Optimization of simplified activated carbon-silica gel reversible columns cleanup methods for analysis of 29 hazardous dioxins in soil, sediment and biological samples

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Introduction

In the analysis of these 29 hazardous dioxins, 7 PCDDs, 10PCDFs and 12 PCBs, are deemed "significantly toxic" by the World Health Organization [1)], the samples are usually finally cleaned up using activated carbon-silica gel (ACS). In the conventional method, 1 g of ACS is used, but we have previously reported that using 0.3 g can save time, manpower and organic solvent without sacrificing reproducibility [2-3)]. However, we previously only evaluated the effectiveness of this method in biological samples [2-4)]. In the study of dioxin pollution in the environment, the ability to evaluate soils or sediments is indispensable. It is important to investigate whether a simplified ACS cleanup method could be adapted to such conditions. With respect to a simplified ACS cleanup method, two specific improvements would be desirable: a reduction in solvent volume, I) by reversing the column and eluting PCDDs and PCDFs by toluene, and II) optimizing the amount of ACS without sacrificing the reproducibility of post-elution target compound analysis. Our approach to simplifying the active carbon dispersed silica gel reversible columns (ACSR) cleanup method while meeting the desired results included the use of a column packed with up 0.1-1 g of ACSR by using three types of sample.

Materials and Methods

Samples

For Soil and sediment samples, two soils and two sediments were sampled at different sites. The samples were filtered through a 2.0-mm mesh sieve, allowed to dry at room temperature, ground into powder using a mortar and pestle, screened through a 0.1 mm-mesh sieve and mixed well by a shaker for 6 hours (soil A and B, sediment A and B). For biological samples, samples of beef and fish, purchased at a grocery store, were homogenized and freeze-dried ground into powder using a mortar and pestle, screened through a 2.0 mm mesh sieve, and mixed well by a shaker for 6 hours. The amount of all samples used in this study was set to 50 g maximum as described by the standard manual for the measurement of dioxins and their related compounds for both soil and sediment in Japan [5,6)].

Stage I - Elution profile testing: Optimization of elution conditions for 0.1-1 g - active carbon dispersed silica gel reversible columns (ACSR)

To determine the optimal amount of sorbent in the columns, we performed a fraction test using [$^{13}C_{12}$]-PCBs 1000 pg, [$^{13}C_{12}$]-T HpCDDs/Fs 200 pg, [$^{13}C_{12}$]-OCDD/F 400 pg as internal standards. After investigating the elution profile for each compound, we determined the amount of solvent needed to elute target compounds from the columns.

Stage II - Reproducibility testing: Outcomes in the use of the 0.1-1 g - ACSR method on various sample matrices.

The reproducibility of outcomes for the use of 0.1-1 g-ACSR columns on several types of pooled sample matrices was determined. Pressurized liquid extraction, H_2SO_4 treatment, (or DMSO/acetonitrile/hexane partitioning [3)], centrifuge and then $AgNO_3$ silica gel cleanup was applied. The method for elution for 0.1- 1 g -ACSR used the method optimized from the result of Stage I.

HRGC-HRMS analysis

For all samples, dioxins were analyzed using a 6890 gas chromatograph (Agilent, Palo Alto, CA) and a JMS-700 mass spectrometer (JEOL Ltd., Tokyo, Japan).

Results and Discussion

Stage I: Elution profile testing

Except for the result of elution profile by hexane for 0.1 g-ACSR and those by toluene for all ACSR, those by hexane for 0.2~1g-ACSR and 25% dichloromethane/hexane for all ACSR, these solvent-volumes for eluting target compounds were proportional to ACS-amounts. For example, consider the hexane elution profile for 0.2 and 1 g -ACSR where a 50-fold ACS volume-weight eluted 10% or less of PCB #114 and 5% or less of PCB #123.

However, with respect to 0.1 g-ACSR, more PCB #114 per volume of ACS was eluted (15%) (Figure 1). As non-*ortho*-PCBs and PCDDs and PCDFs were found to be concentrated in the upper portion of the column, it was thought that the amount of toluene required for elution during column reversal was dependent upon the ACS volume. In the case of both the 0.1 and 0.2 g columns, no differences were noted in the elution profiles. These profiles consisted of the following: approximately 90%-target compounds by 10 ml at elution of approximately 100%-target compounds by 30 ml, and approximately 90%-target compounds by 20 ml at elution of approximately 100%-target compounds by 50 ml. As a short period of time was required for the absorption of the target compounds to ACS in the hexane test solution, target compounds were somewhat diffused in the upper part of the columns. The degree to which this diffusion occurred was almost the same between the 0.1 and the 0.2 g columns. Considering this, we chose the elution method shown in Figure 2 for each 0.1-1 g ACSR column. The concentration of [$^{13}C_{12}$]-congeners (labeled internal standards) in the hexane fractions was higher than previously reported [7] for the propriety of the possibility of slight elution for other mono-*ortho*-PCBs except for PCB #114 and #123.Consequently, other PCBs that were not detected in previous reports were detected but at less than 2% of the elution volume, compared to 50-fold volume of ACS weight. Thus, corroborating previous results, those compounds detected with the hexane elution procedure are PCB #114 and #123.

Stage II: Reproducibility testing

There was no difference among the 0.1-1 g-ACSR columns in regard to recovery rates of the [$^{13}C_{12}$]-congers. On the other hand, with respect to the reproducibility of native concentrations, no difference was found among the average native concentrations obtained from the 0.1-1 g-ACSR columns, using all sample matrices (Table), indicating that there was little influence on native concentration by the low recovery rates. However, the relative standard deviations (RSDs) of congener group-TEQ and Total-TEQ exceeded 10% with the 0.1 g -ACSR columns for all samples, and the RSDs for some compound- concentrations reached about 30% (data not shown about each compounds). In addition, with respect to 0.1g -ACS columns cleanup in our previous report, the RSDs for some compound-concentrations also observed high value in the case, above 20% [7]. Therefore, the data from the 0.1 g -ACSR columns was not valid. On the other hand, the RSD of congener group-TEQ and Total-TEQ didn't exceeded 10% with both of the 0.2 g - and 1g-ACSR columns for all samples, and the RSDs for some compound- concentrations reached below 20%(data not shown about each compounds).We judged that 0.2 g -ACSR is the limit with respect to the reliability of data. Despite the several-fold increase in sample amount, our results revealed good recovery rates and reproducibility of native concentrations. We have no doubt that this simplified method has the power to perform satisfactory sample cleanup using a small amount of ACS.

Acknowledgments

We are grateful to the Kanto Chemical Company of Tokyo, Japan, for the active carbon dispersed silica gel reversible columns containing various content types that were manufactured and offered as a special order for this study.

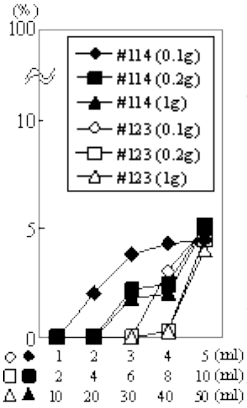

Figure 1 Elution profile for PCB #114 and #123 at n-hexane by 0.1 – 1 g-ACSR column cleanup, x-axis : elution volume, y-axis : elution percents

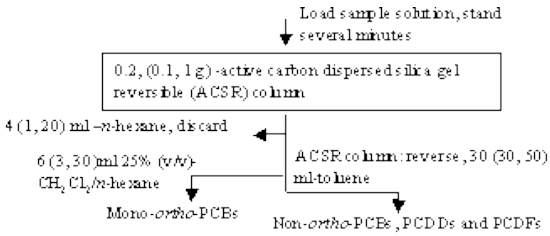

Figure 2 ACSR column cleanup of dioxin fraction from soil, sediment and biological sample.

Table Table Measurement results of 29 hazardous dioxins measurement results in two soils and two sediments and a biological sample in 0.1-1 g-ACSR column cleanup

Sample	Column type	Mean (pg-TEQ / g-dry)				
		PCDDs	PCDFs	Non-*ortho*-PCBs	Mono-*ortho*-PCBs	Total
Soil A	1g	3.4 (6)	2.7 (9)	0.25 (8)	0.030 (9)	6.4 (7)
	0.2g	3.2 (8)	2.6 (9)	0.24 (7)	0.029 (9)	6.1 (8)
	0.1g	3.1 (16)	2.7 (19)	0.26 (15)	0.030 (16)	6.2 (17)
Soil B	1g	13 (7)	12 (2)	1.1 (8)	0.21 (7)	26 (4)
	0.2g	13 (8)	11 (7)	1.1 (8)	0.20 (9)	25 (7)
	0.1g	13 (14)	12 (15)	1.1 (15)	0.20 (10)	26 (15)
Sediment A	1g	16 (8)	12 (9)	1.9 (9)	0.47 (7)	30 (9)
	0.2g	15 (9)	11 (9)	1.8 (9)	0.45 (8)	29 (9)
	0.1g	16 (15)	12 (17)	1.9 (17)	0.46 (13)	30 (16)
Sediment B	1g	16 (5)	25 (9)	3.6 (9)	1.6 (8)	46 (7)
	0.2g	16 (8)	24 (8)	3.4 (6)	1.5 (9)	44 (8)
	0.1g	16 (13)	25 (16)	3.5 (18)	1.6 (14)	46 (15)
Biological sample	1g	0.27 (5)	0.26 (9)	0.61 (8)	0.12 (9)	1.3 (7)
	0.2g	0.27 (8)	0.26 (9)	0.61 (8)	0.13 (9)	1.3 (8)
	0.1g	0.28 (14)	0.27 (11)	0.63 (14)	0.13 (15)	1.3 (14)

(): R.S.D., n=3

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