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On-line coupling of solid-phase extraction to gas chromatography with mass spectrometric detection to determine pesticides in water

E. Pocurull*, C. Aguilar, F. Borrull, R.M. Marcé

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Imperial Tàrraco, 1, 43005 Tarragona, Spain

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Abstract

A group of pesticides with different chemical structures was determined in water by on-line coupling of solid-phase extraction to gas chromatography with mass spectrometric detection through an on-column interface. A 10 mm×2 mm I.D. precolumn packed with PLRP-S was selected for the solid-phase extraction process. The parameters affecting the transfer of the analytes from the precolumn to the GC system (e.g. flow-rate, temperature and solvent vapor exit time) were optimized. An organic modifier was added to the sample before the extraction process to avoid adsorption problems. The use of the MS detector under selected ion monitoring acquisition enabled the analytes to be quantified at sub microgram-per-litre levels preconcentrating only 10 ml of sample, and the limits of detection ($S/N=3$) were between 2 and 20 ng l^{-1}. The method was applied to the determination of the pesticides in tap and river water, and molinate was determined in Ebro river water.

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

The determination of pesticides in water commonly involves a preconcentration step and subsequent separation using a chromatographic technique. The on-line coupling of the sample preconcentration process and the separation–detection process allows automation and prevents contamination from external sources. For such on-line systems, solid-phase extraction (SPE) is generally preferred to liquid–liquid extraction (LLE) because it minimizes some of the drawbacks of LLE such as the need for large amounts of organic solvent [1,2].

In most instances, capillary gas chromatography (cGC) is the chromatographic technique selected because of its excellent separation efficiency, its high speed of analysis and the wide range of sensitive and selective detectors available [3–5]. Mass spectrometric (MS) detection is most used because of its identification capacity [6,7].

The on-line coupling of SPE to GC requires the injection of relatively large volumes of organic solvents, while conventional GC injectors only allow a few microliters. Recently several reviews have been published [8–11] about the injection techniques which have been developed with the aim of enabling large volumes of organic solvent to be injected. These techniques include partially concurrent solvent evaporation (PCSE) using an on-column interface [12–15], fully concurrent solvent evaporation (FCSE) with a loop-type interface [16,17] and the programmed temperature vaporizer (PTV) injection

*Corresponding author.

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technique [18–20]. The loop type interface is more easily optimized, but the on-column interface is more suitable when volatile analytes are to be determined [21]. PTV injection is receiving considerable attention at the moment because it can be used to inject thermally unstable analytes, and volatile compound losses are minimized by using packed liners [22].

So far, only a few methods for determining pesticides in water based on on-line SPE–GC have been published [23–28], most of which use an on-column interface [23,24] because of its wide application range. The methods developed include a drying step to remove water from the precolumn before elution. Gas purge is the approach selected to this end because it is easier to perform [10,25], but some researchers use a drying agent between the precolumn and the analytical column [29]. The elution solvent is usually injected into the GC by a retention gap technique and the vapors generated are mostly eliminated through the solvent vapor exit (SVE) which is between the retaining precolumn and the analytical column in order to minimize losses of the most volatile compounds [23,24]. About 100 μl of solvent is injected into the GC in most of the applications described.

The main aim of the present work is to describe the potential of on-line SPE–GC–MS using an on-column interface to determine a selected group of pesticides in environmental waters. The compounds that have been selected are either used in the Ebro delta or are on the priority list of contaminants and include pesticides with different volatilities and properties.

2. Experimental

2.1. Reagents and standards

The compounds studied were as follows: molinate, dimethoate, fenitrothion, malathion, tetrachlorvinphos, simazine, atrazine, ametryn, prometryn, heptachlor, aldrin, heptachlor-endo, α-endosulfan, dieldrin, α-HCH, γ-HCH and δ-HCH. All compounds were from Riedel-de Häen (Seelze-Hannover, Germany) except fenitrothion and malathion which were supplied by Dr. Ehrenstorfer (Augsburg, Germany). A standard solution of 2000 mg l^{-1} of each compound was prepared in ethyl acetate and stored in the refrigerator. A solution of 100 mg l^{-1} in ethyl acetate was prepared weekly from the standard solutions and used to prepare dilute solutions and to spike water samples to the required concentrations.

Ethyl acetate and methanol, both trace analysis grade, were from Merck (Darmstadt, Germany). Water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Helium and nitrogen were supplied by Carburos Metálicos (Tarragona, Spain) with a quality of 99.995%.

2.2. Equipment

Chromatographic experiments were performed using a Hewlett-Packard HP 6890 Series gas chromatograph (Waldbronn, Germany) equipped with an on-column injector and an HP 5973 mass selective detector. Chromatographic data were recorded using an HP G1701AA CHEMSTATION which was controlled by Windows 95 (Microsoft) and equipped with the Hppest mass spectral library. An HP G2399A SVE kit was installed in order to enable larger volumes to be injected and the chromatographic separation to be carried out. The SVE kit consisted of a 5 m×530 μm I.D. retention gap, a 2 m×250 μm I.D., 0.25 μm retaining precolumn and a 30 m×250 μm I.D., 0.25 μm analytical column, both HP-5MS, and a solvent vent valve. All connections were made with conventional glass press-frits.

For the solid-phase extraction, the precolumn (10×2 mm I.D.) was hand-packed with a styrene–divinylbenzene copolymer (PLRP-S, 100 Å, 20-μm particle size) (Polymer laboratories, Shropshire, UK). Three six-port Valco valves (Houston, USA), controlled by the GC software, were used in the SPE process. An HP 1100 pump was used to deliver the sample and the solvents needed to clean and activate the sorbent. The eluent was delivered with a syringe pump (Cole-Parmer, Illinois, USA). The analytes were transferred from the precolumn to the GC system via a 30 cm×0.10 mm I.D. fused-silica capillary which was permanently mounted in the on-column injector. A 100-μl loop made of polyether ether ketone (PEEK) tubing (HP) was used instead of the precolumn when direct injections were carried out. The scheme of the equipment described

above to perform the on-line SPE–GC–MS method is shown in Fig. 1.

2.3. Chromatographic conditions

The initial temperature of 60°C was maintained constant until the analytes had been preconcentrated and transferred (56.5 min). Then it was increased to 150°C at 25°C min^{-1}, and finally to 205°C at 2°C min^{-1}. The on-column injector worked in the track oven mode and the carrier gas (helium) was maintained at a flow-rate of 1.2 ml min^{-1}. The MS transfer line was kept at 280°C to prevent the analytes from recondensing.

The electron impact (EI) ionization conditions were the following: ion energy 70 eV and mass range 50–400 in the full scan mode. The scan-rate was 4.10 scans s^{-1}. Selected ion monitoring (SIM) acquisition was carried out by acquiring data from the ions in Table 2. The MS was tuned to m/z 69, 219 and 502 for the EI corresponding to perfluorobutylamine (PFTBA).

2.4. On-line trace enrichment

The on-line trace enrichment experiments were performed using three six-port valves connected in series to make the different steps of the preconcentration process possible. Firstly, the precolumn was cleaned and conditioned with 3 ml of methanol and 3 ml of water. Then, 10 ml of the sample containing 30% of methanol was preconcentrated. The flow-rate used throughout all this process was 2 ml min^{-1} and the tubes were purged with the corresponding solution (methanol, water or sample) before it was passed through the precolumn. In the next step, the precolumn was dried with 3 bar nitrogen for 30 min to

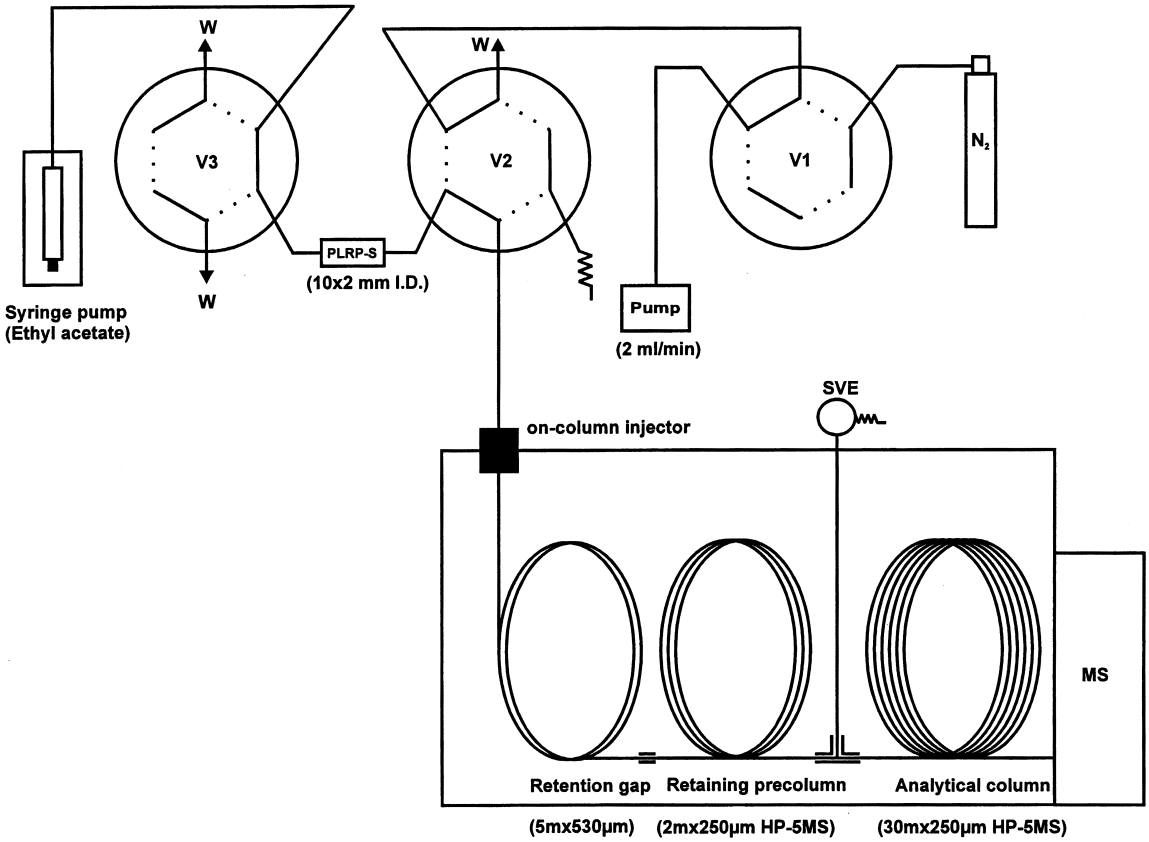

Fig. 1. Set-up of the on-line SPE–GC–MS system.

Table 1
Program for the SPE and transfer processes

Time (min)	Valve	Event
0.01	SVE off V1 off V2 off V3 on	Wash tubes with methanol
2.5	V2 on	Condition precolumn with 3 ml of methanol
4	V2 off	Wash tubes with water
7	V2 on	Activate precolumn with 3 ml of water
8.5	V2 off	Wash tubes with sample
11.5	V2 on	Preconcentrate 10 ml of sample (30% methanol)
16.5	V1 on	Dry precolumn with 3 bar N_2 for 30 min
46.45	SVE on	
46.50	V1 off V2 off V3 off	Transfer analytes with ethyl acetate (100 μl, 47 μl min^{-1})
49.49	V2 on V3 on	End of transfer
50.99	SVE off	
56.5		Start GC program

remove the water. The analytes trapped in the precolumn were desorbed in the backflush mode with 100 μl of ethyl acetate which was pumped at 47 μl min^{-1} with a syringe pump and on-line transferred to the GC system through the transfer line. The SVE was opened a few seconds before the transfer started and closed 1.5 min after the end of the transfer in order to eliminate the ethyl acetate vapors without losing the analytes. The oven temperature was kept at 60°C during the transfer and the temperature program started 5.51 min after the SVE was closed, thus assuring the elution of the solvent peak. The sequence followed in the extraction and transfer process is described in Table 1.

When river and tap water were analyzed, water was filtered through a 0.45-μm filter (MSI, Westboro, MA, USA) and prior to analysis there was no additional treatment.

3. Results and discussion

3.1. Chromatographic separation

The pesticides studied in this paper include compounds from four families: organophosphorous insecticides, organochlorine insecticides, triazines and thiocarbamates. These compounds were selected either because they are used in the Ebro delta region for rice and corn cultivation or because they are on the priority lists of pesticides.

The separation of the seventeen pesticides was optimized by GC–MS by manually injecting 0.5 μl of a standard solution containing 20 mg l^{-1} of each pesticide in ethyl acetate. Separation was completed in less than 33 min.

The ions used to quantify the analytes were selected from the spectrum obtained for each compound under EI ionization. Thus, the base peak of each pesticide was chosen when full scan acquisition was used. Although the m/z values selected for dimethoate, aldrin and dieldrin were low, they corresponded to the base peaks, and higher values caused a significant decrease in sensitivity. The acquisition and quantification under SIM acquisition was carried out by selecting one or two ions of each pesticide (see Table 2).

3.2. Optimization of transfer conditions

The transfer conditions were optimized in order to operate under PCSE conditions using an on-column interface. The parameters optimized were the transfer flow-rate, the transfer temperature and the SVE open

Table 2
Selected ions and analytical data for full scan and SIM acquisition modes for tap water

Compounds	Selected ions[a] (relative abundance)		Full scan			SIM		
			Linearity range ($\mu g\,l^{-1}$)	r^2	LODs ($\mu g\,l^{-1}$)	Linearity range ($\mu g\,l^{-1}$)	r^2	LODs ($\mu g\,l^{-1}$)
Molinate	*126* (100)	55 (71)	0.1–30	0.9987	0.01	0.01–10	0.9997	0.002
α-HCH	*181* (100)	219 (80)	0.1–30	0.9983	0.02	0.01–10	0.9994	0.003
Dimethoate	*87* (100)	–	0.5–20	0.9923	0.1	0.01–10	0.9924	0.003
Simazine	*201* (100)	–	0.5–20	0.9838	0.1	0.05–10	0.9943	0.02
Atrazine	*200* (100)	–	0.1–30	0.9997	0.02	0.01–10	0.9998	0.003
γ-HCH	*181* (100)	–	0.1–30	0.9992	0.02	0.05–10	0.9997	0.02
δ-HCH	*181* (100)	219 (88)	0.1–30	0.9997	0.03	0.05–10	0.9975	0.02
Heptachlor	*100* (100)	272 (76)	0.5–30	0.9974	0.03	0.01–10	0.9994	0.003
Ametryn	*227* (100)	–	0.1–30	0.9991	0.03	0.01–10	0.9999	0.004
Prometryn	*241* (100)	–	0.1–30	0.9991	0.03	0.01–10	0.9957	0.003
Fenitrothion	*125* (100)	–	0.1–30	0.9993	0.03	0.01–10	0.9997	0.004
Aldrin	*66* (100)	–	0.5–30	0.9995	0.06	0.01–10	0.9999	0.003
Malathion	*127* (100)	–	0.1–30	0.9994	0.03	0.01–10	0.9996	0.003
Heptachlor-endo	*183* (100)	81 (94)	0.1–30	0.9995	0.03	0.01–10	0.9997	0.004
α-Endosulfan	*195* (100)	241 (97)	0.5–30	0.9957	0.09	0.05–10	0.9999	0.003
Tetrachlorvinphos	*109* (100)	329 (83)	0.1–30	0.9998	0.03	0.05–10	0.9961	0.003
Dieldrin	*79* (100)	–	0.1–30	0.9992	0.02	0.01–10	0.9998	0.003

[a] The ions in the quantification for full scan acquisition are shown in italics.
LOD=Limit of detection; HCH=hexachlorocyclohexane.

time. They were all optimized by injecting 100 μl of an *n*-alkane standard solution containing 0.1 mg l^{-1} of C_8–C_{20} in ethyl acetate. For these injections, the SPE precolumn was replaced by a 100-μl loop which was filled with the sample using a syringe. Then, the sample was pushed into the retention gap by the ethyl acetate from the syringe pump.

The transfer flow-rate was stepwise increased from 40 μl min^{-1} to the value that caused the analyte peaks to distort, which indicated that the retaining precolumn had been flooded with ethyl acetate. The transfer temperature was also varied from 60 to 70°C depending on the peak distortion observed in the chromatograms. Higher temperatures were not tested so as not to exceed the boiling point of the solvent which would remove the solvent film created in the retention gap. The SVE was opened 3 s before the transfer started and closed 1 min after the transfer finished to eliminate most of the vapor generated during temperature and flow-rate optimization. The optimal temperature and flow-rate were 60°C and 47 μl min^{-1}, respectively. That flow-rate is 4 μl min^{-1} below that which caused flooding to occur and was chosen to ensure that peaks would not be distorted.

Then, the SVE open time was optimized. The SVE was opened 3 s before the transfer started and closed at different times (between 1 and 2 min) after the transfer finished. A time of 1.5 min was selected as optimum because no decrease in peak areas was observed for any of the *n*-alkanes tested and most of the vapor was eliminated.

3.3. SPE process

The sample volume was fixed at 10 ml (see references) because this quantity should be sufficient for analytes to be determined at legal levels with no breakthrough problems.

A polystyrene–polyvinylbenzene copolymer, PLRP-S, was selected as the sorbent for the SPE precolumn because of its ability to retain pesticides, even polar ones [2]. Ethyl acetate was chosen as the desorption solvent because it desorbs analytes with a wide range of polarities from PLRP-S packed SPE precolumns and can also be used under PCSE conditions. Before elution, the sorbent was dried for 30 min with 3 bar N_2 to remove all water from the precolumn. This is a critical step because traces of

water can destroy the deactivation of the retention gap [30].

The elution volume was selected because it has been reported that 100 μl of ethyl acetate should be enough to desorb pesticides into the GC from a 10×2 mm I.D. precolumn packed with PLRP-S [25]. Actually, most of this volume is used to prevent carryover due to memory effects in the transfer line [31]. However, no peaks corresponding to the last eluted compounds appeared in the chromatogram when 100 μl of ethyl acetate was used. Additional experiments showed that no peaks for these compounds were observed even when the elution volume was increased. So we assumed that this was due to analytes being adsorbed in valves and tubes. To test whether this was so, different quantities of methanol were added to the sample which was prepared with Milli-Q water spiked with 1 $\mu g\,l^{-1}$ of each pesticide. The results are shown in Table 3. Recoveries were calculated by comparing the areas with the ones obtained with 100 μl loop injections. The results agreed with our assumption. We chose 30% as the optimum percentage of methanol because quantitative recoveries were obtained for most of the compounds studied. Higher percentages were not studied because this meant that dimethoate would be completely lost.

Several more experiments demonstrated that no carryover effects were observed with the conditions selected. Thus, 100 μl of ethyl acetate was selected to elute the compounds, and samples were prepared by adding 30% of methanol.

3.4. On-line SPE–GC–MS

Once all parameters had been optimized, the method was checked by analysing 10 ml Milli-Q water samples spiked with the pesticides studied.

The linearity for MS under full scan acquisition was checked between 0.1 and 30 $\mu g\,l^{-1}$ and correlation values were between 0.9971 and 0.9998. The limits of detection, calculated assuming a signal/noise ratio of three, were between 0.01 and 0.1 $\mu g\,l^{-1}$. The repeatability ($n=3$) and reproducibility between days ($n=3$) were also checked with a standard solution containing 0.5 $\mu g\,l^{-1}$ of each pesticide. The values obtained, expressed as relative standard deviations (R.S.D.s), were between 8 and 13%, and between 8 and 24%, respectively.

When SIM acquisition was used the linearity was checked in the range from 0.005 to 10 $\mu g\,l^{-1}$ and the responses for most of the pesticides were linear with correlation coefficients between 0.9994 and 0.9999. The limits of detection were between 0.9 and 4 $ng\,l^{-1}$. Repeatability and reproducibility were calculated by preconcentrating a standard solution of 0.1

Table 3
Recoveries obtained by adding different percentages of methanol (MeOH) to the sample before the SPE process

Compounds	Recovery (%)			
	0% MeOH	10% MeOH	20% MeOH	30% MeOH
Molinate	98	96	92	90
α-HCH	82	97	97	98
Dimethoate	89	87	62	14
Simazine	93	93	95	96
Atrazine	96	95	96	96
γ-HCH	90	90	90	91
δ-HCH	68	88	91	97
Heptachlor	–	–	19	53
Ametryn	70	87	90	92
Prometryn	50	98	98	99
Fenitrothion	23	77	89	89
Aldrin	–	–	13	61
Malathion	–	65	87	89
Heptachlor-endo	–	22	87	87
α-Endosulfan	–	20	89	95
Tetrachlorvinphos	–	60	88	90
Dieldrin	–	10	80	97

$\mu g\,l^{-1}$ of each pesticide ($n=3$). The R.S.D. values obtained were between 9 and 18%, and between 10 and 21%, respectively.

3.5. Application to real samples

The performance of the method for real samples was tested in tap and Ebro river water samples.

First, a blank of tap water was analysed to check whether there were any peaks in the corresponding chromatogram at the same retention times as the pesticides being studied, but there were not. The recoveries for tap water for SPE–GC–MS were similar to those obtained when Milli-Q water was analysed, which indicates that the process is not influenced by the matrix. The linearity of the response under full scan acquisition was good for most compounds in the range 0.1–30 $\mu g\,l^{-1}$, and correlation coefficients were between 0.9923 and 0.9998. The limits of detection ($S/N=3$) were calculated to be between 0.01 and 0.1 $\mu g\,l^{-1}$. The results obtained for tap water under full scan acquisition are shown in Table 2.

When SIM acquisition was used, the linearity of the response was checked in the range 0.01–10 $\mu g\,l^{-1}$ and the responses for most of the pesticides were linear with correlation coefficients between 0.9924 and 0.9999. The limits of detection ($S/N=3$) were between 0.002 and 0.02 $\mu g\,l^{-1}$. The results for tap water under SIM acquisition are shown in Table 2. Fig. 2 shows the chromatogram obtained from the analysis of an unspiked tap water sample and tap water spiked at 0.1 $\mu g\,l^{-1}$ in the SIM acquisition mode. The method developed enables levels of 0.1 $\mu g\,l^{-1}$ of the analytes studied to be determined in tap water as required by European Union (EU) rules.

The repeatability and reproducibility between days were determined by performing five extractions for tap water spiked at 1 $\mu g\,l^{-1}$ when full scan acquisition mode was used. The values, expressed as R.S.D., were between 6 and 17%, and between 8 and 26%, respectively. Tap water was spiked at 0.1 $\mu g\,l^{-1}$ when the SIM acquisition mode was selected and R.S.D. values were between 6 and 17% for repeatability and between 11 and 24% for reproducibility.

The performance of the method was also validated for the analysis of Ebro river water samples. The recoveries, linearity of the response, correlation coefficients, limits of detection and precision were similar to those obtained for tap water.

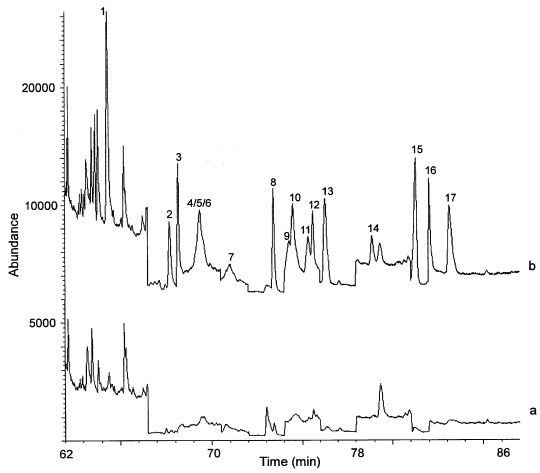

Fig. 2. Chromatograms obtained by on-line SPE–GC–MS (SIM) of: (a) 10 ml of tap water, (b) 10 ml of tap water spiked with 0.1 $\mu l\,l^{-1}$. Peaks: 1=molinate, 2=α-HCH, 3=dimethoate, 4=simazine, 5=atrazine, 6=γ-HCH, 7=δ-HCH, 8=heptachlor, 9=ametryn, 10=prometryn, 11=fenitrothion, 12=aldrin, 13=malathion, 14=heptachlor-endo, 15=α-endosulfan, 16=tetrachlorvinphos, 17=dieldrin. (The times in Figs. 2 and 3 correspond to the total CHEMSTATION program times Table 1.)

Various water samples from areas of the Ebro river close to agriculture zones (e.g. the delta) were analysed. Fig. 3 shows the chromatogram for a sample of Ebro water collected in February under full scan acquisition with the extracted ion chromatogram corresponding to molinate m/z 126 and the spectrum of this compound. One peak was assigned to molinate by comparing the experimental spectrum with that of the library, the match obtained being 90. Quantification was possible for full scan acquisition and the concentration found was 0.1 $\mu g\,l^{-1}$. Some of the other peaks in the chromatogram were assigned to different phthalates.

The PLRP-S precolumn and the retention gap can analyze at least 100 real water samples with no change in performance.

4. Conclusions

SPE was on-line coupled to GC–MS using an on-column interface. Transfer conditions such as flow-rate, temperature and SVE open time were

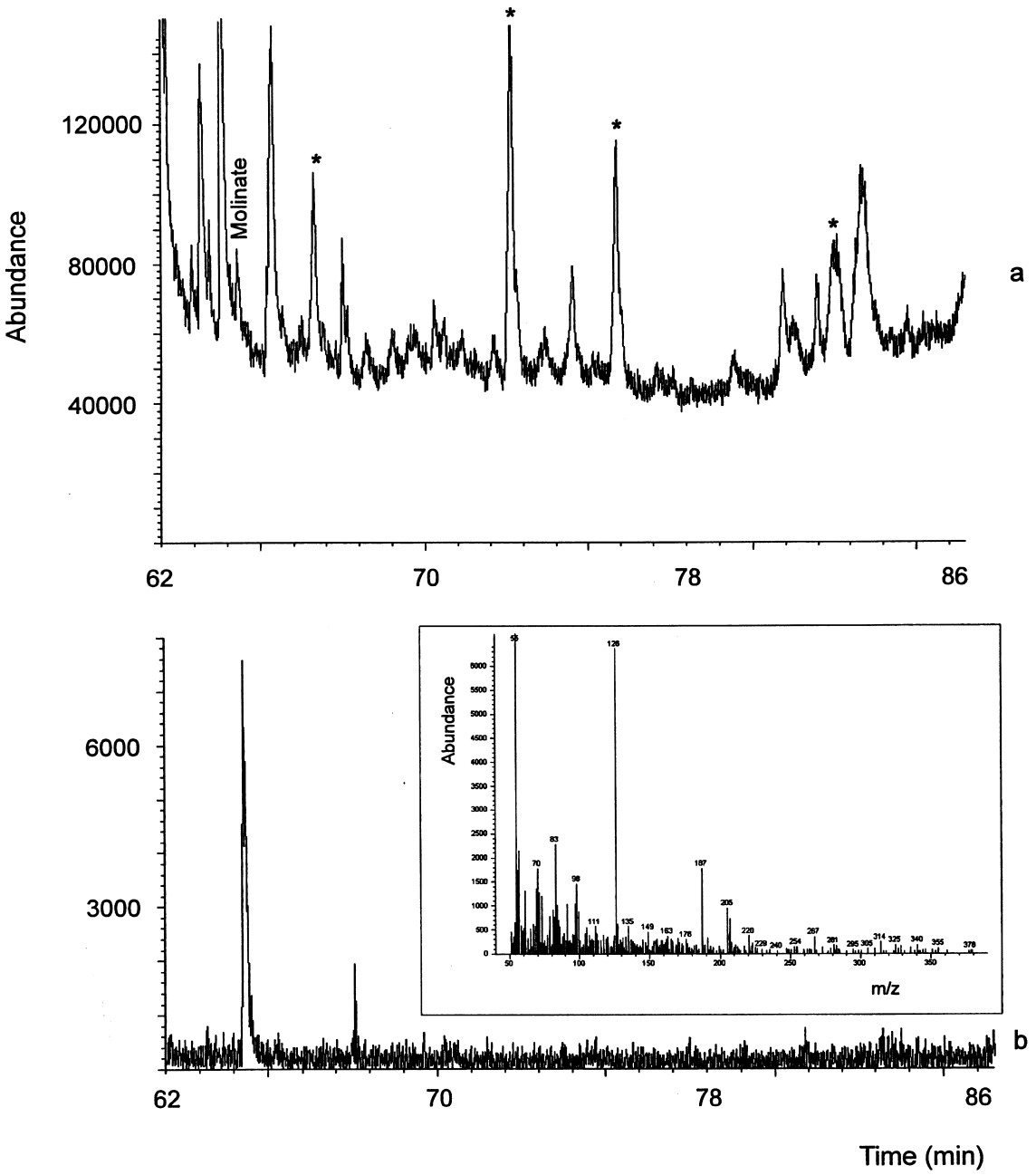

Fig. 3. Chromatogram obtained by on-line SPE–GC–MS for 10 ml of Ebro river water (a) and the extracted ion chromatogram of molinate (m/z 126) (b). The insert shows the spectrum of the peak molinate; * Phthalate.

optimized. The optimum conditions found were 47 $\mu l\,min^{-1}$, 60°C and 1.5 min after the end of the transfer, respectively. Methanol (30%) was added to the sample before the preconcentration step to prevent the analytes from being adsorbed and the recoveries were quantitative for most of the compounds studied.

The potential of the SPE–GC–MS method de-

veloped was demonstrated by analysing tap and Ebro river water to determine different classes of pesticides. The method under SIM acquisition enables the low levels of pesticides permitted by EU regulations in tap water to be quantified by using a small sample volume of 10 ml and only 100 μl of ethyl acetate as the elution solvent.

Molinate was identified and quantified by SPE–GC–MS under full scan acquisition in Ebro river water at a concentration of 0.1 $\mu g\,l^{-1}$.

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