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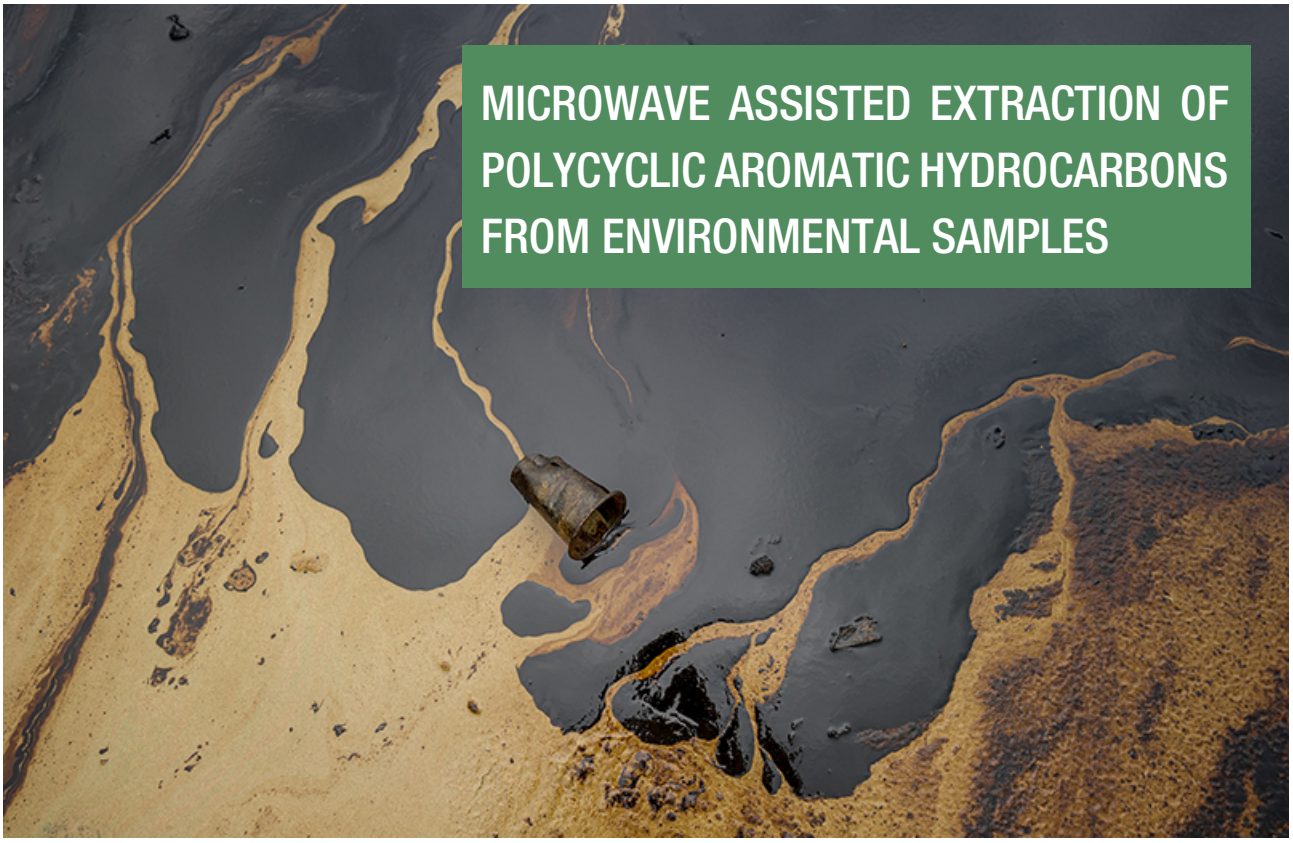

MICROWAVE ASSISTED EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ENVIRONMENTAL SAMPLES

Polycyclic aromatic hydrocarbons (PAHs) are dangerous molecules for the human health and several governments require their analysis in environmental samples. Microwave assisted solvent extraction is a well-established sample preparation technique applied in several official methods. Milestone's ETHOS X with fastEX-24 eT rotor was used in this study to prove its efficacy in the extraction of PAHs from environmental matrices.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants, widely distributed in soils, sediments, wastes, groundwater, and the atmosphere, they are primarily generated during the incomplete combustion of organic materials (e.g. coal, oil, petrol, and wood).

Therefore, anthropogenic activities are the primary sources of PAHs such as residential heating, coal gasification and liquefying plants, coke and aluminum production, petroleum refineries and motor vehicle exhaust just to mention a few.

PAHs are highly lipid soluble and thus readily absorbed from the gastrointestinal tract of mammals. Most of them are toxic, mutagenic, and/or carcinogenic properties[1].

The U.S. Environmental Protection Agency (EPA) have listed 16 priority PAHs as priority pollutants and eight of that are considered to be possible carcinogens.

EPA 3546[2] outlines the procedure for extracting water insoluble or slightly water-soluble organic compounds from soils, clays, sediments, sludges, and solid wastes.

EPA 3546 is a specific method for Microwave Assisted Solvent Extraction (MASE), a well-established sample preparation technique that enables extractions with reduced solvent volume and time. This application note represents a guideline for the extraction of the priority polycyclic aromatic hydrocarbons from both standard reference materials and spiked materials using the official method EPA 3546.

EXPERIMENTAL

EQUIPMENT

- Milestone ETHOS X.
- fastEX-24 eT rotor. [3]
- 100-mL disposable glass vials.
- SFS-24 (Simultaneous Filtration System).
- GC-MS.

Figure 1 – Milestone ETHOS X with fastex-24 eT (left) and SFS-24 filtration system (right).

STANDARD AND REAGENTS

Standards, surrogates and internal standard were purchased by Sigma Aldrich. Grade solvent pesticide were used. Sodium sulfate anhydrous, silica gel (activated for at least 16 h at 130°C) and glass wool or paper filter were used in the clean-up procedure. According to the analytical method EPA 8270e[4], internal surrogates and standards were used.

Analyte	CAS-No
Naphthalene-D8	1146-65-2
Acenaphthylene-D8	93951-97-4
Acenaphthene-D10	15067-26-2
Phenanthrene-D10	1517-22-2
Pyrene-D10	1718-52-1
Benzo[a]pyrene-D12	63466-71-7
Perylene-D12	1520-96-3

Table 1 - Internal Standard Solution

Analyte	CAS-No
Naphthalene	91-20-3
Acenaphthylene	208-96-8
Acenaphthene	83-32-9
Fluorene	86-73-7
Phenanthrene	5801-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benzo(a)anthracene	56-55-3
Chrysene	219-01-9
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8
Dibenzo(a,h)anthracene	53-70-3
Benzo(ghi)perylene	191-24-2
Indeno(1,2,3-cd)pyrene	193-39-5

Table 2 - PAHs Stock solution

SAMPLES

The sandy loam soil LGC6115 and harbour sediment BCR 535 standard reference materials were used for the determination of PAHs. For PAHs not included in the certified materials a spiking stock solution on blank soil was used.

SAMPLE PREPARATION

The samples were collected and stored in accordance with the requirements of EPA 3546.
Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly,

especially composited samples. Grind or reduce the particle size of the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole.

Directly weigh ground samples into the 100 mL disposable glass vials of the fastEX-24 eT rotor. Add 30 ml of acetone-hexane (1:1) solvent mixture.

Add an aliquot of the internal standard solution to the samples just prior to solvent addition, then close the glass vial (automatic capping tool available).

EXTRACTION PROCESS AND CLEAN UP

According to the moisture content, the proper built-in method was selected.

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

Table 3- Microwave Program

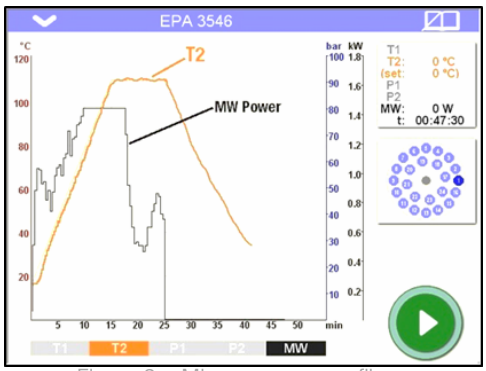

Figure 2 – Microwave run profile

After the extraction, samples were filtered with SFS-24, Milestone simultaneous filtration system using sodium sulfate anhydrous. The vials were rinsed with additional solvent aliquots. SFS-24 allows to filter 24 samples simultaneously with different types of filters available. Extracts and rinse solution were collected together. The extract was subsequently concentrated with nitrogen flow.

If purification is not required, concentrate directly to 0.5 ml and add the suitable amount of surrogate standard solution. If purification is needed, concentrate the extract directly to 2 ml. Purify the solution according to the method (EPA 3611, EPA 3630,EPA 3640). Finally, the extracts obtained by ETHOS X were concentrated for analysis.

ANALITICAL CONDITIONS

A GC-MS equipped with a split-splitless injector, autosampler and mass detector were used. Sample injection volume was 1 µl. A 30 m x 0.25 x 0.25 RXI 5MS Capillary column (Restek) was used for the analyses. The injector was maintained at 290°C and the transfer line at 300°C. A five steps ramp oven program was used:

Rate (°C/min)	Temperature (°C)	Plateaus (min)
20	60	1
50	140	0.5
10	200	0.5
5	260	10
25	300	12

Table 4 – GC oven program

Helium was used as the carrier gas at a linearity velocity of approximately 45 cm/s.

RESULTS AND DISCUSSION

Results from extractions of sandy loam soil LGC6115 and harbour sediment BCR 535 standard reference materials are shown in Tables 5 and 6.
Recovery for all compounds are in the range 70-120% of the certified reference material.

Analyte	Certified Value (mg/kg)	ETHOS X (mg/kg)	Recovery (%)	RSD (%)
Pyrene	2.52	2.16	85.7	4.2
Benzo(a)anthracene	1.54	1.42	92.2	5.1
Benzo(b)fluoranthene	2.29	2.32	101.3	3.5
Benzo(k)fluoranthene	1.09	1.02	93.6	6.1
Benzo(a)pyrene	1.16	0.92	79.3	2.3
Benzo(e)pyrene	1.86	1.66	89.2	5.9
Indeno(1.2.3-cd)pyrene	1.56	1.49	95.5	4.3

Table 5 - PAHs recovery from Fresh Harbor Sediment BCR 535 (1g) (n=4).

Analyte	Certified Value (mg/kg)	ETHOS X (mg/kg)	Recovery (%)	RSD (%)
Phenanthrene	178	200.72	112.8	4.52
Fluoranthene	312	297.29	95.3	5.41
Benzo(a)anthracene	36	33.40	92.8	2.09
Benzo(a)pyrene	0.13	0.15	115.4	11.5
Benzo(ghi)perylene	0.33	0.25	75.8	0.3

Table 6 - PAHs recovery from Sandy loam soil LGC6115 (1 g) (n=4).

Additionally, a PAHs mixture was spiked to a blank soil in order to test the performance of the fastEX24 eT on a wider list of compounds (Table 7).

Analyte	Spike concentration (mg/kg)	ETHOS X (mg/kg)	Recovery (%)	RSD (%)
Naphthalene	1	0.811	81.1	3.9
Acenaphthylene	1	0.777	77.7	2.9
Acenaphthene	1	0.747	74.7	3.6
Fluorene	1	0.867	86.8	2.8
Phenanthrene	1	0.773	77.3	3.7
Anthracene	1	0.79	79	4.9
Fluoranthene	1	0.815	81.5	3.2
Pyrene	1	0.751	75.1	3.8

Benzo(a)anthracene	1	0.781	78.1	7.6
Chrysene	1	0.719	71.9	3.7
Benzo(b)fluoranthene	1	1.003	100.3	5.2
Benzo(k)fluoranthene	1	1.005	100.5	3.5
Benzo(a)pyrene	1	0.772	77.2	2.8
Dibenzo(a.h)anthracene	1	0.892	89.2	4.7
Benzo(ghi)perylene	1	0.974	97.4	2.2
Indeno(1.2.3-cd)pyrene	1	0.872	87.2	6.2

Table 7 - PAHs recovery from Spike solution (n=4)

CONCLUSION

The results demonstrate the efficiency of the ETHOS X with fastEX-24 eT rotor for the PAHs extraction from environmental matrices. High recovery rate even for the most volatile compounds showed the great extraction efficiency. The fastEX-24 eT enables simultaneous solvent extraction of up to 24 samples in only 40 minutes (cooling step included). In turns, this 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 Official Methods.

Thanks to the unique design, fastEX-24 eT is easily applied to even more challenging matrices such as solid wastes and plastics. ETHOS X provides extracts with the lowest solvent usage and significant time saving compared to all the other extraction techniques.

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- Goldman R. Enewold L. Pellizzari E. Beach JB. Bowman ED. Krishnan SS. Shields PG. Smoking increases carcinogenic polycyclic aromatic hydrocarbons in human lung tissue. Cancer Res. 2001;61:6367–6371
2- EPA 3546- Microwave extraction https://www.epa.gov/sites/production/files/2015-12/documents/3546.pdf
3- ETHOS X and fastEX-24 eT https://www.milestonesrl.com/products/microwave-extraction/ethos-x-for-environmental
4- EPA 8270 E – Semivolatile organic compound GC-MS https://www.epa.gov/esam/epa-method-8270e-sw-846-semivolatile-organic-compounds-gas-chromatographymass-spectrometry-gc

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At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology to extraction, ashing and synthesis. Since 1988 Milestone has helped chemists in their work to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.

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