

New method for the determination of polychlorinated biphenyls in air samples

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INTRODUCTION

Polyether-type polyurethane foam (PUF) is widely used as a sorbent for collecting organic air pollutants because PUF has the ability to collect and retain a variety of vapor-phase organic compounds [1]. Furthermore it has a low resistance to air flow during sample collection and it is inexpensive and easy to handle.

The first step in environmental analysis involves separating the organic compounds from the sorbent trap. In most cases this process is achieved by using time-consuming liquid solvent extraction with either a Soxhlet apparatus or sonication, which requires expensive high-purity organic solvents and also generates toxic solvent waste. Thermal desorption has also been applied to sorbents, but the use of thermal desorption is ultimately limited by the thermal stability of the analyte species and the sorbent material and the recoveries of polar and high molecular weight compounds can be unsatisfactory.

The supercritical fluid extraction (SFE) is an alternative to the commonly used desorption methods. The replacement of organic solvents with supercritical fluids results in much faster and more convenient extractions [2].

This paper describes the very first results of the present authors' initial investigation into the use of supercritical CO₂ (modified with methanol, acetone or toluene) and N₂O for the extraction and recovery of PCBs from polyurethane foam sorbents. The objectives of this study were to optimize the extraction conditions in terms of extraction

time, efficiency, and reproducibility and minimize interferences from coextracted compounds.

EXPERIMENTAL

Polyether-type polyurethane foams with various pore-sizes were obtained from KURETA (Stadtallendorf, FRG). The foam traps were precleaned by extractions with supercritical CO₂ at 400 atm and 50°C for 60 minutes. The traps were then stored in screw-top test tubes with teflon-lined caps until further use.

For the recovery studies, PUF plugs were spiked by injecting a small volume of a cyclohexane solution containing an appropriate concentration of the test species into the center of the sorbent plug. The solvent was allowed to evaporate overnight. The recovery of PCBs from PUF was investigated with six PCB congeners at two different spike levels.

All supercritical fluid extractions were performed with a Lee Scientific Modell SFE 703-extraction system (DIONEX, Idstein). Supercritical pressures were maintained inside the cell by using wafer flow restrictors (Lee Scientific). This results in a flow rate of 250 ml/min (as gaseous CO₂ measured at the outlet of the sample vial) at an extraction pressure of 350 atm.

For the recovery studies an internal standard (decachlorobiphenyl, PCB 209) was added to the solvent in each collection vial before the extraction was performed. The collection vials were filled with 15 ml hexane. After extraction, the hexane was evaporated to about 500 μ l. A 1 μ l aliquot was injected into the GC/ECD system for quantification. All GC measurements were carried out on a Varian Modell 3700 instrument equipped with a Varian ⁶³Ni electron-capture detector. Separation was achieved on a SE 54 (50 m x 0.32 mm I.D., Df: 0.25 μ m) using nitrogen as carrier gas. Data were acquired using a Dionex AI 450 data system.

RESULTS AND DISCUSSION

The standard PCBs listed in Table 1 were selected to represent the range of PCB compounds. Supercritical fluid extraction with CO₂ or N₂O alone at 60°C and a pressure of 400 atm gave acceptable extraction efficiencies from 84 % to 107 % in less than 30 minutes as shown in Table 1. The reproducibility in extraction efficiencies obtained for each of the six test compounds from four replicate extractions of spiked PUF sorbent plugs was also acceptable, with the relative standard deviations ranging from 5 to 12%. The extraction efficiency of supercritical fluids can be improved by the addition of a polar modifier [3]. Modifiers can increase the solubility of a substance in a supercritical fluid, but more importantly, the polar modifier molecules are in

competition for the polar adsorption sites on the sorbent, such that modifiers can dramatically reduce the adsorption of the analyte species on the surface of the trap.

To achieve good reproducibility and high recovery rates some instrumental parameters have to be optimized. It is very important to thermostat the restrictor, independent of the extraction cell. We used a restrictor temperature of 150°C, which results in a constant flow of the supercritical fluid and prevents the restrictor from plugging. In addition, the sample vial was cooled down to ~ 1°C, in order to lower the viscosity of the collecting solvent. Because of the lower viscosity, gas bubbles from the depressurized fluid were smaller and a faster transfer of the extracted compounds into the solvent was achieved.

BZ-No.	species	recovery [%]	SD [%]
28	2,4,4'-Trichlorobiphenyl	84.5	6.0
52	2,2',5,5'-Tetrachlorobiphenyl	87.6	8.5
101	2,2',4,5,5'-Pentachlorobiphenyl	92.1	12.0
138	2,2',3,4,4',5'-Hexachlorobiphenyl	99.7	5.2
153	2,2',4,4',5,5'-Hexachlorobiphenyl	99.0	6.0
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	107.1	9.3

Table 1: Recovery rates for six selected PCB congeners from PUF.
Extraction fluid N₂O at 350 atm and 45 °C, Extraktion time 30 min.

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