

Ionic liquid extraction for the determination of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and dioxin-like polychlorinated biphenyls in soil and sediment

Sakatani K¹, Takahashi K¹, Takenaka S¹, Kajiwara J¹, Katsuki S¹, Mitoma C² and Furue M²

¹Fukuoka Institute of Health and Environmental Sciences, 39 Mukaizano, Dazaifu, Fukuoka, Japan, 818-0135, sakatani@fihes.pref.fukuoka.jp; ²Reserch and Clinical Center for Yusho and Dioxin, Kyushu University Hospital, 3-1-1 Maidashi, Higashi-ku, Fukuoka, Japan, 812-8582

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs), which are all commonly known as dioxins, are highly toxic environmental contaminants. Dioxins have been analyzed using different analytical methods in many different environmental matrices, including water, soil, sediment and air. However, these official methods for the routine analysis of dioxins are time consuming, expensive, and use large volumes of solvents.

Ionic liquids are salts composed of a cation and anion that exist as liquids even at room temperature. They have extremely low vapor pressures, are flame retardant, and have high thermal stability. In addition, they have low viscosity and can be used as solvents. Because ionic liquids have low volatility, they are safer than organic solvents.

The aim of the present study was to develop a simple and quick method for analyzing dioxins in soil and sediment using an ionic liquid for extraction. The analytes included 2,3,7,8-chlorine-substituted PCDD/PCDF congeners (seven PCDD congeners and 10 PCDF congeners) and 12 dl-PCB congeners.

Materials and methods

Materials

A river sediment certified reference material (CRM) for dioxins (JSAC0431¹) was purchased from The Japan Society for Analytical Chemistry (Tokyo, Japan). Native soils and sediments were collected in Fukuoka, Japan.

Reagents

The ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF₄]) and 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). The ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF₄]) was purchased from Wako Pure Chemical Industries (Tokyo, Japan), and 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF₆]) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Hexane, nonane, 10% (w/w) silver nitrate impregnated silica gel, Wakogel DX, and anhydrous sodium sulfate were purchased from Wako Pure Chemical Industries. ¹³C₁₂-labeled congeners of the seven PCDDs, 10 PCDFs, and 12 dl-PCBs were used as internal standards, and ¹³C₁₂-1,2,3,4-tetrachlorodibenzo-*p*-dioxin, ¹³C₁₂-1,2,3,4,6,8,9-heptachlorodibenzofuran and ¹³C₁₂-2,2',4,4',5,5'-hexachlorinated biphenyl (PCB 153) were used as syringe spikes. The native and ¹³C₁₂-labeled PCDDs, PCDFs, and dl-PCBs were purchased from Wellington Laboratories (Guelph, Canada).

Analysis of dioxins

Dioxin analysis was performed using an Agilent 7890A (Agilent Technologies, Santa Clara, CA) gas chromatograph with a 7693A series auto injector interfaced with a JMS-800D UltraFOCUSTM (JEOL, TokyoJapan) high-resolution gas chromatograph–high-resolution mass spectrometer (HRGC/HRMS). The separation was conducted on SP-2331 (Supelco, Bellefonte, PA), BPX-DXN (SGE Analytical Science Pty., Melbourne, Australia), and HT8-PCB (SGE Analytical Science Pty.) columns. All columns had the same dimensions (60 m × 0.25 mm i.d., 0.25 μm film thickness).

Examination of the ionic liquid extraction of dioxins

Two hundred nanograms of each internal standard was added to 2 g of the river sediment CRM, followed by 1.5 mL of each ionic liquid ([EMIM][BF₄], [BMIM][BF₄], [HMIM][BF₄], [OMIM][BF₄], [OMIM][Cl] and [OMIM][PF₆]). The mixture was heated at 100 °C for 1 h and centrifuged at 3000 rpm for 5 min, and then the upper ionic liquid layer was recovered. This extraction was repeated three times. Hexane (3 mL) was added to the collected ionic liquid and the mixture was shaken strongly for 1 min, and then the mixture was centrifuged at 3000 rpm for 5 min to recover the hexane layer. This operation was repeated three times, and the extract was applied to a column that was wet-layered as follows: 1 g of 10% (w/w) silver nitrate-impregnated silica gel, 1 g of Wakogel DX, and 2 g of anhydrous sodium sulfate. The column was eluted with 125 mL of hexane and the eluate was collected. Nonane (50 µL) was added to the eluate, and the solvent was evaporated from the mixture at 40 °C, followed by reduction to 50 µL under a stream of nitrogen gas. Finally, 500 ng of each syringe spike was added to prepare the HRGC/HRMS sample.

Uncertainty

Two samples prepared from the same river sediment CRM were repeatedly analyzed by HRGC/HRMS three times in one day, and this protocol was repeated for 5 days. The analytical values were compared with the certified values, and the expanded uncertainty was calculated according to “Guide to the Expression of Uncertainty in Measurement²⁷”.

Comparison with the official Japanese method

The concentrations of dioxins in the soils and sediments were analyzed by both the official Japanese method^{3,4} and our method, and the data were compared. The number of samples was eight. The pretreatment methods used in the official method were Soxhlet extraction, sulfuric acid treatment, multi-layered silica gel column chromatography, and activated carbon column chromatography. To compare the analytical values obtained by our method with those obtained by the official method, percentages (*R*) were calculated using the following equation:

$$R = \frac{C_1}{C_2} \times 100 \quad (1)$$

where *C*₁ is the analytical value obtained by our method, and *C*₂ is the analytical value obtained by the official method.

Results and discussion

Examination of the ionic liquid extraction of dioxins

The internal standards were extracted with six different ionic liquids to determine how the recoveries are affected by changes in cation and anion. First, the effect of cations on the recoveries was studied by keeping the anion [BF₄]⁻ constant. The recoveries in order from highest to lowest were [OMIM][BF₄] > [HMIM][BF₄] > [BMIM][BF₄] > [EMIM][BF₄]. Secondly, the effect of anions on the recoveries was studied by selecting the cation [OMIM]⁺ and varying the anions, such as [Cl]⁻, [BF₄]⁻ and [PF₆]⁻. The recoveries in order from highest to lowest were [OMIM][PF₆] ≥ [OMIM][BF₄] > [OMIM][Cl]. For a series of 1-alkyl-3-methylimidazolium cations, it is known that increasing the alkyl chain length increases the hydrophobicity⁵. And it is known that the hydrophobicity of the anion increases from [Cl]⁻, [BF₄]⁻ to [PF₆]⁻⁵. Therefore, the recoveries obtained in this study could be influenced by the hydrophobicity of the ionic liquid. On the other hand, in the case of certain conditions for ionic liquids composed of [PF₆]⁻, it has been reported that contact with an aqueous phase may result in slow hydrolysis of the [PF₆]⁻ with the concomitant release of HF and PO₄³⁻⁶.

From these results, we developed an analytical method for the determination of dioxins in soil and sediment using the ionic liquid [OMIM][BF₄] for extraction. When [OMIM][BF₄] was used for extraction, the recoveries did not exceed the acceptable limit values of between 50% and 120% set in the official Japanese methods.

Uncertainty

Using the river sediment CRM, the analytical values were compared with the certified values, and the expanded uncertainty of our analytical method was calculated (Table 1). Twenty-five of the 29 dioxins to be

measured were within the mean \pm 20% of the certified value. None of the other four congeners exceeded the mean \pm 40% of the certified value. The expanded uncertainty of the mean value for each congener was 15% to 32%, and we found that our analytical method could be used to determine the concentrations of dioxins in sediment with high accuracy.

Comparison with the official Japanese method

Soils and sediments collected in Fukuoka, Japan were analyzed by both the official Japanese method and our method, and the results were compared using Eq. 1 (Fig. 1). The percentage (R) for each congener was 62.1% to 138%, and 64% of the results were within \pm 20% of the values obtained with the official method. This comparison showed that the data obtained by our method are close to those obtained by the official method.

In addition, the analysis time for our method was one fifth of that for the official method, and the amount of solvent used in our method was one sixth of that used in the official method. Moreover, the present method is better for workers' health than the official method because it does not use highly toxic organic solvents.

Acknowledgement

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Table 1 Analytical values and expanded uncertainties for the method developed in this study

	Certified value ± SD (pg/g-dry)	Mean value (pg/g-dry)	Mean value /Certified value (%)	Expanded uncertainty (%)
2,3,7,8-TeCDD	1.36 ± 0.11	1.17	85.9	18.3
1,2,3,7,8-PeCDD	7.71 ± 0.45	6.96	90.3	26.6
1,2,3,4,7,8-HxCDD	12.31 ± 0.48	14.2	116	24.5
1,2,3,6,7,8-HxCDD	28.9 ± 1.2	24.8	85.7	23.9
1,2,3,7,8,9-HxCDD	23.9 ± 1.3	20.6	86.3	23.5
1,2,3,4,6,7,8-HpCDD	702 ± 41	666	94.8	14.9
OCDD	12010 ± 480	9450	78.7	22.8
2,3,7,8-TeCDF	12.01 ± 0.92	9.22	76.8	31.4
1,2,3,7,8-PeCDF	15.6 ± 1.5	12.6	80.9	17.6
2,3,4,7,8-PeCDF	17.2 ± 1.3	15.0	87.1	14.6
1,2,3,4,7,8-HxCDF	27.4 ± 1.3	24.5	89.4	17.2
1,2,3,6,7,8-HxCDF	24.4 ± 1.0	21.2	86.8	26.1
1,2,3,7,8,9-HxCDF	2.27 ± 0.30	2.41	106	22.5
2,3,4,6,7,8-HxCDF	36.7 ± 3.4	32.7	89.2	19.4
1,2,3,4,6,7,8-HpCDF	142 ± 11	126	88.6	16.7
1,2,3,4,7,8,9-HpCDF	22.0 ± 2.0	21.0	95.4	23.3
OCDF	254 ± 12	226	89.0	20.9
3,4,4',5'-TeCB (81)	149 ± 12	144	96.7	20.7
3,3',4,4'-TeCB (77)	6020 ± 430	4260	70.8	25.1
3,3',4,4',5'-PeCB (126)	64.4 ± 6.2	66.1	103	18.1
3,3',4,4',5,5'-HxCB (169)	6.52 ± 0.91	6.61	101	31.7
2',3,4,4',5'-PeCB (123)	220 ± 36	168	76.2	18.0
2,3',4,4',5'-PeCB (118)	9600 ± 1100	9310	97.0	20.8
2,3,3',4,4'-PeCB (105)	3850 ± 300	3350	87.1	20.6
2,3,4,4',5'-PeCB (114)	311 ± 47	274	88.2	23.7
2,3',4,4',5,5'-HxCB (167)	328 ± 33	284	86.7	31.3
2,3,3',4,4',5'-HxCB (156)	812 ± 70	744	91.6	29.4
2,3,3',4,4',5'-HxCB (157)	212 ± 23	220	104	32.1
2,3,3',4,4',5,5'-HpCB (189)	61.3 ± 6.9	57.9	94.5	21.8

SD: Standard deviation

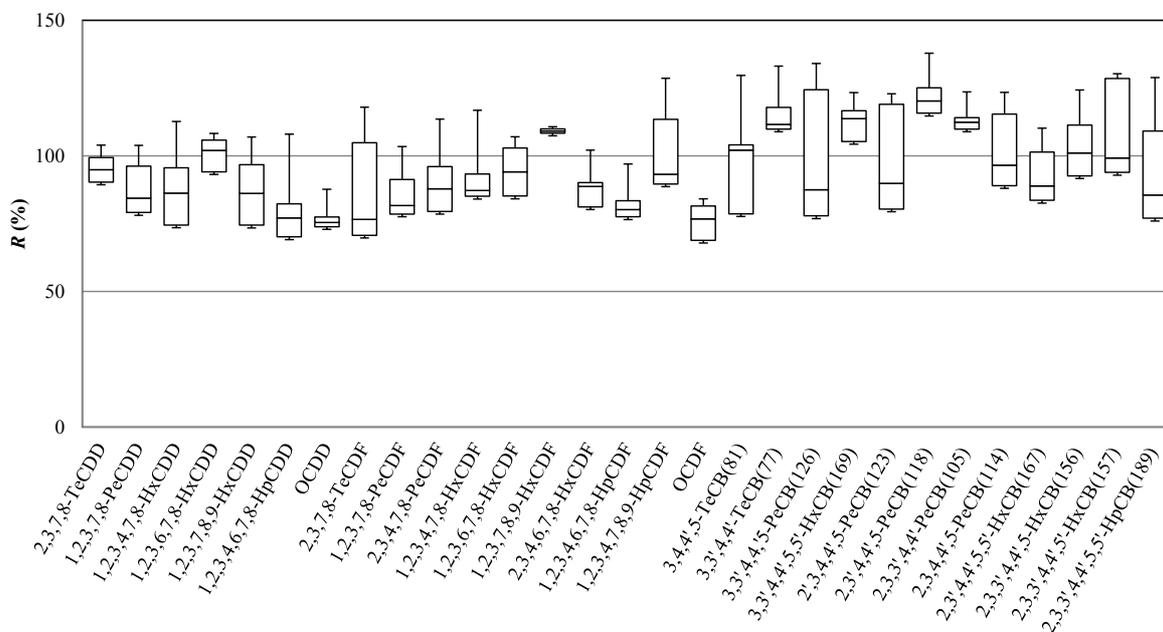


Fig. 1 Analytical values obtained by the method developed in this study as a percentage of those obtained by the official method of Japan.