A Suite of CCQM Studies to Critically Evaluate the Overall Variability in the Analysis of PCB Congeners in Tissue

The Organic Analysis Working Group (OAWG) of the Consultative Committee on the Quantity of Matter (CCQM) conducted a suite of interlaboratory studies designed to identify sources of variability in the analysis of polychlorinated biphenyl (PCB) congeners in shellfish tissue. Four different materials were evaluated by ten national metrology institutes (NMIs) in three concurrent CCQM projects: CCQM-K40/P31.b.1 PCB Congeners in Iso-Octane Solution, CCQM-P57 PCB Congeners in Methylene Chloride Solution and in Mussel Tissue Extract in Methylene Chloride, and CCQM-P67 PCB Congeners in Mussel Tissue.

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All participants in the CCQM studies used gas chromatographic (GC) analysis techniques; however, each participant used a somewhat different methods of extraction, extract clean-up, and GC columns. All participants performed their measurements using the same instruments and calibration solutions for the four materials. For all materials, participants measured the concentrations of five PCB congeners: PCB 28, PCB 101, PCB 105, PCB 153, and PCB170. These target analytes are representative of the volatility range and chemical separation challenges typical of the PCB congeners found in environmental samples. Both the iso-octane and methylene chloride PCB congener materials were gravimetrically prepared. These materials enabled the evaluation of the accuracy and reproducibility of the gas-chromatographic PCB measurements in relatively non-volatile (iso-octane) and volatile (methylene chloride) solvents. Excluding one participant inexperienced in handling highly volatile solvents, the bias (relative to the gravimetric values) was found to be less than 1% and the relative measurement reproducibility, u_{simple}, 1.6% to 3.2% (average of 2.6%) in both solvents.

The PCB congener and mussel tissue extract in methylene chloride materials enabled the evaluation of the effects of interfering compounds on measurement performance. Excluding one participant who analyzed only the neat solutions, one participant inexperienced in measurements of complex materials, and the one congener present in the tissue extract at a mass fraction (≈ 0.6 ng/g) much smaller than the levels evaluated in either of the simple solutions (≈ 30 ng/g to 600 ng/g), the average measurement reproducibility for the four PCBs present in the mussel tissue extract is a remarkably consistent 4.6%. This suggests that the presence of non-target materials in the complex sample (non-PCBs and other PCB congeners) is a source of variability at least as important as the simple instrumental component: $u_{\text{complex}} \approx \sqrt{4.6^2 - 2.6^2} = 3.8\%$.

The mussel tissue extract material was prepared from the same tissue analyzed by the participants. While the extract was prepared to have analyte levels somewhat lower than in the tissue itself, the ratio of the mass-fraction amount of a given compound in the two materials should be the same for all compounds. The per-analyte ratios for one participant were consistently lower than those for the other participants, suggesting that their method did not fully extract the PCBs from the tissue.

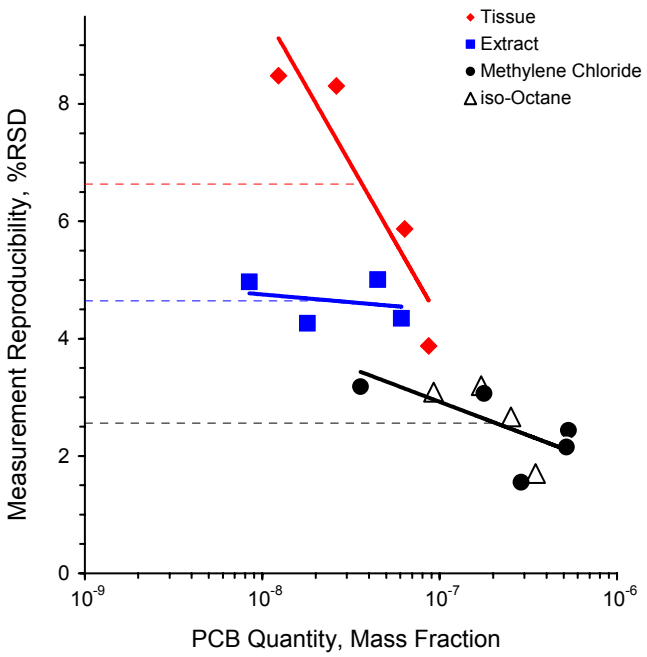
The observed ratio in the results for the five PCBs reported by the six participants with internally consistent results was 1.42 with an expanded uncertainty (95% confidence) of ±0.10. The relative reproducibility of the tissue measurements for these seven participants ranges from ≈4% to ≈9% (average of 6.6%). While the relative reproducibility appears to be a function of analyte level, the rather narrow mass-fraction range (12 ng/g to 90 ng/g) for the four PCBs reliably evaluated suggests that analyte-specific physico-chemical properties or separation challenges are likely to have a role. In either case, extraction can be a significant source of variability in the analysis of PCBs in tissue. The available data suggest that the expected magnitude is about the same as that attributed to the complex sample:

$$u_{\text{extraction}} \approx \sqrt{6.6^2 - 4.6^2} = 4.7\%.$$

An assessment has been made of the experimental difficulties and sources of variability in each step of the analysis for PCB congeners in tissue matrices.

The analysis of the results from this suite of studies has identified the tissue extraction stage of the overall analysis as a major source of interlaboratory measurement variation. If the major extraction-related differences can be identified and reduced, measurement reproducibility for PCBs and other trace analytes in tissue materials can be improved.

Measurement Reproducibility as Functions of Analyte Level for the Four Materials Analyzed in the OAWG "Uncertainty Suite" of PCB-Containing Samples.



The expected analyte levels and reproducibility statistics for the simple solution of PCB congeners in iso-octane (CCQM-K40/P31.b.1, denoted as open black triangles) are estimated from the results reported by all ten participants. The statistics for the simple solution of PCB congeners in methylene chloride (the first component of CCQM-P57, denoted as solid black circles) are estimated from the results of the nine participants who demonstrated their ability to make valid measurements in the volatile solvent. The statistics for the mussel tissue extract in methylene chloride (the second component of CCQM-P57, denoted as solid blue squares) are estimated from the results of the seven participants reporting values who demonstrated their ability to make valid measurements of a complex sample. The statistics for mussel tissue itself (CCQM-P67, denoted as solid red diamonds) are estimated from the results of the six participants who demonstrated their ability to completely extract PCBs from the mussel tissue. The solid lines represent least squares regressions of the relative reproducibility of the measurements onto the $\log_{10}$(mass fraction) of the PCB congeners. The dashed lines denote the mean reproducibility of each set of measurements.