

Extraction under pressure: The sustainable alternative in environmental analysis

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Introduction

Solvent and gas under high pressure at elevated temperatures are becoming more and more important extraction media in environmental analysis. The use of CO₂ at supercritical conditions, with or without modifiers, has increased enormously for both biological and solid samples¹⁻³. Recently also extraction by organic solvents at elevated pressure and temperature has been introduced as accelerated or enhanced solvents extraction. Several organic solvents exhibit much better extraction efficiencies under pressure at higher temperatures.

Which technique to use is dependent on the sample matrix and the compounds to be analysed. An important consideration is how specific the extraction should be. Accelerated or enhanced solvent extractions are in most applications rather unspecific and extract not only the target compounds but also many interfering compounds. Extracts obtained this way often need further sample enrichment or sample clean up. Supercritical fluid extraction has the advantage that it can be very specific by varying the temperature, pressure and the addition of different modifier concentrations. To find the optimum SFE extraction condition for different sample matrices and target compounds demands, however, somewhat more method development. When these optimum conditions are established the advantages of using SFE are obvious and minimal clean up and sample enrichment is needed. So, not only reduction of the use of organic solvents during extraction is achieved, but also extensive use of organic solvent during sample clean up is reduced to a minimum.

Water at sub or supercritical conditions is an even more environmental friendly and attractive solvent than supercritical CO₂^{4,5}. Water at elevated temperature has the unique property that the dielectric (ϵ) constant drops from $\epsilon = 80$ at ambient conditions (20 °C, 1 atm.) to $\epsilon = 27$ at sub critical conditions (250 °C, 50 bar) to $\epsilon = 5-15$ at supercritical conditions (>374°C, >221 bar). Thus water changes from being a very polar solvent to a nearly non-polar solvent. In theory water at sub or supercritical condition should be able to extract for example PCDDs or PCDFs.

Material and Methods

Accelerated solvent extraction were performed with a Dionex ASE 200 accelerated solvent extractor (Dionex Corporation, Sunnyvale, CA) using an experimental design to establish the optimum extraction conditions for PAHs, PCNs, DDT, HxCBz and PCDFs. SFE extractions were done on a HP Hewlett-Packard 7680T SFE extractor (Hewlett-Packard, Wilmington, DE). SFE-LC experiments were performed on a Suprex Autoprep 44 equipped with an Accutrap collection module (Isco Inc., Lincoln, NE). Pressure, temperature and modifier concentration were again varied according to a fractional factorial experimental design to establish the optimum extraction condition for the different sample types and target compounds. In the different studies two MS instruments were used: a VG70S (high resolution) and Fisons Instruments MD800 (low resolution) (both from VG Instruments, Manchester, England). The VG 70S coupled to a HP5890 GC and the MD800 to a Fisons GC 8000 gas chromatograph equipped with a non polar DB-5 column (J&W DB-5, Folsom, CA; 60m x 0.32 mm i.d., 025 um film thickness).

Results and discussion

When analysing biological samples co-extracting fat should be removed before GC/MS analysis. Both destructive (H_2SO_4 /silica columns, KOH) and non-destructive (GPC, SPMD) methods can remove fat but both methods are in general time and resource consuming. When using SFE for biological samples the extraction vessel can be filled partly with absorbent material (Aluminium Oxide). Applied this way aluminium oxide acts as a supercritical chromatographic active phase and retains fat more than for example PCDDs, PCDFs, PBDEs and several pesticides achieving a separation between the fat and the target compounds. Further clean up of the extracts can be achieved on the solid phase trap, which can be used as a LC column⁶. This approach enables to run large number of samples for a variety of compounds and has been used in several epidemiological studies to assess human exposure^{7,8}. In Figure 1 another example of the use of SFE-LC is illustrated, the quantitative analysis of several TeBDEs in Pilot Whale from the Atlantic⁹.

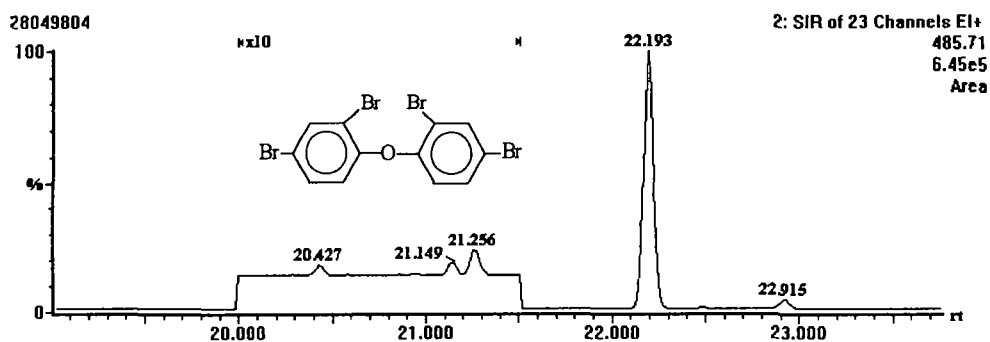


Figure 1. SIR GC/MS chromatogram of Tetra-BDEs in Pilot Whale extracted by SFE-LC

Another approach of using solvents under high pressure is the use of accelerated or enhanced solvent extraction, here an organic solvent under subcritical conditions is used instead of a gas in the supercritical phase. Although the variation in parameters is more limited than using SFE, efficient extractions can be achieved after relatively little method development. Because of the high but unspecific extraction efficiency, most extracts need further clean up. Interferences have to be removed by open column chromatography before GC/MS analysis.

An example of ASE extraction is given in Figure 2, where a reconstructed GC/MS chromatogram of PAHs in soil from a former gasworks facility is presented. The extract has been eluted on a deactivated silica column to remove polar interferences after extraction.

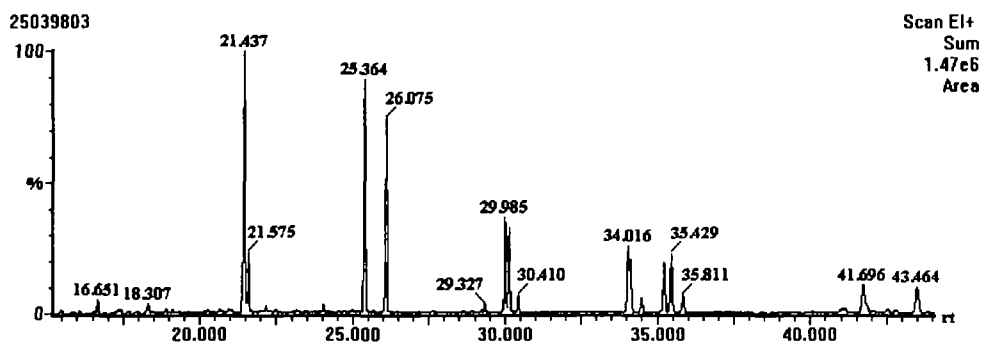


Figure 2. Reconstructed GC/MS chromatogram of PAHs in soil from a former gasworks facility extracted by ASE

Conclusions

Several extraction techniques operating under elevated pressure can be used in environmental analysis for a wide variety of compounds. Application of these techniques has greatly improved the analysis from a scientific, environmental and work condition point of view. The introduction of accelerated or enhanced extraction, still using organic solvents, tends to be more popular because of the simplicity to put this method into practice.

Supercritical fluid extraction, however, shows more potential because of the possibility of very specific extractions. SFE is more complex and method development, preferable with experimental design, will generally take more time

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References

1. Hawthorne, S.B., and Miller, D.J. Extraction and recovery of Organic Pollutants from environmental solids and Tenax-GC using supercritical CO₂. *J. of Chromatographic Science* **1986**, 24 258-264.
2. Hawthorne, S.B., and Miller, D.J. Direct coupled supercritical extraction gas chromatographic analysis of polycyclic aromatic hydrocarbons and polychlorinated biphenyls from environmental samples. *J. of Chromatogr.* **1987**, 403:63-76
3. S.B. Hawthorne. Analytical-Scale Supercritical Fluid Extraction. *Anal. Chem.* **1990**, 62 633A-642A
4. S.B. Hawthorne, Y. Yang and D. Miller. Extraction of Organic Pollutants from Environmental Solids with Sub- and Supercritical Water. *Anal. Chem.* **1994**, 66 2912-2920.
5. Y. Yang, S. Bøwadt, S.B. Hawthorne and D.J. Miller. Subcritical Water Extraction of Polychlorinated Biphenyls from Soil and Sediment. *Anal. Chem.* **1995**, 67, 4571-4576
6. Development of a Solid Phase Carbon Trap for simultaneous Determination of PCDDs, PCDFs, PCBs and pesticides in Environmental Samples Using SFE-LC. B. v. Bavel, M. Järemo, L. Karlsson, G. Lindström. *Anal. Chem.* **1996**, 68 1279-83.
7. L. Hardell, B. v. Bavel, G. Lindström, M. Fredrikson, H. Hagberg, M. Nordström, G. Liljegren and B. Johansson. Higher Concentrations of Specific Polychlorinated Biphenyl Congeners in Adipose Tissue from Non-Hodgkin Lymphoma Patients Compared to Controls without a Malignant Disease. *Int. J. Oncol.* **1996**, 9, 603-605.
8. L. Hardell, G. Lindström, B. v. Bavel, K. Broman, M. Fredrikson, M. Nordström, B. Johansson, G. Liljegren, and H. Hagberg. Increased Concentrations of Chlordane in Adipose Tissue from Non-Hodgkin Lymphoma Patients Compared to Controls without a Malignant Disease. *Int. J. Oncol* **1996**, 9, 1139-1142.
9. G. Lindström, H. Wingfors, M. Dam, B. v. Bavel. Identification of 19 Brominated Diphenylethers, PBDEs, in Long-Finned Pilot Whale (*Globicephala melas*) from the Atlantic. *Submitted*.