Extraction of Semi-Volatile Organic Compounds from Soil

Abstract

Soil is one of the most common matrices in which semi-volatile organic compounds (SVOCs) are present. The extraction of these compounds from soil can be a lengthy and tedious process. The EDGE® is a revolutionary and simple system for many kinds of extractions, including the rapid extraction of SVOCs from soil. The Q-Cup® technology combines the processes of Pressurized Fluid Extraction (PFE) and Dispersive Solid Phase Extraction (dSPE) while also being easy to assemble. The Q-Cup, with its unique open cell concept, creates a dispersive effect and promotes rapid extraction and filtration. The EDGE offers a fast, simple, and efficient extraction while adhering to EPA 3045A.

Introduction

Semi-volatile organic compounds (SVOCs) are a subgroup of Volatile Organic Compounds (VOCs) that have high molecular weights and higher boiling points than VOCs. Among these compounds are polyaromatic hydrocarbons (PAHs), phthalates, plasticizers, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Many of these compounds have been banned due to both their persistence in the environment and human toxicity. Prolonged exposure to these compounds, especially indoors, has raised public health concerns, prompting their categorization by the US EPA as hazardous air pollutants (HAPs). Compounds under this categorization can cause serious health effects, such as allergies, asthma, endocrine and thyroid disruption, reproductive toxicity, fetal and child development delays, and even cancer.

SVOCs consist of compounds with diverse chemical properties and structural features. These differences make it challenging to efficiently extract all analytes of interest with one method. Furthermore, the soil matrix from which the SVOCs are to be extracted often include multiple components, adding to the complexity of extraction. The EDGE automated solvent extraction system is able to handle these issues and effectively extract a difficult set of analytes from complex matrices with a singular, simple method.

Traditional methods, such as Soxhlet, are time consuming and use a large amount of solvent. Other automated methods often require tedious sample preparation and the assembly of complex sample holders. In comparison, the EDGE provides a new automated method that is less time consuming and uses less solvent. The EDGE sample holder, the Q-Cup, is also easier to assemble, being comprised of only two components, allowing the sample to be prepared in seconds.

Because of their persistent nature, SVOCs accumulate and concentrate in our environment due to their persistent nature. To ensure our health and safety, these compounds need to be extracted, accurately and efficiently, following governmental regulations like EPA 3545A. The EDGE complies with EPA 3545A: the extraction of water-insoluble or slightly water-soluble volatile and semi-volatile compounds in soils, clays, sediments, sludges, and waste solids. The EDGE optimizes the process, providing an extract that is filtered, cooled, and ready for analysis in under 20 minutes.

Materials and Method

Reagents

Clean clay, sodium sulfate, and Florisil were purchased from Sigma Aldrich. The sodium sulfate was baked at 400 °C in a CEM Phoenix Microwave Muffle Furnace. A BNAs in Soil CRM was purchased Sigma Aldrich. Deactivated glass wool was purchased from Restek. An SVOC standard (Cat No 31850) containing 76 compounds and a semi-volatile internal standard mix (Cat No 31206) were both purchased from Restek. ACS grade hexane and ACS grade acetone were purchased from Fisher Scientific.

Sample Preparation

For the BNAs in Soil CRM, a Q-Cup was assembled with an S1 Q-Disc stack. Into a Q-Cup was first weighed 20 grams of sample was and then 30 g of sodium sulfate on top. The sample was then mixed using a clean metal spatula. After the sample was thoroughly mixed, the spatula was wiped with a Kimwipe, and the Kimwipe was added into the Q-Cup. On top of each sample was weighed 2 g Florisil, ensuring that the entire top of the sample was covered. A Q-Screen was then inserted into the Q-Cup opening, making sure that the layer of Florisil was not disturbed. The samples were prepared in quadruplet. Each sample was extracted on the EDGE and collected in a 60 mL glass collection vial.

For the wet clay samples, a Q-Cup was assembled with a S1 Q-Disc stack. Into a secondary container was weighed 20 g of the clay sample mixed with 30 g of sodium sulfate. Half the mixture was then added to the Q-Cup and the sample was spiked with 200 µL of 100 µg/mL Semi Volatile Organic Compound spiking standard using an automated pipette for a final concentration of 20 µg. The rest of the sample was then weighed on top. On top of each sample was weighed 2 g Florisil, ensuring that the entire top of the sample was covered. A Q-Screen was then inserted into the Q-Cup opening, making sure that the layer of Florisil was not disturbed. Each sample was prepared in triplet. Each sample was extracted on the EDGE and collected in a 60 mL glass collection vial.

EDGE Method for SVOCs from Soil

Q-Disc: S1 Q-Disc Stack (C9+G1+C9 sandwich)

Cycle 1
Extraction Solvent: Hexane/Acetone (1:1)
Top Add: 15 mL
Bottom Add: 0 mL
Rinse: 0 mL
Temperature: 70 °C
Hold Time: 00:30 (mm:ss)

Cycle 2
Extraction Solvent: Hexane/Acetone (1:1)
Top Add: 15 mL
Bottom Add: 0 mL
Rinse: 0 mL
Temperature: 70 °C
Hold Time: 00:30 (mm:ss)

Cycle 3
Extraction Solvent: Hexane/Acetone (1:1)
Top Add: 15 mL
Bottom Add: 0 mL
Rinse: 0 mL
Temperature: 100 °C
Hold Time: 00:30 (mm:ss)

Cycle 4
Extraction Solvent: Hexane/Acetone (1:1)
Top Add: 15 mL
Bottom Add: 0 mL
Rinse: 0 mL
Temperature: 100 °C
Hold Time: 00:30 (mm:ss)

Wash 1
Wash Solvent: Hexane/Acetone (1:1)
Wash Volume: 30 mL
Temperature: 125 °C
Hold Time: 00:30 (mm:ss)

Wash 2
Wash Solvent: Hexane/Acetone (1:1)
Wash Volume: 30 mL
Temperature: - - -
Hold Time: - -:- - (mm:ss)

Analysis

Extracts were poured over sodium sulfate in glass funnels held in by deactivated glass wool. The sodium sulfate was then rinsed with hexane, and the extracts were evaporated to below 1 mL in a Biotage Turbovap II. Extracts were then spiked with 20 µg of internal standard, brought to volume with hexane, transferred to a GC vial, and injected on an Agilent 7890A GC with a 5975C MSD for analysis. A Phenomenex ZB-5MSplus 30 m, 0.25 mm column was used.

Results and Discussion

The EDGE successfully extracted the SVOC compounds from soil in under 20 minutes, including filtration, cooling, and system washing. The recovery data in **Table 1** (page 3) shows the CRM sample was extracted with high efficiency with most recoveries in the 70% to 120% range.

The resulting RSD values were also low (all less than 15%), indicating that the recovery data was reproducible. The recovery data in **Table 2** (page 4) shows a spiked wet clay soil. The vast majority of recoveries for the compounds was between 70% to 120% and RSD values were for the most part below 20%.

Conclusion

The extraction and determination of the presence of semi-volatile organic compounds in solid matrices are critical for monitoring the environment and subsequently human health. The EDGE provides a fast, simple, and efficient extraction compared to classic techniques. Recovery values for a variety of compounds were within acceptable ranges with low RSD values. Correct sample prep, both mixing the sample with sodium sulfate for sample dispersion as well as the use of Florisil to trap the more volatile compounds, is crucial for the extraction as well.

Table 1. Average Recovery Results and RSD Values for CRM Soil Samples

Compound	Recovery	RSD (n=4)
Phenol	67.78%	5.23%
Bis(2-chloroethyl)ether	87.94%	9.08%
2-Chlorophenol	80.11%	9.66%
2-Methylphenol	115.79%	5.86%
4-Methylphenol	139.09%	6.87%
n-Nitroso-di-n-propylamine	140.68%	9.21%
Nitrobenzene	99.37%	3.46%
Isophorone	83.08%	5.53%
2-Nitrophenol	80.29%	4.88%
2,4-Dimethylphenol	95.41%	1.64%
2,4-Dichlorophenol	96.74%	2.85%
1,2,4-Trichlorobenzene	84.87%	4.73%
Hexachlorobutadiene	88.80%	5.44%
2,4,6-Trichlorophenol	104.06%	3.61%
2,4,5-Trichlorophenol	104.92%	2.29%
2-Chloronaphthalene	91.49%	11.65%
Dimethyl phthalate	108.45%	2.26%
2,6-Dinitrotoluene	110.48%	2.28%
Acenaphthylene	93.11%	1.47%
Acenapthene	99.36%	3.08%
4-Nitrophenol	90.02%	9.38%
Dibenzofuran	100.46%	4.31%
Diethyl phthalate	103.77%	6.17%
Fluorene	97.82%	6.86%
4-Chlorophenyl-phenylether	103.00%	5.89%
4,6-Dinitro-2-methylphenol	54.74%	21.41%
Pentachlorophenol	89.19%	13.53%
Phenanthrene	112.42%	3.15%
Anthracene	118.92%	3.15%
Fluoranthene	110.02%	4.88%
Pyrene	106.42%	3.34%
Benzyl butyl phthalate	107.70%	6.04%
Benz[a]anthracene	106.07%	2.75%
Chrysene	104.31%	6.57%
Bis(2-ethylhexyl)phthalate	117.11%	5.64%
Di-n-octyl phthalate	99.39%	5.89%
Benzo[b]fluoranthene	92.60%	10.50%
Benzo[k]fluoranthene	116.85%	8.13%
Benzo[a]pyrene	100.02%	10.03%
Indol[1,2,3-cd]pyrene	115.71%	6.53%
Dibenz[a,h]anthracene	111.86%	5.66%
Benzo[g,h,i]perylene	112.56%	7.27%

Table 2. Average Recovery Results and RSD Values for Spiked Wet Clay Soils

Compound	Recovery	RSD (n=3)
n-Nitrosodimethylamine	86.92%	3.27%
Pyridine	90.56%	2.39%
Phenol	78.89%	5.85%
Aniline	87.43%	6.51%
Bis(2-chloroethyl)ether	72.80%	11.52%
2-Chlorophenol	74.40%	8.01%
1,3-Dichlorobenzene	53.10%	15.51%
1,4-Dichlorobenzene	37.01%	43.59%
Benzyl Alcohol	85.06%	6.09%
1,2-Dichlorobenzene	43.63%	48.42%
2-Methylphenol	65.61%	12.63%
2,2'-Oxybis(1-chloropropane)	70.83%	27.66%
4-Methylphenol	69.18%	8.83%
n-Nitroso-di-n-propylamine	80.92%	14.40%
Hexachloroethane	39.34%	34.66%
Nitrobenzene	71.46%	20.69%
Isophorone	86.51%	11.64%
2-Nitrophenol	76.19%	14.34%
2,4-Dimethylphenol	30.83%	11.54%
Bis(2-chloroethoxy)methane	75.37%	11.78%
2,4-Dichlorophenol	81.23%	10.65%
1,2,4-Trichlorobenzene	59.78%	21.02%
Naphthalene	74.44%	16.37%
4-Chloroaniline	77.49%	11.04%
Hexachlorobutadiene	69.46%	19.39%
4-Chloro-3-methylphenol	98.53%	8.09%
2-Methylnaphthalene	85.72%	11.80%
1-Methylnaphthalene	85.72%	11.80%
Hexachlorocyclopentadiene	84.79%	12.12%
2,4,6-Trichlorophenol	92.88%	8.14%
2,4,5-Trichlorophenol	101.43%	9.99%
2-Chloronaphthalene	86.57%	15.23%
2-Nitroaniline	96.57%	10.37%
1,4-Dinitrobenzene	94.41%	10.80%
Dimethyl phthalate	98.52%	9.44%
2,6-Dinitrotoluene	101.84%	7.47%
Acenaphthylene	76.74%	9.27%

Compound	Recovery	RSD (n=3)
1,2-Dinitrobenzene	97.03%	8.08%
3-Nitroaniline	94.03%	7.08%
Acenapthene	93.15%	8.31%
2,4-Dinitrophenol	105.27%	1.50%
4-Nitrophenol	100.28%	8.70%
Dibenzofuran	98.40%	8.69%
2,4-Dinitrotoluene	109.36%	5.02%
2,3,5,6-Tetrachlorophenol	101.88%	3.10%
2,3,4,6-Tetrachlorophenol	105.24%	6.31%
Diethyl phthalate	103.54%	4.84%
Fluorene	99.48%	7.88%
4-Chlorophenyl-phenylether	99.18%	7.93%
4-Nitroaniline	105.66%	6.14%
4,6-Dinitro-2-methylphenol	99.87%	4.32%
Diphenylamine	90.24%	3.81%
Azobenzene	100.66%	7.62%
1-Bromo-4-phenoxybenzene	101.63%	5.83%
Hexachlorobenzene	108.48%	6.97%
Pentachlorophenol	105.97%	4.14%
Phenanthrene	99.16%	3.40%
Anthracene	99.16%	3.40%
Carbazole	105.25%	1.13%
Dibutyl phthalate	106.25%	1.12%
Fluoranthene	103.34%	3.98%
Pyrene	103.34%	3.98%
Benzyl butyl phthalate	98.92%	3.71%
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Indol[1,2,3-cd]pyrene	108.34%	7.21%
Dibenz[a,h]anthracene	106.65%	2.25%
Benzo[g,h,i]perylene	102.16%	2.75%

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