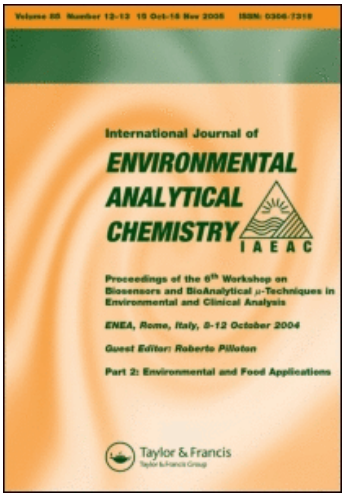

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J. Cacho[a]; J. Salafranca[a]; V. Ferreira[a]; C. Nerín[a]
[a] Depto. Química Analítica, Facultad de Ciencias, Universidad de Zaragoza, Zaragoza, Spain

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FAST MICROEXTRACTION BY DEMIXTURE FOR THE DETERMINATION OF ORGANOCHLORINE COMPOUNDS IN WATER

J. CACHO, J. SALAFRANCA, V. FERREIRA and C. NERÍN

Depto. Química Analítica, Facultad de Ciencias, Universidad de Zaragoza, Campus Universitario s/n, 50009 Zaragoza, Spain

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A microextraction procedure by demixture is applied to the determination of nine chlorobenzene isomers and α, β, γ and δ-hexachlorocyclohexane isomers in water. The procedure consists of demixing an organic phase (iso-propanol) from a homogeneous aqueous solution containing the organochlorine compounds by adding 37.7 g of $(NH_4)_2SO_4$ and 6.85 g of $NaH_2PO_4.H_2O$. In these conditions 120 μL of iso-propanol are separated. The recoveries of the compounds are higher than 80% in all cases and the RSD values for independent replicates are less than 6%. The concentration factor of the procedure is about 350. This procedure is compared to both liquid-liquid and solid-phase C-18 extraction procedures with excellent results.

KEY WORDS: Organochlorine compounds, pesticides, water analysis, demixture procedure, ternary phases diagram.

INTRODUCTION

The determination of organochlorine pesticides and related compounds in water is nowadays a constant problem for the analytical chemists. The low level of concentrations of such compounds and the strict regulations in all countries demand very sensitive procedures. This sensitivity is usually reached through preconcentration steps using either solid-phase cartridges[1–13], solid membranes or liquid-liquid extraction[14–16] and further evaporation of the final organic extracts. However, these procedures have several problems. Liquid-liquid extraction involves a great consumption of organic solvents, which are expensive and have safety problems. On the other hand, the concentration step is often discriminatory for some pesticides and it concentrates the impurities of the solvents as well[17,18].

One alternative to avoid these problems is the use of a microextraction, in which the ratio between the organic and aqueous phase is very high. Several microextraction procedures have been proposed[17–20], one of them by EPA, but most of the times the results are only semiquantitative. The main problem affecting these methods is the distribution factor between both organic and aqueous phases. Nevertheless, if the organic phase could be generated in situ in the aqueous phase through a demixture in a high ionic concentration, the mentioned problems could disappear. Such microextraction by demixture has been described[21,22] as an excellent and efficient technique for the extraction and determination of volatile organic compounds in wine and in water.

This paper shows a procedure of microextraction by demixture applied to the determination of several pesticides and organochlorine compounds in water. The procedure is compared with both the liquid-liquid and solid-phase (C-18) extraction with excellent results.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 5890 series II gas chromatograph fitted with an automatic injector 7673 model and a FID and ECD detectors. A Shimadzu GC-9A gas chromatograph fitted with FID and ECD detectors. Signals were recorded using a NEC computer and processed with the version 3.3 of Maxima 820 software by Waters (Millipore Corporation).

The columns used were: BP-5 (SGE, Ringwood, Australia) 50 m × 0.22 mm i.d., 25 μm film thickness and Supelcowax 10 (Supelco, Bellefonte, P.A.) 60 m × 0.32 mm i.d., 50 μm film thickness.

Chromatographic conditions

The following conditions were used: Hewlett-Packard: splitless injection, splitless time: 3 min, carrier gas: H_2, flow rate: 2 $mL.min^{-1}$, inlet pressure 120 KPa. Make-up gas: N_2 at 30 $mL.min^{-1}$. Detection: FID. Injection volume 1 μL. Temperature program (column Supelcowax 10): 40°C held for 5 min, then raised to 220°C at 4°$C.min^{-1}$. Final time 25 min. Injector and detector temperatures 220°C.

Shimadzu: splitless injection, splitless time: 3 min, carrier gas: H_2; flow rate: 2 $mL.min^{-1}$; inlet pressure: 2.0 $kg.cm^{-2}$. Make-up gas: N_2 at 60 $mL.min^{-1}$. Detection: ECD. Injection volume: 1 μL; temperature program (column BP-5): identical to that described before but starting at 50°C.

Reagents and solutions

All the chlorobenzenes and HCHs (α, β, γ, and δ-hexachlorocyclohexane isomers) were obtained from Chem Service (West Chester, P.A.). $(NH_4)_2SO_4$, $NaH_2PO_4.H_2O$ analytical reagent, nitrobenzene, iso-propanol, ethanol 99%, n-hexane and diethyl ether were supplied from Merck (Darmstadt). Water was obtained from a Milli-Q purification system (Millipore). Sep-pak C-18 cartridges were from Millipore.

A hexane-diethyl ether (85:15, v/v) mixture was prepared as extracting organic phase.

Aqueous samples with known pesticides concentration were prepared by spiking Milli-Q water with a standard ethanol solution containing all the compounds (aprox. 2000 $mg.L^{-1}$ each one). The content of ethanol in the aqueous phase is in all the cases negligible (e.g. 50 mL of an aqueous solution of 100 $ng.L^{-1}$ of pesticides contains only 2.5 nL of ethanol) and it does not affect at all the ternary equilibrium. From this stock solution, 50 μL were taken and diluted up to 1000 mL with Milli-Q water to obtain a 100 $\mu g.L^{-1}$ standard aqueous solution. From this one, and by appropiate dilutions with the same Milli-Q water, the rest of the solutions used in the study were prepared. In each

different study carried-out, new standard aqueous solution was prepared in order to avoid errors due to the degradation of compounds.

The samples prepared in this way were used in all the studies carried-out (linearity, precision, recoveries and detection limits) with the only exception of the comparison among the three methods. In this case, a natural environmental water sample was used in order to apply the procedure to a real matrix, and to take into account the possible difficulties due to the matrix effects that might appear during the analysis.

Procedure for liquid-liquid extraction

Add 250 mL of water sample and 10 mL of a hexane-diethyl ether (85:15, v/v) mixture to a separatory funnel of 500 mL. Shake for 1 minute and transfer the organic phase to a flask. Repeat the extraction three times with 10 mL of the extracting mixture each time. Pass all the extracts together through a small glass column (10 cm, 1 cm i.d.) containing anhydrous sodium sulphate. Wash the column with 5 mL of the extracting mixture and concentrate all the organic phase under nitrogen current at 40°C up to 1 mL. Transfer quantitatively this solution to a volumetric flask of 5 mL containing nitrobenzene as internal standard and dilute to the mark with the extracting mixture. Analyze it under the chromatographic conditions given above.

Procedure for solid-phase extraction with Sep-pak

Activate the C-18 cartridge with 10 mL of distilled water, 10 mL of methanol and 10 mL of distilled water sequentially. Pass 100 mL of water sample through the cartridge at 20 $mL.min^{-1}$. Dry the cartridge under nitrogen current and elute it with 15 mL of extracting mixture. Concentrate the eluate and follow the same procedure described for liquid-liquid extraction.

Procedure for microextraction by demixture

In a separatory funnel of 100 mL add 37.7 g of $(NH_4)_2SO_4$, 6.85 g of NaH_2PO_4. H_2O, 50 mL of the water sample to be analyzed, 10 µL of nitrobenzene as internal standard and 1.2 mL of iso-propanol. Shake the funnel and wait for the separation of phases. Remove the organic phase separated with a Pasteur pippette, transfer it into a vial and analyze it under the chromatographic conditions given above.

RESULTS AND DISCUSSION

Extraction by demixture

The first condition to carry out a demixture process by generating in situ an organic phase is the solubility of the organic solvent in water. Among the solvents which are soluble in water, iso-propanol has been shown as one of the most appropriate. Figure 1 shows the ternary phase diagram of the system water/iso-propanol/ammonium sulphate. The A-point represents the optima conditions of demixture corresponding to a water/iso-

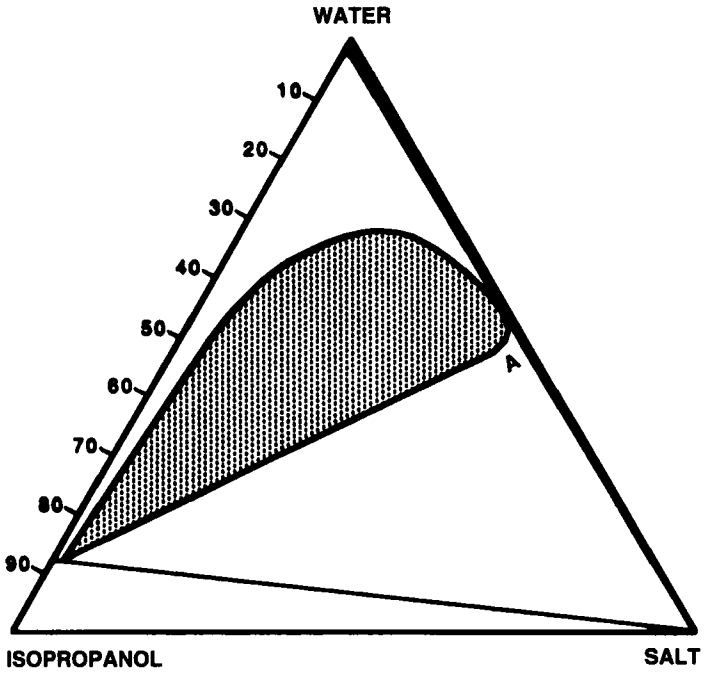

Figure 1 Ternary diagram for the system water/iso-propanol/salt. The dotted area represents the composition of the ternary mixture for which two liquid phases coexist. The A-point indicates the optima conditions of the microextraction.

propanol (50:1.2, v/v) solution with 37.7 g of $(NH_4)_2SO_4$. The addition of a small amount of monosodium phosphate (6.85 g) enables the solution to be further oversaturated and the pH to be regulated, thereby improving the extraction yield of organic compounds, the speed of salt dissolution and phase separation. It can be pointed out that the equilibrium is reached very rapidly and further does not depend on mechanical factors such as shaking speed or time, as the starting solution is perfectly homogeneous and the organic phase is generated in the bulk of this solution. This solves a critical problem in microextraction with solvents, namely the difficulty involved in reaching equilibrium when the number of substances to be extracted is large and their chemical nature is very different.

Total dissolution of the salt takes approximately 8 min and the phases separate by gravity, with no need of centrifugation in further 20 min. The partition is carried out between two phases of very different composition: the aqueous phase, containing less than 1% of iso-propanol, with a high ionic strength and the organic phase with a 13% of water content.

The entire process takes place at ambient temperature thereby avoiding the formation of artefacts. The sample is extracted rapidly and requires no further concentration. No restrictive working conditions are required, and the physical properties of iso-propanol enable it to be injected reproducibly in the splitless mode. In this aspect iso-propanol is clearly superior to the solvents which are normally used in splitless injection for which it is impossible to obtain a good recondensation effect owing to their low boiling points[23].

The volume of organic phase recovered (120 μL) is very reproducible. Only when working with very contaminated waters by surfactants can turn up some problems. Such problems are eliminated if the water sample is diluted 1:1 with distilled water.

Linear range and detection limits

All the compounds studied showed a linear response in all the range studied (10 $ng.L^{-1}$ to 20 $\mu g.L^{-1}$ in water) using both detectors ECD and FID. HCHs were analysed only with ECD for two reasons: the first one, that the column attached to the FID was a Supelcowax 10 which gives very poor separation for these compounds and the second one, that even when working with BP-5/FID, the sensitivity of this detector for HCHs is very low as explained below. Table 1 shows the regression coefficient of the straight lines obtained, the RSD value for six independent analysis and the detection and quantification limits for all the compounds. It can be observed that the RSD is less than 6% which means a good reproducibility. The detection limit has been established as the equivalent concentration to three times the background signal of the chromatogram. The quantification limit was considered in each case as the equivalent concentration to 10 times the background signal. In both cases, the background signal was measured after injecting the extract obtained when an ultrapure (Milli-Q) water sample was extracted under the same conditions described before.

Table 1 shows the results obtained in both detectors. It can be pointed out that when the number of chlorines in the compounds increases both the quantification and detection limits considerably decrease in ECD but they increase in FID. All the values are referred to the aqueous phase and it can be emphasised that all of them are lower than the limits established by the EEC law.

Recovery studies

In order to establish the recoveries for all the compounds, four spiked Milli-Q water samples of different concentration (20, 50, 500 and 1000 $ng.L^{-1}$) were prepared and the procedure described under Experimental was followed. The slope of the straight lines obtained when the concentration found was plotted versus the concentration added for each compound is the recovery value, which is shown in Table 2. It is worth pointing out that all the recoveries are higher than 80%, with the only exception of pentachlorobenzene with 77.4%.

Moreover, the concentration factor of the demixture procedure, which means the ratio between the concentration in organic phase and the concentration in the original aqueous phase, is about 300. This factor is reached in only one step and without evaporation step in which there could be losses of the most volatile compounds such as chlorobenzenes. Both aspects demonstrate that this procedure is an appropriate alternative for the determination of organochlorine compounds in water.

Determination of HCHs and chlorobenzenes in water

To compare the proposed procedure with those well-known ones such as liquid-liquid and solid-phase extractions, after previous studies carried-out with Milli-Q water, a natural contaminated water with chlorobenzenes (CBs) and HCHs was analyzed

Table 1 Regression coefficients (r), linear range, detection and quantification limits and RSD values for the determination of chlorobenzenes (CBs) and HCHs in water by microextraction by demixture. Concentration for RSD values: CBs 10 $\mu g.L^{-1}$, HCHs: 100 $ng.L^{-1}$ (both in water).

Detector	*Flame Ionization (FID)*					*Electron Capture (ECD)*				
Compound	*r coef. (height)*	*RSD, % n=6*	*D. Lim. $\mu g.L^{-1}$*	*Q. Lim. $\mu g.L^{-1}$*	*Linear range ($\mu g.L^{-1}$)*	*r coef. (height)*	*RSD, % n=6*	*D. Lim. $ng.L^{-1}$*	*Q. Lim. $ng.L^{-1}$*	*Linear range ($\mu g.L^{-1}$)*
1-chlorobenzene	0.9995	5.14	0.07	0.2	0.2–20	0.9996	4.73	500	1000	1–5
1,2-dichlorobenzene	0.9988	1.87	0.07	0.2	0.2–20	1.0000	1.98	150	500	0.5–5
1,3-dichlorobenzene	0.9999	3.84	0.07	0.2	0.2–20	0.9995	3.39	150	500	0.5–5
1,4-dichlorobenzene	0.9996	3.18	0.07	0.2	0.2–20	0.9993	3.24	150	500	0.5–5
1,2,3-trichlorobenzene	0.9993	1.95	0.15	0.5	0.5–20	0.9987	2.58	70	200	0.2–5
1,2,4-trichlorobenzene	0.9990	2.97	0.15	0.5	0.5–20	0.9990	3.59	70	200	0.2–5
1,3,5-trichlorobenzene	0.9995	3.05	0.15	0.5	0.5–20	0.9969	2.40	70	200	0.2–5
1,2,3,4-tetrachlorobenzene	0.9998	4.17	0.25	0.8	0.8–20	0.9948	4.61	25	100	0.1–5
1,2,4,5-tetrachlorobenzene	0.9992	2.31	0.25	0.8	0.8–20	0.9974	1.04	25	100	0.1–5
Pentachlorobenzene	0.9992	5.03	0.30	1.0	1.0–20	0.9990	5.63	5	15	0.015–5
α-hexachlorocyclohexane	–	–	–	–	–	0.9994	3.39	2.5	8	0.010–5
β-hexachlorocyclohexane	–	–	–	–	–	0.9994	3.92	2.5	8	0.010–5
γ-hexachlorocyclohexane	–	–	–	–	–	0.9992	2.59	2.5	8	0.010–5
δ-hexachlorocyclohexane	–	–	–	–	–	0.9992	2.86	2.5	8	0.010–5

Table 2 Recoveries obtained in the microextraction by demixture procedure.

Compound	*Recovery (%)*
1-chlorobenzene	83.0
1,2-dichlorobenzene	95.9
1,3-dichlorobenzene	90.0
1,4-dichlorobenzene	88.7
1,2,3-trichlorobenzene	97.0
1,2,4-trichlorobenzene	88.8
1,3,5-trichlorobenzene	85.6
1,2,3,4-tetrachlorobenzene	85.4
1,2,4,5-tetrachlorobenzene	79.3
Pentachlorobenzene	77.4
α-hexachlorocyclohexane	92.6
β-hexachlorocyclohexane	91.8
γ-hexachlorocyclohexane	94.0
δ-hexachlorocyclohexane	97.0

following the three mentioned procedures. This natural water was taken in a pool of lixiviates placed near to an industrial dump. In a preliminary analysis, it was observed that the concentration of CBs was very low (near to the detection limit in some cases or total absence in other ones), whereas the HCHs were between 30 and 60 $ng.L^{-1}$. So that, samples were spiked (in the same way as before) in order to obtain concentrations of aprox. 10 $\mu g.L^{-1}$ (CBs) and 100 $ng.L^{-1}$ (HCHs) allowing in this way the comparison among the three methods with all the compounds. Analysis were carried out by ECD and BP-5 column only to separate all the pesticides. It was noticeable the presence of other organochlorine pesticides (Aldrin, HCB and halomethanes, always in concentrations lower than the ones regulated by law) confirmed by GC-MS.

Six replicates were taken in each case so that a statistical comparison could be achieved. Tables 3 and 4 show the results obtained and also the t-test and F-test values for all the three procedures taken in pairs. It can be marked out that only in the case of 1,2,4,5-tetrachlorobenzene (TCB) and δ-HCH the microextraction by demixture is not comparable to the liquid-liquid. On the other hand, neither the results obtained of 1,2,3,4-TCB nor 1,2,4,5-TCB with sep-pak are comparable to the microextraction by demixture.

The literature mentions different concentration values found in natural waters of rivers, rain or tap water from urban supply[24-26]. Such values range from ≈5 to ≈500 $ng.L^{-1}$, which are at the same concentration level than those mentioned in this paper. Consequently, the microextraction by demixture behaves as a powerful extraction procedure for the direct analysis of organochlorine compounds with minimum sample handling and cost of analysis. As no concentration step is required after the extraction, the procedure is faster than the others above mentioned.

Table 5 contains the main characteristics of both three mentioned procedures.

Table 3 F-test values obtained from a study of six samples analyzed by three different methods. Theoretical value of F = 4.28, confidence level = 95%. (*) = values not according to the test. (L-L) = Liquid-liquid extraction. (PAK) = Solid-phase preconcentration with Sep-pak cartridges C-18, (MICRO) = microextraction by demixture with iso-propanol.

Compound	*L-L/Pak*	*L-L/Micro*	*Pak/Micro*
1-chlorobenzene	–	–	–
1,2-dichlorobenzene	1.12	2.86	2.55
1,3-dichlorobenzene	3.98	2.14	1.87
1,4-dichlorobenzene	5.24 (*)	4.14	1.15
1,2,3-trichlorobenzene	6.06 (*)	4.06	1.39
1,2,4-trichlorobenzene	1.58	1.66	2.62
1,3,5-trichlorobenzene	1.83	2.06	1.13
1,2,3,4-tetrachlorobenzene	3.56	1.43	5.11 (*)
1,2,4,5-tetrachlorobenzene	1.19	5.87 (*)	4.93 (*)
Pentachlorobenzene	1.08	1.38	1.49
α-hexachlorocyclohexane	5.83 (*)	2.61	2.24
β-hexachlorocyclohexane	3.67	1.19	4.15
γ-hexachlorocyclohexane	2.40	1.40	1.71
δ-hexachlorocyclohexane	18.83 (*)	8.52 (*)	2.19

Table 4 t-Test values obtained from a comparison between liquid-liquid extraction vs. microextraction and Sep-pak versus microextraction. Number of samples: 6 by each method. Theoretical value of t (11 freedom degrees) = 3.13, confidence level = 99%. L-L EXT = liquid-liquid extraction, SEP PAK = solid-phase preconcentration with Sep-pak cartridges C-18. (*) = values not according to the test. (**) Concentration given in $\mu g.L^{-1}$ (CBs) or $ng.L^{-1}$ (HCHs).

Compound	*L-L EXT. Conc. found (**)*	*L-L EXT t-Test value*	*SEP-PAK Conc. found (**)*	*SEP-PAK t-Test value*
1-chlorobenzene	–	–	–	–
1,2-dichlorobenzene	10.0	0.38	9.5	2.96
1,3-dichlorobenzene	9.9	3.03	11.0	1.20
1,4-dichlorobenzene	9.4	0.59	9.5	0.58
1,2,3-trichlorobenzene	10.2	2.75	9.6	1.74
1,2,4-trichlorobenzene	10.4	0.16	10.6	0.84
1,3,5-trichlorobenzene	9.8	5.34 (*)	10.1	2.66
1,2,3,4-tetrachlorobenzene	10.8	2.06	10.4	1.30
1,2,4,5-tetrachlorobenzene	9.7	1.56	10.2	4.45 (*)
Pentachlorobenzene	10.9	1.82	9.8	1.35
α-hexachlorocyclohexane	103.6	0.85	103.4	0.63
β-hexachlorocyclohexane	97.5	0.79	97.9	0.75
γ-hexachlorocyclohexane	101.6	2.02	101.5	1.82
δ-hexachlorocyclohexane	101.9	1.44	102.7	1.25

Table 5 Comparison among the three methods (in the conditions carried-out in this study). (*) Typical values from the bibliography. (**) Values corresponding to pentachlorobenzene.

Method	*Sample Preparation Time*	*Solvent Volume*	*Sample Volume (*)*	*Concentr. Required*	*Detection Limits (**)*	*Precision (RSD, %)*
Microext. by demixing	30 min.	1.2 mL	50 mL.	No	5 $ng.L^{-1}$	2.8
Sep-pak	45 min.	25–50 mL	100 mL-2 L	Yes	200 $ng.L^{-1}$	3.5
L-L extraction	60 min.	40–70 mL.	250–500 mL	Yes	50 ng.L–1	4.1

CONCLUSIONS

Several interesting conclusions can be reached from the study carried out:

1.– The microextraction by demixture is a useful alternative, cheap, easy to use and efficient for the determination of organochlorine compounds in water at ultratrace level. The generation in situ of the extracting organic phase together with the existence of only one step, makes the method very advantageous in all aspects against both the conventional liquid-liquid extraction and the solid-phase extraction.

2.– The concentration factors (the ratio between the concentration in organic phase and the concentration in aqueous phase) obtained, are about 300, which involves a considerable economy of solvents. This is the main reason for the reduction of the estimated price for the microextraction procedure. Besides, due to the absence of any evaporation steps, there are not any losses of the most volatile compounds and neither are the impurities from the solvents used concentrated in the final extract. Consequently, no interferences due to the solvents were observed and no special requirements of purity for solvents are needed.

3.– The time required for the analysis is shorter for the microextraction procedure than for the other ones, although this reduction in time is only important when many water samples have to be analyzed.

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