Microwave 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. Microwave-assisted solvent extraction (MASE) is a proven technique that is fast, uses significantly less solvent than conventional techniques, and is cost effective. MASE is ideal for high-throughput labs dealing with hundreds of samples per day. The MARS 6™ with MARSXpress™ or MARSXpress Plus vessels combined with disposable glass liners meets the needs of high-throughput labs, allowing for a fast, clean, and user-friendly extraction process. Adhering to US EPA 3546, the MARS 6 also offers an efficient extraction of up to 40 samples simultaneously.

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. With the MARS 6 running microwave-assisted solvent extraction (MASE), a batch of 40 samples with a difficult set of analytes can be effectively extracted from complex matrices.

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. The MARS 6 is the only batch system available and uses a minimal amount of solvent. The MARSXpress or MARSXpress Plus vessels combined with disposable glass liners allows for simple and clean sample preparation.

Because of their persistent nature, SVOCs accumulate and concentrate in our environment. To ensure our health and safety, these compounds need to be extracted accurately and efficiently, following governmental regulations like US EPA 3546. This is a method for the extraction of water-insoluble or slightly water-soluble volatile and semi-volatile compounds from soils, clays, sediments, sludges, and waste solids. The MARS 6 meets the requirements of US EPA 3546 and is preprogrammed for this method.

Materials and Methods

Reagents

Clean sandy loam and sodium sulfate 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 from Sigma Aldrich. 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, 20 g of sample was weighed into a 75 mL MARSXpress vessel. For spiked samples, 10 g of clean sandy loam was weighed into a 75 mL MARSXpress vessel, 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, then an additional 10 g of clean sandy loam was weighed into the vessel. To each vessel, 25 mL of hexane/acetone (1:1) was added. The vessel was vortexed to ensure full saturation of sample with solvent. The samples were prepared in quadruplet. The vessels were added to the MARSXpress turntable and run with the US EPA 100 °C One Touch Method.

MARS 6 Method for SVOCs from Soil

Control Style: Ramp to Temperature

Stage 1
Temperature: 100 °C
Ramp Time: 15:00 (mm:ss)
Hold Time: 15:00 (mm:ss)
Power: 1800 W
Stirring: Off

Analysis

The vessels were allowed to cool. The extracts were poured over sodium sulfate in glass funnels, held in by a microfiber filter. The solid soil sample was rinsed with hexane, and the rinse was poured over the sodium sulfate, 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 MARS 6 successfully extracted the SVOCs from soil, with all samples in the same batch. 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 16%), indicating that the recovery data was reproducible. The recovery data in **Table 2** (pages 3-4) shows a spiked 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 MARS 6 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.

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

Compound	Recovery	RSD (n=4)
Phenol	68.21	10.61
Bis(2-chloroethyl)ether	77.07	4.37
2-Chlorophenol	75.37	5.25
2-Methylphenol	99.07	11.34
3+4 Methylphenol	97.67	13.67
n-Nitroso-di-n-propylamine	99.86	10.47
Nitrobenzene	102.66	9.12
Isophorone	93.37	9.12
2-Nitrophenol	111.52	8.58
2,4-Dimethylphenol	119.40	8.38
2,4-Dichlorophenol	107.20	10.64
1,2,4-Trichlorobenzene	108.11	8.13
Hexachlorobutadiene	84.20	6.31
2,4,6-Trichlorophenol	86.62	10.93
2,4,5-Trichlorophenol	84.47	10.00
2-Chloronaphthalene	103.77	8.53
Dimethyl phthalate	81.62	13.14
2,6-Dinitrotoluene	84.96	10.98
Acenaphthylene	77.49	10.94
Acenapthene	82.60	7.74
Dibenzofuran	82.16	7.91
Diethyl phthalate	83.18	10.10
Fluorene	83.41	8.41
4-Chlorophenyl-phenylether	87.64	8.25
Phenanthrene	86.06	10.93
Anthracene	91.03	10.93
Fluoranthene	78.79	10.44
Pyrene	78.38	11.24
Benzyl butyl phthalate	78.52	15.39
Benz[a]anthracene	77.47	10.22
Chrysene	92.36	12.62
Bis(2-ethylhexyl)phthalate	81.10	11.69
Di-n-octyl phthalate	78.75	12.99
Benzo[b]fluoranthene	90.97	4.71
Benzo[k]fluoranthene	111.29	5.06
Benzo[a]pyrene	88.14	10.76
Indol[1,2,3-cd]pyrene	103.83	13.96
Dibenz[a,h]anthracene	115.14	10.07
Benzo[g,h,i]perylene	104.17	8.28

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

Compound	Recovery	RSD (n=3)
N-Nitrosodimethylamine	124.96	12.72
Aniline	126.48	32.27
1,4-Dichlorobenzene	125.30	18.41
1,2-Dichlorobenzene	121.60	17.41
2-Methylphenol	100.98	30.40
2,2'-Oxybis(1-chloropropane)	124.66	9.61
4-Methylphenol	102.97	28.47
N-Nitroso-di-n-propylamine	106.31	24.16
Hexachloroethane	118.46	10.40
Nitrobenzene	104.30	17.29
Isophorone	134.43	26.81
2-Nitrophenol	105.50	19.38
2,4-Dimethylphenol	93.10	22.37
Bis(2-chloroethoxy)methane	108.33	15.49
2,4-Dichlorophenol	98.20	24.03
1,2,4-Trichlorobenzene	115.52	10.66
Naphthalene	122.19	6.92
4-Chloroaniline	88.84	23.20
Hexachlorobutadiene	119.98	1.97
4-Chloro-3-methylphenol	89.51	16.72
2-Methylnaphthalene	106.57	5.68
1-Methylnaphthalene	106.44	5.66
Hexachlorocyclopentadiene	109.99	9.12
2,4,6-Trichlorophenol	91.14	19.59
2,4,5-Trichlorophenol	90.81	21.93
2-Chloronaphthalene	105.76	7.40
2-Nitroaniline	83.13	19.47
1,4-Dinitrobenzene	85.41	14.23
Dimethyl phthalate	94.43	22.46
2,6-Dinitrotoluene	100.03	16.40
Acenaphthylene	106.67	9.35
1,2-Dinitrobenzene	81.78	25.08
3-Nitroaniline	77.20	23.64
Acenapthene	114.14	8.11
4-Nitrophenol	102.70	13.21
Dibenzofuran	108.13	9.02
2,4-Dinitrotoluene	98.020	16.04
2,3,5,6-Tetrachlorophenol	73.82	40.48
2,3,4,6-Tetrachlorophenol	78.60	34.79
Diethyl phthalate	100.45	12.29
Fluorene	107.59	9.29
4-Chlorophenyl-phenylether	110.46	9.05

Table 2. Average Recovery Results and RSD Values for Spiked Soils (continued)

Compound	Recovery	RSD (n=3)
4-Nitroaniline	73.34	14.02
4,6-Dinitro-2-methylphenol	71.52	5.70
Diphenylamine	98.30	13.11
Azobenzene	105.01	9.85
1-Bromo-4-phenoxybenzene	102.77	7.26
Hexachlorobenzene	109.95	6.83
Phenanthrene	125.40	7.92
Anthracene	125.40	7.92
Carbazole	102.91	16.72
Fluoranthene	122.77	10.37
Pyrene	116.23	7.32
Benzyl butyl phthalate	111.46	12.75
Benz[a]anthracene	107.71	10.21
Di-n-octyl phthalate	123.96	7.14
Chrysene	130.31	5.11
Benzo[b]fluoranthene	113.27	11.03
Benzo[k]fluoranthene	111.15	9.45
Benzo[a]pyrene	110.50	10.86
Indol[1,2,3-cd]pyrene	116.53	6.61
Dibenz[a,h]anthracene	102.78	12.14
Benzo[g,h,i]perylene	109.67	10.94

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