Development of sediment certified reference material for PCDD/Fs analysis

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Introduction

Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans (PCDD/Fs) were persistent organic pollutants (POPs), which have caused extensive concern due to their adverse effects on the environment and human health. Analysis of POPs, especially PCDD/Fs in the environmental samples is complex, which typically involves many processes. Certified reference materials (CRMs) are strong quality-assurance tools to support PCDD/Fs analysis in sediment and soil samples. Sediment PCDD/Fs CRM was developed in the study, its homogeneity, stability and certification were researched, the mass fractions and associated uncertainty values of the seventeen 2,3,7,8-substituted PCDD/Fs in the candidate reference material (RM) were quantified. The PCDD/Fs CRM was approved as the grade primary reference material by metrological administrative department of state council of China with the certified number GBW08309 in 2016.

Materials and methods

Standard solutions in n-nonane (EPA-1613 CS1 to CS5, EPA-1613 LCS, and EPA-1613 ISS) were purchased from Wellington Labs (USA). All solvents used (n-hexane and dichloromethane) were of pesticide grade (J.T.Baker, USA), n-nonane were purchased from Sigma (USA). Silica gel (100-200 mesh) was purchased from Merck (Germany), alumina (basic) was obtained from Shanghai Hushi Laboratorial Equipment (China).

Concentrations of the seventeen 2,3,7,8-substituted PCDD/F congeners were determined according to the US EPA method 1613. Briefly, spiked the sediment with ^{13}C-labeled surrogates as internal standards; then extracted them using an accelerated solvent extraction (ASE) instrument with 50% dichloromethane in n-hexane; sample extracts cleanuped by multi-layer silica gel column (silver nitrate/acid/base silica included) and alumina column; and then spiked the clean-up extracts with ^{13}C-labeled recovery standards. PCDD/F congeners in extracts determined by HRGC/HRMS (Autospec-Premier, equipped with a DB-5MS capillary column, Agilent Technologies, USA; 60 m×0.25 mm×0.25 μm).

Quality assurance/quality control (QA/QC) measures included analysis of method blanks, duplicate samples, matrix spikes, and laboratory control samples. No target compounds were detected in the method blanks, QA/QC results were within acceptable limits according to USEPA 1613. The recoveries of ^{13}C-labelled internal standards ranged from 50% to 105%. LODs of the seventeen 2,3,7,8-substituted PCDD/F congeners were defined as three times the signal/noise ratio, ranged from 0.1 to 1.3 pg/g dry weight.

Candidate sediment material was collected from the lake in the vicinity of an abandoned chemical plant in Tianjin, 2013. Candidate sediment material collection was based on contaminant levels measured in the previous studies, and intended to provide sufficient raw materials with appropriate PCDD/Fs levels. The CRM developing process followed: surface sediment sample (about 10 cm depth) was collected, freeze-dried, grounded, sieved

(200-mesh), homogenized, dried (110°C for 6 hours), and then packaged (screw-capped brown glass bottles).

Results and discussion

Homogeneity of PCDD/Fs CRM

Homogeneity of candidate CRM was tested by determining the concentrations of the seventeen 2,3,7,8-substituted PCDD/F congeners between and within bottles. Homogeneity testing also included analysis of other constituents (or characteristics) such as metals, organic matter, water content and particle size. The within-bottle standard deviation and the between-bottle standard deviation of PCDD/F congeners were studied by taking 3 sub-samples from each of the 20 random-selected bottles. One-way analysis of variance (ANOVA) was performed to assess homogeneity of candidate CRM, the assessment results of homogeneity indicate that inhomogeneity of PCDD/Fs between bottles were not significant.

Stability of PCDD/Fs CRM

18 bottles of PCDD/Fs candidate CRMs were randomly selected from total 500 bottles, then, 18 bottles were stored at -20°C and 60°C, respectively. The candidate PCDD/Fs CRMs were sampled from these bottles at 1, 3, 5, 7, 14 and 21 days at both the above-mentioned temperatures as a short-term stability test. Other 21 bottles were also randomly selected, and they were stored at 4°C, candidate PCDD/Fs CRMs were sampled from these bottles in 0, 1, 3, 6, 9, 15 and 24 months as a long-term stability test. All the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed by taking 2 sub-samples from each of the three replicate bottles at every storage temperature. Concentrations of the seventeen 2,3,7,8-substituted PCDD/F congeners in these samples were sensitively determined according to the US EPA method 1613, which can ensure that a slight instability of the seventeen 2,3,7,8-substituted PCDD/F congeners could be detected. Line fitting methods were used to assess their stability. The significance of slopes was tested using t test. A significant slope (at 95% or 99% confidence level) can indicate concentration change of the target compounds during the test. The regression analysis results show that all the seventeen 2,3,7,8-substituted PCDD/F congeners were stable in the sediment matrix during both the short-term and long-term stability test.

Certification

Values for the seventeen 2,3,7,8-substituted PCDD/F congeners obtained from the results of the inter-laboratory comparison study among 9 experienced laboratories. Every participating laboratory was required to detect the seventeen 2,3,7,8-substituted PCDD/Fs congeners in the candidate CRM and WMS-01(Wellington Labs, USA) using the same extraction, cleanup and analysis condition. Every laboratory performed six independent, replicate determinations of the target PCDD/Fs.

Every participating laboratory verified the validity of analysis method by recovery experiments and procedure blanks according to the protocol prior to the experiment. All relevant information, such as method description, method-performance characteristics, and final measurement results, were submitted by the participants using a standardized report. All these data were tested using mathematical statistics method, only sound data were accepted. The average values of the 9 participating laboratories were certified as values of PCDD/F congeners in the CRM. The standard uncertainty was estimated by combining the standard uncertainty due to inhomogeneity, the standard uncertainty due to instability, the standard uncertainty due to inter-laboratory certification of the CRM and type B standard uncertainty. The certified mass fraction values and combined standard uncertainty of PCDD/Fs in CRM is summarized in table 1.

Table1 Certified Mass Fraction Values for PCDD/Fs in GBW08309

Name	Mass fraction（$\times 10^{-12}$）		Combined standard uncertainty（$\times 10^{-12}$）
Certified reference material for seventeen PCDD/Fs in lake sediment	2,3,7,8-TCDF	4.0	0.8
	1,2,3,7,8-PeCDF	2.2	0.6
	2,3,4,7,8-PeCDF	3.7	0.7
	1,2,3,4,7,8-HxCDF	43	9
	1,2,3,6,7,8-HxCDF	7.3	1.3
	2,3,4,6,7,8-HxCDF	4.7	1.2
	1,2,3,7,8,9-HxCDF	7.6	1.6
	1,2,3,4,6,7,8-HpCDF	90	15
	1,2,3,4,7,8,9-HpCDF	30	7
	OCDF	3.6×10^2	0.6×10^2
	2,3,7,8-TCDD	11	3
	1,2,3,7,8-PeCDD	3.5	0.8
	1,2,3,4,7,8-HxCDD	22	8
	1,2,3,6,7,8-HxCDD	49	9
	1,2,3,7,8,9-HxCDD	33	8
	1,2,3,4,6,7,8-HpCDD	1.2×10^3	0.3×10^3
	OCDD	9.6×10^3	1.9×10^3

The certified mass fraction values for PCDD/Fs in GBW08309 were established by technical and statistical evaluation. The uncertainties for all the seventeen 2,3,7,8-substituted PCDD/Fs congeners are less than 30% of the certified value. In brief, CRM GBW08309 is suitable for quality assurance in PCDD/Fs analysis for laboratories.

References
1. ISO Guide 35: 2006. International Organization for Standardization (2006).
2. van der Veen A. Revision of the Guide to the expression of uncertainty in measurement. Dutch Metrology Institute (2011).