Analysis of Persistent Organic Pollutants in Complex Matrices by Gas Chromatography—High Resolution Time-of-Flight Mass Spectrometry

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1. Introduction
Persistent Organic Pollutants (POPs) are halogenated organic compounds used for decades as pesticides, flame retardants, and for the manufacture of a variety of commercial goods. They include, but are not limited to, polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) (Figure 1). Unfortunately, these compounds bioaccumulate, and their unfavorable health and environmental effects have led to their regulation in many countries. Analysis of POPs in environmental or biological samples is challenging due to a wide range of concentrations in nature and because of signal reduction and inadequate chromatographic baselines induced by major components in complex environmental matrices. In addition, analysis can be further complicated by POP decomposition products, metabolites or miscellaneous halogenated materials present in samples. Many of these interfering compounds produce similar mass spectral data and can be present in higher concentrations than targeted compounds. The development of instrumental techniques that can provide a comprehensive analysis of environmental samples in a minimal amount of time would significantly improve analysis of POPs.

Figure 1. Structures of four different POP classes.

In this study, polychlorinated biphenyls (PCBs) were targets in the analysis of sediment and fish tissue samples; however, several untargeted classes of POPs were discovered and characterized. LECO’s Pegasus® GC-HRT with Folded Flight Path™ (FFP™) technology provided the required resolving power for accurate mass measurements and robust molecular formula determinations (Figure 2).

2. Experimental Conditions

Samples
Environmental samples were prepared by extraction using dichloromethane:hexane (1:4 v/v), clean up with silica pre-packed cartridges (1g) and elution with 15 mL of dichloromethane:hexane (1:4 v/v). Extracts were evaporated to 1 mL final volume in isooctane.

Experimental
Samples were analyzed on a LECO Pegasus GC-HRT using an Agilent 7890 GC and 7693 auto sampler. Mass spectral data were collected using two of the three possible GC-HRT operating modes (Figure 3): High Resolution (R = 25,000, FWHM at 218.985080) and Ultra-High Resolution mode (R = 50,000, FWHM at 218.985080).

Figure 2. LECO Pegasus GC-HRT (left) and its FFP™ Mass Analyzer (Right).

Figure 3. Pegasus GC-HRT operating modes.

L = 2m
R = 1,000

L = 20m
R = 25,000

L = 40m
R = 50,000
3. Results

Instrument Performance

High resolution (HR) mode analysis of a sediment sample produced the analytical ion chromatogram (AIC) and extracted ion chromatogram (XIC) shown in Figure 4. The XIC highlights three PCBs (CB 47, CB 162 and CB 209) congeners, and Table 1 lists formulas, retention times and areas for all PCBs in the sample. Peak True (deconvoluted) and NIST library mass spectral data for CB 47, CB 162 and CB 209, are shown in Figure 5. Library matches for these PCBs were 953, 826 and 865 respectively. Expansions of the molecular ion regions, as well as, calculated molecular ion, observed molecular ion and mass accuracy values are shown in Figure 6. Further evidence of the high-quality spectral data produced by the GC-HRT can be seen in excellent correlations between expected and observed relative abundance ratios of molecular cluster ions for the PCBs (Figure 7).

Table 1. PCBs (tri- to decasubstituted congeners) in sediment sample.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>R.T. (s)</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>PenCB</td>
<td>C₁₂H₅Cl₅</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>TetCB</td>
<td>C₁₂H₄Cl₅</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>HexCB</td>
<td>C₁₂H₃Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>NonCB</td>
<td>C₁₂H₇Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>HepCB</td>
<td>C₁₂H₃Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>OctCB</td>
<td>C₁₂H₃Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>OctCB</td>
<td>C₁₂H₃Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
<tr>
<td>OctCB</td>
<td>C₁₂H₃Cl₇</td>
<td>1.5e4</td>
<td>1.5e4</td>
</tr>
</tbody>
</table>

Figure 4. AIC (A) and XIC (B) showing PCBs in sediment sample.

Figure 5. Peak True and NIST library mass spectra for CB 47 (A), CB 162 (B) and CB 209 (C).
An example of comprehensive POP analysis is illustrated in Figure 9 where different classes of compounds were extracted from the fish tissue data: Hexachlorobenzene (HCB), octachlorostyrene (OCS), 1-chloro-2,3,3-bis(p-chlorophenyl)ethylene (DDMU), 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (p,p’-DDE), dichlorodiphenyltrichloroethane (DDT), dibromophenyl ether (BDE 47), and 2,2',3,4,4',5,5'-heptachloro-1,1-biphenyl (CB 180). Table 3 lists molecular ion and mass accuracy values for each of these compounds.

Analysis of a fish tissue sample containing elevated levels of PCBs produced the AIC and XIC shown in Figure 8. An average mass accuracy of 1.01 ppm was obtained for 70 PCBs discovered in the sample (Table 2). The enhanced resolving power of the GC-HRT in Ultra-High Resolution (UHR) mode (R = 50,000) facilitates selective extraction of POPs from the “forest of ions” that constitute the total ion chromatogram.

Figure 6. Calculated molecular ion, observed molecular ion and mass accuracy values for CB 47 (A), CB 162 (B) and CB 209 (C).

Figure 7. Expected and observed molecular ion cluster relative isotope abundance ratios for CB 47 (A), CB 162 (B) and CB 209 (C).

Figure 8. AIC (A) and XIC (B) showing different PCB congeners in a fish tissue sample.

Table 2. Mass accuracy values for PCBs in fish tissue sample.

![Image](https://example.com/image1.png)

![Image](https://example.com/image2.png)

![Image](https://example.com/image3.png)
Figure 9. AIC (A) and XIC (B) showing different classes of POPs in fish tissue sample.

Table 3. Mass accuracies for different POP classes in fish tissue sample.

<table>
<thead>
<tr>
<th>POP</th>
<th>Name</th>
<th>Formula</th>
<th>R.T. (s)</th>
<th>Obs.</th>
<th>Mass Accuracy (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB</td>
<td>Hexachlorobenzene</td>
<td>C_{6}H_{6}Cl_{6}</td>
<td>821</td>
<td>281.81263</td>
<td>0.19</td>
</tr>
<tr>
<td>OC3</td>
<td>Octachlorostyrene</td>
<td>C_{8}H_{8}Cl_{8}</td>
<td>1298</td>
<td>281.80770</td>
<td>1.16</td>
</tr>
<tr>
<td>DOMU</td>
<td>2,2-Dichlorodiisocyanurate</td>
<td>C_{6}H_{4}Cl_{2}</td>
<td>1410</td>
<td>281.97669</td>
<td>0.30</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>2,4,5-Trichlorophenol</td>
<td>C_{6}H_{3}Cl_{3}</td>
<td>1410</td>
<td>281.97669</td>
<td>0.30</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>2,4,5-Trichlorophenol</td>
<td>C_{6}H_{3}Cl_{3}</td>
<td>2064</td>
<td>281.97669</td>
<td>0.30</td>
</tr>
<tr>
<td>BDE-47</td>
<td>Decabromodiphenyl ether</td>
<td>C_{12}H_{10}Br_{10}</td>
<td>2064</td>
<td>315.93736</td>
<td>-0.33</td>
</tr>
<tr>
<td>CB-180</td>
<td>Decabromodiphenyl ether</td>
<td>C_{12}H_{10}Br_{10}</td>
<td>2064</td>
<td>315.93736</td>
<td>-0.33</td>
</tr>
</tbody>
</table>

4. Conclusions
LECO Corporation’s Pegasus GC-HRT allows for acquisition of spectral data across a wide mass range, screens for different POP classes in a single run and produces high quality data that can be searched against nominal mass libraries (e.g., NIST, Wiley). The selectivity and exceptional mass accuracy values provided by the high resolution mass spectrometer facilitate robust determination of elemental composition. Operation of the instrument in ultra-high resolution mode resulted in clean separation of isobaric fragments for BDE 47 and CB 180. The Pegasus GC-HRT is an indispensable tool for targeted and non-targeted analysis of persistent organic pollutants in complex environmental matrices.

5. References
1. S.K. Shin and T.S. Kim, J., Hazard Mater., 137(3)
9. LECO Corporation would like to thank Dr. Eric Reiner of the Ontario Ministry of the Environment for providing the environmental samples.

A mass spectrum for coeluting POPs BDE 47 and CB 180 is shown in Figure 6. Mass accuracy values for the molecular ions of CB 180 and BDE 47 were -0.38 and -0.55 ppm. Robust analysis of this data would be difficult without an instrument with high resolving power due to interfering mass fragments with nominal mass of 324: [M-Cl_{2}+2]^{+} for CB 180 and [M-Br_{2}]^{2+} for BDE 47. According to Alaee, resolution of these isobaric fragments would require an MS instrument with a resolving power ≥ 25,000 (m/Δm). Operation of LECO’s Pegasus GC-HRT in ultra-high resolution mode results in baseline resolution for the fragment ions.