A MULTIPLE SAMPLE EXTRACTION AND ON-LINE SYSTEM FOR THE ANALYSIS OF CHLORINATED COMPOUNDS

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ABSTRACT

A multiple sample extraction and on-line analysis system for rapid determination of polychlorinated organics in complex matrices has been developed. The system is based on the direct coupling of supercritical fluid extraction with tandem supercritical fluid chromatography and gas chromatography. The on-line system permits the simultaneous extraction and analysis with high reproducibility and accuracy, while the overall methodology is considerably faster and less laborious than the conventional liquid extraction based analytical procedures.

INTRODUCTION

The efficacy of supercritical CO_2 as an extraction medium for the extraction of chlorinated compounds from environmental samples has been demonstrated by Nam, et al. (1-2). One of the most promising advantages of supercritical fluid based extraction (SFE) is the feasibility of an on-line extraction and analysis system. A number of attempts of direct analysis of polynuclear aromatics have been reported (3-5). However, most of the on-line systems are designed for single samples or relatively small sized samples, typically in the range of 50 to 200 mg. It is difficult to obtain a representative aliquot of this size from most environmental matrices, and sample amounts of 2 to 60 g are generally used for environmental monitoring.

The present study reports on the development and evaluation of a multiple sample extraction and on-line analysis system that is capable of handling sample sizes of up to 20 g.

EXPERIMENTAL

The schematic of the extraction and on-line analysis system is given in Figure 1. The extraction system consists of a pneumatic amplifier, a pressure surge tank and thermostated extraction vessels. The supercritical carbon dioxide extracts are sampled with a fixed volume sampling loop or trapped in a cryogenically cooled trap, and then introduced into the analytical system which is comprised of a packed column supercritical fluid chromatograph (SFC) and a gas chromatograph (GC). The preliminary separation of chlorinated organics and co-extractants is accomplished in the SFC and the final separation is performed in the capillary GC. The performance of the system is being evaluated with an electron capture detector and a quadrupole mass spectrometer.

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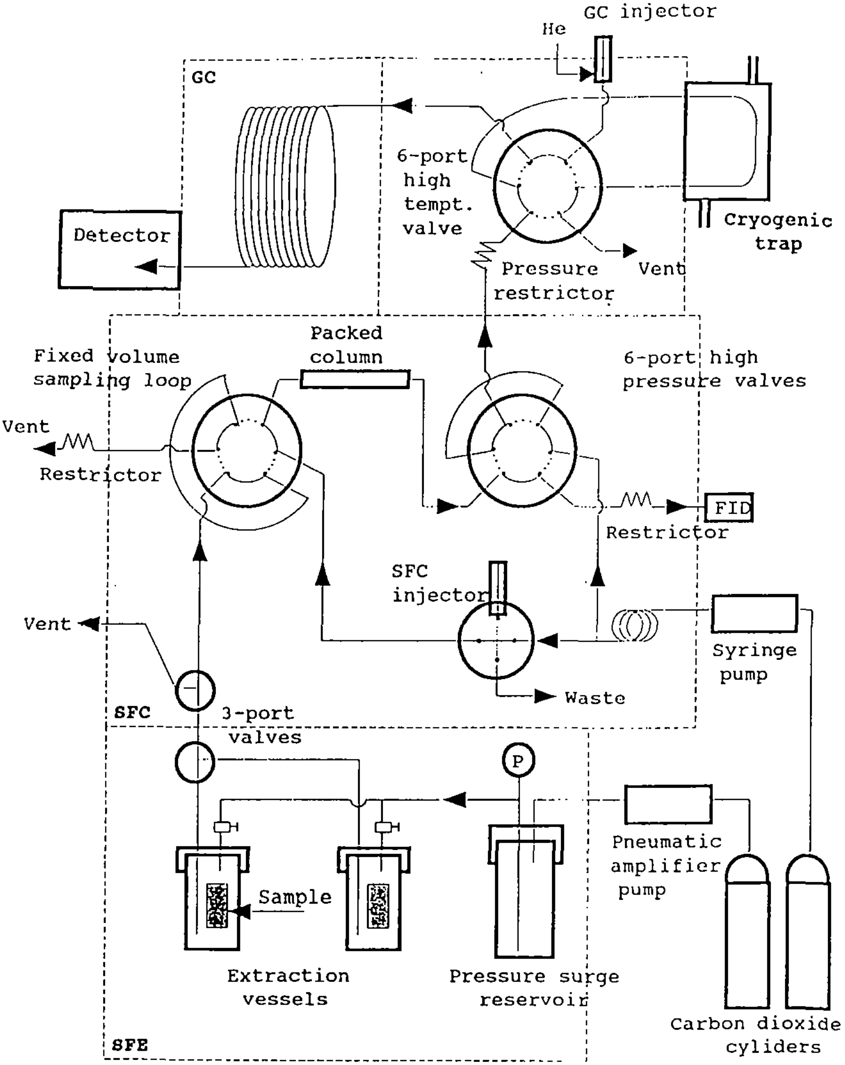
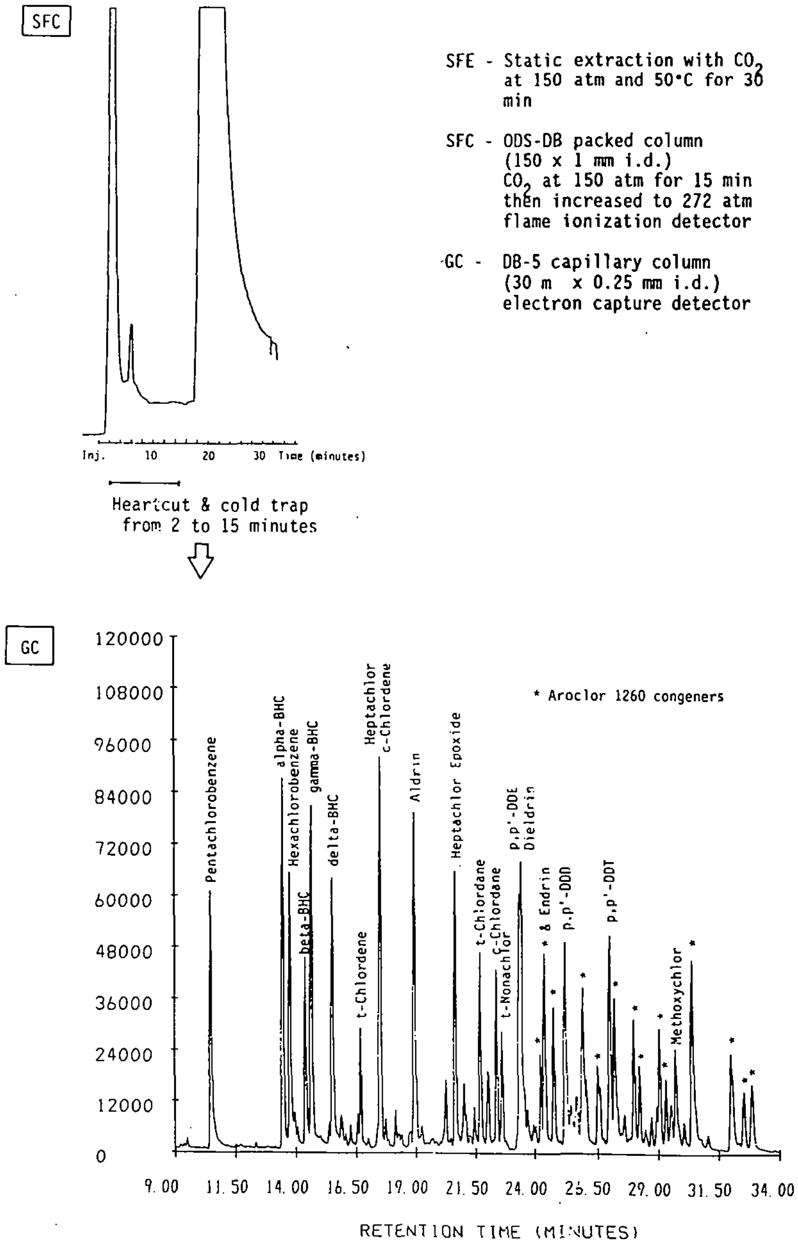


FIGURE 1: Schematic diagram of on-line SFE/SFC/GC system.

RESULTS AND DISCUSSION

In our previous reports, we have shown that high extraction efficiencies (80-100%) for a group of chlorinated organics such as organochlorine pesticides and polychlorinated biphenyls (PCBs) from various biological sample matrices can be readily obtained by static equilibrium extraction with supercritical carbon dioxide at pressures ranging from 100 to 170 atm at a temperature of 50°C (1-2).



SFE - Static extraction with CO_2 at 150 atm and 50°C for 30 min

SFC - ODS-DB packed column (150 x 1 mm i.d.) CO_2 at 150 atm for 15 min then increased to 272 atm flame ionization detector

GC - DB-5 capillary column (30 m x 0.25 mm i.d.) electron capture detector

Heartcut & cold trap from 2 to 15 minutes

Figure 2: SFE-SFC-GC of organochlorine pesticides and polychlorinated biphenyls in the fortified fish fillet tissue.

Extraction at these conditions yielded quantitative recovery of analytes, while maintaining selective extraction to minimize the level of interfering coextractants.

In this study, a supercritical fluid extraction system which has the capacity of extracting gram ranges of sample amounts was directly coupled to a supercritical fluid chromatograph where part of the extract was sampled after 30 minutes equilibration time using a fixed volume sampling loop. The relatively large sample capacity of the extraction system ensured homogeneity in sampling.

The supercritical fluid chromatography separation of directly introduced supercritical carbon dioxide extract of wet fish fillet tissue is shown in the top half of Figure 2. It was found that all of the organochlorine pesticides and PCBs eluted during the 2-15 minute period and separated from most coextractants when SFC was performed at isobaric 170 atm with carbon dioxide as a carrier. SFC eluate during this time period was directed and trapped in a cryogenically cooled trap by switching appropriate valves. Analytes in the trap were then thermally desorbed to a capillary gas chromatograph for high resolution separation and detection by electron capture detector.

The bottom half of Figure 2 shows the final qualitative results obtained from SFE-SFC-GC on-line analysis. The concentrations of each chlorinated analyte in spiked samples were quantitatively determined with relative standard deviations averaging at 5 percent. Complete analysis was accomplished in less than 2 hours, which is two orders of magnitude faster than conventional liquid extraction based analyses. The on-line system is also easily adaptable for automation of entire analytical steps including extraction, separation and detection.

REFERENCES

1. Nam, K.S., S. Kapila, D.S. Viswanath and A.F. Yanders, Chemosphere, 19 (1-6), 33-38 (1989).

2. Nam, K.S., S. Kapila, A.F. Yanders and R.K. Puri, accepted for publication Chemosphere, (1990).

3. Wright, B.W., S.R. Frye, D.G. McMinn, R.D. Smith, Anal. Chem., 59, 640-644 (1987).

4. Levy, J.M., R.A. Cavalier, T.N. Bosch, A.F. Rynaski, W.E. Huhak, J. Chromatogr. Sci., 27, 341-346 (1989).

5. Hawthorne, S.B., D.J. Miller, M.S. Krieger, J. Chromatogr. Sci, 27, 347-354 (1989).