PROMOCHROM TECHNOLOGIES

Application Note
31311

Aroclors with EPA 525.3

AUTOMATED SOLID PHASE EXTRACTION FOR PCBs AS AROCLORS BY GCMS

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ABSTRACT

The need for the detection and quantification of persistent organic pollutants such as PCBs as Aroclors has been of the highest concern since being banned in the USA in 1991. Manual extraction of these compounds is time-consuming and laborious and thus a robust and automated method for its extraction by Solid Phase Extraction (SPE) is required to give labs and government agencies an easier approach to monitor its levels in drinking water. This application note provides a guide on the utilization of PromoChrom's SPE-03 system for the reliable and robust extraction of PCBs as Aroclors with minimal time and excellent recoveries at the minimum reporting limit (MRL) and minimum detection limit (MDL).

INTRODUCTION

The Region of Waterloo laboratory has been providing biological, inorganic, and organic testing of municipal water as an ISO 17025 accredited laboratory since 1996. They have a battery of validated methods for the quantification of various organic pollutants and have employed EPA method 525.3 as the basis for this application note. They have been expanding their labs' capacity for pesticides, herbicides, hydrocarbons and 1,4-Dioxane utilizing the SPE-03 system. Traditionally the solid phase extraction of these compounds was performed on older extractors, while they have switched to the SPE-03 system in 2021 for better cost and work efficiency.

This application note demonstrates the automation of SPE extraction method using PromoChrom's SPE-03 and Empore's C18 Disks.

MATERIALS

- PromoChrom SPE-03 system with MOD-00P (Volume-Matrix Plus configuration and MOD-003 (47mm SPE Disk kit)
- SPE Disk - CDS Empore 2215 C18 Disk
- Reagents and standards following the in-house method below
- GCMS Agilent 6890 & 7890 and Mass Detector Agilent Inert 5973 & 5975.

METHOD SUMMARY

SPE Method

Solvent 1 = Acetone, **Solvent 3** = Dichloromethane, **Solvent 4** = Methanol
Solvent 5 = H_2O, **W1** = Aqueous waste, **W2** = Organic waste

Table 1 – PCB as Aroclors extraction steps programmed on the SPE-03.

Action	Inlet 1	Flow	Volume	*Description*
Elute W2	Solvent 1	50 mL/min	10 mL	*Condition Disks with 10 mL of Acetone*
Wait	Time based		1 min	*Allow 1 minute soak*
Air-Purge W2	Air	50 mL/min	15 mL	*Purge solvent from the Disks*
Elute W2	Solvent 3	50 mL/min	10 mL	*Condition Disks with 10mL of DCM*
Wait	Time based		1 min	*Allow 1 minute soak*
Air-Purge W2	Air	50 mL/min	15mL	*Purge solvent from the Disks*
Elute W2	Solvent 4	50 mL/min	10 mL	*Condition Disks with 10mL of Methanol*
Wait	Time based		1 min	*Allow 1 minute soak*
Air-Purge W2	Air	50 mL/min	15 mL	*Purge solvent from Disks*
Elute W1	Solvent 5	50 mL/min	10 mL	*Condition Disks with water*
Add Sample	Sample	50 mL/min	850 mL	*Load the samples at 50ml/min*
Air-Purge W1	Air	50 mL/min	15 min	*Remove large water droplets from the Disks*
Blow N2	Time based		10 min	*Dry Disks for 10 minutes*
Rinse	Solvent 5	70 mL/min	5 mL	*Rinse the sample bottles with water*
Air-Purge R	Air	70 mL/min	5 mL	*Purge rinse lines*
Collect 2	Sample	60 mL/min	15 mL	*Collect rinsate into fraction 2*
Wait	Time based		3 min	*Allow 3 minute soak*
Collect 2	Sample	70mL/min	10 mL	*Collect any remaining rinsate into fraction 2*
Air-Purge 2	Air	70mL/min	10 mL	*Push any remaining rinsate into fraction 2*
Rinse	Solvent 3	70mL/min	15 mL	*Rinse sample lines and sample bottle with DCM*
Air-Purge R	Air	60mL/min	5 mL	*Push remaining rinsate into the sample bottles*
Collect 2	Sample	60mL/min	10 mL	*Collect rinsate through the Disks into fraction 2*
Wait	Time based		1 min	*Allow 1 minute soak*
Collect 2	Sample	70mL/min	10 mL	*Push any remaining sample through into fraction 2*
Air-Purge 2	Air	70mL/min	15 mL	*Push any remaining sample into fraction 2*

Rinse	Solvent 3	70mL/min	15 mL	*Rinse sample lines and sample bottle with DCM*
Air-Purge R	Air	60mL/min	10 mL	*Push remaining rinsate into the sample bottles*
Collect 2	Sample	60mL/min	15 mL	*Collect rinsate through the Disks into fraction 2*
Wait	Time based		1 min	*Allow 1 minute soak*
Collect 2	Sample	70mL/min	10 mL	*Collect rinsate through the Disks into fraction 2*
Air-Purge 2	Air	60mL/min	15 mL	*Push remaining rinsate into the Disks into fraction 2*

The final sample was dried using a Whatman drying disc and reconstituted to 1ml before internal standards are added.

GC-MS Conditions

Table 2- GCMS Conditions for both GC 1 and 2.

Parameter	Value
GC-MS	GC Agilent 6890 and 7890*
GC Column	HP5-MS or DB5MS capillary column 30 m x 0.25 mm I.D x 0.25 µm film
Injection	220 °C splitless injection Injection volume: 2µL Pressure: 6.1 psi Viscosity delay: 1 second Gas saver on Saver flow: 15.0mL/min Saver time: 3.00min Gas Type Helium Total flow at 50 mL/min
GC Column Conditions	Max temperature: 350 °C Mode: constant flow Initial flow: 0.9 mL/min Nominal initial pressure: 6.11 psi Average velocity: 34 cm/sec MSD Transfer Line Heater: 310 °C
Temperature Program	Initial temperature at 50 °C for 1 min 15 °C/min to 270 °C 45 °C/min to 320 °C hold for 5 mins Total run time 21.28 mins
MS Acquisition Parameters	Mass selective detector, Agilent 5973 and 5975* SIM mode with qualifier masses for each target analyte Solvent delay 7.0min MS Quad: 150 °C to 250 °C MS Source: 230 °C to 250 °C

**Agilent 6890 with mass detector 5973 was used for GCMS1 run and 7890 with mass detector 5975 for GCMS2 run*

Table 3 - Target Ion m/z and Qualifier Ions.

PCB	Target Ion [m/z]	Ion 1 [m/z]
Aroclor 1242 (peak 1-3)	256	
Aroclor 1242 (peak 4-7)	292	222
Aroclor 1254 (peak 1-6, 8)	326	292
Aroclor 1254 (peak 7, 9, 10)	326	362
Aroclor 1260 (peak 1)	360	362
Aroclor 1260 (peak 2-7)	394	360
Phenanthrene-d10 (IS)	188	186
Decachlorobiphenyl (Surr.)	498	428

Scope and Interpretation

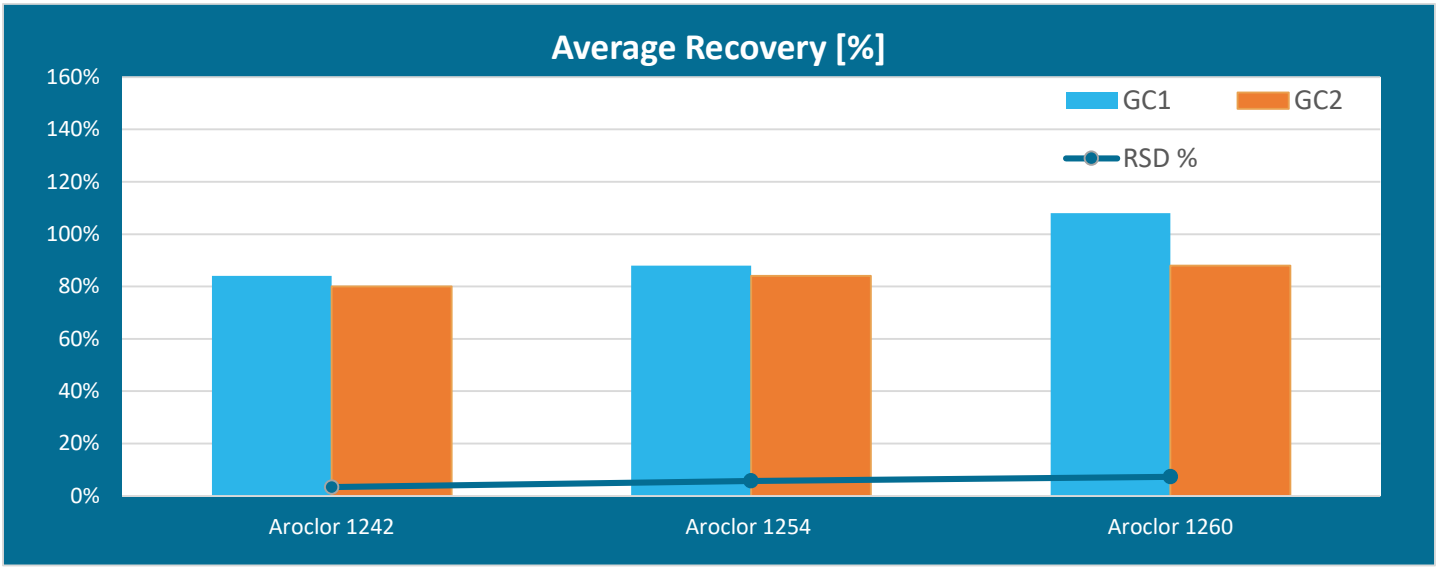
The presence of Aroclors is confirmed by positive detection of individual and unique peaks to each given Aroclor. There are 7 peaks for Aroclor 1242 and 1260 with 10 peaks for Aroclor 1254, concentration for which must be present at ±50% within each set of Aroclor peaks for a positive confirmation for that Aroclor. If they are not at the predetermined level, the set of peaks are not included in the integration. The final concentration of each Aroclor is taken as an average of at least half of all individual peaks.

RESULTS

The data was collected from multiple separate runs, 8 for the MRL and 10 for the MDL with two different GCMS's with the extraction method as described above. The MRL was determined for each of the compounds extracted to establish the method limit of quantification and reporting. In addition to this, 8 analytical runs at mid-level spiking were done for method validation and for demonstration of precision and accuracy. There was no detection of any Aroclors in the blank above 1/3 of the signal-to-noise ratio for all analytical runs.

PCBs as Aroclors Reporting Limit

Figure 1 - Average Reporting Limit Recoveries and RSD % for aroclors using SPE-03 Gen 4 with Empore C18 Disks.



The Aroclors were spiked into 800mL of drinking water with 395µL of spiking solution, extracted, and ran in sets of ten on two separate GCMS instruments with a theoretical expected value of 0.25µg/L. A five-point calibration curve was used, and the recovery values ranged from 80-108% conforming to the limits of 50-150% for the MRL as set in EPA method 525.3 Table 24[1].

On top of the recovery and repeatability of the results, the MRL achieved by the automated extraction is 0.020-0.049 µg/L compared to the previous RL of 0.050 µg/L for all analytes. The %RSD was between 3.48% and 7.37% which have been averaged for each Aroclor above in Figure 1. This was calculated from the standard deviation of each and multiplied by the t value where t = 2.821 at 99% confidence interval.

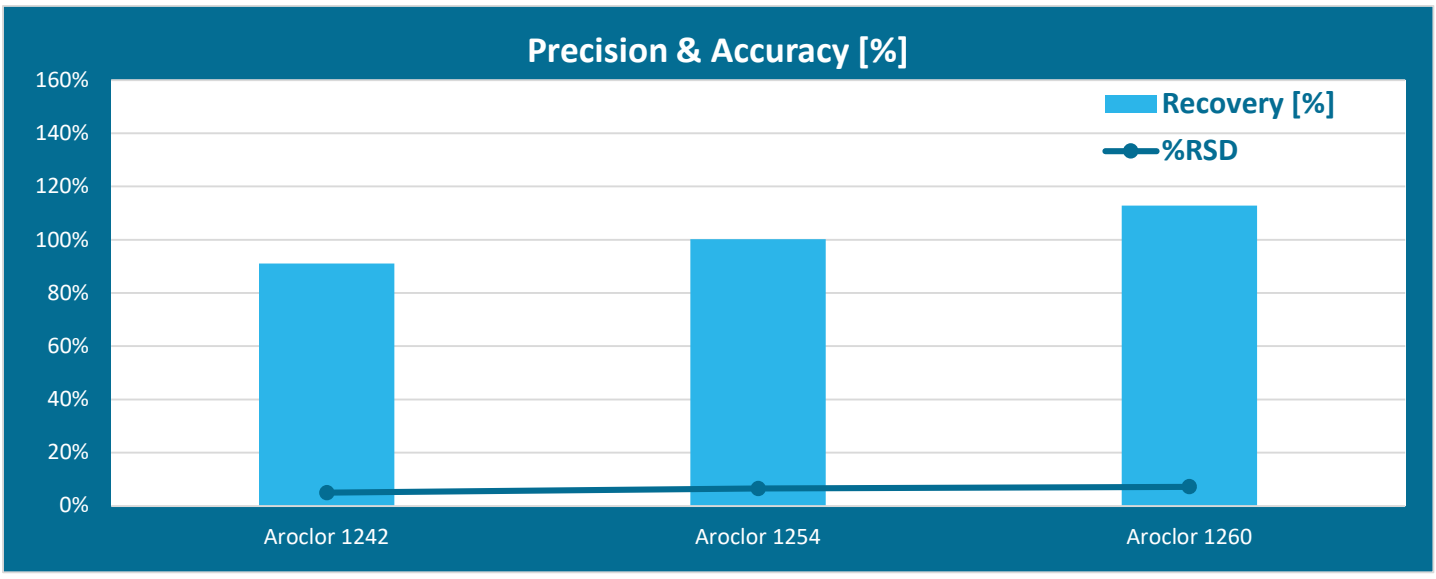
Table 4 - MRL determination of each Aroclor for GC 1 and 2.

Compound & GC Run	Concentration of analytes [µg/L]								Std Dev	MRL [µg/L]
	#1	#2	#3	#4	#5	#6	#7	#8		
Aroclor 1242 GC1	0.21	0.20	0.22	0.21	0.20	0.21	0.20	0.21	0.007	0.020
Aroclor 1242 GC2	0.22	0.20	0.22	0.20	0.19	0.21	0.20	0.19	0.011	0.031
Aroclor 1254 GC1	0.23	0.22	0.23	0.23	0.22	0.22	0.21	0.21	0.008	0.024
Aroclor 1254 GC2	0.22	0.23	0.23	0.23	0.21	0.20	0.20	0.20	0.015	0.044
Aroclor 1260 GC1	0.26	0.27	0.28	0.28	0.26	0.29	0.26	0.24	0.016	0.047
Aroclor 1260 GC2	0.24	0.24	0.23	0.22	0.21	0.22	0.21	0.19	0.017	0.049

PCBs as Aroclors Precision & Recovery

The Aroclors were spiked into 800mL of drinking water with 995µL of spiking solution, extracted, and ran in sets of 8 on GCMS 1 with a theoretical expected value of 0.63µg/L. The average recovery values ranged from 91% to 112% and the %RSD were between 5.01% to 7.19%. These results are within the criteria set out in EPA method 525 Table 24[1] of ±30% of the expected value and <20% RSD for mid-level calibration spikes.

Figure 2 - Average Precision and Recovery for each Aroclors.



PCBs as Aroclors Minimum Detection Limit (MDL)

The Aroclors were spiked into 800mL of MilliQ water with 300µL of spiking solution in two sets of ten on each GCMS system. The MDL was determined by the t value, where t = 2.821 at 99% confidence interval (p = 0.01) multiplied by the standard deviation of the results as listed in table 4.

Table 5 - %RSD (MDL) of each Aroclor for GC 1 and 2.

	Aroclor 1242 GC1	Aroclor 1242 GC2	Aroclor 1254 GC1	Aroclor 1254 GC2	Aroclor 1260 GC1	Aroclor 1260 GC2
%RSD (MDL)	3.29%	2.85%	2.45%	2.50%	3.37%	2.13%

The %RSD for the MDL was between 0.012-0.018µg/L compared to the previous MDL of 0.020µL for all compounds. The overall improvement in the MDL compared to its initial MDL is impressive in its performance for both the Disks and SPE-03 working in tandem. This represents an enhancement in not only extraction time but also recovery limits in an area of residue analysis in which the set limits are only trending to lower legislative limits. The comparable result for each GC system and respective Aroclor is a demonstration of the robustness and repeatability using the SPE-03 as seen in Table 6.

Table 6 – MDL determination for each Aroclor for GC 1 and 2.

Compound & GC Run	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	Std Dev	MDL [µg/L]
Aroclor 1242 GC1	0.20	0.19	0.20	0.19	0.20	0.19	0.19	0.19	0.19	0.18	0.006	0.018
Aroclor 1242 GC2	0.19	0.19	0.19	0.19	0.19	0.18	0.18	0.18	0.18	0.18	0.005	0.015
Aroclor 1254 GC1	0.20	0.20	0.20	0.19	0.20	0.19	0.20	0.20	0.20	0.19	0.005	0.014
Aroclor 1254 GC2	0.20	0.20	0.19	0.19	0.20	0.19	0.19	0.19	0.19	0.19	0.005	0.014
Aroclor 1260 GC1	0.21	0.21	0.22	0.21	0.23	0.22	0.22	0.23	0.22	0.22	0.007	0.021
Aroclor 1260 GC2	0.20	0.20	0.20	0.20	0.20	0.19	0.20	0.19	0.20	0.20	0.004	0.012

CONCLUSIONS

PromoChrom's SPE-03 system, which is compatible with both SPE Disks and cartridges, provides a simple and streamlined solution for extracting PCBs from drinking water simultaneously for up to 8 samples per system. The method has demonstrated excellent recoveries and reproducibility even at the minimum reporting limit and exceeded the previous limits achieved by the lab. Besides Aroclors, the same solution can be used for the full range of pesticides, PAHs, and other semi-volatile organic compounds in water.

References

1. EPA Method 525.3
   https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=505395&Lab=NERL

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