Mineral oil certified reference materials for the determination of polychlorinated biphenyls from the National Metrology Institute of Japan (NMIJ)

Masahiko Numata*, Yoshie Aoyagi, Mayumi Matsuo, Keiichiro Ishikawa, Nobuyasu Hanari, Satoko Otsuka, Yoko Tsuda and Takashi Yarita
The elution profiles of PCBs and the mineral oils with the chromatography columns used for the characterization are shown in Supplemental Figs. 1-4. The GC/MS measurement conditions are summarized in Supplemental Tables 1 and 2.

1) CRM 7903-a and CRM7905-a (Base oil CRMs)

a. Detectable PCB congeners (PCB52, 101, 118, 138 and 153 in CRM 7903-a): The concentrations of target compounds were calculated by inserting each value into the equation given below (Eq. 1). One point calibration was applied, because the linearity was good enough in the range of the solutions tested prior to the sample analyses.

\[
C_u = F_{ana0} \times (R_0 - R_b) \times \frac{C_{nat} \times M_{sur(sample)} \times F_{dilsur} \times f_{dilsur}}{M_{sample} \times M_{sur(cal)}}
\]  

(1)

where \(C_u\) is concentration of analyte in the oil CRMs, \(F_{ana0}\) is introduced as a factor of repeatability of whole analysis (value: unity), \(R_0\) is \(R_{sample} / R_{cal}\), \(R_{sample}\), ratio of peak areas of analyte / surrogate observed for the sample solution; \(R_{cal}\), ratio of peak areas of analyte / surrogate observed for the calibration solution), \(R_b\) is \(R_{blk} / R_{calb}\) (\(R_{blk}\), ratio of peak areas of analyte / surrogate observed for the blank solution (If blank peak is smaller than the limit of detection estimated from the procedural blank test (LOD_{blank}), LOD_{blank}/2 is used. If the limit of detection estimated from the noise near target compounds on the chromatogram of the base oils (LOD_{base}), LOD_{base}/2 is used. LOD is concentration which gives peak height corresponding to S/N=3. The blank analyses were performed three times.; \(R_{calb}\) is ratio of peak areas of analyte / surrogate observed for the calibration solution), \(C_{nat}\) is concentration of analyte in the standard solution, \(M_{sur(sample)}\) is mass of the surrogates solution added to the sample, \(F_{dilsur}\) is dilution factor of the high concentration surrogates solution preparation, \(f_{dilsur}\) is dilution factor of the low concentration surrogates solution preparation, \(M_{sample}\) is mass of the sample taken for analysis, \(M_{nat(cal)}\) is mass of the standard solution of analytes taken for preparation of the calibration solution, \(M_{sur(cal)}\) is mass of the undiluted surrogates solution taken for preparation of the calibration solution. The
results (averages of five independent analyses of samples taken from randomly selected ampoules; result of each sample was average of the two GC/MS measurements) are shown in Table 2.

The results of direct analyses (five independent analyses of samples taken from randomly selected ampoules and two GC/MS measurements for each sample as described above) of the PCB fortified CRMs (Method A-1 to D-5 in Table 1 and Supplemental Table 3) were also calculated by the Eq. 1 (without \(f_{\text{dilur}}\)).

**b. Undetectable PCB congeners:** Their signal-noise ratios (S/N) of the GC/MS signals were lower than 3 or were not higher than the signals obtained from procedural blank tests significantly. The ranges of concentrations equivalent to the respective LOD values (LOD_{blank} or LOD_{base}, as described above) are shown in Table 2 and Supplemental Table 4 as the analytical results (average of randomly selected three data of five independent analyses of samples taken from randomly selected ampoules).

2) CRM 7902-a and CRM7904-a (PCB fortified oil CRMs)

Each certified value was calculated from PCB concentrations in the diluted PCB root solution determined by the direct ID-GC/MS methods, PCB concentrations in the matrices (CRM 7903-a and CRM 7905-a) and dilution factors (mass ratios) for the preparations.

\[
C_f = (F_{\text{ana}} \times R_a - R_b) \times \frac{M_{\text{nat(cal)}} \times C_{\text{nat}} \times M_{\text{sur(pn)}} \times F_{\text{dilur}} \times F_{\text{prep}}}{M_{\text{sample}} \times M_{\text{sur(cal)}}} + C_u
\]

(2) where \(C_f\) is concentration of analyte in the PCB-fortified CRMs, \(F_{\text{prep}}\) is correction factor of PCB spiking (dilution factor from the PCB root solution to the mineral oil CRM / dilution factor from the PCB root solution to the diluted PCB solution), \(M_{\text{pn}}\) is mass of the sample (the diluted PCB solution) taken for analysis, \(M_{\text{sur(pn)}}\) is mass of the surrogates solution added to the sample. Because relatively small amount (ca. 1/1000) of the PCB root solution was added to the oil matrix, and \(C_u\) is much smaller than \(C_f\), no factor was not multiplied to \(C_u\). Uncertainty of \(F_{\text{prep}}\) includes uncertainty associated with weighing and with repeatability of preparation (gravimetric mixing of the PCB root solution and the base oils; \(n=4\)). For the repeatability test, small scale (1/20) preparations were repeated three times, the
results were combined to analytical result of the actual CRM preparation. The analytical results (three independent GC/MS measurements of the diluted PCB root solution) are shown in Table 1 and Supplemental Table 3.

Homogeneity study

The between ampoule homogeneity of the PCB-fortified mineral oil CRMs (CRM 7902-a and CRM 7904-a) was assessed by determining PCB28, PCB153, and PCB194 in three sub-samples taken from ten ampoules randomly selected from the lot of 600 ampoules. In the cases of the non-fortified mineral oil CRMs (CRM 7903-a and 7905-a), analytical values of PCB52, PCB118, and PCB138 were used. The target compounds were determined by the normal phase liquid chromatography-GC/HRMS methods. Analysis of variance (ANOVA) over the data was performed, and mean squares within groups (\(MS_{\text{within}}\)) and among groups (\(MS_{\text{among}}\)) were calculated. Then standard deviations between ampoules (\(s_{bb}\)) were calculated by use of Eq. (3):

\[
s_{bb} = \sqrt{\frac{MS_{\text{among}} - MS_{\text{within}}}{n}}
\]  

(3)

If the repeatability of the measurement method was insufficient, the influence of analytical variation on the standard deviation between units \(u_{bb}\) was calculated and used to estimate inhomogeneity [1, 2]. \(u_{bb}\) was calculated by use of Eq. (4):

\[
u_{bb} = \sqrt{\frac{MS_{\text{within}}}{n} \left( \frac{2}{\nu_{MS_{\text{within}}}} \right)}
\]  

(4)

where \(\nu_{MS_{\text{within}}}\) is the number of degrees of freedom of \(MS_{\text{within}}\).

Except for PCB28 in NMIJ CRM 7902-a, \(u_{bb}\) values were used as uncertainties from the sample inhomogeneity (Supplemental Tables 5, 6 and 7).

Analytical results and calculation for the certified values and uncertainties
Certified values are the weighted means of the results from analytical methods. The uncertainties of the property values were calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM) [3]. The uncertainty of the certified values was estimated from standard uncertainty due to characterization (\(u(\text{char})\)) and material (between ampoule) inhomogeneity (\(u(\text{bb})\)) as described above. The \(u(\text{bb})\) (\(s_{\text{bb}}\) or \(u_{\text{bb}}\)) was estimated by the homogeneity study in the previous section. The \(u(\text{char})\) was a combination of common factor among the analytical methods, \(u(C_{\text{com}})\); analytical method-specific component of uncertainty, \(u(C_{\text{wm}})\) (\(u^2(C_{\text{wm}}) = \sum w_i u_i^2(C_{\text{ind}})\)), where weight, \(w_i = (1/u_i(C_{\text{ind}})) / \Sigma(1/u_i(C_{\text{ind}}))\); and possible bias effects between methods, \(u(C_{\text{bm}})\). Because the GC/MS calibration solutions and surrogate solutions through the analyses of each CRM, \(M_{\text{cal}}, C_{\text{cal}}, M_{\text{sur(cal))}}\), and \(F_{\text{dilsur}}(f_{\text{dilsur}})\) are common factors among the analytical methods, \(u(C_{\text{com}})\) obtained from combination of uncertainties associated these factors, was used as a component of uncertainty common among the analytical methods (\(u^2(C_{\text{com}}) = \sum u^2(x_i)\); \(x_i\): \(M_{\text{cal}}, C_{\text{cal}}, M_{\text{sur(cal))}}, and \(F_{\text{dilsur}}(f_{\text{dilsur}})\). Since other factors depended on the analytical method or measurement, analytical method-specific component of uncertainty, \(u(C_{\text{ind}})\) was obtained from combination of uncertainties associated these factors using a spreadsheet [3]. Between methods variance, \(u(C_{\text{bm}})\) was calculated by analysis of variance (ANOVA) on the data obtained from different methods.

Reciprocals of \(u(C_{\text{ind}})\) (uncertainties associated with each analytical method) were used as weights to calculate certified values from the results of analytical methods. The expanded uncertainty (\(U\)) in the certified values is equal to \(U = ku_c\), where \(u_c\) is the combined standard uncertainty (square root of the sum of squared each uncertainty component, \(u(C_{\text{com}}), u(C_{\text{wm}}), u(C_{\text{bm}}), \) and \(u(\text{bb})\)) with coverage factor, \(k=2\), corresponding to 95% confidence intervals.

The analytical results in Tables 1, 2 and Supplemental Table 3 were combined to provide certified values. Components of the uncertainty of each value are listed in Supplemental Tables 5-7.

Information values for PCB homologues and density
The mass fractions of PCB homologues were the results of analysis by the Japanese official method for the determination of PCBs in waste [4]. Three analyses of samples taken from different ampoules, and two measurements of each treated sample in three different GC/MS conditions (Method 1, 2 and 6; in Supplemental Tables 1 and 2) were performed. The relative standard deviations and the uncertainties associated with sample inhomogeneity were combined, and multiplied by the coverage factor ($k=2$) to estimate uncertainties of the information values, concentrations of PCB homologues in the CRMs. For calculation of homologue concentrations, we assumed that response factors of PCB isomers in each homologue group were same to one of the isomer used for the calibration solution. Because it is possible that the response factors change depending on GC/MS conditions, the information values were calculated from data obtained from three GC/MS conditions (Supplemental Tables 1, 2, 8-10). In the case of CRM 7903-a, the results of the procedural blank tests (Supplemental Table 9) were subtracted from the results of sample analyses. Differences between the analytical results obtained by each GC/MS method were much larger than ones of PCB congeners obtained by the isotope-dilution technique. Uncertainties of the information values were combination of standard deviations of the data obtained by the methods, and uncertainties due to between-ampoule inhomogeneity, $u_{bb}$.

Information values for density were determined by measurements of mixed sample taken from three (CRM 7903-a or CRM 7905-a) or four (CRM 7902-a or CRM 7904-a) ampoules randomly selected from the lot of 600 ampoules with an oscillational density meter, DMA5000EX (Anton Paar, Graz, Austria). The measurements were repeated three times for each temperature. The values at room temperature are shown in Supplemental Table 11. Repeatability of the measurements was smaller than 0.001% (RSD).

References
1. Linsinger TP, Pauwels J, van der Veen AMH, Schimmel H, Lamberty A (2001) Accred Qual Assur 6: 20-25

2. International Organization for Standardization (1989) ISO-guide 35—certification of reference materials—general and statistical principles. Geneva, Switzerland

3. International Organization for Standardization (1993) Guide to the expression of uncertainty in measurement, ISO, Geneva, Switzerland

4. Ministry of Welfare, Japan (1992) Notification No. 192.
|                      | Method 1         | Methods 2 and 5 | Method 3         | Method 4         | Method 6         |
|----------------------|------------------|-----------------|------------------|------------------|------------------|
| **GC/MS**            | AutoSpec         | AutoSpec        | AutoSpec         | AutoSpec         | JMS-700D         |
| **Carrier gas**      | He, 1.0 mL/min   | He, 1.1 mL/min  | He, 1.0 mL/min   | He, 1.0 mL/min   | He, 1.0 mL/min   |
| **Injection**        | Splitless, 200 °C| Splitless, 200 °C| Splitless, 200 °C| Splitless, 200 °C| Splitless, 200 °C|
| **Column**           | HT8-PCB          | DB-XLB          | DB-1701          | DB-1MS           | DB-5MS           |
| **Column temperature** |                  |                 |                  |                  |                  |
|                      | 60 °C (2 min) →  | 80 °C (1 min)   | 80 °C (1 min) →  | 80 °C (1 min) →  | 80 °C (1 min) →  |
|                      | +20 °C/min →     | +50 °C/min →    | +50 °C/min →     | +50 °C/min →     | +50 °C/min →     |
|                      | 190 °C → +1.8 °C/min → | 140 °C → +2.5 °C/min → | 150 °C → +5.0 °C/min → |
|                      | 260 °C → +5 °C/min → | 300 °C (6 min) | 265 °C (2 min) → | 295 °C (2 min) → |                  |
|                      |                  |                 |                  |                  |                  |
|                      |                  | 80 °C (1 min) → |                  |                  |                  |
|                      |                  | +50 °C/min →    |                  |                  |                  |
|                      |                  | 140 °C → +2.5 °C/min → |                  |                  |                  |
|                      |                  | 150 °C → +5.0 °C/min → |                  |                  |                  |
|                      |                  |                  |                  |                  |                  |
|                      |                  |                  |                  |                  |                  |
|                      |                  |                  |                  |                  |                  |
Table S2 MS conditions of the GC/HRMS measurements

| Methods 1, 2, 3, 4, and 6 | Method 5 |
|---------------------------|----------|
| **Ionization**            | Electron ionization (EI) | Negative chemical ionization (NCI), Reaction gas, CH₄ (2x10⁻⁵ torr) |
| **Electron energy**       | 35-40 eV | 70 eV (Emission: 1.5 mA) |
| **Accelerate voltage**    | ca. 8000 V | ca. 3000 V |
| **Ion source temperature**| 250 ºC | 150 ºC |
| **Mass resolution**       | 10000 | 3000 |
| **Monitoring ion, m/z (Target compound)** | 188.0393, 200.0795 (native-, ¹³C₁₂-monoCBs) | 187.0315, 199.0717 (native-, ¹³C₁₂-monoCBs, M-H⁻) |
|                          | 222.0003, 234.0406 (native-, ¹³C₁₂-diCBs) | 220.9925 (native-diCBs, M-H⁻; triCBs, M-H-Cl⁻), |
|                          | 257.9587, 269.9986 (native-, ¹³C₁₂-triCBs) | 233.0327 (¹³C₁₂-diCBs, M-H⁻; triCBs, M-H-Cl⁻) |
|                          | 289.9224, 301.9626 (native-, ¹³C₁₂-tetraCBs) | 290.9116, 302.9518 (native-, ¹³C₁₂-tetraCBs, M-H⁻) |
|                          | 325.8805, 337.9207 (native-, ¹³C₁₂-pentaCBs) | 325.8805, 337.9207 (native-, ¹³C₁₂-pentaCBs, M⁻) |
|                          | 359.8415, 371.8817 (native-, ¹³C₁₂-hexaCBs) | 359.8415, 371.8817 (native-, ¹³C₁₂-hexaCBs, M⁻) |
|                          | 393.8025, 405.8428 (native-, ¹³C₁₂-heptaCBs) | 393.8025, 405.8428 (native-, ¹³C₁₂-heptaCBs, M⁻) |
|                          | 427.7636, 439.8038 (native-, ¹³C₁₂-octaCBs) | 427.7636, 439.8038 (native-, ¹³C₁₂-octaCBs, M⁻) |
|                          | 461.7246, 473.7648 (native-, ¹³C₁₂-nonaCBs) | 463.7216, 475.7619 (native-, ¹³C₁₂-nonaCBs, M⁻) |
|                          | 497.6826, 509.7229 (native-, ¹³C₁₂-decaCB) | 497.6826, 509.7229 (native-, ¹³C₁₂-decaCB, M⁻) |
Table S3 Analytical results for the determination of PCB congeners in CRM 7904-a

|        | Method G-1 | Method G-2 | Method G-3 | Method G-4 | Method G-5 | Method A-1 | Method A-2 | Method A-3 | Method B-2 | Method B-4 | Method C-1 | Method D-2 | Method D-5 |
|--------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| PCB3   | 507 ± 15   | 501 ± 11   | 508.2 ± 3.7| 495 ± 18   | 502 ± 59   | 548.7 ± 3.7| 478.3 ± 1.1| 435.5 ± 8.6| 493.8 ± 3.3| 547.3 ± 3.0| 470.3 ± 4.3| NM         |
| PCB8   | 573 ± 19   | 574 ± 13   | 579.7 ± 3.7| 557 ± 20   | NM         | 584.5 ± 9.1| 581.6 ± 3.7| 572 ± 13   | 523.3 ± 2.0| 590.4 ± 5.5| 593.9 ± 3.0| NM         |
| PCB28  | 173.4 ± 4.1| 172.5 ± 2.6| NM         | NM         | NM         | 181.2 ± 3.1| NM         | 179.4 ± 0.6| 179.8 ± 1.5| 172.5 ± 1.1| 180.5 ± 8.0| NM         |
| PCB52  | 181.8 ± 5.3| 185.9 ± 5.0| NM         | 185.5 ± 5.1| NM         | 189.5 ± 1.7| NM         | 188.2 ± 2.7| 174.8 ± 1.3| 185.7 ± 4.7| 184.7 ± 3.7| NM         |
| PCB101 | 165.7 ± 9.2| 172.3 ± 1.7| 158.3 ± 2.5| 168 ± 10   | NM         | 169.1 ± 2.8| 170.3 ± 3.3| 164.8 ± 7.6| 163.7 ± 2.9| 175.2 ± 2.5| 166.3 ± 0.9| 165 ± 22   |
| PCB118 | 124.1 ± 5.6| 122.3 ± 2.3| 125.1 ± 3.1| 122.8 ± 6.7| 128 ± 10   | 125.3 ± 1.3| 129.2 ± 1.2| 119.9 ± 2.7| 121.7 ± 1.9| 126.5 ± 0.6| 128.4 ± 7.4| 130.7 ± 4.1|
| PCB138 | 129.2 ± 5.5| 135.0 ± 3.6| NM         | NM         | NM         | 135.9 ± 2.1| NM         | 129.0 ± 2.0| 134.8 ± 1.3| 135.4 ± 3.2| 120.6 ± 9.1| NM         |
| PCB153 | 174.7 ± 4.0| 174.9 ± 4.2| NM         | 172.5 ± 5.5| 170.5 ± 9.9| 183.8 ± 3.0| 180.1 ± 1.1| 175.1 ± 2.3| 163.3 ± 2.4| 175.7 ± 1.9| 179.8 ± 3.3| 183.3 ± 2.2|
| PCB180 | 151.3 ± 6.0| 152.8 ± 3.5| 150.4 ± 2.4| 147.8 ± 6.7| 154 ± 14   | 152.1 ± 2.2| 158.4 ± 1.4| 147.8 ± 1.4| NM         | 156.6 ± 4.2| 155.0 ± 2.6| 159.9 ± 1.0|
| PCB194 | 38.6 ± 1.9 | 36.6 ± 1.6 | 36.3 ± 1.8 | 37.6 ± 2.5 | 38.1 ± 3.9 | 41.3 ± 1.5  | 38.9 ± 0.7 | 36.2 ± 0.5 | NM         | 38.6 ± 1.3 | 38.8 ± 2.2 | 38.5 ± 0.2 |
| PCB206 | 8.7 ± 1.1  | 8.39 ± 0.84| 9.92 ± 0.67| 9.9 ± 1.0  | 9.14 ± 0.77| 9.28 ± 0.28| 9.64 ± 0.25| 9.5 ± 1.4  | NM         | 9.37 ± 0.69| 9.65 ± 0.48| 9.21 ± 0.09|

The unit of values is μg kg⁻¹

Uncertainties are u(Cind) (uncertainties associated with each analytical method: G-1 to G-5) or standard deviation (method A-1 to E-5)

The numbers of analytical methods (pretreatment-GC/MS) were shown in Fig. 1.

NM: not measured.

The analytical results were obtained from three independent GC/MS measurements of the diluted PCB root solution (Method G-1 to G-5) or five independent analyses of samples (Method A-1 to D-5).
Table S4 Analytical results for the determination of PCB congeners in CRM 7905-a

|       | Method A-1 | Method B-2 | Method C-1 | Method D-2 |
|-------|------------|------------|------------|------------|
| PCB3  | < 3.41     | < 13.7     | < 0.876    | < 4.71     |
| PCB8  | < 25.5     | < 2.20     | < 0.865    | < 9.56     |
| PCB28 | < 0.213    | < 0.100    | < 0.699    | < 0.219    |
| PCB52 | < 0.113    | < 0.169    | < 0.391    | < 0.513    |
| PCB101| < 0.138    | < 0.155    | < 0.287    | < 0.656    |
| PCB118| < 0.118    | < 0.123    | < 0.242    | < 0.086    |
| PCB138| < 0.229    | NM         | < 0.579    | < 0.124    |
| PCB153| < 0.227    | < 0.141    | < 0.374    | < 0.121    |
| PCB180| < 0.284    | < 0.128    | < 0.223    | < 0.185    |
| PCB194| < 0.322    | < 0.187    | < 0.171    | < 0.256    |
| PCB206| < 0.147    | < 0.122    | < 0.108    | < 0.071    |

The unit of values is μg kg⁻¹

The numbers of analytical methods (pretreatment-GC/MS) were shown in Fig. 1.

NM: not measured.

The results were obtained from randomly selected three data of five independent analyses of samples.
| Congener | Inhomogeneity $u_{(bb)}$ | Relative standard uncertainty | Measurement $u_{(char)}$ | Relative combined uncertainty $u_c$ |
|----------|---------------------------|-----------------------------|--------------------------|-----------------------------|
|          | $u(C_{com})$ | $U(C_{wm})$ | $u(C_{bm})$ | $u(C_{u})$ |
| PCB3     | 0.0069 ($s_{bb}$) | 0.0157 | 0.0089 | 0.0074 | 0.577 | 0.021 |
| PCB8     | 0.0069 ($s_{bb}$) | 0.0147 | 0.0076 | 0.0175 | 0.577 | 0.025 |
| PCB28    | 0.0069 ($s_{bb}$) | 0.0134 | 0.0130 | 0.0022 | 0.577 | 0.020 |
| PCB52    | 0.0034 ($u_{bb}$) | 0.0148 | 0.0160 | 0.0092 | 0.184 | 0.024 |
| PCB101   | 0.0034 ($u_{bb}$) | 0.0143 | 0.0100 | 0.0351 | 0.309 | 0.039 |
| PCB118   | 0.0034 ($u_{bb}$) | 0.0143 | 0.0152 | 0.0160 | 0.183 | 0.026 |
| PCB138   | 0.0034 ($u_{bb}$) | 0.0148 | 0.0231 | 0.0319 | 0.396 | 0.042 |
| PCB153   | 0.0034 ($u_{bb}$) | 0.0128 | 0.0149 | 0.0000 | 0.355 | 0.020 |
| PCB180   | 0.0034 ($u_{bb}$) | 0.0145 | 0.0135 | 0.0150 | 0.577 | 0.025 |
| PCB194   | 0.0058 ($u_{bb}$) | 0.0176 | 0.0250 | 0.0247 | 0.577 | 0.040 |
| PCB206   | 0.0058 ($u_{bb}$) | 0.0196 | 0.0405 | 0.0760 | 0.577 | 0.089 |
Table S6 Uncertainties of the certified values for PCBs in CRM 7903-a

| Congener | Relative standard uncertainty | Measurement $u$(char) | Relative combined uncertainty $u_c$ |
|----------|-------------------------------|------------------------|-----------------------------------|
|          | Inhomogeneity $u$(bb) | Common factor $u$(C<sub>com</sub>) | Analytical result $u$(C<sub>wm</sub>) | Between methods $u$(C<sub>bm</sub>) |
| PCB52    | 0.139 ($u_{bb}$) | 0.0133 | 0.115 | 0.035 | 0.18 |
| PCB101   | 0.055 ($u_{bb}$) | 0.0131 | 0.133 | 0.273 | 0.31 |
| PCB118   | 0.055 ($u_{bb}$) | 0.0131 | 0.123 | 0.122 | 0.18 |
| PCB138   | 0.094 ($u_{bb}$) | 0.0137 | 0.212 | 0.352 | 0.42 |
| PCB153   | 0.094 ($u_{bb}$) | 0.0116 | 0.197 | 0.258 | 0.34 |
Table S7 Uncertainties of the certified values for PCBs in CRM 7904-a

| Congener | Inhomogeneity $u_{(bb)}$ | Common factor $u(C_{com})$ | Analytical result $U(C_{wm})$ | Between methods $u(C_{bm})$ | Non-fortified $u(C_u)$ | Relative combined uncertainty $u_c$ |
|----------|--------------------------|---------------------------|-------------------------------|-----------------------------|------------------------|-----------------------------------|
| PCB3     | 0.0048 ($u_{bb}$)        | 0.0150                    | 0.0089                        | 0.0074                      | 0.578                  | 0.020                             |
| PCB8     | 0.0048 ($u_{bb}$)        | 0.0156                    | 0.0076                        | 0.0175                      | 0.577                  | 0.025                             |
| PCB28    | 0.0048 ($u_{bb}$)        | 0.0191                    | 0.0131                        | 0.0022                      | 0.577                  | 0.024                             |
| PCB52    | 0.0052 ($u_{bb}$)        | 0.0202                    | 0.0162                        | 0.0094                      | 0.867                  | 0.028                             |
| PCB101   | 0.0052 ($u_{bb}$)        | 0.0154                    | 0.0101                        | 0.0355                      | 0.870                  | 0.040                             |
| PCB118   | 0.0052 ($u_{bb}$)        | 0.0154                    | 0.0154                        | 0.0162                      | 0.577                  | 0.028                             |
| PCB138   | 0.0052 ($u_{bb}$)        | 0.0159                    | 0.0233                        | 0.0449                      | 0.578                  | 0.053                             |
| PCB153   | 0.0052 ($u_{bb}$)        | 0.0141                    | 0.0151                        | 0.0000                      | 0.577                  | 0.021                             |
| PCB180   | 0.0052 ($u_{bb}$)        | 0.0156                    | 0.0137                        | 0.0151                      | 0.578                  | 0.026                             |
| PCB194   | 0.0055 ($u_{bb}$)        | 0.0163                    | 0.0253                        | 0.0249                      | 0.577                  | 0.040                             |
| PCB206   | 0.0055 ($u_{bb}$)        | 0.0185                    | 0.0408                        | 0.0766                      | 0.578                  | 0.089                             |
Table S8 Analytical results for the determination of PCB homologues in CRM 7902-a

| Homologue Group | Method A-1  | Method A-3  | Method A-6  | Method G-1*  |
|-----------------|-------------|-------------|-------------|--------------|
| Mono-CBs        | 531 ± 11    | 502 ± 1     | 504 ± 7     | 507 ± 7      |
| di-CBs          | 644 ± 20    | 635 ± 6     | 625 ± 21    | 616 ± 5      |
| tri-CBs         | 818 ± 5     | 961 ± 6     | 870 ± 19    | 812 ± 8      |
| Tetra-CBs       | 1694 ± 44   | 1319 ± 20   | 1341 ± 52   | 1334 ± 5     |
| Penta-CBs       | 969 ± 31    | 923 ± 6     | 1070 ± 12   | 1005 ± 3     |
| hexa-CBs        | 895 ± 41    | 991 ± 13    | 998 ± 26    | 954 ± 8      |
| Hepta-CBs       | 691 ± 19    | 778 ± 7     | 749 ± 32    | 670 ± 5      |
| octa-CBs        | 244 ± 10    | 243 ± 4     | 201 ± 38    | 223 ± 5      |
| Nona-CBs        | 13.7 ± 0.8  | 13.6 ± 1.3  | 12.1 ± 3.4  | 13.9 ± 0.6   |

The unit of values is μg kg⁻¹

Uncertainties are standard deviations.

The numbers of analytical methods were shown in Fig. 1.

* not used for the information values

The results were obtained from three independent analyses of samples taken from randomly selected ampoules.
Table S9 Analytical results for the determination of PCB homologues in CRM 7903-a

| Homologue group | Method A-1 | Method A-3 | Method A-6 |
|-----------------|------------|------------|------------|
|                 | Blank      | Sample     | Blank      | Sample     | Blank      | Sample     |
| mono-CBs        | ND         | ND         | 0.017 ± 0.003 | 0.017 ± 0.015 | 1.11 ± 0.01 | 1.182 ± 0.031 |
| di-CBs          | ND         | 0.62 ± 0.17 | 0.012 ± 0.010 | 0.055 ± 0.015 | ND         | ND         |
| tri-CBs         | 0.059 ± 0.033 | 0.234 ± 0.068 | 0.277 ± 0.061 | 0.87 ± 0.10 | ND         | ND         |
| tetra-CBs       | ND         | 1.396 ± 0.091 | 0.385 ± 0.028 | 1.49 ± 0.24 | 0.186 ± 0.152 | 0.894 ± 0.493 |
| penta-CBs       | ND         | 2.65 ± 0.18 | 0.056 ± 0.061 | 2.88 ± 0.23 | 0.491 ± 0.133 | 3.42 ± 0.68 |
| hexa-CBs        | ND         | 1.15 ± 0.20 | 0.40 ± 0.47 | 1.54 ± 0.22 | ND         | 1.43 ± 0.40 |
| hepta-CBs       | 0.008 ± 0.009 | 0.210 ± 0.026 | ND         | 0.220 ± 0.054 | ND         | ND         |
| octa-CBs        | ND         | 0.022 ± 0.026 | ND         | ND         | ND         | ND         |
| nona-CBs        | ND         | ND         | ND         | ND         | ND         | ND         |

The unit of values is μg kg⁻¹

Uncertainties are standard deviations.

The numbers of analytical methods were shown in Fig. 1.

ND: not detected

The results were obtained from three independent analyses.
Table S10 Analytical results for the determination of PCB homologues in CRM 7904-a

| Homologue Group | Method A’-1 | Method A’-3 | Method A’-6 | Method G-1* |
|-----------------|-------------|-------------|-------------|-------------|
| mono-CBs        | 546 ± 6     | 485 ± 13    | 547 ± 16    | 507 ± 7     |
| di-CBs          | 646 ± 9     | 640 ± 68    | 646 ± 22    | 615 ± 5     |
| tri-CBs         | 862 ± 11    | 870 ± 103   | 889 ± 37    | 803 ± 8     |
| tetra-CBs       | 1589 ± 26   | 1445 ± 197  | 1399 ± 20   | 1318 ± 5    |
| penta-CBs       | 1040 ± 10   | 1028 ± 113  | 1076 ± 34   | 991 ± 3     |
| hexa-CBs        | 976 ± 20    | 993 ± 109   | 991 ± 37    | 942 ± 8     |
| hepta-CBs       | 694 ± 19    | 777 ± 101   | 726 ± 31    | 662 ± 5     |
| octa-CBs        | 217 ± 10    | 240 ± 27    | 229 ± 9     | 221 ± 5     |
| nona-CBs        | 12.1 ± 1.2  | 12.8 ± 0.9  | 11.9 ± 2.6  | 13.7 ± 0.6  |

The unit of values is μg kg⁻¹.
Uncertainties are standard deviations.
The numbers of analytical methods were shown in Fig. 1.
* not used for the information values
The results were obtained from three independent analyses.
Table S11 Information values for density of NMIJ mineral oil CRMs

| Temperature | Information value (density, g/cm³) |
|-------------|-----------------------------------|
|             | CRM 7902-a | CRM 7903-a | CRM 7904-a | CRM 7905-a |
| 20 °C        | 0.87741    | 0.87751    | 0.86266    | 0.86274    |
| 25 °C        | 0.87406    | 0.87417    | 0.85915    | 0.85920    |
| 30 °C        | 0.87072    | 0.87081    | 0.85564    | 0.85570    |
Fig. S1
Elution profiles of PCB homologues and mineral oils on the GPC column. (A) Insulation oil (another commercial one, JIS K2205 Class1-2), (B) Fuel oil; mobile phase, 0–25 mL hexane, 25–35 mL acetone. The chromatographic conditions are described in the Experimental section.
Fig.S2
Elution profiles of PCB congeners and mineral oils on the octadecyl-silica packed column (after the GPC cleanup). (A) Insulation oil, (B) Fuel oil; mobile phase, 0–25 mL acetonitrile, 25–35 mL acetone. The chromatographic conditions are described in the Experimental section.
Elution profiles of PCB congeners and mineral oils on the sulfoxide-bonded silica packed column. (A) Insulation oil, (B) Fuel oil; mobile phase, 0–25 mL hexane, 25–35 mL acetone. The chromatographic conditions are described in the Experimental section.
Fig. S4
Elution profiles of PCB congeners and mineral oils on the Inertsil DIOL column (after the NH2 column cleanup). (A) Insulation oil, (B) Fuel oil; mobile phase, 0–25 mL hexane, 25–35 mL acetone. The chromatographic conditions are described in the Experimental section.