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Note

Use of the photoionisation detector in packed-column supercritical fluid chromatography*

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Supercritical fluid chromatography (SFC) has recently enjoyed a resurgence in popularity and breadth of application, chiefly due to the work of Lee and co-workers[1–6] and other groups[7–10]. As a result of this work, a variety of detection systems has been employed as part of the chromatographic system. However, among the detectors employed, the photoionisation detector apparently has been used by only one group who had limited success[11]. The object of this study was to determine the applicability of the photoionisation detector as a detector in packed-column SFC, and to exploit the selectivity of the detector as an aid in the determination of polycyclic aromatic compounds (PACs) in marine sediments.

Our laboratory is involved in the production of reference materials*** for such determinations and this work is an extension of other investigations of ways to increase the reliability of measurements of PACs in sediment matrices.[12–15]

EXPERIMENTAL

The supercritical fluid employed was carbon dioxide, instrument-grade (Liquid Carbonic Canada), which was used without further purification. Some runs were performed using SFC-grade carbon dioxide (Scott Specialty Gases, Plumsteadville, PA, U.S.A.). No differences (*e.g.*, noise) were observed between the two gases. Fluid pressure was controlled by a Brownlee microgradient system (Brownlee Labs., Chromatography Division of Applied Biosystems; Santa Clara, CA, U.S.A.) configured for use with a single supercritical fluid. A. Rheodyne Model 7520 (Supelco Canada; Oakville, Canada) injector was used, fitted with a 0.5-μl injection loop. The photoionisation detector was a HNU Model PI-52-02 (HNU Systems, Newton, MA, U.S.A.), with a 10.2-eV lamp, tuned to perform to the manufacturer's specifications. Temperature control for the column and the detector interface was obtained by placing

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the column in a Varian Model 6000 gas chromatography (GC) oven and mounting the detector on the detector oven of the GC system. The outlet pressure restrictor was fabricated by crimping the end of a length of 0.010 in. I.D. thin-walled stainless-steel tubing. The gas flow-rate at the restrictor outlet varied from *ca* 20 ml/min at an applied pressure of 2000 p.s.i. to *ca.* 70 ml/min at 5000 p.s.i. with the column at 85°C and the column outlet at ambient pressure. It was necessary to maintain the restrictor and several cm of the 0.010 in. I.D. tubing at high temperature (400°C) to prevent the occurrence of detector "spiking"[7]. The restrictor was positioned so that decompression occurred at the entrance to the ionisation chamber (*ca.* 225-μl volume) of the photoionisation detector, *i.e.*, the ionisation chamber was essentially at atmospheric pressure. This avoids the problems of quenching and of absorption of the exciting radiation observed in the earlier work[11]. The column employed was a Brownlee SS251 5-μm Spheri-5 silica column (25 cm × 1 mm I.D.). All connections pre- and post-column were made with the shortest possible lengths of 0.005 in. I.D. stainless-steel tubing. Column temperature was maintained at 85°C. Data acquisition and plotting were provided by an Apple II$^+$ microcomputer, equipped with an analog to digital converter and programmable attenuation amplifier (Interactive Microware, State College, PA, U.S.A.).

The sample clean-up was similar to that described by Ramos and Prohaska[16]. A Soxhlet extraction was performed on 35 g with 150 ml dichloromethane for 24 h. The extract was reduced in volume to *ca.* 1 ml on a rotary evaporator at low temperature ($\leq$40°C). Then it was passed through a short column of silica gel (7 g of 100–200 mesh activated at 150°C and slurry-packed in hexane), topped with freshly cleaned granular copper (10 g) with 3 ml of 20% dichloromethane in diethyl ether, followed by 60 ml of 40% dichloromethane in diethyl ether. This treatment removed some of the sulfur and polar compounds. The eluate was reduced again to approximately 1 ml and passed through a 30 × 1.9 cm I.D. column packed with 20 g of Sephadex LH20 gel (Pharmacia) using cyclohexane–methanol–dichloromethane (6:4:3). This column had been previously calibrated by eluting azulene. The first fraction (*ca.* 40 ml) containing some of the aliphatic hydrocarbons was discarded, and the remaining fraction (*ca.* 60 ml) containing the PACs was collected, reduced in volume, filtered through a 0.45-μm PTFE filter, transferred to a 25-ml volumetric flask, and made to volume.

RESULTS AND DISCUSSION

Typical photoionisation (PID) and flame ionisation detection (FID) chromatograms of a polycyclic aromatic hydrocarbon (PAH) extract are shown in Fig. 1a and b, with conditions as noted on the figures. The PID trace was obtained from injection of 0.5 μl of a hexane solution of a harbour sediment extract, the FID trace is obtained from injection of 0.5 μl of a five-fold concentrated aliquot of the same solution. Features of the figures may be briefly summarised as follows: the PID trace has much less detector "spiking", a smoother and flatter baseline, and molar response less dependent on the analyte. The photoionisation detector thus permits operation of the column at much higher flow-rates. Interestingly, elemental sulphur (S_8) is also detected as a potential interferant in the photoionisation detector, but this can be readily eliminated by varying the sample preparation chemistry[16]. The FID perform-

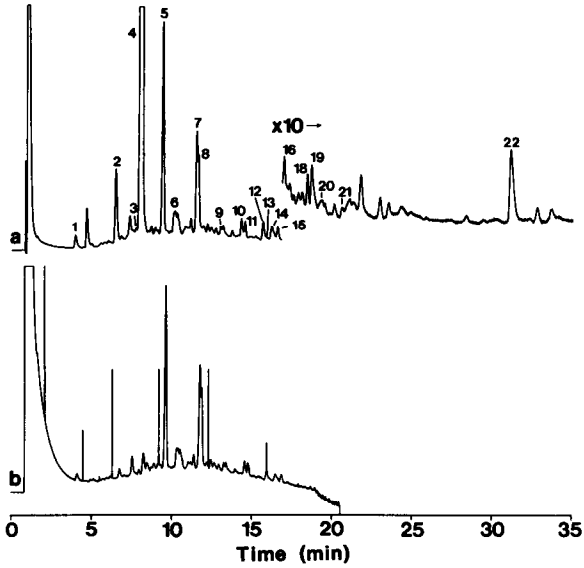

Fig. 1. SFC of a hexane extract of sediment HS-3. Compounds referred to by number are identified in Table I. Conditions: chromatographic fluid, carbon dioxide; column temperature, 85°C; column, 25 cm × 1 mm I.D. Spheri-5 silica. Pressure program: isoconfertic at 2000 p.s.i. for 5 min, then linear pressure ramp to 5000 p.s.i. over 25 min, then isoconfertic at 5000 p.s.i. for 5 min. (a) PID trace, $4 \cdot 10^{-10}$ A full-scale. (b) FID trace, five-fold concentrated aliquot of the extract, $2 \cdot 10^{-11}$ A full-scale.

ance deteriorated as the carbon dioxide flow increased, as shown by the noisy, strongly sloping baseline of Fig. 1b. Cooling and dilution of the flame increased with flow, leading to extinction when column pressures exceeded *ca.* 3200 p.s.i. Maintenance of a viable flame at higher pressures required adjustment of the hydrogen flow-rate to the flame, which increased yet further the baseline noise and spiking. The same effect was observed in similar experiments using a capillary column with a frit type restrictor in place of the crimped tube. This may be a characteristic of the particular flame ionisation detector used in this work. Operation at high pressures is required for eluting the strongly retained oxygenated PACs from the present column. These compounds and others indicated in the figure captions and in Table I have been identified by SFC–mass spectrometry (MS), using the restrictor as part of the usual spray depositor which transfers the eluate onto a VG moving belt liquid chromatography–MS interface[17]. The technique is similar to that developed by Berry *et al.*[18]. Separation of these oxygenated compounds from the PAHs has the advantage of reducing the potential for interferences in the quantitative analysis. SFC–MS was also used to characterise the elution pattern of mixtures of PAH standards used as a reference and calibration standard (*vide infra*).

Sensitivities and dynamic ranges were assessed using a mixture of 13 PAHs prepared for this work. A chromatogram of this solution is shown in Fig. 2. Quantities of compounds injected in the run shown varied from 22 ng for fluorene to 50

TABLE I

PAH STANDARDS AND OTHER COMPOUNDS TENTATIVELY IDENTIFIED IN THE CHROMATOGRAMS OF FIGS. 1 AND 2

Amounts injected (ng) are given in parentheses for the components of the test solution.

Compound No.	*Identity*
1	Naphthalene (23.4)
2	Acenaphthene (23.9)
3	Fluorene (21.6)
4	Sulphur
5	Phenanthrene (22.5)
6	2-Methylanthracene (26.7)
7	Pyrene
8	Fluoranthene (24.9)
9	Benzo[*a*]fluorene (25.5)
10	Benz[*a*]anthracene
11	Chrysene (23.9)
12	Benzo[*b*]fluoranthene
13	Benzo[*j*]fluoranthene
14	Benzo[*k*]fluoranthene
15	Benzo[*a*]pyrene
16	Perylene (29.0)
17	9,10-Diphenylanthracene (50.3)
18	Indeno[1,2,3-*cd*]pyrene (24.2)
19	Benzo[*ghi*]perylene
20	Dibenz[*a,h*]anthracene (23.8)
21	Coronene (21.9)
22	Anthraquinone

ng for 9,10-diphenylanthracene. Detection limits, estimated as three times baseline noise, are of the order of a few hundred picograms for the compounds tested. Detector response was linear from the detection limit to the microgram range for each component of the mixture, a dynamic range of approximately 3.5 orders of magnitude.

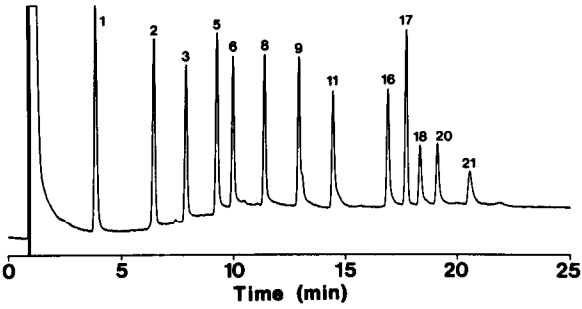

Fig. 2. SFC–PID of a test mixture of 13 PAHs dissolved in hexane–dichloromethane (9:1, v/v). Quantities injected as given in Table I. All conditions as in Fig. 1. Detector attenuation $1 \cdot 10^{-10}$ A full-scale.

CONCLUSION

This work has shown the applicability of the photoionisation detector as a detector for small-bore packed-column SFC. Decompression at the entrance to the ionisation chamber avoids the problems associated with high-pressure cell design and the quenching of ionisation by the carrier fluid. Advantages of PID over FID for this type of chromatography include the added selectivity and sensitivity of PID toward aromatic compounds as well as detector stability when subjected to high gas flow-rates. Work is continuing on developing other applications for this system, including the use of mobile phases that are incompatible with FID.

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