

Development of pressurized subcritical water extraction combined with stir bar sorptive extraction for the analysis of organochlorine pesticides and chlorobenzenes in soils

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Abstract

An analytical method for the determination of several organochlorine pesticides (OCPs) like hexachlorocyclohexanes (HCHs), cyclodiene derivatives (dieldrin, aldrin, endrin, heptachlor, heptachlor epoxide, endrin aldehyde, endosulfan and endosulfan sulphate) and DDX compounds (*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT) as well as chlorobenzenes in soils has been developed. The procedure is based on pressurized subcritical water extraction (PSWE) followed by stir bar sorptive extraction (SBSE) and subsequent thermodesorption–gas chromatography/mass spectrometry analysis. Significant PSWE and SBSE parameters were optimized using spiked soil and water samples. For the PSWE of the organochlorine compounds, water modified with acetonitrile as the extraction solvent, at an extraction temperature of 120 °C, and three cycles of 10 min extraction proved to be optimal. Under optimized conditions, the figures of merit, such as precision, accuracy and detection limits were evaluated. The detection limits obtained for soil samples were in the range 0.002–4.7 ng/g. Recoveries between 4.1 and 85.2% were achieved from samples spiked at a concentration level of 25–155 ng/g. The main advantages of this method are the avoidance of clean-up and concentration procedures as well as the significant reduction of the required volume of organic solvents. The described method was applied to the determination of the pollutants in soil samples collected from a polluted area, the Bitterfeld region (Germany). The results obtained by PSWE–SBSE were in a good agreement with those obtained by a reference method, a conventional pressurized liquid extraction (PLE).

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1. Introduction

The determination of organochlorine pollutants such as organochlorine pesticides (OCPs) and higher chlorinated benzenes is of a high interest, because of their accounted toxic potential, their persistence and their tendency to bioconcentrate. These compounds are ubiquitous among environmental samples, such as air, water, soil, sediments and biological tissues [1,2].

However, the analytical procedures for their determination, such as Soxhlet extraction [3–6], are usually tedious, time-consuming and require large amounts of solvent.

Therefore, improving extraction techniques for the analysis of organochlorine pollutants in solid matrixes is widely investigated in order to minimize waste solvents and to shorten the analytical procedures and the time. Modern technologies includ-

ing the use of new sources of energy have been described, such as microwave-assisted solvent extraction (MASE) [5,7–10], supercritical fluid extraction (SFE) [11,12], pressurized liquid extraction (PLE) [12–17] and subcritical water extraction (SWE) [18,19]. PLE and MASE require a relatively short extraction time and a small amount of solvent. However, tedious clean-up procedures of the extracts obtained by PLE or MASE are necessary in general because the selectivity of the extraction methods is low. SFE and SWE are selective and basically organic solvent free techniques, but a relatively complex system is required. SFE requires much higher pressures and the yields are highly dependent on the matrix. SWE offers the extraction of analytes in a wide range of polarities by changing the temperature and can easily provide class-selective extraction by temperature programming and/or the addition of modifiers.

For SWE, water in the subcritical state was used as solvent for the extraction of organic pollutants from solid matrixes such as contaminated soils. As the temperature of liquid water is raised under pressure, at temperatures between 100 and 374 °C, the

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polarity decreases markedly and it can be used as an extraction solvent for a wide range of analytes. Most interest has been in its application for the determination of polycyclic aromatic compounds (PAHs), polychlorinated biphenyls (PCBs) and pesticides from environmental samples, where it gives comparable results to Soxhlet extraction. But this technique is more rapid and without the use of significant volumes of organic solvents. The recent analytical interest in subcritical water as an extraction solvent began with the work of Hawthorne et al. [20,21] who were interested in environmentally friendly extraction methods for soils and environmental solids. One disadvantage of the described static SWE procedure was the loss of the solvated organic pollutants by reabsorption onto the original matrix after cooling. To avoid this problem, dynamic systems such as the application of the accelerated solvent extractor (ASE, Dionex 200) using water as solvent have been described. With this system the aqueous phase and the soil are separated under the extraction conditions [22,23].

Another disadvantage of SWE is that the extract is a relatively dilute water solution. In an attempt to minimise the dilution of the analytes in the liquid extract, solvent trapping and sorbent trapping on solid-phase extraction (SPE) disk or cartridge [24,25] or on solid-phase microextraction fibers (SPME) [21,23] have been used as concentration/extraction step. SPME is a solvent free and efficient method for the extraction of organic compounds from aqueous samples and needs neither clean-up nor additional concentration steps. The small size of the extraction medium in SPME leads to an incomplete extraction. As an alternative, the stir bar extraction method (SBSE) has been examined [26].

The SBSE technique, first described by Baltussen et al. in 1999 [27], is an efficient procedure for the enrichment

of organic compounds from aqueous samples using PDMS coating. This technique enables a more effective extraction of volatile and semivolatile organic compounds from aqueous samples because of the relatively large volume of the PDMS phase (20–125 μL) compared to SPME (0.5 μL). In combination with thermodesorption–GC/MS, detection limits down to the low nanograms per liter range can be attained. The SBSE was successfully applied to the determination of pesticides in water samples obtained detection limits in the range 0.1–1 ng/L [28].

The aim of this work was to investigate the ability of pressurized subcritical water extraction (PSWE) and subsequent SBSE for determining several OCPs and chlorobenzenes in soils. They are still frequently detected in soils and sediments throughout the world, even though the use of this class of compounds was banned in many countries years ago. The optimization of the PSWE procedure relating to temperature, pressure, extraction time and number of cycles is described. The effect of adding small quantities of organic solvents to the water on the extraction efficiency was studied.

After the optimization of the extraction parameters, the method was applied to samples of soils collected in the Region of Bitterfeld (Germany) and the results were compared against a conventional PLE method.

2. Experimental

2.1. Reagents

The OCPs mixture standard (100–600 $\mu\text{g/mL}$) (see Table 1) was purchased from Promochem (Wesel, Germany) and the

Table 1
Octanol/water partition coefficients (K_{ow}) and m/z of the analytes

Family	Compounds	Selected ions (m/z)	$\log K_{ow}$
Chlorinated benzenes	1,2,4,5-Tetrachlorobenzene (TCB)	216, 214	4.64
	Pentachlorobenzene (PCB)	250, 252	5.17
	Hexachlorobenzene (HCB)	284, 286	5.73
	α-HCH	219, 181	3.80
	β-HCH	219, 181	3.78
	γ-HCH	181, 219	3.72
	δ-HCH	219, 181	4.14
	Heptachlor	272, 274	6.10
	Aldrin	263, 265	6.50
	Heptachlor epoxide	353, 355	4.98
Organochlorine pesticides	Endosulfan I	195, 241	3.83
	Dieldrin	263, 277	5.40
	<i>p,p'</i> -DDE	246, 318	6.51
	Endrin	263, 265	5.20
	Endosulfan II	195, 241	3.83
	<i>p,p'</i> -DDD	235, 237	6.02
	Endrin aldehyde	345, 250	4.80
	Endosulfan sulfate	272, 274	3.66
	<i>p,p'</i> -DDT	235, 237	6.91
	Hexachlorobenzene $^{13}\text{C}_6$	290	
Isotope labelled compounds	α-HCH $^{13}\text{C}_6$	187	
	<i>p,p'</i> -DDE $^{13}\text{C}_{12}$	258	
	<i>p,p'</i> -DDT $^{13}\text{C}_{12}$	247	

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