Troubleshooting in the Trace Analysis of Organochlorine Pesticides in Water Samples

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Summary
As a consequence of the high toxicity of organochlorine pesticides their presence in water for human consumption is limited by legislation. To determine these compounds at trace levels, an extraction procedure and a highly sensitive analytical technique is necessary. In this work we have used laminar disks for the solid-phase extraction of 21 organochlorine pesticides from water. The analytical technique selected is gas chromatography with electron-capture detection. A solid-phase extraction procedure is proposed, and some problems has been encountered. Low recovery of some pesticides has been obtained, because of their adsorption by the walls of containers. To prevent this adsorption, addition of 20% methanol before the sampling step is proposed. Adsorption of pesticides by the organic matter present in water samples was also observed. Pesticides can be adsorbed by the membrane filters usually used to remove suspended particulate matter from water samples. Different kinds of filters have been tested, and the occurrence of the problem has been confirmed. The use of laminar disks in this work has overcome this problem.

Introduction
In the last century the development and use of pesticides played important roles in increasing agricultural productivity. Because of their widespread application, however, pesticides can contaminate natural water, either directly during application or indirectly as a result of drainage of agricultural land [1].

Because pesticides are toxic, persistent, and bioaccumulated, and some are carcinogenic, their presence in water for human consumption must be limited. European Directive 98/83/CE concerning the quality of water for human consumption stipulates the maximum concentration of each pesticide should be 0.1 μg L⁻¹ and the total amount of pesticide should be 0.5 μg L⁻¹. The maximum individual concentration is even lower (0.03 μg L⁻¹) for aldrin, dieldrin, heptachlor, and heptachlor epoxide [2]. As a consequence of the low levels established by this directive, the development of sensitive, fast, and efficient methods of analysis remains of great interest.

Gas chromatography (GC) with highly sensitive electron-capture detection (ECD) is the main analytical technique employed in the determination of pesticide residues in environmental waters, not only because of the sensitivity and specificity of ECD, but also because of the separating power of GC [3].

To reach the detection limit stipulated by the legislation, a concentration procedure for the analytes must be applied. A traditional approach to sample preparation in water analysis is liquid-liquid extraction (LLE). This methodology is time- and solvent-consuming, and laborious. Solid-phase extraction (SPE) with commercially adsorbents has several well-known advantages over LLE. Among the adsorbent materials available for SPE of pollutants from water, octadecyl bonded silica (C₁₈) has become the most popular. Different SPE formats are available, mainly disposable cartridges and membrane disks [4]. For solid-phase extraction of organochlorine pesticides in this work we tested new C₁₈ laminar disks, which consist of a thin bed of microparticles supported in a laminar structure in a pre-assembled disk. Because this arrangement enables better contact between the adsorbent and the analytes, high rates of throughput can be used, even when samples contain suspended solids, without clogging, or previous filtration [5]. This is very important in the determination of organochlorine pesticides because filtration results in losses of some pesticides.
Because of their high hydrophobicity and low water-solubility, pesticides tend to be adsorbed by the walls of the containers used in the handling of aqueous samples. This adsorption is generally higher on Teflon than on glass. These losses are negligible when enrichment experiments are performed with high spiked concentrations, e.g. 50 µg L\(^{-1}\), but not when samples are spiked at the low µg L\(^{-1}\) levels stipulated by drinking water regulations.

Pesticides are, moreover, readily adsorbed on the surface of suspended particulate matter (SPM), and can also be adsorbed by humic and fulvic acids, lipids, and proteins. Although filtration under gravity is typically used to eliminate SPM from samples, losses of the pesticides as a result of adsorption by filter membranes have been reported. Adsorption problems are especially important for isodrin, \(p,p'\)-DDE, \(p,p'\)-DDT, \(a\)- and \(\gamma\)-chlordane, and endrin ketone were from Supelco (Bellefonte, PA, USA), 2,4,5,6-Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl, used as internal standards (IS), were also supplied by Supelco. Isodrin was from ChemService (West Chester, USA).

A working standard mixture of pesticides (0.1 µg mL\(^{-1}\)) was prepared by dissolution in \(n\)-hexane and stored under refrigeration (4°C).

Extraction of the pesticides was performed by use of a Bakerbond Speedisk C\(_{18}\) (J.T. Baker, Deventer, Holland).

 Filters assayed in the prefiltration step were Macherey-Nagel (Düren, Germany) MN GF-6 0.6-µm glass fibre filters, Millipore (Bedford, MA, USA) 0.45-µm cellulose nitrate and acetate filters, and Lida (Rochester, NY, USA) 0.45-µm PTFE filters and 0.2-µm Nylon filter membranes.

**Analysis and Quantification**

Helium (99.999%) was used as carrier gas at 1.2 mL min\(^{-1}\). The column temperature was maintained at 60°C for 1 min after injection, then increased at 25°C min\(^{-1}\) to 220°C, and then at 6°C min\(^{-1}\) to 300°C, which was held for 5 min. The injector and electron-capture detector temperatures were 300 and 350°C, respectively. The detector auxiliary gas was nitrogen (99.999%).

The concentrations of the chlorinated pesticides in samples were obtained from calibration graphs in which the ratio area (pesticide)/area (IS) was plotted against concentration for each pesticide (µg L\(^{-1}\)). Endosulfan sulfate, methoxychlor, and endrin aldehyde were quantified using decachlorobiphenyl as IS; TCMX was used for the other pesticides.

**Extraction Procedure**

Bakerbond Speedisk C\(_{18}\) laminar disks were used for solid-phase extraction of 21 organochlorine pesticides from water samples. They contain 10-µm irregular particles with 60 Å pores in a 50 mm diameter and 1 mm high bed. These disks are recent introductions and their application to the extraction of organochlorine pesticides has not yet been studied in detail.

Disks were preconditioned by washing with hexane (5 mL), ethyl acetate (10 mL), methanol (10 mL), and water (10 mL) from a Milli-Q water purification system (Millipore, Milford, MA, USA). Methanol (for amount, see Results and Discussion) was added to the sample (500 mL) and the mixture was then sonicated for 5 min and percolated through the disks by application of a vacuum membrane pump. Waters (Milford, MA, USA) with a restrictor which ensured an adequate flow-rate of 150 mL min\(^{-1}\). It is necessary to prevent the drying of the disk between conditioning steps with MeOH and Milli-Q water, and sample addition, because a water-air interface is formed in the pores of the disk. Before elution, disks were dried by air flow (aspiration) for 30 min.

Among the elution conditions tested, the best results were obtained when pesticides were eluted from the disk with ethyl acetate (10 mL) then hexane (3 mL). A glass column filled with anhydrous sodium sulphate was used to dry the eluate. The dried eluate was concentrated to low volume by rotary evaporation and then evaporated to dryness by use of a stream of nitrogen (35 mL min\(^{-1}\)). Losses as a result of evaporation were thereby minimized and reproducibility was improved. Finally, the residue was redissolved in hexane (1 mL), each I.S. (10 µL) was added, and the extract (1 µL) was then ready for analysis by GC-ECD.