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Analysis of polycyclic aromatic hydrocarbons with an ion-trap mass detector and comparison with other gas chromatographic and high-performance liquid chromatographic techniques

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ABSTRACT

Some polycyclic aromatic hydrocarbons with a wide range of molecular masses were analysed by high-resolution gas chromatography using an ion-trap mass detector and a flame ionization detector. The sensitivity limits and the possibility of automatic identification through library search were evaluated. The results were compared with those obtained using other analytical techniques: mass spectrometry with a quadrupole analyser and high-performance liquid chromatography with a diode-array UV detector and fluorimetry. The relative sensitivity and the minimum amounts detectable with the various techniques were determined.

INTRODUCTION

Because of the known and potential mutagenic and carcinogenic hazards of polycyclic aromatic hydrocarbons (PAHs), a class of substances now ubiquitous in the human environment [1] because of their presence in combustion products and industrial waste, these compounds require accurate identification and quantification in many environmental samples. Sophisticated extraction and separation procedures have been applied for this purpose [2–9].

The analysis of the purified extracts can be carried out with gas and liquid chromatographic methods and with different detection devices, and obviously the ideal technique should permit perfect resolution of all of the PAHs from interfering substances, a very low detection limit, reproducibility of the retention data in order to help in identification and constancy of response to permit easy quantification without the need for frequent use of reference standards. Some of these goals are often impossible to achieve simultaneously (resolution and analysis speed; high sensitivity and correct identification), and the analyst should therefore apply different techniques offering the best result in a particular field or select the method that has the best performance in each case.

The main problem with the determination of PAHs is the complexity of the environmental matrices and the presence along with the PAHs of many interfering substances that, having physical and chemical behaviour similar to that of PAH, cannot be completely removed by repeated extraction and purification procedures. The identification and quantitation of PAHs therefore require the use of

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methods that simultaneously give high resolution and response selectivity.

High-performance liquid chromatography (HPLC) is therefore associated with diode-array detection systems, which permit simultaneously the identification and quantitation of the compounds, or with fluorescence detectors [10–13].

High-resolution gas chromatography (HRGC) with capillary columns is used in combination with flame ionization detection (FID) and photoionization detection (PID), multimode ionization detection (MMID) and quadrupole analyser mass spectrometry (QUAD) [14–17].

Various combinations of these techniques have also been proposed [18,19]. The highest sensitivity is given by the HPLC–fluorescence (HPLC–FL) method, which permits the determination of PAH amounts in the picogram range. The reported detection limits for the quadrupole mass spectrometer operated in single-ion monitoring (SIM) mode range between 0.1 and 0.5 ng [7]. However, neither the HPLC–FL nor the HRGC–MS–SIM technique permits identification and, for maximum sensitivity in quantitation, should be applied to previously identified compounds in order to select the proper excitation and emission wavelength (HPLC–FL) or the characteristic ion mass free from interferences (HRGC–MS–SIM). Other techniques, having lower sensitivity, should therefore be used for identification purposes.

The use of the ion-trap mass detector permits the entire mass spectra to be obtained with a sensitivity greater than that of quadrupole/SIM and therefore the application of identification algorithms to very small sample amounts. Ion-trap detection (ITD) was therefore used as the detection system in HRGC with bonded-phase open tubular columns, in parallel with FID, and the sensitivities obtained were compared with those obtained by quadrupole MS and by HPLC with constant- or variable-wavelength UV detection and with fluorimetric detection.

Our application of these methods to many environmental samples showed that the HRGC–ITD technique offers a sensitivity that for many compounds is higher than that obtained by HPLC–FL, with the further advantage of permitting the identification of the compounds by means of automatic library search. The simultaneous use of ITD and FID in many instances allows quantitation to be carried out without the need for standard samples of all of the detected PAHs.

EXPERIMENTAL

In order to investigate the behaviour of various detection systems over a wide range of molecular masses of PAHs, a mixture containing sixteen compounds included in the priority pollutants list of the US Environmental Protection Agency (EPA) was used as reference standard (Table I).

The GC–MS analyses were carried out using a Saturn II ion-trap spectrometer (Varian, Palo Alto, CA, USA) connected to a Model 3400 gas chromatograph also equipped with a flame ionization detector. The outlet of the column could be connected simultaneously to the two detectors, by means of a zero-volume "*y*" press-fit glass connector and deactivated capillary tubings. The length of the connecting tubes must be selected in order to act as a restrictor on the ITD side of the system, thus avoiding the backflushing of air and hydrogen from the base of the flame ionization detector to the

TABLE I

MOLECULAR MASS OF THE ANALYSED COMPOUNDS AND THEIR RETENTION TIMES (t_R) ON GC AND HPLC COLUMNS

For analysis parameters see Experimental section.

Compound	Molecular mass	t_R (min)	
		GC	HPLC
Naphthalene	128	13.51	8.24
Acenaphthylene	152	18.52	9.54
Acenaphthene	154	19.29	10.97
Fluorene	166	21.05	11.40
Phenanthrene	178	24.02	12.51
Anthracene	178	24.10	13.34
Fluoranthene	202	27.43	14.61
Pyrene	202	28.24	15.27
Benz[*a*]anthracene	228	32.13	17.92
Chrysene	228	32.21	18.25
Benzo[*b*]fluoranthene	252	35.43	20.65
Benzo[*k*]fluoranthene	252	35.48	21.43
Benzo[*a*]pyrene	252	36.53	22.21
Dibenz[*a,h*]anthracene	278	42.48	23.84
Benzo[*ghi*]perylene	276	44.03	24.72
Indeno[1,2,3-*cd*]pyrene	276	42.29	25.14

vacuum manifold of the ion-trap detector. The flow-rates to the two detectors should be adjusted in order to dispatch to each of them an amount of sample proportional to their sensitivity, thus permitting simultaneously identification by ITD and quantification through FID response (see below). For maximum sensitivity, all the sample must be sent to the ITD, by directly connecting the column to the vacuum system of the ion trap or by closing the FID side of the "*y*" arrangement. A DB5 capillary column was used (J&W Scientific, Folsom, CA, USA), 5% phenyl–95% methyl polysiloxane-bonded phase, 30 m × 0.32 mm I.D., film thickness 0.25 μm. The programmed temperature run used for the determination of sensitivity was: initial isotherm at 50°C for 5 min, programming rate 8°C/min up to 280°C. The injector (Varian 1075 split/splitless) was set at 250°C and the flame ionization detector at 300°C.

Other initial temperatures, programming rates and upper isotherm lengths were also tested. The conditions reported above were found to be suitable for routine analyses, as they allow a complete separation of all of the compounds in a reasonable time.

The acquisition parameters for ITD were: mass range 80–350 u, target 25 000, scan rate 1 s, acquisition time depending on the length of the programmed run, threshold one count, filament delay 240 s, mass defect 100 millimass/100 u, background mass 95 u.

Analyses were also made with the same column type on a Finnigan INCOS-50 quadrupole mass spectrometer connected to a Varian 3400 gas chromatograph, in order to compare the sensitivity and response ratio of ITD and quadrupole analysers.

HPLC analyses were carried out with a Varian Model 9095 liquid chromatograph equipped with Model 9065 diode-array UV detector and a Model 821 FP spectrofluorimeter. A Supelcosil LC-PAH column (Supelco, Bellefonte, PA, USA), 25 cm × 4.6 mm I.D., particle diameter 5 μm, was used. The mobile phase (acetonitrile–water) gradient was: 40% acetonitrile + 60% water for 2 min, increasing linearly up to 100% acetonitrile in 25 min; isocratic 100% acetonitrile up to 35 min. UV detection was performed both at the fixed wavelength of 254 nm and at various wavelengths corresponding to the maximum of the absorption peaks of the different compounds.

The spectrofluorimeter wavelength was programmed during the analysis: the initial values were $\lambda_{ex} = 280$ nm and $\lambda_{em} = 340$ nm; 14 min after the injection the parameters were changed to $\lambda_{ex} = 280$ nm and $\lambda_{em} = 410$ nm; after 25 min elapsed time the values were adjusted again to $\lambda_{ex} = 305$ nm and $\lambda_{em} = 500$ nm.

RESULTS AND DISCUSSION

Table I shows the retention times of the analysed compounds obtained with the temperature and solvent programmes described above during GC and HPLC analysis. The HPLC technique permitted both a better resolution and a shorter analysis time of the standard mixture used but, because in environmental samples the number of interfering compounds may be much greater than in our sample, the higher resolving power of the capillary GC technique is sometimes necessary to permit the analysis of authentic samples. The columns used and the conditions of analysis were not optimized to give the

TABLE II

SENSITIVITY (pg) OF ION TRAP DETECTION AND OF FLUORIMETRIC HPLC DETECTION

For ITD the minimum identifiable amount by means of library search is shown. Note. Fluorimeter settings: from naphthalene to anthracene: λ_{ex} 280 nm, λ_{em} 340 nm; from fluoranthene to benzo[*ghi*]perylene: λ_{ex} 280 nm, λ_{em} 410 nm; for indeno[1,2,3-*cd*]-pyrene: λ_{ex} 305 nm, λ_{em} 500 nm.

Compound	ITD	Fluorimetry
Naphthalene	20	60
Acenaphthylene	20	–
Acenaphthene	2	10
Fluorene	2	100
Phenanthrene	2	100
Anthracene	2	–
Fluoranthene	2	40
Pyrene	2	200
Benz[*a*]anthracene	20	20
Chrysene	20	–
Benzo[*b*]fluoranthene	20	20
Benzo[*k*]fluoranthene	20	20
Benzo[*a*]pyrene	20	20
Dibenz[*a,h*]anthracene	80	40
Benzo[*ghi*]perylene	40	40
Indeno[1,2,3-*cd*]pyrene	20	60

best resolution, but were selected only to give a separation good enough to allow the comparison of different detection systems. When more complex mixtures have to be resolved, other columns and analytical parameters should be used. The knowledge of the retention index of the compounds [20] can assist in the preidentification of many peaks. If different programming speeds have to be used to permit the best resolution to be obtained, computer prediction of the programmed temperature retention times by starting from two or three isothermal run permits tentative identification to be carried out in analysis conditions different from those used for the analysis of standard samples [21–24].

When interfering peaks not belonging to PAH compounds are present in the chromatogram obtained from the environmental samples, identification based on retention times is not adequate. Mass spectrometry with quadrupole detection operated in SIM mode offers a sensitivity similar to that of FID: minimum detectable amounts ranging from 0.1 to 0.5 ng depending on the molecular mass of the compound [7]. The amount necessary to obtain a full-scan spectrum of reasonable intensity is more than one order of magnitude greater, and therefore an amount of some nanograms should be injected for each compound on a HRGC–MS–QUAD system to obtain a spectrum good enough for identification [25–28].

In contrast, using ITD it is possible to obtain with full-scan spectrum a sensitivity higher than that obtained in MS–QUAD–SIM mode, and to apply therefore the automatic library search programmes available. Table II shows for ITD the minimum identifiable quantity, *i.e.*, the minimum injected quantity that produces correct library search identification within first five search hits. ITD also shows a fair linearity of about four orders of magnitude from the minimum identifiable quantity up to 2000 pg, with correlation values higher than 0.997 over a five-point calibration for all of the compounds in the PAH mixture [29–31]. The detection limits of the fluorimetric detector, experimentally measured using the conditions described above, are also reported and show that ITD permits identification at concentrations smaller than those obtained with the HPLC–FL method.

The sensitivity reported for the HPLC–FL method is not the highest possible with this technique, because, as shown in the Experimental section, only three combinations of excitation (λ_{ex}) and emission (λ_{em}) wavelengths were used during the elution of the compounds. It is possible to select for every compound the λ_{ex} and λ_{em} values yielding the highest sensitivity [32,33], by programming the fluorimetric detector and the signal integrator.

In order to obtain accurate results, however, the retention times must be perfectly reproducible and the peaks separated by a baseline segment long enough to permit all the automatic steps for wavelength change to be carried out.

Deactivation of integration, change of λ_{ex} and λ_{em}, equilibration of the signal at the new baseline level, activation of the integrator and monitoring of the new baseline value require two or three times the base width of the peaks, and therefore a resolution on 2.5 or greater is preferable.

This resolution value can only be obtained when few PAHs are analysed, and in the absence of interfering compounds. When the analysis of samples extracted from complex matrices is carried out, it is only possible to change the detector parameters a few times during the elution of the chromatogram. Various PAHs are therefore detected with the same wavelength combination: the first change of λ_{em} from 340 to 410 nm is made after the elution of anthracene; the second (λ_{ex} from 280 to 305 nm, λ_{em} from 410 to 500 nm) before the elution of indeno-[1,2,3-*cd*]pyrene.

This wavelength programme offers a suitable compromise for the analysis of real samples and was therefore used for the determination of the sensitivities reported in Table II.

UV detection yields a sensitivity lower than that of fluorimetry but, by using a diode-array detector, permits the spectrum of every peak to be recorded for identification purposes and, by selecting the wavelength of maximum absorbance, an increase in sensitivity.

Table III shows the minimum concentration detected using non-concentrated samples and different HPLC detection systems: constant-wavelength, variable-wavelength and fluorimetry. The minimum concentration required by the EPA 610 method [34] after concentration of the water sample at a ratio of 1:1000 is also shown. If the same concentration procedure is applied before HPLC analysis, the values in the table (mg/l) should be converted into

TABLE III

MINIMUM DETECTABLE CONCENTRATION USING NON-CONCENTRATED SAMPLES AND VARIOUS HPLC DETECTION SYSTEMS

The sensitivity of the EPA 610 method is based on a water sample after concentration at a ratio of 1:1000.

Compound	Constant wavelength (254 nm) (mg/l)	Variable wavelength		Fluorimetry (mg/l)	EPA 610 method (μg/l)
		mg/l	nm		
Naphthalene	0.5	0.025	215	0.003	1.8
Acenaphthylene	0.5	0.05	224	–	2.3
Acenaphthene	2.0	0.025	224	0.0005	1.8
Fluorene	0.1	0.1	258	0.001	0.21
Phenanthrene	0.05	0.05	249	0.005	0.64
Anthracene	0.025	0.025	249	–	0.66
Fluoranthene	0.2	0.05	234	0.002	0.21
Pyrene	0.2	0.05	239	0.01	0.27
Benz[*a*]anthracene	0.1	0.05	287	0.001	0.013
Chrysene	0.05	0.05	263	–	0.15
Benzo[*b*]fluoranthene	0.1	0.1	254	0.001	0.018
Benzo[*k*]fluoranthene	0.2	0.1	234–239	0.0005	0.017
Benzo[*a*]pyrene	0.5	0.5	254	0.001	0.023
Dibenz[*a,h*]anthracene	0.4	0.05	297	0.002	0.030
Benzo[*ghi*]perylene	0.2	0.2	254	0.002	0.076
Indeno[1,2,3-*cd*]pyrene	0.1	0.1	249	0.003	0.043

the μg/l range. Neither constant-wavelength nor variable-wavelength UV detection can achieve the sensitivity required by the EPA 610 method for some of the late-eluting compounds. Fluorimetric detection, on the other hand, allows the required sensitivity to be obtained with a smaller concentration ratio, less than 100 for the heaviest compounds and about ten-fold for the highest. This method can therefore be used for the analysis of environmental samples when the complexity of the matrix is not so high as to give too many interfering peaks. If the chromatogram is very complex, the HPLC method is not selective enough to permit the separation of all the compounds, and was therefore used as a screening method to measure the overall concentration of PAH and as a preparative and prefractionating method to reduce the complexity of the mixture by separating the components into different HPLC fractions to submit to further HRGC analysis [6,35], and to identify and quantitate by ITD.

As seen above, the INCOS presearch and identification software of the Varian Saturn ion-trap mass spectrometer permits the identification to be successfully carried out with the amounts of PAHs shown in Table II, by comparison with library data. Authentic standard samples of all of the PAHs, often difficult to obtain with sufficient purity, are therefore not necessary for identification. However, Table IV shows that the relative response of ITD to the various PAHs (calibration carried out with the molecular masses listed in Table I) varies within one order of magnitude, and pure standard samples should be necessary for quantitation. Quadrupole mass analysis shows a smaller dependence of response on the compound, but, as seen above, its sensitivity is lower than that of ITD.

If the amount of each PAH in the sample, if necessary after suitable concentration procedures, is high enough to be detected with FID, the near-identical response of this detector to all the compounds having the same general structure allows the use of authentic standard samples of all the PAHs to be avoided [14,17,36].

TABLE IV

WEIGHT RESPONSE FACTORS (RELATIVE TO FLUORANTHENE) OF PAHs TO VARIOUS DETECTION SYSTEMS IN GAS CHROMATOGRAPHY

Compound	ITD	Quadrupole	FID
Naphthalene	1.44	–	1.01
Acenaphthylene	1.61	–	1.01
Acenaphthene	1.09	–	1.04
Fluorene	1.09	0.86	1.04
Phenanthrene	1.59	0.92	1.00
Anthracene	1.52	0.88	0.99
Fluoranthene	1.00	1.00	1.00
Pyrene	1.29	1.07	0.99
Benz[*a*]anthracene	0.66	1.24	0.99
Chrysene	0.70	–	1.01
Benzo[*b*]fluoranthene	0.18	1.33	0.99
Benzo[*k*]fluoranthene	0.14	1.43	1.00
Benzo[*a*]pyrene	0.12	1.32	1.03
Dibenz[*a,h*]anthracene	0.11	–	0.98
Benzo[*ghi*]perylene	0.14	1.36	1.02
Indeno[1,2,3-*cd*]pyrene	0.17	–	1.01

If the flame ionization detector is mounted in parallel with the ion-trap detector at the end of the capillary column by using flow restriction on the ion-trap detector side in order to split the larger amount of the sample to the flame ionization detector, identification through library search can then carried out on the small (but large enough to give a suitable spectrum) amount of sample going to the ion-trap detector, while quantitative analysis is achieved by using the simultaneous FID chromatogram.

Owing to the similar response of FID to the various PAHs (Table IV), the use of non-corrected areas permits an accuracy of $\pm 5\%$ to be obtained, good enough for many applications in environmental analysis, where the main sources of uncertainty are sample pick-up and conservation, extraction and enrichment procedures, different recovery of various compounds, interferences, etc.

CONCLUSIONS

The analysis carried out under standard and reproducible chromatographic conditions on various PAHs permitted the sensitivity of the various detection systems used in HRGC and HPLC to be compared. Instruments of the latest generation commercially available were used, and therefore the relative sensitivities were determined on a common basis, partially confirming previously literature data, and, in some instances, showing a substantial increase in sensitivity.

Using an ion-trap detector sensitivities higher than those previously obtained by MS–QUAD–SIM and HPLC–FL methods were achieved and, at the same time, the compounds could be identified from their mass spectra by using standard library search programmes.

The uniform sensitivity of FID to PAHs with a wide range of molecular masses allows the quantitation to be carried out in routine analyses without frequent use of authentic samples of all the detected compounds, if the amount of sample is great enough to permit the use of this detection system.

In the same concentration range, the connection of ITD and FID in a parallel mode in order to obtain simultaneous chromatograms permits qualitative identification and quantitative determination to be carried out at the same time.

REFERENCES

1 World Health Organization and International Agency for Research on Cancer, *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 32, Polynuclear Aromatic Compounds, Part I: Chemical, Environmental and Experimental Data*, World Health Organization and International Agency for Research on Cancer, Lyon, 1983.
2 EPA, in *Test Methods for Evaluating Solid Waste*, Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 3rd ed., 1986, Ch. 4.
3 L. S. Clesceri, A. E. Greenberg and R. R. Trussel (Editors), *Standard Methods for Examination of Water and Wastewater*, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, 17th ed., 1989, method 6440.
4 M. M. Schantz, B. A. Benner, S. N. Chesler, B. J. Koster, K. E. Hehn, S. F. Stone, R. Kelly, R. Zeisler and S. A. Wise, *Fresenius' J. Anal. Chem.*, 338 (1990) 501.
5 M. C. Kennicutt II, S. T. Sweet, W. R. Fraser, W. L. Stockton and M. Culver, *Environ. Sci. Technol.*, 25 (1991) 509.
6 M. M. Krahn, L. K. Moore, R. G. Bogar, C. A. Wigren, S. L. Chan and C. W. Brown, *J. Chromatogr.*, 437 (1988) 161.
7 N. D. Bedding, D. E. Mc Intyre, J. N. Lester and R. Perry, *J. Chromatogr. Sci.*, 26 (1988) 597.
8 M. L. Lee, M. V. Novotny and K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, London, 1981.
9 A. Bjorseth (Editor), *Handbook of Polycyclic Aromatic Hydrocarbons*, Marcel Dekker, New York, 1983.

10 D. T. Rossi, D. J. Desilets and H. L. Pardue, *Anal. Chim. Acta*, 161 (1984) 191.
11 D. M. Krstulovic, D. M. Rosie and P. R. Brown, *Anal. Chem.*, 48 (1976) 13893.
12 J. R. Jadamec, W. S. Sener and Y. Talmi, *Anal. Chem.*, 49 (1977) 1316.
13 L. W. Hershberger, J. B. Cellis and G. D. Christian, *Anal. Chem.*, 53 (1981) 971.
14 J. Y. Tong and F. W. Karasek, *Anal. Chem.*, 56 (1984) 2129.
15 Y. N. Driscoll, J. Ford, L. F. Janmillo and E. T. Gruber, *J. Chromatogr.*, 158 (1978) 171.
16 J. W. Haas III, M. V. Buchanan and M. B. Wise, *J. Chromatogr. Sci.*, 26 (1988) 49.
17 A. Bemgard and A. Colmsjö, *J. Chromatogr. Sci.*, 30 (1992) 23.
18 M. A. Quilliam and P. G. Sim, *J. Chromatogr. Sci.*, 26 (1988) 160.
19 V. M. Garg, D. D. Bhatt, V. K. Kaushik and K. R. Murthy, *J. Chromatogr. Sci.*, 25 (1987) 237.
20 D. L. Vassilaros, R. C. Kong, D. W. Later and M. L. Lee, *J. Chromatogr.*, 252 (1982) 1.
21 T. C. Gerbino and G. Castello, in P. Sandra and M. L. Lee (Editors), *Proceedings of the 14th International Symposium on Capillary Chromatography*, Foundation for the International Symposia on Capillary Chromatography, Miami, FL, 1992, p. 70.
22 T. C. Gerbino and G. Castello, *J. High Resolut. Chromatogr.*, 16 (1993) 46.
23 T. C. Gerbino, G. Castello and U. Pettinati, *J. Chromatogr.*, 634 (1993) 338.
24 G. Castello, P. Moretti and S. Vezzani, *J. Chromatogr.*, 635 (1993) 103.
25 H. Borwitzky and G. Schomburg, *J. Chromatogr.*, 170 (1979) 99.
26 R. C. Lao, R. S. Thomas, H. Oja and L. Dubois, *Anal. Chem.*, 45 (1973) 908.
27 R. C. Lao, R. S. Thomas and J. L. Monkman, *J. Chromatogr.*, 112 (1975) 681.
28 T. Sauer and P. Bohem, in *Proceedings of the 1991 International Oil Spill Conference, San Diego, CA, March 4–7, 1991*, United States Coast Guard, American Petroleum Institute, U.S. Environmental Protection Agency, Washington, DC, 1991, p. 363.
29 D. F. Gurka, S. M. Pyle and R. Titus, *Anal. Chem.*, 64 (1992) 1749.
30 G. Castello, T. C. Gerbino and S. Nadotti, *Boll. Chim. Igien.*, 42 (1991) 181.
31 S. A. Mc Luckey, G. L. Glish, K. G. Asano and G. J. Van Berkel, *Anal. Chem.*, 60 (1988) 2312.
32 K. Ogan, E. Katz and W. Slavin, *Anal. Chem.*, 51 (1979) 1315.
33 H. C. Kicinsky, S. Adamek and A. Kettrup, *Chromatographia*, 28 (1989) 203.
34 *Federal Register, Guidelines for Establishing Test Procedures for the Analysis of Pollutants*, US Environmental Protection Agency 1984, Method 610 —Polynuclear Aromatic Hydrocarbons, 40 CFR Part 136, 43344; Fed. Reg. 49, No. 209.
35 J. P. F. Palmentier, A. J. Britten, G. M. Charbonneau and F. W. Karasek, *J. Chromatogr.*, 469 (1989) 241.
36 J. T. Scanlon and D. E. Willis, *J. Chromatogr. Sci.*, 23 (1985) 333.