

A Simple Analytical Methodology for Determination of Polychlorinated Compounds in Varied Matrices

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Organochlorines as a class are some of the most persistent organic contaminants in the environment. These chemicals have found wide application in the past, however, due to adverse effect of these chemicals on human health and the environment, their use has been severely curtailed during the past decade. Despite this discontinuation, these chemicals are found in all compartments of the environment. Determination of these compounds in environmental matrices is laborious due to large number of congeners and potential interference posed by co-extractants such as elemental sulfur and lipids. Some of the problems encountered during traditional analytical methodology can be dramatically reduced or eliminated by selective supercritical fluid based extraction techniques¹⁻⁴.

One of the major drawbacks of supercritical fluid extraction has been the concentration of extracts which in principles is very simple but difficult to implement quantitatively. Limited experiments in our laboratory has shown that judicious use of carbonaceous adsorbents can eliminate trapping difficulties in case of polychlorinated hydrocarbons. Present reports deal with a simple analytical scheme for quantitative determination of chlorinated pesticides, polychlorinated biphenyl, polychlorinated dibenzodioxins and polychlorinated dibenzofurans. The scheme is based on supercritical fluid extraction (SFE) and adsorption on activated carbon.

EXPERIMENTAL

All SFE experiments were carried out with a multi-chamber SFE system. The details of the systems have been provided elsewhere⁵. The system consisted of pneumatic amplifier, extraction vessel and adsorbent traps. Experiments were conducted with naturally contaminated samples as well as those fortified with contaminants of interest. Initial evaluations were carried out through a mass balance approach with fortified samples. Organochlorine of interest included hexachlorobenzene, hexachlorocyclohexane, chlordanes, p-p-DDT and its metabolites, Aroclor formulation 1254, 1260 tetra through octa chlorodibenzo-p-dioxins and furans. Concentration of pesticides in the fortified sample was varied from 5.0 to 200 parts per billion (ppb), PCB, was varied from 20-500 ppb and PCDD concentration ranged from 10 ppt-1 ppb.

For determination of contaminants in soil and sediments matrices, samples were homogenized, air dried and sieved to remove stones and aggregated larger than 2 mm. In case of fly ash samples no mechanical treatment was undertaken except homogenization. Biological tissue were homogenized in mechanical blenders. The samples were mixed with anhydrous sodium sulfate and homogenized further with clean pyrex wool, the mixture was placed in a stainless steel wire mesh sample holder. The sample holders were placed in the SFE vessels which were submerged in a thermostated water bath. The vessels were sealed and pressurized with either CO₂ or N₂O. All extractions were carried out in a static mode. Effects of density, temperature and equilibration period on the extractability and the selectivity were monitored.

The extracted sediment components were trapped in solid adsorbent traps. Experiments were carried out to optimize the composition of adsorbent materials. The criteria were minimum breakthrough and high desorption efficiency. To ascertain the breakthrough a series configuration was employed (Figure 1). The high pressure cartridges were of easy to operate snap-on/snap-off type, designed in our laboratories.

For comparative purposes, samples were also extracted in Soxhlet and subjected to classical clean-up steps including chromatographic fractionation on Florisil, size exclusion gels, silica gel, and graphitized carbon.

Figure 1

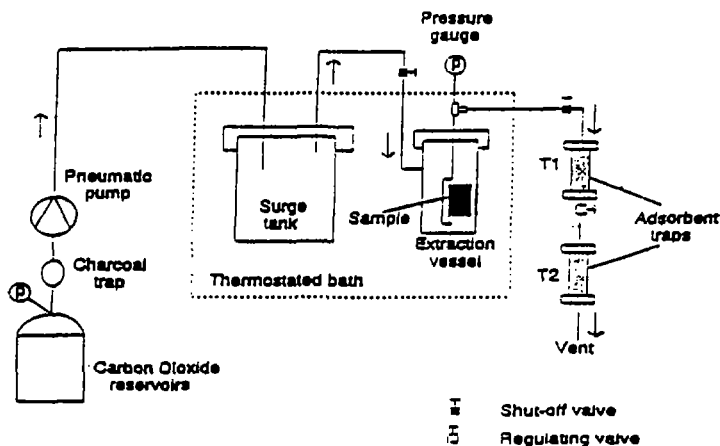


Figure 1: Schematic diagram of the SFE/adsorbent trap system.

RESULTS AND DISCUSSION

The applicability of supercritical fluids for the extraction of non-polar and moderately polar analytes from biological tissues, soils or sediments has been demonstrated by a number of researchers⁶⁻⁹. Extraction efficiencies approaching 100% can be readily obtained even under moderate operating parameters (in the near critical region), especially in the presence of polar modifiers/wetting agents⁶. However, the acceptance of this technique for routine applications has been slow

due to the relatively high cost of the extraction systems and poor precision. The latter problem is related to inefficient trapping of extracted analytes. An ideal trapping system is one which retains all analytes while allowing all of the extracting fluid to escape. The most common approach involves expansion of condensed fluid through a restrictor, where the expansion leads to a drop in the solubility of analytes. Analytes are then collected either on the walls of expansion vessel or in adsorbent traps or liquid impingers. The breakthrough of analytes in condensed CO₂ aggregates is the most severe problem in all trapping systems. The problem can be alleviated by using low volume thermostated restrictors, however this results in long decompression periods. For large extraction vessels decompression periods often exceed extraction equilibration periods. The proper selection of trapping system is thus an important consideration for analytical SFE.

Application of adsorbent traps, in cases where the trap can serve a dual purpose of fractionation and clean-up, is quite attractive.

For the present application, a dual adsorbent trap was found to give the best results. The trap consisted of a stainless steel tube (150 mm X 9 mm i.d.) designed to fit into a swagelok quick connecting fitting. The trap was packed with Florisil and topped with a 20 mm layer of graphitized carbon PX-21 (5-10% by weight on glass filter).

The selection of adsorbent combination was made to maximize adsorption and facilitate fractionation of PCDD, PCBs, chlorinated pesticides and polar co-extractants. This fractionation was accomplished by forward elution with hexane/dichloromethane (5-50% MeCl₂) followed by a reverse extraction with toluene. Further fractionation into sub-classes is feasible but was not optimized for the present study. The evaluation of traps included breakthrough and recovery experiments. Results for selected analytes are summarized in Table 1.

Table 1 Percent Recovery at Different Extraction Pressures and Constant Temperature (323°K)

Analyte	Extraction Pressure, atm					Extraction Pressure, atm			
	136	156	177	197		136	156	177	197
	Percent Recovery					Percent Recovery			
γ-BHC	98	98	92	93	p,p' DDE	95	92	93	93
Hexachlorobenzene	92	95	98	93	p,p' DDD	89	85	84	83
Heptachlor	105	96	96	95	p,p' DDT	85	86	94	87
Heptachlor Epoxide	89	96	98	97	2,3,7,8 TCDD	78	73	85	92
t-Chordane	98	96	96	96	2,3,6,7,8 PCDD	73	76	81	90
cis-Chlordane	95	94	95	98	OCDD	65	66	78	85
Dieldrin	98	93	91	94					

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All components of the mixture were quantitatively recovered from the first trap indicating essentially zero breakthrough. No measurable peaks for spiked components were found in extracts from the second trap.

The SFE experiments were carried out after optimization of trapping systems. The fortified samples, containing 250-250 ppb of pesticides and PCBs were placed in the extraction vessel. Results of extraction carried out at different densities. The results showed that all analytes of interest were extracted quantitatively (Figure 2). An interesting aspect of the experiment dealt with the extraction of interferents such as sulfur. It was under optimized conditions the recovery for sulfur ranged from 1-3%, compared to $\geq 90\%$ with liquid solvent extraction. Thus a 50 fold increase in selectivity for organochlorines over sulfur was obtained. The SFE and associated clean-up methodology is considerably faster. Being essentially a two step process it thus upholds considerable potential for multi-residue analysis compared to multi-step liquid solvent based methodologies.

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