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Rapid analysis of organic microcontaminants in environmental water samples by trace enrichment and liquid chromatography on a single short column

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Abstract

On-column trace enrichment and liquid chromatography using a single short (20 mm length) high-pressure packed column was optimized for the rapid simultaneous identification and quantification of a wide range of organic microcontaminants in environmental water samples. The quality of different C_{18} bonded silica packing materials in terms of their performance (i.e., peak capacity, repeatability) and enrichment/extraction characteristics (i.e., recovery, selectivity) was tested. With 15-ml samples, limits of detection of 0.1–0.4 μg/l and 0.5–1.1 μg/l were achieved for tap and surface water, respectively. The applicability of the system was demonstrated by the screening of real environmental samples and the provisional identification of unknowns.

Keywords: Environmental analysis; Sample handling; Water analysis; Pesticides; Polynuclear aromatic hydrocarbons

1. Introduction

In recent years, the determination of pesticides and other organic microcontaminants in aqueous samples has efficiently been performed by liquid chromatography (LC)-based methods. The on-line monitoring and screening of river and tap water is a well-known application [1–5]. Main advantages of these LC-based methods are the virtual absence of restrictions concerning the polarity, thermolability and volatility of the analytes. UV–Vis absorbance is the most widely used detection method in LC, and often provides adequate sensitivity, but unfortunately lacks selectivity. By recording diode array UV spectra and comparing these with spectral libraries, the lack of identification power has partially been solved.

For the screening of many real samples it is important to monitor the presence of organic microcontaminants at the trace level. In practice this means that prior to LC separation a preconcentration step has to be performed which is nowadays preferably done by on-line solid-phase extraction (SPE). However, in many early-warning and screening situations only a limited number of micropollutants, if any, will actually be present in each individual sample. In other words, if chromatographic resolution is not of primary importance whereas fully satisfactory analyte detectability is, a decrease in

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analysis time by e.g., reduction of the (SPE plus analytical) column length and, consequently, an increase of sample throughput is an attractive option. This was recently studied by combining trace enrichment and LC separation on a single high-pressure packed short column (20 mm long) for the provisional identification of micropollutants in aqueous samples [6,7]. Continuing these rather promising studies, we try to proceed along two different lines. On the one hand, it is of distinct importance to evaluate the quality of different types of packing material to optimize the performance (e.g., peak capacity) as well as the enrichment characteristics (e.g., recovery) of the short analytical column. On the other hand, it will be highly advantageous to combine the rapid screening potential of the short column trace enrichment-cum-separation procedure with the identification power of mass spectrometric (MS) detection. First results of the combination of a single short column with MS detection using an atmospheric pressure chemical ionization interface for the determination of a wide range of microcontaminants were reported recently [8].

The aim of this study was to compare the quality of several C_{18} bonded silica stationary phases to obtain optimum performance with respect to peak capacity and analyte enrichment. Therefore relevant analytical characteristics such as recovery, linearity, repeatability and limits of detection were studied. Furthermore, the applicability of the total set-up was demonstrated by analysing real samples

2. Experimental

2.1. Chemicals

Acetonitrile and methanol, both HPLC-gradient-grade, were from J.T. Baker (Deventer, Netherlands). HPLC-grade water was generated by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA). Buffer solutions were prepared by adding 1 *M* of orthophosphoric acid to a 1 *M* potassium dihydrogenphosphate solution (J.T. Baker) to obtain the appropriate pH and subsequent dilution to 10 m*M*. The pesticide standards were obtained from Riedel-de-Haën (Seelze, Germany), Promochem (Wesel, Germany), the US Environmental Protection Agency Repository (Research Triangle Park, NC, USA) and the Repository of the Food Inspection Laboratory (Alkmaar, Netherlands) and were, as stated by the manufacturers, over 95% pure. All polycyclic aromatic hydrocarbons (PAHs) were from Radiant Dyes Chemie (Wermelskirchen, Germany). A 1000 μg/ml stock solution of each pesticide and PAH was prepared by weighing and dissolving in acetonitrile. Standard mixtures of the pesticides and PAHs were made by diluting a proper amount of the stock solution in methanol. All stock and standard mixtures were stored in a refrigerator at −(4–10)°C during the entire research project. Each day fresh solutions were prepared from the 20 μg/ml standard mixtures by 4-fold dilution with HPLC-grade water.

Tap water samples (Amsterdam, 1995) were taken after having the tap running for 10 min; they were analysed without any prior clean-up. Surface water [rivers Meuse (Eysden, Belgium/Dutch border) and Rhine (Lobith, German/Dutch border), 1995] was sampled by RIZA (Lelystad, Netherlands). The samples were pretreated by filtering 1 l over a 0.45-μm membrane filter (Schleicher and Schuell, Dassel, Germany). The 250-ml samples were spiked by the addition of a standard mixture solution.

2.2. Instrumentation

LC analyses were performed on an HP 1090 LC system equipped with a ternary solvent delivery unit to deliver the solvents for (a) conditioning of the short column, (b) the eluent and (c) the tap or river water samples, a six-port switching valve and an HP 1040 diode array detection (DAD) system (Hewlett-Packard, Waldbronn, Germany).

Both trace enrichment and separation were carried out on a high-pressure packed guard column containing 5-μm C_{18} bonded silica supplied by various manufacturers. Included is this study were a ODS Hypersil column, 20×4.0 mm I.D. (Hewlett-Packard), LC-18-DB columns, 20×4.6 mm I.D. or 2.1 mm I.D. and an ABZ^{+}-plus column, 20×4.6 mm I.D., all from Supelco (Bornem, Belgium), a Symmetry column, 20×3.9 mm I.D. (Waters, Chardds Ford, PA, USA) and a 12.5×4.6 mm I.D. Zorbax SB-C_{18} (Rockland Technologies Europe, Nuenen, Netherlands).

All data were acquired and evaluated by a Hewlett-Packard Pascal Workstation (PAWS), using the Chemstation software (Hewlett-Packard, Böblingen, Germany).

A schematic of the total set-up is given in Fig. 1.

2.3. Analytical procedures

The procedure for analysing the water samples was recently described by Minnaard et al. [7]. First, the short analytical column was flushed at 2.0 ml/min with 10 ml of acetonitrile, and next, with 10 ml of a 10 m*M* phosphate buffer of pH 3. Tap and river water samples of 250 ml were spiked with the mixture of pesticides, and 15 ml were loaded on the column at a flow-rate of 2.0 ml/min. Elution and actual separation were carried out at a flow-rate of 1.5 ml/min, using a 14.25-min linear gradient from pure phosphate buffer to acetonitrile–phosphate buffer (95:5, v/v).

For the analysis of the 16 priority (EPA) PAHs, trace enrichment was performed as mentioned above at a flow-rate of 2.0 ml/min. Desorption of the PAHs and subsequent analysis was performed at a flow-rate of 1.0 ml/min using the following gradient profile: water–acetonitrile (80:20, v/v) for 1 min, which was then changed linearly to water–acetonitrile (20:80, v/v) in 10 min.

DAD-UV detection was performed at a wavelength of 210 nm, which was used for quantification, and a standard bandwidth of 10 nm. It should be added here that different pesticides and PAHs show optimum absorbance at different wavelengths, which can be selected using a software option, such as post-run wavelength extraction. In our experience, 210 nm is the preferred wavelength if multicomponent screening of a variety of microcontaminants is the main aim. Identification was done by using our self-compiled DAD-UV spectral library. In this way, each compound is characterized by its retention time and its match with the appropriate library spectrum.

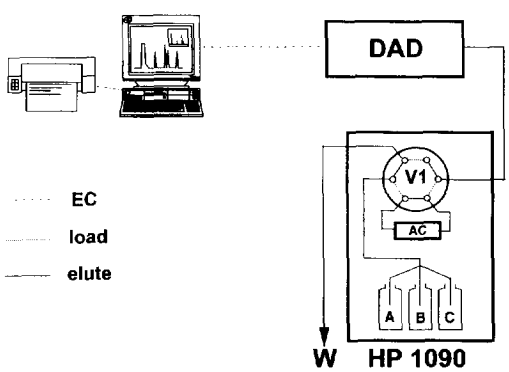

Fig. 1. Experimental set-up of the short-column LC–DAD system; HP 1090=ternary gradient pump; A, B and C=bottles containing phosphate buffer, acetonitrile and water sample, respectively; V1=six-port switching valve; AC=short analytical column; DAD=diode array detector; W=waste flask; EC=electronical connections. For more details, see Section 2.2.

3. Results and discussion

3.1. LC separation of loop injections

A mixture of seventeen pesticides (see Table 1 below) was selected to cover pesticide classes such as the carbamates, organophosphates, triazines, phenylureas and some miscellaneous compounds. These analytes were used to test the quality of the performance of three C_{18} bonded silica columns (ODS Hypersil, Waters Symmetry and Supelco LC-18-DB).

As regards the resolving power of the various short columns, the almost complete separation of the seventeen test compounds can be achieved on all three columns using a 14.25-min linear gradient (Fig. 2). The mutual differences are seen to be very small. The retention times of the test analytes increase slightly upon going from the ODS Hypersil via the Symmetry to the LC-18-DB column. Consequently, the co-eluting compounds barban and neburon (peak Nos. 10 and 11, Fig. 2), are slightly better separated on the LC-18-DB column than on the other two columns. Still, peak widths of the test compounds injected show about the same values (0.07–0.10 min) on all three columns. Direct injection on the short columns was performed at different concentration levels ranging from 0.1 to 10 μg/l. For all three columns, linearity on the short-column LC–DAD system was good results with R^2 values between 0.993 and 1.000 for all test analytes. As regards the retention times, relative standard deviations (R.S.D.s) were in the range of 0.2–0.5% ($n=10$).

Table 1
Calibration data for multiresidue pesticide analysis in tap water (range, 0.3–4 μg/l; $n=5$) and river Meuse water (range, 0.5–10 μg/l; $n=5$) using a Supelco LC-18-DB short column

Compound	t_R	Tap water		River water	
	(min)	Calibration equation[a]	R^2	Calibration equation[a]	R^2
Aldicarb	3.76	$y=1.036(0.020)x-2.598(2.328)$	0.999		
Monuron	4.15	$y=2.968(0.173)x-2.467(3.000)$	0.993		
Propoxur	4.62	$y=1.063(0.030)x-1.058(0.580)$	0.998		
Diuron	5.48	$y=4.160(0.080)x+1.156(1.452)$	0.999	$y=3.572(0.096)x+4.617(1.912)$	0.999
Propazine	5.97	$y=2.707(0.030)x+5.511(5.312)$	0.998	$y=1.039(0.067)x-0.200(1.330)$	0.996
Terbutylazine	6.23	$y=2.390(0.144)x-5.022(2.492)$	0.993	$y=1.159(0.059)x-1.550(1.170)$	1.000
Fenamiphos	7.00	$y=1.754(0.109)x-1.098(1.886)$	0.992	$y=1.554(0.080)x-1.620(1.720)$	0.997
Barban	7.68	$y=3.941(0.161)x+5.366(3.979)$	0.997	$y=3.106(0.018)x-1.063(0.350)$	1.000
Neburon	7.82	$y=3.299(0.117)x+0.880(2.020)$	0.998	$y=2.084(0.040)x+0.483(0.810)$	0.999
Fenthion	8.51	$y=1.794(0.096)x+0.524(1.670)$	0.994	$y=1.741(0.019)x-1.000(0.376)$	1.000
Coumaphos	8.82	$y=1.672(0.114)x+0.068(1.978)$	0.991	$y=3.052(0.033)x-6.652(6.016)$	0.990
Fenchlorphos	9.64	$y=3.161(0.051)x-1.421(0.882)$	0.999	$y=3.871(0.132)x-6.649(2.627)$	0.999
Chlorpyriphos	10.06	$y=0.778(0.019)x-0.167(0.318)$	0.999	$y=1.781(0.020)x-0.877(0.410)$	0.998
Trifluralin	10.27	$y=0.906(0.027)x-0.805(0.476)$	0.998	$y=0.864(0.037)x-0.498(0.730)$	0.996
Bromophosethyl	10.95	$y=1.903(0.081)x-1.882(1.402)$	0.996	$y=2.041(0.031)x-2.965(0.596)$	1.000

[a] y=area; x=concentration (μg/l).

Recently, some preliminary tests were made with a 2 cm long column with a 2.1 mm rather than a 4.0–4.6 mm internal diameter. With the same analytical conditions as were used above, the results obtained for the resolution of the analytes, the linearity of the calibration plots and the repeatability of the retention times were essentially the same as those for the conventional-bore columns.

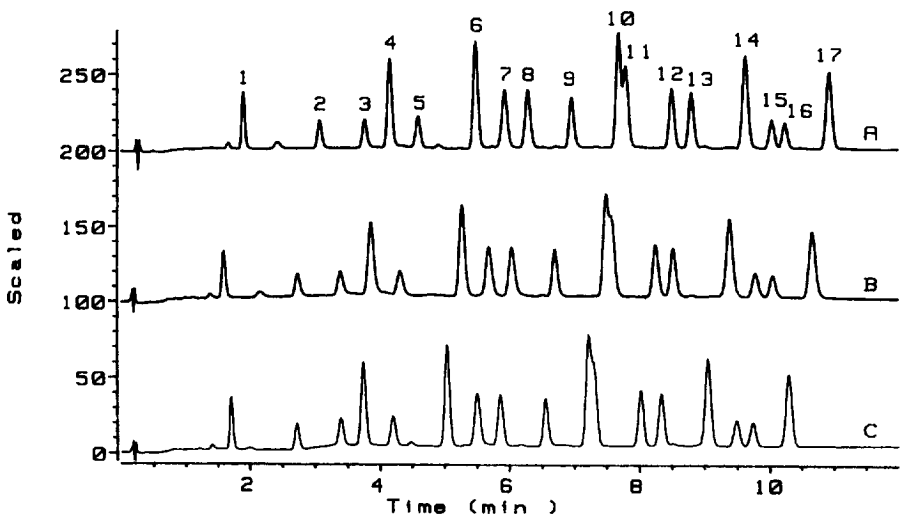

Fig. 2. Short-column LC–DAD chromatogram of a mixture of seventeen pesticides after loop injection (10 μl of 5 μg/ml of each pesticide in the mixture) on (A) LC-18-DB column; (B) Symmetry column; (C) ODS Hypersil column. Peak assignment: (1) oxamyl, (2) dimethoate, (3) aldicarb, (4) monuron, (5) propoxur, (6) diuron, (7) propazine, (8) terbutylazine, (9) fenamiphos, (10) barban, (11) neburon, (12) fenthion, (13) coumaphos, (14) fenchlorphos, (15) chlorpyriphos, (16) trifluralin, (17) bromophos-ethyl. Analytical conditions: 14.25-min linear aqueous phosphate buffer–acetonitrile gradient; UV detection at 210 nm. For all other details, see Section 2.3.

3.2. On-column enrichment and separation

3.2.1. General remarks

Results previously obtained by us for a series of organophosphorus pesticides, showed that when only 15-ml water samples were enriched on a high-pressure packed short column, limits of detection were between 0.5 and 4 μg/l [7]. Of course, depending on the nature of the water samples, i.e., HPLC-grade water, tap or surface water, trace enrichment of other constituents, mainly humic and fulvic acids, can interfere with the detection of the analytes of interest. The position of the matrix peak so created in the chromatogram also depends on the gradient used and the eluent composition [9,10]. Therefore, different water samples, e.g., tap and river water, were analysed to optimize the overall performance of the method.

3.2.2. Analytical performance

Calibration graphs and repeatability

The performance of the response of the short-column LC–DAD method in terms of linearity was tested with spiked tap and river Meuse water. In all cases, 250-ml water samples were spiked with the pesticide mixture at levels ranging from 0.3 to 10 μg/l and 15 ml of these water samples were loaded on the short columns. Typical DAD-UV chromatograms of river Meuse water spiked at the 2 μg/l level obtained with the three columns are shown in Fig. 3. The matrix peak strongly interfered with the detection of the highly polar, early eluting oxamyl and dimethoate. Aldicarb, monuron and propoxur could be identified if the proper retention time windows were selected, but they were difficult to quantify at these low concentration levels. With tap water (results not shown), where interference from the matrix constituents is much less, no problems were encountered with the quantification of the latter three analytes. The calibration graphs obtained for all analytes on the three columns were linear. As an example, results for the LC-18-DB column are reported in Table 1. The regression coefficients were satisfactory with R^2 values between 0.988 and 1.000 for all pesticides in both tap and river water. The repeatability of the retention times was excellent with R.S.D.s of less than 0.5% ($n=10$) for both tap and river water on all three columns.

In order to determine the precision of the total analytical procedure, ten consecutive trace-enrichment experiments of river Meuse water, spiked at the 2 μg/l level, were performed on all three columns. The precision for all compounds eluting after propoxur was quite satisfactory with R.S.D.s of peak

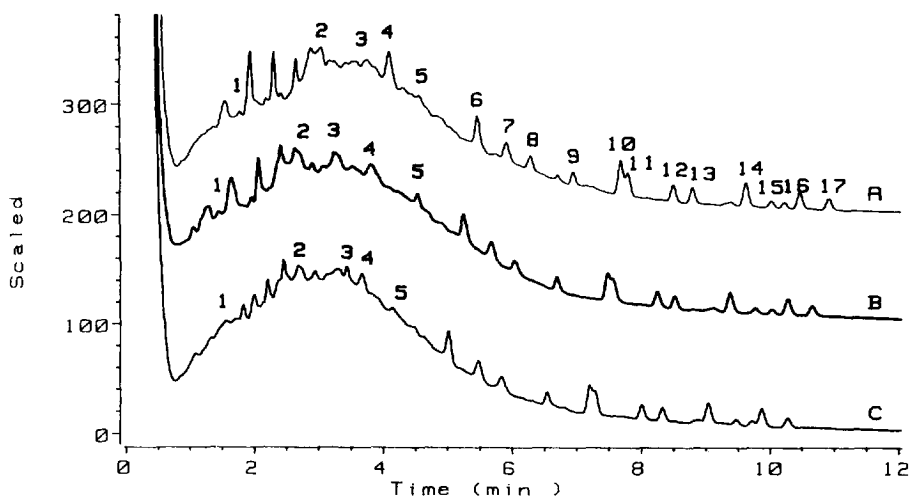

Fig. 3. Typical short-column LC–DAD chromatogram of trace enrichment of 15 ml of river Meuse water spiked with the pesticide mixture at the 2 μg/l level: (A) LC-18-DB, (B) Symmetry and (C) ODS Hypersil column. For analytical conditions, see Section 2.3 and for peak assignment, see Fig. 2.

areas of 1–14% ($n=10$) with only minor differences observed between the columns.

Recovery

Analyte recovery will give an indication of the extraction efficiency of the pesticides from the environmental samples (assuming that desorption creates no problem). The recoveries were calculated by comparing the peak areas of the analytes obtained in the above trace-enrichment experiments with loop injections of the same amount of the test compounds. As can be seen from Table 2, the analyte recoveries from tap water generally were significantly higher than those reported for river water, a typical difference being 10–15%. This no doubt reflects the influence of the more complex nature of river water. The relatively low recoveries observed for the late-eluting non-polar pesticides can be contributed to adsorption to connecting capillaries, etc., as is repeatedly reported in literature [11,12]. Two further observations should be made. Firstly, despite the tap versus surface water differences, the results obtained for each analyte in each matrix were remarkably similar for the three short columns tested. Secondly, unexpectedly low recoveries were obtained for the medium-polar triazines, propazine and terbutylazine, in river water. This phenomenon can probably be explained on the basis of the observation of Hayes et al. [13], who stated that humic substances can adsorb all kinds of analytes and suppress their recovery during enrichment.

Limits of detection

Detection limits (signal-to-noise ratio, 3:1) of the majority of the seventeen analytes on the three short columns are reported in Table 3. For the majority of the test compounds limits of detection in tap water are in the range of 0.1–0.4 μg/l for the three columns. Small mutual differences can be observed and the limits of detection obtained with the LC-18-DB column are slightly better than for the other two columns. Admittedly, the present detection limits do not meet the stringent 0.1 μg/l threshold levels for individual pesticides of the European Union for most of the test analytes, and some improvement still is required. On the other hand, as regards surface water, trace enrichment of 15-ml spiked river Meuse samples gave detection limits ranging from 0.5 to 1.0

Table 2
Comparison of extraction recoveries (in %) for pesticides in tap water and river Meuse water ($n=5$) using different high-pressure packed columns packed with C_{18} bonded silica

Compound	Recovery (%)					
	Tap water[a]			River water[b]		
	ODS Hypersil	LC-18-DB	Symmetry	ODS Hypersil	LC-18-DB	Symmetry
Aldicarb	59	71	62	–[c]	–[c]	–[c]
Monuron	71	87	82	–[c]	45	–[c]
Propoxur	64	80	78	–[c]	67	–[c]
Diuron	97	96	94	85	81	69
Propazine	86	93	78	45	39	40
Terbutylazine	88	84	94	49	59	52
Fenamiphos	89	93	84	71	76	72
Barban	75	86	87	83	71	74
Neburon	78	87	90	82	70	83
Fenthion	82	85	79	75	75	62
Coumaphos	75	84	78	72	70	77
Fenchlorphos	80	74	71	61	78	69
Chlorpyriphos	82	79	70	64	67	65
Trifluralin	79	78	70	65	78	67
Bromophosethyl	65	59	57	45	54	52

[a,b] Calculated at 1 and 2 μg/l level, respectively.
[c] Recoveries difficult to determine because of interfering humic substances.

Table 3
Detection limits (in μg/l; $S/N=3$) for test compounds in 15-ml tap and river Meuse water samples using short-column LC–DAD on three columns high-pressure packed with C_{18} bonded silica

Compound	Detection limit (μg/l)					
	Tap water			River water		
	ODS Hypersil	LC-18-DB	Symmetry	ODS Hypersil	LC-18-DB	Symmetry
Aldicarb	0.8	0.4	0.7	–[a]	–[a]	–[a]
Monuron	0.7	0.2	0.5	–[a]	1.0	–[a]
Propoxur	0.6	0.3	0.5	–[a]	1.2	–[a]
Diuron	0.2	0.1	0.1	0.5	0.4	0.7
Propazine	0.3	0.2	0.3	1.0	0.8	1.0
Terbutylazine	0.3	0.1	0.3	0.5	0.8	1.0
Fenamiphos	0.3	0.3	0.3	0.7	0.8	1.0
Barban	0.2	0.1	0.1	0.6	0.4	0.5
Neburon	0.2	0.1	0.1	1.1	0.4	0.5
Fenthion	0.3	0.3	0.2	0.5	0.5	1.0
Coumaphos	0.3	0.3	0.2	0.6	0.5	0.7
Fenchlorphos	0.1	0.1	0.1	0.8	0.5	0.7
Chlorpyriphos	0.4	0.3	0.4	1.3	0.9	1.0
Trifluralin	0.5	0.3	0.4	1.3	1.0	1.1
Bromophosethyl	0.3	0.3	0.2	0.5	0.5	0.5
Average	0.4	0.2	0.3	0.8	0.6[b]	0.8

[a] Detection limits difficult to determine because of interfering humic substances.
[b] Detection limits for monuron and propoxur not included.

μg/l depending on the analyte of interest and the column used (Table 3). In other words, the alert criterion of 1 μg/l for surface water is met for the majority of the test analytes, Again, the LC-18-DB column gave slightly lower detection limits than the other two columns.

3.2.3. Provisional identification of micropollutants in surface water

The short-column LC–DAD set-up was used to identify unknown compounds in river Rhine water taken at Lobith in June 1995. Fig. 4 shows the trace enrichment/analysis of 15 ml of river Rhine water on the 20×3.9 mm I.D. Symmetry column. From this chromatogram, two peaks were subjected to a comparison with our self-compiled DAD library, using a time-window-selected search. The peaks were tentatively attributed to atrazine and diuron (see inserts of Fig. 4). The presence of these pesticides in river Rhine water during that season is not surprising, because they are used in large amounts for weed killing in villages and fields situated along the banks of the river Rhine.

As another example, a water sample from the river Meuse (Belgium, May 1995), taken from a spot close to a wastewater outlet was analysed (Fig. 5). Numerous unknowns were found to be present in this sample which was analysed using a gradient run appropriately adapted from Ref. [14]. After a library search against our self-compiled DAD library, five peaks were provisionally identified as PAHs. As an illustration, spectral information on two of them, viz. peaks No. 1 (acenaphthylene) and No. 2 (phenanthrene) is provided in the inserts to the figure.

3.3. Overall performance

Within the one-year period of the present project the analytical performance of the system remained fully satisfactory. The only problem which was encountered was the clogging of one of the relatively small-bore capillaries of the LC system. This was probably due to insufficient mixing of the LC solvents and subsequent precipitation of phosphate in the presence of acetonitrile. Actually, one should add that for analyte mixtures such as are used in this

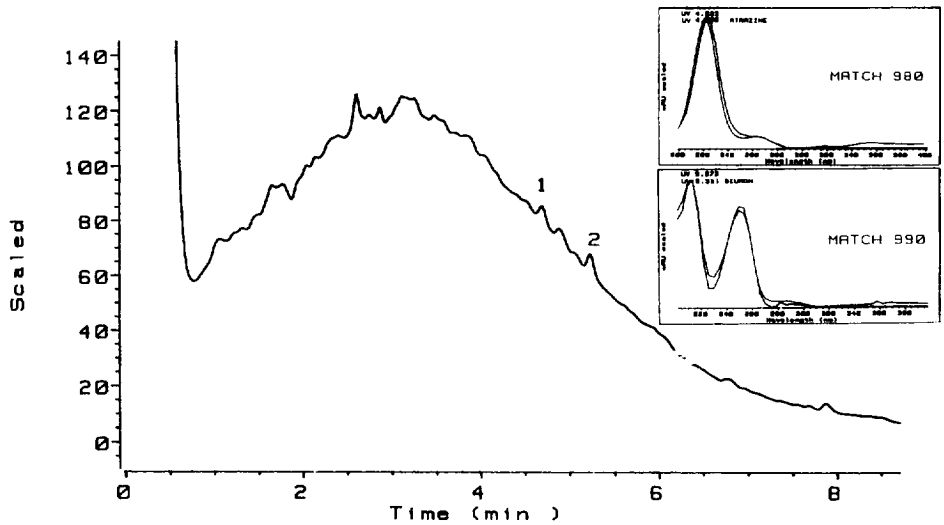

Fig. 4. Identification of microcontaminants in river Rhine water (Lobith, June 1995) using trace enrichment of 15 ml of river water and short-column LC–DAD on a Symmetry column. Inserts: UV spectra of (top) atrazine (peak No. 1) and (bottom) diuron (peak No. 2) compared with library spectra.

paper, HPLC-grade water can be used instead of an aqueous phosphate buffer without any complications [8].

As regards the robustness of the short columns and their overall performance, small mutual differences were observed. On the ODS Hypersil some 30 real samples (15 ml each) could be analysed without any appreciable deterioration, while the Symmetry and the LC-18-DB columns could be used for at least 40 analyses.

Furthermore, the design of the column holders for the LC-18-DB and Symmetry columns appeared to

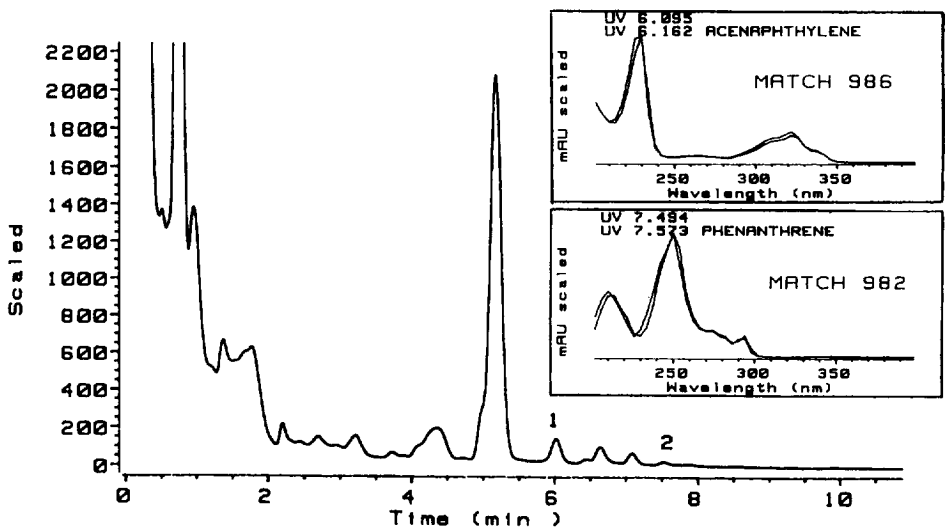

Fig. 5. Identification of some PAHs in a river Meuse (Belgium, May 1995) water sample taken close to a wastewater outlet using short-column LC–DAD on an ODS Hypersil column. Inserts: Comparison of UV absorbance spectra of acenaphthylene (peak No. 1) and phenanthrene (peak No. 2) with library spectra.

be more suitable than that of the holder for the ODS Hypersil column. Leakage problems occasionally occurred, at least in our hands, when using the last-named combination.

4. Conclusions

The potential of single-short-column LC–DAD was studied for the determination of a wide range of organic microcontaminants in environmental samples. The three types of 2-cm long high-pressure packed C_{18} bonded silica columns all gave satisfactory results in terms of analyte recoveries, peak capacity, linearity of response and precision of the various types of data. With detection limits of 0.1–1 μg/l for 15-ml tap and surface water samples and the possibility to run 30–40 samples on a single short column, the present approach is seen to have distinctions. It is interesting to add that, recently, another type of column became available to us, the base-deactivated C_{18} bonded ABZ^{+}-plus. With representative pesticides from all classes tested before, and several "difficult" analytes such as nitralin and 2,4,5-trichlorophenol, good results were again obtained. The only difference with these column types of Fig. 2 was that there were slight changes in elution order, with e.g., propoxur and alachlor eluting relatively late, and coumaphos rather early.

Now that the potential of single short column LC–DAD for monitoring and early-warning purposes has been established, our future research will mainly be in three directions. Firstly, optimization in terms of the dimensions of the short column will be pursued. It is interesting to mention that first results with a 1.25-cm long 5 μm Zorbax SB-C_{18} column were markedly successful. Comparison of the chromatographic traces of Fig. 6 shows that the very short SB-C_{18} column performs less well than the 2-cm Symmetry column used earlier in this study. However, it is also evident that the peak capacity of the short Zorbax column will be sufficient for many environmentally orientated screening purposes, and also for quite a number of applications in e.g., the pharmaceutical/biomedical area. Secondly, more attention will have to be paid to the selection of our short columns. So far, most of these columns have been conventional high-pressure packed guard columns. Although they are therefore manufactured according to specifications which are different from those used for real analytical columns, a large proportion work surprisingly well for analytical purposes, as is demonstrated in the present and several earlier papers. Still, a fair number of these guard columns were found not to meet our analytical standards and it is therefore of interest to improve or change packing procedures and/or obtain access to relevant information from instrument companies.

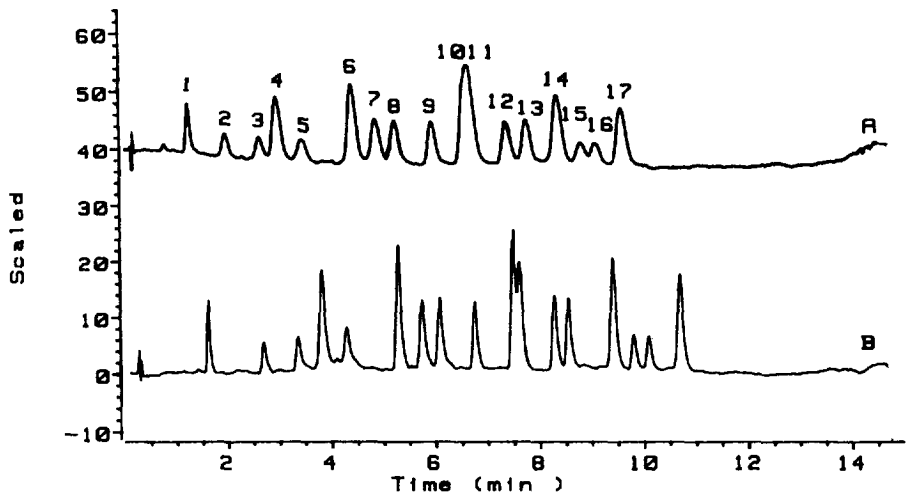

Fig. 6. Short-column LC–DAD chromatogram of a mixture of seventeen pesticides after loop injection (6 μl of 5 μg/ml of each pesticide in the mixture) on (A) the 12.5×4.6 mm I.D. SB-C_{18} Zorbax and (B) 20×4.0 mm I.D. Symmetry column. For peak assignment, see Fig. 2.

Thirdly, the use of DAD UV and (tandem) MS detection will be further explored for the rapid (provisional) identification of a wide range of organic microcontaminants.

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