Discover how chromatography is a
front-line player to monitor persistent organic pollutants.

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Persistent organic pollutants (POPs) are toxic organic compounds that are resistant to the natural degradation processes. They persist in the environment for extremely long periods and can be transported for great distances as they are semi-volatiles. This means they are volatized with the heat, transported by the wind, then moving back in the liquid state. These lipophilic compounds accumulate in the human and animal tissues and are therefore subjected to bio-amplification.

Among the POPs, there are various chemical classes such as the well-known PAHs (polycyclic aromatic hydrocarbons), pesticides, but also the three following classes which this article will focus on:

- **Dioxins**: These are derived from low temperature combustion of chlorinated compounds (Waste disposal, metal combustion and manufacturing process, paper chlorine bleaching or pesticides/herbicides production…).

- **PolyChlorinated Biphenyls** (**PCBs**): PCBs were extensively used as coolant in transformers and capacitors because of their excellent dielectric properties.

- **PolyBrominated DiphenylEthers** (**PBDEs**): Used as flame retardants and can be

found in furniture.

After extensive usage, it was determined that these compounds represent a high toxicity and have been restricted or banned in many areas, including the Stockholm Convention. Therefore, chromatography is a front-line player to monitor such species in Food and Environment matrices.

Dioxins Analysis in Gas Chromatography (GC)

Dioxins are part of a group of 210 tricyclic planar aromatic compounds with one or two oxygen atoms and a chlorination degree from 1 to 8. All these dioxins have very similar chemical and physical properties which makes their separation tricky. Two classes of dioxins can be found: PolyChlorinated Dibenzo Dioxins (PCDDs) and PolyChlorinated Dibenzo Dioxins furans (PCDFs).

Depending on the Chlorine atoms positions, there are 75 congeners of PCDD (See figure 1) and 135 congeners of PCDF.

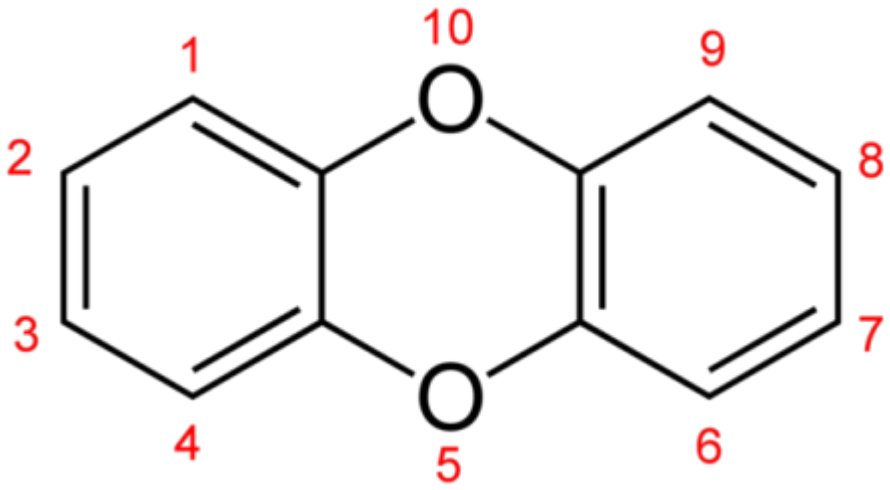


Figure 1- PolyChlorinated Dibenzo Dioxins (PCDDs) structure

According to the International Cancer Research Center (IARC), congeners with 8 chlorine atoms are as carcinogenic as 2,3,7,8 tétrachlorodibenzodioxine classified as group 1.

To separate them using GC-HRMS, 5% Phenyl phases are the most common options and it has been experimentally demonstrated that Phenyl arylen (ZB-5MSPlus or ZB-Semivolatile) with Phenyl groups incorporated in the PDMS polymeric chain offers a better separation than traditional Phenyl phases (such as ZB-5 or ZB-5MSi) as illustrated in Figure 2. This is due to a difference in steric interactions with a planar and non-planar Phenyl group in the GC phase.

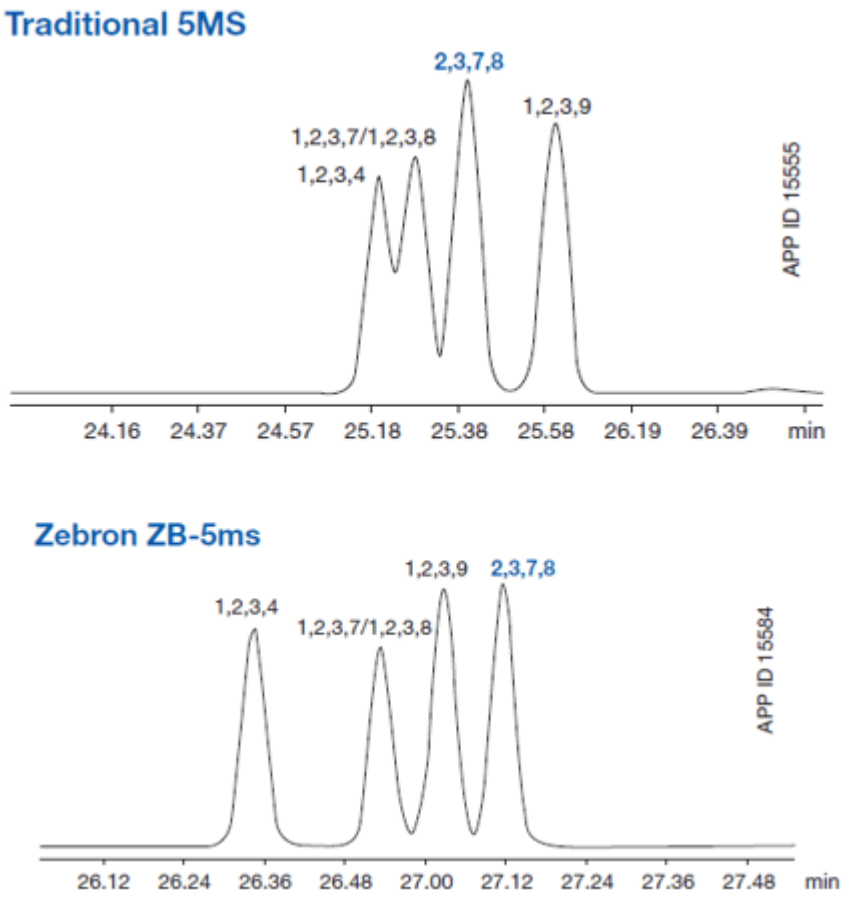


Figure 2- Dioxins congeners separation comparing a traditional 5% Phenyl phase and a 5% Phenylarylen phase

Figure 3 shows a great separation on ZB-5MS 60m x 0.25mm x 0.25µm using a GC-HR/MS of many toxic congeners.

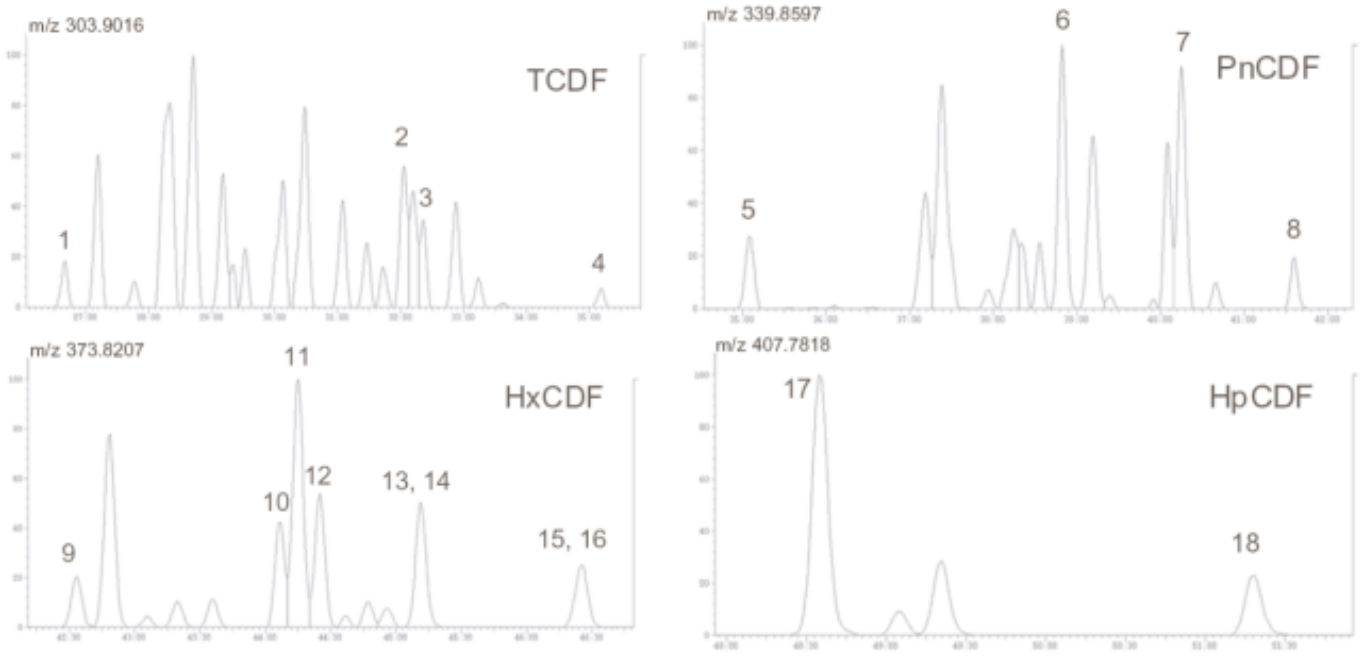


Figure 3 – Separation of TCDF (TetraChloroDibenzoFurans), PnCDF (PentaChloroDibenzoFurans), HxCDF (HexaChloroDibenzoFurans) and HpCDF (HeptaChloroDibenzoFurans) groups using a Zebron 5% Phenylarylen phase. Oven profile : 120°C for 1min to 220°C at 20°C/min for 16min to 235°C at 5°C/min for 7min to 300°C at 5°C/min for 15min

PCBs GC analysis

PCBs (Figure 4) are defined by The International Agency for Research on Cancer (IARC) as carcinogens in humans. Some of them act like dioxins, some other cause endocrine disruption and are neurotoxic. These compounds have contaminated many rivers, schools, buildings, parks or food and all these environmental matrices are analysed to ensure our safety.

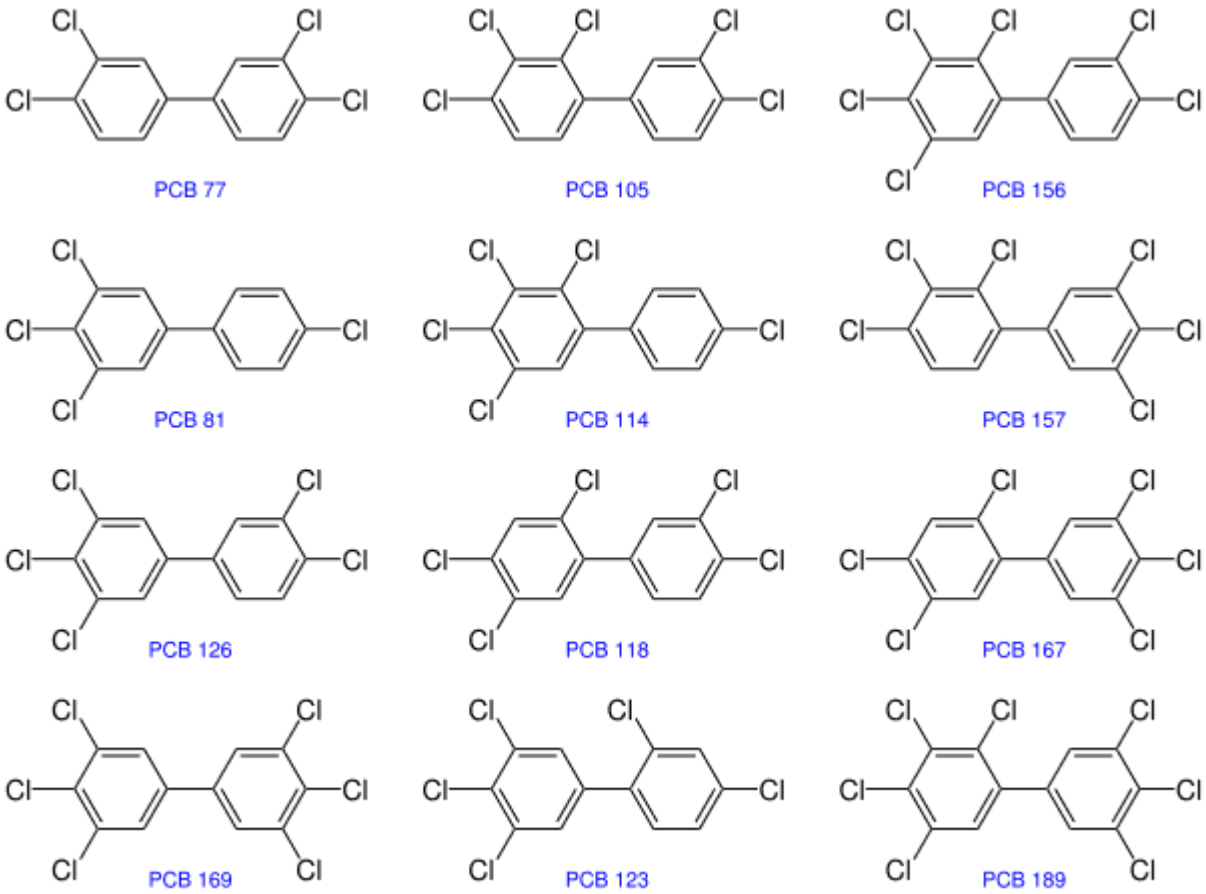
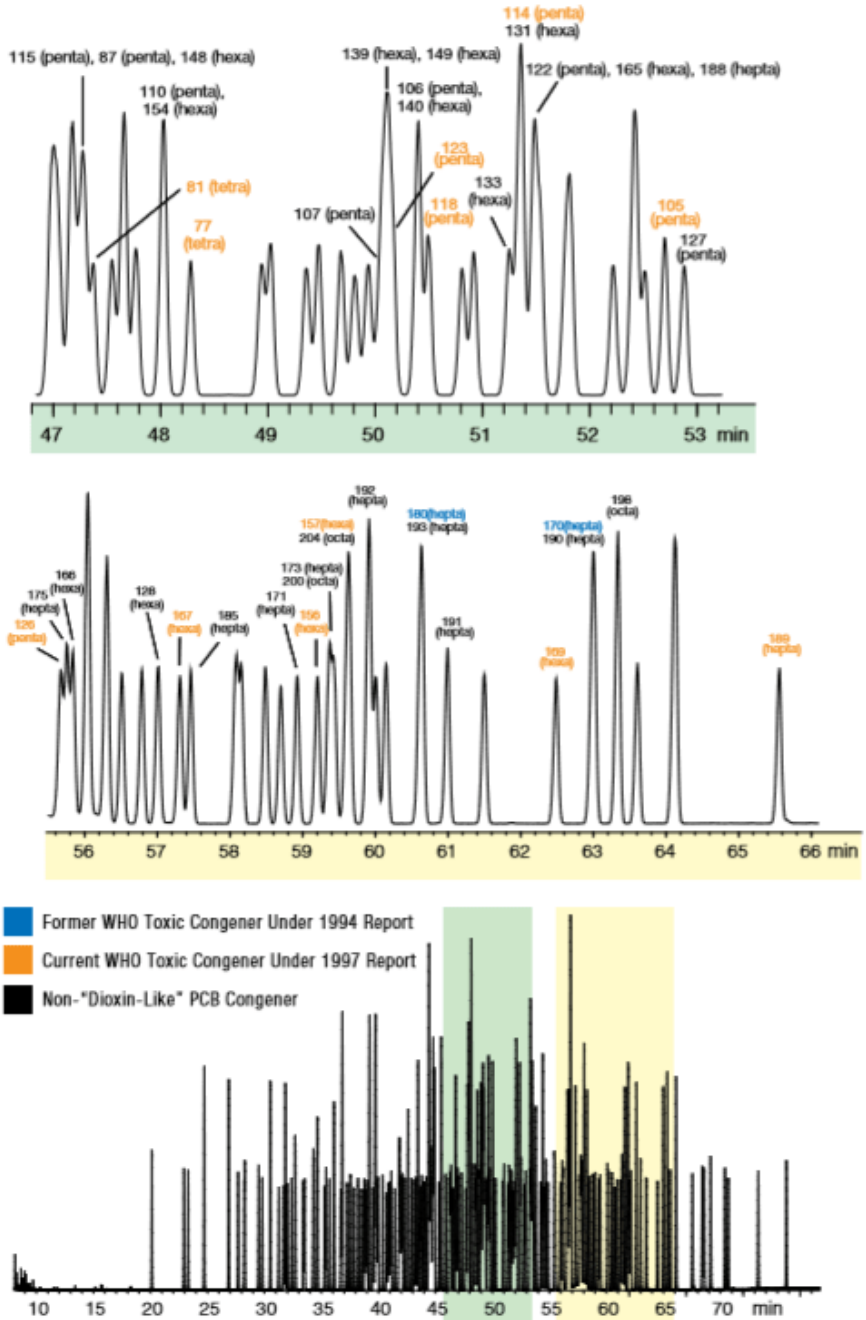


Figure 4 – PCB congeners

Figure 5 shows the type of GC separation of PCBs congeners that can be reached with a Zebron 5MS column. The oven temperature ramp is usually slow to allow a great separation of most of the congeners.



GC/MS Conditions

Column:	Zebron ZB-5ms
Dimensions:	60 meter x 0.25 mm x 0.25 µm
Part No.:	7KG-G010-11
Injection:	Splitless @ 280 °C for 0.5 min (1 µL)
Carrier Gas:	Helium (UHP Grade) at 1.1 mL/min (constant flow)
Oven Program:	60 °C for one minute to 140 °C at 25 °C/min to 290 °C at 2 °C/min
Detector:	MSD; 35-510 amu

Figure 5 – GC separation of PCBs congeners

PBDEs GC analysis

The lack of stability of BDE-209 has forced some labs to add a second PBDE test to analyze this compound separately. This extra testing requires additional instrumentation, extra columns, and decreases the overall productivity of the laboratory. The breakdown of BDE-209 can be attributed to a combination of both temperature stability and column activity. If a lab can reduce either cause, the overall response of BDE-209 can be improved.

With a narrow bore 20 m x 0.18 mm ID x 0.18 µm film Zebron ZB SemiVolatiles GC column, labs are now able to successfully analyze a range of PBDEs from BDE-28 to BDE-209 in a single run (Figure 6). Use of ZB SemiVolatiles roughly cuts the time in half which is required for analysis as there is no longer a need for a second injection with a shorter column.

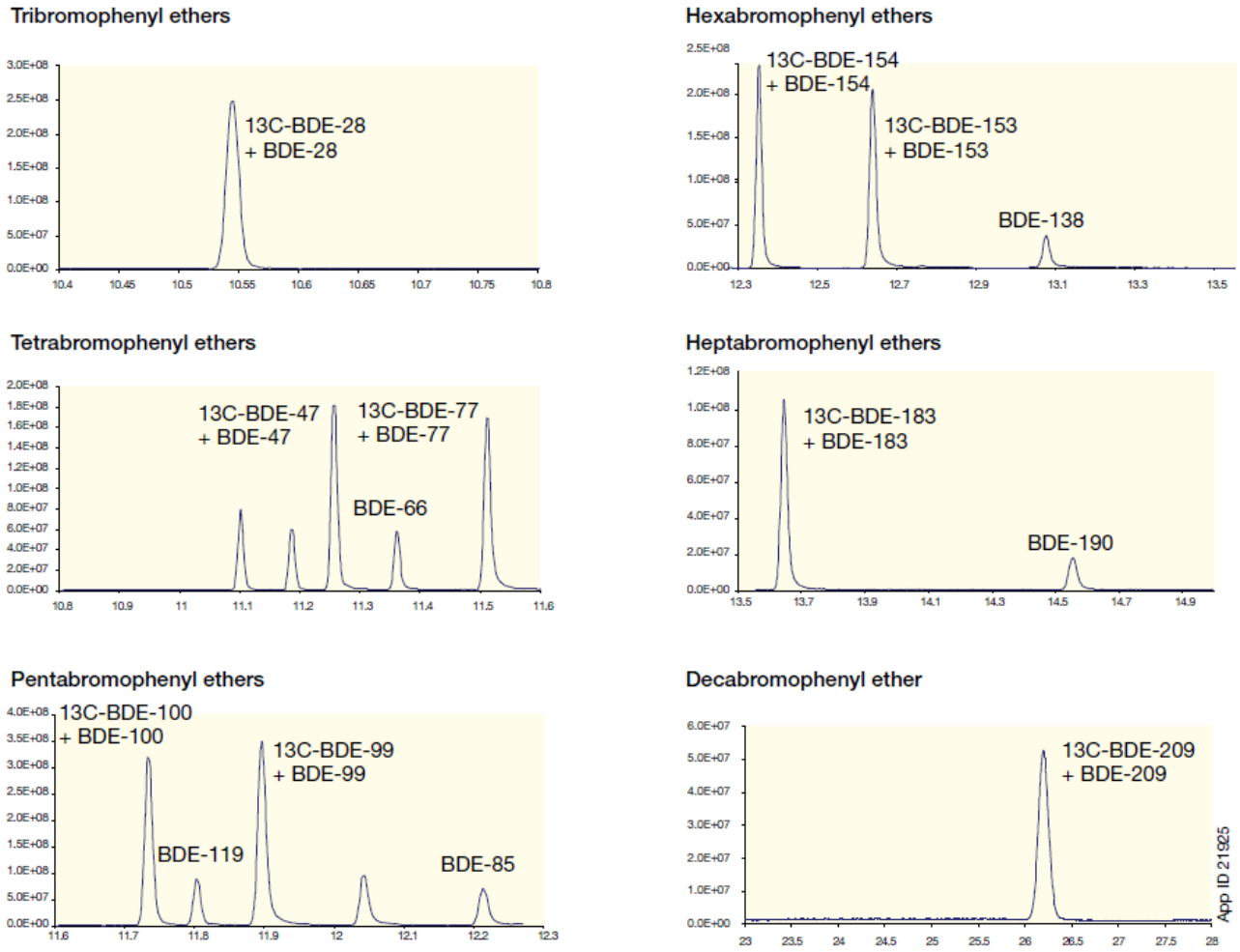


Figure 6 – Separation of PBDE Congeners on a Zebron ZB-SemiVolatiles (20 m x 0.18 mm x 0.18 µm)

Conclusion

GC is the predilection tool for dioxins, PCBs and PBDEs. Due to the chemical structure of these compounds a phenylarylen phase is always preferred and dimensions need to be adapted:

- resolution
  is seeked for PCBs and dioxins analyses and a 60mx0.25mmx0.25µm column is preferred
- short
  columns enable BDE 209 to elute without degradation

As these compounds are active, very inert columns should be used and the premium ZB-Semivolatiles is the must for such separations.

Was this article on persistent organic pollutants helpful? Have a question about it that wasn't answered above? Comment below or reach out to our Technical Experts via Live Chat who are available 24/7. Click the link to talk now: www.phenomenex.com/chat.