US EPA 3546

This paper will discuss the use of Ethos X Microwave Extraction System utilizing fastEX24 rotor with disposable glass vials to extract organic pollutants from certified soils during a recovery study following US EPA Method 3546. Samples were analyzed using GC-MS

Introduction

The United States Environmental Protection Agency's (USEPA's) Test Methods for Evaluating Solid Waste (SW846) provides a comprehensive source of information on sampling, sample preparation, analysis, and reporting. US EPA 3546 is a Microwave-Assisted Solvent Extraction (MASE) procedure for extracting water insoluble or slightly water soluble organic compounds such as organochlorine pesticides, semivolatile organics, PAHs, PCBs, phenoxyacid herbicides, phenols, dioxins, and furans from soils, clays, sediments, sludges, and solid waste. This method was formally included in SW846 in 2008 (1) and most of these compounds have been identified by the US EPA as priority pollutants.

MASE results in a rapid sample preparation technique that enables extractions with reduced amounts of solvents while working at higher temperatures and pressures. The process consist in a partitioning of the compounds of interest from the sample matrix into the solvent within a closed vessel. This accelerates the extraction process, yielding results equivalent to the standard Soxhlet method, but in a fraction of the time and using significantly less solvent.

Milestone's new Ethos X benchtop microwave extraction system offers the ability to extract up to 24 samples simultaneously. With the new fastEX 24 rotor, Ethos X is fully compliant with US EPA 3546 (100-115 °C and 50-150 psi). In addition, disposable glass vials can accommodate sample up to 30 grams of sample if needed, thereby improving the limit of quantitation (LOQ) for analysis. This exceeds by far both the throughput and sample size capabilities of all the other automated techniques, such as pressurized fluid extraction. MASE also uses far less solvent than conventional Soxhlet extractions. This combination of performance and reduced solvent usage provides for the lowest cost per test of any technique available. Today, is possible to process up to 30g of sample thanks to the introduction by Milestone of the largest ever 145 mL weflon vessel in combination with the largest ever 100 mL disposable glass vials that fits inside the new fastEX 24 vessel. This vial improves productivity by providing inexpensive, disposable glass tubes that eliminate the need to clean vessels between batches.

The synergy between the weflon construction and the contact less temperature control in all positions ensure a perfect temperature uniformity and make fastEX24 a unique and innovative solution for the extraction of contaminants from soils, providing unmatched ease of use and low running costs. MASE has definitely become the preferred technique used by the most analytical laboratories for priority pollutants.

Experimental

Instrument

- Milestone Ethos X microwave system equipped with fastEX-24 extraction rotor
- 100 mL disposable glass vials (PN GB00122)
- Gas chromatograph with Mass Spectrometer detector (GC-MS)
- Analytical balance
- Vials for collection of extracts
- Glass funnels for filtration
- Glass fiber filters

Standard and reagents

Pesticide grade or grade solvents and chemicals must be used in all tests. Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentration of interest. The choice of extraction solvent will depend on the analytes of interest. Generally the most applied solvent mixtures are acetone-hexane and acetone methylene chloride as recommended in the EPA analytical methods.

Table 1. Recommended solvents and EPA analytical methods by analyte of interest.

Analyte	EPA analytical method	Solvent mixture
Semivolatile Organics	8270	1:1 acetone –hexane or methylene chloride
PCBs	8082	1:1 acetone –hexane or methylene chloride
PAHs	8270, 8100	1:1 acetone –hexane or methylene chloride
Phenols	8151	1:1 acetone –hexane and phosphate buffer
Chlorinated Pesticides	8081	1:1 acetone –hexane or methylene chloride
Organophosphorus pesticides	8141	1:1 acetone –hexane and phosphate buffer
Chlorinated herbicides	8141	1:1 acetone –hexane or methylene chloride
Dioxins and Furans	-	1:1 acetone –hexane or methylene chloride

Sodium sulfate anhydrous, silica gel and glass wool or paper filter were used in the work up procedure. According to the analytical method surrogate and internal standard could be used.

Sample information

The sandy loam soil standard reference material LGC6115 was used for the determination of PAHs and PCBs (2).
The certified standard reference mineral oil contaminated sediment sample BAM-U015b was used for the determination of TPH (3).

Analytical Procedure

Samples, wet or dried and ground, were weighed directly into the 100-mL extraction disposable glass vials. An aliquot of the surrogate solution were added to the samples just prior to solvent addition then, the glass vials were closed. According to the moisture content, the best suitable built-in method were choose. The extraction procedure so described follows the detailed method provided by U.S. EPA SW-846 Method 3546.

Table 2. Suggested solvent volumes according to the used sample amounts

Sample amount (g)	Solvent mixture (mL)
Up to 10	25
10-20	35
20-30	50

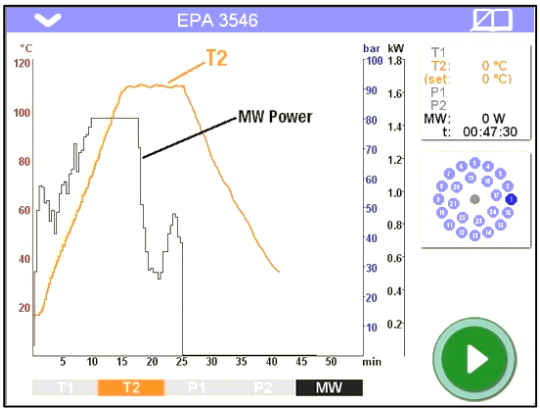

Table 3. Microwave Program

Step	Time (min)	Power (W)	Temperature (°C)
1	15	up to 1600*	110
2	10	up to 1600*	110

**The power applied depends on the moisture content. Dedicated methods are pre-loaded in the ETHOS X software according to the moisture content.*

After the extraction, samples were filtered on glass fiber filters and sodium sulfate anhydrous and the vials were rinsed with additional solvent aliquots. Extracts and rinsates were collected together.

Quantification

PCBs and **PAHs** analyses of the soil extract were performed according to the following method. Injection was through a splitless injector in a GC-MS equipped with VF-17-MS 30 m × 0.25 mm i.d. capillary columns with 5 m guard column. The injector was maintained at 280 °C. The injection was 2µL at 2mL/min flow rate. The oven was hold at 80°C for 2 min, from 80-300°C at 20°C/min than hold for 29 min at 300°C. The detector worked with electron impact chemical ionization mass spectrometer.

TPHs analyses of the soil extract were performed according to the UNI EN 16703 method. Injection was through on column injector in a GC-FID equipped with Select Mineral Oil 15 m × 320 µm i.d. (film 0.1 µm) columns. The injector was maintained at 320 °C. The injection was 1µL with 2mL/min flow rate. The oven was hold at 70°C for 2 min, from, 70-320°C at 30°C/min. The FID detector were programmed at flow rates of 400 mL/min air and 30 mL/min H_2, make up 30mL/min He.

Results and Discussion

Results from extractions of sandy loam soil and sediment sample are shown in Table 4 through 9. The tables show the recovery and the RDSs (%) for PCBs, PAHs and TPH content of these matrices. Recovery for all compounds are in the range 70-120% of the certified standard reference material.
The results demonstrate the efficiency of the Ethos X as sample preparation method for the determination of contaminants. Ethos X provides extracts with the lowest solvent usage and significant time compared to all the other extraction technique.

Table 4. PCBs recovery from 1g sandy loam soil standard reference material (LGC6115)(n=4).

PCB Cogener	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
PCB 101	93	74	80	1.75
PCB 118	116	86	74	4.94
PCB 138	16	14	88	0.2
PCB 153	19	17	89	3.2
PCB 180	9.6	10	104	2.6

Table 5. Semivolatile organics, TPH recovery from 1g certified standard reference mineral oil contaminated sediment sample (BAM-U015b) (n=4).

Analyte	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
TPH	920 ± 100	841.8	91.5	2.4

Table 6. PAHs recovery from 1g sandy loam soil standard reference material (LGC6115) (n=4).

Analyte	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
Phenanthrene	178 ± 6	200.72	113	4.52
Fluoranthene	312 ± 7	297.29	95	5.41
Benz[a]anthracene	36 ± 1	33.40	93	2.09
Benzo[a]pyrene	0.13 ± 0.02	0.16	123	11.5
Benzo[ghi]perylene	0.33 ± 0.06	0.25	76	0.3

Table 7. Recovery of TPH from solid waste sample (1g) – Ethos X compared to Soxhlet extraction (n=4).

Analyte	Soxhlet (mg/kg)	Ethos X (Recovery % of Soxhlet)	RSD (%)
TPH	11354 ± 122	111	5.2

Table 8. Recovery of PCBs from solid waste sample (1g) – Ethos X compared to Soxhlet (n=4).

Analyte	Soxhlet (mg/kg)	Ethos X (Recovery % of Soxhlet)	RSD (%)
PCB 28	4.09	88	5.2
PCB 52	3.70	88	4.8
PCB 95	2.46	79	6.2
PCB 99	1.40	73	3.1
PCB 101	3.18	72	2.6
PCB 105	1.22	90	6.4
PCB 114	0.07	85	7.3
PCB 118	2.68	79	2.0
PCB 123	0.07	114	5.6
PCB 126	0.16	118	4.2
PCB 128	0.55	82	3.4
PCB 138	1.79	80	8.3
PCB 146	0.25	116	6.2
PCB 151	0.17	105	7.4
PCB 153	1.46	90	6.1
PCB 156	0.29	110	7.9
PCB 157	0.10	100	6.5
PCB 169	0.45	104	3.1
PCB 170	0.41	78	2.2
PCB 180	0.36	81	7.7

PCB 183	0.20	80	2.3
PCB 187	0.35	100	5.3
PCB 189	0.21	114	4.7
PCB 77+149	2.37	71	4.9
PCB 81+110	7.03	76	6.1

Table 9. Recovery (n=4) of PCDD and PCDF from sandy soil standard reference material BCR-529 (2g).

Analyte	Certified value (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
2,3,7,8-TCDD	4500±0.6	4236	94	3.4
1,2,3,7,8-PeCDD	440±0.05	515	117	2.8
1,2,3,4,7,8-HxCDD	1220±0.21	1298	106	3.1
1,2,3,6,7,8-HxCDD	5400±0.9	4610	85	2.1
1,2,3,7,8,9-HxCDD	3000±0.4	2522	84	1.9
2,3,7,8-TCDF	78±0.013	75	96	2.7
1,2,3,7,8-PeCDF	145±0.028	116	80	3.5
2,3,4,7,8-PeCDF	360±0.07	329	91	2.6
1,2,3,4,7,8-HxCDF	3400±0.5	3402	100	1.9
1,2,3,6,7,8-HxCDF	1090±0.15	1082	99	3.8
1,2,3,7,8,9-HxCDF	22±0.010	18	82	3.6
2,3,4,6,7,8-HxCDF	370±0.05	445	120	2.2

Conclusions

The ETHOS X enables simultaneous solvent extraction of up to 24 samples (from weighing to filtration steps) in only 40 minutes. This in turns means that is able to extract over 200 samples in 8-hour workday. Contamination, memory effects, and cleaning are completely eliminated due to the use of disposable glass vials. The use of contactless temperature control ensures high reproducibility and full recovery of the target analytes for full compliance with EPA 3546. Moreover thanks to the unique design, ETHOS X ensures reliable extraction also on difficult samples such as solid waste. The ETHOS X with all its unique features fully addresses the need of environmental laboratories in terms of productivity, ease of use, running costs, and extraction quality.

References

(1) Federal Register, Vol. 73, No. 2, Thursday, 3 January 2008, Notices, pages 486489.
(2) https://www.lgcstandards.com/DE/en/Soil-PCBs-and-PAHs/p/LGC6115#
(3) https://www.lgcstandards.com/DE/en/Mineral-oil-contaminated-sediment/p/BAM-U015B