ROLE OF ENTRAINERS IN SUPERCRITICAL FLUID EXTRACTION OF CHLORINATED AROMATICS FROM SOILS AND BIOLOGICAL MATRICES

M.H. Liu, S. Kapila, K.S. Nam, T.E. Clevenger and A.F. Yanders

Environmental Trace Substances Research Center
University of Missouri
Columbia, Missouri

ABSTRACT

The effects of entrainers on extractions of chlorinated aromatics from soils and biological matrices were investigated. A noticeable improvement in the extraction efficiency of all chlorinated phenols was brought about by polar entrainers such as methanol and dimethyl sulfoxide (DMSO).

INTRODUCTION

There has been a resurgence of interest in the application of supercritical fluids, especially carbon dioxide, for the extraction of chemical pollutants from varied matrices. This renewed interest is, in part, due to the high extraction efficiencies that can be obtained with supercritical fluid extraction (SFE) and an anticipated restriction of the use of halogenated organic solvents.

Supercritical carbon dioxide is a nonpolar quadratic fluid, with solvating properties similar to those of alkanes, and is an effective solvent for a number of nonpolar solutes. However, its effectiveness for the extractions of moderately polar to polar solutes is generally low. Increased extraction efficiencies can be brought about by the addition of modifiers (entrainers). The present study was undertaken to monitor the effects of entrainers on extractions of chlorinated aromatics from soil and biological matrices.

EXPERIMENTAL

A supercritical fluid extraction system designed in our laboratory was used during the course of this study. This system was designed for multiple extraction capability and allowed variations in the extraction parameters such as pressure/density as well as the composition of the extracting medium. The samples were suspended in thermostated extraction vessels and modifiers were added either directly to the sample matrix or introduced along with CO_2. Various extraction parameters, such as density, temperature, pressure, and modifier concentration, were studied and optimized for each matrix and class of chlorinated aromatic compounds.

RESULTS AND DISCUSSION

The extraction efficiencies obtained for various chlorinated phenols are given in Table 1. These recoveries were obtained at 172 atm pressure and a temperature of 323°C. The concentration of chlorinated phenol in the soil

TABLE 1

PERCENTAGE EXTRACTION EFFICIENCIES OF CHLORINATED PHENOLS BY SFE

Components*	(log) Kow	mp (°C)	SFE			SFE/MeOH			SFE/Toluene			SFE/DMSO		
			Extraction	Residue	Total	Extraction	Residue	Total	Extraction	Residue	Total	Extraction	Residue	Total
Phenol	1.46	41	39.4	54.0	93.4	82.7	13.0	95.7	45.9	48.1	94.0	79.9	20.2	100.1
2-chlorophenol	2.16	8	64.9	27.8	92.7	76.2	6.3	82.5	62.7	22.4	85.1	77.0	16.7	93.7
4-chlorophenol	2.39	44	27.0	72.1	99.1	82.9	14.3	97.2	40.9	54.0	94.9	70.8	17.9	88.7
3-chlorophenol	2.50	34	30.4	74.3	104.7	84.1	14.3	98.4	44.7	55.1	99.8	74.3	18.3	92.6
2,4-chlorophenol	3.08	42	60.4	33.5	93.9	81.3	7.7	90.0	62.4	26.2	88.6	76.1	12.9	89.0
2,6-dichlorophenol	2.73	65	51.1	48.0	99.1	83.1	10.8	93.9	58.1	34.6	92.7	78.1	19.0	97.1
Trichlorophenol**	2.97	65	37.4	67.8	105.2	85.1	13.6	98.7	51.2	48.6	99.8	76.4	19.8	96.2
Tetrachlorophenol***	4.30	96	24.2	80.2	104.4	83.0	19.0	102.0	39.3	61.9	101.2	72.8	26.1	98.9
Pentachlorophenol	5.01	190	21.9	81.9	103.8	83.3	19.0	102.3	36.3	62.0	98.3	50.9	36.0	86.9

*50 ppm of phenols were spiked in each soil sample

**Trichlorophenol includes 2,4,5-Trichlorophenol (Kow=3.72, mp=68°C) and 2,4,6-Trichlorophenol (Kow=2.97, mp=65°C)

***2,3,4,5-Tetrachlorophenol

sample was 50 ppm. The extraction efficiencies for these compounds using CO_2 with a modifier varied from 22% to 60%. The highest extraction efficiencies were obtained for O-chlorophenol and 2,4-dichlorophenol, whereas the lowest efficiencies were obtained for pentachlorophenol. The extraction data indicate that the extraction efficiency is dependent on the vapor pressure and polarity of the solutes. A noticeable improvement in the extraction efficiency of all chlorinated phenols was brought about by the introduction of polar modifiers such as methanol and dimethyl sulfoxide (DMSO). Better than 80% recovery was obtained with methanol for almost all phenols. The enhancement of extraction efficiencies was comparatively low with nonpolar modifiers such as toluene.

The extraction efficiencies obtained for various chlorinated pesticides and PCBs from soil are similar to those obtained in the case of chlorinated phenols. The highest extraction efficiencies were obtained with polar modifiers, and extraction efficiencies ranging from 70 to 100% were obtained with methanol. These results differ from those obtained earlier with biological matrices, in which case extraction efficiencies of 80% or better were readily obtained with CO_2 without modifiers or with nonpolar modifiers (1-2). The results obtained indicate that the choice of modifiers in supercritical fluid based extraction is dependent not only on the type of the solute molecules but also on the type of matrix.

REFERENCES

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