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Solid Phase Extraction and GC-MS Techniques for the Confirmation of Chlorpyrifos Contamination of Surface Water Supplies

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Chlorpyrifos, O,O-diethyl-O-[3,5,6-trichloro-2-pyridyl]-phosporothioate, is an organophosphorus insecticide which is used in Saskatchewan to protect crops from aphids, armyworms, cutworms, diamondback moths, grasshoppers, and wheat midges. It is the active ingredient in the insectide formulations known as Dursban and Lorsban. Like other organophosphorus insecticides, chlorpyrifos primarily affects the human nervous system by inhibiting the function of the cholinesterase enzyme. In addition to the central nervous system, the cardiovascular and respiratory systems are also impacted by exposure to chlorpyrifos.

Application of chlorpyrifos to crops may be performed using either ground or aerial spraying equipment. In a recent incident in rural Saskatchewan, a landowner claimed that his surface water supply (a dugout) had been contaminated during aerial spraying of his neighbor's crops. Upon inquiry, the claimant discovered that the material sprayed contained the formulation Lorsban. Since this water supply was utilized for drinking purposes (both human and animal), the landowner requested that his water be tested for contamination.

Solid phase extraction disks consisting of an inert membrance impregnated with adsorbents such as octadecylsilane (C18), octylsilane (C8), and styrene-divinylbenzene (SDB) have recently replaced liquid-liquid partitioning procedures in numerous analytical methods. Applications to the determination of pesticides in water samples include chlorinated acid herbicides (Hodgeson 1994), triazine herbicides (Brouwer 1990) organochlorine insecticides (Tang 1993; Hendriks 1993) and organophophorus pesticides (Lacorte 1993). SPE disks have been used for the trace enrichment of various pesticides from river and seawater samples (Barcelo 1993; Durand 1992; Durand 1993). Beltran (1993) compared SPE disks and cartridges for use in extracting organochlorine and organophosphorus pesticides from ground water samples. Chiron and Barcelo (1993) used SPE disks coupled with on-line HPLC analysis for the determination of pesticides in drinking water. In a recent study, SPE disks were used to extract

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organochlorine and organophosphorus pesticides from water samples with subsequent elution using supercritical fluid extraction (Barnabus 1994).

Our laboratory has routinely used solid phase extraction techniques combined with GC-MS detection for the determination of a variety of pesticides in ground and surface water samples. The methodology used for the analysis of a series of chlorinated phenoxyacid herbicides was adapted for use in determining chlorpyrifos (Thompson and Morphy 1995).

MATERIALS AND METHODS

Acetone (Caledon Laboratories Ltd.; Georgetown, Ontario), methanol (Baxter Corp.; Mississauga, Ontario), and ethyl acetate (Fisher Scientific; Nepean, Ontario) were distilled in glass and suitable for pesticide residue analysis. Anhydrous sodium sulphate was obtained from Fisher Scientific.

A neat standard of chlorpyrifos (95% purity) was purchased from PolyScience Inc. (Niles, IL). A standard solution containing 2000 ug/mL of deuterated chrysene, d_{12}-chrysene, in methylene chloride was purchased from Supelco Canada Ltd. (Oakville, Canada).

The solid phase extraction disks utilized in this work were obtained from 3M Empore (St. Paul, MN). The SPE disks consisted of circular polytetrafluoroethylene membranes (47 mm diameter) impregnated with 500 grams of SDB adsorbent.

The sample preparation procedure used for the extraction of chlorpyrifos was based on the method routinely used in our laboratory for the determination of various pesticides in water. Briefly, the 1 L samples were eluted through a conditioned disk over a period of approximately 1 h. It should be noted that ground and treated water samples are generally eluted within 15 min, however the presence of tine particulates in the surface water samples reduces the maximum flow rates obtainable. The organic compounds adsorbed onto the disk were eluted with 50 mL of ethyl acetate and collected in a glass tube placed in the vacuum filtration flask. The organic extracts were dried over anhydrous sodium sulphate and evaporated to approximately 2 mL with a rotary evaporator. The extracts were quantitatively transferred to 5 mL glass centrifuge tubes and the final volumes adjusted to 1 mL under a gentle stream of nitrogen gas. Immediately prior to GC-MS analysis, a 200 uL aliquot of a standard solution containing 40 ng/uL d_{12}-chrysene in toluene was added to each extract. The d_{12}-chrysene was used as an internal standard for quantitation.

As with all analyses, a laboratory reagent blank and a fortified reagent blank (i.e., laboratory spike) were processed with all samples.

All analyses were performed using a GC-MS system that consisted of a Carlo Erba 8000 series gas chromatograph connected via a capillary interface to a Fisons MD 800 quadrupole mass spectrometer. A splitless GC injection port, maintained at 220 C, and a 15 metre x 0.25 mm i.d. fused silica DB-5MS capillary column with a 0.25 u thick stationary film (J & W Scientific; Folsom, CA) were utilized. The GC oven temperature program consisted of an intial temperature of 120 C ramped to 300 C at 10 C/min. The final temperature was then held for 5 minutes.

The quadrupole MS was operated in the electron impact ionization mode with the electron energy set at 70 eV. The source temperature was kept at 200 C for all analyses. The mass spectrometer was programmed to scan from 50 to 5 10 a.m.u. with a cycle time of 0.9 seconds.

Calculation of percent recoveries and quantitation of the chlorpyrifos were performed using the internal standard technique. The potential presence of chlorpyrifos is initially verified by comparing the GC retention time of the peak in the total ion chromatogram (TIC) of the sample with that of a standard solution of chlorpyrifos which was analyzed under identical conditions. The identity of the peak appearing at the correct retention time in the TIC is confirmed by comparing its mass spectrum to that of an authentic standard of chlorpyrifos. Also, it is possible to carry out a computerized search of the GC-MS data system's library of over 60,000 spectra.

RESULTS AND DISCUSSION

The analytical methodology used in our laboratory has been found to be effective in determining levels of numerous pesticides in water at low ppb concentrations and lower. A quick check of the efficiency of the method specifically for chlorpyrifos was made by analyzing a number of fortified reagent water samples. One set of five 1L reagent water samples were spiked at a concentration of 1.23 ug/L while a second set of five samples were fortified to contain the equivalent of 61.5 ug/L. The results of the replicate analyses are given in Table 1. The extraction method was found to be very effective in isolating chlorpyrifos from water.

Table 1. Recovery of chlorpyrifos from spiked reagent water samples (n = 5).

Fortification Level (ug/L)	Average Percent Recovery	Standard Deviation
1.23	112	6
61.5	100	7

The first water sample which was submitted to our laboratory was processed and found to contain approximately 30 ug/L of chlorpyrifos. Figure 1 shows the TICs which were obtained for the water extract and a standard solution containing

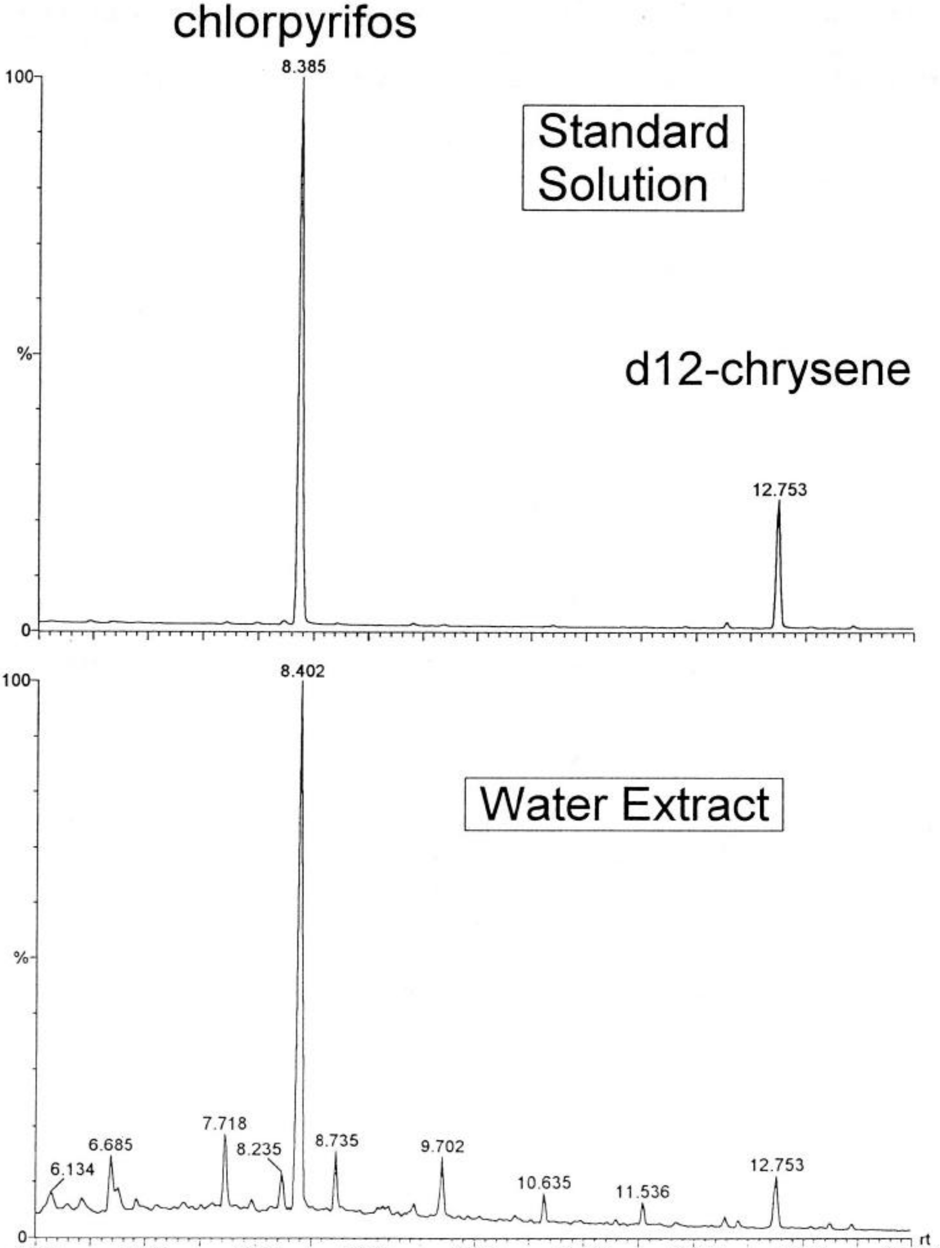

Figure 1. Total ion chromatograms for a standard solution of chlorpyrifos and d12-chrysene (upper trace) and surface water extract (lower trace).

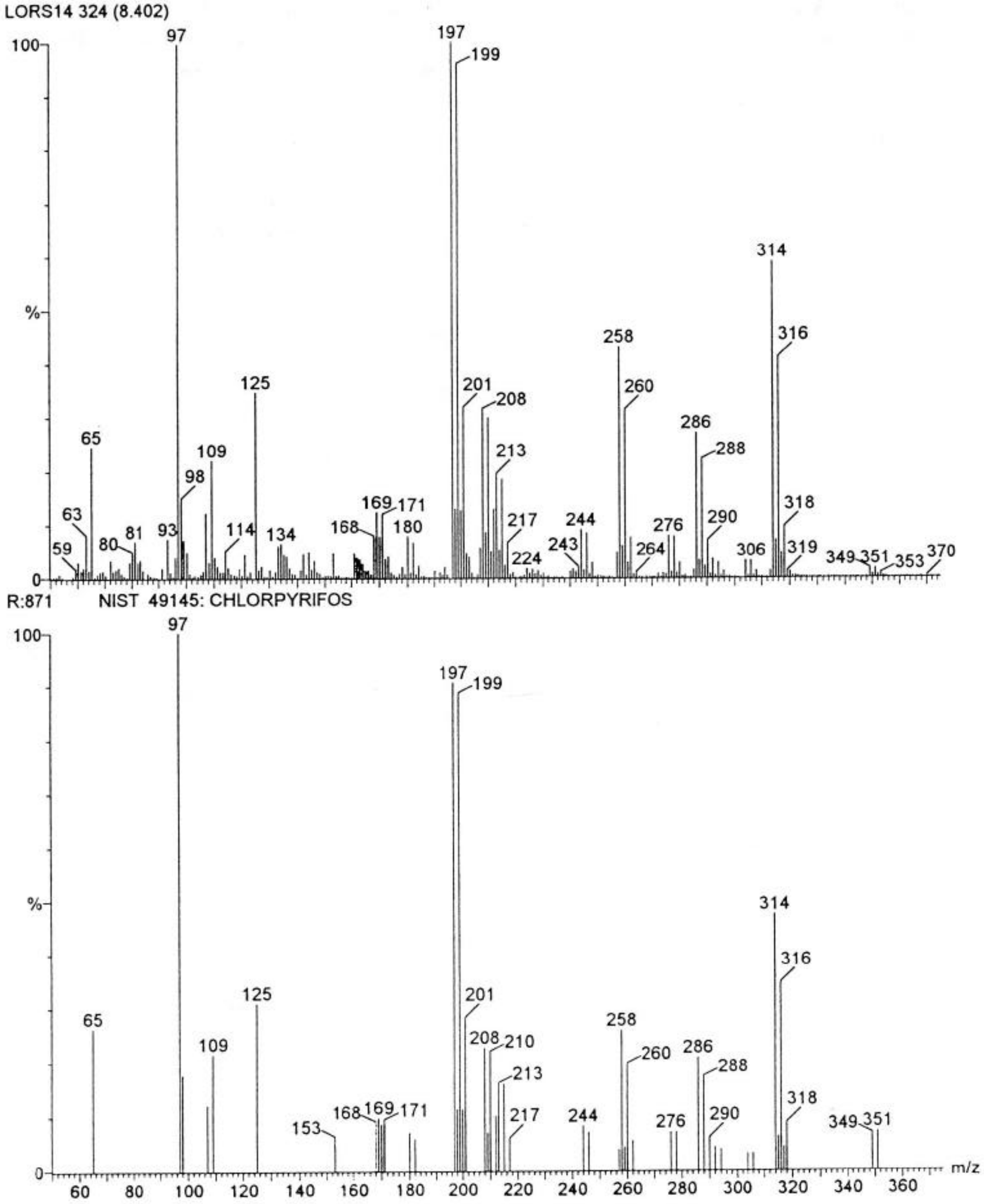

Figure 2. Mass spectra of component eluting at 8.4 min in TIC of water extract (upper spectrum) and chlorpyrifos (lower spectrum) as recorded in data system

chlorpyrifos and the internal standard d_{12}-chrysene. Based on a visual inspection of the respective TICs, it is possible that the water extract contains chlorpyrifos. Identification of the component of interest is performed by examining its corresponding mass spectrum. The mass spectrum of the component eluting at 8.4 min is given in figure 2 (upper spectrum) along with the mass spectrum of chlorpyrifos which is included in the data system's spectral library. Using the GC-MS data system's computerized algorithm for comparing unknown mass spectra to those in the NIST database, a fit of 871 out of 1000 (based on a reverse search) was obtained.

As a result of this finding, our laboratory requested that one of our health officers collect a second sample. This sample, which was taken 20 days after the first, was found to contain 32 ug/L. Given that little natural decomposition of chlorpyrifos would be expected in this short a time period, the results are consistent with those originally obtained. A third sample was collected approximately 61 days after the first sample. Analysis of this sample revealed that chlorpyrifos was present at a concentration of approximately 22 ug/L. As would be expected, the level of chlorpyrifos has dropped.

Solid phase extraction utilizing adsorbent disks has been proven to be a useful technique for isolating many different pesticides from aqueous samples. Combined with the unambiguity obtained from the use of mass spectrometric techniques, this type of procedure is well suited to the rapid analysis of pesticides in water.

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