

A RAPID METHOD FOR DETERMINATION OF COPLANAR POLYCHLORINATED BIPHENYLS IN SOIL

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Introduction

Polychlorinated biphenyls (PCBs) are a class of compounds which containing 209 individual compounds that differ in the number and position of the chlorine atoms. Among these compounds, four non-ortho substituted PCB and eight mono-ortho substituted PCB are called “dioxin-like”, which are structural similar with dioxins and also are the same mechanism of toxicity as dioxins. They have been assigned a toxic equivalence factor (TEF) that refers to the toxicity of the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).¹ Sample preparation for the analysis of PCBs is the most time-consuming and labor-intensive task involved in the analytical scheme.² The aim of this study was to establish a fast pretreatment method for PCBs in soil.

Materials and Methods

Materials

All organic solvents used were pesticide quality and purchased from J.T.Baker Chemical Company, USA. Diatomaceous Earth (DE) was purchased from Dionex, USA. The ¹³C-labelled internal standard solution was purchased from Cambridge Isotope Laboratories.

Sample extraction, cleanup and HRGC/HRMS analyses

Sample extraction was carried out using a Dionex ASE (accelerated solvent extraction) 300.10 g soil was spiked with ¹³C-labelled internal standard solution (EC-4977) then mixed with DE and placed in an extraction cell (34ml volume). Solvents were hexane/acetone (1:1). An oven heat-up time of 5 min, static time of 5 min and oven temperature of 100°C were chosen. The flush volume amounted to 60% of the extraction cell volume. After extraction, the extract was concentrated and exchanged into hexane.

Cleanup was performed on an automated cleanup system, i.e. Power-PrepTM, Fluid Management Systems, Inc. Three disposable columns including multilayer silica, basic alumina and carbon/celite column were used as absorbents. 110 ml hexane:dichloromethane (1:1) and 110ml hexane were eluted through the whole system for washing. Prior to the automated cleanup process, the three columns were conditioned by 90ml, 20ml and 20ml hexane at 10ml/min respectively. Then the extracts spiked ¹³C-labelled cleanup standard solution (EC-4978) were diluted in 14ml hexane before loading on the multilayer silica column at 5ml/min. The detailed flow chart of the cleanup process was indicated in Figure.1. Four fractions (F2, F3, F5 and F6) were collected in a flask. The fractions were concentrated to approximately 1ml and then transferred to a 100µl conical vial for final concentration. Reduce the volume of the fractions to about 20µl using nitrogen. The ¹³C-labelled injection standard solution (EC-4979) was added to the fractions before HRGC/HRMS analysis.

The analysis was performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms (60m×0.25mm I.D., 0.25µm film thickness)

Sample preparation and analysis

capillary column was used for separation of the PCB congeners. The GC temperature program was optimized as follows: splitless injection of 1 μ l at 90 °C, initial oven temperature of 90 °C for 1min, then increased at 20 °C/min to 180 °C held for 1min, finally increased at 3 °C/min to 300 °C and held for 1min. He was used as the carrier gas. The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring (SIM). Electron energy was set to 38eV. Source temperature was 280 °C. The mass system was tuned to a minimum resolution of 10000 (10% valley) using PFK (perfluorokerosene) as lock mass. The detailed quantitative determination of PCBs was referred to US EPA method 1668A.³

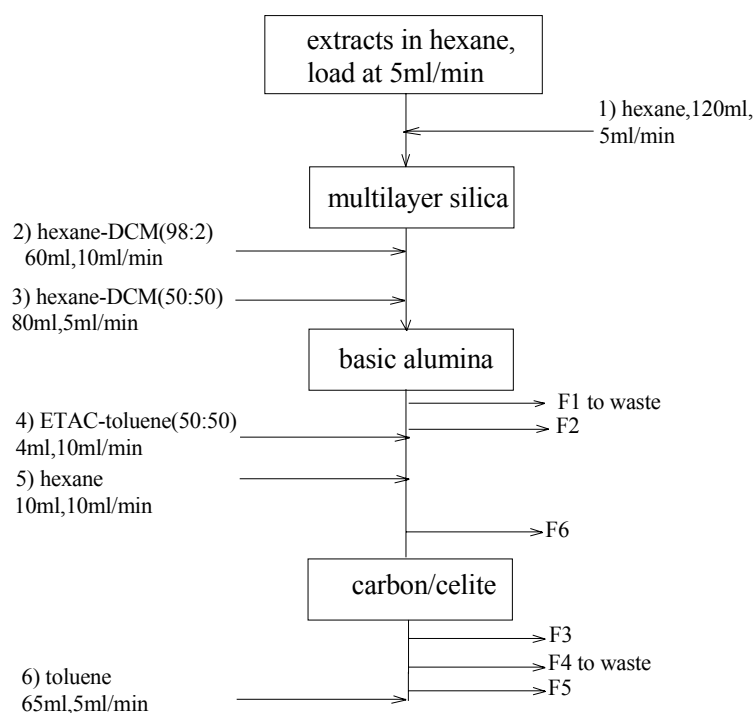


Fig.1. The flow chart for the PCBs cleanup using the Power-Prep™ system

Results and Discussion

Standard solution was used to check the efficiency of the FMS system firstly. Five fractions, i.e., F2, F3, F4, F5 and F6 were collected respectively. Table 1 showed the distribution of the 12 coplanar PCBs in the five fractions. Four non-ortho substituted PCB (77,81,126 and 169) with planar geometry were all collected in the toluene fraction (F6) because of their structural properties, which was also similar with the results of Pirard, C. et al.¹ So the non-ortho substituted PCB could not be isolated with dioxins, which were also back-flushed with toluene, using FMS system. Eight mono-ortho PCB were dispersed in the F2, F3, F5 and F6 fractions. So we collected four fractions when performing FMS cleanup process of soil extracts.

Sample preparation and analysis

Table 1 Distribution of the 12 coplanar PCBs in different fraction (%)

Congener	F2	F3	F4	F5	F6
PCB77	-	-	-	-	100
PCB 81	-	-	-	-	100
PCB 105	-	57.9	-	16.9	25.2
PCB 114	17.7	62.6	-	8.2	11.5
PCB 118	45.5	29.7	-	11.6	13.2
PCB 123	56.8	26.7	-	7.3	9.2
PCB 126	-	-	-	-	100
PCB 156	16.4	37.8	-	20.1	25.7
PCB 157	8.8	34.5	-	24.7	32
PCB 167	86	4.6	-	4.3	5.1
PCB 169	-	-	-	-	100
PCB 189	47.9	13.5	-	15.9	22.8

Note: “-” means not detected.

The recoveries of the ^{13}C -labelled internal and cleanup standard solution in soil were shown in Table 2. The recoveries for the 12 coplanar PCBs and 3 cleanup standard solution ranged from 60% to 71% and from 64% to 114%, respectively. However, the recoveries for the lowly chlorinated congeners (below Tri-CBs) were lower than 30%, which was also found in the results of Kim et al's research.⁴ The lowly chlorinated congeners might be lost during the concentration process.

Table 2 Recoveries of ^{13}C -labelled internal and cleanup standard solution

Congener	Recovery (%)	Congener	Recovery (%)
PCB 1	<10	PCB 155	60
PCB 3	25	PCB 156	62
PCB 4	<10	PCB 157	65
PCB 15	28	PCB 167	62
PCB 19	121	PCB 169	60
PCB 37	58	PCB 188	79
PCB 54	58	PCB 189	68
PCB 77	61	PCB 202	84
PCB 81	64	PCB 205	79
PCB 104	58	PCB 206	75
PCB 105	62	PCB 208	85
PCB 114	62	PCB 209	65
PCB 118	67	PCB 28	64
PCB 123	71	PCB 111	104
PCB 126	64	PCB 178	114

Sample preparation and analysis

Note: PCB 28, 111 and 178 were cleanup standard solutions.

The proposed simple process for the total coplanar PCB analysis, including ASE, Power-Prep system cleanup and HRGC/HRMS analysis requires about 8h. This method was time effective and greatly reduced the exposure between lab worker and solvents comparing with the traditional pretreatment method.

References

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