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On-line trace enrichment of polar pesticides in environmental waters by reversed-phase liquid chromatography–diode array detection–particle beam mass spectrometry

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Abstract

The determination of a group of pesticides by RPLC–diode array detection, coupled on-line to particle beam MS, is developed for the analysis of different environmental waters. On-line trace enrichment of 100 ml of sample on a PLRP-S precolumn allows the determination of most pesticides at levels between 0.2 and 5 $\mu g\ l^{-1}$ and detection limits in the range 0.05–0.5 $\mu g\ l^{-1}$ for diode array detection and 0.02–0.5 $\mu g\ l^{-1}$ for particle beam MS. With real-life samples, a distinct matrix effect is observed in particle beam MS detection, which is caused by coeluting compounds acting as carriers. This improves analyte detectability and requires standard addition to be used for quantification. Different river and drinking waters were analysed and some pollutants were detected at sub- $\mu g\ l^{-1}$ levels.

1. Introduction

The determination of medium and highly polar pollutants in water is mainly carried out by RPLC [1–6] using a variety of detectors, the UV–visible absorbance detector being the most popular one because of its robustness and wide application range. Fluorescence and electrochemical detectors provide higher sensitivity and selectivity but, because of the latter aspect, the number of compounds that can be detected is rather limited. The lack of confirmatory power of absorbance detection is partially solved by the use of diode array detection (DAD), but the UV spectra within one compound class often are not very different and the confirmatory power of DAD is limited.

Mass spectrometric (MS) detection in LC is becoming increasingly important, because of its high confirmatory power, which is very important in environmental analysis because of the legal implications of analytical data. Different interfaces have been developed [7–10] and, although thermospray is the most popular one for the analysis of environmental pollutants [11–13] because of its high sensitivity, the advantage

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of obtaining electron impact (EI) spectra when using the particle beam (PB) interface makes PB-MS very powerful in the detection and determination of pollutants. In fact, the determination of medium and highly polar pesticides by RPLC–PB-MS is reported in literature [14–16]. The possibility to obtain positive and/or negative chemical ionization spectra increases the confirmatory power of MS detection.

The poor sensitivity of the particle beam interface is quite well known. Several attempts have been made to improve it, such as the addition of a carrier to the eluent [17] or of compounds with a structure similar to that of the analytes of interest to improve transport through the interface. The use of isotopically labelled analogues of each compound has also been applied to increase the sensitivity [18,19]. Two further drawbacks for quantitation are the non-linearity of calibration plots and the enhancement of the analyte signal because of coeluting compounds acting as a carrier. However, in one recent study [20], good linearity was obtained for several compounds.

Since the detection limits typically obtained in RPLC–PB-MS do not allow to determine pesticides at the low tolerance levels of 0.1 $\mu g\ l^{-1}$ for drinking water and 1–3 $\mu g\ l^{-1}$ for surface water, a preconcentration system prior to LC is necessary. The advantages of on-line trace enrichment procedures include better sensitivity, lower consumption of organic solvents, higher automation potential and simplicity of the analysis compared with off-line procedures and are widely described in Refs. [21–24]. The applicability of on-line trace enrichment–RPLC has been demonstrated for the determination of many pesticides with DAD [1–3,24,25] and also for MS detection with the thermospray [26–28] and PB interfaces [20].

Some authors use LC–DAD for quantitative analysis because of its robustness and an additional analysis by LC–MS is carried out when any pesticide is suspected in order to confirm its presence. Although this is a proper procedure, two analytical runs are now required. Therefore, in the present paper on-line trace enrichment–RPLC–DAD–PB-MS has been used for the determination of a group of pesticides in drinking and surface water and quantitative results from DAD and PB-MS are compared.

2. Experimental

2.1. Chemicals

All pesticides were of 98–99% purity; they were obtained from Riedel-de Häen (Seelze, Germany). Stock solutions of each compound were prepared at the 1000 $\mu g\ ml^{-1}$ level in HPLC-grade methanol (Scharlau, Barcelona, Spain). If stored in a refrigerator at 8°C, the solutions were stable for several months. Working stock solutions of all pesticides at a concentration of 40 $\mu g/ml$ were prepared in methanol; they were diluted to different concentrations with methanol for calibration graph construction.

HPLC-gradient-grade methanol (Scharlau) and 0.1 *M* ammonium acetate were used to prepare the LC eluent. Ammonium acetate was from Panreac (Montcada i Reixac, Spain). An appropriate amount of the salt was dissolved in water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and pH was adjusted to 5 with acetic acid (Probus, Badalona, Spain). The ammonium acetate solution was filtered through a 0.45-μm nylon filter prior to use.

Helium for the PB interface was 99.995% pure from Carburos Metalicos (Barcelona, Spain).

2.2. Instrumentation

LC was performed on a HP 1090 liquid chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with two pumps, a diode array detector, a six-port rotary valve and an autosampler. The system was controlled by a HP Workstation HP79994A which also performed data acquisition from DAD. Helium was used for solvent degassing. The analytical column was a 200×4.0 mm I.D. stainless-steel column packed with Spherisorb ODS2, 5 μm (Teknokroma, Barcelona, Spain). The precolumn consisted of a holder and a 10×2.0 mm cartridge packed with

15–25 μm PLRP-S styrene–divinylbenzene copolymer (Spark Holland, Emmen, Netherlands). An Applied Biosystems (Ramsey, USA) pump was used to deliver the sample and wet the precolumn.

The diode array detector was set at 240, 254 and 280 nm and spectra were recorded in the range 200–400 nm.

A Hewlett-Packard 5989 A MS Engine, equipped with a dual EI/chemical ionization source was connected to the DAD outlet via a Hewlett-Packard PB interface. All data were acquired on a HP UX 59944C data system. The ion source block and quadrupole temperatures were set at 250 and 100°C, respectively. The MS Engine was tuned to m/z 69, 219 and 502 corresponding to perfluorotributylamine. The scan range was m/z 64–400 u, in order to avoid noise due to ammonium acetate, at 2 s/scan.

Interface tuning and signal optimization were conducted by injecting solutions of 500 ng monuron by flow injection analysis using methanol–0.1 *M* ammonium acetate (60:40, v/v) as the carrier stream. The desolvation chamber temperature was set at 65°C and the helium nebulizer pressure at 50 p.s.i. (1 p.s.i. = 6894.76 Pa). Typical operating pressures were 0.5 Torr (1 Torr = 133.322 Pa) at the second-stage momentum separator and $1.5 \cdot 10^{-5}$ Torr in the ion source chamber.

After background subtraction the spectrum of each compound was compared with those in the Wiley library and good confidence levels were obtained although the reference spectra were generated using either a direct insertion probe or GC.

The area of the base peak ion for each compound extracted from the total ion chromatogram was used in the quantification procedure of PB-MS data.

2.3. Analytical procedure

The PLRP-S precolumn was flushed at 5 ml min^{-1} with 5 ml of methanol and 5 ml of methanol–ammonium acetate (pH 5.0) (30:70, v/v). Subsequently, a 100-ml sample was preconcentrated (4 ml min^{-1}) on the precolumn. The analytes trapped on the precolumn were desorbed in the backflush mode with methanol–0.1 *M* ammonium acetate (pH 5.0) (30:70, v/v) and transferred on-line to the analytical column. The actual separation of the analytes was carried out using a linear gradient of methanol–0.1 *M* ammonium acetate (pH 5.0) from 30:70 to 88:12 in 34 min. The flow-rate of the HPLC eluent was 0.4 ml min^{-1} and the column temperature was 40°C.

3. Results and discussion

3.1. RPLC–DAD–PB-MS

The scheme of the total system used is shown in Fig. 1. Firstly, chromatographic conditions

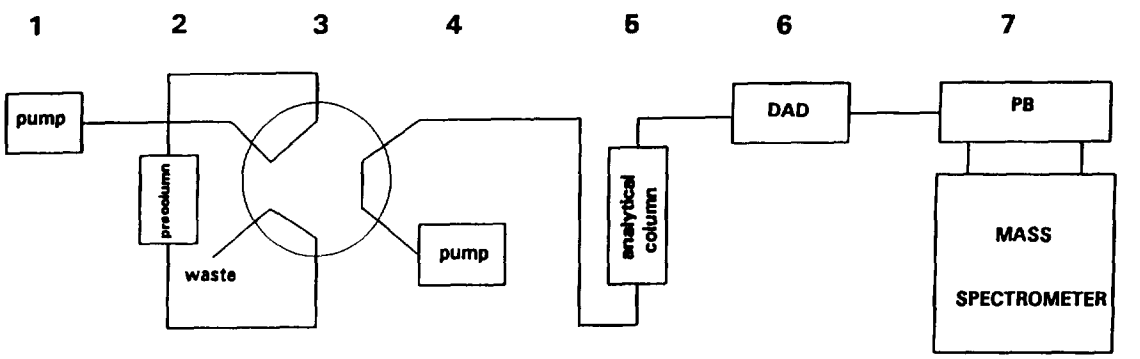

Fig. 1. Scheme of the experimental set-up. 1 = Pump delivering sample; 2 = PLRP-S precolumn; 3 = six-port rotatory valve; 4 = eluent pump; 5 = analytical column; 6 = diode array detector; 7 = particle beam interface and mass spectrometer.

were optimized based on previous results [20]. The ammonium acetate added to the eluent acts as a carrier and extends the PB-MS linear range [29]. Methanol was chosen as this is the solvent to be recommended from the PB-MS point of view. Although 2.1 mm I.D. analytical columns are preferred for PB-MS analysis, because of the relatively low flow rates which are permitted, a 4.6 mm I.D. column was selected as this implies better results when an on-line trace enrichment cartridge is connected to the column. A flow of 0.4 ml min^{-1} was selected because it is the recommended flow for the PB interface, and does not cause undue peak broadening.

A linear gradient of methanol–ammonium acetate (pH 5) from 30:70 to 88:12 in 34 min was used to carry out the separation of the analytes. The retention times of each analyte with the gradient profile are included in Table 1. As can be seen, all compounds are eluted in 30 min. Monuron and propuxur coeluted; still at low concentrations and when detecting at 280 nm they could be quantified separately. Unfortunately, at this wavelength the sensitivity was much lower than at 254 nm which is conventionally used for analytes.

For DAD chromatograms were recorded at 240, 254 and 280 nm. The wavelength used to quantify each compound is included in Table 1. Although lower wavelengths are sometimes used for some compounds, with the present eluent a serious distortion of the baseline was observed at lower wavelengths, mainly due to the presence of ammonium acetate.

Coupling PB-MS to the outlet of the DAD system did not cause noticeable additional peak broadening and satisfactory data from DAD and MS could be obtained from a single injection. As an illustration, Fig. 2 shows a total ion chromatogram obtained with PB-MS and a chromatogram using DAD after 5 μl injection of a standard solution of 40 μg ml^{-1} of each pesticide.

As regards MS detection, the base peak of each compound is included in Table 1. It must be pointed out that the m/z range for acquisition was 64–400, even though some compounds, such as linuron, have their base peak (m/z 61) at lower m/z values which implied a loss of sensitivity. The m/z range was selected in order to avoid noise caused by ammonium acetate [7].

Good linearity was obtained for all compounds from 1 to 40 μg ml^{-1} at the wavelengths shown in Table 1, with R^2 values between 0.986 and 0.9998. Calibration plots for the base peak of each compound obtained from the total ion chromatogram were constructed from 2 to 40 μg

Table 1
Name of pesticides studied, class of pesticide, retention time, λ used for measuring the absorbance and base peak used for quantification from chromatogram under full-scan acquisition conditions

Compound	Class	t_R (min)	λ_{selec} (nm)	Base peak (m/z)
Oxamyl	C	7.12	240	72
Methomyl	C	8.55	240	105
Aldicarb	C	16.87	254	68
Cyanazine	T	18.47	240	212
Monuron	P	19.84	254	72
Propoxur	C	19.84	280	110
Carbofuran	C	20.36	280	164
Simazine	T	21.14	240	201
Carbaryl	C	21.85	280	144
Fluometuron	P	22.99	240	72
Atrazine	T	25.10	240	200
Diuron	P	25.81	254	72
Linuron	P	28.12	254	161
Barban	C	28.60	240	153

C = Carbamates; P = phenylureas; T = triazines.

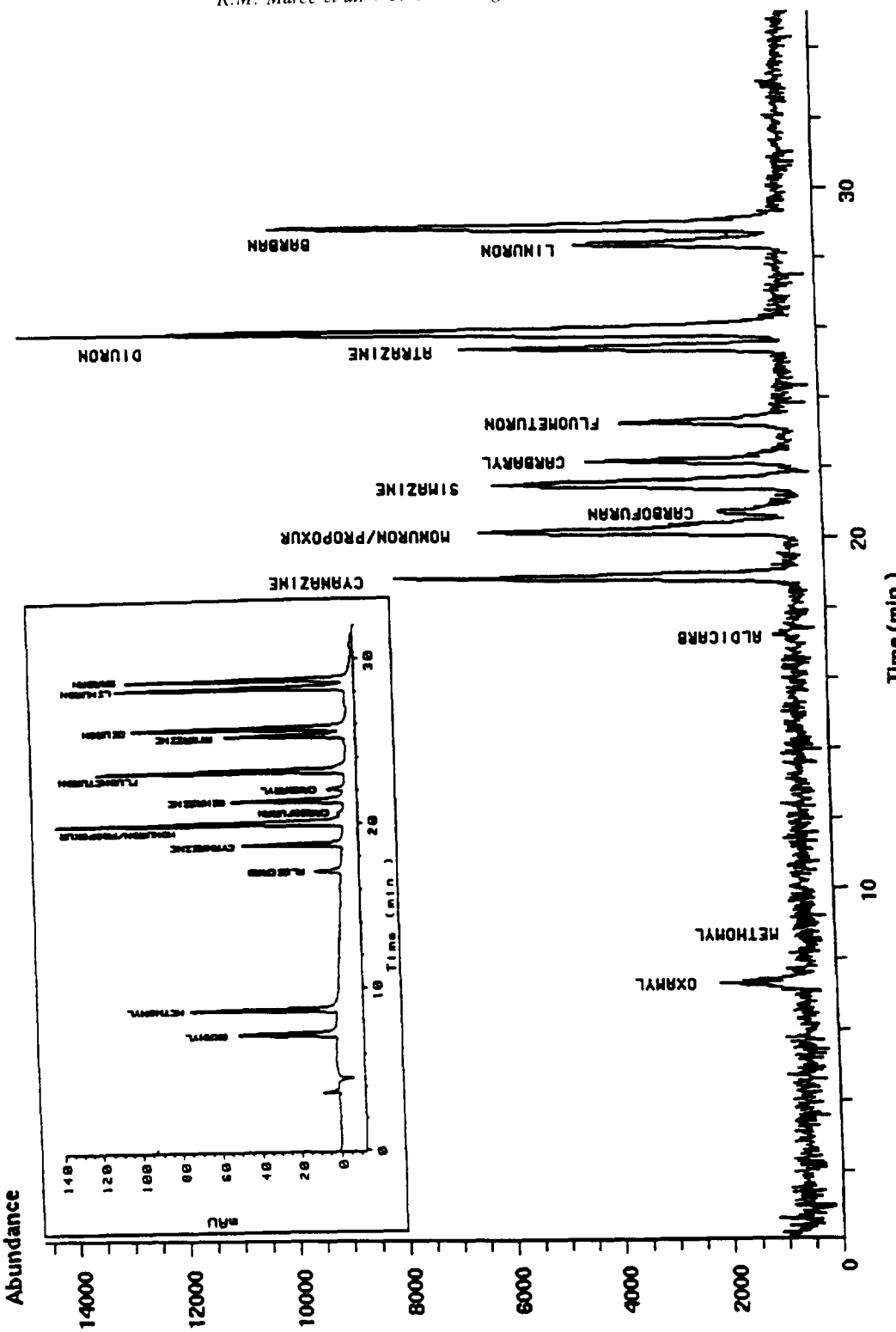

Fig. 2. RPLC–PB-MS total ion chromatogram of a standard solution of 14 pesticides at 40 $\mu g\ ml^{-1}$. The insert shows the RPLC–DAD chromatogram at wavelength 240 nm.

ml^{-1}. For most compounds the linearity was quite good (R^2 between 0.982 and 0.9990); an exponential response was obtained for compounds such as methomyl, aldicarb and simazine. Although better sensitivity could be obtained by using selected ion monitoring (SIM), full-scan acquisition was preferred since the spectrum of each pesticide can then be obtained.

3.2. Trace enrichment

Trace enrichment was carried out by using an on-line solid-phase extraction system. A highly hydrophobic styrene–divinylbenzene precolumn was selected because of the higher breakthrough volumes for most compounds studied, compared with C_{18}-bonded silica material.

Different sample volumes were preconcentrated and the recoveries for each compound were calculated using DAD (25, 50 and 100 ml of Milli-Q water, without any pH adjustment; spiking at 1 $\mu g\ l^{-1}$, see Table 2). From these results, and taking into account the level of these pesticides allowed in drinking water (0.1 $\mu g\ l^{-1}$), a volume of 100 ml was selected for further studies although with this volume, the recoveries of methomyl and oxamyl were lower than 20% due to early breakthrough.

Linearity of the response for the total analytical system, including the preconcentration step, was checked for a sample volume of 100 ml of Milli-Q water spiked at different concentrations. Good linearity was obtained from 0.2 to 5 $\mu g\ l^{-1}$ for all compounds (with the exception of methomyl, oxamyl and aldicarb) using both DAD and PB-MS. R^2 values obtained were between 0.990 and 0.9996 for DAD and between 0.984 and 0.996 for PB-MS. The early eluting compounds, methomyl and oxamyl, were not included because their recoveries were very low. The detection of aldicarb was not very sensitive with either DAD or PB-MS (Fig. 2) and linearity was therefore checked from 1 to 5 $\mu g\ l^{-1}$ (R^2 values of 0.994 and 0.990, respectively).

Fig. 3 shows a chromatogram obtained for 100 ml of Milli-Q water spiked at 1 $\mu g\ l^{-1}$ of each pesticide using DAD. Although some peak broadening is apparent it is not really detrimental for monitoring purposes.

Table 2
Recovery and relative standard deviation ($n = 4$) of pesticides at 1 $\mu g\ l^{-1}$ in Milli-Q water at different sample volumes

Compound	Sample volume (ml)					
	25		50		100	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Oxamyl	38	7	45	9	20	11
Methomyl	30	10	16	9	8	14
Aldicarb	94	6	86	7	85	6
Cyanazine	86	8	90	6	92	7
Monuron	93	5	84	4	82	5
Propoxur	95	4	94	5	80	6
Carbofuran	102	3	98	4	97	4
Simazine	88	4	85	6	82	6
Carbaryl	90	5	92	3	94	4
Fluometuron	96	2	101	3	92	2
Atrazine	96	4	92	3	87	5
Diuron	92	3	87	5	85	5
Linuron	94	5	85	4	82	6
Barban	80	6	76	7	70	7

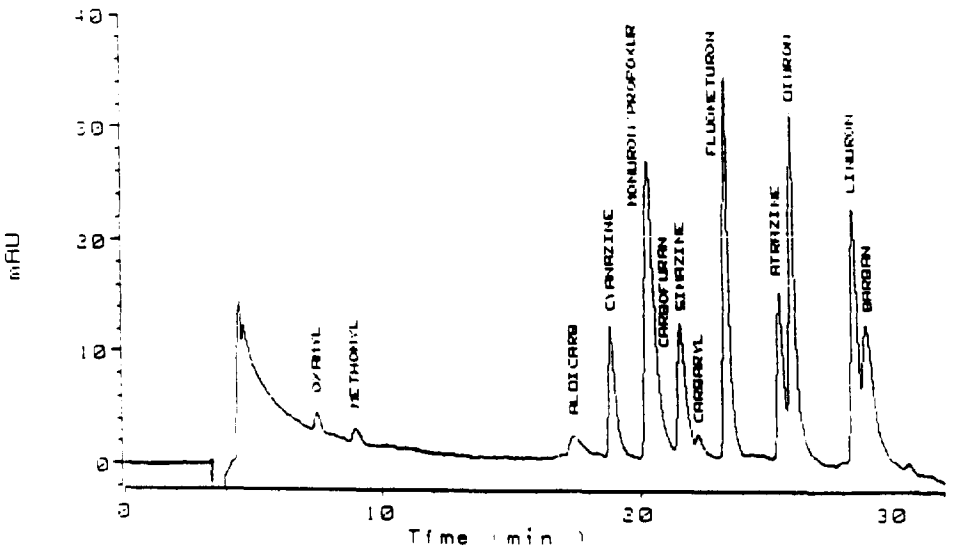

Fig. 3. On-line trace enrichment–RPLC–DAD chromatogram recorded at 240 nm of 100 ml Milli-Q water spiked with 14 pesticides at 1 $\mu g\ l^{-1}$ without any pH adjustment (pH about 6). For conditions, see text.

3.3. Performance of the total system

The analytical performance of the system was tested with tap and river water. Initially the influence of the pH of the sample solution was tested. No significant differences were found between recoveries obtained at pH 3 and at pH 6. However, adjusting the sample pH to 3 gave a larger matrix peak. We therefore preferably carried out the preconcentration at pH about 6, which actually meant that the samples could be preconcentrated without any pH adjustment. It should be point out that no clogging of the cartridge was observed with river water previously filtered through 0.45 μm.

The matrix peak which is mainly due to humic and fulvic acids did not appear in the PB-MS chromatograms. However, quantitative analyses showed a matrix effect at both pH values tested, higher responses being obtained compared with those found for preconcentration of Milli-Q water. This is due to a carrier effect [30] which is caused by the coelution of compounds acting as carriers; it was observed with both tap and surface water. This implies that quantification using PB-MS detection can not be carried out with calibration curves constructed for Milli-Q water; instead, standard addition must be used. The matrix effect caused the detection limits for some compounds in real samples to be lower than those obtained with Milli-Q water.

As regards linearity, this was essentially as good for the real-life water samples as for Milli-Q water. In the relevant ranges, the R^2 values were between 0.984 and 0.9990 for DAD (river water, 0.5–5 $\mu g\ l^{-1}$; tap water, 0.2–5 $\mu g\ l^{-1}$) and between 0.975 and 0.990 for PB-MS (0.2–5 $\mu g\ l^{-1}$ for both types of water). It should be added that, with the total analytical system, linear rather than the earlier exponential calibration plots were also observed for simazine and aldicarb.

Using DAD, it was found that the recovery for the complete on-line procedure with water samples spiked with 0.5 $\mu g\ l^{-1}$ of each pesticide was higher than 80% for both tap and river water, except for the first two eluting compounds, as was expected on the basis of the breakthrough volumes.

The repeatability of the method was checked with a 100-ml tap water sample spiked at the 1 $\mu g\ l^{-1}$ level. R.S.D. values were between 0.4

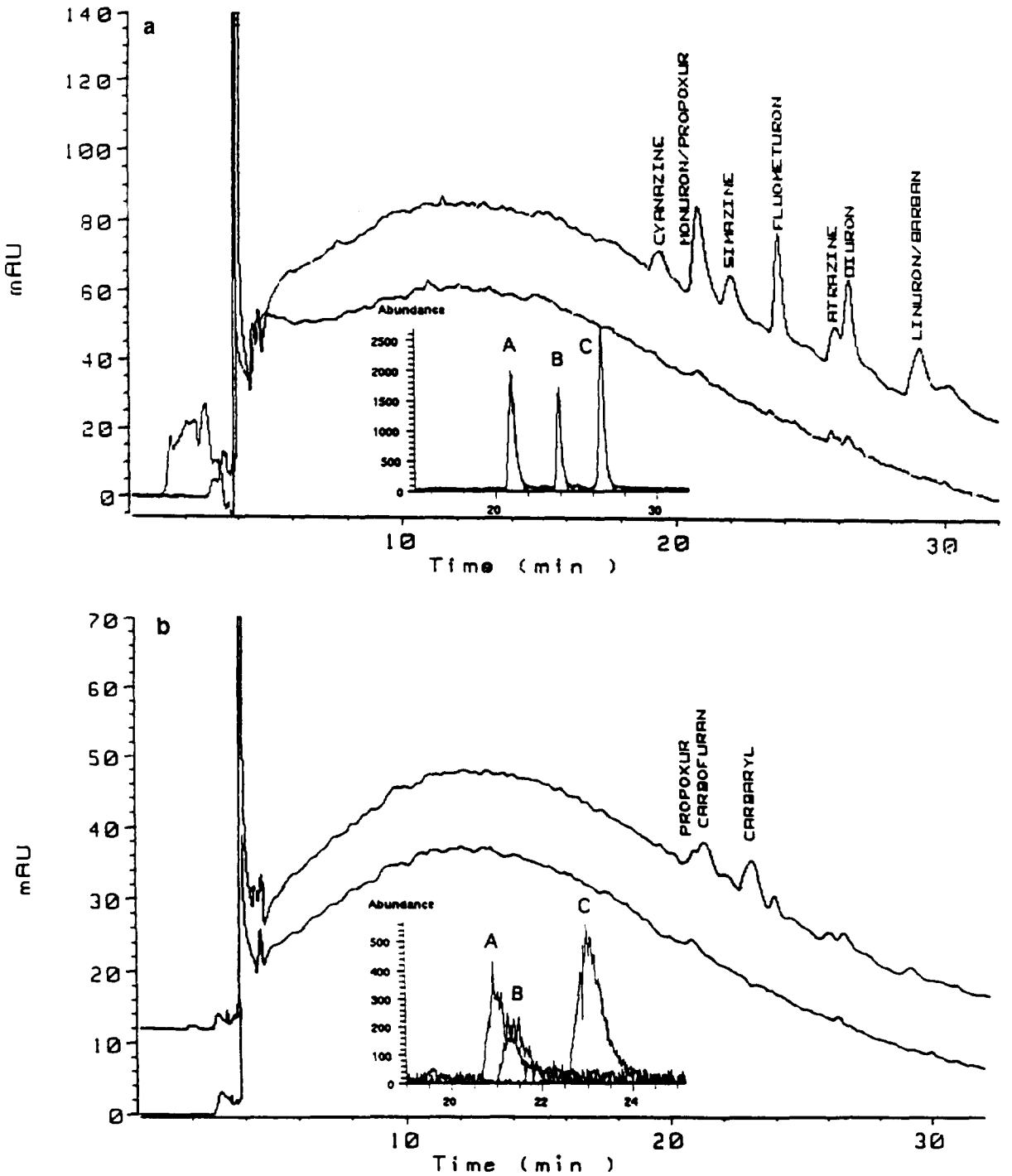

Fig. 4. On-line trace enrichment–RPLC–DAD chromatograms of 100 ml of river water and 100 ml of river water spiked with 14 pesticides at 1 $\mu g\ l^{-1}$. (a) Recorded at 240 nm; inset shows the PB-MS mass chromatogram of m/z 72: A = monuron, B = fluometuron, C = diuron. (b) Recorded at 280 nm; inset shows the PB-MS mass chromatograms of: A = propoxur (m/z 110), B = carbofuran (m/z 164), C = carbaryl (m/z 144).

and 9% for DAD and between 3 and 16% for PB-MS ($n = 4$). These are quite satisfactory results for the low concentration studied.

The limit of detection ($S/N = 3$) of the method varied between about 0.5 and 0.05 $\mu g\ l^{-1}$ for DAD and between about 0.5 and 0.02 $\mu g\ l^{-1}$ for PB-MS detection (full scan acquisition but quantification of highest peak), depending on the sample type and the analyte. It should again be pointed out that the matrix effect improves the response using PB-MS detection with real samples, especially for atrazine and carbofuran.

Fig. 4 shows the RPLC–DAD chromatograms of 100 ml of a river water sample (no pH adjustment) recorded at 240 nm and at 280 nm and the chromatograms for the same samples spiked with 1 $\mu g\ l^{-1}$ of each pesticide. The inserts show the RPLC–PB-MS mass chromatograms of the same sample using proper m/z values for the selective detection of several of the test analytes. The difference in both analyte detectability and selectivity is striking.

In order to further illustrate the potential of LC–PB-MS, Fig. 5 shows mass chromatograms at m/z 72, 144, 200 and 164 which were recorded after trace enrichment of 100 ml of tap water spiked with the several pesticides at the 0.1 $\mu g\ l^{-1}$ level.

3.4. Applications

Various river Ebro water samples were analysed and some pesticides were found. The mass chromatogram at m/z 72 obtained for one such sample is shown in Fig. 6. The peak which was eluted at 25.8 min could be assigned to isoproturon on the basis of a comparison with the retention time and the PB-MS spectrum of a

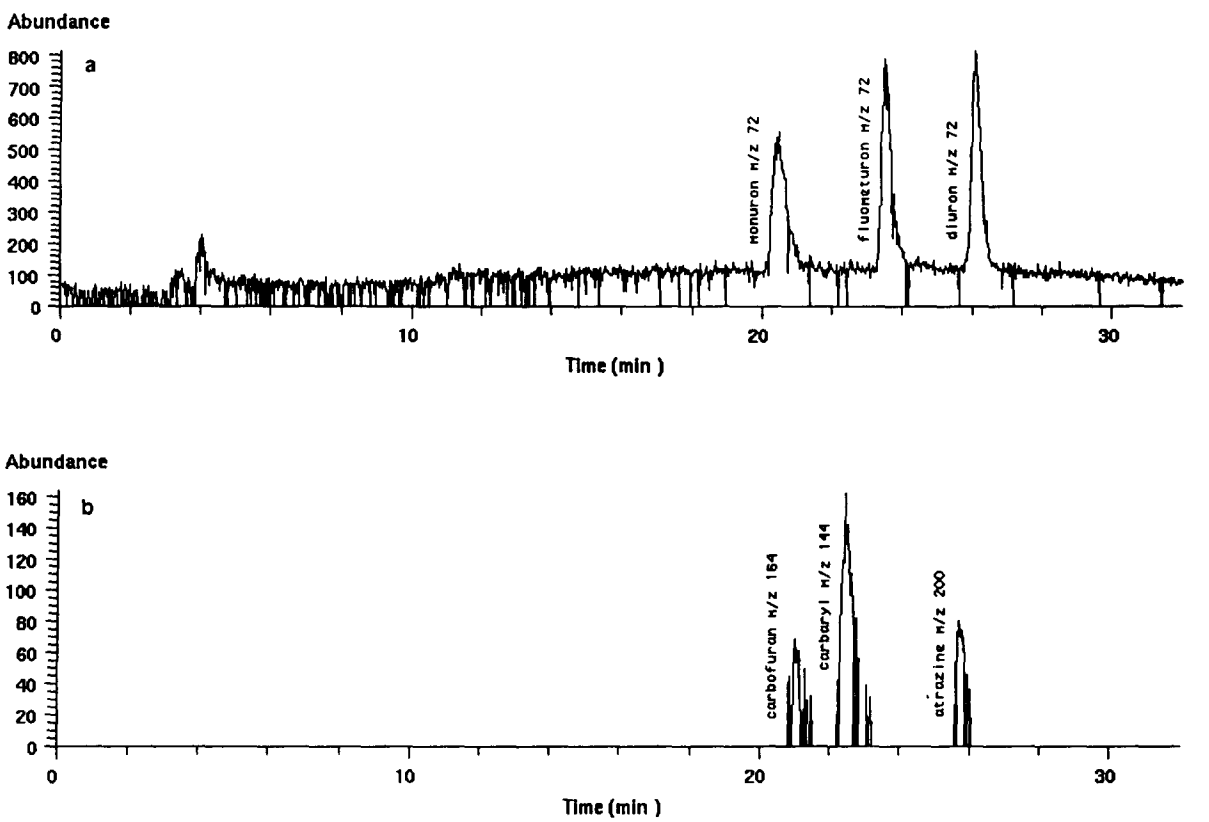

Fig. 5. On-line trace enrichment–RPLC–PB-MS extracted ion chromatogram of 100 ml tap water spiked with pesticides at 0.1 $\mu g\ l^{-1}$: (a) m/z 72; (b) m/z 164 (carbofuran), m/z 144 (carbaryl) and m/z 200 (atrazine).

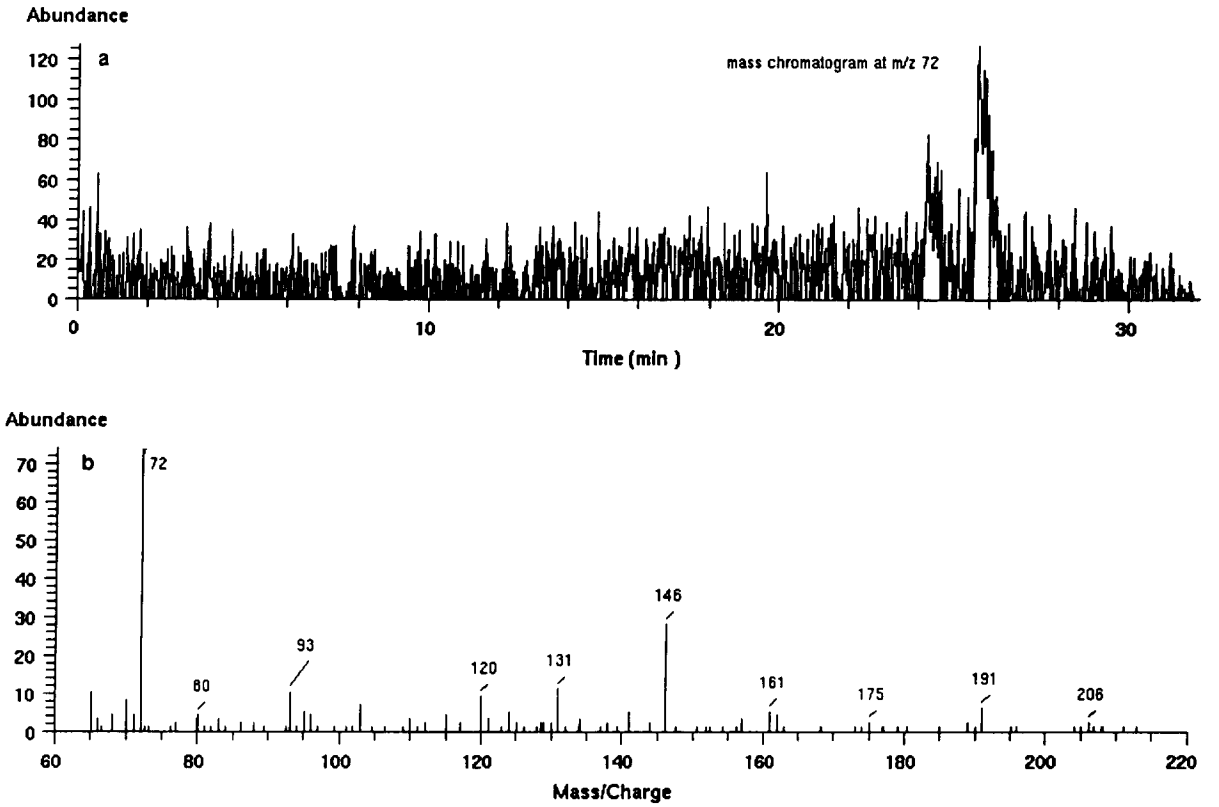

Fig. 6. (a) On-line trace enrichment–RPLC–PB-MS mass chromatogram (m/z 72) of 100 ml river Ebro water. (b) PB-MS spectrum of peak assigned to isoproturon (25.8 min). The peak at 24.3 min has not been identified as yet.

standard. It should be pointed out that although the peak intensity of the mass chromatogram was low, the spectrum showed a good match with the spectrum of the standard (95%). When using DAD instead of PB-MS detection, a small peak was observed at the proper retention time but spectral identification turned out to be impossible. After construction of PB-MS and DAD calibration curves, quantitation gave isoproturon levels of 0.074 $\mu g\ l^{-1}$ (standard addition) and 0.070 $\mu g\ l^{-1}$, respectively. The close similarity of these values is rather gratifying. Actually, in other river water samples isoproturon could be quantified by RPLC–PB-MS down to 0.05 $\mu g\ l^{-1}$; in these instances, no noticeable signal was observed with DAD.

Another example of a pollutant that was detected by means of on-line trace enrichment–RPLC with PB-MS, but not with DAD is presented in Fig. 7, which shows the mass chromatogram at m/z 77 of a 100-ml river Ebro sample, the mass spectrum of the peak of interest and the best match from the Wiley library. On this basis, the peak could be tentatively assigned to N-benzenesulfonamide which has been detected in the river Ob [20] and in water from several other rivers [31].

4. Conclusions

The present study demonstrates that on-line trace enrichment–RPLC–DAD–PB-MS presents no experimental problems and can be used for the trace-level determination of micropollutants in surface and tap water at levels of, typically, 0.2–5 $\mu g\ l^{-1}$ and 0.5–5 $\mu g\ l^{-1}$, respectively. Quantification is possible with both detection

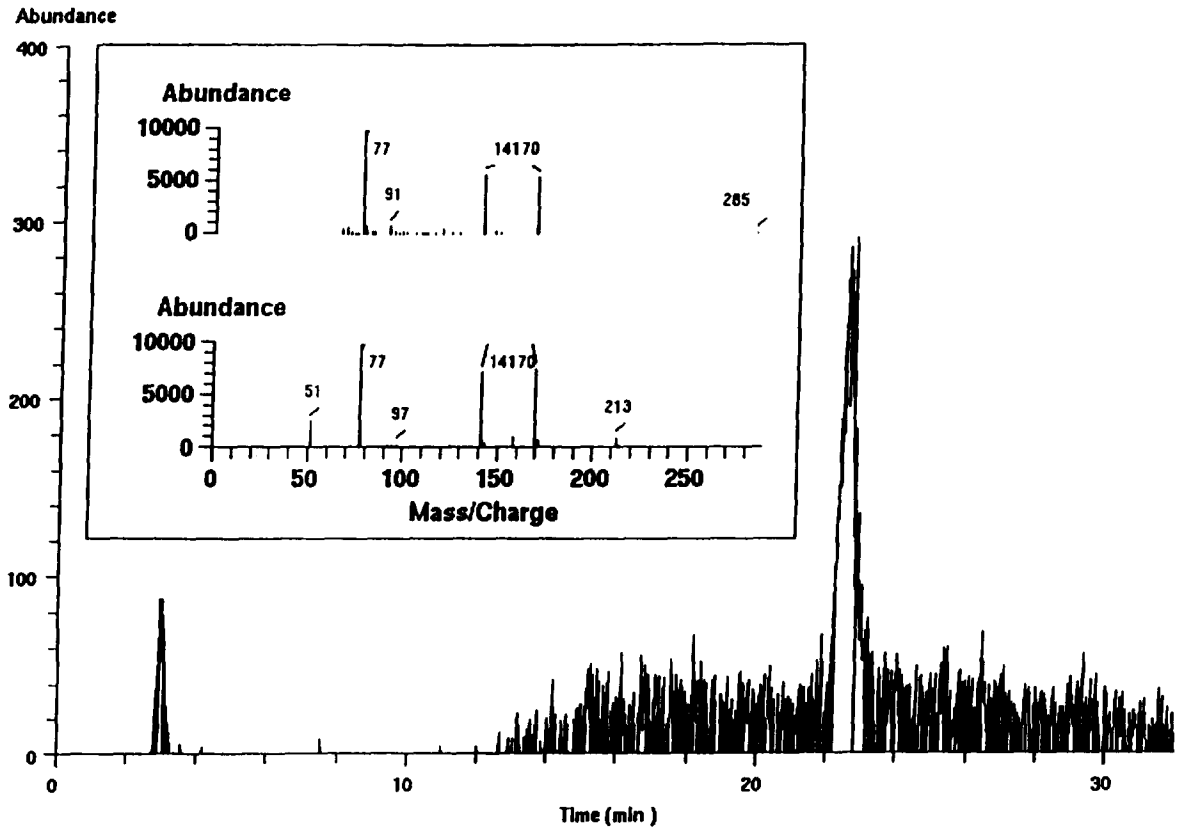

Fig. 7. Ion chromatogram at m/z 77 of 100 ml of river water and PB-MS spectrum of the peak at 22.5 min (inset, top; 22.462–22.736 min) and the PB-MS spectrum of N-benzenesulfonamide from the Wiley library (inset, bottom).

modes, although standard addition is required with PB-MS detection because of a beneficial carrier effect due to coeluting compounds in real samples. The main advantage of the present set-up is that complementary UV–Vis absorbance and EI-type mass spectral data are collected in one run. The high confirmatory power is illustrated with isoproturon and N-benzenesulfonamide as examples. It is worthwhile to add that the analyte detectability observed with PB-MS is rather better than is often assumed.

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