IDENTIFICATION OF THE BROMINE COMPONENT PRESENT IN INDOOR DUST

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Introduction

Recently, brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have been detected in indoor dust at relatively high concentrations¹⁻³. Many researchers pointed out the importance of house dust as a route of human exposure to PBDEs and HBCDs. Recent research has revealed that the PBDEs present in house dust are bioavailable to mammals as those dissolved in an oil vehicle⁴, stressing the importance of dust ingestion as a pathway of exposure to BFRs. Our previous study showed that brominated compounds are transferred from TV set components onto dust through various pathways such as vaporization, migration and adsorption, although the major transfer pathway of brominated compounds such as PBDEs from TV sets onto dust is still unknown. It is thought that BFRs in indoor dust are associated with BFR containing products such as TV sets and personal computers (PCs) in room interiors. However, contribution of various sources to BFR load in indoor dust has not been characterized. Such knowledge would be useful for determining the main sources and transfer pathways of BFRs and devising their control strategy in indoor environment. In this study, we investigated the presence of bromine as BFR indicator in indoor dust collected from households, offices in universities/research institutions, fire fighting facilities and interior of TV sets in Japan.

Materials and Methods

Sampling and preparation. Indoor dust samples were collected from households, offices in universities/institutions, fireproof facilities at business hotels, private companies, restaurants, electrical shops, cleaning shops, hospitals, day care centers, kindergartens and elderly homes in Japan from 2005 to 2007. Indoor dust samples were collected from vacuum cleaner bags. Dust from inside of TV sets was collected from waste TV sets using a vacuum cleaner⁵. Five used TVs were obtained from an electronic retail store in Japan. Interior dust samples were collected from the inside of the TVs. Indoor dust collected from household and offices in universities/institutions was transferred to a stainless steel sieve (< 1.0 mm), covered with a steel lid and shaken using an automatic Sieve Shaker (AS300, Retsch Co., Ltd.)². For other dust samples, impurities such as small stones, chips, clips, and human and animal hair were removed using tweezers. All the samples were stored at room temperature until analysis. Indoor dust (equivalent to 1 mg) was sparsely attached to cellophane on the cellophane tape using tweezers and analyzed by X-ray fluorescence spectroscopy (XRF). BFR containing products were cut into small pieces with scissors, attached to the tape and also analyzed by XRF.

Energy dispersive micro X-ray fluorescence spectrometer. Indoor dust was analyzed using the energy dispersive micro XRF (μEDX-1200, SHIMADZU Co., Ltd), which can detect bromine and other elements in a small area of 50 μm across for solid samples. Micro XRF was basically operated in mapping mode to obtain detailed images of bromine distribution. Mapping was conducted at step sizes of 50 μm in the x- and y-direction and 0.5 sec dwell time at each point within the range of 10 mm². When matrix containing bromine in indoor dust was not detected under 0.5 sec dwell time at any point, dust was analyzed again by 100 sec dwell time mode for detecting such lower concentrations of bromine.

a. Electronic retail stores

BrKa

 $\overline{0.80mm}$ 4.0 x 3.0mm

b. Day care center dust

150.0

BrKa

c. Flame proof curtain d. Personal computer casing

 $\overline{0.0}$ 38.88 [cps] **BrKa**

Figure 1: Images of test samples (upper) and bromine-mapping (lower) for indoor dust samples (a and b) and small pieces of BFR containing products (c and d). Bromine content of the flameproof curtain (c) and the personal computer chassis (d) were 1.0 % and 0.1%, respectively.

[cps] [cps]

Observation of dust matrix with stereoscopic microscope. After bromine-mapping for indoor dust thinly applied on the tape, dust matrices which contained high concentration of bromine (0.1 % or more) were picked up by using tweezers, and their magnification pictures were taken using digital optical microscope (VHX-200/100F, KEYENCE Co., Ltd) in order to estimate the origin of bromine component in indoor environment.

Results and Discussion

The images of bromine-mapping for indoor dust samples and small pieces of BFR containing products are shown in Fig. 1. Presence of bromine component was confirmed in 27 out of 48 dust samples (Figs. 1-a & 1-b). Pieces of the flame proof curtain (bromine content: 1.0%) and the personal computer casing (bromine content: 0.1%) of known bromine content were investigated to estimate the concentration of bromine in the bromine-abundant components detected in indoor dusts (Figs. 1-c & 1-d). Based on the intensity in mapping for BFR containing products, the bromine concentration of the component found in indoor dust from the electronic retail store was estimated to be 1.0% or more, which was higher than the flame proof curtain (Fig. 1-a). Bromine content in the indoor dust collected from the day care center was estimated to be about 0.1%, and this was relatively higher than in the personal computer chassis. It was possible to detect indoor dust components which contain the bromine of about 0.1% using micro XRF in analytical condition of 0.5 sec mapping mode. Our results suggest that products containing high concentration of brominated compounds such as BFRs might be very small and ubiquitous in indoor dust.

This study examined not only the distribution of matrices containing bromine in indoor dust collected from households, offices in universities/institutions and firefighting facilities but also those in dust inside TV casings. It has been reported that PBDE levels in the dust inside TV sets were two to three orders of magnitude higher than those in house dust samples in Japan, North America and European countries⁵. However, as shown in Fig. 2-a, distribution of bromine in the dust inside TVs was not often observed in analytical condition of 0.5 sec mapping mode, indicating that there is no indoor dust components which contain the bromine of about 0.1% in this instance. In order to detect the dust matrix with 0.1% or less of bromine content, the dust sample was analyzed using 100 sec dwell time mode for enhancing the detection sensitivity of the mapping. As a result, presence of bromine component was imaged in the dust from inside of the TV cases (Fig. 2-b). Although lead-mapping for TV dust was also performed at the same time, presence of lead component was not detected, unlike bromine (Fig. 2-c and 2-d). While bromine components were distributed widely throughout TV dust thinly attached to tape, a few lead components were dotted in dust coating inside TV sets. These results suggest that bromine is transferred from products to dust matrices not only via miniaturized migration, but also through other pathways such as vaporization.

The dust matrices containing bromine of about 0.1% or more were examined using stereoscopic microscope to identify their source materials in indoors. Although the 14 dust fractions of about 0.5 to 2 mm across were picked up carefully with tweezers and set onto microscope stage, it was impossible to pick up fractions less than 0.5 mm due to handling difficulties. Bromine components were classified roughly into two categories according to their visual appearance. Eleven out of 14 dust matrices were particulates with various surface characteristics and colors. The other matrices were fibrous substances such as lint. However, it was difficult to identify indoor sources of bromine components at the present stage. In near future, we will try to collect data for further surface information and elemental composition of bromine components with scanning electron microscope/energy dispersive X-ray spectrometry (SEM/EDS), and then search for indoor origin of the detected bromine component.

Figure 2: Images of bromine-mapping (a and b) and lead-mapping (c and d) for the dust inside TV. After analyzing under 0.5 sec dwell time at each point (a and c), TV dust was also analyzed by 100 sec dwell time mode for detecting very low concentration of bromine (b and d).

We have initiated the work on the presence of bromine as BFRs in indoor dust matrices and tried to identify their indoor origin. Transfer pathways of BFRs from products are thought to be direct migration through plastic fragments and waste textile and secondary migration such as vaporization. It is crucial to identify major transfer pathways of BFRs from products to dusts for designing the control strategy of BFRs in the indoor environment. Regarding human exposure via dust ingestion, information on the existence of BFRs in indoor dust might be useful to assess the bioavailability of BFRs contained in dust samples⁴. It is possible to propose appropriate preventive measures in order to indoor exposure to BFRs, if the major origin of BFRs in dusts is identified.

Reference

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