INSIGHTS FROM AN IN-DEPTH INVESTIGATION OF PCB ANALYTICAL STANDARDS

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Introduction

Analysis of individual PCB congeners using EPA Method 1668 requires use of a standard containing all 209 PCB congeners[1]. This standard is available from only one vendor, and, thus, no independently prepared standard containing all 209 PCB congeners is available to verify the accuracy of this standard. Observations made independently by the authors suggested that some inaccuracies might exist in this standard. The present work aims to evaluate this standard versus other available PCB congener standards and assess accuracy and agreement amongst commercially available PCB congener mixes.

Materials and methods

We compare three commercially available PCB congener analytical standards and a NIST SRM containing PCB congener standards. The analysis of the standards used SGS Analytical Perspectives' implementation of EPA Method 1668 (1668/8223). Each native PCB congener analytical standard was used to prepare replicate calibration standards (RCSs). We systematically removed as many sources of bias as practical. We also strove to ensure that any bias introduced was introduced to all RCSs equally. To this end, we took the following steps:

1. All RCSs were prepared using the same labeled standard mix. The only differences in composition were the native analytical standards.
2. One analyst prepared all RCSs using the same equipment.
3. A third party verified the accuracy of all equipment used in preparing the RCSs.
4. All RCSs were prepared using native standard vials that had never been opened, to prevent alterations in concentration through evaporation of solvent.
5. We analyzed all RCSs in one continuous analytical sequence on the same instrument operated by the same analyst.
6. All RCSs were analyzed in a random order.
7. The HRMS analyst integrated all RCSs before quantifying them.
8. Multiple levels of native standards were used for one provider of native standards, allowing us to ensure that the concentrations we believed we prepared were, in fact, correct.

Results and discussion

Some statistical differences were found between the three commercially available PCB native analytical standard mixes, although many congeners were not statistically significantly different at the 5% confidence level (Figure 1). Many of the statistically significant differences between the commercially available native analytical PCB standards were relatively small in magnitude, although some are large enough to be a significant source of error. All commercially available standards agreed equally well with the NIST SRM on average. However, differences in the magnitudes of individual congener disagreements varied from vendor to vendor (Table 1).

While the verification of standards through this project indicates that many of the congeners in the commercially available mix of all 209 PCBs are acceptably accurate, we cannot address over 100 of these congeners independently. Those standards for which both a statistically and practically significantly difference exists pose a particular concern, as we cannot rule out the possibility of more differences of this type in those congeners we cannot verify.

In summary, there are some significant differences from one PCB analytical standard to another for individual congeners. These differences may be important depending on the application for which the measurement is being performed. Also, there remains a gap in the ability of practitioners to verify the accuracy of commercially available standards.

References:
1. EPA Method 1668C

	p-values		
Analyte	**A v. B**	**A v. C**	**B v. C**
PCB-77 33'44'-TeCB	5.60E-22	1.17E-29	1.88E-02
PCB-81 344'5-TeCB	1.87E-13	6.97E-18	4.04E-03
PCB-105 233'44'-PeCB	8.62E-12	7.38E-13	6.93E-01
PCB-114 2344'5-PeCB	8.63E-32	6.40E-26	2.27E-07
PCB-118 23'44'5-PeCB	2.14E-15	5.46E-13	1.93E-01
PCB-123 2'344'5-PeCB	1.21E-16	1.80E-19	3.51E-02
PCB-126 33'44'5-PeCB	7.95E-02	1.09E-08	4.32E-12
PCB-156/157 233'44'5/233'44'5'	2.80E-20	6.77E-30	1.68E-06
PCB-167 23'44'55'-HxCB	5.56E-21	3.15E-32	1.27E-09
PCB-169 33'44'55'-HxCB	9.51E-25	3.00E-32	6.28E-04
PCB-189 233'44'55'-HpCB	1.63E-30	7.06E-23	7.75E-04
PCB-209 DeCB	6.62E-30	4.86E-37	3.32E-03
PCB-1 2-MoCB	4.27E-04	4.98E-01	1.37E-04
PCB-3 4-MoCB	2.19E-07	8.71E-01	4.60E-06
PCB-4 22'-DiCB	1.52E-01	3.28E-08	1.41E-08
PCB-15 44'-DiCB	3.60E-18	6.25E-18	5.19E-01
PCB-19 22'6-TrCB	2.52E-06	3.92E-15	1.54E-03
PCB-37 344'-TrCB	7.67E-19	2.16E-42	3.16E-33
PCB-54 22'66'-TeCB	7.57E-01	1.11E-07	3.54E-06
PCB-153 22'44'55' -HxCB	3.74E-22	5.00E-23	1.36E-01
PCB-155 22'44'66'-HxCB	1.36E-20	3.05E-27	8.37E-07
PCB-188 22'34'566'-HpCB	4.93E-14	4.16E-07	3.27E-05
PCB-202 22'33'55'66'-OcCB	1.72E-13	5.25E-17	2.28E-02
PCB-205 233'44'55'6-OcCB	1.33E-11	3.40E-15	3.21E-01
PCB-208 22'33'455'66'-NoCB	1.46E-23	6.14E-18	4.40E-02
PCB-206 22'33'44'55'6-NoCB	3.29E-03	7.52E-12	2.20E-14

Figure 1. p-values of t statistics comparing relative response factor means for each of the congeners in the ICAL. Cells colored green indicate differences that are statistically significant at the 5% confidence level.

Table 1. Mean, minimum, and maximum percent differences and sums of squares obtained from the differences of measured and certified values from NIST SRM 2259 measured using two different native PCB standards.

	Vendor A	Vendor C
Mean PD	9.2%	9.3%
Sum of Squares	150.6%	370.4%
Min PD	0.2%	0.6%
Max PD	43.3%	52.9%