

ENRICHMENT OF CHLOROPESTICIDES AND PCB FROM WATER PRIOR TO ANALYSIS:  
A COMPARISON OF FOUR METHODS

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ABSTRACT

Chloropesticides and PCB in the ng/l-concentration range are best extracted from water by liquid/liquid extraction. Two methods showed higher recovery rates with low standard deviation and lower method standard deviations than liquid/solid extraction with commercial C-18 phase cartridges or extractive steam distillation.

INTRODUCTION

Several established procedures for the extraction of low polar organic micropollutants from water are existing, and a thorough investigation of their relative usefulness is needed. A new method for enrichment of chloropesticides and PCB from water with light phase rotation perforator is described and compared with 3 established procedures (1/1-extraction by a German DIN-method, 1/s-extraction with C-18 phase cartridges, extractive steam distillation). 18 Chloropesticides and 6 PCB-congeneres were investigated. Analyses were performed with GC-ECD Slope, rest standard deviation, method standard deviation of a linear regression, limits of detection and recovery rates were determined applying statistical means.

EXPERIMENTAL PART

For each method, 5 parallel experiments were carried out on 5 concentration levels between 1,5 and 50 ng/l. Synthetic samples were made up from aqua bidest., which had been further purified: the water was extracted by the corresponding method before endowing it with a solution of the 24 compounds in acetone. The sample volume was always 1 l. All chemicals used were specified for analytical use. Pentane had to be further rectified before being suitable.

Gas chromatography:

The Vega 6130a gas chromatograph (Carlo Erba) was equipped with a split/splitless injector and a  $^{63}\text{Ni}$  electron capture detector. A retention gap (FS-Phenyl-Sil desakt., 0,32 mm x 2,5 m, C&S) preceded the analytical column (CP-Sil-8-CB, 0,32 mm x 50 m, film thickness 0,26  $\mu\text{m}$ , Chrompack).

Carrier gas was nitrogen, make up gas argon/methan (95:5). Injection of the "1  $\mu$ l" probe (1.85  $\mu$ l including needle volume) was carried out by the 'hot needle' method, followed by a splitless time of 60 s (split ratio 1:40). A temperature program was used

#### Methods of enrichment

Light-phase rotation perforator:

In a 1 l rotation perforator (figure 1, according to *Brodesser and Schoeler* [1]), the sample was extracted with pentane, refluxing from a 50 ml round flask for 1 h. After transfer of the organic phase to a calibrated flask, 2 ml i-octane were added and the extract reduced to 0.5 ml at about 14 Torr in air bath.

DIN-method [2]:

Placed in a 1 l Erlenmeyer flask, the sample was strongly mixed with 10 ml Pentane for 10 min. After standing for another 10 min, the organic phase was separated by help of a microseparator and after addition of 1 ml i-octane reduced to 0.5 ml as described above.

Solid phase extraction [3]:

The commercially available cartridges (C-18 phase, 500 mg, Analytichem) were treated with 5 ml hexane, methanol and purified water respectively, before the sample (containing 1 % methanol) was extracted by help of a slight vacuum with a flow rate of 7-17 ml/min. After drying with nitrogen, the solid phase was treated with 3 x 1 ml hexane, the eluate reduced to 0.5 ml upon addition of 1 ml i-octane as described above.

Extractive steam distillation [4]:

The sample was boiled in a round flask for 2 hours (heating output 450 watts). The condensed steam flowed into an extraction device, where it passed through a 15 ml layer of cooled hexane before continually returning into the bottom flask. After transfer to a calibrated flask and addition of 1 ml i-octane, the hexane phase was reduced to 0.5 ml.

Evaluation:

Directly preceding each chromatogram of an extraction solution, a chromatogram of a standard solution of the 24 investigated compounds of comparable concentration in i-octane was taken up. Recoveries were determined by relating the 2 sets of data for each experiment. The recoveries given are average values, determined from sets of 5 experiments that were carried out for each concentration level and each method of extraction. As characteristic values for the procedures, slope (or sensitivity), rest standard deviation and method standard deviation of linear regressions and limits of detection were determined.

By help of the chromatographic data of the standard solutions, the area values of each set of 5 parallel experiments were standardized and average values determined, which were then used for the linear regression.

#### RESULTS AND DISCUSSION

A linear relationship could be established for all methods except the solid phase extraction, where for most compounds sensitivity dropped dramatically at 50 ng/l. This is thought to be caused by an altogether insufficient extraction capacity and a selective adsorption of compounds with higher affinity to the active sites. For the sake of comparability, a linear regression was always applied.

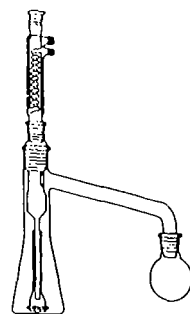


Figure 1.

The sensitivity values were generally the highest for the methods of liquid/liquid extraction and the lowest for the steam distillation. Very low rest standard deviations on the other hand resulted in method standard deviations for the steam distillation procedure that were quite comparable with the liquid/liquid methods (figure 2). Average values of method standard deviation were 2.9 ng/l for the rotation perforator, 3.4 ng/l for the DIN-method and 3.8 ng/l for the steam distillation. The solid phase method does for most compounds not fit into the picture due to its strongly non-linear extraction behaviour.

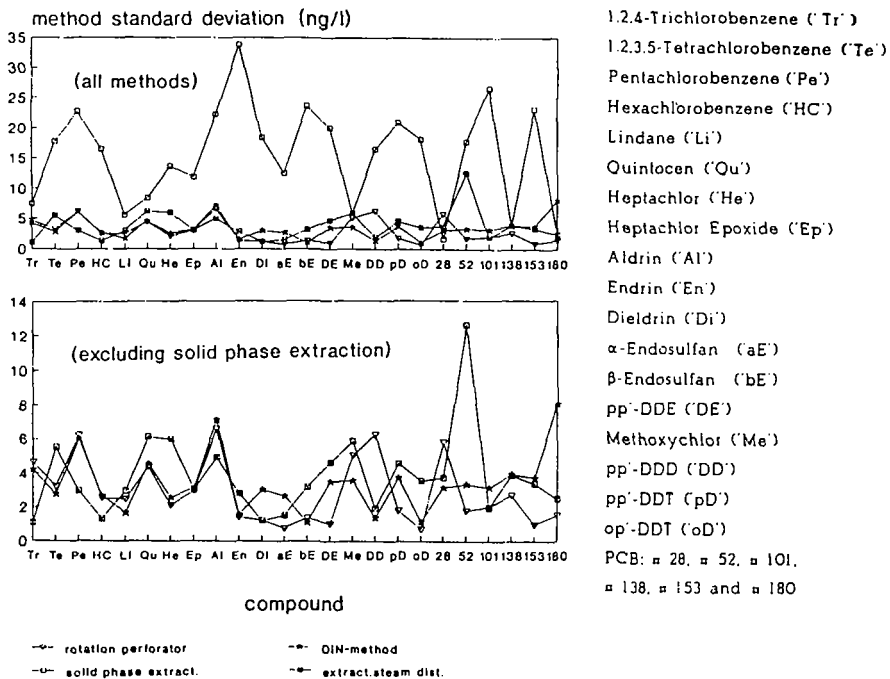


Figure 2: Method Standard Deviation Values

Table 1: Chloropesticides and PCB-Congeneres used in the Investigations

Recoveries ranged between about 80 and 90 % for the liquid/liquid methods. At 50 ng/l, the DIN-method was found to be more efficient, while near the limits of detection, extraction by rotation perforator produced higher recoveries. For both procedures, recovery was always better than 70 %. Standard deviations were typically about 10 %. Unacceptably low, still almost constant at all concentration levels were the recoveries with the extractive steam distillation. Only occasionally, values above 70 % were obtained. Recoveries even below 20 % were found for β-endosulfan and heptachlor. The solid phase procedure gave recoveries between about 80 and 100 % and standard

deviation values between 15 and 30 % at 4 and 10 ng/l, respectively. At 25 and 50 ng/l, recoveries declined, leaving only lindane and quintocen above 70 % at 50 ng/l. Methoxychlor,  $\beta$ -endosulfan and to a certain extent endrine, dieldrine and  $\alpha$ -endosulfan showed unreliable values of recovery, independent of the concentration. Results for all methods at 10 ng/l are shown in figure 3.

The best degree of enrichment was obtained by the extraction with the rotation perforator. Regarded also from a practical viewpoint, the DIN-method was still more appealing, since with simple, inexpensive equipment, the extraction was accomplished easily and fast with relatively small amounts of highly purified solvent. Problems with phase separation may occur with both methods on analyzing real samples. Extractive steam distillation and solid phase extraction both revealed high deficiencies in their respective extraction behaviours. A steep decline in permeability was observed with the solid phase system when analyzing real samples containing considerable amounts of microorganisms, making extraction difficult. The cause for the low enrichment potential of the steam distillation is probably insufficient exchange between the condensed steam and the organic solvent.

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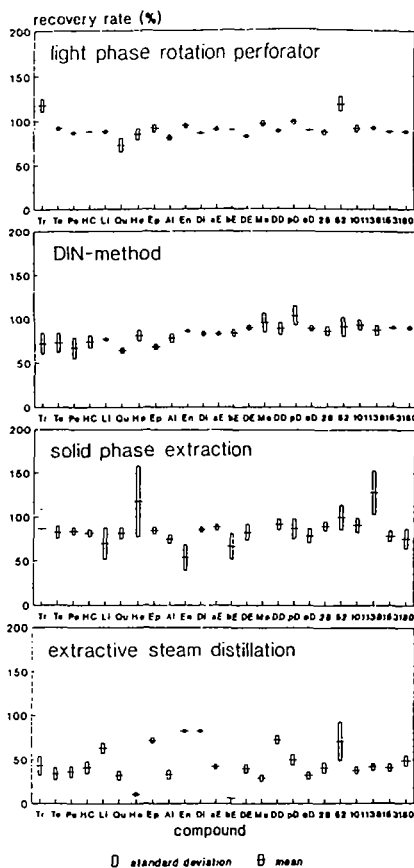


Figure 3: Recoveries at 10 ng/l