A study on the behavior of Dioxins in various coated silica gel

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Introduction

Multilayer silica gel column (see Fig. 1) treatment is well known cleanup technique for Dioxins analysis and has been employed by many Dioxins analysis official methods in Japan. For contaminated PCB reduction, heated silica gel has been used to prepare the coated silica gel for multilayer silica gel column in our laboratory. Sometimes the recovery rate of some ^{13}C labelled PCDD used as internal standards were below the line of the QA/QC requirement (50-120 %) of each methods (see Table 1). The loss of internal standards generally appears on rich matrix interferences containing samples, however, this phenomenon also appeared on low matrix interferences containing samples such as blank test samples and treated waste waters. On basic alumina column treatment or activated carbon column treatment, the loss of OctaCDD and OctaCDF is recognized but not of Tetra, Penta and HexaCDD. Therefore multilayer silica gel column treatment is possibly a cause of this phenomenon. Focused on two of the constitutions of multilayer silica gel column, silver nitrate coated silica gel and sulfuric acid coated silica gel, this study investigated the behavior of dioxins on them individually.

Materials and Methods

Reagents: silica gel 60(Merck, 63-200 µm), silver nitrate (Wako Pure Chemical, JIS special grade), sulfuric acid (Wako Pure Chemical, super special grade), anhydrous sodium sulfate (Kanto Kagaku, pesticide residue and PCB analysis grade), n-hexane (Kanto Kagaku, dioxin analysis grade), ^{13}C labelled PCDD/PCDF solution (Wellington laboratories, 100 ng/mL or 200 ng/mL for each compounds), ^{13}C labelled DL-PCB solution (Wellington laboratories, 100 ng/mL for each compounds), syringe spike solution for PCDD/PCDF(Wellington laboratories, 100 ng/mL for each compounds), syringe spike solution for DL-PCB(Wellington laboratories, 100 ng/mL for each compounds).

Methods: (1) Treatment of silica gel; at this study, following treated silica gels were used. (a) not heated, (b) flash heated from room temperature to 400 ºC and held for 4 hours and (c) held 105 ºC for 4 hours and heated to 400 ºC at 10 ºC/minute and held for 4 hours. (2) Coated silica gel preparation; (a) 25 g of silver nitrate was dissolved in 40 mL of pure water. 225 g of silica gel was added to this aqueous solution and shaken well. Then, it was evaporated at 50 ºC for 3 hours with light shielding and silver nitrate coated silica gel was obtained. (b) 44 g of sulfuric acid was added to 56 g of silica gel or 22 g of sulfuric acid was added to 78 g of silica gel and shaken well. Then 44 % or 22 % sulfuric acid coated silica gel was obtained. (3) Elute examination; the individual coated silica gel columns were prepared as shown in Fig. 1 respectively. Each 10 µL of ^{13}C labelled PCDD/PCDF solution and ^{13}C labelled DL-PCB solution were added to coated silica gel columns and eluted with 100 mL of n-hexane. The eluate was concentrated to 50 µL and before HR-GC/MS measurement, added each 10 µL of syringe spike solutions of PCDD/PCDF and DL-PCB. Then the recovery rates of ^{13}C labelled PCDD/PCDF and DL-PCB were calculated from the peak area ratio of related compounds with the results of HR-GC/MS measurement.

Results and Discussion

The recovery rates of ^{13}C labelled PCDD/PCDF and DL-PCB were shown in Table 2. On all of the silver nitrate coated silica gel columns, the recovery rates were sufficient. On the sulfuric acid coated silica gel columns by using heated silica gel, the average recovery rates of Tetra and PentaCDD were not satisfied to the requirement, especially, those of TetraCDD were less than 10 %. On the other hands, those of PCDF and DL-PCB were acceptable on each sulfuric acid coated silica gel. From these results, the sulfuric acid coated silica gel by using heated silica gel is concluded to be one of the causes of low recovery phenomenon. Meanwhile, the further investigation of the coated silica gel is necessary for other possible causes of this phenomenon.

Acknowledgements

The authors would like to appreciate Yasutaka Hirata, Akemi Yamamoto and Eiko Sasaki for their support of this study.

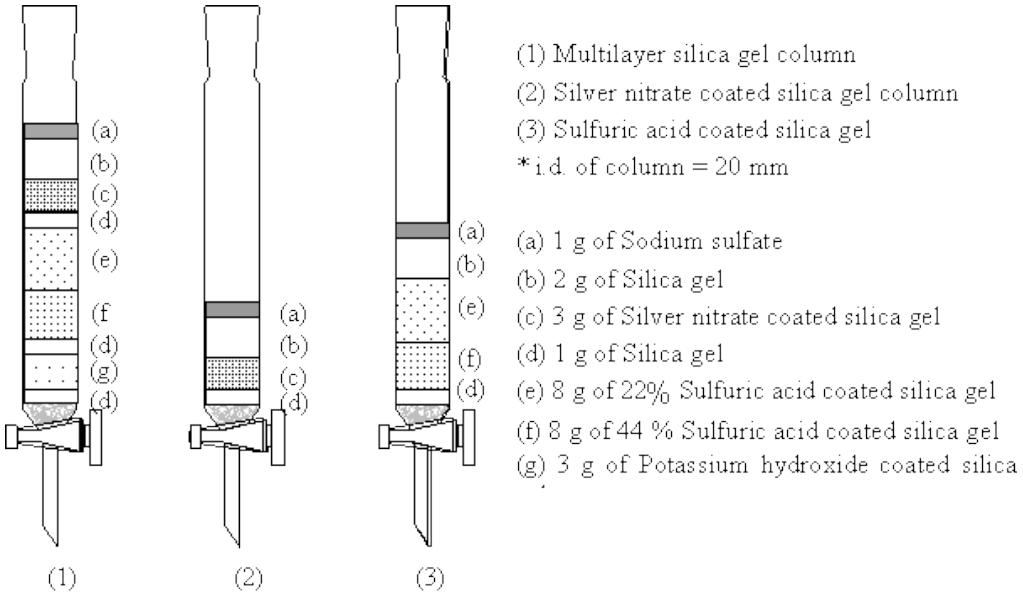

Fig.1 Multilayer silica gel column and coated silica gel

Table 1 The example of low recovery rates of ^{13}C labelled PCDD/PCDF and DL-PCB

	Type of sample	
	Blank test	Treated waste water
$^{13}C_{12}$-2,3,7,8-TetraCDD	31	49
$^{13}C_{12}$-1,2,3,7,8-PentaCDD	72	25
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDD	73	15
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDD	75	17
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDD	77	23
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD	96	12
$^{13}C_{12}$-OctaCDD	86	10
$^{13}C_{12}$-2,3,7,8-TetraCDF	83	59
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	91	82
$^{13}C_{12}$-2,3,4,7,8-PentaCDF	100	105
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDF	85	95
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDF	87	99
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDF	103	96
$^{13}C_{12}$-2,3,4,6,7,8-HexaCDF	98	95
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF	101	95
$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF	102	102
$^{13}C_{12}$-OctaCDF	86	86
$^{13}C_{12}$-3,3',4,4'-TetraCB	103	83
$^{13}C_{12}$-3,4,4',5-TetraCB	109	86
$^{13}C_{12}$-3,3',4,4',5-PentaCB	120	90
$^{13}C_{12}$-3,3',4,4',5,'5-HexaCB	103	94
$^{13}C_{12}$-2,3,3',4,4'-PentaCB	108	95
$^{13}C_{12}$-2,3,4,4',5-PentaCB	105	94
$^{13}C_{12}$-2,3',4,4',5-PentaCB	113	91
$^{13}C_{12}$-2',3,4,4',5-PentaCB	108	93

$^{13}C_{12}$-2,3,3',4,4',5-HexaCB	92	93
$^{13}C_{12}$-2,3,3',4,4',5'-HexaCB	93	88
$^{13}C_{12}$-2,3',4,4',5,5'-HexaCB	90	91
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaCB	100	103

Unit: %

Table 2 The average recovery rates of ^{13}C labelled PCDD/PCDF and DL-PCB

	Type of coated silica gel					
	Silver nitrate coated			Sulfuric acid coated		
	(a)	(b)	(c)	(a)	(b)	(c)
$^{13}C_{12}$-2, 3,7,8-TetraCDD	97	103	108	101	6	0
$^{13}C_{12}$-1,2,3,7,8-PentaCDD	106	98	100	101	61	28
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDD	104	97	100	105	69	68
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDD	103	96	98	102	72	81
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDD	101	101	100	110	77	71
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDD	105	99	94	94	111	95
$^{13}C_{12}$-OctaCDD	96	93	94	113	108	97
$^{13}C_{12}$-2,3,7,8-TetraCDF	98	102	102	99	102	106
$^{13}C_{12}$-1,2,3,7,8-PentaCDF	103	104	101	106	108	85
$^{13}C_{12}$-2,3,4,7,8-PentaCDF	101	101	107	101	105	99
$^{13}C_{12}$-1,2,3,4,7,8-HexaCDF	106	96	97	104	109	91
$^{13}C_{12}$-1,2,3,6,7,8-HexaCDF	104	98	97	104	110	100
$^{13}C_{12}$-1,2,3,7,8,9-HexaCDF	107	107	98	112	118	92
$^{13}C_{12}$-2,3,4,6,7,8-HexaCDF	100	105	90	104	107	94
$^{13}C_{12}$-1,2,3,4,6,7,8-HeptaCDF	104	103	93	111	113	101
$^{13}C_{12}$-1,2,3,4,7,8,9-HeptaCDF	99	101	99	117	122	105
$^{13}C_{12}$-OctaCDF	92	98	94	107	111	99
$^{13}C_{12}$-3,3',4,4'-TetraCB	95	89	102	88	79	99
$^{13}C_{12}$-3,4,4',5-TetraCB	100	88	99	85	85	97
$^{13}C_{12}$-3,3',4,4',5-PentaCB	104	84	107	112	88	91
$^{13}C_{12}$-3,3',4,4',5,'5-HexaCB	104	90	115	86	92	93
$^{13}C_{12}$-2,3,3',4,4'-PentaCB	99	90	95	85	93	97

$^{13}C_{12}$-2,3,4,4',5-PentaCB	98	88	97	88	92	94
$^{13}C_{12}$-2,3',4,4',5-PentaCB	94	89	97	86	89	95
$^{13}C_{12}$-2',3,4,4',5-PentaCB	94	89	101	86	91	95
$^{13}C_{12}$-2,3,3',4,4',5-HexaCB	94	87	105	97	94	94
$^{13}C_{12}$-2,3,3',4,4',5'-HexaCB	94	89	102	93	89	94
$^{13}C_{12}$-2,3',4,4',5,5'-HexaCB	94	86	101	87	90	96
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaCB	96	90	101	98	97	98

Unit; %

Number of experiment; 3

Type of silica gel;

(a) not heated

(b) flash heated from room temperature to 400 ºC and held for 4 hours

(c) held 105 ºC for 4 hours and heated to 400 ºC at 10 ºC/minute and held for 4 hours.