

Polynuclear Aromatic Hydrocarbons in Environmental Materials: Extraction by Supercritical Fluid Extraction

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INTRODUCTION

Supercritical fluid extraction (SFE), usually with carbon dioxide and, often, with a modifier, has become of increasing interest in the last few years because of its selectivity, preconcentration effect, efficiency, simplicity, rapidity, cleanness, and safety, mainly concerning the extraction of organic compounds prior to separation and detection by chromatographic techniques. It has several advantages over classical solvent extractions, in comparison with recent extraction techniques. Approaches to obtain quantitative extractions, including fluid choice, extraction flow rate, modifiers, pressure, and temperature, are presented, as well as the potential for SFE to extract polynuclear aromatic hydrocarbons (PAHs) from soils, sediments, and biota. Improvements and new environmental applications are also reported.

PARAMETERS INFLUENCING THE SUPERCRITICAL FLUID EXTRACTION PROCESS AND APPLICATIONS

Since the first applications of SFE were published by Zosel in 1978, this extraction technique has developed into a key method for the separation of the contaminants from both sediment and biological matrices. Supercritical fluid extraction has a number of advantages over classical solvent extraction methods: It is faster, more selective, and less toxic, particularly when compared with techniques using solvents such as dichloromethane, thus reducing safety hazards. It has received the attention of some researchers who have reviewed and developed this technique and its suitability to the analysis of environmental matrices.^[1–3] The application of SFE to PAHs was reviewed, and new analytical strategies involving the need for modified supercritical fluids to improve extraction efficiency, restrictor prevention from blocking, collection form of the eluant, and general operation conditions, has been demonstrated. This technique is radically different from liquid–solid extraction (LSE), subcritical water extraction, microwave-assisted extraction (MAE), and accelerated solvent extraction (ASE)—also known as pressurized liquid extraction or pressurized fluid

extraction—because the main constituent of the solvent system, CO₂, separates from the extracts upon venting to the atmosphere, leaving the analytes that are trapped either on a solid phase, such as C₁₈, or in an organic solvent. The influence in the extraction process of various parameters will depend on a number of steps controlling the transport of analytes from the matrix to the bulk fluid, e.g., temperature, pressure, solvent type, and extraction time. Interested readers should consult an excellent review regarding the mechanisms controlling the binding, release, and transport in environmental materials.^[4] Supercritical fluid extraction, at low (50°C) and high (200°C) temperatures, and an 18-hr Soxhlet extraction with dichloromethane for railway soil and diesel soot samples were compared for the PAHs extraction.^[5] The samples were mixed with anhydrous Na₂SO₄. The mean recoveries for the 17 PAHs examined in the railway soil was 50% at 50°C, 81% at 200°C, and 90% at 350°C. For the diesel soot, the recovery for 13 PAHs was 51% at 50°C, 71% at 200°C, and 118% at 350°C. Although higher temperatures favored better recoveries for the higher-molecular-weight PAHs, it was also suspected that the two- to three-ring PAHs were actually generated at these elevated temperatures. So a 30-min extraction at 200°C was selected as the optimum. Temperature and organic modifiers—10% MeOH, diethylamine, and/or toluene—using a marine sediment (SRM 1941) diesel soot and air particulate matter (SRM 1649) were also examined. The best recoveries were obtained with CO₂–diethylamine at 200°C with a 15-min-static and 15-min-dynamic extraction time. Also, supercritical water at 250°C, CO₂ at 200°C, and CO₂ with 19% toluene at 80°C were compared for the extraction of PAHs from urban air. Surprisingly, the water was generally as effective as the other solvents under these conditions.^[2] However, unlike CO₂, the water had to be subsequently removed from the extract. After optimization of the SFE-CO₂ extraction method for PAHs, similar results were obtained by using the acetone with MAE, ASE with acetone/dichloromethane, or Soxhlet with dichloromethane.

The use of a binary modifier, which is added to the extraction cell at the time of the extraction, rather than continuously, in the CO₂ stream showed an almost matrix-independent SFE method for the PAHs.^[6] The

