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Automated high-performance liquid chromatographic method for the determination of organophosphorus pesticides in waters with dual electrochemical (reductive–oxidative) detection

R. Carabias Martínez*, E. Rodríguez Gonzalo, F. Garay García and J. Hernández Méndez

Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Salamanca, 37008 Salamanca (Spain)

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ABSTRACT

A highly sensitive method for multi-residue analysis of organophosphorus pesticides by HPLC with dual electrochemical detection has been developed. It involves the detection of reduction products from the upstream electrode in an oxidative mode at the downstream electrode. This reductive–oxidative detection mode allows detection limits below 4 μg/l. When a preconcentration device was coupled on-line with the HPLC system, detection limits as low as 0.03 μg/l were achieved for only 100 ml of sample. The relative standard deviations were in an acceptable range for trace analysis. The overall analysis time for the five pesticides investigated (paraoxon, guthion, methyl-parathion, ethyl-parathion and fenitrothion) was 25 min.

INTRODUCTION

Organophosphorus pesticides are in widespread use because of their relatively rapid decomposition and low accumulation in the biological food chain. Because there is a need to determine trace levels of pesticides in complex matrices such as water, soil and crops, analytical methods have to be both highly sensitive and selective. Organophosphorus pesticides are mainly determined by using chromatographic techniques [1]. As far as HPLC, which is the only separation technique to be discussed in this paper, is concerned, ultraviolet detection is the most common choice [2–4], but electrochemical detection (HPLC–ED) is becoming a popular technique [5,6]. Most reports describe the use of amperometric detectors with only a single working electrode, but dual-electrode detectors (series or parallel configuration) are more versatile; they can provide improved analyte specificity and lower detection limits, especially in the series (upstream–downstream) configuration [7,8]. The series configuration is also applied for electrochemical derivatization of the analyte to a product with favourable properties for electrochemical detection.

This paper describes an HPLC method for the determination of paraoxon, methyl-parathion, ethyl-parathion, guthion and fenitrothion in a reductive–oxidative detection mode with a series dual-electrode system. These organophosphorus pesticides can be directly determined by reductive electrochemical detection due to the presence of nitro or azo groups in their structures. However, reductive HPLC–ED requires an exhaustive deoxygenation because of the high

* Corresponding author.

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residual current due to the reduction of dissolved oxygen. Although direct oxidative electrochemical detection is not possible for these pesticides, they can be electrochemically converted into derivatives which are then suitable for oxidative detection. A dual-electrode detector in the series mode provides a simple and rapid way for performing this detection. Improvements in electrochemical detection are described here, the detection limits obtained being a significant improvement over the results of all other HPLC methods previously reported [9–12].

The proposed method was applied to the determination of pesticide residues in waters. Preconcentration prior to HPLC–ED is required when it is desirable to measure analyte concentrations of less than 0.1 μg/l. In recent years, much attention has been paid to sample preconcentration techniques involving the use of a solid-phase sorbent, as an alternative to conventional liquid–liquid extraction techniques [13–17].

In a previous work [12], extraction and preconcentration of organophosphorus pesticides on a C_{18}-bonded phase silica cartridge were successfully accomplished. In this paper, a microprocessor-controlled system for automated on-line pesticide extraction and preconcentration is described, the solid-phase sorbent cartridge being placed in the sample loop of a six-port valve. The overall HPLC–ED system was optimized.

EXPERIMENTAL

Apparatus

The HPLC system consisted of a Spectra-Physics Model SP-8800 ternary pump, a PAR 400 electrochemical detector equipped with an MP 1304 glassy carbon series dual electrode, an Ag/AgCl/1.0 *M* KCl reference electrode and a gold auxiliary electrode and a Spectra-Physics SP 4290 integrator. A Rheodyne injection valve with a 10-μl sample loop and a 5-μm Spheri-5-RP-18 column (250 × 4.6 mm I.D.) from Brownlee Labs. were used in all experiments. All solvents and samples were filtered through 0.45 μm pore-size nylon membrane filters (Millipore).

A PAR 384 B polarograph with a Metrohm E-628 glassy carbon rotating electrode, a platinum auxiliary electrode and a saturated calomel reference electrode was used for cyclic and anodic stripping voltammetry.

The on-line preconcentration system consisted of commercially available Sep-Pak C_{18} bonded-phase silica cartridges (Waters) placed in the sample loop of a Rheodyne Model 5020 six-port injection valve; a Gilson 231-401 microprocessor-controlled diluter–autosampling injector, equipped with a piston pump and a fraction collector, was used to elute and inject the sample into the chromatograph. A Gilson Minipuls-3 peristaltic pump with vinyl tubing was used for pumping the pesticides through the cartridge.

Reagents

All organophoshorus pesticides were obtained from Riedel-de Haën (Seelze-Hannover, Germany); the purities of the individual standards ranged from 97 to 99%. The pesticides, listed in the order in which they appear in the chromatograms, were (1) paraoxon, (2) guthion, (3) methyl-parathion, (4) fenitrothion and (5) ethyl-parathion. Ultra-high-quality water was obtained with an Elgastat UHQ water-purification system. Standard solutions were prepared in HPLC-grade methanol (Carlo Erba, Milan, Italy). All other chemicals were of analytical-reagent grade.

Water samples

Stock standard solutions containing a mixture of the five pesticides were prepared in pure methanol. Working standard aqueous samples were prepared by diluting 1.0 ml of the stock standard solution to 100.0 ml with ultra-pure water. River water samples investigated were taken from the Tormes river (Salamanca, Spain) as representative samples of surface waters in this agricultural area. They were collected directly in 1-l glass containers, stored at 4°C in the dark and analysed within 24 h after collection. All river water samples were filtered through sintered-glass filters (No. 5) to remove suspended particulate matter.

Procedure

The HPLC operating conditions were optimized in a previous study [12], the mobile phase

being methanol–water (70:30, v/v) containing 0.025 *M* acetic acid–acetate buffer (pH 4.8). The flow-rate was set at 1.25 ml/min.

Electrochemical detection with series dual electrodes was carried out as follows: pesticides were reduced at the upstream electrode (W_1) set at a potential $E_1 = -1.500$ V, the reduction products being detected in an oxidative mode at the downstream electrode (W_2) set at $E_2 = 0.400$ V. Both electrodes were electrochemically pretreated every day. Injected amounts higher than 20 ng required reactivation of the upstream electrode at a potential of +1.600 V for 5 min prior to each measurement.

Determination of pesticides in waters. The preconcentration step was carried out with the on-line system depicted schematically in Fig. 1. Analytes were adsorbed in the cartridge by a single pass of a 100-ml water sample with a peristaltic pump (B_1) at a flow-rate of 10 ml/min. The valve was then switched to the injection position and the cartridge eluted with 2.0 ml of pure methanol using a piston pump (B_2); the microprocessor-controlled diluter–injector allowed the collection, in a conical vial, of the fraction eluting between 1.0 and 1.4 ml, sending to waste the remainder of the liquid eluted. A 10-μl aliquot of the 400 μl collected was injected into the chromatographic system. The cartridge was rinsed with 10.0 ml of methanol and the system was then ready for the next sample. All operations (cartridge elution, fraction collection, sample injection and wash cycle) were done automatically under the control of the microprocessor.

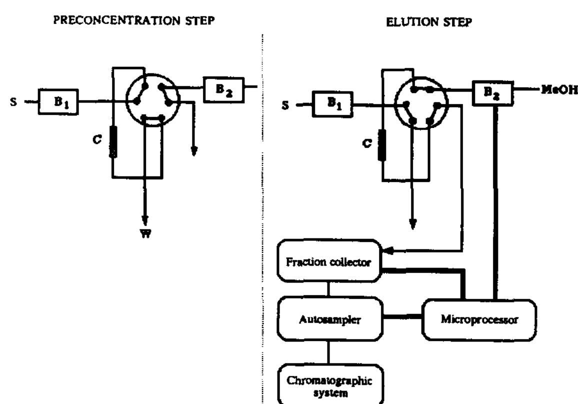

Fig. 1. Schematic diagram of the automatic on line preconcentration system used for river water analysis. B_1, B_2 = Peristaltic and piston pumps, respectively; S = sample; C = preconcentration cartridge; W = waste.

The cartridges were equilibrated with 5.0 ml of methanol and 5.0 ml of ultra-pure water before use for pesticide concentration. In the analysis of river waters, a new cartridge was used for each sample.

Quantification was carried out by using the external standard method, bracketing samples and standards under identical conditions (preconcentration, elution and injection) and taking the mean peak area value of three injections.

RESULTS AND DISCUSSION

Voltammetric studies

An initial study by cyclic voltammetry was performed on solutions of the same composition as the chromatographic mobile phase. Moreover, in order to check whether the products generated by electrochemical reduction are available for oxidative detection, anodic stripping voltammetry after application of an extreme reduction potential was also investigated.

Cyclic voltammograms of paraoxon (Fig. 2a) were scanned from 0.800 to −1.200 V; this pesticide exhibits a cathodic peak at −0.930 V and an ill-defined anodic peak at 0.300 V on the reverse scan, which represent the oxidation of the species generated in the reduction process. The anodic stripping voltammogram (Fig. 2b) obtained by an anodic potential sweep in the differential pulse mode, after preconcentration at −1.200 V, showed two well defined peaks, one of them due to reduction of pesticide free in solution and another (at $E = 0.270$ V) due to oxidation of the reduced product at −1.200 V. These results are consistent with those described by Toral *et al.* [18], who suggested that the cathodic peak represented the reduction of the nitro group to hydroxylamine, while the anodic peak was derived from the oxidation of the hydroxylamine to a nitroso derivative. A similar electrochemical behaviour was exhibited by fenitrothion and ethyl- and methyl-parathion because they all have the same electroactive aromatic nitro group.

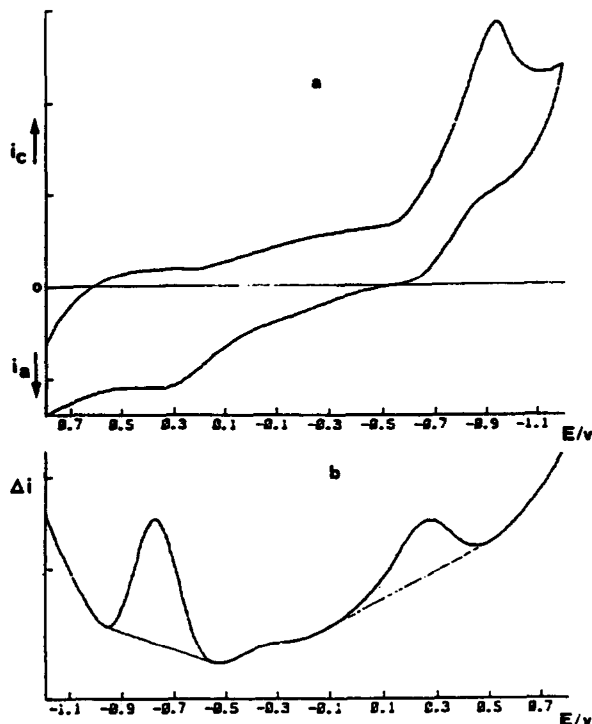

Fig. 2. (a) Cyclic voltammogram for paraoxon. $E_{initial} = 0.800$ V; $E_{final} = -1.200$ V; scan rate, 50 mV/s. (b) Anodic stripping voltammogram. $E_{preconcentration} = -1.200$ V.

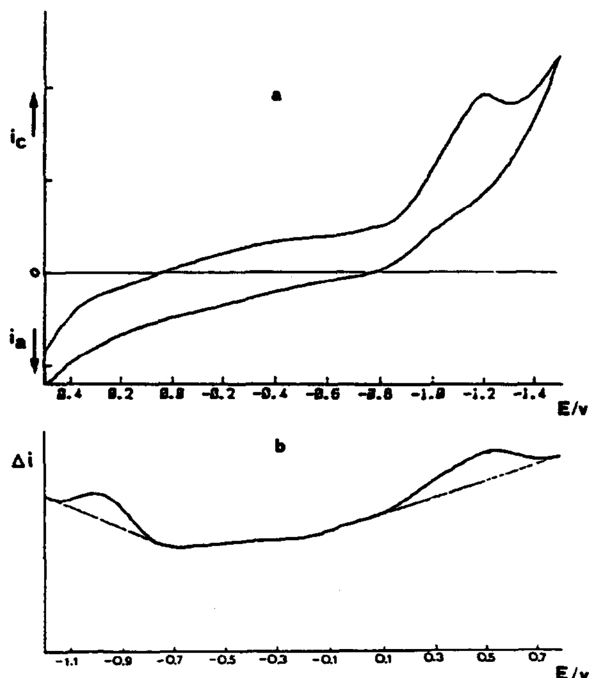

Fig. 3. (a) Cyclic voltammogram for guthion. $E_{initial} = 0.500$ V; $E_{final} = -1.500$ V; scan rate, 50 mV/s. (b) Anodic stripping voltammogram. $E_{preconcentration} = -1.200$ V.

Cyclic and anodic stripping voltammograms for guthion with a glassy carbon electrode are shown in Fig. 3. The voltammograms for this pesticide (which has an –N=N– electroactive group) exhibit a reduction process at more negative potentials (−1.200 V) than the other pesticides investigated, the oxidation of the reduced products having taken place at 0.500 V.

It can be concluded that electrochemical detection is feasible either by using a single working electrode set at a high cathodic potential or with a series dual-electrode device, the upstream electrode operating as a "generator" electrode to convert the analyte into its reduced form which will be detected in the oxidative mode at the downstream "detector" electrode.

Single-electrode detection

The high negative potential required for the reduction of guthion (−1.400 V) makes direct reductive (single-electrode) electrochemical detection of organophosphorus pesticides unsuitable for trace determinations as the residual current and noise level become very high. Thus, detection limits calculated by reductive electro-

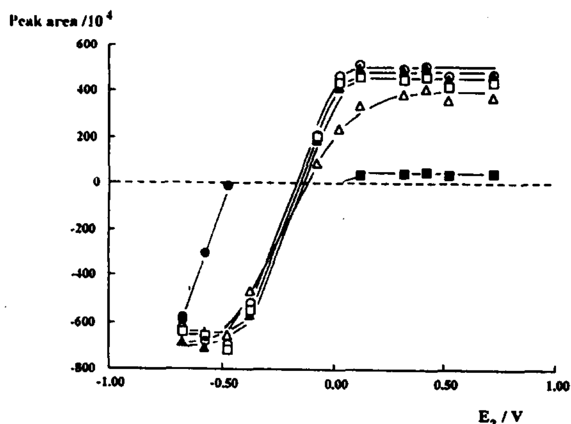

Fig. 4. Influence of downstream electrode potential (E_2) on the analytical signals. Upstream electrode potential E_1 = −1.200 V in all experiments. Amount injected, *ca.* 275 ng of each pesticide. Negative peak area means reduction peak. △ = Paraoxon; ■ = guthion; ▲ = methyl-parathion; ○ = fenitrothion; □ = parathion; ● = oxygen.

chemical detection, on a single electrode, are similar to those previously obtained with ultraviolet detection [12], but no improvements are achieved.

Series dual-electrode detection

The primary advantage of the series dual-electrode approach is the ability to employ the upstream electrode as a "generator" electrode essentially ignoring the unwieldy background current and other problems associated with the high potential. The downstream electrode is then the "detector" electrode, which will remain unaffected.

Hydrodynamic voltammograms were obtained considering $E_1 = -1.200$ V as the operating potential for the upstream electrode (W_1) and incrementally changing the potential E_2 of the downstream electrode (W_2) from -0.700 to 0.700 V (Fig. 4). Signals for dissolved oxygen were only obtained when the downstream electrode (W_2) was set at potentials lower than -0.500 V. The responses for paraoxon, methyl-parathion, fenitrothion and ethyl-parathion were very similar, as expected from their similar structures, reaching a limiting plateau at potentials higher than 0.400 V. Guthion did not exhibit an analytically useful response at any of these potentials. It was necessary to set the upstream electrode (W_1) potential at $E_1 = -1.500$ V in order to increase the oxidative current of guthion in the downstream electrode (Table I).

Optimum potential values of $E_1 = -1.500$ V and $E_2 = 0.400$ V for the upstream (W_1) and downstream (W_2) electrodes, respectively, were therefore chosen for further experiments, to permit the most universal practical response for the five pesticides. Under these conditions, an anomalous behaviour for guthion was again observed: no response at all for this pesticide was obtained when the mobile phase was poorly deoxygenated (Fig. 5a); when helium was continuously bubbled through the mobile phase, guthion exhibited a good and reproducible response (Fig. 5b). The electrochemical behaviour of guthion has been described by Hernández Méndez *et al.* [19]; the electrochemically reduced form of this pesticide is unstable, being subject

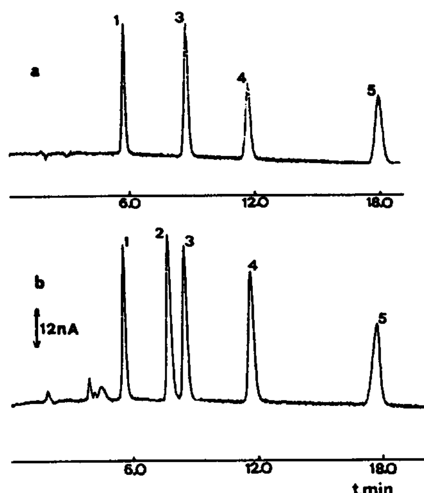

Fig. 5. Chromatogram for dual-electrode detection. (a) Poorly deoxygenated mobile phase and (b) mobile phase continuously deoxygenated by bubbling helium. Experimental conditions and numbers on peaks as described under Experimental.

TABLE I

INFLUENCE OF UPSTREAM ELECTRODE APPLIED POTENTIAL (E_1) ON THE ANALYTICAL SIGNALS

Downstream electrode potential $E_2 = 0.400$ V in all experiments. Amounts injected as in Fig. 4.

E_1(V)	10^4 Area units				
	Paraoxon	Guthion	Methyl-parathion	Fenitrothion	Parathion
−1.200	384	29	479	487	436
−1.300	416	314	514	523	458
−1.400	406	443	498	499	444
−1.500	374	467	459	456	405

to subsequent chemical reactions with oxygen. According to the reported mechanism, the upstream reduced guthion is oxidized by dissolved oxygen, leading to compounds that are electroinactive at the downstream detector. Therefore, a rigorous and continuous deoxygenation of the mobile phase was required to ensure sufficient removal of any oxygen.

Electrode pretreatment

Solid electrodes are known to be subject to fouling of their surfaces, resulting in decreased sensitivity. At present, there is no simple solution to the problem of electrode poisoning and many procedures have been reported, including electrochemical treatments [20,21], to avoid or minimize the gradual decrease in activity.

To improve the detector performance, different kinds of electrochemical pretreatments were tested, the most efficient being the application to both electrodes of several potential pulses (Fig. 6). Even applying such pretreatment everyday, a gradual diminution of chromatographic signals with time was still observed (Fig. 7a). However, the signal reproducibility was improved when, in addition to this daily pretreatment, a potential of 1.600 V was applied for 5 min to the upstream electrode (W_1) after each injection (Fig. 7b). The possibility of applying a positive potential pulse to the upstream electrode (reduction process) without any noticeable deterioration of the baseline at the downstream detector is another important advantage of series dual-electrode detection that allows the injection to be made once the cleaning pulse is finished. By

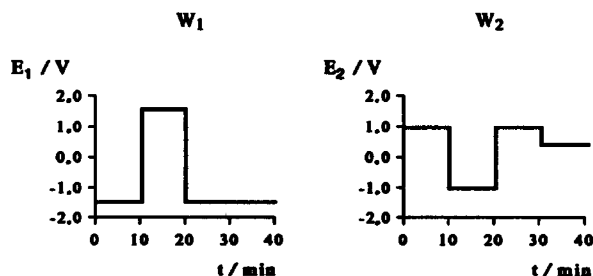

Fig. 6. Electrochemical pretreatment for series dual-electrode detection. Applied potential *versus* time for both electrodes (W_1 and W_2).

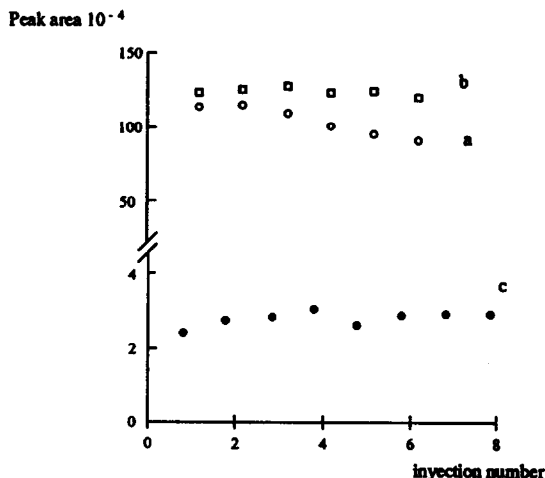

Fig. 7. Enhancement of reproducibility of response with the electrode pretreatment. (a) Signals for 138 ng of paraoxon injected, electrodes being pretreated daily as described in Fig. 6; (b) same as (a) but including an additional step where W_1 was set at 1.600 V for 5 min before each injection; (c) same as (a) for a smaller amount injected (4.2 ng of paraoxon).

using this upstream electrode reactivation step, the precision of the analytical responses for repetitive injections, expressed as their relative standard deviations, were in the range 1.6–4.9%.

As the decrease in electrode performance depends on the concentration injected, it was checked that no upstream electrode (W_1) reactivation was required for injected amounts lower than 20 ng (Fig. 7c).

Influence of flow-rate on the optimum electrochemical detection

Flow-rate is an important parameter in HPLC–ED because it determines not only the chromatographic separation but also the optimum electrochemical detection as hydrodynamic conditions influence the detector response for a given flow cell geometry. The experimental relationship between peak area (A) and flow-rate (q) was as predicted for a thin-layer flow cell configuration [22], fitting the equation $A = \text{constant} \cdot q^{-0.64}$ ($r = 0.98$) in the range investigated (0.50–1.75 ml/min) for all pesticides except guthion. For this pesticide, its behaviour was as expected theoretically only at

flow-rates higher than 0.90 ml/min because at lower flow-rates the electrochemically reduced form of guthion can be chemically oxidized [19] by traces of oxygen in the mobile phase.

Although exhaustive deoxygenation of the mobile phase was shown to be very efficient at moderate flow-rates, at lower flow-rates, when the time delay between upstream reduction and downstream oxidative detection becomes significant, even traces of oxygen in the mobile phase seem to be sufficient for chemical oxidation of the reduction products of guthion and, consequently, a decreased oxidative response at downstream electrode is observed. Hence flow-rates higher than 0.90 ml/min are recommended in order to prevent these products becoming electroinactive before downstream detection.

According to all these results and bearing in mind the requirements for the chromatographic separation [12], a flow-rate of 1.25 ml/min was considered the most appropriate for optimum overall performance.

Analytical data

Under the optimum conditions described above, linear relationships were found between peak area and pesticide concentration over the whole range studied, between about 0.1 and 280 ng injected for each pesticide. The calculated detection limits, for a signal-to-noise ratio of 2, are given in Table II. These values, about 40 pg of injected pesticide, represent a considerable improvement on those reported by Clark *et al.* [11] for electrochemical determination of ethyl- and methyl-parathion with a single-electrode detector (0.8–0.9 ng injected) and to those reported by Ding and Krull [10] for guthion and ethyl-parathion (0.20 and 0.2 mg/l, respectively) using photolysis followed by electrochemical detection. The sensitivity is also ten times higher than that reported for ultraviolet detection [12] under the same chromatographic conditions.

The relative standard deviations at a concentration level of 4.2 ng injected were in the range 4–11% (Table II); the values decreased to 2–5% when 138 ng of each pesticide were injected.

Determination of pesticides in river waters

There is an increasing need for sensitive and reliable methods to determine pesticide concentrations below μg/l levels in natural waters. The maximum concentration of individual pesticides in drinking waters allowed by European Community (EC) legislation is 0.1 μg/l [23]; hence analyte preconcentration prior to HPLC–ED determination is required in order to reach sensitivity levels below the legal limits.

Most reported methods for pesticide analysis involve liquid–liquid extraction for analyte isolation and sample handling, but such procedures frequently require hazardous solvents and make automation of the analysis more difficult. Nowa-

TABLE II

CALIBRATION FITS WITHOUT PRECONCENTRATION

Concentration range between *ca.* 0.1 and 275 ng injected of each pesticide.

Pesticide	Intercept (10^2 area units)	Slope (10^4 area units/mg l^{-1})	Correlation coefficient	R.S.D. (%)[a]		DL (mg/l)[b]
				A	B	
Paraoxon	4.8 ± 3.1	5.57 ± 0.03	0.9998	4.8	1.9	0.004
Guthion	3.4 ± 3.6	5.59 ± 0.03	0.9998	3.7	3.2	0.004
Methyl-parathion	4.8 ± 2.7	6.23 ± 0.03	0.9999	3.5	1.6	0.003
Fenitrothion	5.7 ± 5.6	6.42 ± 0.05	0.9995	4.5	2.5	0.003
Ethyl-parathion	6.8 ± 8.2	5.21 ± 0.08	0.9985	11.0	4.9	0.004

[a] R.S.D. = Relative standard deviation ($n = 10$); (A) 4.2 ng of each pesticide, only daily electrode pretreatment; (B) 138 ng of each pesticide, daily pretreatment plus a pulse of 1.600 V to the upstream electrode (W_1) prior to each measurement.

[b] DL = Detection limit ($2N/m$, where N is the noise and m is the slope of the calibration graph).

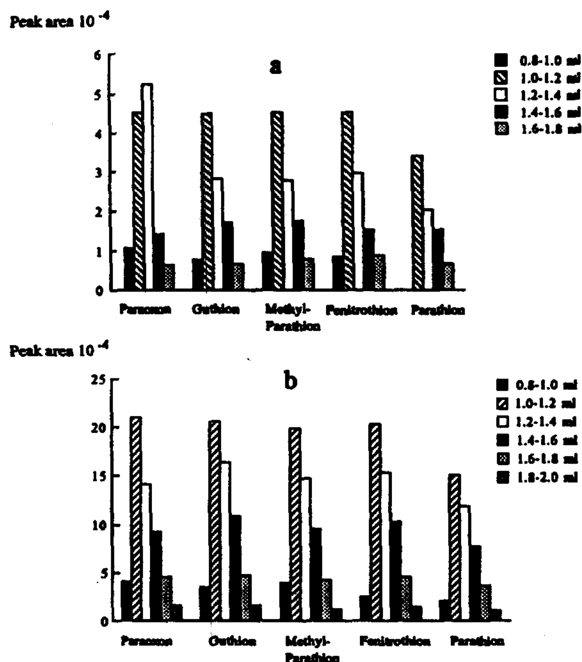

Fig. 8. Elution profiles for each pesticide from different volume fractions collected. (a) 4.2 μg/l; (b) 19 μg/l.

days, investigations are focused on the optimization of solid–liquid extraction procedures.

Standard samples in ultra-pure water were used to check the automated on-line preconcentration system (Fig. 1) in the different steps in the overall process. After sorption of pesticides in the solid-phase cartridge, the latter was eluted with 2.0 ml of methanol; elution profiles for each pesticide were determined by analysing the different volume fractions eluted (0.2 ml each). For the five pesticides and at all concentrations tested (0.1–19 μg/l), the richest fractions were the sixth and the seventh (between 1.0–1.2 and 1.2–1.4 ml) (Fig. 8). Once the richest fractions were known, subsequent studies were made by programming the diluter–injector to collect solely the fraction between 1.0 and 1.4 ml and injecting a 10-μl aliquot.

The experimental relationships between peak area and pesticide concentration in water samples were found to be linear over the whole range tested (Table III). Detection limits, calculated at a signal-to-noise ratio of 2, were 0.03 μg/l for ethyl-parathion and 0.02 μg/l for all others pesticides investigated, all of them being 3–5 times lower than the legal limits allowed in drinking waters. The lowest detectable concentration can be improved by using sample volumes greater than 100 ml; the recovery data obtained showed that no loss of pesticide occurred on increasing the water volume passed through the extraction cartridge from 100 to 1000 ml. Relative standard deviations for ten replicates at concentration levels of 4.2 and 0.2 μg/l are also given in Table III.

In order to check the applicability of the proposed method to real matrices, river water samples from different points of the Tormes river (Salamanca, Spain) were analysed (Fig. 9).

TABLE III

CALIBRATION FITS WITH PRECONCENTRATION

Concentration range between *ca.* 0.1 and 6 μg/l of each pesticide. Preconcentration of 100 ml of sample.

Pesticide	Intercept (10^3 area units)	Slope (10^3 area units/$\mu g\, l^{-1}$)	Correlation coefficient	R.S.D. (%)[a]		DL (μg/l)[b]
				A	B	
Paraoxon	−1.2 ± 0.8	8.5 ± 0.2	0.9991	9.4	12.3	0.02
Guthion	−2.1 ± 0.9	9.3 ± 0.2	0.9992	6.8	10.8	0.02
Methyl-parathion	−0.9 ± 0.8	9.3 ± 0.2	0.9990	6.4	8.6	0.02
Fenitrothion	0.3 ± 0.5	9.0 ± 0.1	0.9997	8.6	10.9	0.02
Ethyl-parathion	1.3 ± 0.5	6.9 ± 0.1	0.9994	9.3	12.8	0.03

[a] R.S.D. = Relative standard deviation ($n = 10$). Fortification level: (A) 4.2 μg/l; (B) 0.2 μg/l.
[b] DL = Detection limit, defined as in Table II.

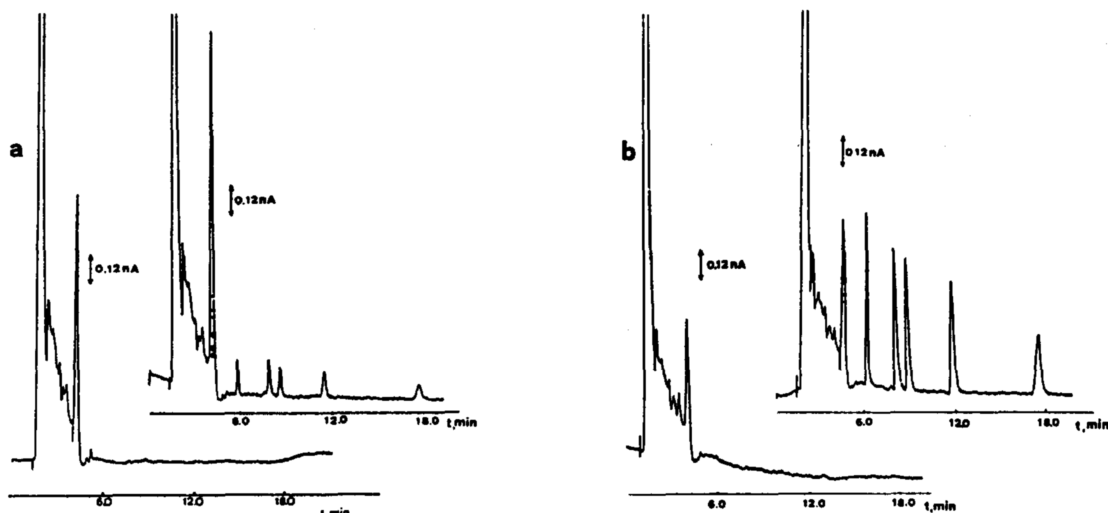

Fig. 9. Chromatograms of river water samples from different points of the Tormes river fortified at (a) 0.2 and (b) 1.4 μg/l.

A 100-ml aliquot of each sample was firstly analysed following the same procedure to provide ambient-level analyte concentrations; none of the samples showed naturally occurring pesticides. Samples were then fortified at four concentration levels between *ca.* 0.2 and 2 μg/l of each pesticide. The analytical recoveries from this matrix ranged from 84% to 124% (Table IV).

TABLE IV

PESTICIDE RECOVERIES FROM RIVER WATER SAMPLES

Pesticide	Fortification level (μg/l)	Recovery (%)	*n*
Paraoxon	0.20	114	2
	0.42	108	2
	1.47	91	4
	2.11	105	4
Guthion	0.20	124	2
	0.44	113	2
	1.73	84	4
	2.22	103	4
Methyl-parathion	0.19	100	2
	0.41	112	2
	1.62	86	4
	2.15	109	4
Fenitrothion	0.20	100	2
	0.44	113	2
	1.66	90	4
	2.20	109	4
Ethyl-parathion	0.20	98	2
	0.44	95	2
	1.57	92	4
	2.26	100	4

CONCLUSIONS

HPLC coupled with dual electrochemical detection in the reductive–oxidative mode was applied to multi-residue organophosphorus pesticide analysis, the proposed method being more sensitive than all other HPLC methods previously reported. An improvement in electrochemical detection by using a series dual-electrode detector was established; the possibility of activation of the upstream electrode by applying a high-potential pulse prior to each analysis, without any baseline deterioration at the downstream detector, is an important advantage of the series dual-electrode configuration, not previously reported; this treatment was shown to be the best way to obtain good signal reproducibility independent of the working time (without problems of electrode surface activity).

In the computer-controlled on-line preconcentration scheme proposed, problems with analyte losses or contamination are minimal because the extracts could be injected automatically into the

chromatographic system, having the important advantage of eliminating the solvent-removal step, which in some instances is extremely critical. The linearity of the calibration graphs show the integrity of the overall system, including adsorption, desorption, chromatographic separation and dual-electrode detection. The limits of sensitivity of this method for organophosphorus pesticides were set at sub-pg levels by sampling only 100 ml of water, whereas most extraction procedures require 1–2 l of water. The relative standard deviations obtained are in an acceptable range for trace analysis.

The method of on-line preconcentration with an automated sampling device provides a rapid and easy means of pesticide trace enrichment prior to their analysis by HPLC and it is obviously advantageous from the viewpoint of sensitivity, rapid sample handling and costs, when large monitoring programmes are to be performed.

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