

Extraction of Tetrachloroethylene from Weathered Soils: A Comparison between Soxhlet Extraction and Microwave-Assisted Extraction

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Abstract : The inadvertent ingestion of contaminated soil can be an important source of xenobiotic exposure to the humans. Our study focuses on chlorinated hydrocarbons in soil, particularly tetrachloroethylene. Tetrachloroethylene is used for dry cleaning and textile processing, as a chemical intermediate and as a degreasing agent. It is also used for rubber coatings, solvent soaps, printing inks, adhesives, polishes, lubricants and as a cooling gas in electric transformers. Chemical discharges from industry, both intentional and unintentional, contribute to a growing concern about the levels of this compound in soil. The amount of time required for sample preparation and analysis of a single sample is often considerable and is accompanied by the accumulation of significant volumes of waste solvent. The thermal desorption method is a step towards minimizing analysis time as well as the volume of solvent waste generated. We report a comparison of the recoveries of tetrachloroethylene spiked into two model solids and also native contaminated soil using Soxhlet extraction and microwave assisted extraction methods. Recoveries by both the methods show good agreement with each other.

Key words: *soxhlet extraction, microwave assisted extraction, tetrachloroethylene, hazardous compounds*

Abstrak : Pengambilan secara tidak sedar melalui pemakanan, tanah yang telah tercemar adalah sumber utama pendedahan xenobiotik kepada manusia. Kajian ini memberi penumpuan kepada hidrokarbon-hidrokarbon klorina didalam tanah, khususnya, tetrakloroetilina. Tetrakloroetilina digunakan untuk pembersihan kering dan proses tekstil, sebagai bahan kimia perantaraan dan sebagai ejen nyah minyak. Ia juga digunakan untuk menyalut getah, pelarut sabun, dawat percetakan, pelekat, pelincir dan sebagai gas penyejuk dalam alat ubah elektrik. Pembuangan bahan kimia dari industri-industri, samada secara sengaja atau tidak, adalah penyumbang kepada masalah paras tetrakloroetilina di dalam tanah pada takat yang membimbangkan. Masa untuk penyediaan dan penganalisaan sesuatu sampel adalah panjang dan biasanya memerlukan banyak bahan-bahan pelarut. Disini kami melaporkan satu perbandingan jumlah terakloroetilina yang diekstrak dari tanah yang di cemari dan dua tanah model menggunakan kaedah pengekstrakan Soxhlet dan pengekstrakan menggunakan gelombang mikro. Keputusan daripada kedua-dua kaedah menunjukkan persamaan dari segi peratus hasilan.

Received : 5.6.02; accepted : 5.5.03

Introduction

Soil contaminated by chemicals, pesticides and other xenobiotic compounds used in various industries and agricultural activities can be a major source of exposure to the human. When contaminated soil is inadvertently consumed, the amount of such compounds to which a person is exposed will depend not only on the amount of the compound that is in the soil, but also on the quantity of the contaminant released from the soil as it passes through the digestive system. The amount of a particular compound extractable from the soil depends on the chemical properties of the compound, the characteristics of the soil, and the contact time of the contaminant with the soil.

The quantity of a compound that is removed from the soil and then transferred into the human body circulation is referred to as the bioavailable fraction [1]. Current techniques to determine bioavailability involve animal or bacterial models or complex models of the human digestive system [1-3]. The total amount of a compound that is desorbed from the soil, whether it is further absorbed into circulation or not, is defined as the bioaccessible fraction, sometimes referred to as the "mobile" fraction [4]. It is potentially an overestimate of bioavailability and can be seen as a conservative estimate of possible risk.

In this work, we examine two simple analytical extraction methods, namely the Soxhlet extraction and microwave-assisted extraction (MAE) with an

organic solvent. This study will focus on the chlorinated hydrocarbon in soil, namely tetrachloroethylene.

Tetrachloroethylene is used for dry cleaning and textile processing, as a chemical intermediate and degreasing agent. It is also used for rubber coatings, solvent soaps, printing inks, adhesives, polishes, lubricants and as a cooling gas in electric transformers. There is a growing concern about the levels of this compound in soil due to discharges from industries.

In this study, series of controlled experiments were performed on the contaminated soil and two model solids to determine the extraction efficiency of two methods, namely the Soxhlet extraction and the microwave-assisted extraction. Soxhlet extraction is a continuous solvent extraction method and is the standard technique used in most EPA methods [5]. It is a lengthy process, involving 24-hour extraction times and large volumes of organic solvent (up to 150 ml), and large sample sizes (up to 10 g). MAE is a similar extraction method which reduces the extraction time to a shorter duration using smaller samples and solvent amounts. MAE uses polar organic solvents in contact with solid samples heated in a microwave oven to extract organic contaminant [6]. In order to study the effects of organic components of the soil on the retention of the tetrachloroethylene, model solids were chosen to distinguish between retention by organic and inorganic portions of the soil. The model solids: sand, and humic acid amended sand were chosen to determine the influence of the organic content of soil on extraction efficiency. Test was also carried out on native contaminated soil (not spiked).

Materials and Methods

Native Soil collection and Total Organic Carbon (TOC) Determination

Native contaminated soil was obtained from the stream sediments located near an adhesive and lubricant factory in Klang, Selangor. The waste-water discharged from the factory was previously tested for the presence of tetrachloroethylene. Samples were taken approximately 10 cm below the soil surface. Samples were dried in oven (50°C) and were sieved to less than 150 µm. The samples were sealed in polypropylene bags and kept at 4°C until use. Total organic carbon (TOC) was measured using an elemental analyser (Carlo Ebra model NA 1500, Italy) [7]. The instrument uses a combustion method converting all the carbon into carbon dioxide gas. The sieved soil samples were first pre-treated with 1 M hydrochloric acid to remove the carbonates and bicarbonates (major component of inorganic carbon). The dried treated samples were then placed in the induction furnace. Combustion was carried out in the furnace at 1000°C in pure dry oxygen to convert

organic carbon in the sample to CO₂. The CO₂ evolved from the reaction was carried through to the CO₂ coulometer for determination of total carbon.

Extraction of tetrachloroethylene using both the methods was carried out as described in section 2.5. Recovery of tetrachloroethylene was calculated based on total organic carbon in the native soil.

Model Solid Preparation

In an effort to study the portions of soil that interact most strongly with the contaminant, two different model solids were studied. Pure inorganic sand was chosen to study the interaction of the contaminant with the inorganic portion of soil, while a humic acid-amended sand (HA-sand) was used to study the interaction of the compounds with a "soil" that had a controlled organic component. Humic acid was chosen as the organic component for this research as it was the most readily available and is usually the larger organic component of soil.

The two model solids were prepared using washed sea sand (Fisher Scientific, S-25-10). The sand was first sieved to less than 150 µm and then washed with 1:1 (v/v) acetone:hexane, five times. Humic acid (sodium salt, Aldrich Co.) was purified by first removing free fulvic acid in acidic solution, dissolving in basic solution, and then precipitating in acidic solution. Precipitated humic acid was collected by vacuum filtration and rinsed with 0.1 M HCl. To prepare 5 % by weight humic acid-amended sand, 95.0 g of blank sand which was cleaned as described above, was mixed with 5.0 g of purified humic acid and 150 ml deionized water and stirred with a mechanical stirrer for 24 h. The humic acid-amended sand (HA-sand) was then allowed to dry in the hood and tested for the stability of HA on sand in several solvents (acetone, hexane, water, dichloromethane). HA-sand was aged in an amber glass bottle at room temperature for approximately three months before being spiked with tetrachloroethylene.

Spiking

Approximately 50 g of each model solid (sand and HA-sand) was placed in a 150 ml beaker to which was added 7 ml of the standard solution of 1000 µg/ml of tetrachloro-ethylene in acetone to obtain about 145 µg/g of tetrachloroethylene in the sample medium. Approximately 60 ml of acetone were added to thoroughly wet the medium. The solid-solvent mixture was sealed with several layers of Parafilm and stirred with a mechanical stirrer intermittently for 24 h. The Parafilm was then removed to allow the solvent to evaporate with intermittent stirring.

Aging

Each spiked sample was aged at room temperature in a sealed amber glass bottle for 12 weeks prior to analysis.

Extraction

Soxhlet Extraction

A micro Soxhlet extractor (Ace Glass, Inc. 6776) was used for all Soxhlet extractions with a 10 x 50 mm single layer cellulose extraction thimble (Whatman International Ltd, 2800105). Extraction time was 24 h with about 1.0 g of the sample and 20 ml of 1:1 (v/v) acetone:hexane solvent with a cycle time of about 6 min. Recovered solvent was diluted to 25 ml with acetone before analysis. All analyses were performed by direct injection into gas chromatography with electron capture detector (GC-ECD).

Microwave-Assisted Extraction (MAE)

A microwave acid digestion bomb (45 ml capacity, Parr 4782) was used for all microwave extractions. The sample to be tested (0.10 – 0.15 g) was weighed into a Teflon cup followed by the addition of 4 ml 1:1 (v/v) acetone:hexane solvent by pipette. The Teflon cup was sealed with a Teflon O-ring and lid. The assembly was placed in the bomb body and sealed. The bomb was heated in a microwave oven (1.52 kW, 900 W output, Sharp Carousel) for 3 min. The sealed bomb was cooled outside of the microwave oven for 30 min. The Teflon cup was then opened and the supernatant was transferred to a glass vial by pipette. All analyses were performed by direct injection into a GC-ECD.

Analysis

Samples were analysed using a Hewlett Packard Model 5890 Series II GC with an autosampler, a DB5-MS column (30 m long; 0.25 mm i.d.; 0.25 µm film thickness), and electron capture detector (ECD). Samples were analysed by direct injection of 1 µl into an injection port held at 250 °C. The ECD was held at 200 °C. The GC oven temperature was held at 50

°C for 2 min and then ramped to 250 °C at 20 °C/min, where it was held for the remainder of the run with a column head pressure of 15 psi (He gas with N₂ make-up gas). Calibration curves were created for tetrachloroethylene using standard dilutions of the spiking solution.

Results and Discussion

The micro-Soxhlet extraction was successful in recovering an average of 77 % of the tetrachloroethylene that was spiked into each of the model solids with a range of 75 to 79 % (Table 1).

Microwave-assisted extraction with 1:1 (v/v) acetone:hexane solvent gave recoveries that were slightly higher than those found by Soxhlet extraction. The average recovery of tetrachloroethylene ranged from 77 to 86 %, with an average of 82 %. The lower recoveries of tetrachloroethylene by both the methods for sand compared to H-A sand may be due to kinetics preference for tight interaction of the compound with the inorganic portion of the sample. For the native contaminated soil, similar results were obtained where the recoveries by the Microwave-assisted extraction with 1:1 (v/v) acetone:hexane solvent were slightly higher compared to those of Soxhlet method. Recovery was calculated based on total organic carbon (TOC) in the contaminated soil. TOC was determined to be 22.3 mg/g of the soil.

Study of the efficiency of Soxhlet extraction and MAE confirms their use as total extraction methods. Soxhlet is the standard extraction method used to determine the contamination level of organic compounds in soil [5]. It is, however a tedious plus solvent and sample consuming process. Many different techniques have been proposed to replace Soxhlet extraction, some recovering more than twice the amount of a compound that is

	Mean Percentage Recovery ^a (std dev)						
	SPIKED SAND			SPIKED H-A SAND		CONTAMINATED SOIL	
	Soxhlet ^b	MAE ^c		Soxhlet ^b	MAE ^c	Soxhlet ^d	MAE ^e
Tetrachloroethylene	75 (2)	77 (3)		79 (4)	86 (5)	15 (4)	18 (5)

Table 1. Average Percent Recovery of Tetrachloroethylene By Each Method From Spiked Sand, H-A Spiked Sand and Contaminated Soil

^a Percent recoveries as measured by fraction recovered of amount originally spiked onto soil or for the case of contaminated soil, amount recovered per TOC.

^b Each value represents an average of four, 24-hour mini-Soxhlet extractions with 1:1 (v/v) Acetone:Hexane.

^c Each value represents an average of five, 3-minute microwave extractions with 1:1 (v/v) Acetone:Hexane

^d Each value represents an average of four, 24-hour mini-Soxhlet extractions with 1:1 (v/v) Acetone:Hexane. Recovery was calculated based on the amount of TOC in a gram of the contaminated soil sample.

^e Each value represents an average of five, 3-minute microwave extractions with 1:1 (v/v) Acetone:Hexane. Recovery was calculated based on the amount of TOC in a gram of the contaminated soil sample.

recovered by Soxhlet extraction [6,8,9]. MAE is one such technique. In this work, a simple domestic microwave oven and an inexpensive extraction vessel were used. Although the equipment used allowed no control of pressure and temperature, good reproducibility was found for extractions of all samples studied. In addition, the recoveries were all in good agreement with Soxhlet extraction (Table 1). Using a two-sided t-test for independent samples, no statistically significant differences ($\alpha=0.05$) were found between recoveries by MAE and Soxhlet extraction for tetrachloroethylene.

The sample sizes, solvent volumes, and extraction times used for MAE in this work were generally less than those used in other MAE studies [6,10], but were sufficient for achieving good recoveries as well as reproducible results. The methods used to spike the matrices reduce the possibility of the compounds being removed from solution before binding takes place. Since the spiking solvent was evaporated rather than decanted from the solids, the low volatility of the compound means that all of the spiked compounds remained with the matrix rather than with the spiking solvent, as is the case in some spiking methods which involve removing non-adsorbed compounds immediately after spiking [11,12]. In the cases where non-adsorbed compounds are immediately washed off, there is no allowance for slow adsorption of contaminants into the matrix and only immediate adsorption is investigated. There is evidence, however, that adsorption of some contaminants, especially those migrating into the pore volume, may take place over an extended period of time [13,14].

Acknowledgements

The authors would like to thank Biochemistry Department at the University of Malaya Kuala Lumpur, Malaysia for instrumentation during the preliminary portion of this research. Technical assistance of Tan, K.L. is gratefully acknowledged

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