

Supercritical Fluid Extraction of Water Samples Containing Ultratrace Amounts of Organic Micropollutants

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Received 26 May 1998; accepted 25 June 1999

Abstract: A true solventless off-line supercritical fluid extraction (SFE) method has been developed, which does not use organic solvents for trapping and for washing out of analytes. Determination of polynuclear aromatic hydrocarbons, chlorinated pesticides, and polychlorinated biphenyls in aqueous solutions based on their direct SFE extraction and on off-line solventless SFE/gas chromatography coupling has been done. This new method has a detection limit at the parts per billion/parts per trillion level. For the ultralow concentration level of 0.1–1 ppt, direct SFE from water was more accurate, faster, and more reproducible than conventional sample preparation methods based on micro-liquid/liquid extraction and solid-phase extraction. © 1999 John Wiley & Sons, Inc. *J Micro Sep* 11: 729–736, 1999

Key words: *water analysis; trace organics; supercritical fluid extraction; liquid-liquid micro-extraction*

INTRODUCTION

Most dangerous environment pollutants [polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins, polychlorinated dibenzofurans, chlorinated pesticides (CPs), polynuclear aromatic hydrocarbons (PAHs), etc.] have to be determined in water. Therefore, sample preparation methods are widely used. These methods, based mainly [according to Environmental Protection Agency (EPA) procedures] on liquid/liquid extraction (LLE), usually include multistep procedures and are very time consuming. Another method based on solid-phase extraction (SPE) of targeted compounds from water also uses different approaches for elution of targeted compounds from sorbent [organic solvent, supercritical fluid extraction (SFE)]. The main disadvantages of these approaches are use of organic solvents during isolation of impurities and collection of extract and use of only 0.001–0.01 part of the final extract for determination of analyte after the preconcentration stage. These drawbacks cause dilution of the analytes, contamination of analytes with impurities present in organic solvents, loss of analytes during the evaporation stage or trapping period, the need to use a large water sample, increased analysis time, etc. [1]. Use of the modern variants of the methods mentioned above—solid-phase mi-

croextraction and micro-LLE—eliminates some of these drawbacks but only partially.

An alternative approach to the commonly used methods of water sample preparation is direct off-line SFE from aqueous solutions.

The region of supercritical or near-critical fluid is very interesting as an extraction medium, especially in ultratrace analysis. The density and solvent power of supercritical fluids are close to the respective values for liquids. The viscosity of supercritical fluids is close to the viscosity of gases, and diffusion coefficients are between gas and liquid values. Thus, we can note some possible advantages of supercritical fluids as an extraction medium for ultratrace analysis:

- minimization or complete exclusion of organic solvent use;
- the possibility of selective extraction due to minor changes of pressure and temperature in extraction system;
- a much higher degree of extractant purity than with organic solvents because carbon dioxide and nitrous oxide (commonly used fluids) are gases at ambient conditions;
- simplicity of concentrating and removing extractant from extract; and

- the possibility of analysis of the whole extract, not only a small part of it.

There are some publications reporting direct SFE of a limited number of organic compounds. The concentrations of analytes in the water sample were not lower than the parts per billion level and extraction time was up to 2h. In addition, organic solvent is used in most cases for collection of the targeted compounds from the flow of supercritical fluid at the outlet of SFE cell when off-line SFE was carried out [2,3].

In this case the SFE extract is contaminated with organic solvent impurities. Therefore, these works only demonstrate the possibility of direct SFE from aqueous solutions and do not represent the true features of direct SFE sample preparation for ultratrace organic analysis.

There are opinions also that direct SFE has several limitations. First, although the solubility of H₂O in CO₂ is quite low, any H₂O that is transported from the extraction cell may contribute to restrictor plugging. This H₂O also causes problems in the analyte collection step as it collects in the trap also. Second, when trace levels of pollutants are present, the extraction of a large sample volume (such as 1 L) may be necessary to concentrate the analyte sufficiently to exceed the detection limit imposed by the analysis method [4].

In our opinion these limitations concern only the analyte trapping technique and may be eliminated. The trapping of small quantities of organic compounds from the flow of supercritical fluid is the key point of the general SFE method in its off-line use. There are some approaches to solving this problem. The most widely used approach is based on trapping extracted analytes into a small quantity (≥ 1 mL) of organic solvent [5–9]. The disadvantages of this approach are dilution of the analytes, contamination of analytes with impurities present in organic solvent, and loss of analytes during the trapping period. The degree of recovery depends largely on the volatility of analytes, and it is higher for compounds with low volatility.

Another approach is based on the sorption of analytes on solid sorbents or in empty glass vials and subsequent washing out with the help of organic solvent [5–11]. The main drawbacks of this approach are the contamination of the extract solution with impurities present in the organic solvent and higher loss of analytes with use of empty vials.

The third approach includes use of short capillary columns with bonded stationary phases for trapping of analytes and washing out with the help of a small quantity (0.1 mL) of organic solvent [12]. This

method seems to be superior to other SFE off-line methods of sample preparation. However, the main limitation of the latter method as with the former ones also is that only a small amount (1–2 μ L) of the final organic solution of analytes is injected onto the gas chromatographic (GC) column. Therefore, a decrease in the sensitivity of analysis and discrimination of the composition of the analyte mixture is seen. The drawbacks mentioned above are most critical when ultratrace amounts of organic compounds need to be determined.

In this article, the aim of our research was the development of a SFE trapping technique that will allow analyte collection from supercritical fluid flow without use of organic solvents and transfer of the total quantity of all analytes present in the sample onto the GC column. Such a technique is very important for the general SFE method and for direct SFE from aqueous solutions. The aim was also to compare the water analysis technique based on direct SFE we developed with some other water sample preparation methods.

EXPERIMENTAL

Compounds investigated. We used mixtures of the following compounds: *n*-alkanes C8–C24 (Polyscience Corp., Niles, IL, USA) PAHs [acenaphthylene, acenaphthene, fluorene, fenanthrene, anthracene, fluoranthene, pyrene, benzo(α)anthracene, and chrysene (Absolute Standards, Hamden, CT, USA)]; CPs [α -HCCH, β -HCCH, δ -HCCH, heptachlor, aldrin, heptachlorepoide, α -endosulfan, dieldrin, 4,4'-DDE, endrin, β -endosulfan, 4,4'-DDD, endrin aldehyde, endosulfan sulfate, 4,4'-DDT (Absolute Standards)]; and PCBs [2,3,4,4',6-pentachlorobiphenyl (115), 2,2',3,4,6-pentachlorobiphenyl (88), 2,2',3,4,4',5-hexachlorobiphenyl (137), 2,2',3,3',4,4',5,5'-octachlorobiphenyl (194), 2,2',3,3',5,5',6,6'-octachlorobiphenyl (202), and Aroclor-1260 (Absolute Standards)], which have to be determined in accordance with different EPA methods, as model compounds.

Direct SFE. The SFE 30 extraction unit (CE Instruments, Milan, Italy) with a homemade SFE extraction cell (inner volume 15 mL) described earlier [13] was used. Figure 1 illustrates the SFE instrumentation for water sampling. Supercritical CO₂ and N₂O were used as extraction media. An activated carbon trap was used for additional purification of CO₂. The water sample volume in all cases was about 10 mL. The extraction cell was spiked with a mixture of analytes and then dynamic SFE was carried out. The extraction was performed at different pressures (from 8.0 to 25.0 MPa) using a heated metallic restrictor (5 cm long). The flow rate

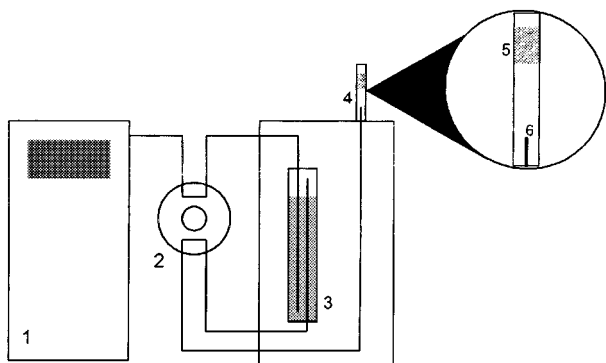


Figure 1. Schematic-diagram of the SFE instrumentation for water sampling (1, pump; 2, switching valve; 3, extraction cell; 4, trapping cartridge; 5, silanized quartz wool; 6, restrictor outlet).

in this case was 0.7–2.6 mL/min (for liquid measured in the pump). The outlet of the restrictor was heated (100–150°C).

Trapping technique. Solventless analyte trapping after SFE was performed by means of extracted analyte collection on special adsorption cartridge. The adsorption cartridge was a glass GC injector liner filled with 10 mg of silanized quartz wool (Alltech Associates, Inc., Deerfield, IL, USA) and placed after the restrictor (Figure 1). During collection of the analytes the cartridge was cooled owing to rapid evaporation of supercritical fluid at the restrictor outlet.

Micro-LLE. Our research was performed using a special vessel for micro-LLE (J & W Scientific, Folsom, CA, USA). The water sample volume was 10 mL. Compounds to be investigated were spiked into an extraction vessel and extraction with 0.3 mL of hexane was performed during 2 min. The extract was separated and the whole extract volume was injected into the gas chromatograph.

SPE. Standard equipment for solid-phase extraction (J. T. Baker Company, Criesheim, Germany) was used. Model compounds were extracted using C18 and Purasep 200 cartridges and C18 extraction disks. Sorbent conditioning was performed: 5 mL of methylene chloride/ethyl acetate (1:1) (for Purasep 200 5 mL of acetone) and 5 mL of methanol were used for this purpose. Model compounds were spiked to a water sample (10 mL), and then the latter was adjusted to pH 2 with 6 N HCl. The extraction was performed with a water sample flow rate of 1 mL/min for cartridges and 3–5 mL/min for the disks. The elution of analytes was performed with 5 mL of ethyl acetate and 5 mL of methylene chloride. Eluates were combined and concentrated

under N_2 to 0.5 mL. Then the whole extract volume was injected into the gas chromatograph.

GC extract analysis. The extract analysis was carried out using a capillary gas chromatograph model 4160 with a split/splitless injector, an on-column injector, and flame-ionization and electron capture detectors (CE Instruments). Make-up gas (nitrogen) for electron capture detection (ECD) was purified using an oxygen purifier (Supelco, Bellefonte, PA, USA). Micro-LLE and SPE analyses of whole organic extract were performed using a large volume injection system as shown in Figure 2 (on-column injector). It included a “gas curtain” for prevention of penetration of solvent vapors into the separating column and detector. During long sample injection times carrier gas was moved from the injector (2) and gas regulator (7), so that gas flow was not via the separation column (“gas curtain”). The gas flow rate at the outlet of the split valve (6) was 100 mL/min. Injection speed was 5 μ L/s. After injection, the gas regulator (7) was shut off and separation of extracted compounds was performed using a 25-m \times 0.32-mm fused silica capillary column with SE-54 and 0.15- μ film thickness (Mega, Legnano, MI, USA).

With direct SFE thermodesorption (splitless injector at 250°C) and cryofocusing (at –20°C) were used for injection of interesting compounds trapped on the cartridge onto the GC column. The cryofocusing was performed on the retention gap, SE-52 1 m \times 0.32 mm \times 5 μ m (Mega), using the homemade cooler based on the Peltier effect. The cartridge (injector liner, 70 mm \times 4 mm) was put into the GC injector. Acquiring and acquisition of chro-

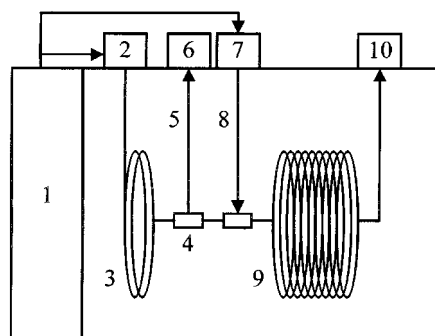


Figure 2. Schematic diagram of the gas chromatographic system used for direct-SFE, SPE, and micro-LLE extract analysis. 1, gas controller; 2, injector (on-column for SPE and micro-LLE extracts and splitless for SFE extracts); 3, retention gap; 4, T-press-fit; 5, solvent split; 6, split valve; 7, carrier gas flow regulator; 8, “gas curtain”; 9, separation column; 10, ECD (fluid ionization detector).

matographic data were performed using the Chrom-Card Data System (CE Instruments).

RESULTS AND DISCUSSION

The effect of the flow rate of gaseous CO_2 and N_2O at the outlet of the SFE system on the efficiency of model compound trapping using a cartridge has been investigated. The extraction cell filled with silica wool was spiked with model mixtures of *n*-alkanes (2×10^{-9} g), PAHs (2×10^{-9} g), chlorinated pesticides (2×10^{-11} g), and PCBs (4×10^{-12} g) and then dynamic SFE (pressure, 25 MPa; temperature, 50°C; time, 10 min; restrictor temperature, 120°C) was performed. The flow rate of gaseous CO_2 at the end of the restrictor was measured (5–1500 mL/min). It was shown that for flow rates higher than 400 mL/min (gaseous CO_2 or N_2O at the restrictor outlet) a collection efficiency higher than 70% could be achieved (Table I). In this case the cooling effect of the rapidly expanding supercritical fluid during evaporation on trapping of the analytes without use of the sorbents or solvents for analyte collection was used. The range of small supercritical fluid flow rates (2–30 mL/min for gas or ca. 0.1 mL/min for liquid) was not useful because in this case the SFE stage is too long and there is the problem of plugging of the restrictor. These problems were very important especially when direct SFE from water was performed. Use of high fluid flow rates (up to 2.5 mL/min for liquid) has solved these problems. It was shown also that there were no loss of the analytes from the cartridge during about 10 min, when gas flow rate was less than 1200 mL/min. The influence of restrictor temperature (50–200°C) and extraction cell pressure and temperature on collection efficiency of the analytes was also investigated. Heating of the restrictor prevents its plugging but at temperatures higher than 150°C, a decrease in collection efficiency was observed. Changes in the extraction cell pressure and temperature in the range of 8.0 to 25.0 MPa and 40 to 100°C, respectively, did not affect collection efficiency when the flow rate of gaseous CO_2 or N_2O at the outlet of the SFE system was higher than 400 mL/min. Then direct SFE of the model compound mixtures from aqueous solutions was performed using the trapping system described. An extraction cell with 10 mL of water was spiked with 5 μL of acetone solution of hydrocarbon (2×10^{-9} g per component in extraction cell), chlorinated pesticide (2×10^{-11} g per component in extraction cell), and PCB (4×10^{-12} g per component in extraction cell) mixtures and dynamic direct SFE (supercritical fluid flow, 2 mL/min for liquid; pressure, 25 MPa; temperature, 70°C; time, 2–5 min; restrictor tempera-

ture, 120°C) was performed. Owing to the high supercritical fluid flow rate and heating of the restrictor, the extraction time was very short (about 2–5 min) and plugging of the restrictor was not observed.

The results obtained for solventless off-line SFE/GC analysis of mixtures of different hydrocarbons, CPs and PCBs are shown in Table I. The recovery from silica wool in this case includes only values for the collection efficiency using the trapping system, but for direct SFE from water the values presented in the table include collection efficiency for the trapping system and recovery from water. On the basis of data shown in the Table I it is possible to conclude that the trapping system present permits trapping of the model compounds with about 70–80% efficiency (even for volatile hydrocarbons and for trace amounts of analytes up to the 10^{-12} g level). As shown in the Table I the values for recovery with direct SFE from water and with SFE from inert matrixes were very close. This means that recovery (without taking into consideration the collection efficiency) for direct extraction from water is higher than 90% and that the small amount of water present in the extract in this case does not influence the efficiency of the trapping system. The same results for trapping efficiency were obtained for all PAHs, CPs, and PCBs investigated using both CO_2 and N_2O .

The regularities of direct SFE from aqueous solutions of CPs, PCBs, and PAHs have been investigated using the method developed for solventless off-line direct SFE/GC coupling. Our research included investigation of the influence of extraction conditions (pressure, temperature, analytes and supercritical fluid type, kinetics of direct SFE, etc.) on the analyte recovery. Concentrations of targeted compounds in water were in the range of 0.1–1 ppb for hydrocarbons, 1–100 ppt for CPs, and 0.1–10 ppt for PCBs. The sample of water solution was 10 mL. Thermodesorption efficiency was about 90% and trapping efficiency about 70–80%, depending on the compound. SFE recoveries of toxicants from water samples were higher than 90%. On the basis of the results a method to determine PAHs, CPs, and PCBs in water based on off-line direct SFE/GC was developed. The optimum extraction conditions were the following: pressure, 25.0 MPa; temperature, 90°C; extraction time, 5 min; supercritical fluid flow rate, 2 mL/min for liquid; restrictor temperature, 120°C. Injection time (thermodesorption) was 2 min, thermodesorption temperature was (250°C), and cryofocusing temperature was (–20°C). The chromatograms of model mixtures after direct SFE from aqueous solutions are presented in Figure 3. The

Table I. Collection efficiency from supercritical fluid flow.

Component	Recovery (%)			
	Extraction from silica wool		Direct extraction from water	
	CO ₂	N ₂ O	CO ₂	N ₂ O
<i>N</i> -alkanes				
Octane	83 ± 5	84 ± 7	75 ± 7	73 ± 7
Nonane	85 ± 4	87 ± 6	73 ± 5	78 ± 8
Decane	88 ± 6	82 ± 7	75 ± 6	77 ± 6
Undecane	86 ± 6	80 ± 5	74 ± 7	72 ± 9
Dodecane	82 ± 7	85 ± 8	80 ± 8	84 ± 8
Tetradecane	80 ± 5	83 ± 6	70 ± 7	75 ± 7
Hexadecane	84 ± 6	84 ± 8	72 ± 8	76 ± 6
Octadecane	81 ± 5	85 ± 6	76 ± 5	72 ± 8
Eicosane	78 ± 7	79 ± 5	77 ± 8	76 ± 9
Docosane	88 ± 6	80 ± 6	76 ± 6	69 ± 8
Tetracosane	80 ± 7	81 ± 8	72 ± 5	79 ± 8
PAH				
Acenaphthylene	80 ± 9	82 ± 11	86 ± 11	84 ± 8
Acenaphthene	82 ± 6	86 ± 7	82 ± 7	85 ± 9
Fluorene	86 ± 8	79 ± 6	84 ± 8	81 ± 7
Fenanthrene	86 ± 6	77 ± 8	73 ± 9	72 ± 8
Anthracene	85 ± 7	83 ± 11	78 ± 10	79 ± 9
Fluoranthene	78 ± 8	76 ± 6	67 ± 8	77 ± 8
Pyrene	84 ± 6	81 ± 6	68 ± 6	72 ± 7
Benzo(α)anthracene	81 ± 9	86 ± 8	65 ± 9	75 ± 10
Chrysene	78 ± 7	75 ± 9	60 ± 10	70 ± 9
CP				
α -HCCH	83 ± 11	85 ± 9	80 ± 9	83 ± 10
β -HCCH	86 ± 8	84 ± 7	74 ± 7	76 ± 9
δ -HCCH	81 ± 9	79 ± 9	68 ± 8	68 ± 9
Heptachlor	83 ± 9	87 ± 10	71 ± 7	81 ± 7
Aldrin	82 ± 12	83 ± 10	73 ± 12	72 ± 11
Heptachlorepoxyde	75 ± 9	86 ± 9	65 ± 9	67 ± 10
α -Endosulfan	84 ± 10	81 ± 9	64 ± 9	69 ± 9
Dieldrin	81 ± 9	76 ± 8	61 ± 10	68 ± 9
4,4'-DDE	78 ± 7	85 ± 9	70 ± 9	74 ± 9
Endrin	88 ± 6	82 ± 7	62 ± 8	67 ± 7
β -Endosulfan	86 ± 7	81 ± 8	64 ± 9	61 ± 9
4,4'-DDD	79 ± 9	84 ± 7	72 ± 12	76 ± 10
Endrin aldehyde	77 ± 8	83 ± 10	66 ± 9	76 ± 11
Endosulfan sulfate	83 ± 11	80 ± 7	59 ± 13	69 ± 10
4,4-DDT	76 ± 9	77 ± 9	63 ± 9	73 ± 9
PCB				
115	73 ± 14	75 ± 15	75 ± 13	71 ± 13
88	78 ± 12	84 ± 11	84 ± 15	74 ± 15
137	82 ± 9	79 ± 9	78 ± 14	78 ± 14
194	76 ± 10	83 ± 10	67 ± 12	67 ± 12
202	77 ± 11	84 ± 9	65 ± 10	69 ± 12

characteristics of these methods are presented in Table II. The advantage of the proposed methods is that the quantitative determination of targeted compounds has to be more reliable and sensitive due to high efficient transfer of the extracted compounds from water onto the capillary GC column, eliminating contamination from impurities present in or-

ganic solvents. The transfer efficiency in the proposed off-line SFE/GC methods has to be close to the efficiency of on-line SFE/GC method.

Comparison of micro-LLE, SPE, and direct SFE from water for ultratrace amounts of PCBs (10^{-12} – 10^{-9} g) was performed. The influence of quantity of analyte in the water sample on recovery by the

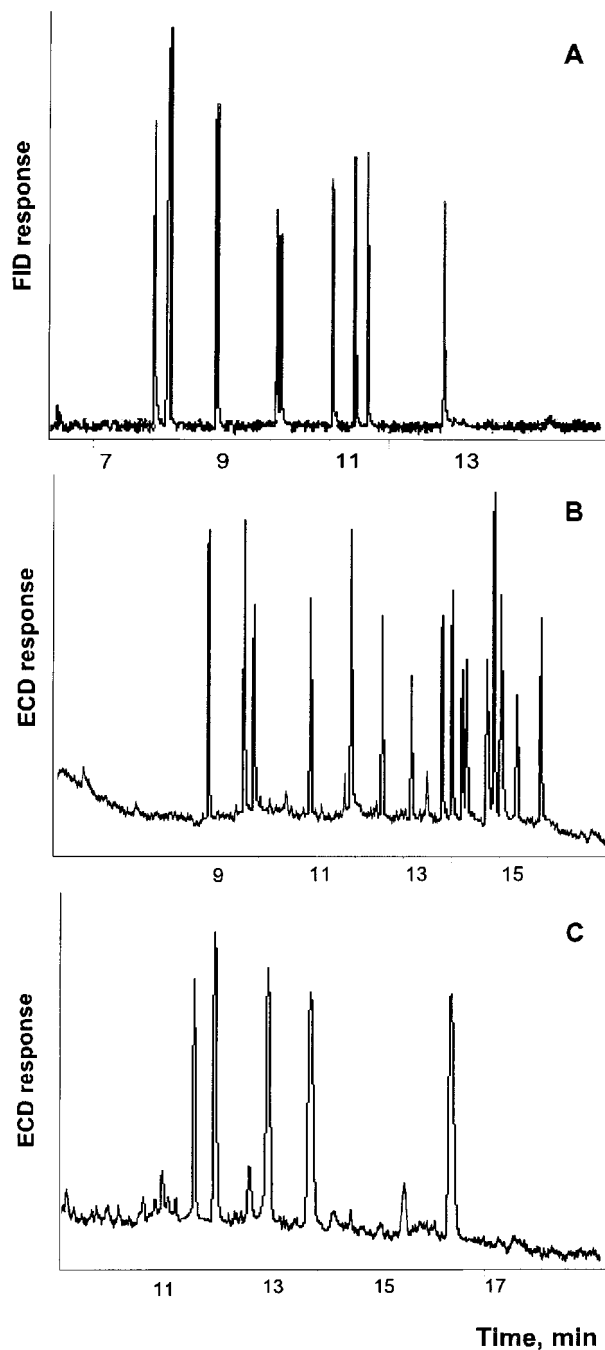


Figure 3. Chromatograms of SFE extracts obtained from 10mL aqueous solutions of PAHs (A), CPs (B), and PCBs (C). Extraction conditions: pressure, 25.0 MPa; temperature, 90°C; extraction time, 5 min; dynamic extraction mode; supercritical fluid flow rate, 2 mL/min for liquid (N_2O); restrictor temperature, 120°C; solventless trapping on injector liner; thermodesorption (250°C) and cryofocusing ($-20^\circ C$), 2 min; amount of analytes, PAHs 3×10^{-9} g per component, CPs 3×10^{-11} g per component, PCB 4×10^{-12} g per component. Chromatographic conditions: (A) isotherm 50°C hold 5 min, heating to 170°C with rate 30°C/min, heating to 270°C with rate 8°C/min, hold 10 min; (B) isotherm 50°C hold 2 min, heating to 270°C with rate 20°C/min, hold 10 min; (C) isotherm 50°C hold 2 min, heating to 270°C with rate 15°C/min, hold 10 min.

Table II. Characteristics of the organic pollutant determination method in aqueous solutions, based on solventless off-line direct-SFE / GC coupling.

Organic compounds	Water sample volume (mL)	Direct SFE recovery (%)	Analysis time (SFE and GC) (min)	Detection limit (signal to noise ratio 10:1) (ppt)
PAHs	10	60–86	18	10
CPs	10	59–83	21	1.0
PCBs	10	65–84	24	0.1

respective methods was investigated. The results are presented in Table III. As it is seen from the Table III the direct SFE recovery is not influenced by quantity of analytes but SPE is not suitable when the quantity of analytes in the sample is less than 0.1 ng. It was shown also (Table III) that only micro-LLE could be compared with direct SFE at an ultratrace concentration level, but in this case the reproducibility was less than with SFE. The poor results for SPE, especially for ultratrace levels, can be explained by incomplete elution of small quantities of analyte

from the sorbents used in SPE. It was shown (Table IV) that for the ultralow concentration level of 0.1–1 ppt (10^{-12} – 10^{-11} g of analyte in the water sample, respectively) direct SFE from water was more accurate and reproducible than micro-LLE and SPE.

CONCLUSION

A true solventless off-line SFE method was developed, which does not use organic solvents for trapping and for washing out of analytes. The trapping system used in this method allowed high collec-

Table III. Comparison of the efficiency of micro-LLE, SPE, and direct SFE from water depending on quantity of analytes.^a

Quantity of PCB in the sample (g)	Concentration (%)	Recovery (%) ^b				
		Direct SFE	Micro-LLE	SPE ^c		
				C18 (cartridge)	Purasep 200 (cartridge)	C18 (disk)
10^{-9}	10^{-8}	97 ± 9	92 ± 7	92 ± 7	87 ± 8	89 ± 6
10^{-10}	10^{-9}	91 ± 8	90 ± 6	30 ± 8	9 ± 4	7 ± 3
10^{-11}	10^{-10}	94 ± 8	93 ± 11	5 ± 2	—	—
10^{-12}	10^{-11}	88 ± 11	60 ± 30	—	—	—

^aWater sample, 10 mL; Sample, mixture of 5 PCBs (115, 88, 137, 194, 202); whole extract analysis by GC (ECD); concentration, 0.1–100 p.p.t.

^bRecovery includes sorption and elution degree.

^c— indicates that there were no model compounds registered on the detection limit.

Table IV. Comparison of micro-LLE, SPE, and direct SFE from water (accuracy and reproducibility).^a

Quantity of PCB spiked in the water sample ($\times 10^{-11}$ g)	Quantity of PCB determined in the water sample ($\times 10^{-11}$ g)				
	Direct SFE	Micro-LLE	SPE ^b		
			C18 (cartridge)	Purasep 200 (cartridge)	C18 (disk)
100	96 ± 9	92 ± 7	95 ± 7	87 ± 8	93 ± 7
10	9 ± 1	8 ± 1	2.0 ± 0.2	1.0 ± 0.3	1.0 ± 0.2
1	0.9 ± 0.1	1.1 ± 0.2	0.08 ± 0.03	—	—
0.1	0.11 ± 0.02	0.07 ± 0.03	—	—	—

^aWater sample, 10 mL; sample, mixture of 5 PCBs (115, 88, 137, 194, 202); whole extract analysis by GC (ECD); concentration, 0.1–100 p.p.t.

^b— indicates that there were no model compounds registered on the detection limit.

tion efficiency for compounds with different volatilities, e.g., supercritical extraction from solid (and dry) matrixes and direct SFE from water.

Methods for determination of polynuclear aromatic hydrocarbons, chlorinated pesticides, and polychlorinated biphenyls in aqueous solutions based on their direct SFE and on off-line solventless SFE/GC coupling have been developed. High SFE recovery of targeted compounds from water and high efficiency of their solventless transfer onto a GC column have been achieved. Detection limits to the 0.1–10 p.p.t. level have been achieved with the methods developed.

It is shown that direct SFE of investigated compounds from aqueous solutions is more preferable. In this case no organic solvent is used and whole extract volume analysis is provided. For an ultralow concentration level of 0.1–10 p.p.t. direct SFE from water was more accurate, faster and more reproducible than conventional sample preparation methods based on LLE and SPE.

In addition, because of the short analysis time, the proposed method of ultratrace organic pollutant determination in aqueous matrixes may be used for fast screening of water samples when measurement of pollutant content is needed quickly.

ACKNOWLEDGMENTS

We are very grateful to Neolab and J. T. Baker Companies supplying analytical equipment to our analytical chemistry chair.

REFERENCES

1. Revelsky, I. A.; Golovko, I. V.; Yashin, Yu. S.; Efimov, I. P.; Zirko, B. I.; Glazkov, I. N.; Revelsky, A. I.; Vulikh, P. P.; Zolotov, Yu. A., *Anal Methods Instrum* 1995, 2, 163.
2. Barnabas, I. J.; Dean, J. R.; Hitchen, S. M.; Owen, S. P. *J Chromatogr A* 1994, 665, 307.
3. Kane, M.; Dean, J. R.; Hitchen, S. M.; Dowel, C. J.; Tranter, R. L. *Analyst* 1995, 120, 355.
4. Reighard, T. S.; Olesik, S. V. *Crit Rev Anal Chem* 1996, 26, 1.
5. Barnabas, I. J.; Dean, J. R. *Analyst* 1994, 119, 2381.
6. Chester, L.; Pinkston, J. D.; Raynie, D. E. *Anal Chem* 1996, 68, 487R.
7. Hüsters, N.; Kleiböhmer, W. *J Chromatogr A* 1995, 697, 107.
8. Wenklawiak, B. W.; Heemken, O. P.; Sterzenbach, D.; Schipke, J.; Theobald, N.; Weigelt, V. *Anal Chem* 1995, 67, 4577.
9. Mulcahey, L. J.; Taylor, L. T. *Anal Chem* 1992, 64, 2352.
10. Miller, D. J.; Hawthorne, S. B.; McNally, M. P. *Anal Chem* 1993, 65, 1038.
11. Levy, J. M.; Ravey, R. M.; Houk, R. K.; Ashraf-Khorassani, M. *Fresenius J Anal Chem* 1992, 344, 517.
12. Vejrosta, J.; Ausorgova, A.; Fanta, J.; Janda, V. In P. Sandra, Ed; *Proceedings of the 16th International Symposium on Capillary Chromatography*, Riva del Garda, May 27–30, 1994; Hüthig: Heidelberg.
13. Hedrick, J. L.; Taylor, L. T. *Anal Chem* 1989, 61, 1986.