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Note

Supercritical fluid extraction procedure for the removal of trace organic species from solid samples

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In recent years, there has been increasing interest in supercritical fluid extraction of organic chemical substances, including the separation of organic chemicals from water, caffeine from coffee beans, oils from natural products[1] polychlorinated biphenyls from transformer oils[2] and pesticide residues from plant sources[3]. There are several advantages of supercritical extraction over liquid extraction[4]. The solvent power of the supercritical fluid can be varied by controlling the pressure whereas the solvent power of liquids is varied by changing temperature or solvent composition. The extract can be separated from the supercritical fluid by reducing the pressure whereas liquid extraction requires an evaporation step to remove the extracting solvent. Traditional industrial solvents, used in liquid extraction, are under increasing scrutiny due to their toxicity and environmental effects. In addition, liquid extraction typically requires more time and energy costs.

Supercritical fluids have densities that are greater than those of gases but comparable to those of liquids. The viscosities and diffusivities are intermediate to those properties for liquids and gases. Thus, supercritical fluids have the solvent power of liquids with better mass transfer characteristics than typical liquid solvents; therefore, extraction efficiencies using supercritical fluids may be higher than those using liquid solvent extractions[1].

Carbon dioxide which has a critical temperature of 304.20 K, a critical pressure of 7583 kPa (73.86 bar) and a critical density of 0.468 g/ml (ref. 5) has been the supercritical fluid of choice, for several reasons[2]. The critical point is accessible, and it is a good solvent for organics. It is non-toxic and non-flammable, and is readily available at a low cost. In addition, by adding small amounts of polar modifiers, such as methanol, the extracting power of the fluid can be varied[4]. Density appears to be of primary importance in determining the extracting potential of supercritical carbon dioxide, with solvent properties increasing as a function of increasing density[6]. At densities greater than 0.9 g/ml, carbon dioxide is expected to produce an extract similar to the one made with methylene chloride[7].

The majority of supercritical fluid extraction set-ups consist of a source of supercritical fluid joined to an extraction vessel containing the substance(s) to be extracted. Valves and tubing are used to connect the extraction vessel to a separation vessel, into which the dissolved material is condensed out of the supercritical fluid.

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A version of this general set-up is that used by Braun and Schmidt[8] to extract crude montan wax. They used supercritical carbon dioxide and ethylene at pressures of 15 500–51 500 kPa (150–500 bar) and temperatures of 293–373 K. The extract was precipitated by lowering the pressure from 2550 to 6150 kPa (25 to 60 bar) and the temperature 5–10 K below the critical temperature of the solvent. Eisenbach[9] described two methods of separating the dissolved material from the supercritical fluid: an isobaric method, and an isothermal method. In the isobaric method, the supercritical fluid plus dissolved material moves from the extraction vessel to a heat exchanger where the supercritical fluid is heated. The density decreases, and the dissolved material falls out and is collected in the separation vessel. In the isothermal method, the supercritical fluid plus dissolved material is expanded after the extraction vessel. When the pressure drops below the critical pressure, the material falls out into the separation vessel.

Supercritical fluid extraction instrumentation also has been directly coupled to a high-performance liquid chromatograph[10] and to a supercritical fluid chromatograph[11]. In the latter case, an extraction cartridge (50 × 4.6 mm I.D.) packed with ground coffee beans was connected to a trap loop which was part of the supercritical fluid chromatograph or to a secondary trapping column packed with activated carbon. The trap column could be disconnected from this set-up and eluted with methanol–water mixture for other analyses.

In this paper, the supercritical extraction of polychlorinated biphenyls (PCBs) from sediment and polyaromatic hydrocarbons (PAHs) from an urban particulate sample (NBS SRM 1649) is described. A commercial supercritical fluid chromatograph (Hewlett-Packard), designed for use with packed columns is employed for temperature and pressure control, and a gas chromatograph equipped with an electron-capture detector is used for PCB analysis, or a flame ionization detector is used for PAH analysis. The supercritical extraction is compared to Soxhlet extraction for the sediment material, and to certified values for the urban particulate sample.

EXPERIMENTAL*

A 25 cm × 6.35 mm (1/4 in.) O.D. stainless-steel column was packed with approximately 6 g of sediment or 1 g of urban particulate matter held in place by stainless-steel frits. The inlet of the column was connected to the carbon dioxide inlet of the supercritical fluid chromatograph, and the outlet of the column was connected to a 66-cm section of 60 μm I.D. fused-silica capillary. The capillary served to reduce the carbon dioxide pressure to atmospheric pressure. A 5-cm section of 6.35 mm (1/4 in.) O.D. stainless-steel tubing packed with C_{18} packing material (μBondapak C_{18}/Corasil, Waters Assoc.), also held in place by frits, was attached to the end of the capillary. The 25-cm column and the fused-silica capillary were inside an oven maintained at 313 K. The extractor column was left outside the oven at room temperature. Liquid carbon dioxide was pumped through both columns and the capillary

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* Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the products are necessarily the best available for the purpose.

at an inlet pressure of approximately 35 500 kPa (345 bar) and density of 0.93 g/ml, for 4 h. After this, the column containing C_{18} packing material was disconnected, and connected to a high-performance liquid chromatography pump. Methylene chloride (40 ml) was passed through the C_{18} column to extract any compounds deposited from the supercritical carbon dioxide. The methylene chloride extract was then evaporatively concentrated to 500 μl and held for gas chromatographic analysis. The final extracts were analyzed on a 30 m × 0.25 mm I.D. fused-silica column coated with an immobilized methyl silicone (DB-5) phase to a thickness of 0.25 μm. Helium was used as the carrier gas for the PCB analysis, while hydrogen was used for the PAH analysis. Either an electron-capture detector, for the PCB analysis, or a flame ionization detector, for the PAH analysis, was used. The constant-current electron-capture detector was maintained at 320°C and utilized a nitrogen purge gas. The flame ionization detector was maintained at 300°C. Samples were injected through an all-glass injector (splitting mode) maintained at 300°C. Chromatographic data were collected, stored and reduced using a computer–integrator.

RESULTS AND DISCUSSION

For the sediment samples, a second C_{18} column (packed as above) was used in tandem during carbon dioxide extraction to detect any breakthrough of extracted PCBs from the first C_{18} column. Analysis of the second column showed that no breakthrough had occurred. For comparison of extraction efficiency, a 6-g sample of the same sediment material was Soxhlet extracted for 16 h using a methylene chloride solvent. Internal standards were added to the supercritical and Soxhlet extracts to determine the absolute amount of PCBs present in the extract. Two supercritical fluid extractions and two Soxhlet extractions were carried out on aliquots of the sediment. The results are given in Table I. These data suggest that comparable amounts of PCBs were extracted using Soxhlet and supercritical fluid extraction.

TABLE I

CONCENTRATION OF AROCLOR 1254 IN SEDIMENT

Data are given as average values ± S.D.

Extraction No.	*Aroclor 1254 concentration (μg/g)*	
	Soxhlet	*Supercritical fluid*
1	6.61 ± 0.21	6.84 ± 0.18
2	6.71 ± 0.16	6.61 ± 0.19

The concentration of five PAHs in NBS SRM 1649 were determined using supercritical extraction and gas chromatography with flame ionization detection. This sample had been previously certified using analytical methods employing Soxhlet extraction[12]. Two supercritical extractions were carried out on separate samples and a quantitative analysis of PAH content was performed. Prior to gas chromatography, the extracts were fractionated on an aminosilane semi-preparative liquid chromatographic column in order to separate the alkane fraction and the polar fraction from the aromatic fraction. Internal standards were added before extraction so that the amount of PAH in the particulate matrix, not in the extract, would be measured. The results are compared to the certified values in Table II. Other than for indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylone, the certified values and supercritical fluid extraction values are in good agreement. The indeno[1,2,3-*cd*]pyrene supercritical extraction value, however, is 30% higher than the certified value and the benzo[*ghi*]perylene value 18% higher, suggesting that the supercritical extraction is more efficient than Soxhlet extraction in removing large PAH species. This hypothesis will be investigated further.

TABLE II

CONCENTRATION OF SELECTED PAHs IN NBS SRM 1649

Compound	*Concentration (μg/g)*	
	Certified[12,*]	*Supercritical fluid extraction***
Fluoranthene	7.1 ± 0.5	7.2 ± 0.1
Benz[*a*]anthracene	2.6 ± 0.3	2.3 ± 0.2
Benzo[*a*]pyrene	2.9 ± 0.5	3.1 ± 0.1
Benzo[*ghi*]perylene	4.5 ± 1.1	5.3 ± 0.5
Indeno[1,2,3-*cd*]pyrene	3.3 ± 0.5	4.3 ± 0.1

* The estimated uncertainty corresponds to approximately 95% confidence limits.
** Data are given as average value ± S.D.

Additionally, two supercritical extractions were made of a single SRM urban dust sample to check on the completeness of the extraction process. No PAHs appeared to be extracted the second time. The same urban dust was then removed from the extraction column of the supercritical fluid chromatograph and placed in a Soxhlet extractor, where it was extracted for 16 h using methylene chloride. Chromatographic analysis of this concentrated Soxhlet extract showed that no additional PAHs were removed, suggesting that the total extractable PAHs were removed in the first supercritical fluid extraction.

CONCLUSIONS

Both the PCBs and PAHs are extracted from their respective matrices by supercritical fluid extraction. The method of supercritical fluid extraction is an alternative to other classical extraction methods. The supercritical procedure appears to require less time for completion than does the Soxhlet extraction. The possibility exists to extend supercritical extraction to more polar compounds by adding a modifier such as methanol to the carbon dioxide mobile phase.

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