flow-rate, in contrast to the flame-ionization detector, where the response is proportional to the mass flow into the detector and decreases with decreasing flow-rate. This fact is advantageous when using PID in capillary chromatography, and this is discussed in more detail in Section 5.

(d) Properties of the chromatographic column and purity of the carrier gas. Because of its high sensitivity, the photoionization detector is more sensitive to the

quality of the chromatographic column, leakage of stationary phase and impurities in the carrier gas. Considering that the detection limit depends on, among other factors, the background current of the detector[23], as the detector signal is the summation of the detector response to the substance to be determined and to other substances present (impurities, stationary phase), the partial pressure of which decreases during elution of the substance to be detected, it is obvious that the detection limit decreases with low leakage of the stationary phase when using purified carrier gas and suitable columns.

The linear dynamic range of the photoionization detector is given between 10^4 and 10^7 by various workers for various PID constructions; the best design configurations are superior in linear dynamic range to flame-ionization detectors.

Fig. 2 shows a comparison of the sensitivity and linear dynamic range of different detectors for GC. Photoionization detectors studied by various workers are compared in Table 4 and photoionization and flame-ionization detectors are compared in Table 5.

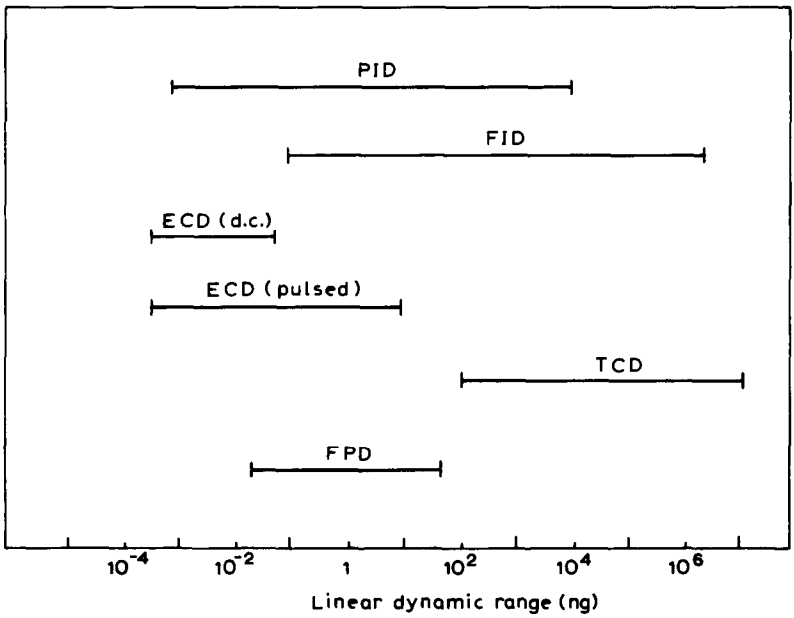

Fig. 2. Linear dynamic range of some detection methods for GC. TCD = Thermal conductivity detection.

3.3. Operating temperature

As can be seen from Table 4, the highest operating temperature of a photoionization detector depends on the material used for its construction. Detectors in which PTFE is used are operated at temperatures up to 250°C, whereas detectors of newer design in which ceramic materials are used can be operated at temperatures up to 300°C, so that the temperature of the column can be up to 280°C. This operating range is suitable for most gas chromatographic applications.

TABLE 4

COMPARISON OF CHARACTERISTICS OF SOME PHOTOIONIZATION DETECTOR CONSTRUCTIONS

Parameter	*Ref. 11*	*Ref. 16*	*Ref. 17*	*Ref. 18*	*HNU 52-02*
Ionization efficiency	10^{-3}	10^{-3}	$1.6 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$8 \cdot 10^{-4}$
Background current (A)	$2 \cdot 10^{-10}$	$6 \cdot 10^{-9}$	$9 \cdot 10^{-11}$	$3 \cdot 10^{-10}$	$1.5 \cdot 10^{-11}$
Linear dynamic range	10^5	10^4	10^5	10^5	10^7
Detection limit (g benzene)	$1 \cdot 10^{-12}$	$4 \cdot 10^{-11}$	$2 \cdot 10^{-11}$	$3 \cdot 10^{-10}$	$2 \cdot 10^{-12}$
Noise (A)	10^{-13}	$4 \cdot 10^{-11}$	$3 \cdot 10^{-13}$	$5 \cdot 10^{-13}$	$4 \cdot 10^{-14}$
Discharge	Ar	He	H_2	Ar, H_2	H_2
Closed discharge region	No	No	Yes	Yes	Yes
Maximum operating temperature (°C)	–	250	100	350	300

TABLE 5

COMPARISON OF SOME SPECIFICATIONS OF PHOTOIONIZATION AND FLAME-IONIZATION DETECTORS

Parameter	*Photoionization detector*	*Flame-ionization detector*
Linear dynamic range	10^7	10^6
Noise (A)	$4 \cdot 10^{-14}$	$5 \cdot 10^{-14}$
Background current (A)	$1.5 \cdot 10^{-11}$	$2 \cdot 10^{-11}$
Detection limit (pg benzene)	2	50
Sensitivity (C/g)	0.3	0.01
Maximum operating temperature (°C)	300	400

4. MAIN FIELDS OF APPLICATION

4.1. Analysis of noxious substances in industrial and environmental samples

Since the beginning of the development of the photoionization detector, its application in the analysis of industrial and environmental atmospheres has been considered. However, the first practical applications did not appear before the development of the first commercial detectors by HNU Systems (U.S.A.). One of the first applications was the detection of vinyl chloride monomer in the atmosphere by means of gas chromatography using PID[24]. The photoionization detector permitted the detection of vinyl chloride monomer at ppb (10^{-7}%) levels because of its 40-fold higher sensitivity to this compound, so that direct detection in atmospheric samples without previous concentration was possible.

The photoionization detector is also one of the most sensitive detectors for the detection of sulphur compounds, usually being ten times more sensitive than flame-photometric detection (FPD). In comparison with the FPD response, which has a parabolic course[25], the linear response of PID lies in the concentration range from tens of picograms to tens of micrograms in the sample. The lowest detected amounts of some low-molecular-weight sulphur compounds when using gas chromatography with photoionization detection are summarized in Table 6. The PID sensitivity for sulphur compounds was utilized for the detection of CS_2 after desorption from char-

TABLE 6

LOWER LIMITS OF DETECTION (LLD) FOR SOME LOW-MOLECULAR-WEIGHT SULPHUR COMPOUNDS BY PID

Compound	*LLD (pg)*
H_2S	15
$(CH_3)_2S$	20
$(CH_3)_2S_2$	22
CH_3SH	20
CS_2	30

coal using acetonitrile[26]. Smith and Krause[26] concluded that desorption of CS_2 with acetonitrile was complete and stated that the method permits detection down to 0.1 ppm of CS_2 in 10 l of air with a relative standard deviation of the overall detection method of 4.78%. Driscoll and Spaziani[27] used PID for detection of odorous sulphur compounds emitted from different industries, including H_2S, CH_3SH, $(CH_3)_2S$, $(CH_3)_2S_2$, CS_2 and other organic sulphur compounds, with a detection limit of 0.1 ppm.

High sensitivity has been achieved in determination of tetraethyllead using gas chromatography with a photoionization detector[28]. After adsorption on Amberlite XAD-2, tetraethyllead was desorbed by pentane and detected directly using gas chromatography with PID after separation on a column packed with 5% Carbowax 20M. The detection limit was 150 pg of tetraethyllead and the relative standard deviation was 25%.

Langhorst and Nestrick[29] used PID for the detection of mono- to hexachlorobenzenes at ppb levels in air. The method consists in adsorption of chlorobenzenes on Amberlite XAD-2, desorption with tetrachloromethane and gas chromatographic analysis with PID. A special column packed with Synerg C with PEG 40M (HNU Systems) was used for the separation of eleven chlorobenzene isomers. The efficiency of absorption and desorption in the concentration range from 5 ppb to 15 ppm was reported to be 95 ± 12%. The number of chlorine atoms on the benzene nucleus did not affect the detector response.

Oyler *et al.*[30] used PID for the GC detection of aromatic hydrocarbons and products of their reaction in drinking water. The substances were adsorbed in an auxiliary column packed with RP C_{18} and eluted with acetonitrile–water. The individual eluted fractions were injected directly into the gas chromatograph. Detection was 10–40 times more sensitive than when using flame-ionization detector; the detection limit ranged between 0.05 and 0.1 ng of the substance injected.

An interesting application of the photoionization detector is in the detection of traces of oil in carbon dioxide used as a cooling medium in atomic reactors[31], with a detection limit of 2 ppb. Here, one takes advantage of the fact the photoionization detector does not respond to methane, present in the cooling gas as an inhibitor of graphite corrosion by radiolysis, making the application of FID impossible.

Moeckel *et al.*[32] evaluated the application of PID in the detection of noxious substances in the atmosphere of pharmaceutical manufacturing plants. The very high response for compounds containing nitrogen and sulphur in their molecule and for hydrocarbons is important. The above workers developed a method for the detection

of noxious substances after adsorption on activated carbon or silica gel and desorption. The non-destructive character of the detector was also utilized for the further identification of unknown components using mass spectrometry.

The photoionization detector has also been preferred for use in the gas chromatographic analysis of pesticides, amines and nitrosamines[33–36] in environmental samples; these substances have attracted attention in recent years because of their potential carcinogenicity and mutagenicity. Driscoll *et al.*[33] detected some sulphur- and phosphorus-based pesticides using gas chromatography with PID after separation of the mixture in a column packed with OV-1 on Chromosorb W HP. When detecting pesticides with an aromatic nucleus in the molecule, the sensitivity of PID is comparable to that of ECD, whereas in the detection of aliphatic pesticides the sensitivity of PID is approximately ten times lower than that of ECD but is comparable to that of FPD.

The determination of organic amines using GC–PID after adsorption of the compounds on silica gel and their desorption with water–methanol was described by Woods and Nickols[34], who reported that PID is 15–66 times more sensitive than FID in this application. Some problems arose owing to the bad separation of underivatized amines and their tailing on the column used (Carbowax 20M + 2% KOH on Chromosorb W AW). The amines were derivatized to benzylidenes; according to more recent papers, this can be avoided when using columns with stationary phase covalently bonded to the carrier, *e.g.*, Synerg C-AP columns (HNU Systems).

Meili *et al.*[35] described the detection of nitrosamines in biological and environmental samples.

An important application of PID is the detection of trace amounts of organic nitro compounds in industrial and environmental samples and in biological samples. Many of these compounds, especially those containing condensed aromatic nuclei in the molecule, have various degrees of carcinogenicity and mutagenicity. Although other methods have been often used, *e.g.*, high-performance liquid chromatography (HPLC) and direct analysis using mass spectrometry (DI-MS), most methods are based on gas chromatography because of the lower limit of detection attainable and the availability of instruments that can be designed to be portable.

Langhorst[36] reported the relative molar responses (RMR) of some organic nitro compounds related to benzene when using PID. Krull *et al.*[37] considered problems in the detection of these compounds. They use PID–ECD and PID–ECD–FID combinations for the trace analysis of nitro compounds, to determine the detection limit of large amounts of aliphatic and aromatic nitro derivatives and to study methods for the detection of these compounds. For the separation of nitro compounds, like other workers, they preferred to use columns packed with a stationary phase covalently bonded to the carrier (Ultrabond 20 M and Permabond)[29,38].

In addition to the reported examples of the application of PID to the gas chromatographic detection of noxious substances in industrial and environmental samples, it has also been successfully used for the detection of phosphine[39], benzene and alkylbenzenes in air[40] and arsine, ammonia, hydrogen sulphide and emissions of sulphur oxides and other noxious compounds that often do not respond when using FID.

The photoionization detector has also been used in the construction of portable gas chromatographic analysers[41–43], where its simplicity, the need for only a single

carrier gas and its high sensitivity excel. Also, specialized gas chromatographic analysers for the analysis of toxic chemicals have been constructed using the advantages of PID, especially for the analysis of environmental samples[44].

4.2. Analysis of drugs in biological samples

Chemicals that have pharmacological effects at low concentrations in the organism, so that they have lower toxicity and secondary effects, often appear in concert with the development of new drugs. Especially with some drugs for blood circulation, psychopharmaceuticals and new anti-inflammatory drugs, the doses are often very low and the levels of the drugs in blood, plasma and serum range from one to several hundred nanograms per millilitre. This trend leads to an increase in the analytical requirements in pharmacological and pharmakinetic studies as the need arises to detect lower and lower concentrations of drugs in large excesses of other biological substances.

Research on new methods and detection possibilities has led on the one hand to a search for new, more effective methods for extraction and purification of samples for analysis and, on the other, to the application of new chromatographic methods and a search for more suitable detectors for this level of analyses.

In spite of some difficulties, gas chromatography has maintained its important position, alongside HPLC, in the detection of drugs in biological samples. Some new detection methods have been used, *e.g.*, combined GC–MS and GC–IR[45–49], but their expansion has been hindered by their complexity and expense. Combined GC–PID has many advantages in addition to its simplicity, one of the greatest being its higher sensitivity than FID. It has been reported that the sensitivity of PID is 8–16 times greater than that of FID for barbiturate drugs; the limit of detection where also the other conditions of detection play important roles (see Section 2.2) is 20–70 times lower[50]. The sensitivity of PID in individual instances is determined by the structure of the drug and it is especially advantageous that many drugs contain an aromatic nucleus in the molecule. It is well known that the sensitivity of PID to aromatic compounds is generally higher than that to the aliphatic compounds.

Another substantial advantage of PID is the small or zero response of the detector to many solvents. A very small negative peak of the solvent arising from the decrease in the background current of the detector permits the quantitative determination of small amounts of quickly eluting substances that are hidden in the tail of the solvent peak when using FID.

Finally, it has been observed that higher sensitivity of PID is not accompanied by an increased number of interfering substances. On the contrary, the background current of the detector is lower than the background current of the flame-ionization detector in detection in biological samples[50].

With respect to the other already mentioned advantages of this detector, such as simplicity, application of one carrier gas only and large linear range, the application of the photoionization detector in the analysis of drugs brings many advantages. Nevertheless, the number of papers published so far dealing with this problem is small. In addition to the mentioned detection of sixteen drugs of the barbiturate group in serum and urine, PID has preferably been used in our laboratory for the study of the metabolism of acetylsalicylic acid, for the detection of levels of benzo-

phenac, a non-steroid anti-inflammatory drug developed in the Research Institute of Pharmacy and Biochemistry, Prague, in the serum of volunteers after application in suppository form and for the detection of plasma levels of diclophenac (Voltaren) administered to volunteers per os[51]. In the last case, PID replaced the previously used ECD; its application was necessary because of the low concentration of the drug in the plasma, but this brought some problems with a broad range of concentrations in view of the small linear range of ECD.

The utilization of the possibilities and advantages of the photoionization detector in this field is a question for the immediate future and will, obviously, depend to a great extent on its commercial availability.

4.3. Identification of substances in mixtures

One of the most interesting applications of the photoionization detector is its use in the qualitative and quantitative analysis of substances in mixtures, and in this respect it is referred to as the "poor man's mass spectrometer". The recent application of several detectors connected in series often permits the qualitative identification of individual substances in a sample. Most often, a combination of a non-selective detector with a selective detector is used[52–59]. Application of the photoionization detector as a selective detector in combination with a flame-ionization or electron-capture detector brings many advantages resulting from the advantages of the photoionization detector itself, as already discussed.

With respect to the non-destructive character of the photoionization detector, the detectors are arranged in the following series in practical application: photoionization–flame-ionization detector, photoionization–electron-capture detector and electron-capture–photoionization detector. The measured parameters are the relative responses of the photoionization detector and the subsequent detector in combination, which are calculated from peak areas or heights and normalized to any *n*-alkane (*e.g.* *n*-hexane) or to another standard. The calculated "normalized PID/FID ratio" specified by some workers as the normalized relative response factor (NRRF) is characterized for certain groups of substances, and often also for individual substances in a given group. In common with the retention time of the unknown substance, it permits the identification or at least classification of a substance in a certain group.

This procedure with PID was first applied to the identification of hydrocarbons in complex mixtures, *e.g.*, in a light hydrocarbon feedstock for a synthetic natural gas plant[60]. In consideration of the responses of PID to hydrocarbons, it has been found that compounds having a PID/FID NRRF of 2–4 belong to alkenes, those having a PID/FID ratio of 5–10 to aromatic hydrocarbons and those with a PID/FID ratio of less than 2 to alkanes. A similar dependence has been found in a group of pesticides having sulphur or chlorine in the molecule; the normalized PID/FID ratio was 12–16 for aromatic pesticides, 5–10 for unsaturated aliphatic pesticides and 2 or less for saturated aliphatic pesticides.

This principle of identification has been subjected to some modifications and practical applications[44,61–63]. One of the most important papers in this field is that of Krull *et al.*[37], who used combined ECD–PID and PID–FID for the gas chromatographic detection of trace amounts of organic nitro compounds and for their

identification. The paper contains a large volume of data on the PID, FID and ECD responses for nitro compounds and the normalized ECD/PID ratios of these compounds, which can be used together with retention times for their identification.

An interesting modification is the connection in series of several photoionization detectors. A source giving various energies of radiation (*e.g.*, 9.5, 10.2 and 11.7 eV) is used in each detector[64]. The sample can also be analysed several times and the sources can be interchanged between the measurements. The response ratios obtained for each source are then used for the identification of alkanes, alkenes and aromatic and polyaromatic compounds in crude oil when using capillary gas chromatography.

4.4. Application of photoionization detectors in capillary gas chromatography

Capillary gas chromatography (high-resolution gas chromatography, HRGC) is a rapidly developing sphere of gas chromatography. Its practical use has been enhanced by recent significant progress such as the development of elastic silica (fused silica, vitreous silica), capillary columns, special methods of deactivation of the inner surface of capillaries, stationary phases bonded to the inner capillary surface (bonded phases, cross-linked phases) and new methods of sample proportioning, including their automation so that quantitative dosage of the sample is achieved and discrimination of substances with high boiling points can be prevented.

Problems remain in the application of a suitable detector. The most common is the application of a flame-ionization detector with respect to its high sensitivity, linearity and small dead volume attainable when the column exit is placed directly in the detector. Other detectors have also been modified for application in HRGC.

An advantage of the application of the photoionization detector in HRGC is, in addition to the advantages mentioned above, the fact that it is a concentration detector so that a low flow-rate of the carrier gas used in capillary columns, leads to a substantial increase in the sensitivity of the detector.

The first application of PID in HRGC was described by Jennings *et al.*[65], who used the photoionization detector in combination with glass capillary columns for the detection of flavours. Jaramillo and Driscoll[61] compared PID and FID in HRGC, especially the efficiency of the chromatographic system when using FID and PID expressed in terms of the plate height (H, mm) and efficiency expressed by the relationship

$$N = \frac{t_R^2}{\sigma_{tot,t}^2}$$

where t_R = retention time of the given substance and $\sigma_{tot,t}^2$ = time-based peak variance resulting from the contribution of the individual parts of the chromatographic system to this variance:

$$\sigma_{tot,t}^2 = \sigma_{inj}^2 + \sigma_{con}^2 + \sigma_{det}^2 + \sigma_{tc}^2 + \sigma_{col}^2$$

the right-hand terms being the peak variance contributions of the injector, connections, detector, time constants (electronics and detector) and column, respectively.

The dependences of the variance contribution of the cell volume of the photoionization detector to the chromatographic peak variance ($\sigma^2_{det,PID}$) and the efficiency of the chromatographic system on the flow-rate of the carrier gas were given and the conclusion was drawn that the difference between the efficiency of the system, N, when using PID and FID is higher at higher flow-rates of the carrier gas, ranging from 25% at flow-rates of 0.3 to 0.5 ml/min up to approximately 65% at flow-rates exceeding 2 ml/min.

The interesting conclusion was also drawn that the efficient cell volume variance contribution to $\sigma^2_{det,PID}$ is only one sixth to one quarter (35–54 μl) of the total volume of the cell (this volume was 225 μl in the detector used), depending on the flow-rate of the carrier gas.

Practical applications of the photoionization detector include the detection of crude oil components[61,64], where a similar resolution to that given by the flame-ionization detector application has been achieved. The selectivity of PID when using UV lamps giving various energies of ionizing radiation was used for the identification of the individual components of the mixture in nanogram amounts.

The non-destructive character of PID was employed by Jennings and Alyes[66] when collecting the individual fractions after the separation of mixtures on a capillary column for further identification or for subsequent connection to another capillary chromatographic column for investigation of the homogeneity of peaks eluted from the first column.

Kapila and Vogt[67] studied the possibility of application of combined PID–FID to HRGC in the same manner as it has been used for packed columns. They found that commercial photoionization detectors do not meet here the high requirements for tightness and small dead volume and, therefore, they suggested a new design of detector meeting these requirements. The PID–FID combination can be then used for the identification of substances in mixtures after analysis on a capillary column as described in the previous section.

These examples of the application of the photoionization are surely only the start of its application in HRGC. The rapid development of this method will, together with further development of the detector and, as we hope, more general commercial availability, contribute to further applications of combined HRGC–PID.

5. CONCLUSION

As already mentioned, more extensive application of the photoionization detector in gas chromatography began at the end of the 1970s. However, many important improvements in its construction and function to meet the requirements of practical use have been achieved. Many practical applications have been described. The first commercial photoionization detectors manufactured by HNU Systems were amongst the most progressive instruments for use in development and research. The advantages of the combination of these detectors with high-quality chromatographic columns resulted in the development of Permabond columns with very low bleeding of the stationary phase, which is covalently bonded to the carrier and has a high resolution in comparison with the usual columns. These columns have been successfully used in other applications of gas chromatography.

Despite the above facts and the evident advantages resulting from the appli-

cation of the photoionization detector, the number of applications is not yet very high, and practical applications relate rather to the illustration of possibilities than real routine examples. An exception is the detection of noxious substances in the environmental atmosphere, where the application of PID is included in the methods of the Environmental Protection Agency, the Occupational Safety and Health Agency and the National Institute of Occupational Safety and Health in the U.S.A.

Evidently, other factors are also important. One of them is the limited commercial availability of this detector, which is now offered as an integral component of gas chromatographs by a few manufacturers and as an accessory to other instruments (also older makes) only by HNU Systems. Another important factor is the relatively scarce published information about this type of detector; so far no comprehensive report has been published on its principles and applications (except a review by Hsueh and Chou[68] in an obscure journal).

Because of the advantages of the photoionization detector, an increasing number of applications and further development of its construction can be expected.

6. SUMMARY

The photoionization detector for gas chromatography became commercially available at the end of the 1970s. This review outlines the history of its development, the theory of its operation and some theoretical relationships describing its response to eluents. Also discussed are various features of the detector and some factors that influence its performance. Its applications in gas chromatography are reviewed, and advantages of its use in high-resolution gas chromatography are discussed.

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