

Evaluation Of Supercritical Fluid Extraction For Eliminating Interferences During Multiresidue Pesticide Analysis

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INTRODUCTION

Sediments are the primary reservoir of lipophilic xenobiotic contaminants in the aquatic systems, and a long term assessment of the environmental quality of these systems can be made through the measurements of these contaminants in the sediments. One of the major problems in multiresidual analysis of sediment results from interferences posed by elemental sulfur, which occurs as a result of anoxic degradation of biological matter. These interferences are a serious problem when an electron capture detector (ECD) or a flame photometric detector (FPD) is used as the monitoring device during the gas chromatographic analysis. The normal methodology for removal of sulfur from sediment extract is treatment of the extract with metallic mercury or copper¹. The treatment results in conversion of soluble sulfur to insoluble sulfides which are readily removed as precipitates. This methodology is quite effective in removing sulfur; however, the treatment leads to degradation of a number of pesticides and chemicals of environmental interest. An alternate to the treatment of extract with metal is being evaluated in our laboratory. This procedure is based on preferential extraction of non-polar analytes by supercritical fluids. The objective of the present study was to explore the applicability of selective supercritical fluid extraction (SFE) for elimination or reduction of sulfur interference.

EXPERIMENTAL

The evaluation of SFE was carried out with sediment samples from streams in Missouri. A batch of sediment was air dried, homogenized and sieved to remove particles larger than 2 mm. A ten-gram aliquot was used for each analysis. Some of the samples were spiked with elemental sulfur in addition to the naturally occurring sulfur. Selected samples were also fortified with five thiophosphate pesticides (terbufos, malathion, diazinon, methyl parathion and chlorpyrifos) and/or organochlorine pesticides and other contaminants (chlordanes, heptachlor-epoxide, p,p'-DDD, p,p'-DDE, p,p'-DDT, endrin and PCBs).

Sediment samples were homogenized with equal amount of anhydrous sodium sulfate. The mixture was transferred to the SFE vessel. All extractions were carried out in the static mode at various temperature and pressure conditions. An equilibration period of one hour was used for all extractions. The extracted sediment components were trapped in chilled

liquid impingers.

Sediment samples were prepared in an analogous manner for Soxhlet extraction. All extractions were carried out with methylene chloride for a 12 hr period. Extracts were concentrated and processed through adsorption gel column chromatography (florisil, gel permeation and silica gel). A standard Cu metal treatment was carried out to remove elemental sulfur from selected extracts. Approximately 0.6 g of powdered Cu, freshly acid-washed and cleaned, was added to the extract. The mixture was shaken for 10 min. or until almost all of the greenish-yellow color had disappeared.

Gas chromatographic analyses of extracts were carried out with fused silica capillary columns. A FPD, an ECD or a mass spectrometer was used as the monitoring device. Chromatographic conditions were selected to optimize separation of analytes of interest.

RESULTS AND DISCUSSION

The initial experiments were designed to monitor the selectivity of elemental sulfur extraction under SFE conditions optimized for the extraction of chlorinated and organophosphate pesticides²⁻⁴. The results were compared with those obtained through soxhlet extraction and are shown in Figure 1, which represents the output of the flame photometric

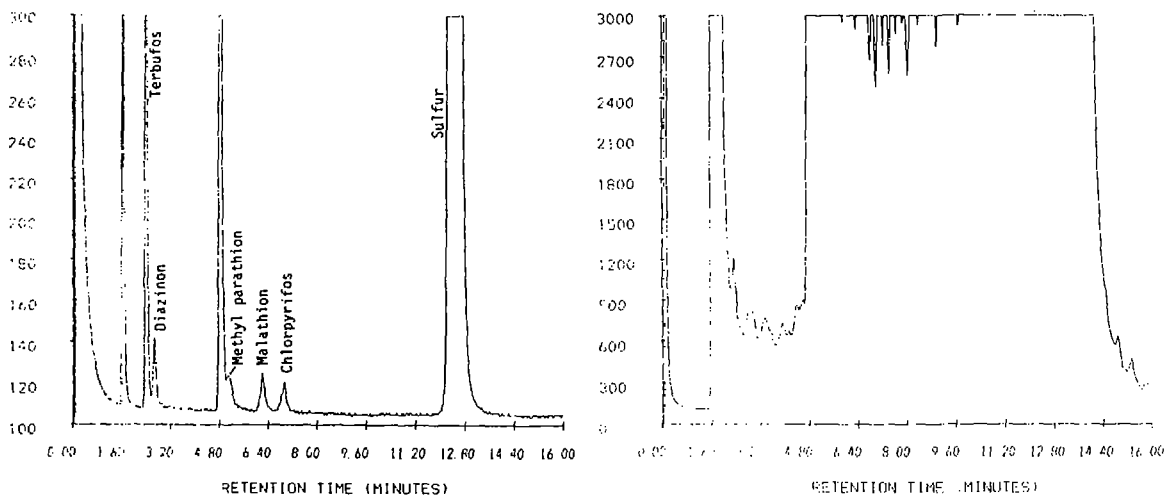


Figure 1: GC/FPD chromatograms of fortified sediment samples extracted via (A) SFE and (B) Soxhlet extraction.

detector operating in the sulfur mode (with a 394 nm filter). Quantitation revealed that less than 2 percent of the fortified sulfur was present in the SFE extracts. By contrast, $\geq 90\%$ of the xenobiotics of environmental interest were extracted. A measure of SFE's superiority in an environmental monitoring program can be seen in Figure 2, which depicts results obtained for selected thiophosphate pesticides in sediment. The analysis was carried out by a quadropole mass spectrometer interfaced to a gas chromatograph. It is quite clear that the sulfur interference poses little or no problem in determination of these analytes (Figure 2A),

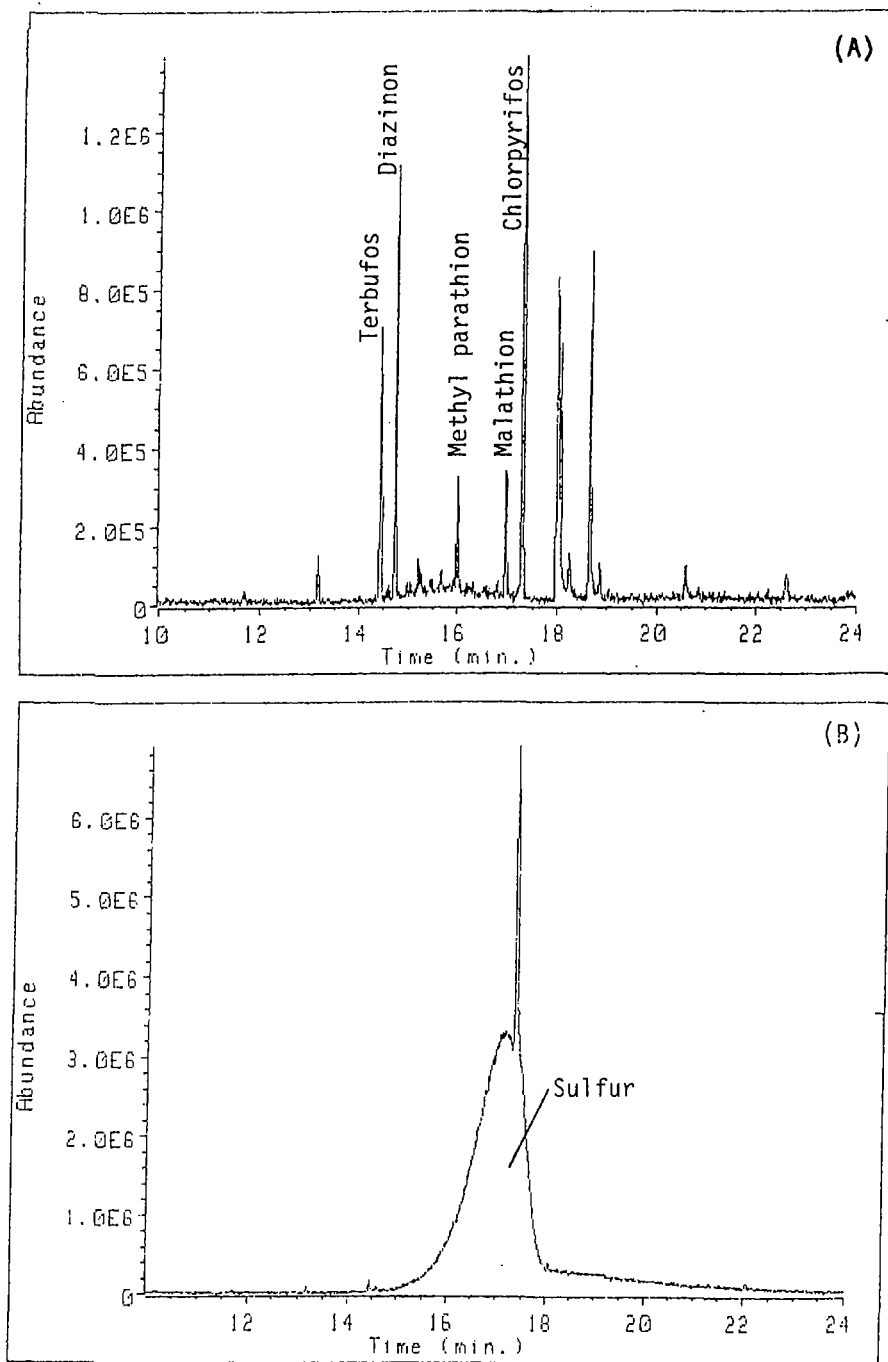


Figure 2: GC/MS chromatograms of fortified sediment samples, extracted via (A) SFE, (B) Soxhlet extraction.

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whereas it is a severe problem in Soxhlet extracts (Figure 2B). As expected, elimination through traditional treatment with metallic Cu leads to decomposition of all analytes (Figure 3). Clearly, SFE holds considerable potential in environmental monitoring programs.

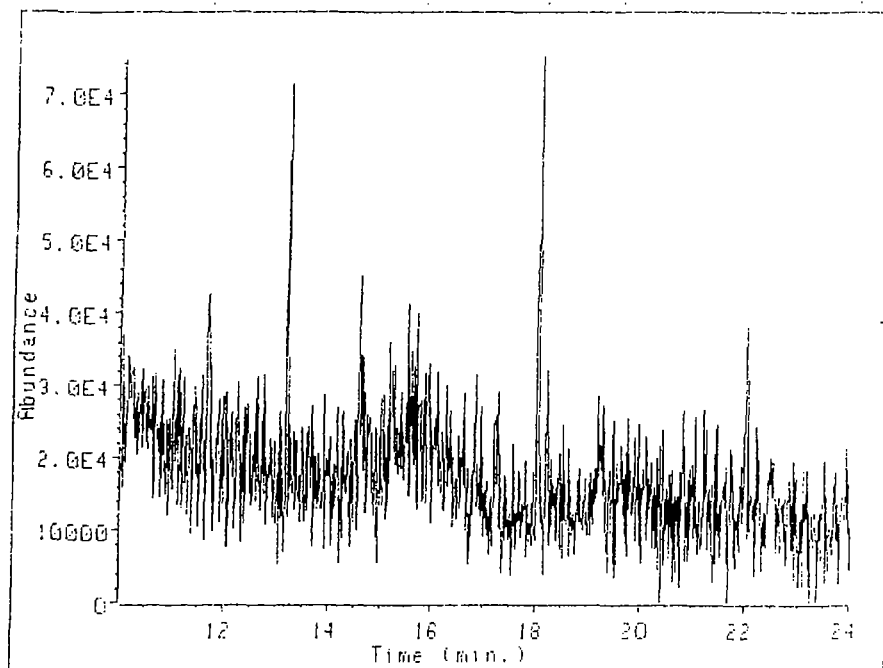


Figure 3: GC/MS chromatogram of fortified sediment sample, extracted via Soxhlet extraction and treated with metallic Cu to remove elemental sulfur interference.

ACKNOWLEDGEMENTS

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