STUDY OF EXTRACTION AND CLEANUP METHODS OF DIOXINS IN HOUSE DUST

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Introduction

The dioxins unintentionally generated by waste incineration are polluting the ecosystem and food supply. Based on a current research, it has been clarified that the intake of dioxins from food accounts for 90% or more as the exposure route of dioxins to humans, and that the proportion of exposure to dioxin from the environment such as atmosphere and the soil is low. However, the exposure due to indoor pollution has been hardly examined so far. In general, young generations such as newborn babies and infants mainly spend their life indoors. Moreover, there is a pressing need to investigate the exposure influence from house dust because they live in the space near the floor. However, there have been few reports concerning house dust polluted by dioxins[1] and PCB[2-4]. We then did a comparative study using soxhlet extraction and accelerated solvent extraction (ASE) as extraction methods of dioxins from house dust. In addition, we also made a comparative study of the alkali decomposition method and the multilayer silica gel cartridge method as cleanup operation. Moreover, the pollution levels of dioxins in house dust in two districts (n=10) in Japan were clarified.

Experimental Methods

Extraction (soxhlet extraction and ASE)

The house dust was collected from 10 residential houses in two districts in Japan. All the dust samples were collected from the dust bags of vacuum cleaners, and were passed through two kinds of sieves (mesh size; 1 mm and 75 μm). The comparatively big solids and minute powders were removed. The dust samples having a particle size of 75 μm-1 mm were used for the analysis. Each sample was divided into two for the soxhlet extraction and ASE. Five gram samples were used for the soxhlet extraction and ASE, and the soxhlet extraction was carried out for 16 hours with toluene as the extraction solvent. On the other hand, the ASE was carried out using a Dionex ASE 200 with toluene as the extraction solvent at a temperature of 150 °C, and pressure of 2000 psi, with three extracting cycles per sample. Each extracted material was concentrated with a rotary evaporator in order to remove the toluene, and the resulting fatty residue was obtained. The obtained residue was considered the amount of lipids in the house dust.

Alkali decomposition

According to the conventional method, the stable isotopes of the dioxins ($^{13}C_{12}$-PCDD/Fs) were added as dioxin surrogates after the lipid was extracted from the samples. Then 40ml of 1N KOH/EtOH was added. It was stirred, and the solution was then allowed to stand at room temperature overnight. The alkaline solution was diluted with 40ml of water, followed by liquid-liquid extraction with 40 ml of n-hexane (twice). After the hexane layer was dehydrated and concentrated, the extracted material was processed using a three-layer sulfuric acid silica gel cartridge (silica gel 0.5 g, 44% sulfuric acid silica gel 2 g, and silica gel 1 g; product of Supelco), followed by activated carbon silica gel column chromatography

Multilayer silica gel cartridge

The extracted lipid was dissolved in a small amount of hexane, the surrogates were added to the lipid, and then charged into a pre-packed multilayer silica gel cartridge (product of GL Science) previously well washed with hexane. After 150 ml of hexane was added for elution, the eluate was concentrated, followed by activated carbon silica gel column chromatography.

GC/MS measurement

The PCDD/Fs were analyzed by HR-GC/MS using a JEOL JMS-700 mass spectrometer equipped with a capillary column of CP-SIL88 (30 m x 0.25 mm i.d., 0.1 μm film thickness) for the 4-6CDD/Fs, DB-17HT (30 m x 0.25 mm i.d., 0.15 μm film thickness) for the 7-8CDD/Fs and non-ortho Co-PCBs, and DB-5MS (30 m x 0.25 mm i.d., 0.25 μm film thickness) for the mono-ortho PCBs. The MS was operated in the selected ion monitoring mode with a mass resolution of 10000. The toxic equivalent quantity (TEQ) was calculated using WHO-TEF(1998).

Results and Discussion

Extraction procedure

House dust is composed of complicated matrices, which are of outdoor origin and of indoor origin. Examples of the former include atmospheric descent particles, soil, etc., which have been carried by the wind or clothes. The latter are fiber rubbish from indoor carpets or clothes, dead skin, dirt, hair, etc., which are of animal or human origin. We made a comparative study of the extraction efficiency of the lipid and the dioxin isomer concentration as indexes for the soxhlet extraction method and the ASE method.

Five samples were divided half, and each sample was extracted using the soxhlet extraction and ASE methods. Both methods yielded approximately the same lipid content, i.e., about 6 % each sample. The values are almost similar to those values reported by Johanna[5] for the lipid content in house dust. It is an interesting fact that the lipid content rate in house dust of residential house origins that are not mutually related indicated almost the same value. Fig. 1 shows the total dioxin content (net value) that is composed of the 29 kinds of dioxin isomers having TEF, and Fig. 2 shows their TEQ. The dioxin level (net value), which had been obtained by the ASE method indicated low values, compared with those obtained by the soxhlet method, though the TEQ level obtained by the ASE method was almost equal to those obtained by the soxhlet extraction. When the content of each dioxin isomer was examined in detail, the low chlorinated isomers that significantly contributed to the TEQ value showed approximately the same level. The OCDD content (net value) displayed the highest among the dioxin isomers. The soxhlet extraction

yielded a higher OCDD content than the ASE method. It seemed that this difference is reflected in Fig. 1 and Fig. 2. As for the pattern of each isomer, the house dust showed the patterns of no biological origins such as human milk and blood, etc., but environmental origins such as the atmosphere or soil. These results suggested that the dioxins in house dust significantly depended on the environmental influence such as the atmosphere or soil, which had entered the residential house from the outdoors. Consequently, in order to extract completely OCDD, it was understood that the soxhlet extraction method was much better than the ASE method, although a longer extracting time was needed for the soxhlet extraction than the ASE.

Simple cleanup using a multilayer silica gel cartridge

A cleanup method for the analysis of human milk, in which alkali decomposition and a three-layer sulfuric acid silica gel cartridge are used, was reported at the dioxin symposium last year[6]. Although an excellent cleanup effect can be obtained by employing this method, it requires an overnight alkali decomposition treatment (about 12 hours) and a liquid-liquid distribution extraction using hexane. In this study, we tried to develop a simpler cleanup method that allows the extracted lipid to be directly treated using a multilayer silica gel column without subjecting it to alkali decomposition. There used to be a drawback to this in that the preparation of a multilayer silica gel column required complicated procedures, however, a pre-packed multilayer silica gel in a disposable cartridge has now become available.

On the other hand, we processed other house dust samples using the above-mentioned alkali decomposition method in order to compare them with the multilayer silica gel cartridge method. We studied the recoveries of the dioxin surrogates and the influence of coexisting impurities on the GC/MS chromatograms. As a result, although the recoveries of the dioxin surrogates (PCDD/Fs, non-ortho Co-PCBs, mono-ortho PCBs) were indicated as sufficient in both methods, the multilayer silica gel cartridge method showed higher recoveries than the alkali decomposition method (Table 1). Moreover, as for the GC/MS chromatograms, the influence of the coexisting impurities was not observed in either cleanup method.

On the basis of these results, it was determined that the combination of the soxhlet extraction, the multilayer silica gel cartridge treatment, and the activated carbon silica gel column chromatography was suitable for the extraction and cleanup operation for the house dust analysis.

Dioxins in house dust

The samples that had been measured at this time were collected from five residential houses in two districts in Japan. These two districts (city A and city B) were located in the center (city A) of Japan and the northern section (city B), and were far apart, for the measurement results, the average value from city A was 15.6 pg TEQ/g (8.6 - 26.0 pg TEQ/g), on the other hand, that of city B was 16.0 pg TEQ/g (5.9 - 30.5 pg TEQ/g); consequently, a significant regional difference was not admitted. However, the level of the dioxin content measured at this time is almost the same as the level usually measured in soil, furthermore, the house dust exists in the space where humans always live. Especially, a newborn baby and infant spend in the life (i.e., breathing and meals) in the space near the floor compared to adults. Accordingly, it is necessary to consider the influence of house dust at the exposure levels to humans from the environment.

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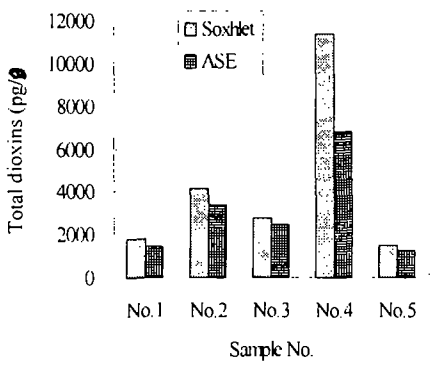

Fig.1. Comparison of total dioxin contents obtained from the soxhlet extraction and ASE methods

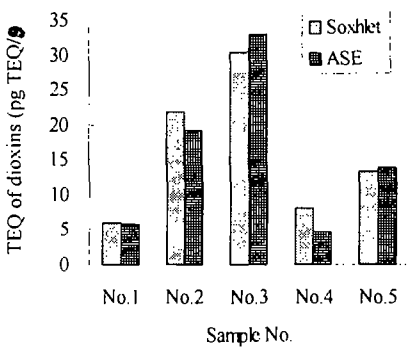

Fig. 2. Comparison of dioxin TEQ obtained from the soxhlet extraction and ASE methods

Table 1. Comparison of recovery rate of dioxin surrogates obtained from alkaline decomposition and multilayer silica gel cartridge method

	Alkali decomposition Recovery (%)		Multilayer silicagel cartridge Recovery (%)	
	Mean (n=5)	Range	Mean (n=5)	Range
PCDD/Fs	74.0	66.0 - 78.3	89.6	75.6 - 90.8
Co-PCBs	78.1	53.3 - 90.1	94.4	88.2 - 99.7
PCDD/Fs & Co-PCBs	76.2	64.5 - 82.3	92.2	86.7 - 98.8