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Determination of chlorpyrifos in water by large-volume direct aqueous injection capillary gas chromatography

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SUMMARY

A technique is described for the injection of large-volume aqueous samples in capillary gas chromatography for the direct determination of chlorpyrifos in well water. An uncoated inlet of suitable length coupled to a thin-film methyl phenyl silicone capillary column was employed for the determination of low parts-per-10^9 (ppb) levels of the pesticide in water. Samples were injected without prior clean-up steps by using a 10-port valve, and detection was performed by electron capture. The method yielded high accuracy, precision (4.8% with 95% confidence at 0.9 ppb), and suitable linearity range (0.9–18 ppb). The method presented circumvents the extraction, filtration and centrifugation steps commonly used in the determination of trace organic components in aqueous matrices.

INTRODUCTION

The emphasis on the analysis of trace organic compounds in aqueous samples has increased in the past two decades[1]. A major problem in this area has been the gas chromatographic quantitation of organic pollutants at trace levels by the direct injection of aqueous samples[2–6]. Pesticide analysis in particular has usually been performed by extraction using an organic solvent and subsequent concentration prior to injection of small volumes into a gas chromatograph[7,8].

Recently, advancements have been recognized in the on-line coupling of reversed-phase liquid chromatography (LC) with capillary gas chromatography (GC) for the determination of organic trace constituents in complex matrices[9,10]. This paper presents a gas chromatographic system for the analysis of chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphothioate] by the direct injection of relatively large volumes of an aqueous sample with electron-capture detection. The analysis procedure reduces the number of off-line manipulation and concentration steps thereby providing simplicity and automation, and the possibility of higher sample throughput. By employing a non-deactivated fused-silica inlet (retention gap) coupled to a thin-film methylsilicone capillary column, chlorpyrifos was sufficiently resolved from inter-

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ferences while maintaining peak shape integrity at the party-per-billion[a] (ppb) level. Though the "retention gap" technique is generally recognized as not being compatible with aqueous solvents[11], preliminary data obtained in our laboratories[12] indicated that relatively large volumes of water could be injected into a capillary GC column without detrimental effects on peak shape and resolution, and the present chromatographic set-up takes advantage of phase-ratio focusing[13] and cold-trapping mechanisms[14], while utilizing the non-deactivated fused-silica inlet to allow complete solvent vaporization prior to reaching the separation column.

EXPERIMENTAL

A system diagram for the determination of chlorpyrifos in water is presented in Fig. 1. The gas chromatograph used was a Hewlett-Packard (Avondale, PA, U.S.A.) 5890. A 10-port valve (Model A4C10WT, Valco, Houston, TX, U.S.A.) was mounted 5 cm outside the oven wall and was equipped with a stainless-steel external sample loop of 20 μl volume. A 20 m × 0.25 mm non-deactivated fused-silica capillary (Polymicro Technologies, Pheonix, AZ, U.S.A.) used as an inlet was contained within the oven and was directly attached to the valve. This uncoated inlet was connected via a low dead volume union (ICT, Model IC25250) to a 30 m × 0.25 mm, 5% phenylmethylsilicone capillary of 0.25 μm film thickness (J&W Scientific, Folsom, CA, U.S.A.). An electron-capture detector operated at 350°C was used. Integration and recording of the signals was performed by a Hewlett-Packard 3392A integrator. Typical operating conditions were helium carrier at 6.4 ml/min (at 130°C) and oven temperature of 130°C for 15 min followed by a program of 20°C/min to 280°C. Make-up flow to the detector was argon–methane (10:90) at 32 ml/min.

A Hewlett-Packard 19405A sample/event control module was set up to control a Valco digital valve interface (DVI) and an a Hewlett-Packard 3392A integrator. The DVI drove a Valco helical-drive air actuator (AT104) which in turn rotated the 10-port

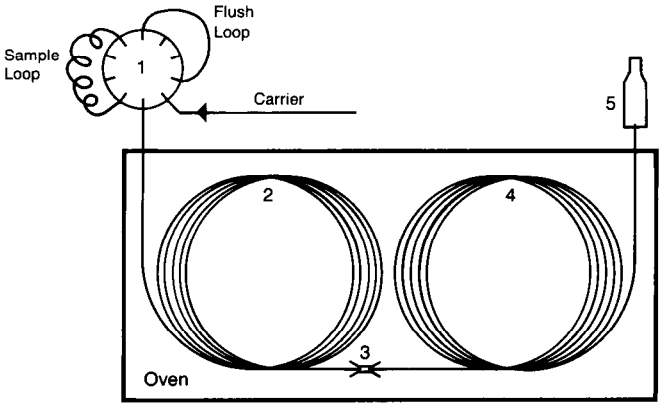

Fig. 1. Schematic diagram of the system for chlorpyrifos determination in water. 1 = Injection valve with sample loop (20 μl stainless steel) and flush loop; 2 = uncoated inlet; 3 = press-fit connector; 4 = capillary GC column; 5 = electron-capture detector.

[a] Throughout this paper, the American billion (10^9) and trillion (10^{12}) are meant.

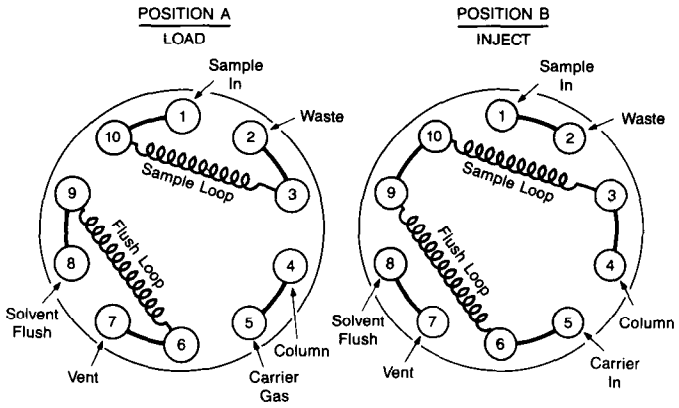

Fig. 2. 10-Port injection valve. Position A: loading of sample and solvent flush; position B: injection of sample onto the capillary GC column.

valve between load and inject positions. A Micromeritics 725 autoinjector was used to fill the sample loop of the valve and control the timing between each run. A schematic of the 10-port injection valve configuration is shown in Fig. 2. A flush loop was installed ahead of the sample loop on the valve to study the effects of flushing the aqueous sample with organic solvent in order to minimize possible carry-over.

RESULTS AND DISCUSSION

To achieve sufficient resolution and undistorted peak shapes, the component of interest must be retained at the head of the capillary GC column while the injected water is eluted at or near its boiling point. Once the component of interest was reconcentrated, the oven temperature was increased to elute the higher boiling component. All of the water passed through the 5% phenylmethylsilicone capillary and the electron-capture detector. Collection and processing of the detector signal was started after all the water had passed through the detector. Several variables were examined in the development of the optimum chromatographic conditions, as a critical balance had to be made between injecting sufficient sample size to provide an adequate detection limit and the volume of uncoated inlet necessary to allow solvent evaporation without allowing liquid to reach the stationary phase of the capillary GC column. Carrier gas flow-rate was adjusted well above optimum (6.4 ml/min at 130°C) so as to rapidly move the sample out of the injection loop and through the tandem capillar system. Flow was mantained by a constant pressure regulator, thus the helium carrier decreased in flow-rate to 4.4 ml/min at 280°C.

Initially, injections were made by using a stainless-steel sample loop with the loop open to the carrier for the full length of the analysis. A long band of baseline noise appeared after the majority of water eluted, attributed to residual water adsorbed to the walls of the injection loop (Fig. 3A). This was also observed by using a non-deactivated section of fused silica as the injection loop, and has been previously reported[10]. Timed injections of 30–45 s eliminated the noise (due to slow desorption of water in the loop), without observed carry-over of sample or detrimental effects in

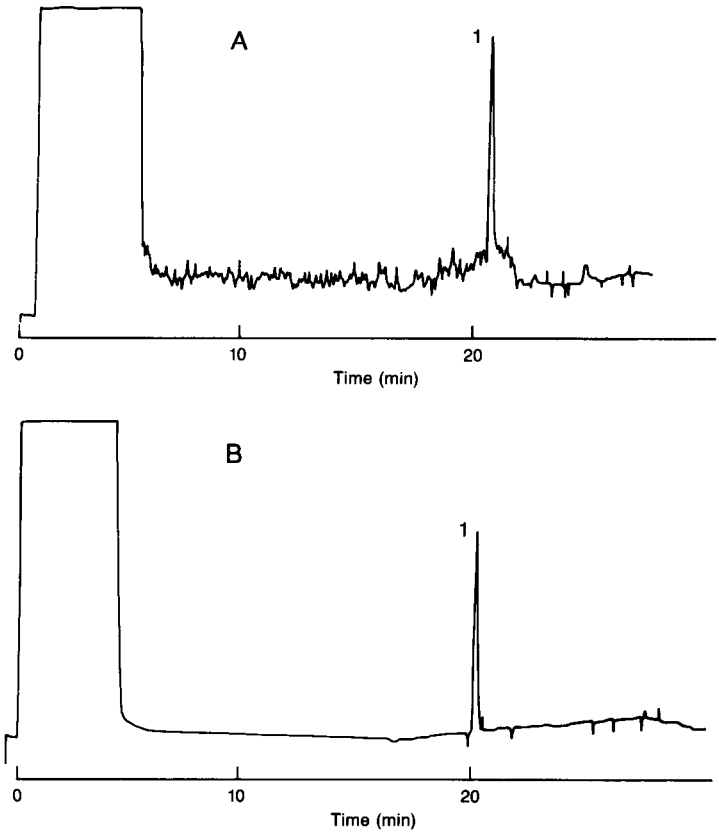

Fig. 3. Chromatograms of chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate] in water. Column: 20 m × 0.25 mm I.D. DB-5, 0.25-μm film. Uncoated inlet: 20 m × 0.25 mm I.D. non-deactivated fused silica. Oven temperature: 130°C for 15 min, program to 250°C at 10°C/min. Carrier gas: helium at 6.4 ml/min. Detector: electron-capture detector at 350°C. Make-up gas: argon–methane (10:90) at 32 ml/min. Injection size: 20 μl. (A) Valve in the inject position for the full length of the analysis. (B) Valve in the inject position for 45 s. Peak 1 = chlorpyrifos 12 ng/ml.

quantitation (Fig. 3B). By using the conditions listed, the use of a solvent in the flush loop was found to be unnecessary.

Linear response for the electron-capture detector

Linearity of the electron-capture detector response for chlorpyrifos in the water matrix was investigated by using two different make-up gases. A linear range of response with a correlation coefficient of 0.97 was obtained in the range of 0.9 to 18 ppb chlorpyrifos with either nitrogen or argon–methane (10:90) as the detector make-up gas. This is a range typically seen for this selective detector[15]. In spite of the limited linear range of the electron-capture detector, this procedure lends itself well to expanding the workable range of chlorpyrifos concentrations through appropriate dilution of the sample or decreased injection volumes.

Precision of analysis

The precision of the method was tested at a level of 0.9 ppb (ng/ml) chlorpyrifos dissolved in distilled water. Table I lists the results obtained for replicate determinations at the 0.9 ppb level. It was observed that the precision of the analysis could be greatly increased by determining peak height with forced baseline at the valley points (4.8 *vs.* 33% when using integrated areas for calculation). The detection limit of the reported procedure was calculated as 220 ppt (three times baseline random noise level).

TABLE I

RECOVERY OF 0.9 PARTS PER BILLION (ng/ml) CHLORPYRIFOS IN WATER

	Concentration found (ng/ml)	
	Integrated peak area	*Peak height with forced baseline*
	0.73	0.89
	0.87	0.88
	0.99	0.87
	1.02	0.89
	0.71	0.84
Mean	0.86	0.87
S.D.	0.14	0.02
R.S.D. (%)	16	2.3

Column performance and stability

Much of the hesitancy to perform aqueous GC on a routine basis is the suspected incompatability and deleterious effect that water has on the stationary phases used. The question in our research group concerned the possibility of phase alteration that might lead to increased adsorbtion and column activity toward the component of interest and/or non-reproducible retention times. As a result, detailed records were maintained of the number of injections, the volume of water, and the volume of organic wash solvents introduced to the system. A polar test mixture (CP-8) was chromatographed prior to the aqueous injections and, later, periodically to track the column integrity. Typical observations for the bonded 5% phenylmethylsilicone capillary columns were 150 aqueous injections of 20 μl each without discernable change in column activity or retention times. Columns that have had more than 3 ml of water passed through them at elevated column temperatures are still being used and do not appear to have experienced measurable degradation. It is concluded that the original column retention behavior is maintained for a sufficient number of aqueous injections to make the daily routine use of this method quite economical.

Automation of the analytical instrument

The chromatographic system lends itself well to computer-controlled automated analysis. A Micromeritics LC autosampler, a Valco DVI and a Valco helical-drive air

actuator (AT104) were connected to a Hewlett-Packard 19405A sample/event control module. Approximately 50 samples (calibration standards, water blanks, and organic wash solvents) can be analyzed along with the actual well water samples without manual intervention. It should be noted that carry-over can take place with samples of particularly high levels of chlorpyrifos (>100 ppb); however, the positioning of acetone or methanol in sample vials between each sample on the autosampler effectively eliminated detectable carry-over, thereby safeguarding all analytical runs. Samples with high chlorpyrifos levels could be diluted with water and reanalyzed.

Well water sample analysis

Test were conducted to determine whether direct aqueous injection would provide comparable results to the method typically used for this type of analysis. In this method, a 40-ml aliquot of the water sample is extracted with 2 ml of hexane. After shaking for 15 min and centrifuging for 3 min at 6 *g*, a 5-μl portion of the hexane layer is injected onto a 180 cm × 3 mm I.D. × 6.4 mm O.D. borosilicate glass column packed with a mixed phase of OV-17 and QF-1 with 11% loading on 80–100-mesh Gas-Chrom Q, at an oven temperature of 205°C. Carrier gas used was nitrogen at 20 ml/min and detection via a flame photometric detector. Calibration of the instrument was performed with a 1 ppb standard of chlorpyrifos in hexane.

In the direct aqueous injection procedure, external standard calibration was performed by forming a least squares plot of three standards containing between 0.9 and 18 ppb chlorpyrifos. The direct injection procedure indicated variability of ± 5% at levels of 30 ppb and ± 25% at 1 ppb compared to the values generated by existing methodology.

CONCLUSIONS

Large-volume direct aqueous injection GC for the determination of chlorpyrifos in water shows advantages over existing methodology by providing rapid and reliable analyses of environmental water samples. Extraction steps are completely eliminated and it has been shown that the integrity of the capillary column can be maintained and that precision is adequate at quantitation levels of 0.9 to 18 ppb. Based on the results obtained and preliminary data on other common pesticides reported previously[10], it is expected that quantitative analysis using the procedure presented here can be extended to other common pesticides.

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