PROMOCHROM TECHNOLOGIES

Application Note
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Mini-disk Phenol

Mini-disk:
A balance between cartridges and disks for solid phase extraction

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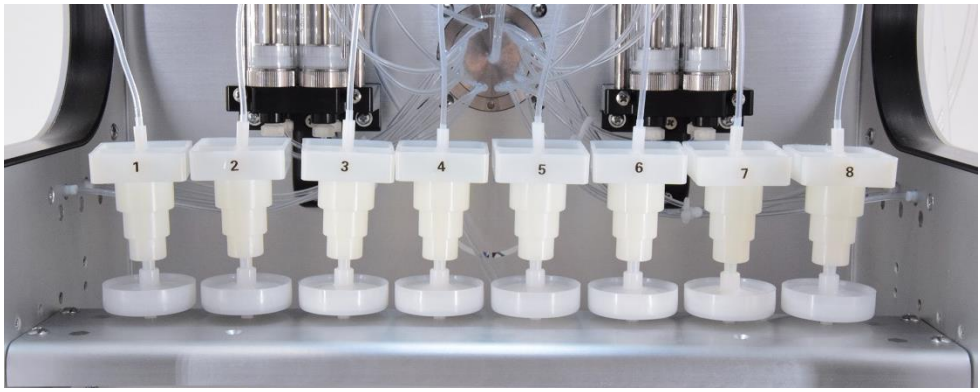
Keywords

EPA Method 528, Phenol, Mini-disk, SPE-03, Automated SPE, water

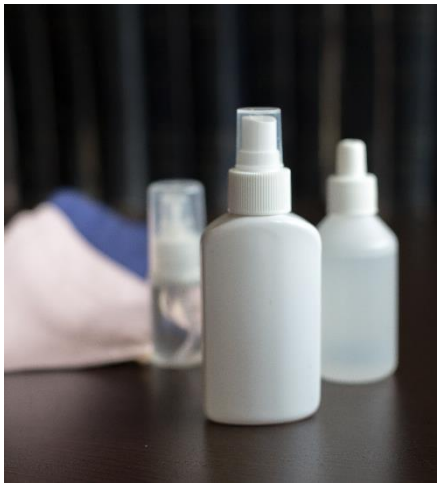


ABSTRACT

Solid phase extraction is often the most challenging and time-consuming process in the analysis of large volume water samples. Majority of solid phase extractions are performed using SPE cartridges, even though SPE disks offer much higher flow rate and clogging resistance. This is due in part to the higher cost and larger volume of solvent usage. In addition, most automated SPE systems are only compatible with SPE cartridges, thereby further limiting the use of disks.

To capture the advantages of SPE disk in extraction speed and overcome its disadvantages in solvent consumption and automation, PromoChrom developed a suite of Mini-disks. The Mini-disks come in a format size similar to a 30-mm syringe filter and a cross section area 5 times of a 6-mL SPE cartridge. The increased cross section area and optimized sorbent properties enables the Mini-disks to work with much higher flow rates than SPE cartridges, whereas a smaller size than conventional disks makes the Mini-disks easily adaptable to cartridge type SPE instruments and consume less solvents. This application note discusses the extraction of phenols in water using our mixed-mode Mini-disks, MD-BNA-30, with the SPE-03 automated solid phase extraction system.

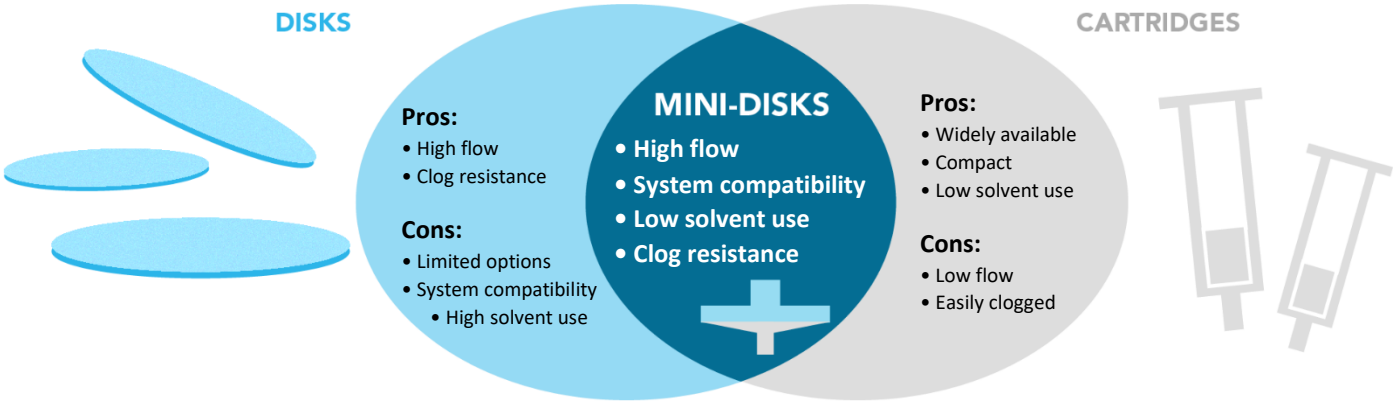
INTRODUCTION



Phenols are class of man-made and naturally-occurring compounds consisting of one or more hydroxyl groups (–OH) bonded directly to an aromatic hydrocarbon group. Phenol is used primarily as a precursor to produce various plastics such as nylon and polycarbonate. It is also used as a disinfectant and antiseptic. Combustion and waste water discharge from manufacturing industries are the main source of Phenol pollution in the environment[1]. Toxic effects of Phenol include shortened lifespan and reproductive problems in animals and nose, eye and skin irritation to humans. Severe exposure could lead to deaths and respiratory syndromes.[2]

Solid phase extraction can be used to extract phenols from water samples for analysis. Per EPA Method 528, 1 L of samples are extracted with 6 mL SPE cartridges at 20 mL/min[3]. Even though SPE disks offer faster sample loading speed and better tolerance to clogging, they require more solvent usage and have limited market options and compatibility with automated systems. SPE cartridges are more affordable, widely available and compatible with most extraction platforms.

In this application note, we bring forth a novel Mini-disk that combines the advantages and eliminates the shortcomings of cartridges and disks. The hybrid design can achieve high flow rates and tolerance to particulate matter while using similar amounts of solvent as cartridge-based extraction. Compared to EPA Method 528, flow rates of 45 mL/min to 50 mL/min was used throughout the extraction in this example. The diameter of the Mini-disk measures only 30 mm and is packaged to fit standard luer slip connections, making it suitable for cartridge-based automated SPE systems and vacuum manifolds.



The sorbent material for the Mini-disks are made up of 25-um spherical beads with very narrow size distribution. This smaller bead size increases sample capacity while the uniform distribution offers lower resistance to liquid passing through the disk. PromoChrom's Anti-clogging Frit technology is also applied to the Mini-disk for enhanced tolerance to particulates from sample matrices.

This application note demonstrates the use of PromoChrom mixed-mode Mini-disks with the SPE-03 automated solid phase extraction system for extracting phenols in water.

MATERIALS

- Standards for sample spiking and HPLC analysis: Phenols Mix for 8040A (Sigma-Aldrich, part number 48235U) diluted with methanol.
- Mini-disk: PromoChrom Mini-disk packed with mixed-mode polymers and capable of extracting basic, neutral and acidic pollutants in water (Cat. No.: MD-BNA-30)
- Mobile phase for HPLC: Mobile phase A is acetonitrile + water + phosphoric acid (90:10:0.2). Mobile phase B is water containing 0.2% phosphoric acid.
- Instrument for Extraction: SPE-03 8-channel SPE system with MOD-00P configuration for automatic rinsing of up to 1L sample bottles.
- Instrument for analysis: Agilent 1100 HPLC system consisting of a G1312A binary pump and a G1314A VWD detector. An AQ-C18 column with 4.6X200 mm dimension from Agela Technologies was used for chromatographic separation.

METHODS

Sample Extraction

Four samples consisting of 500 mL of mineral water in 1-liter glass bottle (VWR® TraceClean® Boston Round Bottles) was acidified using 0.5 mL formic acid (88%) to pH 3-4 and then spiked with 9 phenols at a concentration of 3 ug/L. The samples were extracted using the method shown in table 1. Two sets of fractions were collected and analyzed using HPLC without further concentration.

Table 1 – SPE procedures programmed on the SPE-03
***Solvent 1** = Methanol , **Solvent 2** = Water, **W1** = Aqueous waste, **W2** = Organic waste*

Action	Inlet 1	Flow	Volume	***Description***
Elute W2	Solvent 1	50 mL/min	10 mL	*Condition disks with 10 mL MeOH at 50 mL/min*
Elute W1	Solvent 2	50 mL/min	10 mL	*Condition disks with 10 mL water at 50 mL/min*
Add Samp W1	Sample	45 mL/min	550 mL	*Load samples at 45 mL/min, using 550 mL to ensure all sample liquid in the bottles are loaded*
Rinse	Solvent 2	45 mL/min	10 mL	*Rinse bottles with 10 mL water*
Add Samp W1	Sample	45 mL/min	20 mL	*Transfer rinsate from sample bottles through disks and out of Waste 1. Using additional volume to purge the tubing and Mini-disks with air*
Rinse	Solvent 1	70 mL/min	15 mL	*Rinse sample bottles with 15 mL MeOH*
Collect 1	Sample	50 mL/min	25 mL	*Transfer rinsate from sample bottles through disks and into Fraction 1. Using additional volume to purge residual solvent from disks into Fraction 1*
Collect 2	Solvent 1	50 mL/min	5 mL	*Elute disks with another 5 mL MeOH and collect into Fraction 2 to study amount of left over analytes in Mini-disks*
Air-Purge 2	Air	50 mL/min	10 mL	*Purge residual solvent from disks into Fraction 2*

HPLC Analysis

During the analysis, mobile phase A was increased from 20% to 100% over 14 mins and then maintained for 6 mins. Mobile phase A is then reduced to 20% over 1 min to get ready for the next run. The VWD detection wavelength was set at 275 nm for the first 8 minutes and then changed to 235 nm. Injection volume was 20 uL. Flow rate was 1.2 mL/min. Below is a typical chromatogram of the phenols under these conditions.

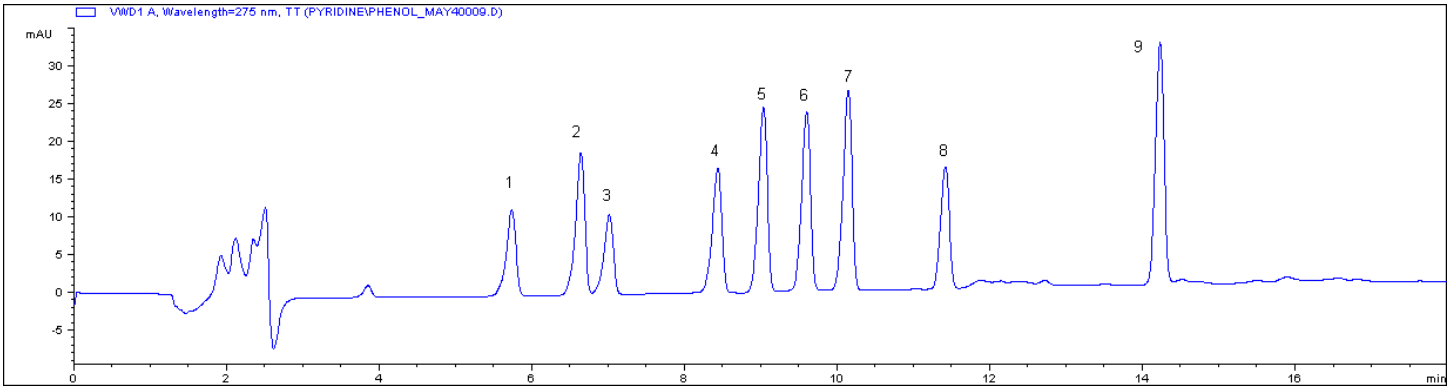


Figure 1 - Chromatogram for 9 phenols at 5 ug/mL. 1. phenol, 2. 4-nitrophenol, 3. 3-methylphenol, 4. 2-nitrophenol, 5. 4-chloro-3-methylphenol, 6. 2,4-dichlorophenol, 7. 2-methyl-4,6-dinitrophenol, 8. 2,4,6-trichlorophenol, 9. pentachlorophenol.

RESULTS AND DISCUSSION

The recoveries of the phenols from the first fraction are summarized in Table 2. All recoveries are above 80% except for one sample that had 77% recovery for Phenol. Phenol is the most hydrophilic amongst these 9 compounds, which could made it more sensitive to solid phase extraction parameters. A further optimization on extraction conditions should make the recovery of phenol more reproducible.

Table 2 – Recoveries of phenols from 4 spiked samples

Analytes	Recovery [%]				Average	RSD [%]
	#1	#2	#3	#4		
Phenol	116	77.0	96.0	80.0	92.3	19.4
4-nitrophenol	93.8	93.8	100	`87.5	93.8	5.4
3-methylphenol	98.3	84.7	94.9	84.7	90.7	7.7
2-nitrophenol	96.2	94.3	96.2	83.0	92.4	6.9
4-chloro-3-methylphenol	90.9	92.4	86.4	93.9	90.9	3.6
2,4-dichlorophenol	111	103	83.5	91.2	97.2	12.6
2-methyl-4,6-dinitrophenol	94.0	107	91.3	85.3	94.4	9.7
2,4,6-trichlorophenol	87.9	101	82.2	85.5	89.2	9.2
pentachlorophenol	88.9	99.4	98.2	81.0	91.9	9.4

The second fraction from the 5 mL methanol elution does not contain any phenols, suggesting that 15 mL methanol is sufficient to elute all the trapped analytes from the Mini-disk. The solvent consumption of this method is similar to cartridge-based extraction. The Mini-disk can be used with the standard SPE-03 configuration without modifications or using extra adapters.

Time Savings

SPE cartridges are typically conditioned at 10mL/min and eluted at 5 mL/min. Sample loading per EPA Method 528 is performed at 20 mL/min. By enabling much higher flow rates of 45 to 50 mL/min on the Mini-disks, approximately 25 minutes is saved on each 500 mL sample extraction and 40 minutes is saved on each 1000 mL extraction.

ORDERING INFORMATION FOR MINI-DISKS

Part number	Description	Application
MD-BNA-30	Packed with 25-um spherical mixed-mode polymer. 50 Mini-disks per box.	For simultaneous extraction of basic, neutral and acidic compounds.
MD-525-30	Packed with 25-um spherical mixed-mode polymer. 50 Mini-disks per box.	For extraction of hydrophobic and hydrophilic compounds.
MD-C18-30	Packed with C18 bonded 25-um spherical silica. 50 Mini-disks per box.	For extraction of PAHs, PCBs, organochlorine, pyrethroids and organophosphorus pesticides.
MD-WAX-30	Packed with 45-um spherical WAX polymer. 50 Mini-disks per box.	For extraction of PFAS and other acidic compounds.

REFERENCES

1. Phenols, Lake Simcoe Region Conservation Authority, https://www.lsrca.on.ca/Pages/Phenols.aspx#:~:text=Phenols%20can%20occur%20in%20small,harmful%20effects%20to%20the%20environment.

2. Phenol, Australian Government Department of Climate Change, Energy, the Environment and Water https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/phenol

3. EPA Method 528, https://www.epa.gov/sites/default/files/2015-09/documents/m_528.pdf

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