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Microwave assisted extraction of pesticides from environmental samples

This report was extracted from the Milestone Application Report ETHOS X - Pesticides - EPA 3546 Method

Pesticides are extensively used in modern agriculture, which could lead to serious consequences due to their biomagnification and persistent nature. 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 equipped with fastEX-24 eT rotor was used in this study to prove its efficacy in the extraction of pesticides from environmental matrices

INTRODUCTION

Pesticides are pivotal chemical compounds for the modern agriculture production, used to control pests' diffusion. Depending on their target function, pesticides are used to treat insects, rodents, fungi and unwanted plants (weeds). For example, since 1940s, organochlorine pesticides and organophosphate pesticides are used extensively not only in agriculture but also for mosquito control.

The action mechanism of these chemicals is mostly designed to disturb the physiological activities of the target organism, leading to dysfunction and reduced vitality. Despite their fundamental use in the modern agriculture, these molecules can cause neurological damage, endocrine disorders, and have acute and chronic health effects on human[1]. Moreover, some of these chemicals belong to the class of persistent organic pollutants (POPs) with high persistence in the environment[2].

EPA 3546[3] 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 pesticides from both standard reference materials and spiked materials using the official method EPA 3546.

EXPERIMENTAL

Equipment

- Milestone's ETHOS X.
- fastEX-24 eT rotor.[4]
- 100-mL disposable glass vials.
- SFS-24 (Simultaneous Filtration System).
- GC-MS/MS
- HPLC MS/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[5], internal surrogates and standards were used.

Table 1. Pesticides Stock solution

Analyte	CAS-No	Analyte	CAS-No
α-BHC	319-84-6	Endosulfan Sulfate	1031-07-8
γ-BHC	58-89-9	Endrin aldeide	7421-93-4
β-BHC	319-85-7	Endrin ketone	01/10/7378
δ-BHC	319-86-8	Heptachlor Epoxide	1024-57-3
Aldrin	309-00-2	Methoxychlor	72-43-5
Heptachlor	76-44-8	Demeton	8065-48-3
γ-\α-chlordane	5103-74-2\57-74-9	Dimethoate	60-51-5
α-Endosulfan	1031-07-8	Malathion	121-75-5
4,4'-DDE	72-55-9	Parathion	56-38-2
Dieldrin	60-57-1	Parathion-methyl	298-00-0
Endrin	72-20-8	Mevinphos	7786-34-7
β-Endosulfan II	33213-65-9	Phorate	298-02-2
4,4'-DDD	72-54-8	Fenitrothion	122-14-5
2,4'-DDT	789-02-6	Isocarbophos	24353-61-5
4,4'-DDT	50-29-3	Methidathion	950-37-8
Mirex	2385-85-5	Toxaphene	8001-35-2
Dichlorvos	62-73-7		

Table 2. Internal Standard Solution

Analyte	CAS-No
Isoproturon-d6	217487-17-7
Biphenyl-d10	1486-01-7
Atrazina-d5	163165-75-1
Phenanthrene-d10	1517-22-2
Pirimicarb-d6	1015854-66-6
PCB 138	35065-28-2
Triphenylphosfate	115-86-6

Samples

The clay loam 1 - CRM847 certified reference material were used for the determination of pesticides. For pesticides 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 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 extraction disposable glass vials of the fastEX-24 eT rotor. 30 mL of acetone-hexane (1:1) was used as extraction mixture. 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).

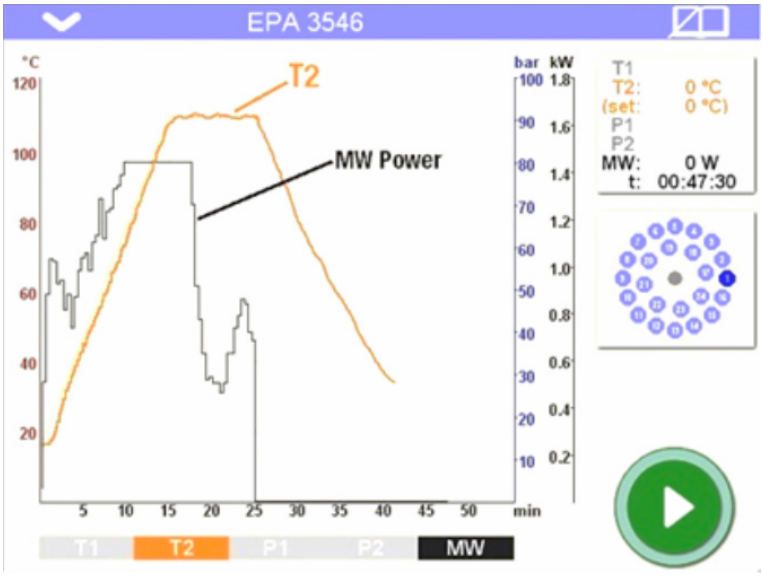

Figure 2. Microwave run profile.

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, concentrate the extract directly until 2 mL. Purify the solution according to the method (EPA 3610, 3620, 3630, 3640, 3660). Finally, the extracts obtained by ETHOS X were concentrated for analysis.

Analitical conditions

Based on the pesticide compositions both GCMS/MS and HPLC MS/MS with triple quadrupole were used.

GC-MS/MS is equipped with a split-splitless injector, autosampler and triple quadrupole mass spectrometer. 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. A five steps ramp oven program was used:

Table 4. GC-MS/MS oven program

Rate (°C/min)	Temperature (°C)	Plateaus (min)
20	50	2
30	150	0
7	260	0
20	290	11

Helium was used as the carrier gas at a linearity velocity of approximately 65 cm/s.

HPLC MS/MS was used to ensure the recovery data and to better quantify some compounds. An oven temperature of 40 °C is used with an injection volume of 0.25 µL.

Mobile phase:

- Water 0,1% formic acid 5 mM ammonium formate.
- Methanol 0,1% formic acid 5 mM ammonium formate.

Table 5. HPLC-MS/MS gradient method

Time (min)	Water (%)	Methanol (%)
0.2	95	5
11	0	100
13	0	100
13.1	95	5

RESULTS AND DISCUSSION

Results from extractions of Clay loam 1 - CRM847 are shown in Table 6. Recovery for all compounds is in the range 70-120% of the certified standard reference material.

Table 6. Pesticides recovery from Clay loam 1 - CRM847 (1g) (n=4)

Analyte	Certified value (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
δ-BHC	138	128.89	93.4	8.7
α-BHC	221	188.95	85.5	7.0
β-BHC	295	342.2	116	2.2
α-Chlordane	309	330.63	107	3.3
γ-Chlordane	171	182.28	106.6	2.4
4.4'-DDD	120	107.28	89.4	3.1
4-4'-DDE	315	290.74	92.3	3.3
4-4'-DDT	92.1	84.27	91.5	11.5
Dieldrin	53.3	54.79	102.8	9.6
Endosulfan I	211	162.25	76.9	4.8
Endosulfan II	225	160.65	71.4	7.9
Endosulfan Sulfate	159	159.63	100.4	4.0
Endrin Ketone	170	139.57	82.1	6.3
Endrin	162	156.81	96.8	4.4
Heptachlor epoxide	127	119.25	93.9	3.7
Methoxychlor	290	260.13	89.7	6.6

Additionally, a pesticide mixture was spiked to a blank soil in order to test the performance of the fastEX-24 eT on a wider list of pesticides (Table 7).

Table 7. Pesticides recovery from Spike solution (n=4)

Analyte	Spike concentration (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
α-BHC	50	52.00	104.0	4.6
γ-BHC	50	50.00	100.0	8.1
β-BHC	50	60.00	120.0	3.2
δ-BHC	50	56.67	113.3	4.1
Aldrin	50	53.33	106.7	5.2
Heptachlor	50	56.67	113.3	2.6
alfa clordano	50	48.40	96.8	4.8
gamma clordano	50	52.67	105.3	6.1
4.4'-DDE	50	56.67	113.3	3.2

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Table 7. Pesticides recovery from Spike solution (n=4) [continuation]

Analyte	Spike concentration (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
Dieldrin	50	53.33	106.7	1.3
Endrin	50	52.05	104.1	1.9
β-Endosulfan II	50	50.00	100.0	4.1
4.4'-DDD	50	56.67	113.3	3.8
2.4'-DDT	50	46.65	93.3	2.4
4.4'-DDT	50	45.70	91.4	2.9
Mirex	50	53.05	106.1	5.1
Dichlorvos	50	40.00	80.0	9.3
Demeton	50	41.45	82.9	6.8
Dimethoate	50	52.50	105.0	4.2
Malathion	50	45.70	91.4	3.6
Parathion	50	43.95	87.9	2.7
Parathion-methyl	50	53.33	106.7	2.9
Mevinphos	50	54.20	108.4	3.9
Phorate	50	46.67	93.3	4.6
Fenitrothion	50	56.67	113.3	5.8
Isocarbophos	50	46.25	92.5	6.4
Methidathion	50	43.15	86.3	8.9
Endosulfan Sulfate	50	46.90	93.8	10.6
Endrin aldeide	50	39.45	78.9	3.5
Endrin Ketone	50	39.70	79.4	4.9
Heptachlor Epoxide	50	47.30	94.6	6.3
Methoxychlor	50	53.35	106.7	5.5
Toxaphene	50	41.80	83.6	4.9

CONCLUSION

The results demonstrate the efficiency of the ETHOS X with fastEX-24 eT rotor for the pesticides extraction from environmental matrices. High recovery rate for all the tested molecules 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.

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