Effect of Long-time X-ray Irradiation on Cr and Hg in a Polypropylene Disk Certified Reference Material Observed during Measurements by X-ray Fluorescence Spectrometry

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The effect of long-time X-ray irradiation on Cr and Hg in a polypropylene disk certified reference material (PP disk CRM, NMIJ CRM 8136-a) during measurements by X-ray fluorescence (XRF) spectrometry was examined in the present study. The XRF intensities of Cr (Kα), Hg (Lα) and Pb (Lα), obtained by an energy-dispersive (ED)-XRF spectrometer, showed the different intensity trends and the obtained XRF intensity ratios of Cr/Pb and Hg/Pb revealed decreasing and constant ratios, respectively, for long-time X-ray irradiation of up to 430 h. A similar decreasing trend of the Cr/Pb intensity ratio was also observed by wavelength-dispersive (WD)-XRF measurements for 120 h. Moreover, Cr, Hg and Pb in the PP disks obtained after long-time measurements by the WD-XRF spectrometer were measured by an ED-XRF spectrometer, and the loss of Cr was confirmed. From these results, Cr in the PP disk CRM, whose chemical form was an organometallic compound, was considered to be possibly lost during the XRF analysis for long-time or frequent measurements.

Keywords X-ray fluorescence (XRF) spectrometry, energy-dispersive (ED)-XRF spectrometer, wavelength-dispersive (WD)-XRF spectrometer, long-time X-ray irradiation, Cr/Pb XRF intensity ratio, organometallic compound

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Introduction

According to legislation of the EU RoHS (restriction of the use of hazardous substances in electrical and electronic equipment) directive, which has been effective since July in 2006,1,2 the concentration values of hazardous substances, such as Cd, Cr(VI), Hg, Pb, PBB (poly-brominated biphenyl) and PBDE (poly-brominated diphenyl ether), in electrical and electronic equipment produced in EU and transported from other areas should be restricted. Since plastic materials are well known to be widely used in electrical and electronic equipment regulated in the RoHS directive, standard analytical procedures and certified reference materials (CRMs) of hazardous substances in plastics are of great interests and are being demanded. X-ray fluorescence (XRF) spectrometry is applied for a direct and speedy analysis of hazardous substances in plastics of great interests and are being demanded. X-ray fluorescence (XRF) spectrometry is applied for a direct and speedy analysis of hazardous substances in plastics and electronic equipment,3,9 and is also described in the IEC 62321 as a screening method with respect to the RoHS directive.10

On the other hand, the loss of element in plastics during XRF measurements was of concern and was reported concerning an organometallic compound of Hg in plastic CRM due to its volatility,3 which might result in serious analytical errors in the determination of hazardous substances.

In the present study, the effect of long-time X-ray irradiation on Cr and Hg in a polypropylene (PP) disk CRM was examined by XRF spectrometry. Since the chemical forms of Cr for both inorganic and organometallic compounds were mixed in the PP disk CRM, the organo one was of concern to be possibly lost during long-time XRF measurements. Though any Hg contained was considered to be stable due to its inorganic chemical form,8,9 it was also measured and compared to that of Cr. The XRF intensities of Cr (Kα), Hg (Lα) and Pb (Lα) as well as the XRF intensity ratios, either Cr/Pb or Hg/Pb, were obtained by both an energy-dispersive (ED)-XRF spectrometer and a wavelength-dispersive (WD)-XRF spectrometer with many replicated measurements, which corresponded to long-time X-ray irradiation. The measurements of Cr, Hg and Pb in the PP disk CRMs obtained after long-time WD-XRF measurements was also performed by an ED-XRF spectrometer. The effect of long-time X-ray irradiation on Cr and Hg was discussed and evaluated from the obtained results.

Experimental

Sample and instrumentation

The PP disk CRM (later transcribed as PP disk) used in the present study was NMIJ CRM 8136-a, which was developed by National Metrology Institute of Japan (NMIJ, Tsukuba, Ibaraki, Japan).8,9,11 The diameter and the thickness of these disks are 30 and 2 mm, respectively. The chemical forms of Cr contained in the PP disk were lead chromate (PbCrO4) and chromium acetylacetonate (Cr(C5H7O2)3) which can be expressed as Cr(acac)3, as inorganic and organometallic compounds,

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respectively. The chemical form of Hg contained in the PP disk was mercury sulfide (HgS). The concentrations for both Cr and Hg in the PP disk were 890.6 and 952 mg kg\(^{-1}\), respectively. The ED-XRF and WD-XRF spectrometers used in the present study were Rayny EDX-720 (Shimadzu Co., Japan) and ZSX 100e (Rigaku Co., Japan), respectively. The operating conditions of the XRF spectrometers are listed in Tables 1 and 2, and the measurements were repeated up to 430 times during 10 different periods (4 days for one period), which corresponded to 430 h. On the other hand, a WD-XRF analysis was carried out for Cr and Pb measurements, since the loss of Cr was observed, whereas Hg and Pb were shown to be slightly increasing, as well as similar trends. The enhanced XRF intensities of Cr were observed, whereas Hg and Pb were shown to be stable even if it was exposed to long-time X-ray irradiation. In order to investigate whether or not a similar phenomenon could be observed, Cr and Pb were measured by an ED-XRF spectrometer, due to the long-time X-ray irradiation, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h. From this point of view, the XRF intensity ratios of Cr/Pb and Hg/Pb could be good indicators to evaluate the stability of Cr and Hg in the PP disk. As can be seen in Fig. 1, constant XRF intensities of Cr were observed, whereas Hg and Pb were shown to be slightly increasing, as well as similar trends. The enhanced XRF intensities of Hg and Pb could be due to an uncaused change in the sensitivity of the ED-XRF spectrometer, which was operated at different measurement periods. Figure 2 shows the relative XRF intensity ratios of Cr/Pb and Hg/Pb calculated from XRF intensities shown in Fig. 1. The constant intensity ratios were obtained for Hg/Pb, whereas Cr/Pb showed decreasing ratios, as can be seen in Fig. 2(a). From these results, it was considered that Hg was stable in the PP disk, whereas Cr was considered to be lost during the measurements by an ED-XRF spectrometry, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h. From this point of view, the XRF intensity ratios of Cr/Pb and Hg/Pb could be good indicators to evaluate the stability of Cr and Hg in the PP disk. As can be seen in Fig. 1, constant XRF intensities of Cr were observed, whereas Hg and Pb were shown to be slightly increasing, as well as similar trends. The enhanced XRF intensities of Hg and Pb could be due to an uncaused change in the sensitivity of the ED-XRF spectrometer, which was operated at different measurement periods. Figure 2 shows the relative XRF intensity ratios of Cr/Pb and Hg/Pb calculated from XRF intensities shown in Fig. 1. The constant intensity ratios were obtained for Hg/Pb, whereas Cr/Pb showed decreasing ratios, as can be seen in Fig. 2(a). From these results, it was considered that Hg was stable in the PP disk, whereas Cr was considered to be lost during the measurements by an ED-XRF spectrometry, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h. From this point of view, the XRF intensity ratios of Cr/Pb and Hg/Pb could be good indicators to evaluate the stability of Cr and Hg in the PP disk. As can be seen in Fig. 1, constant XRF intensities of Cr were observed, whereas Hg and Pb were shown to be slightly increasing, as well as similar trends. The enhanced XRF intensities of Hg and Pb could be due to an uncaused change in the sensitivity of the ED-XRF spectrometer, which was operated at different measurement periods. Figure 2 shows the relative XRF intensity ratios of Cr/Pb and Hg/Pb calculated from XRF intensities shown in Fig. 1. The constant intensity ratios were obtained for Hg/Pb, whereas Cr/Pb showed decreasing ratios, as can be seen in Fig. 2(a). From these results, it was considered that Hg was stable in the PP disk, whereas Cr was considered to be lost during the measurements by an ED-XRF spectrometry, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h.

**Results and Discussion**

Figures 1(a) - 1(c) show the relative XRF intensities of Cr (K\(_a\)), Hg (L\(_a\)) and Pb (L\(_a\)) obtained by an ED-XRF spectrometer for a total 430 h (one data was obtained by 1 h measurement, as listed in Table 1). It could be considered that Pb in the PP disk was sufficiently stable even if it was exposed to long-time X-ray irradiation, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h. From this point of view, the XRF intensity ratios of Cr/Pb and Hg/Pb could be good indicators to evaluate the stability of Cr and Hg in the PP disk. As can be seen in Fig. 1, constant XRF intensities of Cr were observed, whereas Hg and Pb were shown to be slightly increasing, as well as similar trends. The enhanced XRF intensities of Hg and Pb could be due to an uncaused change in the sensitivity of the ED-XRF spectrometer, which was operated at different measurement periods. Figure 2 shows the relative XRF intensity ratios of Cr/Pb and Hg/Pb calculated from XRF intensities shown in Fig. 1. The constant intensity ratios were obtained for Hg/Pb, whereas Cr/Pb showed decreasing ratios, as can be seen in Fig. 2(a). From these results, it was considered that Hg was stable in the PP disk, whereas Cr was considered to be lost during the measurements by an ED-XRF spectrometry, because Pb was recovered quantitatively during the dry-ashing sample pretreatment procedure at 350°C for 6 h.

**Fig. 1** Relative XRF intensities of (a) Cr (K\(_a\)), (b) Hg (L\(_a\)) and (c) Pb (L\(_a\)) obtained by ED-XRF measurements as a function of the X-ray irradiation time.

Table 1: Operating conditions of ED-XRF spectrometer (Rayny EDX-720, Shimadzu Co.)

| X-ray irradiated diameter (circle) | X-ray tube: |
|-----------------------------------|------------|
|                                    | End-window type Rh target (water cooling) |
| Tube voltage:                      | 50 kV      |
| Tube current:                      | 80 mA      |
| Filter:                            | Not used   |
| Sample chamber:                    | Vacuumed   |
| X-ray Irradiated diameter to sample: | 10 mm      |
| X-ray tube:                        | End-window type Rh target (water cooling) |
| Tube voltage:                      | 50 kV      |
| Tube current:                      | 80 mA      |
| Filter:                            | Not used   |
| Sample chamber:                    | Vacuumed   |
| X-ray Irradiated diameter to sample: | 10 mm      |
| Wavelength range measured (2\(\theta\)) | 67.500 to 70.500 deg for Cr and 32.000 to 35.000 deg for Pb |
| Measurement time/s                 | 3600       |
| Measurement time/s                 | 3360 s (9.6 s/0.020 deg) |

Table 2: Operating conditions of a wavelength dispersive X-ray fluorescence spectrometer (ZSX 100e, Rigaku Co.)

| Operating condition | Operating condition |
|---------------------|---------------------|
| Measurand and their integrated energy range/keV for compton scattering | 18.12 – 19.88 |
| Detectors            | Scintillation counter |
| Measurand and their integrated energy range/keV for compton scattering | 18.12 – 19.88 |
| Detectors            | Scintillation counter |
| Measurand and their integrated energy range/keV for compton scattering | 18.12 – 19.88 |
| Detectors            | Scintillation counter |
| Measurand and their integrated energy range/keV for compton scattering | 18.12 – 19.88 |
| Detectors            | Scintillation counter |
Figs. 3(b) and 3(c), respectively. Since the observed temperature on the surface of the PP disk was about 90°C after 1 h measurement by the WD-XRF spectrometer, the X-ray irradiation and heat generated were considered to influence the charred surface. Figure 4 shows the relative XRF intensities of Cr and Pb as well as the Cr/Pb ratio obtained by WD-XRF measurements for up to 120 h at 80 mA of the X-ray tube current condition. The different trends of the XRF intensities between Cr(Kα) and Pb(Lα) were observed, resulting in the decreasing XRF intensity ratios of Cr/Pb. From these results, it could be considered that Cr in the PP disk was lost during 120 h of measurement by the WD-XRF spectrometer. The larger decreasing rate of the Cr/Pb ratio observed for the WD-XRF measurement (Fig. 4(c)) could be attributed to higher X-ray irradiation compared to that of the ED-XRF measurement (Fig. 2(a)). We also measured Cr, Hg and Pb from the charred surface of the PP disks, which was obtained after the WD-XRF measurements for 32 and 120 h, by the ED-XRF spectrometer, and evaluated the intensity ratios of Cr/Pb and Hg/Pb, as shown in Fig. 5. Although the Hg/Pb ratios obtained showed 1 to 2% lower ratios compared to that of the PP disk without the WD-XRF measurement, it could be considered that Hg was sufficiently stable for XRF analysis with high X-ray irradiation for a long time since the chemical form of Hg was HgS with a melting point of 580°C. In the case of Cr, the Cr/Pb ratio observed from the charred surface of the PP disk with 32 h measurement showed almost unity; however, about 10% lower ratio was observed for the PP disk after the WD-XRF measurement for 120 h. On the other hand, the Cr/Pb ratio obtained from the reverse side of the charred disk surface with 120 h of measurement showed about 2% higher ratio, which suggested that the Cr contained in the disk side was stable without the effect of long-time X-ray irradiation. From these results, it could be considered that the loss of Cr was observed from an X-ray irradiated surface of the PP disk during the WD-XRF measurement for a long time. Since the chemical forms of Cr in the PP disk 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 XRF measurement for a long time.

**Conclusions**

The effect of long-time X-ray irradiation on Cr and Hg in the PP disk was evaluated. The observed XRF intensities and XRF intensity ratios for up to 430 h of measurement by the ED-XRF spectrometer revealed a loss of Cr from the PP disk, even though no obvious change of surface morphology could be seen by a visual observation. A decreasing Cr/Pb intensity ratio was also observed, and the surface of the PP disk was charred by the long-time WD-XRF measurement. Moreover, a lower Cr/Pb intensity ratio was observed from the charred disk surface by the ED-XRF spectrometer, whereas Hg/Pb showed almost unity. From these results, it was considered that the organometallic compound of Cr in the PP disk CRM, which revealed a lower melting point, might be lost during long-time XRF analysis. Since the long-time XRF measurement demonstrated in the present study is not carried out for general routine XRF analysis, the loss of Cr cannot be found unless the PP disk is frequently measured.
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