

AUTOMATED EXTRACTION OF **TCLP SEMI-VOLATILES** USING **MINI-DISK** TARGETING **BASIC/NEUTRAL/ACIDIC** COMPOUNDS

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ABSTRACT

This application note brings forth a novel mixed-mode Mini-disk, MD-BNA-30, for the extraction of basic, neutral and acidic compounds from the TCLP semi-volatile organic compounds (SVOCs) list¹. The Mini-disk is capable of high flow rates similar to SPE disks while its compact and optimized design allows for easy handling and improved performance.

INTRODUCTION

Merit Labs performs a range of sample testing, one of which includes TCLP SVOCs in water and leachate samples using Solid Phase Extraction (SPE) per EPA Method 3535² and GCMS analysis per EPA Method 8270.

The SPE process was originally performed using proprietary 47mm disks and an extractor that loads samples using vacuum, hereon referred to as the “benchmark”. To overcome the limitations in sample throughput and variations in extraction time due to sample matrices, PromoChrom’s MD-BNA-30 mixed-mode Mini-disk and SPE-03 8-Channel fully-automated extractor were introduced.

The Mini-disk comes in a compact format similar to a 30mm syringe filter that can be directly attached to the SPE-03 system. As shown in **Figure 1** below, the two Mini-disks on the right take up minimal space compared to the six disk holders for 47mm disks. Using a disk holder also requires additional handling for inserting the 47mm disk and cleaning the holder after extraction.



Figure 1 - 47mm Disks and Mini-disks on the SPE-03 Disk Rack

Despite the relatively tiny footprint of the Mini-disk, it has 5 times the cross-sectional area of a 6mL SPE cartridge. The larger area and optimized sorbent properties enable the Mini-disk to work with much higher flow rates than SPE cartridges, while requiring less solvents than 47mm disks to condition and elute.

Positive-pressure syringe pumps on the SPE-03 deliver constant flow determined by the user and thus ensures that all 8 samples are always completed in the same amount of time.

This application note demonstrates the automated extraction of TCLP SVOCs using both 47mm disks and PromoChrom's MD-BNA-30 mixed-mode Mini-disks on the SPE-03 system. It also compares recoveries with the existing benchmark.

MATERIALS

- PromoChrom SPE-03 system with MOD-00P (Volume-Matrix Plus configuration) and MOD-003 (Disk kit including rack and holders, only required for 47mm disks)
- PromoChrom mixed-mode Mini-disk, MD-BNA-30
- Benchmark - proprietary 47mm mixed-mode disk and existing extractor
- Reagents and standards following EPA Method 3535
- Agilent GCMS



Figure 2 - SPE-03 Setup with Mini-disks which does not require the Disk Rack

METHOD SUMMARY

Solvent 1 = DCM, **Solvent 2** = 80:20 DCM:Acetone, **Solvent 3** = MeOH, **Solvent 4** = Acidified H₂O (1000 H₂O : 1 HCl by volume), **Solvent 5** = H₂O , **Solvent 6** = 5% NH₄OH

W1 = Aqueous waste, **W2** = Organic waste

Below is the SPE-03 method for the Mini-disk developed based on the benchmark's procedure. The orange section elutes the acidic and neutral compounds while the blue section covers basic compounds.

Table 1 - SPE-03 Method for BNA Extraction using Mini-disks

Action	Inlet 1	Flow	Volume	Description
Elute W2	Solvent 1	50 mL/min	20 mL	Condition disks with 20 mL DCM
Air-Purge W2	Air	50 mL/min	15 mL	Purge DCM from disks using air
Elute W2	Solvent 3	50 mL/min	20 mL	Condition disks with 20 mL MeOH
Elute W2	Solvent 5	50 mL/min	15 mL	Wash disks with 20 mL H ₂ O
Elute W1	Solvent 4	50 mL/min	15 mL	Wash disks with 15 mL Acidified H ₂ O
Add Samp W1	Sample	50 mL/min	520 mL	Load samples (acidified to pH 5) at 50 mL/min, using 520 mL to ensure all samples are loaded
Elute W1	Solvent 4	50 mL/min	15 mL	Wash disks with 15 mL Acidified H ₂ O
Air-Purge W1	Air	50 mL/min	15 mL	Purge large water droplets out of disks
Blow N2	Time based		6 min	Dry disks with nitrogen for 6 mins (5L/min and 40 psi)
Rinse	Solvent 2	70 mL/min	8 mL	Rinse bottles with 8mL of 80:20 DCM:Acetone
Collect 2	Sample	60 mL/min	10 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based		1 min	Pause to allow 1 min soak time
Rinse	Solvent 2	70 mL/min	8 mL	Rinse bottles with 8mL of 80:20 DCM:Acetone
Collect 2	Sample	60 mL/min	10 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based		1 min	Pause to allow 1 min soak time
Rinse	Solvent 2	70 mL/min	8 mL	Repeat 3 rd bottle rinse and elution with 80:20 DCM:Acetone. Purge rinse lines to ensure all solvents are delivered to the sample bottles
Air-Purge R	Air	70 mL/min	4 mL	
Collect 2	Sample	60 mL/min	15 mL	
Wait	Manual Resume			Pause system to remove acid/neutral extracts
Rinse	Solvent 6	70 mL/min	5 mL	Rinse bottles with 5% NH ₄ OH to adjust pH
Collect 2	Sample	60 mL/min	8 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based		1 min	Pause to allow 1 min soak time
Rinse	Solvent 2	70 mL/min	10 mL	Rinse bottles with 10mL of 80:20 DCM:Acetone
Collect 2	Sample	60 mL/min	10 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based			Pause to allow 1 min soak time
Rinse	Solvent 6	70 mL/min	5 mL	Rinse bottles with 5% NH ₄ OH to adjust pH
Collect 2	Sample	60 mL/min	20 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based		1 min	Pause to allow 1 min soak time
Rinse	Solvent 2	70 mL/min	8 mL	Rinse bottles with 8mL of 80:20 DCM:Acetone
Collect 2	Sample	60 mL/min	8 mL	Collect rinsate and elute cartridges into fraction 2
Wait	Time based		1 min	Pause to allow 1 min soak time
Rinse	Solvent 2	70 mL/min	8 mL	Repeat 3 rd bottle rinse and elution with 80:20 DCM:Acetone. Purge rinse lines to ensure all solvents are delivered to the sample bottles
Air-Purge R	Air	70 mL/min	4 mL	
Collect 2	Sample	60 mL/min	20 mL	

The acidic/neutral fraction is passed through 30-85g of sodium sulfate and washed with 2 x 30mL of DCM. The basic fraction is later passed through 30-85g of sodium sulfate and washed with 1 x 30mL of DCM. The combined extracts are then evaporated to <1mL and re-constituted to 1mL with DCM.

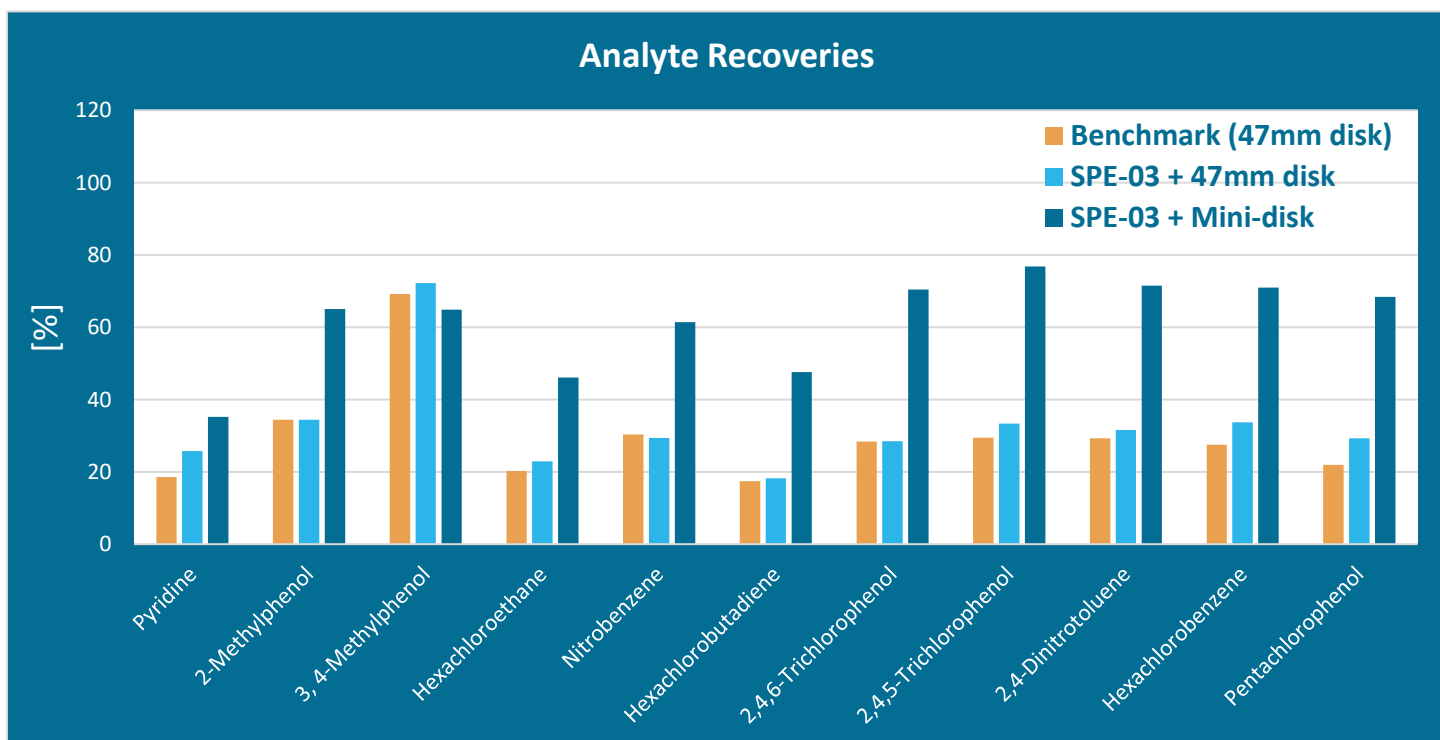
RESULTS

The SPE-03 was first validated using 47mm disks to achieve similar results to the benchmark. This involved some method development, including the use of nitrogen drying to effectively purge liquids during conditioning and elution. This was not required for the Mini-disks. The sample line design was also improved to include a cap as shown in **Figure 2** to minimize the evaporation of volatile compounds from the wide sample containers used by Merit Labs. PromoChrom's mixed-mode Mini-disks were then validated and introduced into routine extractions. The Mini-disk results were taken from LCS and LCS duplicates across 8 different extraction batches on different days, totalling 16 samples.

Analyte Recoveries

As shown in **Figure 3**, recoveries comparable to the benchmark (**orange**) was achieved by the SPE-03 using 47mm disks (**light blue**) after the aforementioned method optimizations. Compared to using 47mm disks on the benchmark and SPE-03, the Mini-disk (**dark blue**) demonstrated a significant improvement in overall analyte recoveries, especially for the acidic phenols. The basic compound, Pyridine, has also been a challenging analyte before due to its low recoveries, which saw more than 30% improvement on the Mini-disk.

Figure 3 - BNA Analyte Recoveries on the SPE-03 and Benchmark System

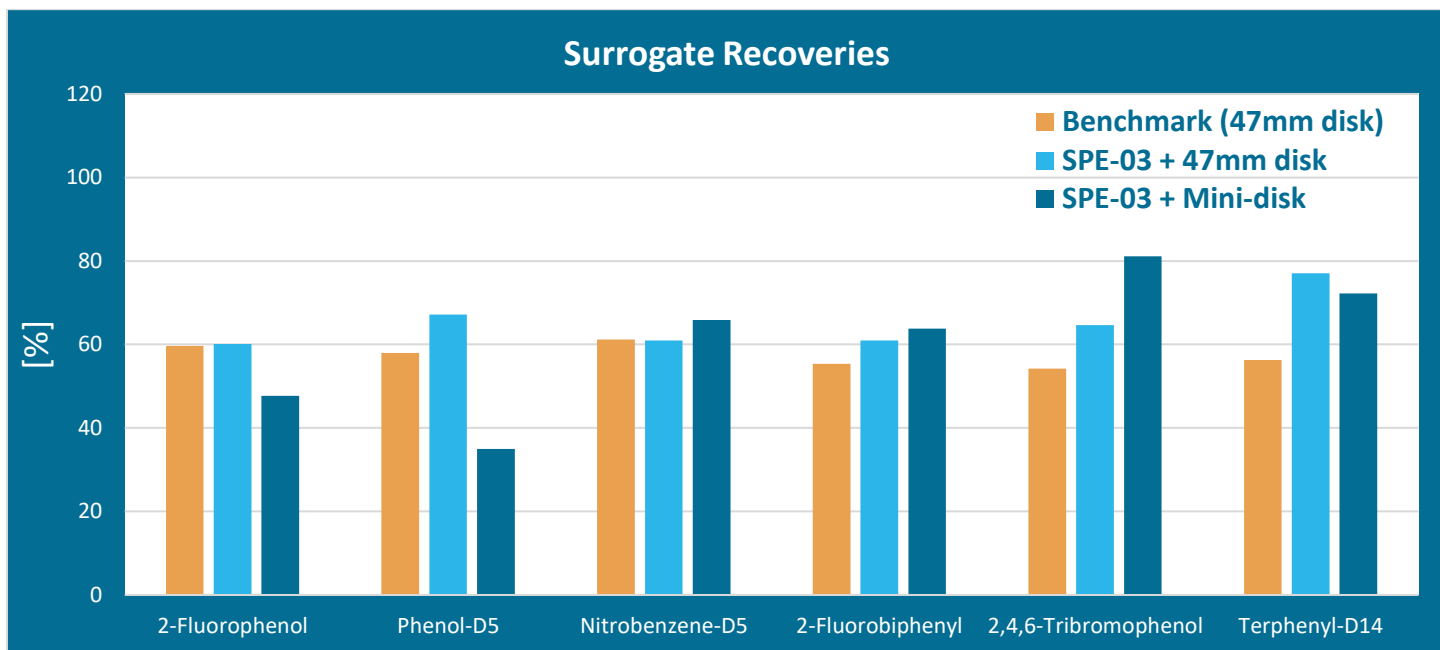


The improved performance of the Mini-disk is attributed in part to the optimized sorbent proportion, packing distribution and flow design within its housing. The smaller disk area also allows for easier conditioning, drying and elution.

Surrogate Recoveries

The corresponding surrogate recoveries are shown in **Figure 4**. Using the same 47mm disk as the benchmark, better results were seen on the SPE-03. This may be attributed to the constant flow rate of the positive pressure pumps. When switching to Mini-disks, recoveries were further improved on some surrogates while 2-Fluorophenol and Phenol recovered lower. Since the performance was acceptable, the Mini-disks were incorporated into routine extractions without further method optimization. PromoChrom's application note 31107³ shows that an average of 92.3% recovery can be achieved on phenol using a more tailored method.

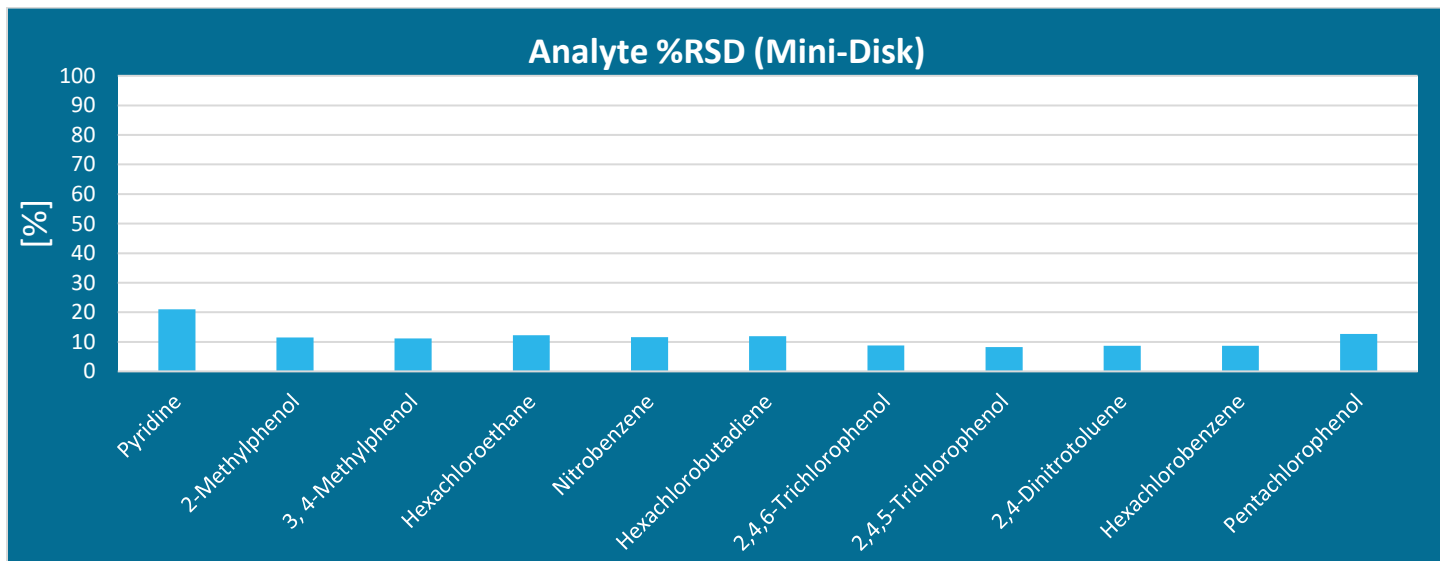
Figure 4 - BNA Surrogate Recoveries on the SPE-03 and Benchmark System



REPRODUCIBILITY

Looking at %RSD of the 16 samples using Mini-disk (**Figure 5**), all analytes had a variation of less than 13% across 8 days, except for Pyridine which is more susceptible to variations during disk drying.

Figure 5 - BNA Analyte %RSD on the SPE-03 using Mini-disk



CONCLUSION

Compared to 47mm disks, Mini-disks have demonstrated improved results and easier handling. The compact and pre-packaged format also makes them easily integrable with the SPE-03, or even vacuum manifolds. Regardless of which type of disk is used, PromoChrom's SPE-03 system provides an efficient and versatile platform that extracts 8 samples simultaneously. The fixed extraction time using positive-pressure syringe pumps provides laboratories with predictable turnaround times.

References

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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 hydrophobic compounds.
MD-WAX-30	Packed with 45-um spherical WAX polymer. 50 Mini-disks per box.	For extraction of PFAS and other acidic compounds.

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