



A Novel, Versatile Polymeric Sorbent for Solid Phase Extraction of Various Organic Compounds in Water

UCT Part Numbers:

ECHLD156-P - 500 mg Enviro-Clean® HL DVB in 6 mL cartridge

VMFSTFR12 - Sample transfer tubes

ECSS25K - 25 kg sodium sulfate, anhydrous, ACS grade, granular 60 mesh

RFV1F15P - 15 mL reservoirs with 1 frit, 10 micron porosity

ECSS15M6 - 5 g anhydrous sodium sulfate in 6 mL cartridge

AD0000AS - Cartridge adaptors

Introduction

This application describes the use of a novel, versatile polymeric sorbent for the solid phase extraction (SPE) of a range of organic compounds. Depending on the extraction protocol used analysts are able to extract acids, bases, and neutrals including non-polar and even some mid-polar to polar compounds. Several of the compounds extracted are typically not well retained by silica-based sorbents, such as C8 and C18. The analytical performance of this new sorbent is demonstrated by selectively extracting acidic compounds (phenols), neutrals (explosives, organophosphorus pesticides, triazine herbicides, and other polar/non-polar compounds), and bases.

The SPE methods are simple and easy to use. It involves cartridge washing and conditioning, sample loading, cartridge drying and analyte elution with proper organic solvents. To ensure good extraction efficiency, the water sample must be de-chlorinated and the sample pH adjusted so that the target analytes are in their uncharged molecular forms. It is only in the neutral form that the analytes are retained by reverse phase functionality on the polymeric sorbent. For acidic compounds, sample pH should be adjusted to 2 units below the lowest pKa of the compounds to be extracted. For basic compounds, sample pH should be 2 units above the highest pKa of the compounds. For neutral compounds sample pH is not as critical as with acids or bases and can be extracted as received, unless one or more compounds to be extracted are sensitive under certain pH. Sample pH should be adjusted to the value at which any sensitive compounds are most stable to avoid low recovery caused by analyte hydrolysis or degradation. For example, captan and flumioxazin degrade much faster under alkaline conditions; therefore the sample should be adjusted to acidic conditions to avoid analyte

degradation. Some compounds hydrolyze under both alkaline and acidic condition (e.g. organophosphorus esters), thus the optimum sample pH is neutral. Knowing the chemical and physical properties of the target analytes helps reduce overall method development time.

UCT has created a new sample transfer tube (**VMFSTFR12**) that fits SPE cartridges of varying sizes (1, 3, 6, 10, 15, and 25 mL). These transfer tubes allow analysts to load large sample volumes onto SPE cartridges with limited attendance. Simply connect the transfer tube to the SPE cartridge and drop the opposite end, outfitted with a SS sinker into the sample container.

Another time and effort saving option is utilized by connecting a drying cartridge (**ECSS15M6**) directly to the end of the SPE cartridge (**ECHLD156-P**) using a cartridge adaptor (**AD0000AS**) during the elution step. This eliminates the need for an additional eluate drying step. This procedure can be used when the elution solvents are more non-polar, such as ethyl acetate or dichloromethane. Another drying option is available when eluting using more polar solvents, such as methanol or acetone. Pack 15 gm of bulk sodium sulfate (**ECSS25K**) into a 15-mL fritted reservoir (**RFV1F15P**) and place in-line at the end of the SPE cartridge. Polar solvents elute more water residue from the SPE cartridges than non-polar solvents. The use of the 15mL reservoir with 15 gm of bulk sodium sulfate ensures plenty of drying capacity.

SPE applications of various organic compounds in water

1: Acidic compounds

SPE procedure	
Sample pretreatment	1 L water sample, pH adjusted to < 2
Cartridge washing	3 x 3 mL dichloromethane (DCM)
Cartridge conditioning	3 x 3 mL methanol (MeOH); 4 x 3 mL 0.05 N HCl
Sample loading	15 mL/min
Cartridge drying	15 min under full vacuum
Elution with in-line drying	10 mL DCM bottle rinse; 3 mL DCM to cartridge
Eluate evaporation	Nitrogen at 40 °C to 1 mL

Analyte	Single-lot results		Multiple-lot results	
	Recovery%	RSD% (n=5)	Recovery%	RSD% (n=35)
Phenol	88.2	2.2	86.4	4.0
2-chlorophenol d4 (Surr)	88.7	1.6	87.3	4.7
2-chlorophenol	87.4	1.3	85.3	3.5
2-methylphenol	88.6	1.5	86.8	3.6
2-nitrophenol	85.6	0.8	85.5	3.8
2,4-dimethylphenol d3 (Surr)	88.5	1.4	86.9	6.6
2,4-dimethylphenol	88.4	1.1	85.1	6.5
2,4-dichlorophenol	87.4	1.3	86.5	3.8
4-chloro-3-methylphenol	90.4	1.0	89.5	2.9
2,4,6-trichlorophenol	88.3	0.6	87.8	3.2
2,4-dinitrophenol	103.2	7.6	108.4	5.6
4-nitrophenol	96.5	1.2	97.4	4.2
2-methyl-4,6-dinitrophenol	92.9	2.5	97.9	6.7
2,4,6-tribromophenol (Surr)	88.7	0.9	89.5	4.3
Pentachlorophenol	94.3	1.1	95.8	4.7

2: Neutral compounds

2a. Explosives

SPE procedure	
Sample pretreatment	1 L water sample, pH as received
Cartridge washing	3 x 5 mL ethyl acetate (EtOAc)
Cartridge conditioning	3 x 5 mL MeOH; 2 x 10 mL DI water
Sample loading	15 mL/min
Cartridge drying	10 min under full vacuum
Elution with in-line drying	5 mL EtOAc bottle rinse; 5 mL EtOAc to cartridge
Eluate evaporation	Nitrogen at 40 °C to 1 mL

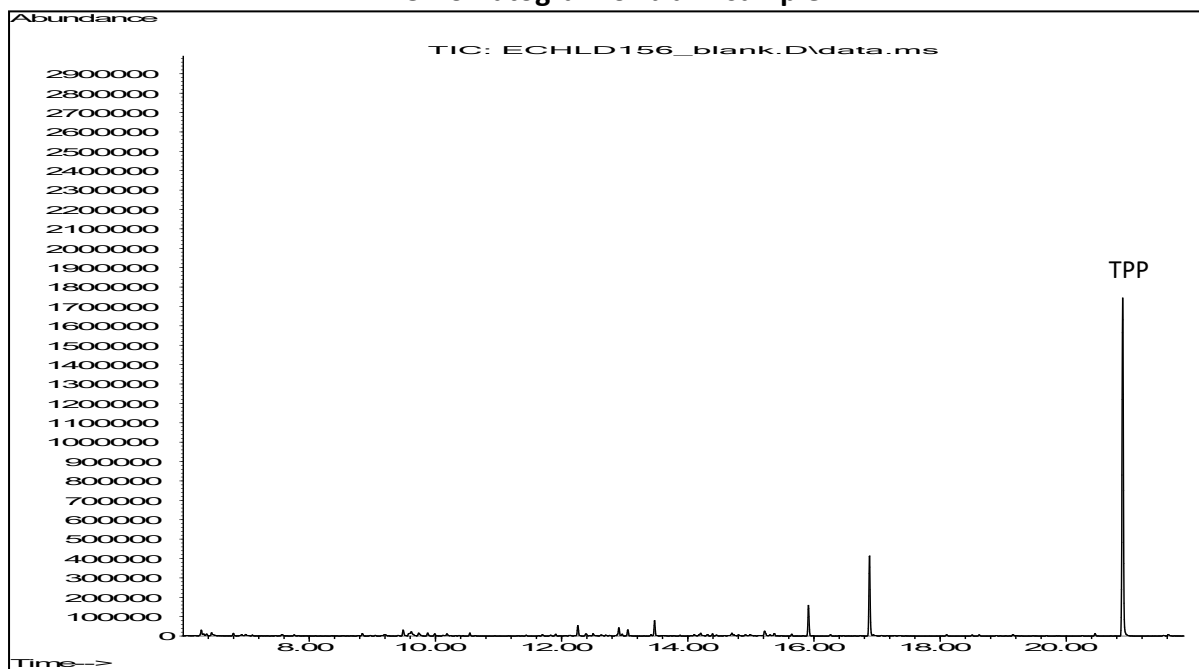
Analyte	Single-lot results		Multiple-lot results	
	Recovery%	RSD% (n=5)	Recovery%	RSD% (n=25)
Nitrobenzene d5 Surr	92.4	3.5	88.9	4.3
Nitrobenzene	86.8	2.7	88.8	4.6
2-Nitrotoluene	87.6	3.6	89.1	4.7
3-Nitrotoluene	86.6	3.6	87.7	4.6
4-Nitrotoluene	84.4	3.3	87.2	4.9
1,3-Dinitrobenzene	102.4	5.3	99.7	4.2
2,6-Dinitrotoluene	98.2	5.7	97.3	4.8
2,4-Dinitrotoluene	91.2	5.3	92.9	4.2
1,3,5-Trinitrobenzene	100.0	9.1	100.4	5.5
2,4,6-Trinitrotoluene	103.0	6.3	100.9	5.3
RDX	107.0	1.7	111.1	5.8
4-Amino-2,6-Dinitrotoluene	100.1	7.5	99.6	5.8
3,5-Dinitroaniline	104.3	5.6	103.6	6.3
2-Amino-4,6-Dinitrotoluene	103.3	5.2	105.7	5.0
Tetryl	102.2	3.7	105.4	4.7

2b. Organophosphorus pesticides and triazine herbicides

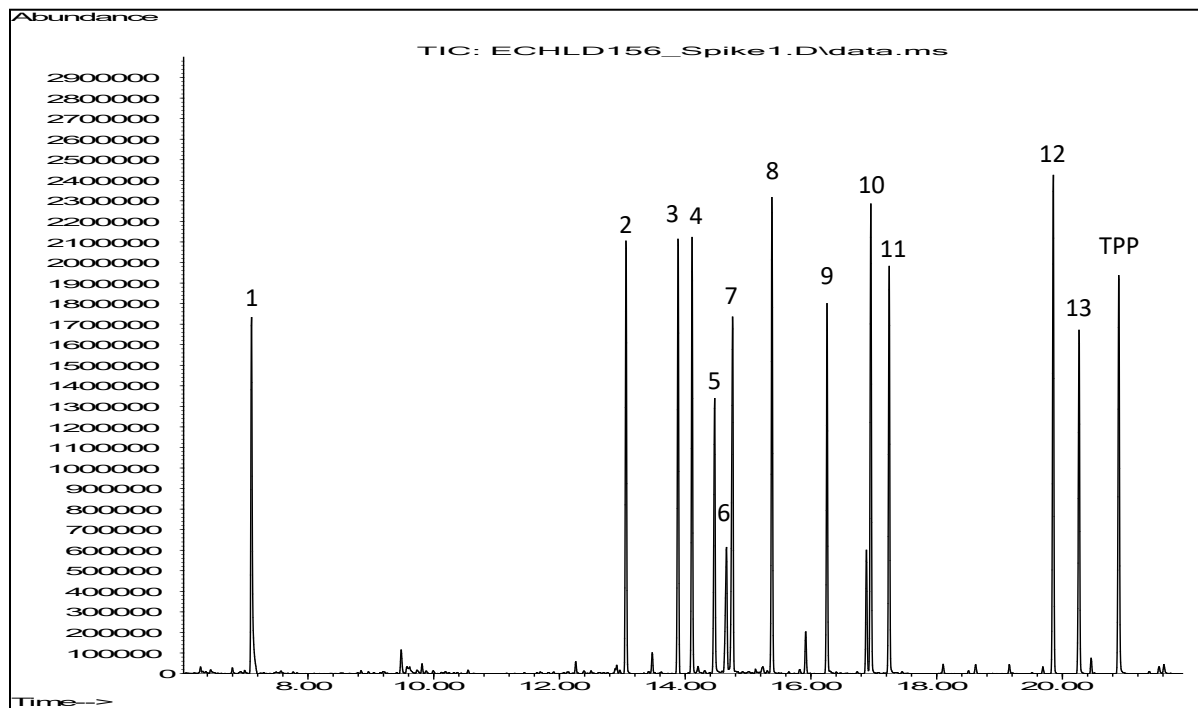
SPE procedure	
Sample pretreatment	1 L water sample, at neutral pH
Cartridge washing	3 x 5 mL DCM
Cartridge conditioning	2 x 5 mL MeOH; 2 x 5 mL DI water
Sample loading	15 mL/min
Cartridge drying	10 min under full vacuum
Elution	5 mL acetone bottle rinse; 5 mL DCM bottle rinse; 5 mL DCM to cartridge
Eluate drying	15 g sodium sulfate in 15 mL fritted reservoir
Eluate evaporation	Nitrogen at 40 °C to 0.5 mL
Solvent exchange	Solvent exchange to n-hexane

Analyte	Class	Recovery%	RSD% (n=5)
o,o,o-Triethyl phosphorothioate	Organophosphorus	87.8	1.8
Thionazin	Organophosphorus	100.9	1.8
Sulfotep	Organophosphorus	96.2	0.9
Phorate	Organophosphorus	93.0	1.2
Dimethoate	Organophosphorus	108.7	7.3
Simazine	Triazine	104.2	2.1
Atrazine	Triazine	101.5	1.2
Disulfoton	Organophosphorus	85.5	1.7
Methyl parathion	Organophosphorus	112.4	1.8
Malathion	Organophosphorus	110.7	1.3
Parathion	Organophosphorus	106.8	1.3
Ethion	Organophosphorus	107.8	0.7
Famphur	Organophosphorus	120.0	1.8

Chromatogram of blank sample



Chromatogram of a sample spiked with 10 µg/L analytes



Peak list: 1. o,o,o-Triethyl phosphorothioate; 2. Thionazin; 3. Sulfotep; 4. Phorate; 5. Dimethoate; 6. Simazine; 7. Atrazine; 8. Disulfoton; 9. Methyl parathion; 10. Malathion; 11. Parathion; 12. Ethion; 13. Famphur.

2c. Other polar and non-polar neutral compounds

SPE procedure	
Sample pretreatment	1 L water sample, pH adjusted to <5
Cartridge washing	3 x 5 mL DCM
Cartridge conditioning	3 x 5 mL MeOH; 10 mL DI water
Sample loading	15 mL/min
Cartridge drying	10 min under full vacuum
Elution with in-line drying	2 x 5 mL DCM
Eluate evaporation	Nitrogen at 40 °C to 1 mL

Analyte	Chemical properties	Recovery%	RSD% (n=4)
Dicrotophos	Polar, LogP -0.24	96.0	2.0
Dimethipin	Polar, LogP -1.53	105.3	3.1
Butylated hydroxyanisole	Non-polar, LogP 3.06	102.5	0.5
Diethyl phthalate	Non-polar, LogP 2.42	96.7	0.6
Methyl parathion	Non-polar, LogP 2.8	97.4	2.2
Carbaryl	Non-polar, LogP 2.36	101.3	3.5
Malathion	Non-polar, LogP 2.36	101.9	1.0
Captan	Non-polar, LogP 2.35	100.6	1.8
Nitrofen	Non-polar, LogP 4.62	93.7	1.9
Ethion	Non-polar, LogP 3.93	99.9	1.4
4,4'-DDT	Non-polar, LogP 6.46	96.1	1.8
Captafol	Non-polar, LogP 3.95	103.2	3.2
Bis(2-ethylhexyl) phthalate	Non-polar, LogP 4.89	96.5	1.7

3: Basic compounds

SPE procedure	
Sample pretreatment	1 L water sample, pH adjusted to > 7
Cartridge washing	3 x 5 mL DCM
Cartridge conditioning	3 x 5 mL MeOH; 10 mL DI water
Sample loading	15 mL/min
Cartridge drying	10 min under full vacuum
Elution with in-line drying	2 x 5 mL DCM
Eluate evaporation	Nitrogen at 40 °C to 1 mL

Analyte	Chemical properties	Recovery%	RSD% (n=4)
o-Toluidine	Basic, pKa 4.48	94.8	4.2
Quinoline	Basic, pKa 4.50	112.1	2.1

Conclusions

- A novel and versatile polymeric sorbent effectively retains a variety range of organic compounds, including acids, neutrals (polar and non-polar compounds), and bases
- Cross-linked polymeric sorbent with > 5 times greater capacity than silica-based sorbents
- Stable in samples with pH ranged from 0 to 14
- Straightforward SPE extraction protocols with excellent precision and accuracy
- Unique polymeric structure contributed to consistent analytical performance with minimum lot-to-lot variations

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