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MICROWAVE ASSISTED EXTRACTION OF PHTHALATES FROM ENVIRONMENTAL SAMPLES

Phthalates are released in the environment during the dismantling of electronic waste. As they are dangerous molecules for the human health, their analysis in environmental samples is of important value. Microwave assisted solvent extraction is a well-established sample preparation technique applied in several official methods. Since phthalates can be released in the sample from laboratory plastics, the use of proper laboratory equipment is fundamental. Milestone's ETHOS X equipped with fastEX-24 eT rotor and disposable glass vial was used in this study to prove its efficacy in the extraction of phthalates from environmental samples

INTRODUCTION

Phthalate esters (PAEs) comprise a class of synthetic chemicals commonly used in numerous consumer products, such as floorings, food packages, personal care products, and electronic items. They are mainly used as plasticizers, substances added to plastics to modify their physical properties such as flexibility, transparency, etc. Phthalate esters can be released into the environment during the dismantling of electronic waste (e-waste); PAEs have been detected in indoor dust, air, food, and drinking water.[1]

PAEs are endocrine-disrupting chemicals and therefore present considerable risk to human health.[2] Adverse effects on the respiratory system (such as bronchial obstruction and asthma), immune system, and neuropsychological development have also been observed.[3]

EPA 3546[4] 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 PAEs from both standard reference materials and spiked materials using the official method EPA 3546.

EXPERIMENTAL

EQUIPMENT

- Milestone's ETHOS X.
- fastEX-24 eT rotor. [5]
- 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 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[6], internal surrogates and standards were used.

Analyte	CAS-No
Bis(2-ethylhexyl) phthalate	85-68-7
Benzyl butyl phthalate	117-81-7
Dibutyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Di-n-octyl phthalate	117-84-0

Table 1- Phthalates Standard Solution

SAMPLES

The CRM47643 certified reference material were used as spiking stock solution on blank waste.

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 otherwise 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.

Ground samples, wet or dried, were weighed directly into the 100 mL disposable glass vials of the fastEX-24 eT rotor. 30 ml of acetone-hexane (1:1) solvent mixture was used. An aliquot of the internal standard solution was added to the samples just prior to solvent addition then the glass vials were closed (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 2 - Microwave Program

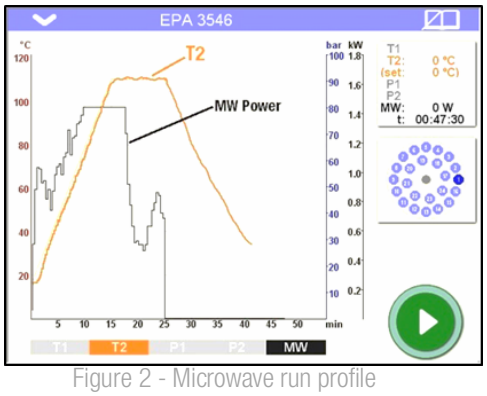

Figure 2 - Microwave run profile

After the extraction, samples were filtered with milestone SFS-24 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 until 0.5 ml and add the appropriate surrogate standard solution to achieve the surrogate standard concentration. If purification is necessary (EPA 3610, 3620, 3640), concentrate the extract directly until 2 ml. Purify the solution according to the method. 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 three steps ramp oven program was used:

Rate (°C/min)	Temperature (°C)	Plateaus (min)
20	60	1
30	120	0.5
15	300	5

Table 3 – GC oven program

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

I RESULTS AND DISCUSSION

Analyst, in phthalates analysis, generally have to pay attention on the possible contamination introduced during the entire analytical process from laboratory plastics material. Working with fastEX-24 eT, this issue can be easily overcome thanks to the use of disposable glass vials and PTFE caps. In order to proof the validity of the fastEX-24 eT rotor for this purpose, a blank test, carried out using the same microwave method and the same solvent mixture of the official method, was performed prior the sample extraction.
As reported in table 4, the material blank values were very low, enabling the fastEX-24 eT for this application.

Analyte	ETHOS X (mg/kg)
Bis(2-ethylhexyl) phthalate	< 0.01
Benzyl butyl phthalate	< 0.01
Dibutyl phthalate	< 0.01
Diethyl phthalate	< 0.01
Dimethyl phthalate	< 0.01
Di-n-octyl phthalate	< 0.01

Table 4 – fastEX-24 eT Blank test

Results from the certified reference material CRM47643 (Certified Value: 2 mg/kg) are showed in the table 5. Recovery for all compounds are in the range 70-120% of the certified standard reference material.

Analyte	ETHOS X (mg/kg)	Recovery (%)	RSD (%)
Bis(2-ethylhexyl) phthalate	1.9	95	2.1
Benzyl butyl phthalate	1.85	92	3.3
Dibutyl phthalate	1.88	94	1.9
Diethyl phthalate	1.78	89	2.0
Dimethyl phthalate	1.78	89	3.1
Di-n-octyl phthalate	1.79	89	4.5

Table 5 - PAEs recovery from CRM47643 (Certified Value: 2 mg/kg) (n=4).

CONCLUSION

The results demonstrate the efficiency of the ETHOS X with fastEX-24 eT rotor for the Phthalate esters extraction. Moreover, the specific fastEX-24 eT construction ensures the extraction without sample contamination thanks to the use of disposable glass vials.

The fastEX-24 eT enables simultaneous solvent extraction of up to 24 samples in only 40 minutes. In turns, his means that is able to extract over 200 samples in 8-hour workday.

Contamination, memory effects, and cleaning are completely eliminated thanks to the use of disposable glass vials. The use of contactless temperature control ensures high reproducibility and full recovery of the target analytes, in full compliance with Official Methods.

Thanks to the unique design, fastEX-24 eT is easily applied also on difficult samples 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.

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ABOUT MILESTONE

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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