



A NEW POLYMERIC SORBENT FOR SOLID PHASE EXTRACTION OF PHENOLS, EXPLOSIVES, BASES, AND POLAR COMPOUNDS IN WATER

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INTRODUCTION

UCT has developed a new polymeric sorbent for solid phase extraction of a range of compounds, including acids, bases, neutrals, and even some mid-polar to polar compounds. Some of the compounds which can be extracted are often not well retained on silica-based sorbents, such as C8 and C18. This new sorbent is applicable to multiple EPA methods, including EPA method 526 (semi-volatile organic compounds), method 527 (pesticides and flame retardants), method 528 (phenols), methods 529 and 8330 (explosives), method 537 (perfluorinated alkyl acids), method 553 (benzidines and nitrogen-containing pesticides), and method 8141B (organophosphorus pesticides and triazine herbicides). The analytical performance of this new sorbent for the extraction of phenols, explosives, organophosphorus pesticides and triazine herbicides, and other compounds, including bases, polar and non-polar analytes is presented.

The SPE method using this new sorbent is 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 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, the 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. The sample pH should be adjusted to the value at which any sensitive compounds are most stable. This will help minimize 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 also developed a new sample transfer line (VMFSTFR12) that fits SPE cartridges of varying sizes (1, 3, 6, 10, 15, and 25 mL). These transfer lines allow analysts to load large sample volumes onto SPE cartridges with limited analyst attendance. 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 (when non-polar solvents are used for elution). This eliminates the need for an additional eluate drying step. A new collection rack (VMF02125) that can hold larger containers, such as 40-60 mL vials, has also been created for environmental applications where larger elution volumes are often needed.

MATERIALS

Item	Description	UCT part#
SPE cartridge	500 mg Enviro-Clean® HL DVB in 6 mL cartridge	ECHLD156-P
Sample transfer tube	Fits 1, 3, 6, 10, 15, and 25 mL SPE cartridges	VMFSTFR12
Drying cartridge	5 g anhydrous sodium sulfate in 6 mL cartridge	ECSS15M6
Cartridge adaptor	Fits 1, 3, 6, 10, and 15 mL cartridges	AD0000AS
SPE collection rack	Designed for 40-60 mL vials	VMF02125



Solid Phase Extraction Setup for 12 Water Samples

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SPE APPLICATIONS OF VARIOUS ORGANIC COMPOUNDS IN WATER

Application 1:

EPA Method 528 (Phenols, acidic compounds)

Analyte	Spiked (ug/L)	EPA requirement		Single-lot results		Multiple-lot results	
		Recovery%	RSD%	Recovery%	RSD% (avg)	Recovery%	RSD% (avg)
Phenol	10	90-100	±30	88.2	2.2	88.4	4.5
2-chlorophenol (d) (Sur)	2.5	75-100	±20	88.7	1.8	87.3	4.7
2-chlorophenol	10	75-100	±20	87.4	1.3	85.3	3.5
2-methylphenol	10	75-100	±20	88.6	1.5	88.8	3.8
2-nitrophenol	10	75-100	±20	85.6	0.8	85.5	3.8
2,4-dimethylphenol (d) (Sur)	2.5	75-100	±20	88.9	1.4	88.9	6.6
2,4-dimethylphenol	10	75-100	±20	88.4	1.1	88.4	6.5
2,4-dinitrophenol	10	75-100	±20	87.4	1.3	86.5	3.8
4-chloro-3-methylphenol	10	75-100	±20	88.4	1.0	88.5	2.9
2,4,6-trichlorophenol	10	75-100	±20	88.3	0.8	87.8	3.3
2,4-dinitrophenol	10	75-100	±20	102.2	7.5	108.4	5.5
4-nitrophenol	10	75-100	±20	98.5	1.2	97.4	4.2
2-methyl-4-nitrophenol	10	75-100	±20	82.8	2.5	87.9	6.7
2,4,6-trinitrophenol (Sur)	5	60-100	±20	88.7	0.9	88.5	4.3
Pentachlorophenol	10	75-100	±20	84.3	1.1	85.8	4.7

Application 2:

EPA Method 529 (explosives, neutral compounds)

Analyte	Spiked (ug/L)	EPA requirement		Single-lot results		Multiple-lot results	
		Recovery%	RSD%	Recovery%	RSD% (avg)	Recovery%	RSD% (avg)
Nonobenzene dl Sur	5	75-100	±20	92.4	3.5	89.9	4.3
Nonobenzene	5	75-100	±20	88.8	3.7	88.8	4.8
2-Nitrobenzene	5	75-100	±20	87.8	3.8	88.1	4.7
3-Nitrobenzene	5	75-100	±20	86.6	3.8	87.7	4.6
4-Nitrobenzene	5	75-100	±20	84.4	3.3	87.2	4.9
1,3-Dinitrobenzene	5	75-100	±20	102.4	5.3	99.7	4.2
2,6-Dinitrobenzene	5	75-100	±20	98.2	5.7	97.3	4.6
2,4-Dinitrobenzene	5	75-100	±20	91.2	5.3	92.8	4.2
1,3,5-Trinitrobenzene	5	75-100	±20	100.8	9.1	100.4	5.5
2,4,6-Trinitrobenzene	5	75-100	±20	103.8	6.3	100.9	5.3
BDX	5	75-100	±20	107.8	1.7	111.1	5.8
4-Amino-2,6-Dinitrobenzene	5	75-100	±20	100.1	7.5	99.8	5.8
3,5-Dinitrobenzene	5	75-100	±20	104.3	5.6	103.6	6.3
3-Amino-4,6-Dinitrobenzene	5	75-100	±20	103.3	5.2	106.7	5.0
Tetryl	5	75-100	±20	102.2	3.7	105.4	4.5

Application 3:

EPA Method 8141B (organophosphorus pesticides and triazine herbicides, neutral compounds)

Analyte	Class	Spiked (ug/L)	Recovery%	RSD% (n=5)
o,o-Diethyl phosphorothioate	Organophosphorus	10	87.5	1.8
Thionazin	Organophosphorus	10	100.9	1.8
Sulfotep	Organophosphorus	10	96.2	0.9
Phorate	Organophosphorus	10	93.0	1.2
Dimethoate	Organophosphorus	10	106.7	7.3
Simazine	Triazine	10	104.2	2.1
Atrazine	Triazine	10	101.5	1.2
Disulfoton	Organophosphorus	10	85.5	1.7
Methyl parathion	Organophosphorus	10	112.4	1.8
Malathion	Organophosphorus	10	110.7	1.3
Parathion	Organophosphorus	10	106.8	1.3
Ethion	Organophosphorus	10	107.8	0.7
Famphur	Organophosphorus	10	120.0	1.8

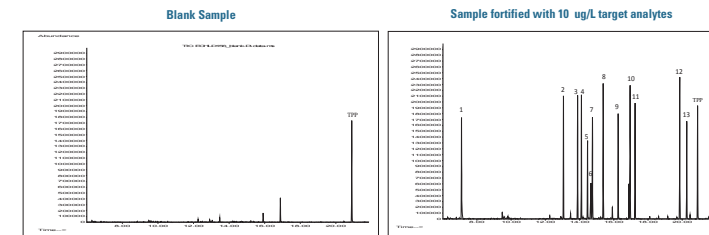
Application 4:

Other applications (bases, polar and non-polar compounds)

SPE procedure		Spiked (ug/L)	Recovery%	RSD% (n=4)
Sample pretreatment	1 L water sample, pH 7	5	94.8	4.2
Cartridge washing	3 x 5 mL DCM			
Cartridge conditioning	3 x 5 mL MeOH, 10 mL DI water			
Sample loading	15 mL/min	20	96.0	2.0
Cartridge drying	10 min under full vacuum	5	102.5	3.1
Elution with in-line drying	2 x 5 mL DCM	20	96.7	0.6
Eluate evaporation	Nitrogen at 40 °C to 1 mL			

Analyte	Chemical properties	Spiked (ug/L)	Recovery%	RSD% (n=4)
o-Toluidine	Basic, pKa 4.48	5	94.8	4.2
Quinoline	Basic, pKa 4.50	5	112.1	2.1
Quartraphos	Polar, LogP -0.24	20	96.0	2.0
Dimetipen	Polar, LogP -1.53	5	102.5	3.1
Bisulfated hydrazinolate	Non-polar, LogP 3.06	20	97.4	2.2
Diallyl phthalate	Non-polar, LogP 2.42	20	96.7	0.6
Methyl parathion	Non-polar, LogP 2.8	20	97.4	2.2
Carbazyl	Non-polar, LogP 2.38	20	101.3	3.5
Malathion	Non-polar, LogP 2.36	20	101.9	1.0
Captan	Non-polar, LogP 2.35	20	100.6	1.8
Nitrofen	Non-polar, LogP 4.02	20	93.7	1.9
Ethion	Non-polar, LogP 3.95	20	99.9	1.4
4,4'-DDT	Non-polar, LogP 6.46	20	96.1	1.8
Captafol	Non-polar, LogP 3.95	20	103.2	3.2
But(2-ethylhexyl) phthalate	Non-polar, LogP 4.89	20	96.5	1.7

REPRESENTATIVE CHROMATOGRAMS (APPLICATION #3)



Peak list: 1. O,O-Diethyl 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.

CONCLUSIONS

- A novel and versatile polymeric sorbent effectively retains a variety range of organic compounds (acidic, neutral, and basic)
- Cross-linked polymeric sorbent with over 5 times greater capacity than silica-based sorbents
- Sorbent is stable for 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
- Newly designed sample transfer tubes for extracting large samples and collection racks for holding elution vials up to 60 mL eases time burden on analysts.