

## Supercritical Fluid Extraction as an Extraction and Clean up Technique in Environmental Analyses.

**Bert van Bavel<sup>1</sup>** and **Gunilla Lindström**

Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden

<sup>1)</sup> Present address: Department of Environmental and Sanitary Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan.

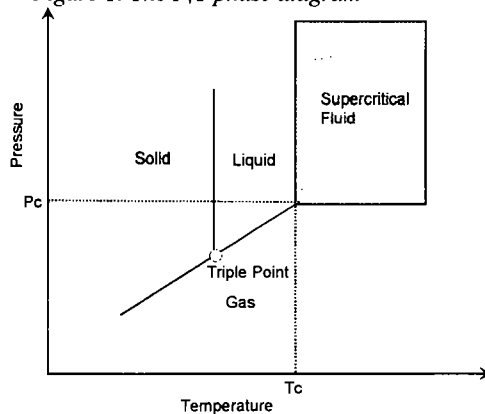
### 1. The principles of SFE

The superior solvation qualities of supercritical fluids over liquids have been known for more than a century when, in 1879, Hannay and Hogarth<sup>1</sup> investigated the solubility of different inorganic salts in supercritical ethanol. It was however not until the late sixties that the potential of extraction with supercritical fluids was recognised. A gas or a liquid becomes a supercritical fluid above the critical point in the temperature/pressure phase diagram (Figure 1). This point is defined by the critical temperature ( $T_c$ ) and the critical pressure ( $P_c$ ). In the supercritical state a substance is neither a gas nor a liquid. The properties of a supercritical fluid are therefore intermediate between the gas and the liquid phase. The density is comparable with that of a liquid whereas the viscosity is equivalent to a gas (Table 1).

As a consequence, the diffusion rate is somewhere in-between the liquid and the gas phase. Supercritical fluids can be compressed to almost the same density as a liquid, and thus show liquid-like solvation properties. With respect to extraction, a supercritical fluid has a higher diffusion rate than a liquid, while still exhibiting the solvation capacity of a liquid. This makes a supercritical fluid very suitable as an extraction medium. The mass transfer kinetics are rapid, and by controlling the pressure and temperature the solvent strength can be adjusted<sup>2</sup>. Optimisation by changing the pressure and temperature, to achieve selective extraction, is thus possible.

Several liquids or gases can be brought into the supercritical phase. Different solvents, as an extraction medium for the use in analytical-scale SFE, can be selected. Carbon dioxide is most commonly used as an SFE medium because of its desirable properties and ease of handling. Carbon dioxide has a relatively low  $T_c$  and  $P_c$  and is a non toxic gas at atmospheric conditions at room temperature. Carbon dioxide is also relatively inexpensive and commercially available at a purity grade acceptable for most

Figure 1. The P,T phase diagram



analytical applications. Another advantage of carbon dioxide is that the polarity can easily be adjusted by adding modifiers, for example methanol, to the supercritical fluid or to the extraction vessel.

## 2.1 SFE Instrumentation

Substantial improvements have been achieved in recent years concerning the SFE instrumentation going from crude home made instruments to sophisticated commercial instruments with the convenience of autosamplers and computer operation. The instrumentation required is basically rather simple (Figure 2). A gas cylinder where liquid CO<sub>2</sub> is withdrawn from the bottom is connected to a pump where the liquid is compressed to the desired pressure. The gas is preheated to the extraction temperature by a special preheater unit or a GC oven in which the extraction vessel is placed. A restrictor placed after the extraction chamber controls the CO<sub>2</sub> flow and variable pressure regulation systems are available controlling the pressure in the extraction chamber. Two extraction modes can be used, either static or dynamic. In the static mode the valve system is closed and no flow through the extraction cell is possible. In the dynamic mode CO<sub>2</sub> is passed through the sample at a certain flow rate. Collection of the target compounds after expansion where upon the density of the supercritical liquid drops, can be done in a liquid or on a solid phase.

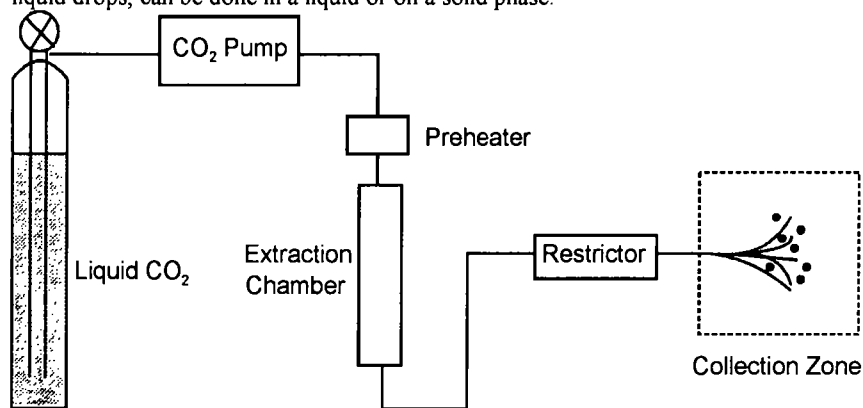


Figure 2. A block diagram of a supercritical fluid extraction system.

### 2.1 SFE in Environmental Analysis

SFE is very suitable for the extraction of chlorinated organic pollutants from different sample type. By optimising the extraction conditions cleaner extracts are obtained which need less further sample clean up. It is also possible to combine sample extraction and clean up using SFE-LC. As an illustration the SFE-LC extraction of human adipose tissue for different chlorinated compounds, including dioxins, furans, PCBs and different pesticides, is described.

Prior to extraction the samples were homogenised, mixed with Na<sub>2</sub>SO<sub>4</sub> and spiked with several <sup>13</sup>C labelled internal standards. At optimum extraction condition for the extraction of the target compounds (40°C, 281 bar) unfortunately also fat starts to co-extract from the extraction chamber. To avoid the extraction of fat, the extraction chamber was filled with basic alumina oxide as a fat retainer. This fat retainer works like a packed SFC column and fat and target compounds can be separated this way. Both long and thin extraction vessels enhance the supercritical chromatographic separation of fat and target compounds on alumina oxide. In chromatographic terms, the column length L is increased and the column diameter D is reduced; both factors increase the resolution R.

## 2.2 SFE-LC

The extracts obtained by means of SFE are very clean and allows direct GC/MS analyses of PCBs and pesticides without further clean up<sup>3</sup>. The selective extraction of only the target compounds also tolerates the use of the solid phase trap of the SFE as an LC system for the on line separation of the PCDDs, PCDFs and planar PCBs from the bulk PCBs and different pesticides. The 'bulk' PCBs and pesticides are present at a relative high concentration and are interfering during HRGC/HRMS analyses of the dioxins and furans which are present at much lower concentrations. A specially designed carbon trap<sup>4</sup> was used for the on line SFE-LC separation of the compounds mentioned above. The SFE-LC is outlined in Figure 3 and has been used within an epidemiological study in which over 60 samples were analyzed<sup>5</sup>. For this study simultaneous analyses of one sample for PCDDs, PCDFs, planar PCBs, 'bulk' PCBs, HxCBz, DDE, and chlordane was performed.

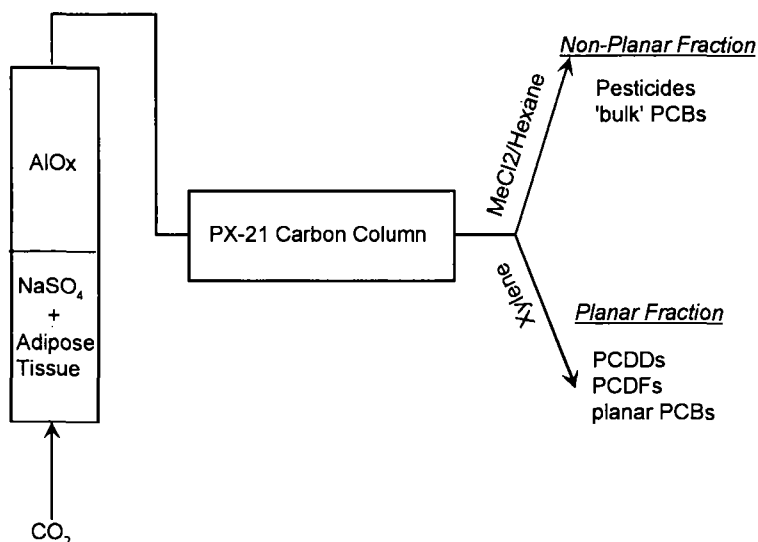


Figure 3. Flow scheme of the SFE-LC system.

## 3 Conclusion

SFE-LC is superior to the traditional extraction and clean up for organochlorine compounds in biological samples in every aspect;

- Solvent use is reduced to a minimum
- Analysis time is reduced to 2-3 hours
- Large sample put through is possible by using automated systems
- The repeatability is better than the traditional analysis
- Optimisation for different compound classes is possible
- Simultaneous analyses of many different organochlorine compounds of one sample is possible

The considerable reduction in analysis time and cost open the possibility for performing large monitoring studies including many different organochlorine compounds. This substantial improvement in the simultaneous analysis PCDDs, PCDFs, planar PCBs, 'bulk' PCBs and pesticides as HxCBz, DDE and the Chlordanes will improve our understanding of the behaviour of these compounds in the environment and the human population.

## 4 References

---

- <sup>1</sup>) Hannay J.B., and J. Hogarth (1879): On the Solubility of Solids in Gases. *Proc. Roy. Soc. (London)*, 29, 324-326.
- <sup>2</sup>) Hawthorne S.B. (1990): Analytical-Scale Supercritical Fluid Extraction. *Anal. Chem.* 62 (1990) 633A-642A.
- <sup>3</sup>) van Bavel B., P. Dahl, L. Karlsson, L. Hardell, C. Rappe and G. Lindström (1995): Supercritical Fluid Extraction of PCBs from Human Adipose Tissue for HRGC/LRMS Analyses. *Chemosphere* 30, 1229-1236.
- <sup>4</sup>) van Bavel B., M. Järemo, L. Karlsson and G. Lindström (1996): Development of a Solid Phase Carbon Trap for Simultaneous Determination of PCDDs, PCDFs and PCBs in Environmental Samples using SFE-LC. *Anal. Chem.* 68, 1279-1283.
- <sup>5</sup>) Hardell L., B. v. Bavel, G. Lindström, M. Fredrikson, H. Hagberg, M. Nordström, G. Liljegren, B. Johansson (1996): Higher Concentrations of Specific Polychlorinated Biphenyl Congeners in Adipose Tissue from Non-Hodgkin Lymphoma Patients Compared to Controls without a Malignant Disease. *Submitted.*