

OPTIMIZATION OF SUPERCRITICAL FLUID EXTRACTION FOR THE DETERMINATION OF PCBs, PCDDs AND PCDFs IN SOIL

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ABSTRACT

Supercritical fluid extraction (SFE) was evaluated as an alternative procedure to conventional solvent extraction for the determination of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from soil. Extraction temperature and pressure conditions were optimized using a central composite experimental design approach. This three-level two-factor design allowed fitting of the extraction data to a six-parameter mathematical model which included second order effects in each factor as well as an interaction term. The resulting model provided a range of operating conditions where the highest recoveries could be obtained. A number of samples were then analyzed under the optimum conditions and compared to conventional analytical methodologies. The results confirm that SFE is indeed a viable alternative to solvent extraction. However, because of the competing effects of solubility and volatility, a single set of operating conditions cannot be defined.

INTRODUCTION

Supercritical fluids have been used in engineering applications for many years. Recently, these unusual fluids have found applications in analytical chemistry either as mobile phases for chromatography or as extraction fluids. The most common fluids for these applications is supercritical carbon dioxide. This material is of particular interest because it is a gas at room temperature, allowing for easy evaporation. Under supercritical conditions, carbon dioxide has solvating properties similar to conventional

solvents such as the freons or hexane. In addition carbon dioxide has a low toxicity, with no special disposal requirements.

The objective of this study was to optimize the extraction conditions in terms of temperature and pressure. Optimization was necessary to balance the competing effects of analyte solubility and volatility. This manuscript represent the first report of the application of a statistical experimental design approach to the SFE experiment.

EXPERIMENTAL SECTION

INSTRUMENTATION

Samples were extracted using a Suprex Model SFE/50 extraction system. Samples were packed into a 5 mL extraction vessel. Approximately two to three g of soil could be packed into each vessel. A length of 25 μm i.d. capillary tubing provided pressure regulation for the extraction experiment.

Sample extracts were quantified using a VG Model 70SE High Resolution Mass Spectrometer. The instrument was operated in the electron impact ionization mode at a mass resolution of 10,000 ($M/\Delta M$, 10% valley definition). Data were acquired by selected-ion-recording using a VG Model 11-250J Data System.

PROCEDURE

The extraction vessel was filled with the sample. Sample spiking (native or isotopically-labelled standards) was performed using a minimum volume of solvent. When necessary, the sample was mixed with diatomaceous earth to facilitate handling. The vessel was then assembled and tested for leaks. Each sample was extracted immediately for 30 minutes under conditions specified by the experimental design. Collection of extracted components was achieved by immersing the outlet of the capillary restrictor in 6 - 7 mL of hexane. Bubbles of carbon dioxide were readily observed at the end of the restrictor.

After extraction, the hexane was evaporated to dryness and reconstituted in 20 μL of tridecane. No other analyte enrichment procedures were employed before the initial analysis. A 2 μL aliquot was injected into the GC/MS system for quantification.

RESULTS AND DISCUSSION

Extraction conditions were based on a central composite design, or "star-cube" design. Nine separate experiments and four replicates were spread out within the established boundaries for temperature and pressure (temperature: 35 to 150 °C; pressure: 75 to 350 atmospheres). The data were fit to a six parameter model using C-Comptm software (Statistical Programs, Inc.). A complete Analysis of Variance (ANOVA) was possible from the data obtained. All first- and second-order parameters were significant with greater than 80 percent confidence. The interaction term was not significant.

A representative plot of analyte response (arbitrary units) over the established temperature-pressure range is shown in the attached figure. This figure was calculated using the parameter estimates obtained from linear regression on data from the extraction of model compounds. The plot shows a minimum response at intermediate temperature and pressure ("L"). Higher response is obtained near the boundaries, with the best response at lower temperatures (the upper left part of the plot, "H"). This result suggests that solubility is more important than volatility for this system.

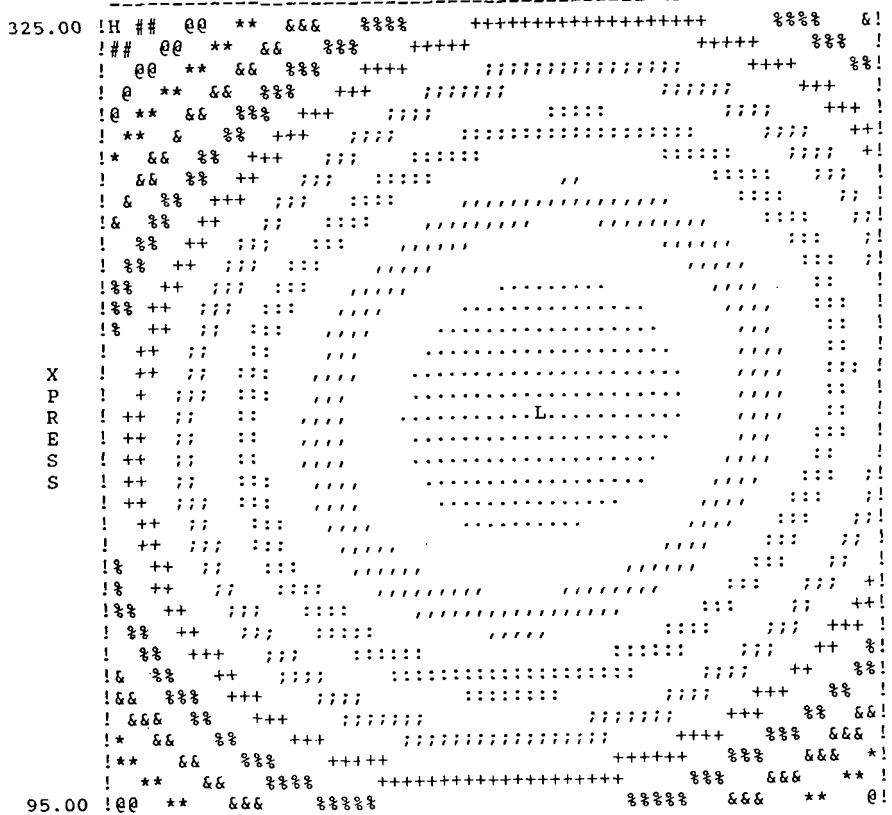
However, because of variations in analyte solubility and volatility, as well as differences in the activity of the matrix surface, optimization is necessary for each new system study. We have collected information on a number of different analyte classes and substrates as part of our efforts to build a database of optimized SFE conditions for a wide range of environmentally significant compounds.

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Plot of Response versus XPRESS and XTEMP



	40.00	XTEMP	140.00
L<=	6.776E+01	%	1.643E+02 TO 1.740E+02
.	6.776E+01 TO	&	1.836E+02 TO 1.933E+02
,	8.708E+01 TO	*	2.029E+02 TO 2.126E+02
:	1.064E+02 TO	@	2.223E+02 TO 2.319E+02
;	1.257E+02 TO	#	2.416E+02 TO 2.512E+02
+	1.450E+02 TO	H>=	2.609E+02

	RESPONSE	XTEMP	XPRESS
(L)	6.7764712E+01	9.6666667E+01	2.1000000E+02
(H)	2.6087531E+02	4.0000000E+01	3.2500000E+02