PROMOCHROM TECHNOLOGIES

Application Note
31309

Mini-disk 525

Extraction of **EPA Method 525 Semi-Volatile Organic Compounds** in Water using **Mini-Disks and Presto Automated SPE Extractor** by **Maryland Department of Health (MDH)**

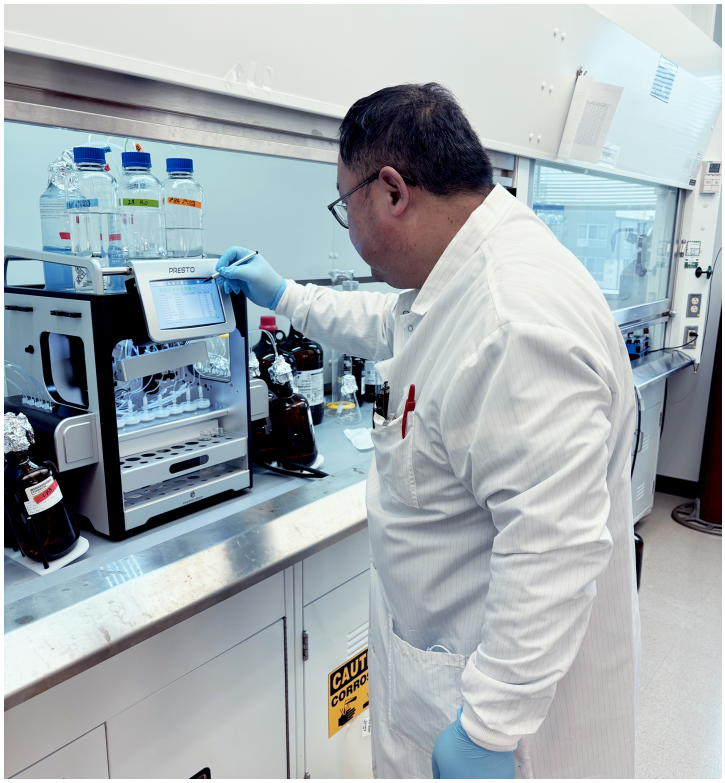
Authors

Raymond Chen, Manger
Heidi Li, Analytical Specialist
Ian Wan, General Manager
PromoChrom Technologies
Richmond, BC, Canada

Sinisa Urban, Ph.D, Division Chief
Xiaoli Hu, Public Health Laboratory Scientist G3
Division of Environmental Sciences
Laboratories Administration
Maryland Department of Health
1770 Ashland Ave. Baltimore
MD 21205 USA

Keywords

EPA Method 525, semi-volatile, Mini-disk, Presto Automated SPE, water



ABSTRACT

Solid phase extraction (SPE) is commonly used in the analysis of semi-volatile organic compounds (SVOCs) in drinking water. To capture the full advantages of SPE disks and cartridges, PromoChrom developed a suite of Mini-disks which come in a format similar to a 30 mm syringe filter and have a cross-sectional area 5 times that of a 6 mL SPE cartridge. The increased cross-sectional area and optimized sorbent properties enable the Mini-disks to work with much higher flow rates than SPE cartridges while consuming less solvent than SPE disks. Its compact size makes it easily adaptable to any PromoChrom automated extraction system, especially when paired with the latest Presto automated SPE system, which significantly shortens

the time needed for sample loading. This application note demonstrates the extraction of 22 SVOCs in water using our MD-525-30 Mini-disk with the Presto automated SPE system validated by MDH.

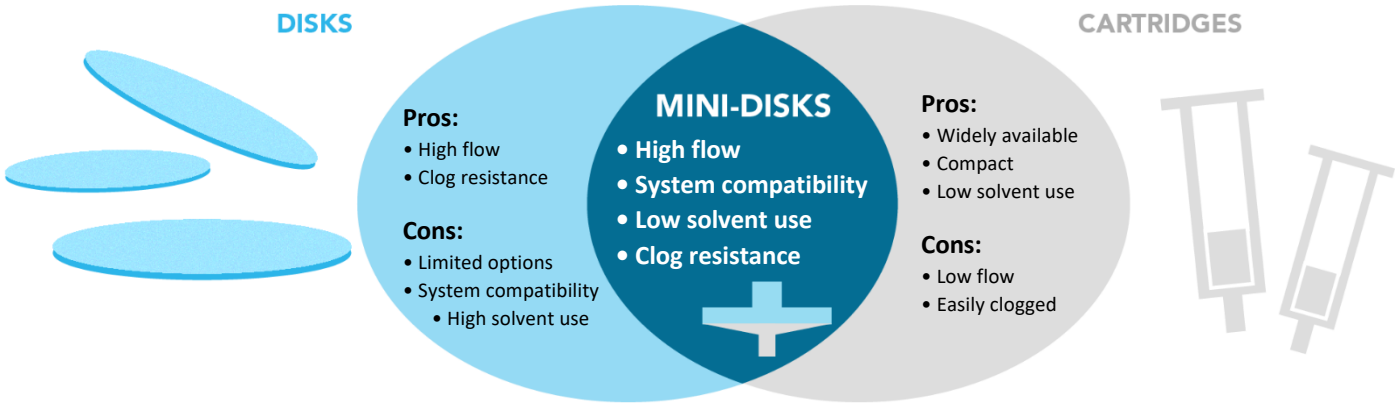
INTRODUCTION

Pesticides are widely used in agriculture to protect crops and improve yields, but their persistence in the environment can pose risks to water quality and public health. Detecting and quantifying trace levels of pesticides in water is essential for ensuring compliance with environmental regulations and safeguarding drinking water supplies.

As a major regional monitoring and testing government body, 'Maryland Department of Health-Laboratories Administration (MDH)' performs a wide range of sample testing, which includes testing for trace organic pesticides in tap water, well water and drinking water samples per EPA Method 525.2 to ensure the well-being of citizens. They are constantly looking for innovative techniques to optimize their workload and improve their performance.

EPA method 525.2 is a method for the determination of organic compounds in drinking water by extracting with liquid solid extraction (LSE) and identifying/quantifying by Gas Chromatography-Mass Spectrometry (GCMS). Per EPA Method 525, 1 L samples are extracted with LSE cartridges, SPE disks, or SPE cartridges. 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 addresses the shortcomings of cartridges and disks. 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. In combination with the PromoChrom Presto, a 50 mL/min flow rate can be achieved for the conditioning step, with a 35 mL/min sample loading rate and 5 mL/min for the final elution. The total extraction time is within 90 minutes and the total collection solvent volume is 19 mL (less than 50 mL after drying).



This application note demonstrates a series of tests that MDH has performed using MD-525-30 Mini-disk with the Presto automated solid-phase extraction system to extract 22 SVOCs from water samples for analysis.

MATERIALS

- Standards for sample spiking and GCMS analysis: Alachlor, Aldrin, Atrazine, Benzo(a)pyrene, Bis(2-ethylhexyl) Adipate, Bis(2ethylhexyl) Phthalate, Butachlor, Cis-Chlordane, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachlorocyclopentadiene, Lindane, Methoxychlor, Metolachlor, Metribuzin, Propachlor, Simazine, Trans-Chlordane, Trans-Nonachlor (see Appendix Table 1 for details)
- Internal standards: Acenaphthalene-d10, Phenanthrene-d10, Chrysene-d12 (see Appendix Table 1 for details)
- System Monitoring Compound (Surrogate): Perylene-d12 (see Appendix Table 1 for details)
- Mini-disk: PromoChrom Mini-disk packed with mixed-mode polymers and capable of extracting both hydrophilic and hydrophobic organic compounds in water (Cat. No.: MD-525-30).
- Equipment for Extraction: PromoChrom Presto automated SPE system.
- Instrument for analysis: Agilent GCMS system including a 7890B GC with split/splitless inlet, a 7693 autosampler and a 5977A Inert MSD. The column is an Agilent J&W HP-5MS 30m x 0.25mm x 0.25 µm.

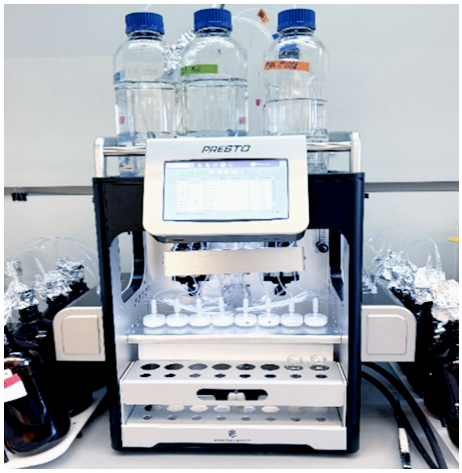


Figure 1: Presto SPE

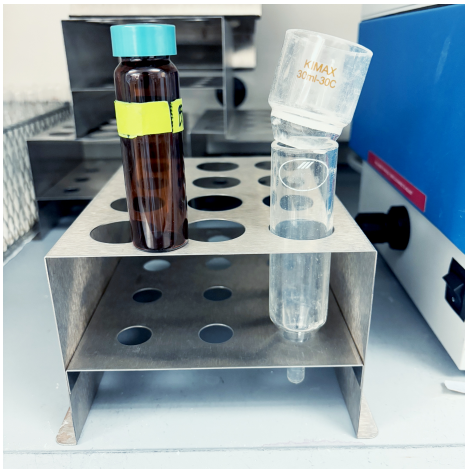


Figure 2: Collection Drying Apparatus


Figure 3: MD-525-30 Mini-Disk

METHOD

Sample Extraction

Sample extraction and GCMS analysis were performed by MDH.

Prior to the extraction, eight samples consisting of 950 mL of reagent water in 1liter amber glass bottle were prepared by addition of 40-50 mg of sodium sulfite as preservative, and then acidified to pH <2 using 6N hydrochloric acid. 5 mL of methanol was then added to the sample to assist dispersing of the standards. An aliquot of 40 µL stock standard solution (containing 2 µg for each analyte, added to Laboratory Fortified Blank (LFB), Laboratory Fortified Sample Matrix (LFM) samples), 100 µL stock Internal Standard (IS) and Surrogate Standard (SS) (containing 5 µg for each IS/SS) were added to the water samples.

Samples were extracted using the method shown below:

Procedures programmed on the Presto automated SPE system
***Solvent 1** = Methanol (MeOH), **Solvent 2** = Water, **Solvent 3** = Ethyl Acetate (EtOAc), **Solvent 4** = Methylene chloride (DCM);*
***W1** = Aqueous waste, **W2** = Organic waste*

Action	Inlet 1	Flow	Volume	***Description***
Elute W2	Solvent 4	50 mL/min	10 mL	*Condition Mini-disks with 10 mL of DCM*
Elute W2	Solvent 3	50 mL/min	10 mL	*Condition Mini-disks with 10 mL of EtOAc*
Wait	Time based		1 min	*Allow 1 minute soak*
Elute W2	Solvent 3	50 mL/min	5 mL	*Condition Mini-disks with 5 mL of EtOAc*
Air-Purge W2	Air	50 mL/min	10 mL	*Purge residual solvent from Mini-disks to waste 2*
Elute W2	Solvent 1	50 mL/min	10 mL	*Condition Mini-disks with 10 mL MeOH*
Wait	Time based		1 min	*Allow 1 minute soak*
Elute W2	Solvent 1	50 mL/min	5 mL	*Condition Mini-disks with 5 mL MeOH*
Elute W1	Solvent 2	50 mL/min	10 mL	*Condition Mini-disks with 10 mL water*
Add Sample W1	Sample	35 mL/min	10 mL	*Load samples at 35 mL/min, to prime the pump*
Add Sample+ W1	Sample	35 mL/min	1060 mL	*Load samples at 35 mL/min through presto pump, using 1060 mL to ensure all sample liquid in the bottles are loaded*
Elute W1	Solvent 2	50 mL/min	20 mL	*Wash Mini-disks with 20 mL water*
Air-Purge W1	Air	70 mL/min	10 mL	*Remove water droplets from the Mini-disks*
Blow N2	Time based		20 min	*Use nitrogen to dry the Mini-disks @**30psi** which gives about ~4-4.5 L/min flow rate for 8 channels*
Rinse	Solvent 3	70 mL/min	5 mL	*Rinse sample bottle with 5 mL EtOAc*
Air-Purge R	Air	70 mL/min	5 mL	*Purge rinse lines*
Collect 2	Sample	5 mL/min	5 mL	*Collect rinsate into Fraction 2*
Wait	Time based		1 min	*Allow liquid to settle for 1 minute*
Rinse	Solvent 4	70 mL/min	5 mL	*Rinse sample bottle with 5 mL DCM*
Air-Purge R	Air	70 mL/min	5 mL	*Purge solvent out of rinse line*
Collect 2	Sample	5 mL/min	5 mL	*Collect rinsate into Fraction 2*
Wait	Time based		1 min	*Allow liquid to settle for 1 minute*
Rinse	Solvent 4	70 mL/min	3 mL	*Rinse the sample bottle with 3 mL DCM*
Air-Purge R	Air	70 mL/min	5 mL	*Purge rinse lines*
Collect 2	Sample	5 mL/min	10 mL	*Collect rinsate into fraction 2*
Collect 2	Solvent 4	5 mL/min	3 mL	*Elute the Mini-disks directly with DCM and collect into fraction 2*

Action	Inlet 1	Flow	Volume	*Description*
Wait	Time based		1 min	*Allow liquid to settle for 1 minute*
Collect 2	Solvent 3	5 mL/min	3 mL	*Elute the Mini-disks directly with EtOAc and collect into fraction 2*
Air-Purge 2	Air	50 mL/min	15 mL	*Push any remaining sample into fraction 2*

The extraction took 81 minutes for a batch of 8 samples. The final extract in the collection vial was about 19 mL. 6-10 g of sodium sulfate was then added to the collection vial and the vial was vortexed. The mixture was then passed through 3-5 g of sodium sulfate and washed with 3 × 10 mL of DCM. The sample was concentrated to <1 mL (above 0.5 mL mark) using an evaporator with an endpoint detection sensor. Then, 10 µL of Recovery standard (RS) was added, and the volume was adjusted to 1.0 mL prior to GC-MS analysis.

Evaporator parameters: 45°C with a N_2 pressure setting of 9-10 psi. The N_2 pressure setting will start low at about 3-5 psi to avoid splashing when the liquid level is high in the collection vials.

GCMS Analysis

The parameters for GCMS analysis are listed below:

Parameters for GCMS analysis

Injection Volume	2 µL
Inlet	270 °C; Pulsed splitless injection mode
Oven Temperature Program	80 °C (hold for 0.5 minutes), 18 °C/min to 260 °C 6 °C/min to 310 °C (hold for 1 minute) Total run time: 19.83 mins
Carrier Gas and Flow Rate	Helium at 1.22 mL/min, constant flow
Transfer Line Temperature	280 °C
Ion Source Temperature	230 °C
Quadrupole Temperature	150 °C
Scan	50 to 550 *m/z*

RESULTS AND DISCUSSION

The recoveries of 22 compounds are summarized in Appendix Table 1. All analytes were spiked at 2 ppb and all recoveries fall within the 70-130% range, which meets the criteria of EPA 525.2 (as shown in Figure 4). The %RSD for most of the compound's are within 10% for 8 replicates conducted over 2 days.

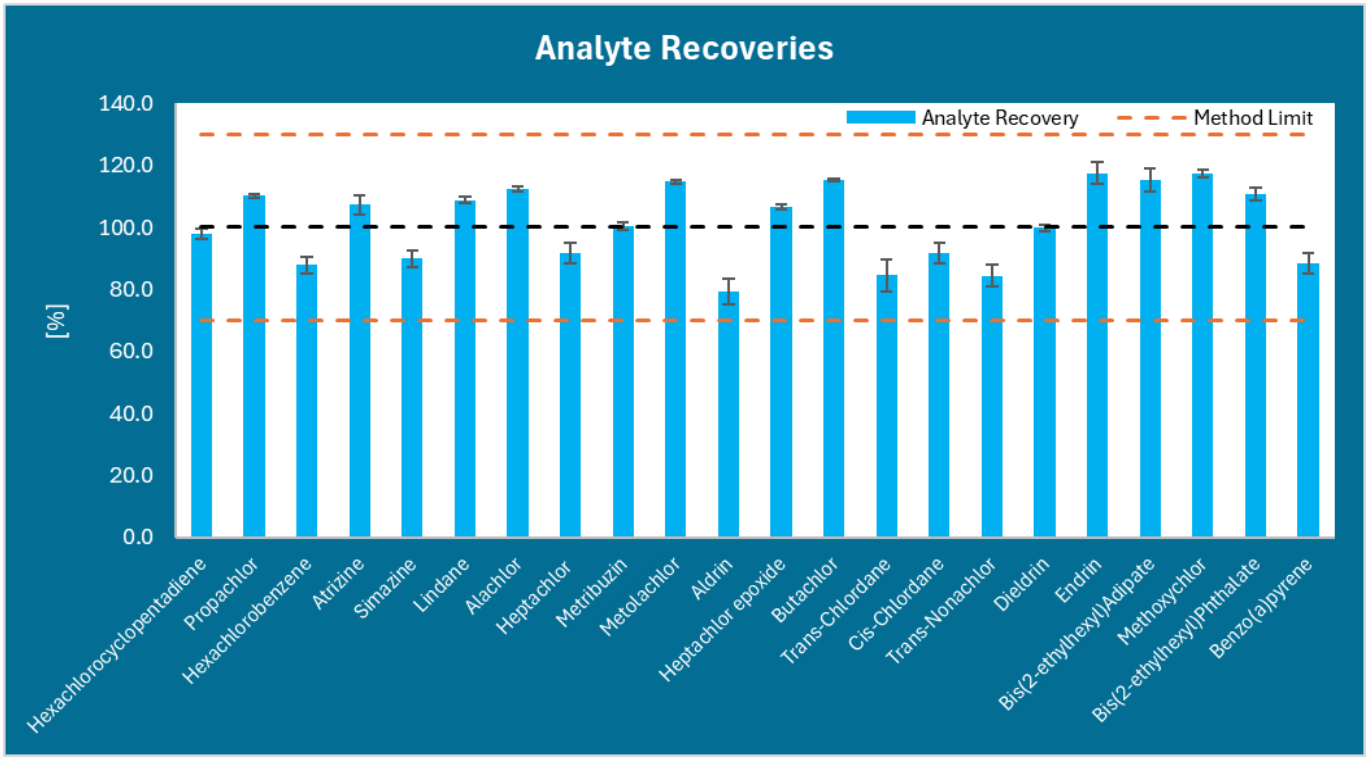


Figure 4: Analyte Recoveries on the Presto-SPE System: The method limits are illustrated as the red dashed line, with %RSD shown as an error bar. The black dashed line is 100%. Note: *Technical Chlordane: average of Trans-Chlordane, Cis-Chlordane and Trans-Nonachlor

The method detection limit (MDL) and reporting limit (RL) are shown in Figure 5. MDL verification was performed by running seven spikes at the following concentrations: 0.5 µg/L for pesticides and low level (LL) pesticides, and 1.0 µg/L for high level (HL) pesticides. The lab reagent blank (LRB) are reported to be lower than the detection limits. RL of lindane, Heptachlor, Heptachlor epoxide and Benzo(a)pyrene are 0.1 µg/L as validated on a separate RL study by 7 replicates spiking at 0.1 µg/L.

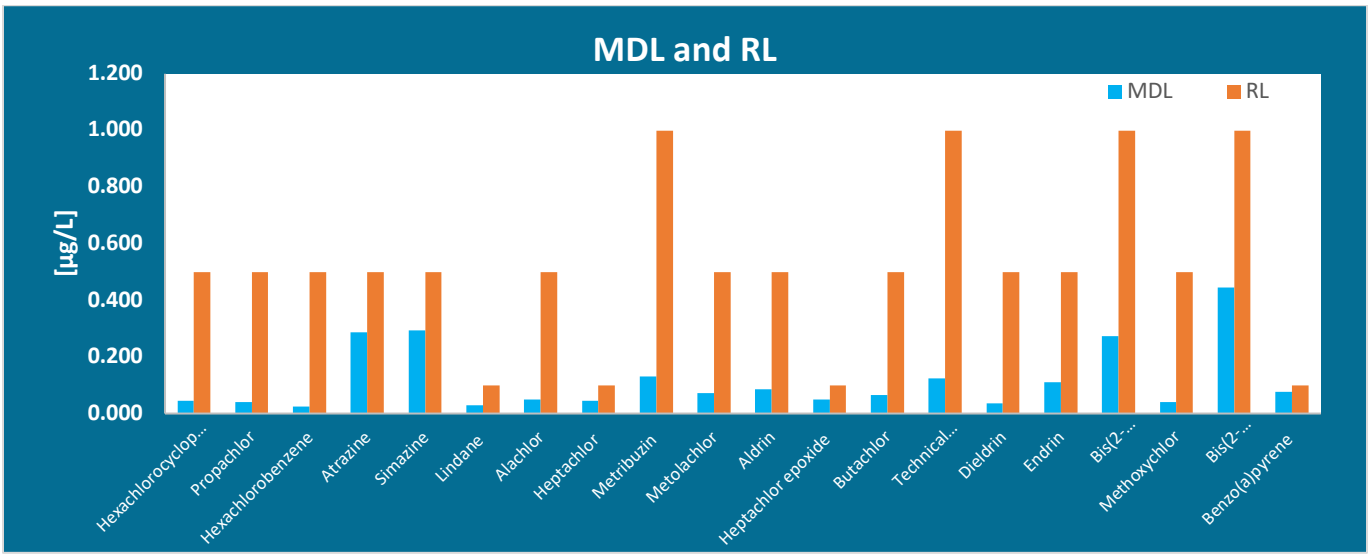


Figure 5: MDL and RL of Analytes on the Pesto-SPE System.

The average recovery of internal standards (IS), surrogate standards (SS) and recovery standards (RS) are in Figure 6. All recoveries also fall within the 70-130% for the EPA requirement. Please note that for EPA 525.2, IS/SS were spiked with 5 µg per liter of sample (pre-spiking), and RS was added at 5 µg per mL of the extracted sample in the final micro-vial (post-spiking). The %RSD for most of the compound's are within 10%.

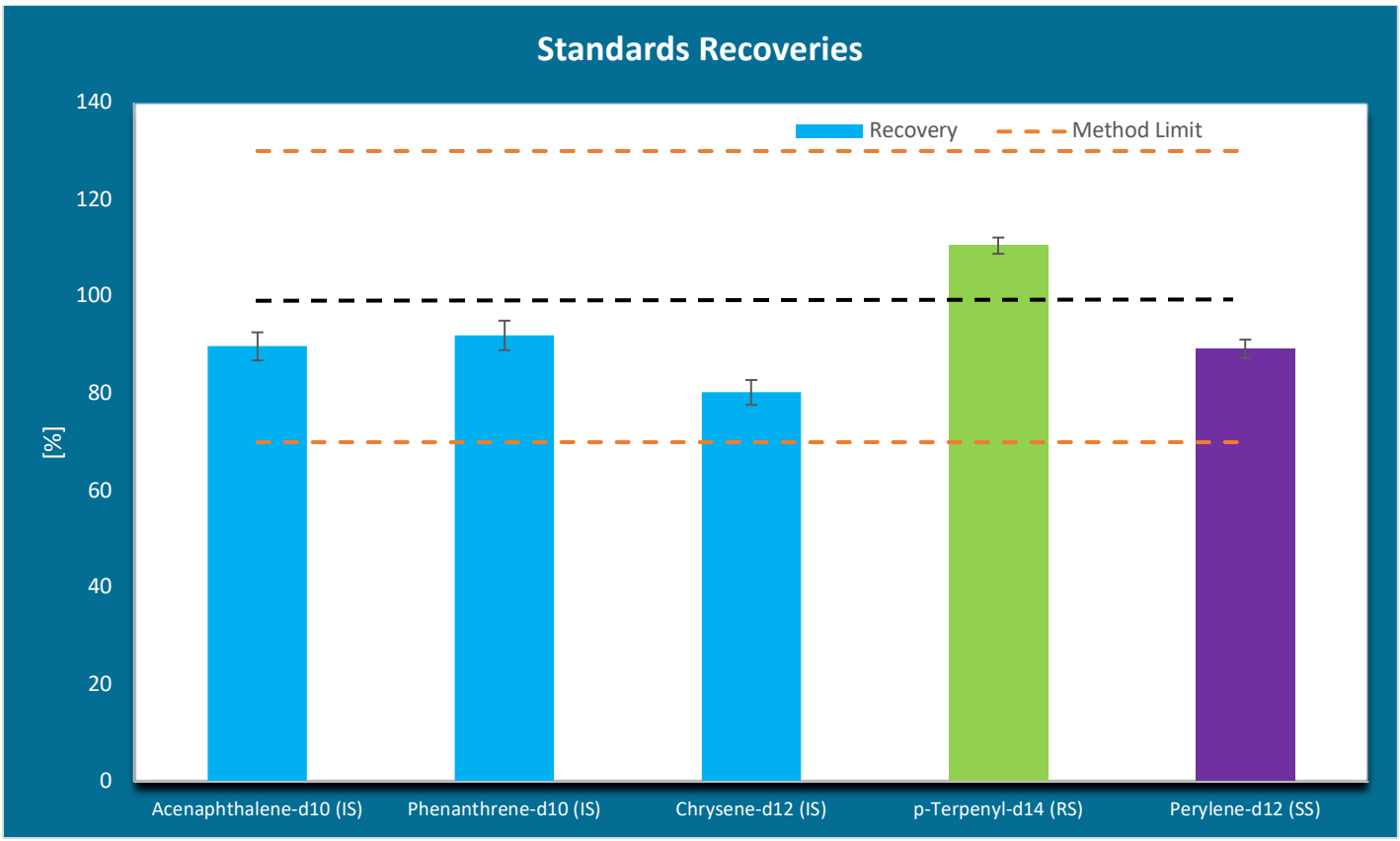


Figure 6: Recoveries of Internal standards (IS), Recovery standard (RS) and Surrogate standard (SS) on the Presto-SPE System with %RSD shown as an error bar. The method limits are illustrated as red dashed line, with %RSD shown as an error bar. The black dashed line is 100%.

CONCLUSION

The PromoChrom MD-525-30 mini-disk in combination with the PromoChrom Presto can effectively extract the 22 SVOCs monitored by MDH while meeting the EPA 525.2 certification criteria. This solution offers an efficient extraction approach taking 81 minutes for 950 mL samples and using a relatively small amount of final collection solvent of 19 mL. MDH diligently serves its community by performing a wide range of tests using automated SPE and developing optimal workflows through automation.

ORDERING INFORMATION FOR MINI-DISKS

Part number	Description	Application
MD-525-30	Packed with 25-um spherical mixed-mode sorbent, pack of 40	For extraction of hydrophobic and hydrophilic compounds.

REFERENCES

1. EPA method 525.2, EPA Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extractions and Capillary Colum Gas Chromatography/Mass Spectrometry .

Appendix

Table 1 – Average recoveries of analytes from 8 spiked samples

No.	Analytes	CAS No.	Average	RSD (%)	MDL (µg/L)	RL
1	Hexachlorocyclopentadiene	77-47-4	97.9	2.97	0.044	0.50
2	Propachlor	1918-16-7	110.3	1.19	0.041	0.50
3	Hexachlorobenzene	118-74-1	87.9	5.49	0.024	0.50
4	Atrazine	1912-24-9	107.3	6.00	0.287	0.50
5	Simazine	122-34-9	89.9	5.18	0.294	0.50
6	Lindane	58-89-8	108.8	2.07	0.029	0.10
7	Alachlor	15972-60-8	112.4	1.56	0.049	0.50
8	Heptachlor	76-44-8	91.8	6.42	0.044	0.10
9	Metribuzin	21087-64-9	100.4	2.78	0.130	1.00
10	Metolachlor	51218-45-2	114.8	1.21	0.072	0.50
11	Aldrin	309-00-2	79.2	8.25	0.086	0.50
12	Heptachlor epoxide	1024-57-3	106.5	1.66	0.049	0.10
13	Butachlor	23184-66-9	115.3	1.06	0.065	0.50
14	Trans-Chlordane	5103-74-2	84.5	10.41	0.124*	1.00
15	Cis-Chlordane	5103-71-9	91.7	6.95	0.124*	1.00
16	Trans-Nonachlor	39765-80-5	84.4	7.12	0.124*	1.00
17	Dieldrin	60-57-1	99.9	2.10	0.036	0.50
18	Endrin	72-20-8	117.6	7.03	0.111	0.50
19	Bis(2-ethylhexyl)Adipate	103-23-1	115.3	7.46	0.274	1.00
20	Methoxychlor	72-43-5	117.4	2.53	0.039	0.50
21	Bis(2-ethylhexyl)Phthalate	117-81-7	110.7	3.90	0.446	1.00
22	Benzo(a)pyrene	50-34-8	88.4	6.84	0.076	0.10
Acceptance Criteria			70-130	< 30	MDL<RL	

Note: *Technical Chlordane: average of 3 (Trans-Chlordane, Cis-Chlordane and Trans-Nonachlor)

Table 2 - Recoveries of Internal standards (IS) Recovery standard (RS) and Surrogates (SS)

Analytes	CAS No.	Average Recovery (%)	RSD (%)
Internal standards (IS)			
Acenaphthalene-d10	15067-26-2	89.8	5.78
Phenanthrene-d10	1517-22-2	92.0	6.08

Analytes	CAS No.	Average Recovery (%)	RSD (%)
Chrysene-d12	1719-03-5	80.3	5.13
Recovery standard (RS)			
p-Terpenyl-d14	1718-51-0	110.5	3.35
System Monitoring Compound (SS)			
Perylene-d12	1520-96-3	89.3	3.77
Acceptance Criteria		70-130	

NOTE: MDH does not endorse or recommend any products including those described herein.

Learn more at
www.promochrom.com

PROMOCHROM TECHNOLOGIES