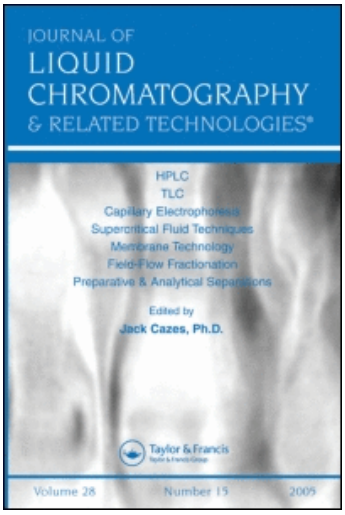

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PHOTOIONIZATION DETECTION IN PACKED-CAPILLARY LIQUID AND SUPERCRITICAL-FLUID CHROMATOGRAPHY

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ABSTRACT

A photoionisation detector (PID) was coupled to packed-capillary liquid and supercritical-fluid chromatography to study its performance. Several mobile phases were tested to evaluate the potential of liquid chromatography with photoionisation detection, LC-PID. The behaviour of the PID was not as good as in gas chromatography (GC), due to the absorption of photons by the mobile phase vapour. Therefore, the minimum detection limits (MDLs) were high compared to those in GC-PID, being at the low nanogram level for, e.g., ketones, aldehydes and amides. Coupling of the PID with supercritical-fluid chromatography (SFC) using modified carbon dioxide gave more satisfactory results. For aromatic compounds like phenanthrene and pyrene MDLs were found to

be 12 and 20 pg, respectively. These values were almost the same as found in GC-PID. Separation and detection of aliphatic C_4-C_{13} carboxylic acids and some organosulphur/phosphorus pesticides (disulfoton, ethion and sulfotepp) showed the possibility to detect several classes of compounds at the low nanogram level using methanol-modified carbon dioxide.

INTRODUCTION

The photoionisation detector (PID) is a commonly used detector in gas chromatography [1], but so far it is hardly applied in column liquid (LC) and supercritical-fluid (SFC) chromatography. However, since LC is the most versatile chromatographic separation technique for polar to medium polar compounds, combination of this technique with the PID is of interest. After the introduction of miniaturised LC, i.e. the introduction of columns with internal diameters of ≤ 1.0 mm, it became possible to use LC on-line with most gas chromatographic detectors. An excellent review on this topic is given by Kientz *et al.* [2]. The use of the PID in SFC is especially of interest when modified carbon dioxide is used as the mobile phase, since using a flame-ionisation detector (FID) then is impossible.

Reactions that can take place inside the ionisation chamber of a PID are schematically shown in Fig. 1. In Step 1 the photoionisable analyte (AB) absorbs UV light (wavelength is determined by the lamp choice). Ionisation (Step 4) of the excited analyte (AB*) occurs if the ionisation potential is equal to or smaller than the energy of the photons ($h\nu$) used. After ionisation AB^+ is directed by an electric field, present in the ionisation chamber, to the collector electrode (cathode) and the generated current, i, is measured (Step 9) [1]. There are however, several side reactions limiting the efficiency of these processes. The mobile phase (E) and the make-up gas (G) can also absorb UV light (Steps 2 and 3). The

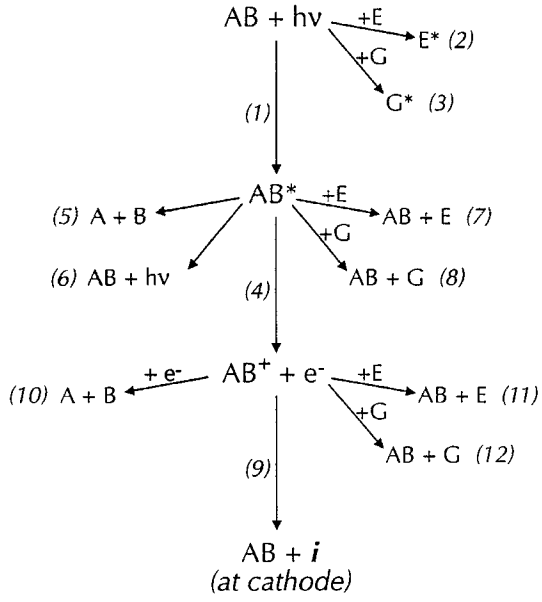

Figure 1. Reaction scheme for photoionisation detection. Abbreviations: AB, analyte; E, mobile phase and G, make-up gas.

excited AB* can, in addition to Step 4, dissociate to A and B (Step 5), emit fluorescence (Step 6), and be quenched by the mobile phase (Step 7) or by the make-up gas (Step 8) to AB. Furthermore, AB^+ can recombine with an electron (Step 10), with the mobile phase (Step 11), or wih the make-up gas (Step 12) to AB, instead of being directed to the collector electrode [5,8].

In the literature helium is frequently recommended as make-up gas because of its high ionisation potential (24.6 eV), which means that it can not be ionised under the conditions conventionally used. Moreover, it hardly absorbs at 10.2 eV (121 nm), the energy of the light source most frequently used, so Step 3 is almost negligible. The collisional quenching efficiency (Step 8) and the electron-capture efficiency (Step 12) are both

rather low and can be neglected also [8]. Another important aspect is the nature of the mobile phase. In the vapour state, normal-phase solvents like hexane and toluene can not be used with a 10.2 eV lamp because their ionisation potentials are 10.2 and 6.7 eV, respectively. Reversed-phase solvents like methanol, water and acetonitrile have, in the vapour state, ionisation potentials above 10.3 eV, but from literature it is known that they absorb rather strongly at 121 nm [9-11]. For carbon dioxide it is known that it hardly absorbs at 121 nm [12].

In principle, there are two possibilities to couple a chromatographic system with a PID. One is to use an interface to evapourate both the analytes and the mobile phase before their introduction into the detector. The other possibility is to allow direct introduction of the mobile phase containing the analytes into the detector, without evapouration (LC) or decompression (SFC) of the solvent.

Using the interface approach, Schmermund et al. [3] designed the first LC-PID system in 1975 and in 1984 Driscoll et al. [4] evaluated the applicability of LC-PID for several classes of analytes, reporting minimum detection limits (MDLs) of 3 - 700 ng. The best analyte detectability was found for halobenzenes. These studies were all performed using conventional-bore LC with flow splitting before detection. In 1987 De Wit and Jorgenson reported coupling of the PID with open-tubular LC columns (I.D. 5-10 μm). The MDL for toluene was 10 fmole and linearity was observed over three orders of magnitude [5].

The second approach was used by Locke et al. [7]. In this case only normal-phase LC can be used as the ionisation potential of water (liquid state) is very low (6.05 eV). Detection limits for polycyclic aromatic hydrocarbons (PAHs) varied between 4 and 250 pg, while the analyte detectability for substituted benzenes was 100-fold worse. Linearity was found over more than six decades. No response was found for phenols and chlorinated compounds.

The first report of using a PID for both packed-column and open-tubular SFC discussed three detectors designed for use with pressurized

mobile phases was rather disappointing [13]. With carbon dioxide the sensitivity for benzene was 10^6 times lower than when using an FID. Both argon and carbon dioxide were used as mobile phase; the detection limits found were 1000-fold lower when using argon instead of carbon dioxide. The dramatic difference was explained by different degrees of light absorption and different quenching effects.

The use of the PID under atmospheric pressure conditions in SFC seems promising. Sim et al. compared PID with FID detection for packed-column SFC and found that pressure programming had less effect on PID than on FID as the flame was quenched with the latter detector [14]. Detection limits for polyaromatic hydrocarbons were ca. 200 pg and linearity was observed over three orders of magnitude.

In the present paper the use of the PID is studied for both LC and SFC, and the results are compared with those obtainable in GC-PID. In both cases, packed-capillary columns (I.D. = 0.32 mm) were used without flow splitting and detection took place in the vapour phase. For LC-PID, this required the use of a simple interface to evapourate the LC effluent. Reversed-phase LC was performed because this mode allows the use of high-energy lamps. For SFC the use of packed columns meant that it was necessary to modify the mobile phase (carbon dioxide) with methanol and formic acid. In both cases the performance of the system was first tested with three polyaromatic hydrocarbons. Next, the potential of the system was evaluated by separating and detecting compounds without chromophoric groups.

EXPERIMENTAL

LC-PID Instrumentation

A Phoenix-20 syringe pump (Carlo Erba Strumentazione, Milan, Italy) was used to deliver the mobile phase. Samples were injected

manually using a 60 nl home-made injection valve (Free University, Amsterdam, The Netherlands). Fused-silica capillaries of different lengths (I.D. 0.32 mm; SGE, Ringwood, Australia and Chrompack, Middelburg, The Netherlands) were slurry packed with 5 μm LiChrosorb RP-18 (Merck, Darmstadt, Germany) or 5 μm RoSil C-8 (RSL, Eke, Belgium) and used as the analytical column. For detection a 52-02A PID (HNU systems, Newton, MA, USA) with a 9.5 or 10.2 eV krypton lamp was used. Signals were recorded on a Kipp & Zonen BD40 recorder (Delft, The Netherlands).

Fig. 2 shows the detector set-up. Via a low-dead volume union (Valco, Schenkon, Switzerland) the column was connected to a fused-silica capillary (SGE; I.D. 0.050 mm) which entered the glass-lined inlet (length 14.85 cm; I.D. 0.70 mm) of the detector through a capillary column adaptor. The fused-silica capillary was tightened in the capillary column adaptor by a vespel ferrule (SGE), while the other end of the adaptor was connected with a helium line from which the helium flows between the fused-silica capillary and the inner wall of the glass-lined inlet. The fused-silica capillary ended just beneath the top of the glass-lined inlet. Helium swept the mobile phase vapour into the ionisation chamber of the detector via the two holes present at the top of the glass-lined inlet and left the chamber via the glass-lined exhaust.

SFC-PID Instrumentation

A μLC-500 Micro Flow-syringe pump (ISCO, Lincoln, NE, USA) was used for mobile phase delivery and pressure control. All samples were introduced manually through a 60 nl Valco injection valve (Type CI4W) positioned on a PU 4500 gas chromatograph (Pye Unicam, Philips, The Netherlands). Fused-silica columns of different length (0.32 mm I.D.) were slurry packed with Rosil CN (5 μm; RSL), or LiChrosorb RP-18 or RP-8 (both 5 μm; Merck). The column temperature was controlled at 50°

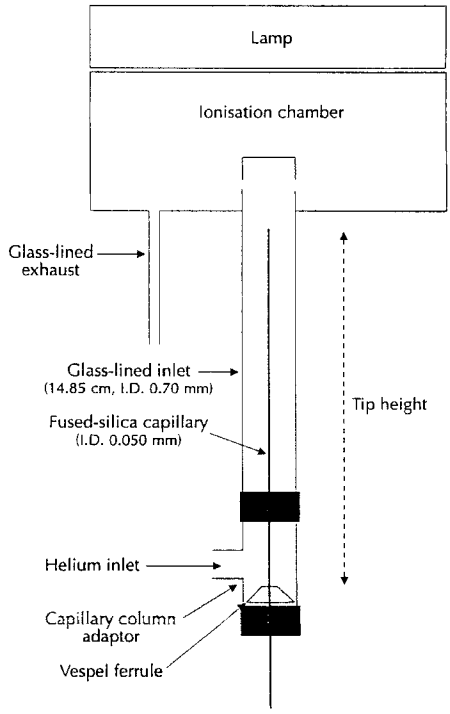

Figure 2. Design of LC-PID interface.

C by the GC oven. The PID was mounted in one of the detector positions of the GC, temperature being controlled by both the detector oven of the GC and the heater of the PID. Signals were recorded on a Kipp & Zonen BD40 recorder. Fused-silica capillaries (10 μm I.D.; Polymicro Technologies, Phoenix, AZ, USA) of different length were used for pressure restrictor or a 100 μm frit restrictor (Dionex/Lee Scientific, Salt Lake City, UT, USA) was shortened to give a flow rate of 5 μl min^{-1} at 150 bar. The restrictor was mounted in the same way as the fused-silica capillary in the LC-PID system described above. It was necessary to cool the syringe of the ISCO pump during the filling procedure in order to

obtain a maximum filling percentage. This was done by slightly releasing a nut at the top of the syringe and allowing the carbon dioxide to expand adiabatically. To obtain modified carbon dioxide a known volume of modifier was added to the syringe. The resulting percentages (expressed as % mol mol^{-1}) were calculated with interpolated carbon dioxide densities at various temperatures, taken from the tabulated data of Angus et al. [15], and the known densities of the modifiers used.

Chemicals

Helium (99.999%) and carbon dioxide (99.97%) were both obtained from Hoek Loos (Schiedam, The Netherlands). Hexane, water and methanol were of HPLC-grade and were obtained from J.T. Baker (Deventer, The Netherlands). 2-Propanol (99%), phenol (99%), acetonitrile (>99%), chloroform (>99%), N,N-dimethylformamide (>99%) and formic acid (98%) also came from J.T. Baker. 1-Butanol (99.7%), N-methylacetamide (98.5%), butanoic acid (>99%), hexanoic acid (>99%), heptanoic acid (>99%), octanoic acid (>99%), decanoic acid (>99%), dodecanoic acid (>99%), tridecanoic acid (>99%), naphthalene (>99%) and pyrene (>99%) were purchased from Merck. 2-Butanone (99%), 2-hexanone (99%), 2-heptanone (99%), acetamide (99%) and N,N-dimethylaniline (99%) came from Aldrich (Brussels, Belgium). N,N-Diethylformamide (>99%) was supplied by Lamers & Indemans ('s-Hertogenbosch, The Netherlands) and phenanthrene (99%) by Eastman Kodak (Rochester, NY, USA). 2-Pentanone (99%) came from Huls (Marl-Kreis - Recklinghausen, Germany). Propionaldehyde (97%), butyraldehyde (>99%), capronaldehyde (>98%) and valeraldehyde (98%) were purchased from Fluka Chemie (Buchs, Switzerland). Disulfoton, ethion and sulfotepp were gifts from the Governmental Food Inspection Service (Alkmaar, The Netherlands).

RESULTS AND DISCUSSION

LC-PID

The LC-PID system was optimised to obtain the best signal-to-noise ratio by varying parameters such as the detector temperature, tip height (i.e. length of the fused-silica capillary in the glass-lined inlet) and lamp intensity in the flow-injection mode. The injection valve was coupled directly to the PID via the interface capillary. Phenanthrene (11.6 ng/60 nl methanol) was chosen as test compound because of its high boiling point (340°C) and good PID response. With a tip height of 11.6 cm, a methanol flow of 3 μl min^{-1} and a helium flow of 26 ml min^{-1}, the detector temperature was varied over the range 180-300°C. It was found that the temperature should be kept at 200-250°C, i.e. significantly above the boiling point of the mobile phase, in order to prevent condensation, but it was not necessary to go up to 340°C (the boiling point of phenanthrene) because the analyte was swept into the ionisation chamber by the mobile phase vapour and the helium.

Next the influence of the tip height was investigated. When the tip position is not high enough less volatile compounds will not evapourate instanteneously at the tip end, and consequently band broadening will occur. On the other hand, when the tip position is too high, analytes can condense inside the fused-silica capillary and clog the capillary after evapouration of the mobile phase. For a relatively non-volatile compound like phenanthrene no peak broadening was observed when the tip was positioned above 8 cm. Clogging problems started to occur at tip heights of over 12.2 cm. For volatile compounds it was not necessary to optimise the tip height as no clogging was observed even at maximum tip height (13.5 cm).

Fig. 3 shows the effect of the lamp intensity on the signal-to-noise ratio (test compound, phenanthrene). The best ratio was obtained at the

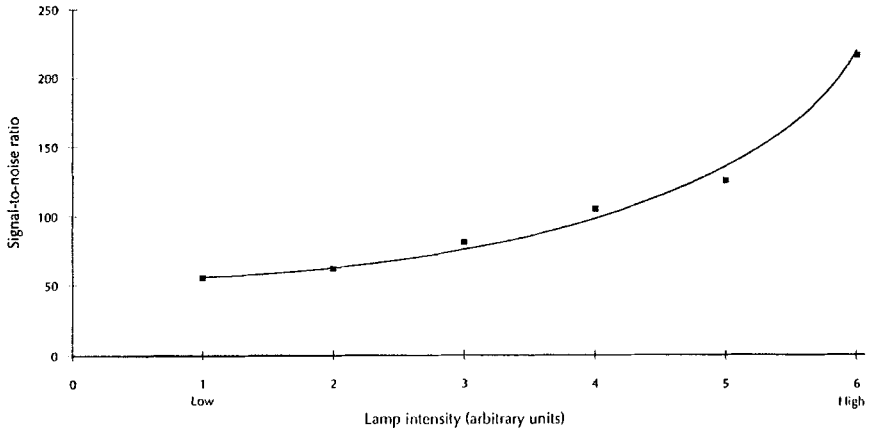

Figure 3. Signal-to-noise ratio as function of the lamp intensity in LC-PID. Conditions: injection volume, 60 nl; sample, phenanthrene, 11.6 ng; mobile phase, methanol 3 μl min^{-1} ; helium flow rate, 26 ml min^{-1}; lamp energy, 10.2 eV; detector temperature, 250°C; tip height, 11.6 cm.

highest lamp intensity, which illustrates the importance of a high photon flux because most of the photons are absorbed by mobile phase molecules.

The influence of the helium flow rate was studied in the LC mode. In the interface helium flows between the capillary and the glass-lined inlet and forces the mobile phase into the ionisation chamber. It is also used to cool both the lamp and the mobile phase in the capillary; the mobile phase evapourates only at the end of the capillary, just before the ionisation chamber. Fig. 4 shows the effect of varying the helium flow rate from 21 to 49 ml min^{-1} on the signal-to-noise ratio of a phenanthrene solution (25 ng/60 nl). The optimum helium flow rate was ca. 40 ml min^{-1}. For higher helium flow rates two opposite effects were observed. First of all, the helium dilutes the mobile phase; the background current reduction is therefore less pronounced (cf. below) and the signal-to-noise

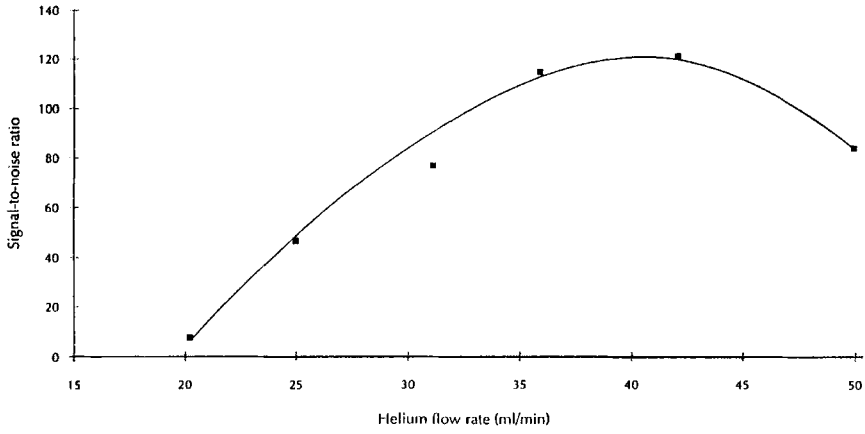

Figure 4. Signal-to-noise ratio as function of the helium flow rate in LC-PID. Conditions: packed-capillary column, 80 x 0.32 mm I.D., packed with 5 μm LiChrosorb RP-18; injection volume, 60 nl; sample, phenanthrene, 25 ng; mobile phase, methanol 3 μl min^{-1} ; lamp energy, 10.2 eV; detector temperature, 240°C; tip height, 8.3 cm.

ratio increases. Secondly, the analyte is in the detector for a shorter period of time which will decrease the signal-to-noise ratio.

Background current in LC-PID

The background current of some frequently used mobile phases was measured to study the influence on the PID response. This was done at mobile phase flow rates of 0, 1 and 3 μl min^{-1} using lamp energies of 9.5 and 10.2 eV. The helium flow rate was varied between 6 and 58 ml min^{-1}.

The background current is caused by the gold used to coat the ionisation chamber. The ionisation potential of gold is 4.71 eV, so both lamps are able to ionise the gold. The mobile phase vapour present in the

ionisation chamber can reduce the background current by absorbing the lamp radiation. This can be seen as a process competing with photoionisation of the analytes. The level of the background current is influenced by the efficiency of Steps 2 ($E + h\nu \rightarrow E^*$), 7 ($AB^* + E \rightarrow AB + E$) and 11 ($AB^+ + E + e^- \rightarrow AB + E$) of Fig. 1. Obviously these efficiencies should be as low as possible.

The background currents of the mobile phases at different mobile phase flow rates and lamp energies are listed in Table I. The background current with no mobile phase vapour present in the ionisation chamber (mobile phase flow rate, 0 μl min^{-1}) is 1.3 nA for the 9.5 eV lamp and 0.31 nA for the 10.2 eV lamp. The data in Table I show that at a mobile phase flow rate of 3 μl min^{-1}, the background current is reduced more than at 1 μl min^{-1}. This is due to the fact that at higher flow rates more mobile phase flows into the ionisation chamber and diminishes the ionisation of the gold. The only exception was found for pure water when using the 9.5 eV lamp. When the 10.2 eV lamp was used, some of the mobile phases were ionised. These are n-hexane, 1-butanol and 2-propanol with ionisation potentials of 10.18, 10.04 and 10.16 eV, respectively [8]. As a result these mobile phases yield a high background current. But even with these mobile phases the background current is lower at 3 than at 1 μl min^{-1}.

The effect of the helium flow rate on the ionisation efficiency of the 9.5 eV lamp is shown in Fig. 5. If there is only helium present in the ionisation chamber (mobile phase flow rate, 0 μl min^{-1}) there is no effect on the background current when changing the helium flow rate. When hexane was introduced as mobile phase the background current decreased, the decrease becoming larger at a higher flow rate. An increase of the helium flow rate led to higher background currents (cf. Fig. 5), because helium dilutes the mobile phase vapour.

In summary one can conclude that with flow rates of around 3 μl min^{-1} generally used in packed-capillary LC, the decrease of the

TABLE I

BACKGROUND CURRENTS FOR SEVERAL MOBILE PHASES AT DIFFERENT MOBILE PHASE FLOW RATES AND LAMP ENERGIES*.

Mobile phase	Background current (nA) at			
	lamp energy: 9.5 eV and mobile phase flow rate of:		lamp energy:10.2 eV and mobile phase flow rate of:	
	1 μl min^{-1}	3 μl min^{-1}	1 μl min^{-1}	3 μl min^{-1}
n-Hexane	1.2	0.7	2.1	1.2
Methanol	1.0	0.4	0.1	0.01
Methanol-water (70:30)	1.2	0.7	0.1	0.01
Methanol-water (30:70)	1.6	1.2	0.1	0.05
Water	1.8	2.0	0.1	0.02
Acetonitrile	1.1	0.8	0.02	0.01
Chloroform	1.0	0.7	0.1	0.03
1-Butanol-methanol-water (5:30:65)	1.6	1.3	0.5	0.4
1-Butanol	1.1	1.0	3.0	2.5
2-Propanol	1.4	1.2	1.5	0.9

* Conditions: LC column 8.0 cm x 0.32 mm I.D., packed with 5 μm LiChrosorb RP-18; detector temperature, 240°C; helium flow rate, 57 ml min^{-1}; tip height, 8.1 cm; n = 3.

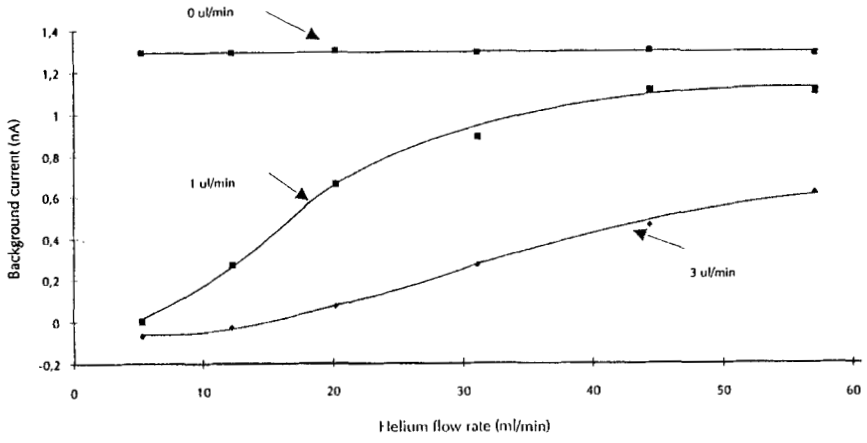

Figure 5. Background current of n-hexane versus different helium flow rates in LC-PID. Conditions: packed-capillary column, 80 x 0.32 mm I.D., packed with 5 μm LiChrosorb RP-18; lamp energy, 9.5 eV; detector temperature, 240°C; tip height, 8.1 cm.

background current will be such that a serious loss of detector sensitivity must be expected.

Analytical data

Calibration curves were constructed for several groups of compounds by injecting 60 nl samples into the system and MDLs (signal-to-noise ratio of 3) were determined. The helium flow rate was 40 ml min^{-1} and the flow rate of the mobile phase 3 μl min^{-1}. The detector temperature was set at 210°C. A 10.2 eV lamp was used because of its highest photon flux. Data concerning the calibration curves and the MDL values are given in Table II. The concentration range of the calibration curves is between 5 and 1200 ng per 60 nl injection. Each calibration curve consisted of 12 data points measured in duplicate, except the curves

TABLE II

MINIMUM DETECTION LIMITS (MDL) OF THE LC-PID SYSTEM*.

Compounds	MDL (ng)	Calibration curve $y = a (\sigma_a) x + b (\sigma_b)$	R^2
2-Butanone[I]	0.5	y = 3.45 (0.01) x + 0.4 (0.4)	0.999
2-Pentanone[I]	1.5	y = 2.25 (0.01) x + 0.7 (0.5)	0.999
2-Hexanone[I]	0.2	y = 1.77 (0.01) x + 0.6 (0.4)	0.999
2-Heptanone[I]	2.5	y = 1.18 (0.01) x + 0.3 (0.3)	0.999
Propionaldehyde[II]	1.0	y = 7.51 (0.09) x + 2.2 (0.9)	0.999
Butyraldehyde[II]	1.5	y = 5.46 (0.09) x + 1.8 (1.1)	0.998
Capronaldehyde[II]	2.0	y = 4.55 (0.15) x + 3.5 (2.1)	0.994
Valeraldehyde[II]	2.5	y = 1.31 (0.03) x + 1.1 (0.6)	0.997
Acetamide[III]	2.5	y = 3.18 (0.02) x + 2.6 (0.9)	0.999
N-Methylacetamide[III]	1.5	y = 3.76 (0.06) x + 8.0 (2.6)	0.997
N,N-Dimethylformamide[III]	1.5	y = 4.09 (0.04) x + 3.7 (1.7)	0.999
N,N-Diethylformamide[IV]	3.0	y = 8.16 (0.09) x + 4.4 (4.5)	0.999
Phenanthrene[V]	1.0	y = 1.81 (0.02) x - 0.2 (0.1)	0.999
Phenol[VI]	4.5	y = 1.63 (0.01) x - 0.5 (0.2)	0.999
N,N-Dimethyl-aniline[VII]	2.5	y = 8.95 (0.05) x + 5.7 (2.4)	0.999

* Conditions: injection volume, 60 nl; mobile phase flow rate, 3 μl min^{-1}; helium flow rate, 40 ml min^{-1}; lamp energy, 10.2 eV; detector temperature, 210°C unless otherwise stated.

I: conditions as in Fig. 6A. II: Conditions: LiChrosorb RP-18 column; mobile phase, acetonitrile-water (1:1); tip height, 10.1 cm; III: conditions as in Fig. 6B; IV: Conditions: RP-18 column; mobile phase, methanol; tip height, 8.1 cm; V: conditions: RP-18 column; mobile phase, methanol; tip height, 9.5 cm; detector temperature, 240°C; VI: conditions: RP-18 column; mobile phase, methanol; tip height, 8.0 cm; detector temperature, 240°C; VII: conditions: RP-18 column; mobile phase, methanol; tip height, 8.1 cm.

for the aldehydes which consisted of 10 data points measured in duplicate. Figs. 6A and 6B show LC-PID chromatograms for the separation of several ketones and amides, respectively.

In literature the MDLs of N,N-dimethylformamide and N,N-diethylformamide for LC-PID are 500 and 600 ng, respectively [3]. In other words, the data of Table II show values which are more than 100-fold improved. In the same paper the MDLs reported for 3-hexanone and anthracene are 700 and 75 ng, respectively. For similar compounds like 2-hexanone and phenanthrene the MDL values found with the present system are 4600 and 80 times lower. These rather remarkable gains in analyte detectability can not be explained by the fact that there is less mobile phase introduced into the detector because for phenol and N,N-dimethylaniline the MDL values found are the same as those published before [3]. It was also observed that better MDLs were invariably obtained using the 10.2 eV lamp, which is in contrast with the literature where the 9.5 eV lamp gave the best results for N,N-dimethylaniline and anthracene [3].

Although most of the compounds in Table II can also be determined by GC which provides more sensitive detection, separation by LC can be helpful because of a different selectivity of this technique [10]. On an average, the loss of sensitivity of LC-PID compared with GC-PID is about two orders of magnitude. In essence this means that LC-PID should be combined with on-line trace enrichment in order to perform trace analysis for compounds which can not be separated by GC and have no chromophoric group.

SFC-PID

Optimisation of the SFC-PID system

The composition of the mobile phase is the most interesting parameter when using PID in SFC. The 10.2 eV lamp was used

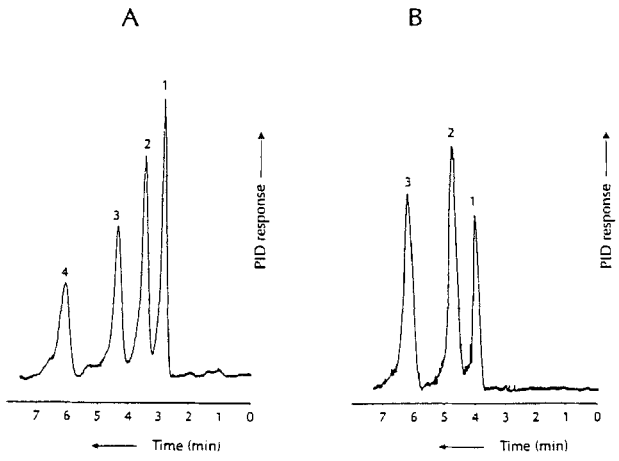

Figure 6. LC-PID of ketones (6A) and amides (6B). Conditions: helium flow rate, 26 ml min^{-1}; lamp energy, 10.2 eV; detector temperature, 240°C. (A) Packed-capillary column, 100 x 0.32 mm I.D., packed with 5 µm LiChrosorb RP-18; mobile phase, acetonitrile-water (55:45), 3 µl min^{-1} ; tip height, 11.4 cm; injection volume, 60 nl; sample, (1) 2-butanone, 85 ng; (2) 2-pentanone, 94 ng; (3) 2-hexanone, 82 ng; (4) 2- heptanone, 91 ng. (B) Packed-capillary column, 150 x 0.32 mm I.D. , packed with 5 µm Rosil C-8; mobile phase, acetonitrile-0.1mM formic acid (5:95), 3 µl min^{-1} ; tip height, 11.7 cm; injection volume, 60 nl; sample, (1) acetamide, 50 ng; (2) N-methylacetamide, 49 ng; (3) N,N-dimethylformamide, 47 ng.

throughout because of the results presented above for LC-PID. First of all the influence of the mobile phase composition on the backgound current was studied. In LC reduction of the background current caused by the mobile phases used was responsible for the low sensitivity of the detector. As expected from the literature [12], the introduction of carbon dioxide in the detector had no influence on the background current. The use of modified carbon dioxide reduced the background current of the 10.2 eV lamp with maximally 10% (ca. 4.7 mol% methanol in carbon dioxide, 5 µl min^{-1}; helium flow rate, 5 ml min^{-1}). Therefore, it was not necessary to

use high helium flow rates because helium only serves to lower the dead volume of the detector. Because, moreover, low mol% (< 2.5 mol%) of modifier are normally used in SFC, one may expect that the performance of the detector will not seriously be affected.

A problem in SFC is that the injection medium can not be the same as the mobile phase. Especially with the PID this problem is not easily solved. Common injection solvents like acetone and hexane can not be used because they cause a large PID response. Therefore, more polar solvents like ethanol, methanol or acetonitrile had to be used as injection medium. From among these solvents there is a slight preference for ethanol because it has least influence on the separation efficiency. However, even these solvents disturb the PID signal due to a solvent peak, because they do absorb light and this causes a decrease of the background current. As a consequence optimisation of the SFC-PID system could not be carried out using flow-injection.

Phenanthrene was chosen as test compound for optimisation of the system. When studying the influence of the detector temperature on the signal-to-noise ratio, it was found that an increase of the temperature from 200 to 300°C reduced this ratio 2-fold. It is therefore recommended to use a detector temperature which is as low as possible. The limitation in going to a lower detection temperature self-evidently is the nature of the analyte (e.g., volatility). The ensuing problem was partly circumvented by using the detector oven of the GC on which the PID was mounted, to heat up the glass-lined inlet of the PID in which the restrictor was situated.

Another parameter is the lamp intensity of the detector. The result was virtually identical with that observed for LC-PID shown in Fig. 3. That is, the highest lamp intensity should be chosen in order to measure under optimum conditions. One should add that working with high lamp intensities will reduce the lifetime of the lamp.

In Fig. 7 the influence of the helium flow on the signal of phenanthrene is shown for four different modified carbon dioxide phases.

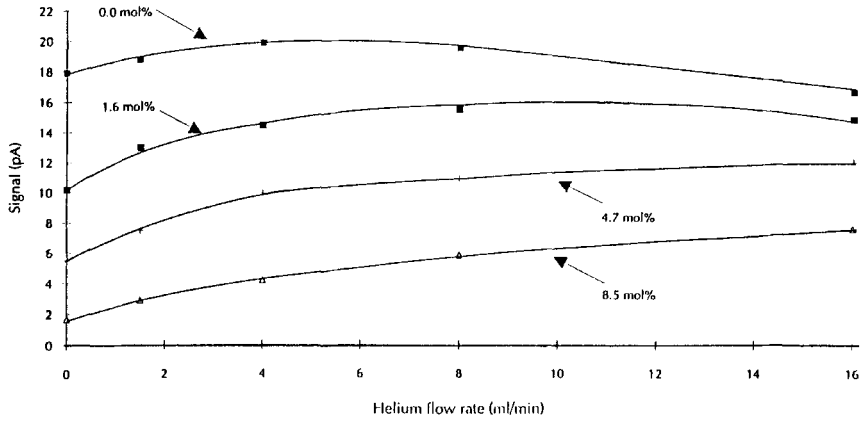

Figure 7. Influence of the helium flow rate on the signal of phenanthrene in SFC-PID for different modified mobile phases. Conditions: packed-capillary column, 150 x 0.32 mm I.D., packed with 5 µm LiChrosorb RP-18; column temperature, 54°C; restrictor length, 250 mm; pressure, 152 bar; injection volume, 60 nl; sample, phenanthrene, 450 pg in ethanol; detector temperature, 200°C; lamp energy, 10.2 eV; lamp intensity, high.

The influence of helium is rather limited when there is no methanol in the mobile phase. However, with an increasing flow rate of helium the residence time of the analyte in the detector is reduced and a somewhat lower signal is observed. If methanol is added to the mobile phase, a much stronger decrease of the sensitivity is observed which may be explained by increasing competition of side reactions such as Steps 2, 7 and 11 (cf. Fig. 1). In these instances, increasing the helium flow rate has no negative effect on the analyte signal intensity because it helps to reduce the amount of methanol in the detector. However, as Fig. 8 shows the real situation, expressed by the signal-to-noise ratio, is somewhat different: the increase in the flow rate obviously causes a noticeable increase of the noise level. Consequently, an optimum is obtained at about 2 ml min^{-1}.

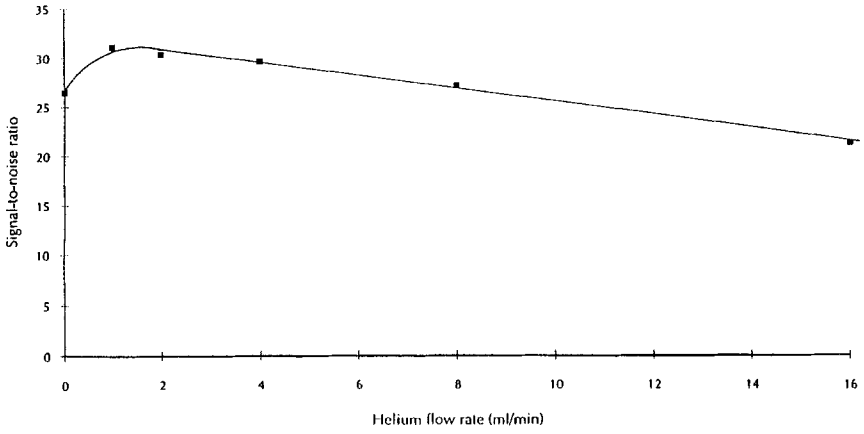

Figure 8. Signal-to-noise ratio as function of the helium flow rate in SFC-PID. Conditions: packed-capillary column, 150 x 0.32 mm I.D., packed with 5 µm LiChrosorb RP-18; column temperature, 54°C; restrictor length, 250 mm; pressure, 152 bar; mobile phase, 1.5 mol% methanol; injection volume, 60 nl; sample, phenanthrene, 130 pg in ethanol; detector temperature, 200°C; lamp energy, 10.2 eV; lamp intensity, high.

The influence of the mobile phase flow on the signal-to-noise ratio was studied using another model compound, butanoic acid. The data of Fig. 9, which was constructed at the optimal helium flow rate of 2 ml min^{-1}, show the influence at three different pressures. The highest signal-to-noise ratio is reached at the highest chromatographic pressure, which is of course due to the fact that peak broadening is larger at low mobile phase densities. As is to be expected, as regards the influence of the restrictor length, at a low mobile phase flow (long restrictor) signal-to-noise ratios are highest.

Analytical data

In order to test the analytical performance of the SFC-PID system using 1.5 mol% methanol in carbon dioxide as mobile phase, a mixture of

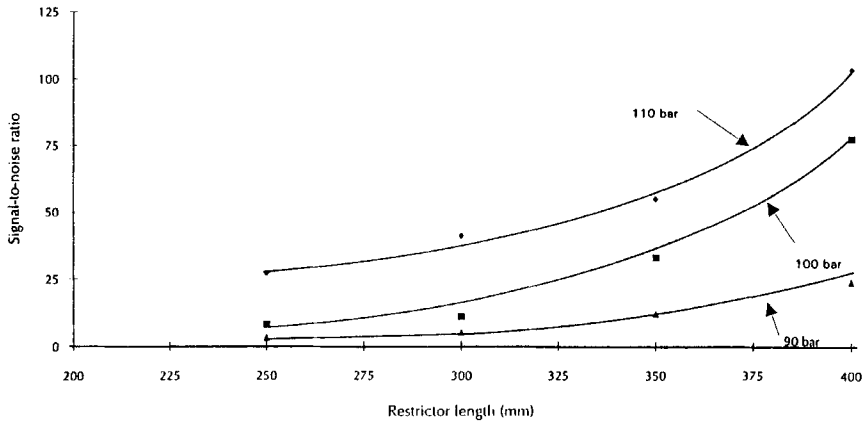

Figure 9. Signal-to-noise ratio of butanoic acid as function of the restrictor length in SFC-PID for different column temperatures and pressures. Conditions: packed-capillary column, 150 x 0.32 mm I.D., packed with 5 μ m LiChrosorb RP-18; column temperature, 40°C; mobile phase, 0.48 mol% methanol and 0.24 mol% formic acid; injection volume, 60 nl; sample, butanoic acid, 45 ng in ethanol; helium flow rate, 2 ml min^{-1}; detector temperature, 200°C; lamp energy, 10.2 eV; lamp intensity, high.

three PAHs was analysed. The PAHs were dissolved in ethanol, but as can be seen in the chromatogram the peak of naphthalene is disturbed by a solvent peak (Fig. 10). Therefore, the MDL for this compound could not be determined. For the other two compounds, phenanthrene and pyrene, the MDLs were 12 and 20 pg, respectively. The MDL for phenanthrene is 100-fold lower than that found in LC-PID (cf. above) and is in the same order as the MDL found with GC-PID [1]. The calibration curve for phenanthrene showed good linearity (see Table III); that is, use of modified carbon dioxide does not deteriorate the detector performance.

For a further demonstration of the potential of SFC-PID fatty acids were used as test analytes. For the separation of these compounds a strongly modified mobile phase is needed making it impossible to use FID

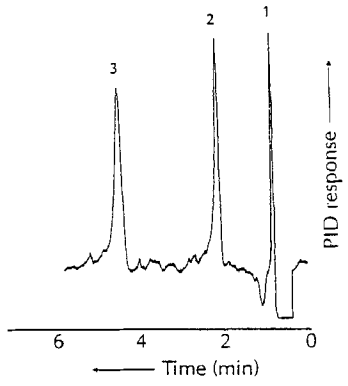

Figure 10. SFC-PID of some PAH's. Conditions: packed-capillary column, 150 x 0.32 mm I.D., packed with 5 μm LiChrosorb RP-18; column temperature, 54°C; restrictor length, 250 mm; pressure, 152 bar; mobile phase, 1.5 mol% methanol; injection volume, 60 nl; sample, (1) naphthalene, 200 pg, (2) phenanthrene, 220 pg and (3) pyrene, 290 pg in ethanol; helium flow rate, 1 ml min^{-1}; detector temperature, 200°C; lamp energy, 10.2 eV; lamp intensity, high.

detection. The acids also lack a chromophoric group necessary for UV detection. Formic acid was used as modifier in combination with methanol to obtain sufficient polarity of the mobile phase. The highly polar mobile phase used to separate the acids even allowed the use of pure water as injection solvent without a negative effect on the separation. In Fig. 11 the separation of butanoic, hexanoic, heptanoic and octanoic acid is shown. Obviously analysis of these rather polar compounds can be achieved without derivatisation. The calibration curves and the MDL values for these and some longer-chain fatty acids are included in Table III. Linearity is good; the detection limits are significantly higher than those found for phenanthrene and pyrene. This is due to the different molecular structures of these classes of compounds and consequently, different ionisation efficiencies [1].

TABLE III

MINIMUM DETECTION LIMITS (MDL) OF THE SFC-PID SYSTEM*.

Compounds	MDL (ng)	Calibration curve $y = a (\sigma_a) x + b (\sigma_b)$	R^2
Phenanthrene[I]	0.01	y = 1.47 (0.02) x - 7.0 (4.5)	0.999
Butanoic acid[II]	5.5	y = 0.16 (0.01) x + 5.0 (1.8)	0.995
Hexanoic acid[II]	3.5	y = 0.40 (0.01) x + 8.6 (2.6)	0.998
Heptanoic acid[II]	2.5	y = 0.88 (0.02) x + 6.1 (8.9)	0.995
Octanoic acid[II]	3.0	y = 1.31 (0.05) x + 7.7 (3.6)	0.995
Decanoic acid[III]	6.0	y = 1.77 (0.03) x - 5.0 (2.1)	0.998
Dodecanoic acid[III]	4.0	y = 2.33 (0.05) x - 0.4 (0.3)	0.999
Tridecanoic acid[III]	3.5	y = 2.17 (0.04) x - 0.3 (0.2)	0.999

* Conditions: LiChrosorb RP-18 column, 150 x 0.32 mm I.D.; injection volume, 60 nl; helium flow rate, 2 ml min^{-1}; lamp energy, 10.2 eV; lamp intensity, high; detector temperature, 200°C unless otherwise stated.

I: Conditions: column temperature, 54°C; mobile phase, 1.5 mol% methanol; pressure, 152 bar; restrictor length, 250 mm. II: Conditions: column temperature, 52°C; mobile phase, 0.48 mol% methanol, 0.24 mol% formic acid; pressure, 110 bar; restrictor length, 400 mm; detector temperature, 225°C. III: Conditions: column temperature, 54°C; mobile phase, 1.0 mol% methanol, 0.50 mol% formic acid; pressure, 152 bar; restrictor length, 250 mm.

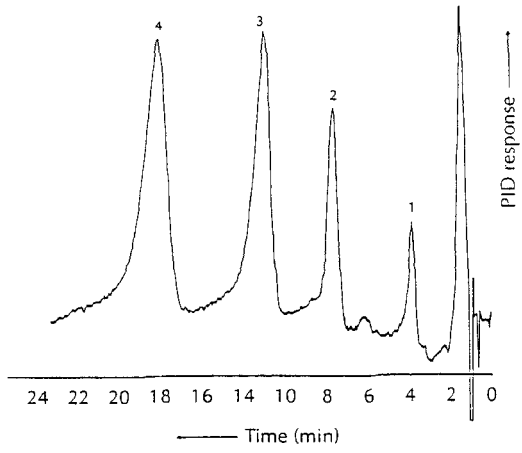

Figure 11. SFC-PID of some short-chain fatty acids. Conditions: packed-capillary column, 150 x 0.32 mm I.D., packed with 5 µm LiChrosorb RP-18; column temperature, 52°C; restrictor length, 400 mm; pressure, 140 bar; mobile phase, 0.48 mol% methanol, 0.24 mol% formic acid; injection volume, 60 nl; sample, (1) butanoic acid, (2) hexanoic acid, (3) heptanoic acid and (4) octanoic acid, all compounds 30 ng in ethanol; helium flow rate, 3 ml min^{-1}; detector temperature, 200°C; lamp energy, 10.2 eV; lamp intensity, high.

Finally, a mixture of three organosulphur/phosphorus pesticides, sulfotepp, disulfoton and ethion,was analysed (Fig. 12). They could be detected down to a level of 1 ng. Admittedly, this is much higher than reported for packed-capillary SFC with thermionic detection (ca. 50 pg; [16]). However, the result clearly illustrates the potential of the PID as a detector for widely varying classes of compounds. During this research two PID lamps were used as the 10.2 eV lamp already used in the LC-project lossed intensity during the SFC work. The new lamp is still in use after a working period of eight months. During the whole project (lC and SFC, two years) the PID broke one time down as the inlet in the ionisation

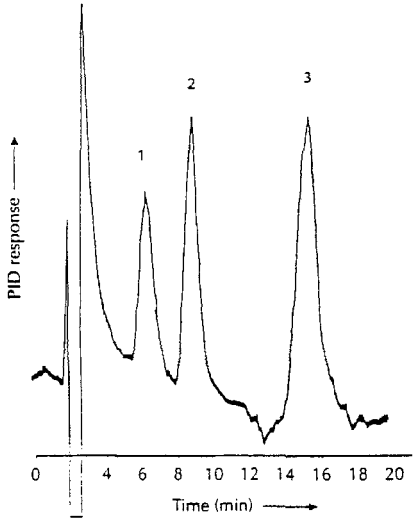

Figure 12. SFC-PID of some organo sulphur/phosphorus pesticides. Conditions: packed-capillary column, 210 x 0.32 mm I.D., packed with 5 μ m LiChrosorb RP-18; column temperature, 52°C; restrictor length, 280 mm; pressure, 133 bar; mobile phase, 0.97 mol% methanol; injection volume, 60 nl; sample, (1) sulfotepp, 23.7 ng, (2) disulfoton, 12 ng and (3) ethion, 24.7 ng , in ethanol; helium flow rate, 3 ml min^{-1}; detector temperature, 260°C; lamp energy, 10.2 eV; lamp intensity, high.

chamber was broken. Working with the PID in SFC is quite simple, the system can be used for months without changing any component, in LC the system is robust and care should be taken with the positioning of the interface capillary.

CONCLUSIONS

The present study shows that the optimum conditions for photoionisation detection in combination with packed-capillary LC are: a

10.2 eV lamp, a high lamp intensity, a helium flow rate of about 40 ml min^{-1} and a high temperature (between 200-250°C). The minimum detection limits for ketones, aldehydes and amides are in the low nanogram range. Although, for several analytes, detectability was 2 - 3 orders of magnitude better than reported in the literature, it is still true that the sensitivity of LC-PID is relatively low compared with GC-PID, the main problem being the quenching of the ionisation radiation due to the absorption of photons by the mobile phase. However, by combining LC-PID with, e.g., on-line trace enrichment the sensitivity problem can largely be solved. Besides, the tedious sample clean-up sometimes required for GC-PID, can then be avoided. Future work should be directed at exploring the practicality of such procedures.

Combining packed-capillary SFC with PID is a highly successful approach; the performance of the detector is almost the same as in GC. Under optimum conditions (10.2 eV lamp, high lamp intensity, helium flow rate of about 2 ml min^{-1}, temperature of 200°C) the MDLs for phenanthrene and pyrene are about 10 pg. Since strongly modified mobile phases can be used it is possible to perform separations of underivatised fatty acids and organosulphur/phosphorus pesticides down to the 2 - 5 ng level. Actually, this is the main - and extremely important - advantage of the PID over the more conventional FID.

One should of course realize that the main problem of (packed-capillary) SFC, i.e., the rather low injection volumes which are permitted, is not solved by utilizing another detector. A second problem with injection in SFC is the choice of the injection solvent. With injection volumes of typically ca. 60 nl and MDLs in the low-nanogram range, detection limits in the samples offered for analysis are in the 10 -100 ppm range. It is therefore interesting to briefly quote the developments made with regard to large-volume injections in SFC by using solid-phase extraction columns. With such an on-line set-up, sample injection volumes can be increased at least 1000-fold and no injection solvent is introduced into the detector [17]. In principle, this means that MDLs can

be improved down to in the range of 10 -1000 ppb. On-going research is directed at the further exploration of this approach.

Finally, it be interesting to mention that during the present study three PID lamps were used because the 10.2 eV lamp used for the LC work started to lose intensity during the SFC-orientated studies. The new lamp is still in use after a working period of 8 months. During the total work period, the PID broke down once because the inlet in the ionisation chamber broke. Working with the PID in SFC is especially simple; the system could be used for several months on end without exchanging any part of the total set-up.

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