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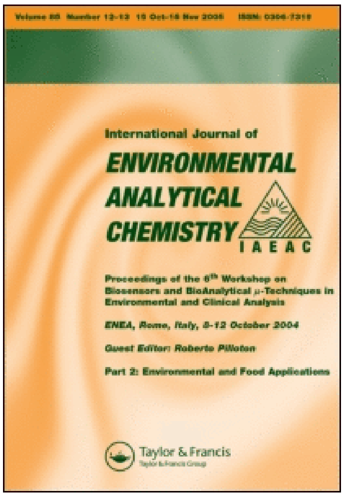

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Treatment and Determination of Organophosphorous Pesticides in Waste Water by Using Continuous Flow Methodologies Coupled On Line With High Performance Liquid Chromatography*

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The treatment of waste water containing three organophosphorous pesticides: diazinon, azinphos-methyl and fenthion by using continuous flow methodologies coupled on line with HPLC-UV detection is presented.

Two continuous flow techniques: completely continuous flow and flow injection, both combined with two separation methods: liquid–liquid extraction and adsorption

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resins are discussed, as well as the influence of physical and chemical parameters on the analysis.

Adsorption resins seem to be more suitable for the treatment of waste water at low pesticide concentrations while liquid–liquid extraction is more selective.

KEY WORDS: HPLC, organophosphorous pesticides, continuous flow methodologies, liquid–liquid extraction, adsorption resins.

INTRODUCTION

Organophosphorous pesticides are widely used because of their relatively rapid decomposition and low accumulation in biological food chain.

Analysis of these pesticides are done generally by using chromatographic techniques,[1] in particular high performance liquid chromatography (HPLC).[2] However, previous sample work-up is necessary in order to enrich the sample if the pesticide concentration is very low.

The most common separation methods for the treatment of waste water samples are classical liquid–liquid extraction using different organic solvents[3,4] and more recently, enrichment by adsorption techniques using XAD-resins[5,6] and C_{18} bonded phases.[7] Batch procedures are considered time consuming because of the considerable amount of glassware and are easily liable to contamination. On the other hand, the increasing costs of reagents and equipments force the analyst to scale down the size of the sample clean-up, the volume of chemicals used and the time of analysis and at the same time to increase the whole productivity of the process.

Reduction in scale opens new ways to automatization of pesticide analysis.[8,9] In this context, continuous flow methodology has shown great possibilities to analyze pesticides using segmented[10] and unsegmented[11] flow systems.

In this work, some unsegmented flow manifolds are considered for the treatment, by using liquid–liquid extraction or adsorption resins, of waste water samples containing organophosphorous pesticides: a completely continuous flow system (CCFA) and a flow injection system (FIA) both coupled on line with a HPLC-UV detector. Three organophosphorous pesticides commonly used in Spain have been selected: diazinon, azinphos-methyl and fenthion. The influence of physical and chemical parameters on the analysis are discussed.

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EXPERIMENTAL

Reagents

Organophosphorous pesticides (azinphos-methyl, diazinon and fenthion) were supplied by Bayer.

Organic solvents were Scharlau HPLC grade.

Distilled water was microfiltered by Millipore filters (0.45 μm).

Standard organic solutions were prepared by direct weight of the pesticide. Standard aqueous solutions were prepared from dilutions of 1000 mg L^{-1} methanolic stock solutions.

Amberlite XAD-2 Adsorber Resin (Merck) with a particle size between 0.3–0.9 mm has been used in this work. Resin was purified according to the method of Junk *et al.*[12]

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The HPLC system consisted of a Spectra–Physics Model SP-8700 solvent delivery unit, an injection valve (Rheodyne) with a 10 μl sample loop, an UV-Vis detector (SP-8440), an integrator (SP-4270) and a Knauer Nucleosil C-18 column (120 × 4 mm i.d.). The working wavelength was 220 nm. The mobile phase was 80:20 methanol:water and its flow rate was set at 1 ml min^{-1}.

Under these conditions, the retention time of each pesticide was: diazinon (1.3 min), azinphos-methyl (1.9 min) and fenthion (3.2 min). No differences in these values were observed when injecting samples in water and in organic solvents.

MANIFOLDS

Figure 1 shows the flow liquid–liquid extraction manifolds: (A) CCFA and (B) FIA. Standard Tygon pump tubing was used for pumping water while the organic solvent was delivered through a displacement flask. Teflon tubing (0.5 mm i.d.) was employed in the whole system. In CCFA mode, the pesticide sample is introduced into the system by means of a peristaltic pump while in FIA mode a fixed sample volume is introduced by using an injection valve.

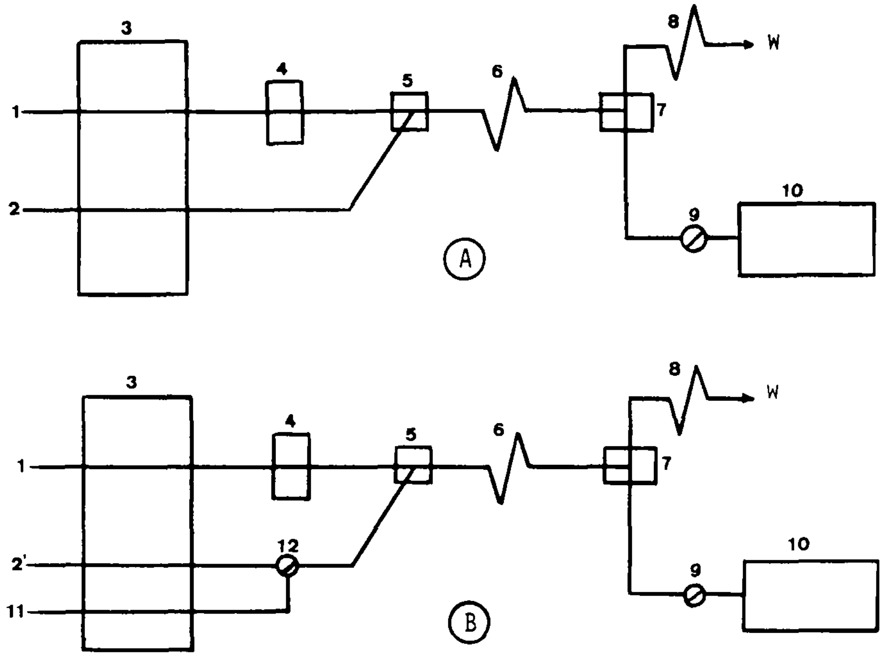

Figure 1 Flow liquid–liquid extraction manifolds: (A) CCFA and (B) FIA. 1 organic phase; 2 sample; 2′ carrier; 3 peristaltic pump; 4 displacement flask; 5 segmentor; 6 extraction coil; 7 phase separator; 8 restrictor; 9 injection valve; 10 HPLC; 11 sample; 12 FIA injection valve; W waste.

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In both cases, the sample merges with the organic phase in a Y-piece segmentor and the extraction takes place in the extraction coil. Both phases are separated with the aid of a Teflon membrane (0.5 μm) placed in a phase separator of the type already described.[13] Aqueous phase is wasted through a restrictor and the organic phase feeds the injection valve of the HPLC system.

Figure 2 shows the flow adsorption resin manifolds: (A) CCFA and (B) FIA, both including an adsorption resin glass column. In CCFA mode, the pesticide sample is introduced by a peristaltic pump while in the FIA mode, it is introduced by an injection valve. In both cases, pesticides are retained by the resin and afterwards, by stopping pump 3 and starting pump 3′, eluted by the organic solvent

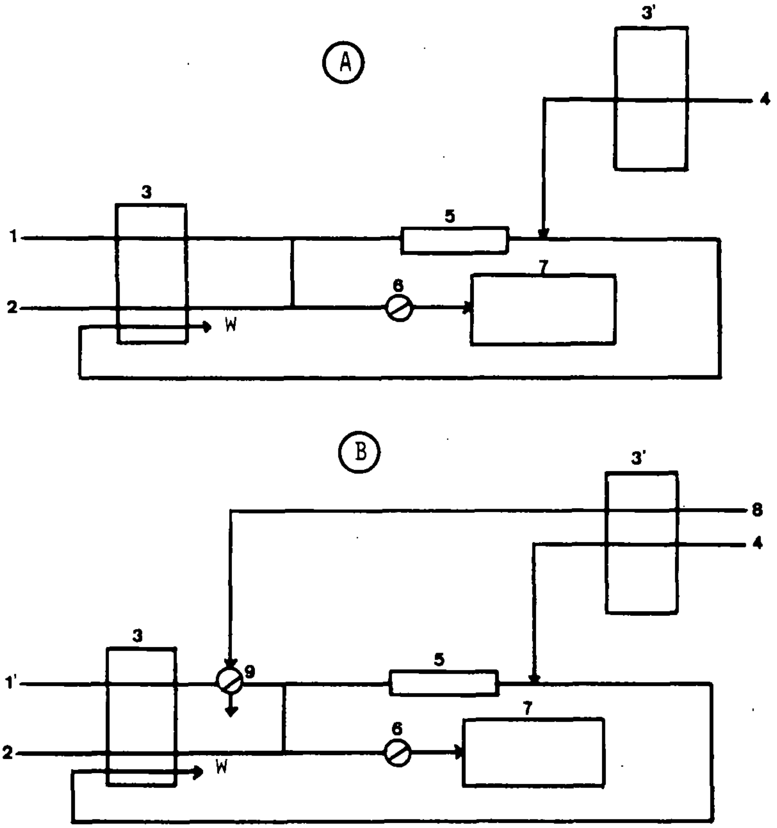

Figure 2 Flow adsorption resin manifolds: (A) CCFA and (B) FIA. 1 sample; 1' carrier; 2 water; 3 and 3' peristaltic pumps; 4 eluent; 5 resin column; 6 injection valve; 7 HPLC; 8 sample; 9 FIA injection valve; W waste.

which feeds the injection valve of the HPLC system. Standard Tygon pump and Teflon tubing (0.5 mm i.d.) were also employed in this case for both manifolds.

RESULTS AND DISCUSSION

Table 1 shows the most important chemical and physical parameters which have to be optimized in this kind of analysis. Chemical

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Table 1 Chemical and physical parameters to be optimized using continuous flow methodologies

Chemical parameters	*Physical parameters*
Organic phase solvent	Total flow rate
Organic eluent	Organic flow rate
Type of resin	Aqueous flow rate
Amount of resin	Internal diameter
pH	Extraction coil length
	Resin column length
	Injection volume (only in FIA)

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parameters are normally the same used in batch experiments. On the other hand, because the chromatographic-UV determination is done on line in the organic solvent, this solvent should not absorb at the working wavelength.

In liquid–liquid extraction, the preconcentration of the sample depends on the ratio between the aqueous and the organic flow rate. However, it is necessary to take into account that the total flow rate should be lower than 6 ml min^{-1} in order to obtain good phase separations in the separator. The preconcentration by using adsorption resins depends on the time which the waste water sample passes through the resin column.

In FIA methodology, the injection volume should be higher than 1 ml in order to preconcentrate the sample several times and to avoid sample dilution in the liquid–liquid extraction technique due to the phase separator.

Experiments with different extraction coil and resin column length must be carried out in order to find the best results.

Chemical and physical parameters used in this study for the preconcentration of pesticide water samples are shown in Table 2.

Chromatograms obtained before and after the treatment using both methodologies are shown in Figure 3. It can be observed that the pesticides are concentrated and interferences due to the water are removed. It is necessary to point out that diazinon is not extracted in *n*-heptane in our study because of its polarity but it can be preconcentrated using adsorption resins.

Calibration curves can be determined using these methodologies.

Table 2 Chemical and physical parameters used in this work for continuous flow methodologies

Liquid–liquid extraction	*Adsorption resin*
Solvent: *n*-heptane	Eluent: methanol
Extraction coil length: 4 m	Column: 180 × 3 mm i.d.
Total flow rate: 2.5 ml min^{-1}	Resin: XAD-2
Aq/org phase ratio: 4	Aq. flow rate: 2 ml min^{-1}
pH: 6–7	Org. flow rate: 1.6 ml min^{-1}
Injection volume: 0.5–2 ml	Injection volume: 1–4 ml
	Amount of resin: 0.3 g
	Elution time: see Figure 5

In order to carry out these curves, some interesting experimental findings have to be taken into account.

In the flow liquid–liquid extraction methodology, the extraction percentage, $\%E$, depends on different chemical and physical parameters, like aqueous and organic flow rate, coil length, nature of the organic solvent and so on. Anyway, all these parameters must be optimized in order to obtain the best extraction percentage.[14] At the same time, $\%E$ also depends on the initial aqueous pesticide concentration as it is shown in Figure 4. Hence, calibration curves can be only obtained when the extraction percentage is constant. The behaviour showed in Figure 4 can be explained as follows: when the concentration of azinphos-methyl increases, the mass transfer between both phases has a slow kinetic process and the distribution of the pesticide does not reach the equilibrium and consequently decreases. On the other hand, the increase of extraction percentage when the concentration of fenthion increases can be attributed to the possibility of pesticide aggregation in *n*-heptane.[15]

In the flow adsorption resin methodology, the chromatographic signal depends on the elution time because there is an elution gradient of the pesticides. The time corresponding to the maximal signal varies as a function of the initial pesticide concentration as it is shown in Figure 5. Therefore, calibration curves have to be determined in short ranges of concentration in order to avoid this effect. Some other parameters also modify the chromatographic signal, like the kind of eluent and its flow rate but they can be kept constant easily.[16]

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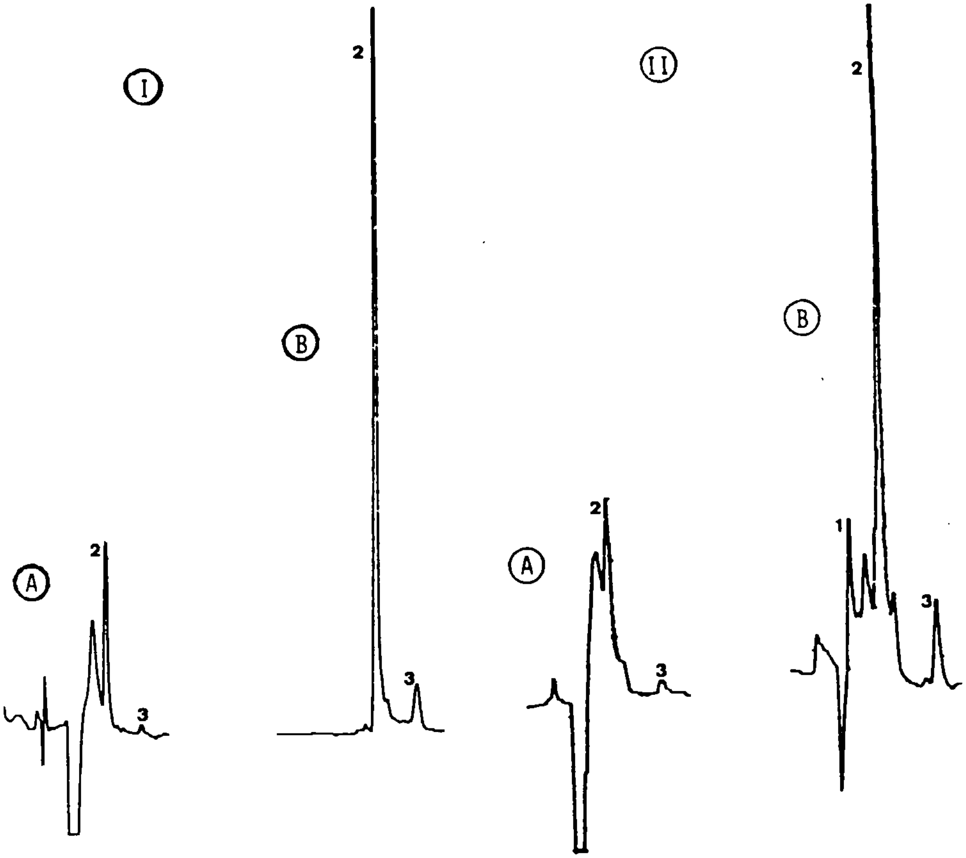

Figure 3 Chromatograms of pesticide samples. (I) By using continuous flow liquid–liquid extraction: (A) in water before extraction and (B) in *n*-heptane after extraction. Initial concentration: $1\,\mathrm{mg\,L^{-1}}$; extraction coil: 4 m; total flow rate: $2.5\,\mathrm{ml\,min^{-1}}$; aq/org volume ratio: 4. (II) By using continuous flow adsorption resins: (A) in water before adsorption, (B) in methanol after desorption. Initial concentration: $1\,\mathrm{mg\,L^{-1}}$; organic flow rate: $1.5\,\mathrm{ml\,min^{-1}}$; elution time: 60 s; resin: XAD2. 1 diazinon, 2 azinphos methyl and 3 fenthion.

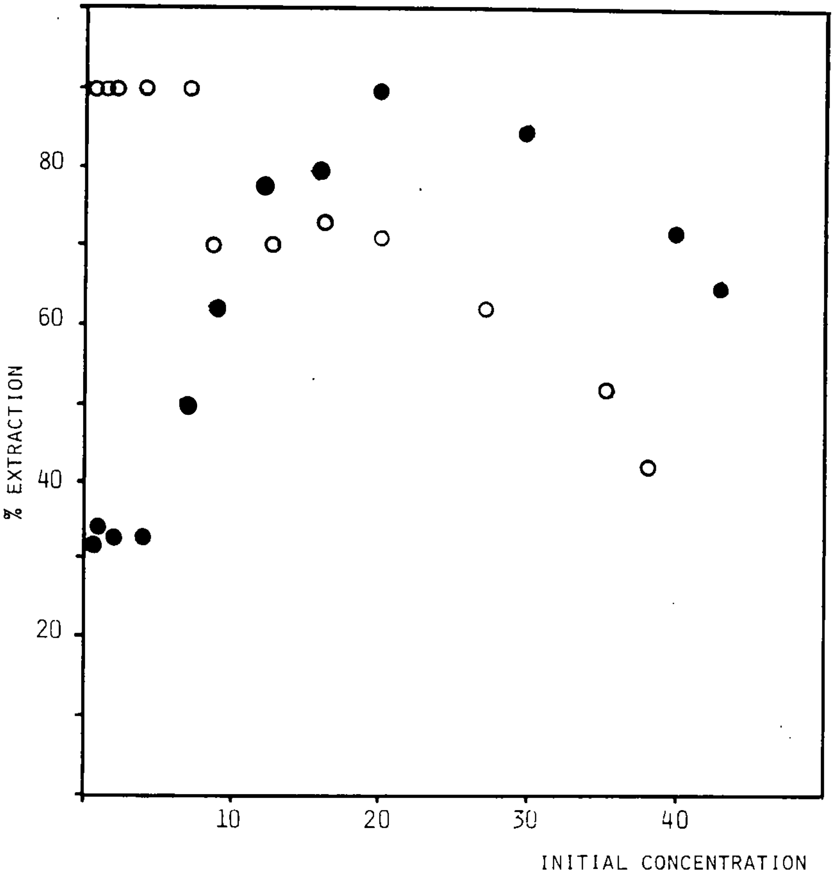

Figure 4 Percentage of the extraction *vs* initial aqueous concentration of the pesticide in mg L^{-1}. Total flow rate: 2.5 ml min^{-1}; aq/org volume ratio: 4; extraction coil length: 4 m. ○ Azinphos methyl; ● Fenthion.

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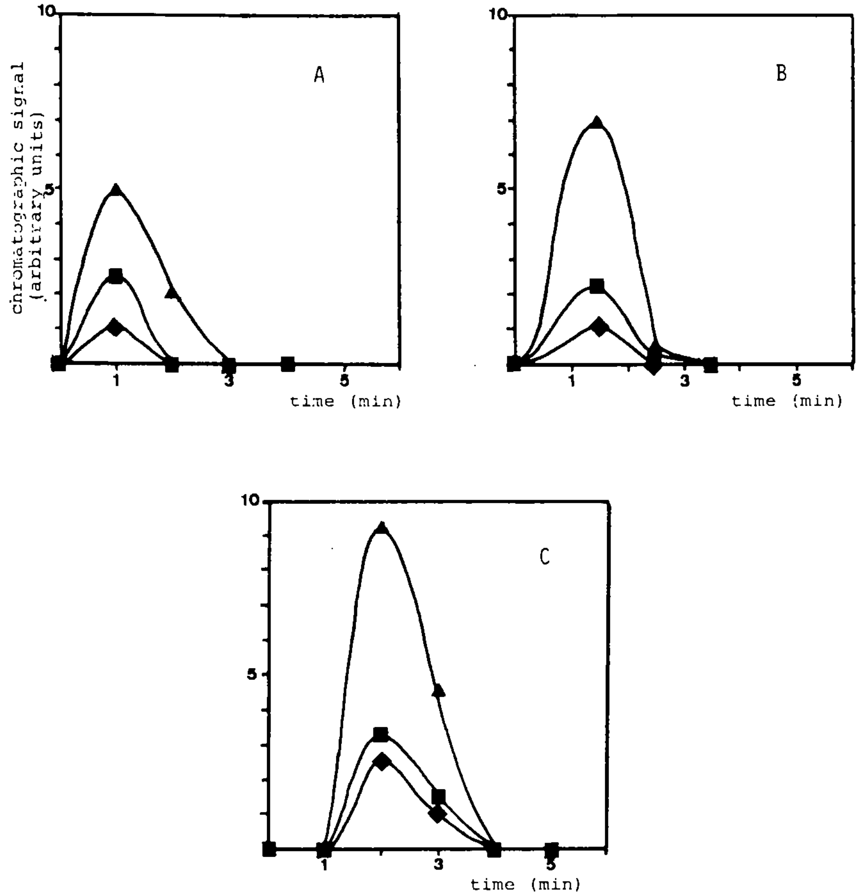

Figure 5 Relationship between elution time and chromatographic signal at three initial aqueous concentrations of the pesticides (A: 0.25; B: 2 and C: 10 mg L^{-1}). ■ Diazinon; ▲ Azinphos methyl; ◆ Fenthion.

Table 3 summarizes the main characteristics of both methodologies used in this work. As it can be observed the treatment with adsorption resin seems to be more suitable for samples containing low concentration of pesticides, although this methodology is less selective. Using both methodologies sample handling is easier and the sample throughout ($\approx 15\,h^{-1}$) allows to use them in routine analysis of waste water containing organophosphorous pesticides.

Table 3 Main characteristics of continuous flow methodologies for the treatment of waste water samples containing organophosphorous pesticides

Liquid–liquid extraction	*Adsorption resin*
Phase separator increases sample dilution	Chromatographic signal depends on elution time
Low sample preconcentration (max 10 times)	High sample preconcentration
Preconcentration depends on flow rates	Preconcentration depends on time
More selectivity	Manifolds more complicated
Similar sample throughput $\approx 15\,h^{-1}$	
No differences in the chromatograms (*n*-heptane and methanol)	
Difficult selection of the organic solvent (no absorption at 220 nm)	

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References

1. J. Sherma, *Anal. Chem.* **59**, 18R (1987).
2. J. F. Lawrence, *High Performance Liquid Chromatography of Pesticides*, (G. Zweig and J. Sherma, eds.) (Academic Press, New York, 1982), Vol. 12.
3. V. López-Avila, P. Hirata, S. Kraska, M. Flanagan, J. H. Taylor, Jr and S. C. Hern, *Anal. Chem.* **57**, 2797 (1985).
4. P. F. Blanchet, *J. Chromatogr.* **179**, 123 (1979).
5. G. A. V. Rees and L. Au, *Bull. Environm. Contam. Toxicol.* **22**, 561 (1979).
6. G. L. LaBel, D. T. Williams, G. Griffith and F. M. Benoit, *J. Assoc. Off. Anal. Chem.* **62**, 241 (1979).

7. W. A. Saner and J. Gilbert, *J. Liq. Chromatogr.* **3**, 1753 (1980).
8. K. Ramsteiner, *Inter. J. Environ. Anal. Chem.* **25**, 49 (1986).
9. R. J. Hemingway, N. Aharonson, P. A. Greve, T. R. Roberts and H. P. Thier, *Pure and Appl. Chem.* **56**, 1131 (1984).
10. D. A. Burns, *ACS Symposium Series* **136**, 15 (1980).
11. A. Farran and J. de Pablo, *Inter. J. Environ. Anal. Chem.* **30**, 59 (1987).
12. G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, H. J. Fritz and G. V. Calder, *J. Chromatogr.* **99**, 745 (1974).
13. K. Bäckström, L.-G. Danielson and L. Nord, *Anal. Chim. Acta* **169**, 43 (1985).
14. A. Farran, J. de Pablo and S. Hernández, *Proceedings of EUROANALYSIS VI, Paris, 7–11 September 1987*, p. 385.
15. T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry* (Marcel Dekker Inc., New York, 1977).
16. A. Farran, E. Figuerola, S. Hernández and J. de Pablo, to be published.

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