Effect of Long-time Heating for Polyvinyl Chloride and Polypropylene Resin Pellet Certified Reference Materials for Heavy Metal Analysis

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The effect of long-time heating for both polyvinyl chloride (PVC) and polypropylene (PP) resin pellet certified reference materials (CRMs) for heavy metal analysis, which contained Cd, Cr, Hg and Pb, was examined in the present study. The temperature of the drying oven was 80°C, which was used for drying these CRMs before analysis, and the long-time heating was carried out for up to 480 h. As a result, a relative decrease in mass of *ca.* 0.3% was observed for both CRMs. Moreover, a decrease in concentration of *ca.* 10% was observed for Cr, even though the concentrations for other elements did not change during the long-time heating. Since the chemical form of Cr was an organometallic compound with lower melting point, it was considered that concentration decreased due to the heat.

Keywords Long-time heating, PVC resin pellet CRM, PP resin pellet CRM, organometallic compound, chromium acetylacetonate

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Introduction

The directive on the restriction of the use of hazardous substances in electrical and electronic equipment (RoHS) is one of the directives of European Union (EU) that became effective in July 2006.^{1,2} There was a great upheaval in Japan, because the export of electrical and electronic equipment to EU would not be possible unless the requirements of the directive were met. Since the parts and the final products of electrical and electronic equipment are made from raw materials and by assembling the parts, respectively; any relevant industries and societies could not remain indifferent to the directive. The targeted hazardous substances were Cd, Cr(VI), Hg, Pb, PBB (poly-brominated biphenyl) and PBDE (poly-brominated diphenyl ether) and the threshold values were 100 and 1000 mg kg⁻¹ for Cd and other substances, respectively. It was well known that plastic materials were widely used in electrical and electronic equipment; therefore, standard analytical procedures³ and certified reference materials (CRMs) of hazardous substances in plastics were demanded from relevant industries and societies. In line with the requirements, National Metrology Institute of Japan (NMIJ) has been made efforts to develop plastic CRMs for heavy metal analysis with respect to RoHS directive.⁴⁻¹³ So far, acrylonitrile-butadiene-styrene (ABS),^{4-7,9} polyvinyl chloride (PVC)⁸ and polypropylene (PP)^{8,10-13} resin CRMs for the determination of Br, Cd, Cr, Hg and Pb have been developed. These plastic CRMs were pellet or disk forms and were developed for chemical analysis^{4,8,10-12} or X-ray fluorescence spectrometry,^{5-7,9,13} respectively. A X-ray fluorescence (XRF) spectrometry is expected for direct and

speedy analysis of the hazardous substances in electrical and electronic equipment¹⁴⁻¹⁷ and also described in the IEC 62321 as a screening method with respect to RoHS directive.³ However, the loss of elements in plastics during XRF measurement was a concern and reported for an organometallic compound of Hg in plastic CRM due to its volatility,¹⁴ which might result in serious analytical error for the determination of hazardous substances. In our previous study, we also observed the loss of Cr from the PP resin disk CRM (NMIJ CRM 8136-a) for long-time measurements by XRF spectrometry.¹³ The temperature observed at the surface of the PP resin disk CRM was *ca.* 90°C after 1 h measurement by wavelength dispersive XRF (WD-XRF) spectrometer and the loss of *ca.* 10% Cr was observed during the long-time measurement for 120 h from the side of the surface irradiated by X-ray. Since the chemical forms of Cr for both inorganic and organometallic compounds were mixed in the PP resin disk CRM, the organo one was considered to be lost by the heating from the long-time X-ray irradiation. If the heat is the main source for the loss of elements, it is considered that the similar phenomenon can be observed during drying procedure for a long-time using a drying oven.

In the present study, the effect of long-time heating was examined for both PVC and PP resin pellet CRMs to explore the source of the loss of elements. These CRMs were heated at 80°C in a drying oven, which was the temperature used for drying these CRMs before analysis, and the changes in mass of the CRMs and concentrations of elements were evaluated for long-time heating up to 480 h.

Fig. 1 Relative change in mass of PVC resin pellet CRM as a function of heating time at 80°C for up to 384 h (16 days). The initial mass of the PVC resin pellet CRM examined was 0.5 g. The bar indicated shows standard deviation ($n = 3$).

Experimental

Sample and instrumentation

The PVC and PP resin pellet CRMs examined in the present study were NMIJ CRM 8123-a and 8133-a, respectively, which were developed by NMIJ (Tsukuba, Ibaraki, Japan).^{8,18,19} The masses of one pellet were *ca.* 30 mg and *ca.* 10 mg for PVC and PP resin pellet CRMs, respectively.⁸ The chemical forms of Cd, Hg and Pb contained in both the CRMs were inorganic compounds such as cadmium oxide (CdO), mercury sulfide (HgS) and lead chromate (PbCrO₄), respectively.^{8,18,19} On the other hand, the chemical forms of Cr contained in both the CRMs were not only PbCrO₄ but also chromium acetylacetonate (Cr(C₅H₇O₂)₃) which can be expressed as Cr(acac)₃, as inorganic and organometallic compounds, respectively;^{8,18,19} in order to increase total concentration of Cr to be closer to threshold value of 1000 mg kg⁻¹, even though hexavalent chromium (Cr(VI)) was a subject in RoHS directive.¹⁻³ The melting points of CdO, HgS, PbCrO₄ and Cr(acac)₃ are 900 – 1000, 580, 844 and 210°C, respectively; and the concentrations of Cd and other elements in both the CRMs are *ca.* 95 mg kg⁻¹ and *ca.* 950 mg kg⁻¹, respectively.^{8,18,19} A drying oven with maximum temperature of 250°C was used for long-time heating at 80°C in the present study. The heating temperature of 80°C is the drying temperature for these pellet CRMs^{8,18,19} to remove any moisture before analysis. The heating temperature was also close to the temperature of *ca.* 90°C observed at the surface of the PP resin disk CRM (NMIJ CRM 8136-a) after 1 h measurement by WD-XRF spectrometer in our previous study.¹³ Approximately 0.5 g of both the pellet CRMs was weighed accurately by electric balance (AX 205, Mettler-Toledo International Inc.) and heated in the drying oven at 80°C. After the heating, the mass and the concentrations of elements were measured. In case of mass measurement, the electric balance was used to weigh the mass of the CRMs. The concentrations of elements were determined by inductively coupled plasma mass spectrometry (ICPMS) with microwave acid digestion procedure which was along the analytical procedure described in Refs. 4 and 8.

Results and Discussion

Figure 1 shows the relative change in the mass of PVC resin pellet CRM as a function of heating time at 80°C for up to

Fig. 2 Relative change in concentrations for (a) either Cr or Hg and (b) either Cd or Pb in PVC resin pellet CRM as a function of heating time at 80°C for up to 384 h (16 days). The relative concentrations obtained were normalized with respect to the initial concentrations of each element, which were normalized as 100%. The bar indicated shows standard deviation ($n = 3$).

384 h (16 days). The decrease in the mass was observed and it was *ca.* 0.25% until the heating for 96 h (4 days). The decrease in the mass remained almost constant at 0.25 – 0.28% from 96 to 384 h. From the results, it was considered that the change in the mass of PVC resin pellet CRM was not so large; therefore, concentration of elements was expected to remain constant during the long-time heating. Figure 2 shows the change in concentrations of elements in PVC resin pellet CRM as a function of the heating time. It could be seen from Fig. 2, only the decrease in the concentration of Cr was observed even though the other elements did not show any loss during the heating for a long-time. The relative decrease in the concentration of Cr was *ca.* 10% after the heating for 96 h. The loss of Cr was considered to be dependent on its chemical form, which resulted in the loss of Cr during the long-time heating. A similar examination was also carried out for PP resin pellet CRM as listed in Table 1. In case of the PP resin pellet CRM, relative decreases in the mass and the concentration of Cr observed were *ca.* 0.3% and *ca.* 10%, respectively, during the heating time for 480 h (20 days). Since the chemical forms of Cr in both the CRMs were PbCrO₄ and Cr(acac)₃ whose melting points were 844 and 210°C, respectively; the organometallic compound of Cr(acac)₃ was considered to be lost during the heating for a long-time. In our previous study, the loss of

Table 1 Relative changes in the mass of PP resin pellet CRM and the concentration of elements after heating at 80°C for 480 h

Mass ^a	Relative change, %
	99.72 ± 0.07
Cd	99.6 ± 0.5
Cr	89.7 ± 4.6
Hg	100.9 ± 0.8
Pb	100.0 ± 1.0

a. Initial mass of the PP resin pellet CRM examined was 0.5 g. The value indicated after ± shows standard deviation ($n = 4$).

ca. 10% Cr from the PP resin disk CRM (NMIJ CRM 8136-a), which was prepared from the PP resin pellet CRM (NMIJ CRM 8133-a) examined in the present study, was observed during long-time measurements for 120 h (5 days) by WD-XRF spectrometer.¹³ The temperature observed at the surface of the PP resin disk CRM was ca. 90°C after 1 h measurement by WD-XRF spectrometer, which temperature was close to the drying temperature of 80°C examined in the present study. Although the surface areas between the pellet and the disk CRMs were different, the loss of similar amounts of Cr (ca. 10%) was observed for both 120 h (5 days) measurement by WD-XRF spectrometer as in our previous study and the long-time heating for 480 h (20 days) as listed in Table 1. Moreover, since the loss of Cr in the disk CRM was observed from the side of the surface irradiated by X-ray in our previous study, it could be considered that the loss occurred predominantly from the surface area compared to the inside for both pellet and disk CRMs. From these results, the cause of the loss of Cr could be considered to be the heat and the amount of loss became constant after the heating for a few days since the loss occurred predominantly from the surface of the plastics. The similar phenomena may be observed for other plastic materials if they contain similar organometallic compounds. It was also considered that the loss of ca. 10% Cr(acac)₃ corresponded to a loss of ca. 0.05% of mass for both the CRMs. The loss of the mass observed for pellet CRMs was larger than that speculated from the loss of Cr(acac)₃. It was considered that both CRMs contained additives such as ultra violet absorber, hindered amine light stabilizer and anti-oxidation reagents to keep the resin stable, even though their chemical forms and concentrations were not known. Consequently, the additives were considered to be lost during the long-time heating examined in the present study.

Conclusions

The effect of long-time heating for both PVC and PP resin pellet CRMs for heavy metal analysis was examined in the present study. The relative decreases in the mass of ca. 0.3% and the concentration of ca. 10% for only Cr were observed, even though the concentrations for other elements did not change during the long-time heating. The organometallic compound of Cr with lower melting point resulted in the loss of Cr by the heating for a long-time. Although the loss of mass observed for

both CRMs could not be explained by only the loss of Cr(acac)₃, the additives contained were also considered to be lost during the long-time heating. Since the heat was considered to be generated during the drying procedure as well as the measurements by XRF spectrometry demonstrated in previous studies,^{13,14} it should be noted that there could be a loss of elements if the plastics measured contained organometallic compounds, which could result in serious analytical error for accurate determination of elements in plastics.

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