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Simultaneous quantitation of sixteen organochlorine pesticides in drinking waters using automated solid-phase extraction, high-volume injection, high-resolution gas chromatography

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Abstract

A method is described for the simultaneous determination of sixteen organochlorine pesticides in drinking water using automated solid-phase extraction followed by high-volume (80 μl) injection capillary column gas chromatography using electron capture detection. The fully automated extraction method followed by high-volume injection permits rapid sample analysis compared to previously described procedures since no further pre-concentration of the analytes is necessary after they have been eluted from the octadecyl solid-phase extraction cartridge. The lowest detectable concentrations of the pesticides are between 1–5 ng l^{-1}, relative recoveries range from 92–105% in tap water spiked at 100 ng l^{-1} and the relative standard deviations are in the range 5–12%.

Keywords: Drinking water; Organochlorine compounds; Pesticides

1. Introduction

European legislation (EC Directive 80/778/EEC, Water Act, 1989) requires that many pollutants must be detected when present at very low concentrations in drinking water. This has produced a need for rapid and precise multi-residue analytical techniques for the isolation and detection of these compounds at concentrations of <100 ng l^{-1} in potable water. In addition to organochlorine pesticides still in use in modern farming practises, stocks of expired organochlorine compound containing chemicals may still exist which present a potential hazard through inadvertent dumping into watercourses. Furthermore, the persistence of organochlorine compounds in the natural environment for many years and their concentration within organisms as they are passed through food webs is well documented [1–3] (and references therein) and warrants routine monitoring in drinking water supplies.

Liquid–liquid extraction (LLE) of pesticides from natural water samples (usually 1–2 l volumes) using organic solvents such as hexane, dichloromethane and petroleum ether are effective [4], but time-consuming and difficult to automate. In addition LLE uses large volumes of costly organic solvents, and complications such as the formation of emulsions can occur [5].

Solid-phase extraction (SPE) is increasingly used

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for the routine concentration of trace pollutants in natural waters. A variety of solid-phase supports in cartridge or disc form are available for the extraction of pesticides from water [5–7]. The technique is simple and easy to automate [8], and the cartridge may be used as an on-line pre-column in tandem with liquid chromatography instrumentation [9–11] or gas chromatography (GC) [12–14]. Sorbed compounds on solid supports may be thermally desorbed in the injection port of a gas chromatograph and analysed directly [15].

A Zymark Autotrace Workstation™ facilitates automated extraction, drying and elution of pesticides. Although small elution volumes (<10 ml) are used, it is generally necessary to concentrate the eluate further, using nitrogen aspiration prior to GC analysis to ensure that nanogram detection levels are achieved. Large volume injection (80 μl) eliminates the necessity for a final evaporation step, thus decreasing sample preparation time and eliminating losses through volatilisation. Large volume injection is also a simple way of improving analyte detectability [16,17]. Recent investigations [18] showed that large volume injection may be optimised according to the volatility and thermostability of the analytes by using different injection volumes, injector liner diameters and speed controlled injection.

This paper describes a sensitive, precise, rapid and cost effective method for the identification and quantitation of sixteen organochlorine pesticides in drinking waters.

2. Experimental

2.1. Preparation of sample

One liter water samples were fortified with 5 ml of MeOH and 25 ml of pH 7 phosphate buffer. All solid chemicals and solvent were of "Analar" and residue analysis grade, respectively. Water was purified with a Milli-Q 18™ (Millipore, Bedford, MA, USA) water purification system.

2.2. Preparation of standards

Organochlorine pesticide standards (>95% purity) were supplied by Dr. S Ehrenstorfer (Augsberg, Germany). Individual standard solutions were prepared by dissolving 20 mg of each pesticide in 100 ml of ethyl acetate. A 2 mg l^{-1} intermediate composite standard solution was prepared by mixing 1 ml of each standard solution and diluting to 100 ml with ethyl acetate. A 200 μg l^{-1} working composite standard was prepared by diluting 1 ml of the intermediate standard in 10 ml of ethyl acetate and this was used to spike 1 l of deionised water or laboratory tap water to produce water standards containing 200, 100 and 20 ng l^{-1} of the pesticide suite. Blank deionised water and laboratory tap water were extracted and analysed by an identical procedure to that of the standards.

3. Sample extraction procedure

A Zymark Autotrace™ (Zymark Corporation, Hopkinton, MA, USA) fitted with 3 g octadecyl silica based cartridges (J T Baker, Deventer, Netherlands) was used for fully automated SPE [19]. Six samples were extracted in one batch by the following procedure:

1. Condition cartridge with 2×10 ml of MeOH at a flow-rate of 10 ml min^{-1}.
2. Condition cartridge with 10 ml of deionised water at a flow-rate of 10 ml min^{-1}.
3. Load 1030 ml of spiked water on to SPE cartridge at a flow-rate of 10 ml min^{-1}.
4. Rinse cartridge with 10 ml of distilled water.
5. Dry cartridge with compressed air for 20 minutes to remove any traces of water.
6. Wash syringe with 10 ml of ethyl acetate.
7. Elute cartridge under positive pressure with 5 ml of ethyl acetate.
8. Wash syringe with 10 ml of dichloromethane.
9. Elute cartridge with positive pressure with 5 ml of dichloromethane.

Aliquots from the final 10 ml of eluent (5 ml ethyl acetate+5 ml dichloromethane) were dispensed into vials and 80 μl was injected onto the GC. The preparation and extraction procedure produces a 100-fold enhancement in analyte concentration.

Subsequently, a pilot repeatability study involving six deionised water samples spiked at 100 ng l^{-1} indicated that a final eluent with a volume of only 2 ml (1 ml of ethyl acetate and 1 ml of dichloromethane) provided satisfactory recoveries. This has the advantage that reduced solvent volumes are used and

provides a 500-fold enhancement in the concentration of target compounds relative to the original sample. In this pilot study the relative standard deviations (R.S.D.) were between 2–12% for all of the pesticides tested. The loading of the sample onto the SPE cartridges is as described above (steps 1–6). Thereafter, the Zymark Autotrace™ functions, detailed in steps 7–11 (below) should be applied for low volume (<2 ml) elution:

7. Soak and collect 0.5 ml of ethyl acetate.
8. Elute and collect 0.5 ml of ethyl acetate.
9. Wash syringe with 10 ml of dichloromethane.
10. Soak and collect 0.5 ml of dichloromethane.
11. Elute and collect 0.5 ml of dichloromethane.

It is recommended (particularly when eluting with volumes as low as 0.5 ml) to wash the syringe prior to soaking and elution in order to ensure that the solvent lines are sufficiently purged and accurate final eluate volumes are obtained.

4. Analysis of pesticide residues using high-volume injection-GC–ECD

The analysis of extracts containing the organochlorine pesticides studied (Table 1) was performed using an AI Cambridge GC94 equipped with a CTC Analytics Liquidsampler A200 SE, optic high-volume injector and ECD using the conditions outlined below: Column: J&W Scientific DB-5 capillary column 30 m×0.25 m×0.25 μm; carrier gas: helium; column temperature: 60°C initially then programmed at 20°C min^{-1} to 140°C and finally at 4°C min^{-1} to 280°C. High-volume injector conditions: split mode for 1 min at 50°C then splitless mode for 1 min while the temperature is programmed to 250°C at 16°C s^{-1}. Speed of injection 40 μl s^{-1}; injector liner: glass, 8 cm×3 mm, manually packed with silanised glass wool (Jones Chromatography Ltd., Mid-Glamorgan, UK); detector temperature: 300°C.

4.1. Validation of method

Eleven batches of standards and blanks were analysed. A batch consisted of three calibration standards (200, 100 and 20 ng l^{-1} of all sixteen pesticides) in deionised water, a "high" and a "low" standard (100 and 20 ng l^{-1}, respectively) in deionised water, a sample (laboratory tap water) containing 100 ng l^{-1}, a blank tap water and a blank deionised water.

Table 1
The mean and standard deviation of the extraction efficiency of 100 ng l^{-1} for each pesticide from deionised water, the repeatability of the extraction when compared to a calibration curve composed from co-extracted standards and the mean R^2

Pesticide	Extraction efficiency (%) of 100 ng l^{-1} in deionised water		Mean R.S.D. (%, n=11)			R^2 (n=11)
	Mean	S.D. (n=11)	100 ng l^{-1} in deionised water	100 ng l^{-1} in tap water	20 ng l^{-1} in deionised water	
Trifluralin	87	12	5.5	8.2	8.3	0.995
α-HCH	94	13	5.7	8.0	10.6	0.991
β-HCH	95	11	6.5	7.4	7.0	0.997
γ-HCH	93	12	6.4	9.1	7.6	0.994
Heptachlor	78	18	7.8	7.8	9.6	0.995
Aldrin	77	19	7.2	8.1	9.4	0.995
Heptachlor epoxide	92	9	4.7	7.0	7.1	0.996
α-Endosulphan	90	7	5.8	8.1	6.9	0.996
pp′ DDE	77	16	8.8	9.6	9.7	0.994
Dieldrin	90	10	6.3	7.7	6.9	0.996
op′ TDE	84	14	7.1	7.4	9.3	0.996
Endrin	90	9	6.4	9.5	9.0	0.998
β-Endosulphan	87	5	5.9	7.0	8.3	0.996
pp′ TDE	83	14	5.2	7.5	7.4	0.996
op′ DDT	79	17	6.4	8.0	10.2	0.996
pp′ DDT	78	15	7.4	11.6	5.6	0.979

R^2=Mean correlation coefficient.

5. Results and discussion

The mean correlation coefficients obtained from the calibration curves plotted from eleven batches are shown in Table 1 and indicate the excellent linearity of the method. Calibration curves were forced through the origin. Each batch was run in duplicate, 12 h or more separating a set of two batches.

The chromatogram obtained from an 80-μl injection of an extract from drinking water spiked with the sixteen pesticides at 100 ng l^{-1} and 20 ng l^{-1} concentrations (Fig. 1A) is similar to that obtained approximately six weeks (ca. 300 injections) later (Fig. 1B). These results demonstrate the long term chromatographic stability of the technique. The data used in this study has been obtained using 10 ml of elution solvent (5 ml ethyl acetate+5 ml dichloromethane), however, similar results were obtained using only 2 ml (1 ml ethyl acetate+1 ml dichloromethane), which has the advantage of providing a 500-fold enhancement of the analytes relative to the original sample and uses lower volumes of expensive organic solvent.

Extraction efficiencies, determined by comparing peak areas of 100 ng l^{-1} standards extracted from deionised water relative to those injected neat, ranged from 77–95% (S.D.=5–19, n=11) for the sixteen pesticides investigated. A reproducibility study indicated relative standard deviations between 5 and 12% for pesticide concentrations of both 100 and 20 ng l^{-1} extracted from deionised and drinking waters (Table 1). These values were obtained by comparison with calibration curves composed from co-extracted standards.

The CTC Analytics Liquidsampler™ used here was fitted with a 100-μl injection syringe. In this study an 80-μl injection volume was chosen to allow a plug of air (20 μl) to be drawn into the syringe

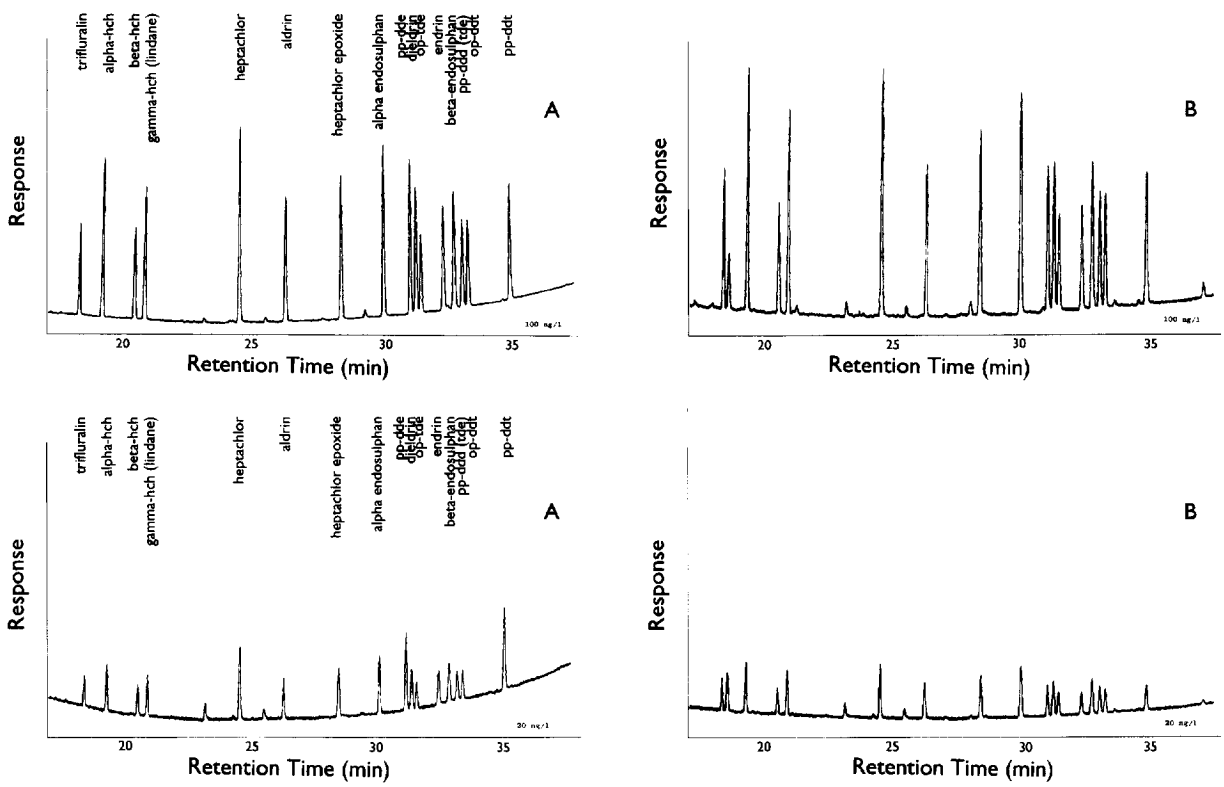

Fig. 1. High-volume (80 μl) gas chromatograms showing the separation of sixteen organochlorine pesticides at a concentration of 100 (top) and 20 ng l^{-1} (bottom). 300 injections (six weeks) separate the analysis of (A) and (B) illustrating the long term chromatographic stability of the procedure with minor deterioration of the chromatographic column.

after the sample. The maximum volume of liquid which can be injected in order to obtain optimum detectability and baseline resolution of all compounds is determined by the volume of liquid that can be retained in the injection liner. This is in turn dependent on the liner dimensions, the surface area of the packing material and the way in which it is packed [18]. The speed of injection may also be important as it controls nebulisation of the sample as it emerges from the injection needle. Nebulisation assists sample adsorption onto the silica wool packing. If the sample were to enter the injector within a solvent slug, part of it may be lost via the split exit at the bottom of the liner due to its poor adsorption within the liner in this state [18]. Other parameters which may improve the detection limit of the procedure include altering the solvent venting time and the length of time the split is closed while the sample is transferred from the injector to the column.

Increasing the injection volume increased the sensitivity of the method (Fig. 2). Sample volumes of >80 μl were carried out manually because the autosampler used was limited to carry a maximum injection syringe of 100 μl. Although some injections of up to 140 μl of neat standard provided results with high quality chromatography (Fig. 2), in general, volumes >100 μl were not always reproducible and occasionally led to column overloading. Injection liner packing seems at least partially responsible for this effect. Upon renewing the packing, overloading occasionally occurred at volumes as low as 120 μl. Under similar conditions, volumes of up to 140 μl could achieve baseline resolution for all sixteen pesticides. As has been noted previously,

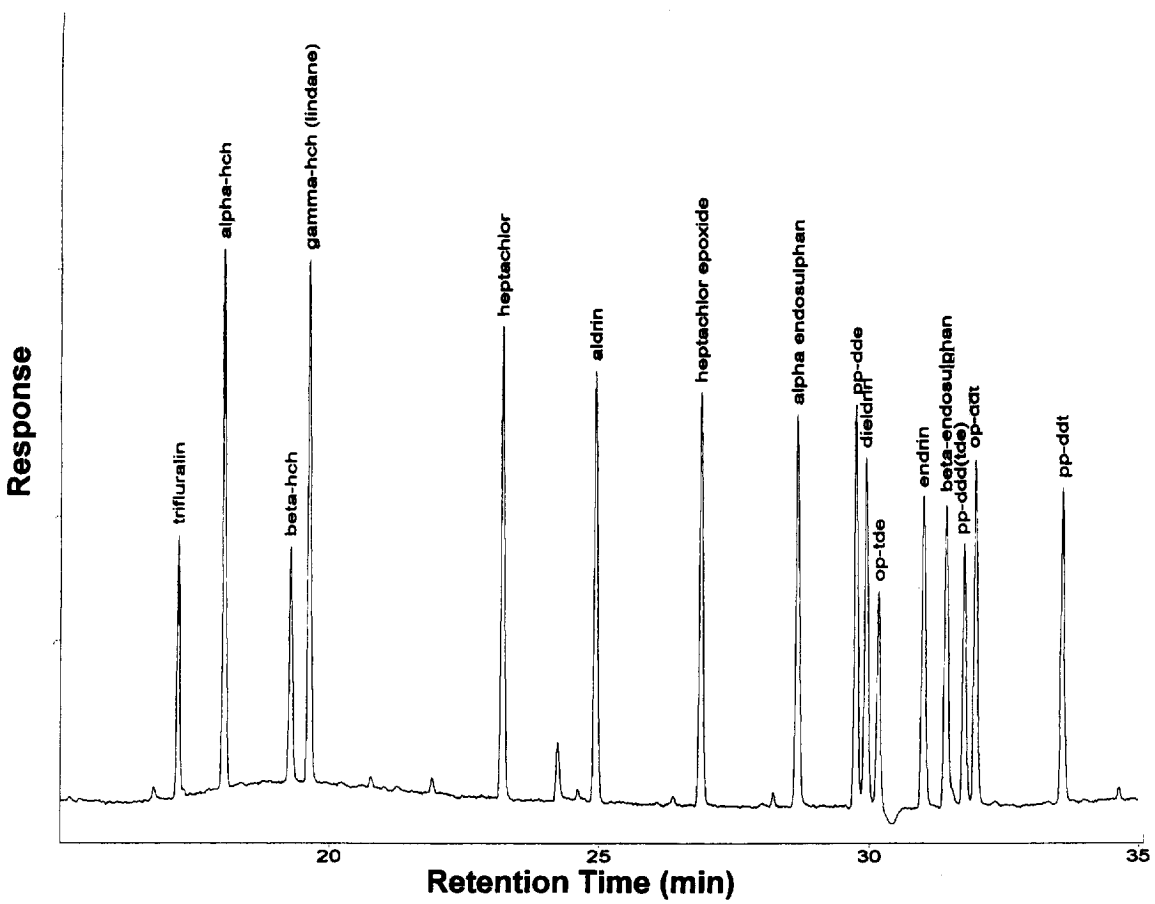

Fig. 2. Chromatogram showing a 140 μl injection volume for the suite of sixteen organochlorine pesticides.

liner packing reproducibilty is difficult to attain owing to the irregular, fibrous nature of silica wool [18].

In this study an 80-μl injection volume provided the reproducibility and chromatographic quality required for routine monitoring of the sixteen pesticides listed in Table 1 in drinking water. Further investigations may be carried out to investigate the effect that liner packing, different liner dimensions and solvent venting times have in the chromatography quality and reproducibility of the method using >80-μl injection volumes.

The method has been used routinely for analysing drinking waters for six months with no obvious problems. During this period none of the sixteen organochlorine pesticides specified here were detected in drinking waters from Northumberland, UK.

6. Conclusions

The fully automated SPE followed by high-volume injection-GC method described here is a rapid, reproducible and sensitive technique for the analysis of organochlorine pesticides in drinking waters. In this study large volume injection has been shown to be a robust technique that was useful for increasing the detectability of the GC procedure. It eliminated the need for further concentration of the eluate following desorption from the SPE cartridge. It saved preparation time and reduced losses of trace organics during sample preparation. An 80-μl injection volume was used for performance testing in this study. Preliminary investigations suggest that injection volumes of up to 140 μl can be used to provide high resolution chromatographic separation, and with further work, may be able to provide similar reproducibility to 80 μl, while enhancing the detectability of the method.

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