

# Analysis of PCBs in environmental matrices using triple quadrupole GC-MS/MS

Mark T Belmont<sup>1</sup>, Giulia Riccardino<sup>2</sup>, Adam Ladak<sup>3</sup>, Paul Silcock<sup>3</sup>, Kjell Hope<sup>4</sup> and Daniel Kutscher<sup>5</sup>

<sup>1</sup>Thermo Fisher Scientific, USA, <sup>2</sup>Thermo Fisher Scientific, IT, <sup>3</sup>Thermo Fisher Scientific, UK, <sup>4</sup>Pacific Rim Laboratories, Canada, <sup>5</sup>Thermo Fisher Scientific, DE

## ABSTRACT

**Purpose:** Polychlorinated biphenyls (PCBs) were used in hundreds of industrial and commercial applications, but their production was banned because of their persistence in the environment and their tendency to enter the food chain and bioaccumulate in living organism. They have been classified as persistent organic pollutants (POPs) and they have been regulated under the Stockholm Convention for POPs since 2001.

**Methods:** Recent advances in gas chromatography triple quadrupole mass spectrometry (GC-MS/MS) allowed for high sensitivity and selectivity leading to consider GC-MS/MS as a reliable tool for PCBs analysis as well as high resolution accurate mass spectrometry. The Thermo Scientific™ GC-MS/MS was used for the determination of PCBs in water and soil samples.

**Results:** The results obtained in these experiments demonstrate that the Thermo Scientific™ TSQ™ 9610 mass spectrometer equipped with the Thermo Scientific™ NeverVent™ AEI ion source represents a reliable tool for analysis of PCBs in environmental samples.

## INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of industrial organic chemicals consisting of carbon, hydrogen, and chlorine atoms. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, hydraulic equipment, plasticizers, plastics, rubber products, and dyes but they were banned because of their persistence in the environment and their tendency to enter the food chain and bioaccumulate in living organism. There are currently 209 known PCBs congeners that can be divided into two groups according to their structural and toxicological characteristics: the non-dioxin like PCBs (non-DL-PCB) representing the majority of the PCB congeners with a lower degree of toxicity and the dioxin-like PCBs (DL-PCBs) representing the 12 most toxic congeners, which have structure and toxicity similar to dioxins. DL-PCBs are classified as persistent organic pollutants (POPs), and they have been regulated under the Stockholm Convention for POPs since 2001. In this study, GC-MS/MS was used for the determination of PCBs in water and soil samples. Linearity and instrument detection limits (IDLs) as well as an extended robustness study were assessed to evaluate the instrument performance for the detection of trace levels of PCBs.

## MATERIALS AND METHODS

### Sample Preparation

Water and soil samples were extracted following the workflow reported in Figure 1.

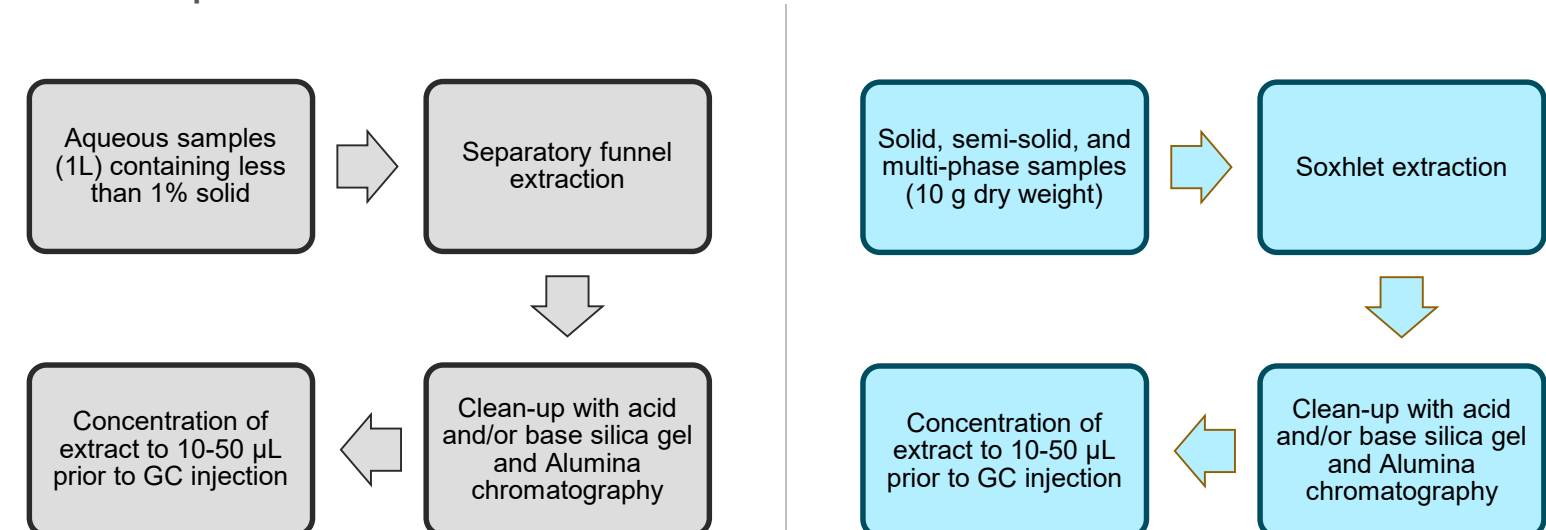
### Test Method

The EPA Method 1668C standard solution kit (Wellington laboratories, Inc., P/N 68C-CVS) containing native and <sup>13</sup>C mass-labeled PCB congeners and mass-labeled PCB internal standards was used to assess system linearity. The lowest calibration level was further diluted 1:2 in nonane to expand the calibration curve from 0.1 to 2,000 ng/mL. For the calculation of IDLs, the lowest calibration level was diluted 1:4 in nonane.

### Data Analysis

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. PCB quantitative analysis requires the use of isotope dilution (this feature is available in Chromeleon CDS from software version 7.2.9 onwards).

Figure 1. Sample preparation procedure for aqueous, solid, semi-solid and multi-phase samples



## RESULTS

### Chromatography

Two specific precursor ions, each with one specific corresponding product ion, were used to set up the timed-selected reaction monitoring (t-SRM) acquisition method. This allowed for high selectivity to discriminate between the target compounds and the complex matrix, thus ensuring a confident and selective identification of analytes. As an example, the total ion chromatograms (TIC) of a real sample acquired in EI, full-scan (FS, *m/z* 100–600) showing the complexity of the matrices and the selectivity of the SRM acquisition is reported in Figure 2. Moreover, chromatographic resolution of the target analytes, including the pentachlorobiphenyl critical pair PCB-123/PCB-118, was obtained in 21 minutes (Figure 3).

Figure 2. TIC (A) FS: *m/z* 100–600, and (B) t-SRM acquisitions for environmental sample extracts containing PCBs showing the complexity of the matrix (FS acquisition) and the selectivity of the t-SRM acquisition

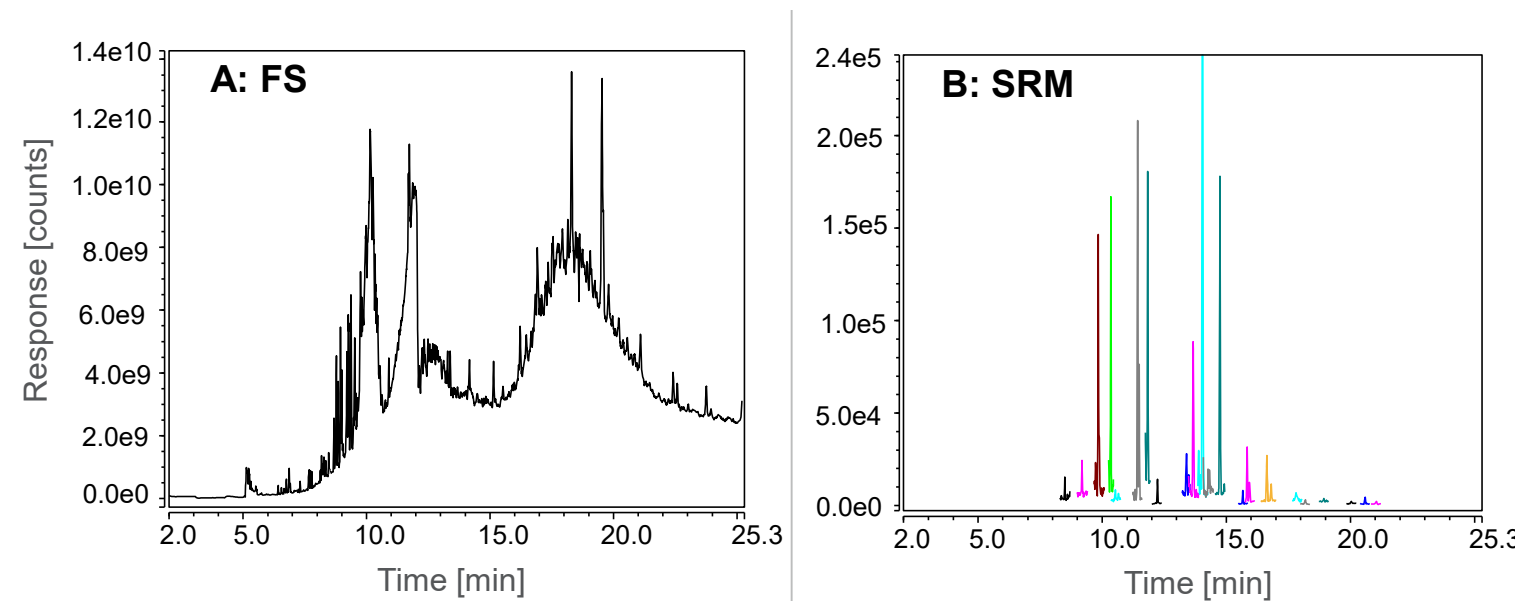
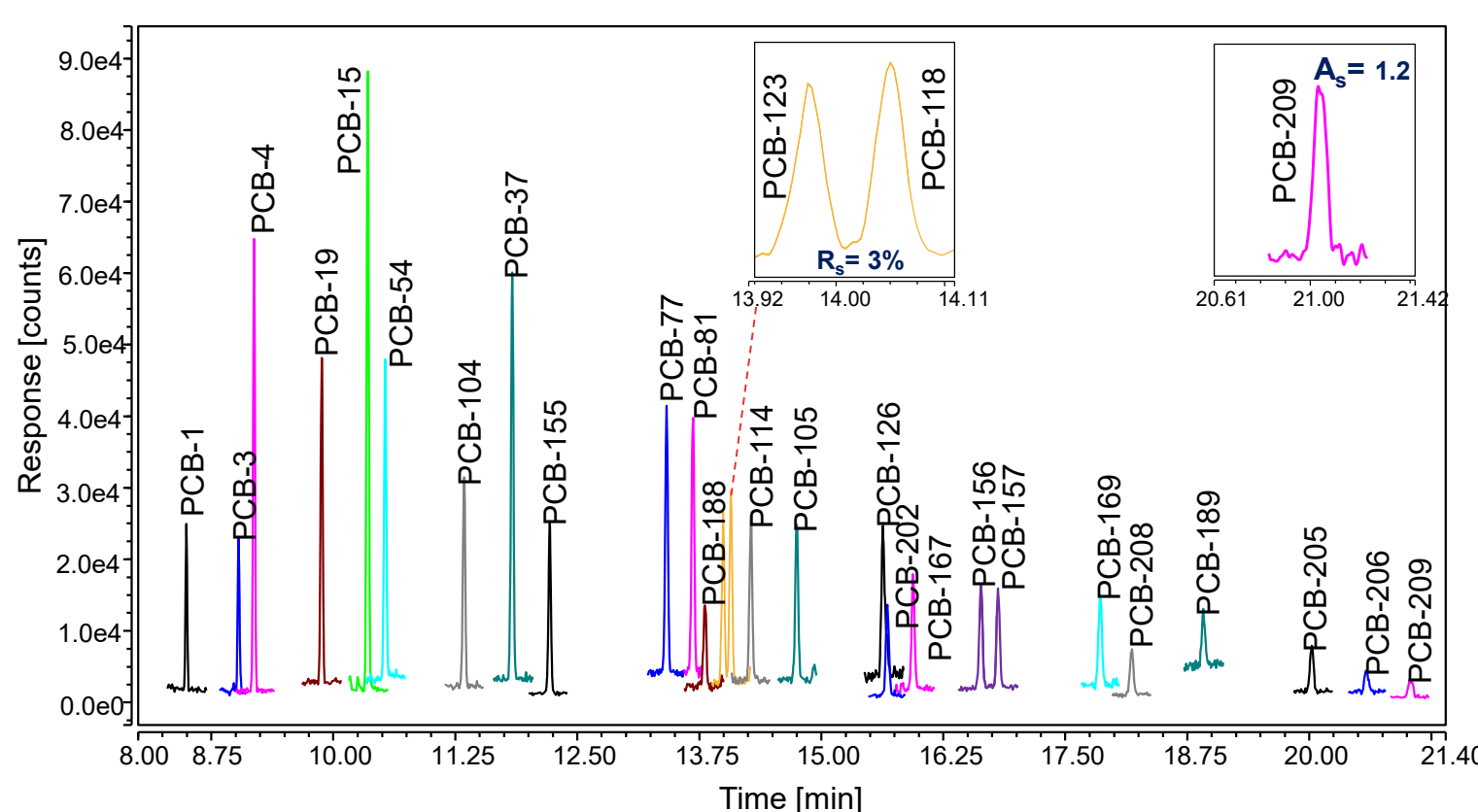


Figure 3. t-SRM acquisition showing baseline chromatographic separation for the investigated compounds in the lowest calibration standard diluted 1:2 (0.1 ng/mL)

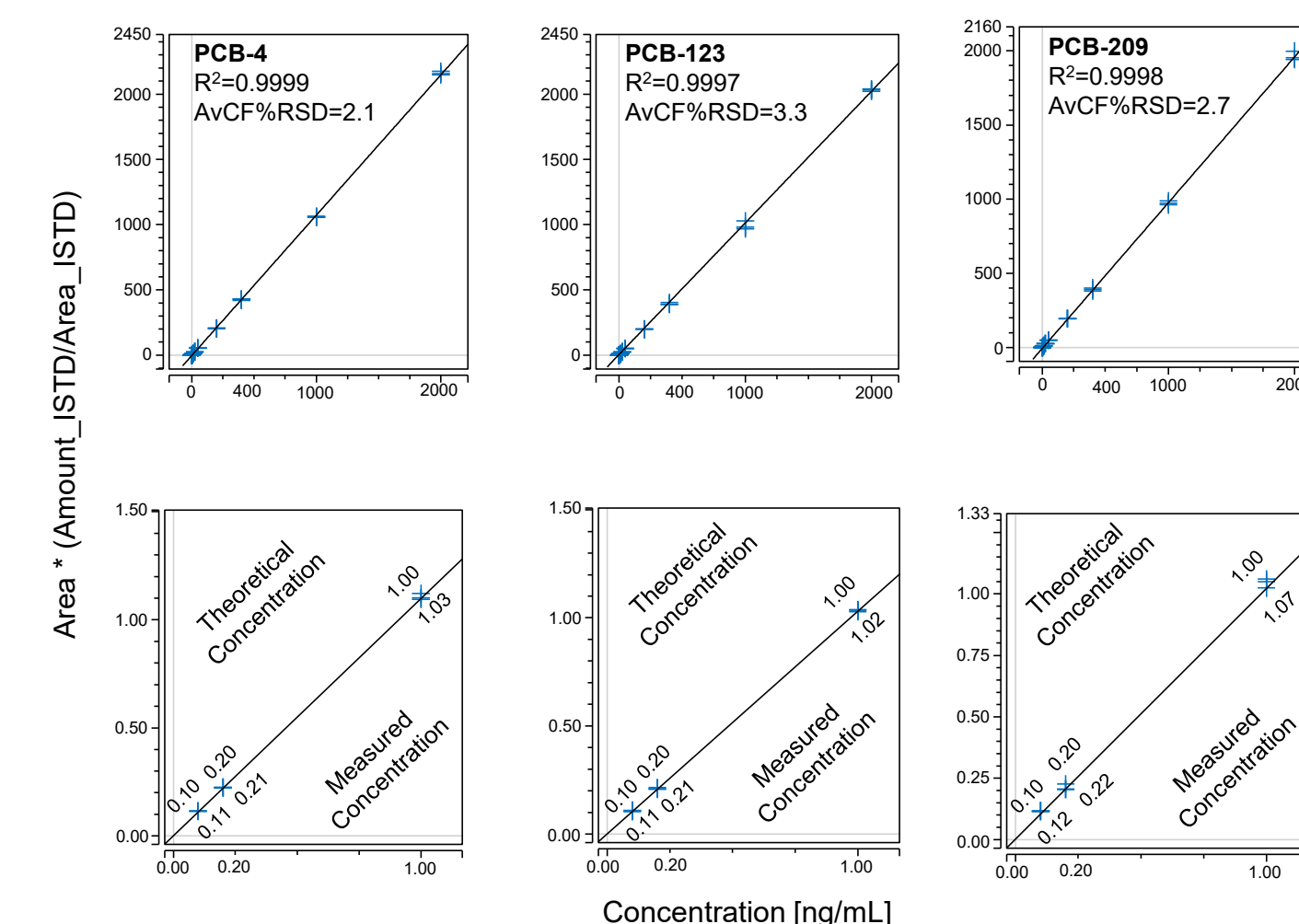


The insets highlight the resolution ( $R_s$ ) of the critical pair and the calculated asymmetry factor ( $A_s$ ) for the high boiling point congeners (PCB-209).

### Linearity

The TSQ 9610 GC-MS/MS is equipped with the Thermo Scientific™ XLXR™ detector, which is an electron multiplier that offers extended detector lifetime and dynamic range. Calibration curves ranging from 0.10 to 2,000 ng/mL were prepared as detailed in the *Test Method* section. Each calibration level was injected in triplicate. Native PCB congeners were quantified using their corresponding isotopes using isotope dilution quantitation, the target analytes showed a linear trend with coefficient of determination ( $R^2$ ) > 0.990 and residual values (measured as %RSD of average response factors, AvCF %RSD) < 20%, thus confirming a wider linear range can be easily achieved. Full range calibration curves (0.10–2,000 ng/mL) for some selected DL-PCBs (PCB-123) and non-DL-PCBs (PCB-4, 209) are shown as examples in Figure 4.

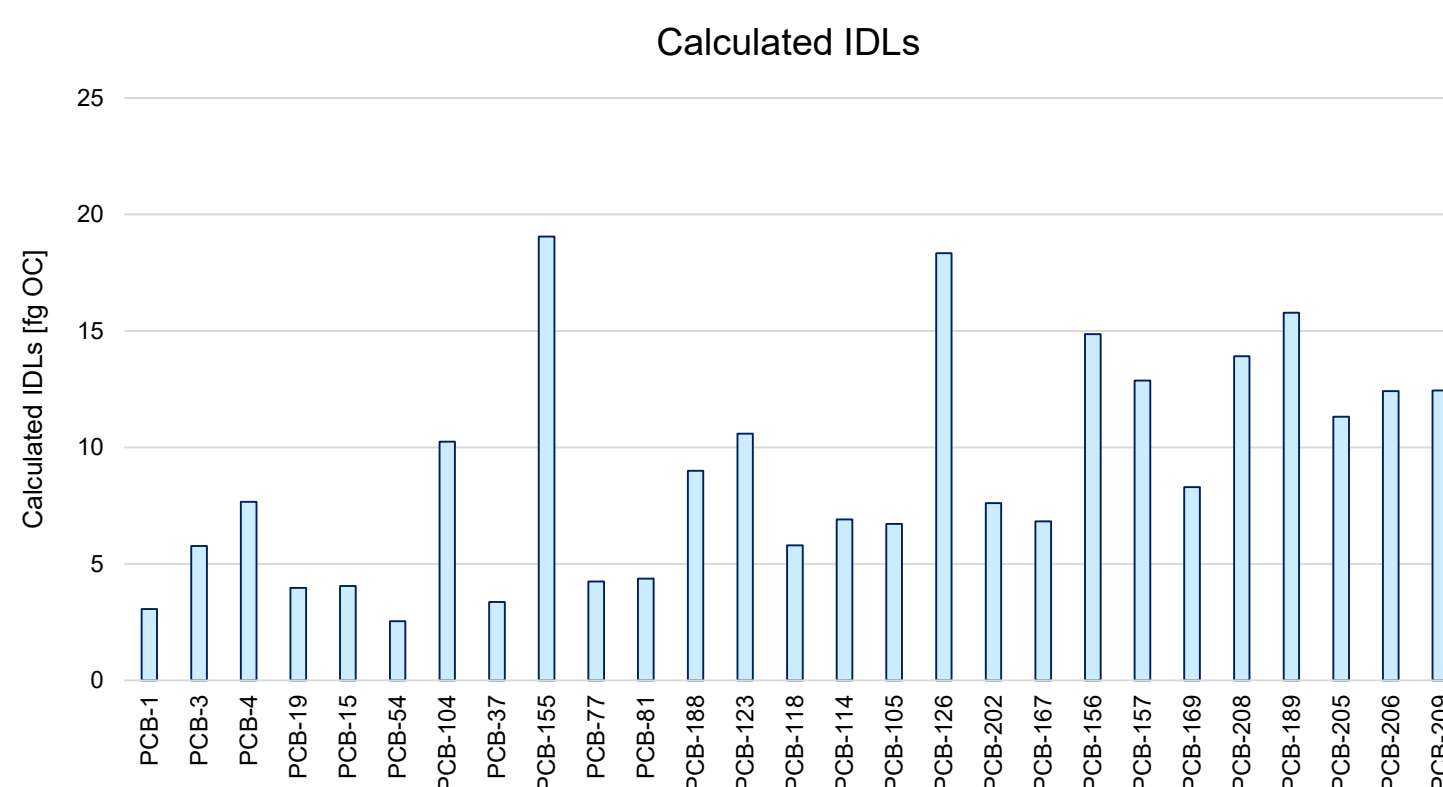
Figure 4. Example of solvent (nonane) calibration curves for some selected DL-PCBs (PCB-123) and non-DL-PCBs (PCB-4, 209) and zoomed detail (0.1–1.0 ng/mL)



### Instrument detection limit (IDL), and limit of detection (LOD)

Very often, data acquired using t-SRM have little noise, therefore the calculation of the IDLs and the LOQs based on the signal-to-noise (S/N) approach may be inadequate. The IDL was therefore determined for the individual congeners by diluting the CS0.2 standard four times, so that a final concentration of 0.05 ng/mL was achieved. This solution was repeatedly injected ( $n=10$ ). IDLs were calculated taking into account the one-tailed Student's *t*-test values for the corresponding  $n-1$  degrees of freedom at 99% confidence, the injected on-column (OC) concentration, and the absolute peak area %RSD (<15%) for each analyte. Calculated IDLs ranged from 3 fg to 19 fg OC, corresponding to 0.15 pg/L to 0.95 pg/L in water and to 0.015 to 0.095 ng/kg in soil samples as reported in Figure 5. The standard concentration used to assess the IDL was chosen as LOQ as (i) the ion ratios were within  $\pm 15\%$  of the expected values calculated as an average across a calibration curve ranging from 0.10 to 2,000 ng/mL, (ii) the absolute peak area repeatability, and (iii) the response factor (RF) RSD were <15%.

Figure 5. Calculated IDLs for PCB individual congeners

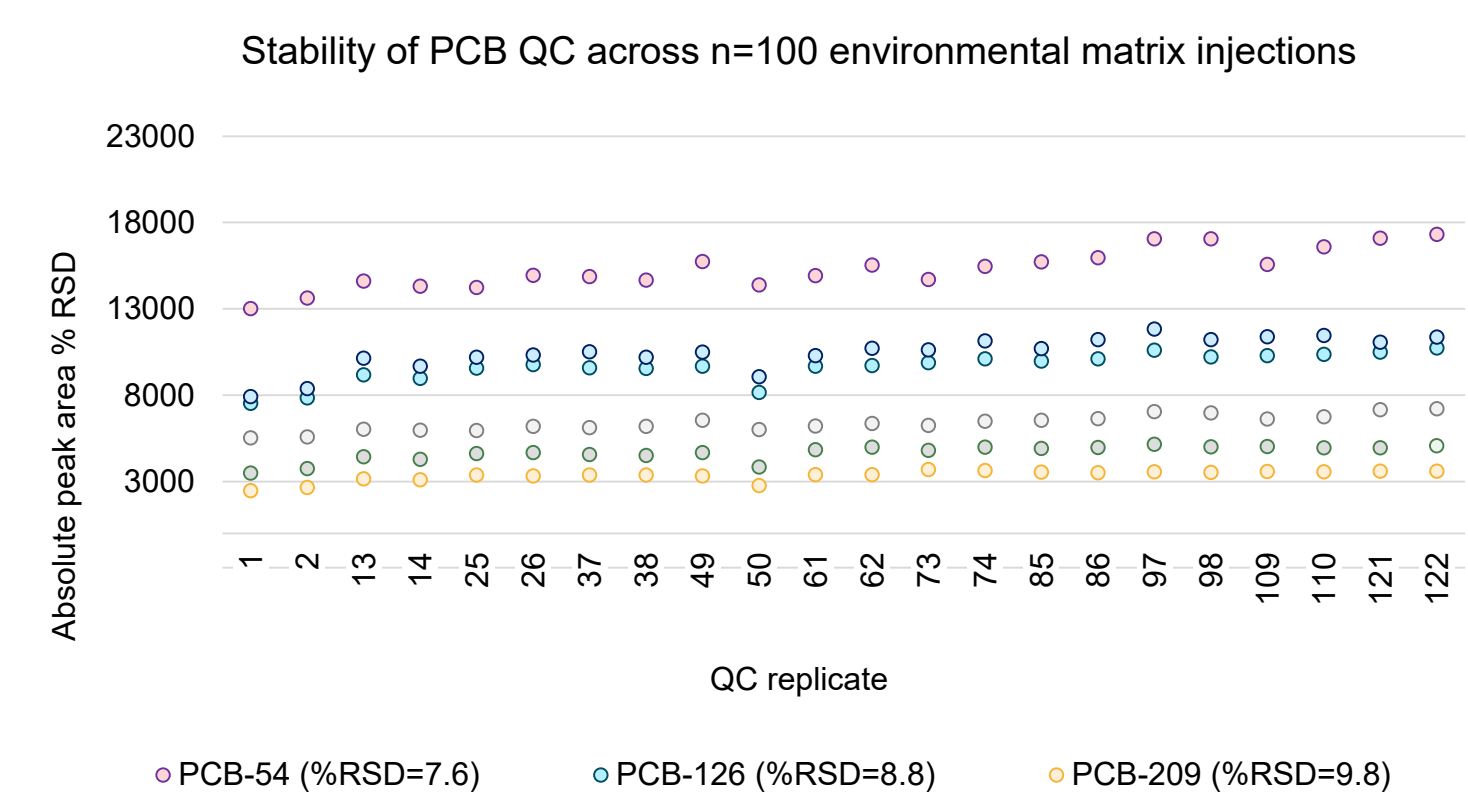


Calculated IDLs ranged from 3 fg to 19 fg OC, corresponding to 0.15 pg/L to 0.95 pg/L in water samples and to 0.015 ng/kg to 0.095 ng/kg in soil samples.

### Robustness

Analytical testing laboratories need to process a high number of samples every day, therefore it is critical that the instrument performs consistently. The Thermo Scientific™ SmartTune™ tool allows the user to check the tune status of the system with a few mouse clicks in an easy and quick fashion. The SmartTune tool uses the MS parameters established during the initial tuning with a clean source and intelligently assesses the performance of the system, only re-tuning when MS performance has been compromised. Instrument robustness for everyday analysis and quantitative performance was evaluated by repeatedly injecting various environmental extracts ( $n=100$ ). A quality control standard in nonane (QC) at a concentration of 1.0 ng/mL was injected in duplicate every 10 samples to monitor the system stability. The SmartTune feature was used to check the instrument status at the beginning, middle, and end of the sequence. No inlet or MS re-tuning or maintenance was required during the robustness evaluation. The QC showed stable response across the injections with ion ratios consistently within  $\pm 15\%$  of the calculated average from the calibration curve, calculated concentration within  $\pm 20\%$  of the spiked level, and QC absolute peak area %RSD <11% as shown in Figure 6.

Figure 6. QC absolute peak area and %RSD across a sequence of  $n=100$  injections of various environmental extracts



## CONCLUSIONS

The results obtained in these experiments demonstrate that the TSQ 9610 mass spectrometer equipped with the NeverVent AEI ion source in combination with the Thermo Scientific™ TRACE 1610 GC and the Thermo Scientific™ AI/AS 1610 liquid autosampler represents a reliable tool for analysis of PCBs in environmental samples.

- The high selectivity of the Thermo Scientific™ TRACE™ TR-PCB column ensured chromatographic separation of the target analytes in about 21 minutes. Calculated resolution of the critical pair PCB-123 / PBDE-118 was 3%. Furthermore, the column thin film phase, high thermal stability, and low column bleed ensured elution of the high boiling point PCBs (e.g., PCB-209) with improved peak shapes.
- The XLXR detector allowed for extended linearity over a concentration range of 0.10 to 2,000 ng/mL with coefficient of determination of  $R^2 > 0.990$  and AvCF %RSDs <20. Moreover, the CM advanced reprocessing capability allowed for isotope dilution quantitative analysis.
- The engineered design and the improved sensitivity of the NeverVent AEI ion source allowed for low instrument detection limits ranging from 3 fg to 19 fg OC (corresponding to 0.15 pg/L to 0.95 pg/L in water samples and to 0.015 to 0.095 ng/kg in soil samples) and LOQ set at 0.05 ng/mL, showing ion ratios within 15% of the expected values calculated as an average across a calibration curve, absolute peak area and RF %RSD < 15 even at such low analyte concentrations.
- The enhanced robustness and reliability of the AI/AS 1610 liquid autosampler combined with the inertness of the flow path and the stability of the NeverVent AEI ion source allowed for  $n=100$  matrix injections without requiring any system re-tuning or MS or inlet maintenance.

## REFERENCES

- United States Environmental Protection Agency, U.S. EPA, Method 1668C Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, April 2010, [https://www.epa.gov/sites/default/files/2015-09/documents/method\\_1668c\\_2010.pdf](https://www.epa.gov/sites/default/files/2015-09/documents/method_1668c_2010.pdf).

## ACKNOWLEDGEMENTS

We would like to thank Dr. Kjell Hope from Pacific Rim Laboratories Inc., Canada for supplying the samples.

## TRADEMARKS/LICENSING

© 2022 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others.

PO66142-EN0422S