Reducing Instrument Downtime for Polychlorinated Biphenyl Sample Analysis Using an Optimized Graphitized Carbon Black Cartridge for Extract Cleanup

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Abstract

Some of the most commonly encountered problems experienced by those analyzing environmental samples for polychlorinated biphenyls are instrument downtime and shortened calibration periods, both of which are due to the deleterious effects of co-extracted matrix components that are introduced into the analytical instrument during sample injection. In addition to this, chromatographic interferences complicating identification and quantification have also made life difficult for environmental analysts. Although there are cleanup options such as Florisil, silica gel, and alumina, these normal phase solutions often do not adequately remove the less polar and high molecular weight compounds that are responsible for diminishing instrumental performance and sample path inertness.

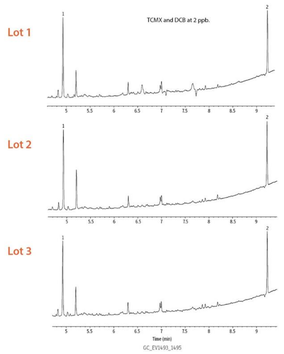
In this presentation, a cartridge is introduced that is designed specifically to be utilized exactly like the commonly employed Florisil cartridge, but to a much superior effect for highly pigmented and inlet degrading samples. What this means for the analyst, is calibration intervals that can be maintained longer and reduced instrument maintenance, ultimately leading to higher sample throughput.

Introduction

Although PCBs generally are not easily degraded by injector and column fouling, the organochlorine pesticides that may be analyzed with them in EPA methods like 608 and 508.1 are, requiring that a GC degradation mix be analyzed and pass to ensure system inertness in order to continue analyzing samples. Even though these two classes of compounds are not always analyzed together, having their own distinct analytical methods in the case of EPA 8081 and 8082, in smaller labs with limited instrumentation, they may both be analyzed using a common GC requiring the PCB extracts to be cleaned as effectively as the pesticides so as not to contaminate the instrument and cause samples to be held up while the instrument is being maintenanced for the sake of the more sensitive pesticide samples.

A potential pitfall exists, however, in blindly adopting the cleanup method developed to address pesticide cleanup for PCB Aroclor analysis in that the nature of graphitized carbon retention has the possibility to excessively retain the planar, non-ortho congeners. This aspect of the carbon needs to be evaluated in order to ensure that characteristic congeners of certain Arochlors are not lost, leading to an inability to identify and quantify the various Aroclors.

Figure 1. Illustration of the minimal level of interferences eluting from CarboPrep Plus cartridges when compared to reference compounds spiked at only 2 ppb.



Peaks
1. 2,4,5,6-Tetrachloro-*m*-xylene (TCMX)
2. Decachlorobiphenyl (DCB)

Column	Rtx-CLPesticides, 30 m, 0.32 mm ID, 0.32 µm (cat.# 11141)
Sample	2,4,5,6-Tetrachloro-*m*-xylene (cat.# 32027) Decachlorobiphenyl (BZ #209) (cat.# 32029)
Diluent:	Hexane
Injection	
Inj. Vol.:	4 µL splitless (hold 0.75 min)
Liner:	Topaz 4.0 mm ID single taper inlet liner w/wool (cat.# 23303)
Inj. Temp.:	250 °C
Purge Flow:	50 mL/min
Oven	
Oven Temp.:	90 °C (hold 0.5 min) to 330 °C at 25 °C/min (hold 2 min)
Carrier Gas	He, constant flow
Flow Rate:	3.5 mL/min
Detector	Micro-ECD @ 340 °C
Make-up Gas	
Flow Rate:	50 mL/min
Make-up	
Gas Type:	N_2
Data Rate:	50 Hz
Instrument	Agilent/HP6890 GC
Notes	Conditioned a Resprep CarboPrep Plus SPE cartridge (cat.# 25845) by adding one cartridge volume of hexane:acetone (90:10) and letting it stand for five minutes before drawing the solvent down to frit level. Then, 1 mL of sample extract was loaded onto the cartridge and eluted with 9 mL of hexane:acetone (90:10).

Objectives

- To show the cleanup capabilities of Resprep® CarboPrep Plus SPE Cartridges for PCB Aroclor sample extracts.
- To illustrate the low background of extractable material from the cartridge and how it compares to the response of typical Aroclor components.
- To demonstrate the instrument performance advantages of the Resprep® CarboPrep Plus SPE Cartridges using the specified method conditions.
- To show minimal effect on the elution pattern of PCB Aroclors as a result of passing through a graphitized carbon black cartridge.

Materials and Method

- Resprep® CarboPrep Plus SPE Cartridges were evaluated in the format: 3 mL, 95 milligram (cat.# 25845) using a Resprep 12-post vacuum manifold (cat.# 28298-VM)
- An Agilent 7890 GC-ECD with autosampler was used for this work
- Reference standards (Restek Corporation, unless otherwise specified):

  Figure 1: Tetrachloro-*m*-xylene, (cat.# 32027), Decachlorobiphenyl, (cat.# 32029)

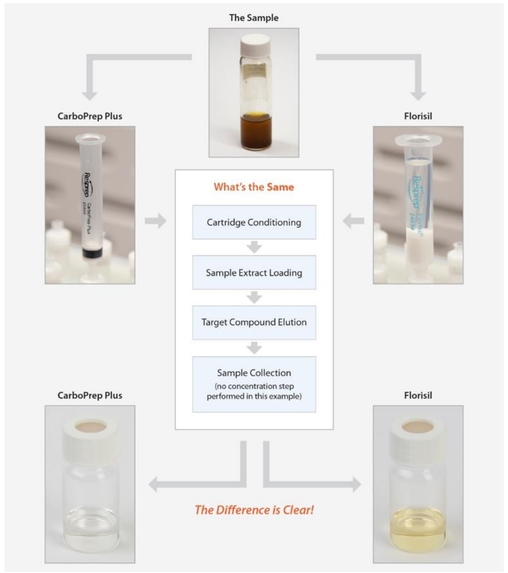
  Figure 3: Organochlorine Pesticide System Check Mix, (cat.# 32417)

  Table 1: PCB Congener Mix #1 - #9, (cat.# C-CS-01 – C-CS-09), AccuStandard, New Haven CT.

  Figure 4: Aroclor 1221, (cat.# 32007)

  Figure 5: Aroclor 1254, (cat.# 32011)

Figure 2. Illustrates the visual difference between an extract using CarboPrep Plus and Florisil cartridge cleanups



Results and Discussion

- Background extractable testing suggests clean, consistent background signal not always observed with common cleanup SPE products (**Figure 1**).
- Only a few congeners that appear in Aroclor mixes are not recovered completely as illustrated in **Table 1**.
- An obvious visual removal of all pigmented interferences in the extract are apparent as compared with standard SPE cleaning techniques (**Figure 2**).
- Cleanup of a complex sample extract using CarboPrep Plus can allow the GC Degradation Breakdown standard to pass for many more injections compared with cleanup using Florisil (**Figure 3**).
- The Aroclor most affected by the retention of non-ortho congeners is 1221 with PCB-15 being the most obvious preventing that congener from being used to quantitate samples, but even here, the overall ability to identify the Aroclor as 1221 is not diminished (**Figure 4**).
- The heavier Aroclors, such as 1254, are not affected by this excess retention at all **(Figure 5).**

Figure 3. Graphic of the advantage of CarboPrep Plus over Florisil for maintaining system inertness for longer periods allowing more samples to be analyzed prior to performing instrument maintenance.

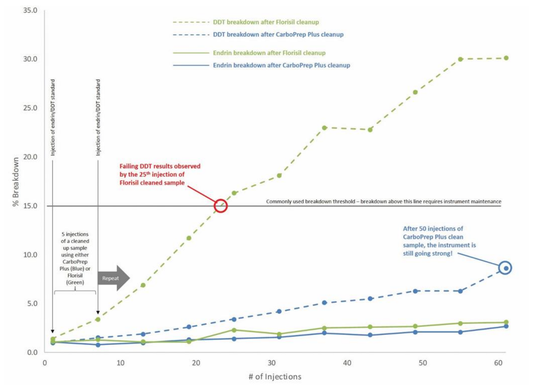


Table 1. Illustrates the list of retained congeners and their % composition in the listed congeners

Congener	Total # of Cl's in PCB congener	Percentage of congener collected in the 1st 5 mL	Percentage of congener collected in the 2nd 5 mL	Percentage of congener collected in the 3rd 5 mL	Percentage of congener collected in the 4th 5 mL	Percentage of congener collected in the 5th 5 mL	Percentage of congener found in Aroclors[1]	Aroclors where congener is present (Aroclor in bold contains the highest % makeup of congener)
PCB-13	2	95	5				1.1	**1221**,1232
PCB-11	2	93	7				<<0.3	
PCB-12	2	45	44	9	2		0.6	**1221**,1232
PCB-14	2	70	24	5			<<0.3	
PCB-15	2	4	36	33	18	9	4.2	**1221**,1232,1016,1242
PCB-36	3	86	13	1			<<0.3	
PCB-39	3	41	39	13	5	2	<<0.3	
PCB-38	3	41	43	12	4	2	<<0.3	
PCB-35	3	27	40	18	9	5	<<0.3	
PCB-37	3		16	32	29	23	2.2	**1242**,1232,1016,1248
PCB-80	4	81	17	2			<<0.3	
PCB-78	4	16	43	22	12	7	<<0.3	
PCB-79	4	12	42	23	14	9	<<0.3	
PCB-81	4	2	11	27	32	27	<<0.3	
PCB-77	4				36	64	0.5	**1248**,1242
PCB-126	5	7	39	29	16	9	<<0.3	
PCB-127	5			9	33	57	<<0.3	
PCB-169	6			9	32	59	<<0.3	

Conclusions

- Resprep® CarboPrep Plus SPE Cartridges possess a unique selectivity that allows interference removal unsurpassed by typical normal phase SPE cartridges.
- Although a few congeners are retained on the GCB surface, the overall ability to recognize and quantify PCB Aroclors is not diminished.
- The ability of the cartridge to remove inertness robbing contaminants that otherwise would result in additional instrument downtime is significantly better than that of Florisil.

Figure 4. Highlights the most strongly retained congener in the most affected Aroclor illustrating overall, minimum effect on the ability to identify and quantify it.

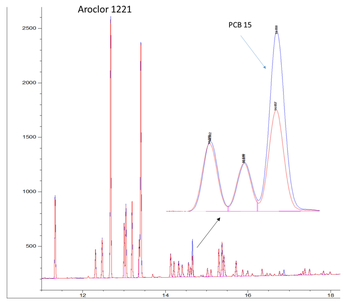


Figure 5. Illustrates that Aroclor 1254 is not affected in the least.

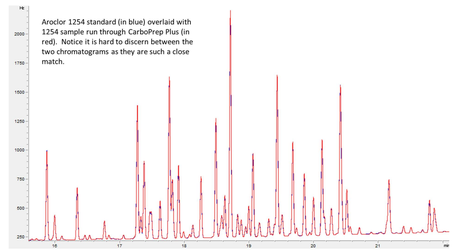
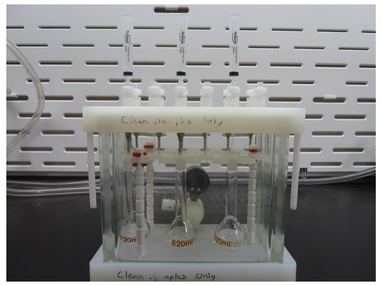


Figure 6. A 12-port vacuum manifold in combination with the CarboPrep Plus cartridges was used to evaluate the performance possibilities of SPE cleanup for PCB Aroclor samples.



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