Development of Plastic Certified Reference Materials for XRF analysis
(JSAC 0611-0615) containing Pb, Cd, Cr;

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Abstract
New plastic certified reference materials (CRMs) with Pb, Cd and Cr for XRF analysis have
been developed in cooperation with the Japan Society for Analytical Chemistry. These CRMs
(named as JSAC 0611 – 0615) were prepared by casting polyester including a toluene solution
of organometallic compounds as a standard. The disk was removed from the glass plate after
12 h of hardening at room temperature. Concentrations of the three trace elements ranged
from 0 to 200 mg/kg for Pb, 0 to 50 mg/kg for Cd, and 0 to 200 mg/kg for Cr. A
homogeneity test by XRF measurement showed that the three metals were uniformly
distributed in the disk.
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INTRODUCTION
On July 1st, 2006, European Union’s “RoHS (Restrictions on Hazardous Substance) Directive”[1], which is controlled with the maximum level of Pb, Cr(IV), Cd, Hg, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in almost all electric and electronic industrial materials, is enforced. Especially, it has caused the serious problem on the plastic industry and materials because RoHS directive were applied to the plastic in the electrical and electronic equipment. Therefore, quantitative determination of hazardous metals in plastic materials is very important for quality control and for monitoring.

Various studies have been conducted on the determination of trace metals in plastics by spectrometric techniques, i.e., ICP-AES [3], ICP-MS [4], and AAS [5-8]. However, these methods require the time-consuming pretreatment, such as dry ashing, wet ashing, and acid digestion. On the other hand, XRF analysis is suitable for simple, quick, nondestructive and direct determination, but certified reference materials (CRMs) for calibration are necessary to certify the reliability of the analytical value.

Certified Reference Materials (CRMs) are essential tool in order to confirm the accuracy and precision of used analytical procedure and analytical results. At present, several plastic CRMs containing trace amounts of metals have been available. VDA 001-0042) is the first plastic CRMs for the determination of cadmium in polyethylene. BCR 680 and 6813-7) that contain As Br, Cd, Cl, Cr, Hg, Pb and S in polyethylene, are available from the Institute for Reference Materials and Measurement (IRMM; Belgium). However, the lack of the plastic CRMs is ongoing problem from a viewpoint of the analytical needs because the amounts of the industrial plastic product are enormous.

In order to satisfy these analytical needs, the Japan Society for Analytical Chemistry (JSAC) have established the committee for the plastic CRMs for hazardous metals since 2004.

In the JSAC, the new plastic CRMs (named as JSAC0611 to 0615) containing Pb, Cd and Cr for using X-ray fluorescent analysis were developed and certified. In this paper, the sample preparation and the homogeneity of the analyte are mainly described.

EXPERIMENTAL
Apparatus
A Rigaku Rix 3100 X-ray fluorescence spectrometer equipped with an end window 4 kW Rh X-ray tube and an automatic 50-sample changer was used. An IBM PL 3100 Windows computer was used for machine control, data processing and analytical calculations. The analyzing crystal and detector were used a LiF (200), and a scintillation counter for CrKα, CdKα, and PbLα. X-ray intensity of the analytical line was measured on the peak line. The theoretical X-ray florescent intensities for the critical depth of the plastics were calculated using the fundamental parameter method. The instrumental conditions are listed in Table 1.
Table 1 Instrumental conditions for X-ray fluorescence spectrometry of Pb, Cd and Cr

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical line</td>
<td>Lα</td>
<td>Kα</td>
<td>Kα</td>
</tr>
<tr>
<td>Tube voltage / kV</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Tube current / mA</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Crystal</td>
<td>LiF(200)</td>
<td>LiF(200)</td>
<td>LiF(200)</td>
</tr>
<tr>
<td>Detector</td>
<td>SC</td>
<td>SC</td>
<td>SC</td>
</tr>
<tr>
<td>Filter</td>
<td>-</td>
<td>Zr-filter</td>
<td>-</td>
</tr>
<tr>
<td>Peak angle / degree</td>
<td>33.93</td>
<td>15.28</td>
<td>69.34</td>
</tr>
<tr>
<td>( Counting time / s )</td>
<td>10</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>PHA</td>
<td>100-300</td>
<td>100-300</td>
<td>90-310</td>
</tr>
</tbody>
</table>

Plastic resin and Chemicals
The raw materials of the plastic CRMs were used for the commercially available polyester resin (Clear polyester resin, Epoch Co. ltd., Japan). Chemicals were used for the organometallic reagents, i.e., chromium(III) acetylacetonate (ACROS), cadmium cyclohexylbutylate (ACROS), and tetraphenyl lead (ACROS). Toluene (Junsei, JIS guaranteed grade reagent) was used to make solutions of organometallic compounds.

RESULT AND DISCUSSIONS
Preparation of the CRMs [14, 15]
The reference materials consisting of polyester resin were prepared at Environmental Technology Service Corporation (Tobata-ku, Kitakyusyu, Fukuoka; Japan) in the following steps:

1. The Clear polyester resin (2000 g) and 170 g of a toluene solution of organometallic reagents were mixed and stirred for 10 min in a 18 L-PE vessel. The amounts of organometallic reagents were weighed such that the target concentrations could be obtained.

2. The mixture from Step 1 was divided into 100 g units in a glass beaker, and 1 g of headner (2-Butanone Peroxide, Permeck N) was mixed.

3. The mixture obtained from Step 2 was stirred quickly for 1 min, and cast into 250 Al-molds (42 mmφ, 5 mmt) on the glass plate immediately.

4. The cylindrical disks obtained from Step 3 were removed from the glass plate and Al mold after 12 h of standing at room temperature. The prepared concentration of these CRMs was estimated by the mixing ratio of the sample amount.

A total of 232 disks of JSAC 0611 and JSAC 0613, 242 disks of JSAC 0614 and JSAC 0615, and 226 disks of JSAC 0612 were produced. The prepared concentrations of these CRMs are shown in Table 2.
Table 2  Prepared concentrations of Pb, Cd and Cr for JSAC 0611 - 0615.

<table>
<thead>
<tr>
<th>Prepared concentration / mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>JSAC 0611 (Blank)</td>
</tr>
<tr>
<td>JSAC 0612</td>
</tr>
<tr>
<td>JSAC 0613</td>
</tr>
<tr>
<td>JSAC 0614</td>
</tr>
<tr>
<td>JSAC 0615</td>
</tr>
</tbody>
</table>

**Homogeneity test**

The homogeneity of the disks was investigated by XRF measurement in order to confirm the deviations of XRF intensities of the analytes. XRF measurement results of all produced disks and disk weight are given in Table 3. Each of the values in the table is the average intensity of all the disk measurement; the relative standard deviations are 0.58 – 0.62 % for Pb, 3.0 – 4.1 % for Cd, and 0.56 – 1.7 % for Cr. As a measurement result, the precision of CdKα intensity was larger than of PbLα and CrKα intensity. It is because of the critical depth of the analytical line.

Table 3  Homogeneity test by XRF intensities of Pb, Cd and Cr in JSAC 0611 - 0615.

<table>
<thead>
<tr>
<th>XRF intensities / kcps</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
<th>Sample weight / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>JSAC 0611</td>
<td>26.083 (0.58)</td>
<td>1.0670 (3.6)</td>
<td>0.9257 (1.9)</td>
<td>7.1688 (4.3)</td>
</tr>
<tr>
<td>JSAC 0612</td>
<td>31.208 (0.82)</td>
<td>1.1144 (4.1)</td>
<td>1.6828 (1.0)</td>
<td>7.0459 (4.6)</td>
</tr>
<tr>
<td>JSAC 0613</td>
<td>37.094 (0.62)</td>
<td>1.1962 (3.1)</td>
<td>2.4829 (0.73)</td>
<td>7.0946 (3.5)</td>
</tr>
<tr>
<td>JSAC 0614</td>
<td>47.300 (0.65)</td>
<td>1.3817 (3.1)</td>
<td>3.8725 (0.56)</td>
<td>7.0765 (3.5)</td>
</tr>
<tr>
<td>JSAC 0615</td>
<td>65.870 (0.69)</td>
<td>1.6497 (3.0)</td>
<td>7.3143 (0.57)</td>
<td>7.1236 (3.4)</td>
</tr>
</tbody>
</table>

( ) : Relative standard deviation ; n = 242 (JSAC 0615, 0614), n = 232 (JSAC 0611, 0613), n = 226 (JSAC 0612).

The critical depths of the three elements calculated by the FP method (Fig. 1) are 1 - 2 mm for CrKα, 5 - 7 mm for PbLα, and more than 40 mm for CdKα. Therefore, CdKα intensity was sensitive with the variation of the thickness, because it was regarded as “thin layer model”. This is also evident that CdKα intensity were strongly correlated with the intensity of RhKα - Compton scattering x-ray, and the disk weight given in Fig. 2 and Fig. 3. Hence, the CdKα intensity can be corrected with the intensity of RhKα - Compton scattering x-ray or the disk weight.
Fig. 1 Critical depth of CrK$\alpha$, CdK$\alpha$ and PbL$\alpha$ in polyester calculated by fundamental parameter method.

Fig. 2 CdK$\alpha$ intensities vs. RhK$\alpha$ Compton scattering X-ray intensities plot.

Fig. 3 CdK$\alpha$ intensities vs. disk weight plot.
Effect of the Sample Grinding

The variation of CdKα intensity in case of the critical depth was able to overcome by correction of the Compton scattering X-ray or disk weight. In other words, if the disk thickness were uniform, these corrections were not necessary. Disk surfaces were prepared by both grinding and polishing by a milling machine at 4.00 ± 0.02 mm thick. Polished disks obtained by a milling machine were kept constant. XRF measurement results of 25 disks after polishing are given in Table 4. The values obtained by the polished disk have greater precision than the values obtained by raw disks. Especially, the precision of CdKα intensity was improved remarkably as shown in Fig. 4.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>XRF intensities of Pb, Cd and Cr with polished sample in plastic standard disk.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRF intensity / kcps</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td>JSAC 0611</td>
<td>25.431 (0.16)</td>
</tr>
<tr>
<td>JSAC 0612</td>
<td>30.349 (0.25)</td>
</tr>
<tr>
<td>JSAC 0613</td>
<td>35.840 (0.15)</td>
</tr>
<tr>
<td>JSAC 0614</td>
<td>45.477 (0.19)</td>
</tr>
<tr>
<td>JSAC 0615</td>
<td>63.057 (0.15)</td>
</tr>
</tbody>
</table>

( ) : Relative standard deviation ; n= 25

Fig. 4 Deviations from the mean value of CdKα intensities with the raw samples (□), and the polished samples (■) in JSAC 0611 - 0615.
* : Error bar defined by the confidence interval (95 % ; n = 25).
CONCLUSIONS

New plastic CRMs have been produced and performed the homogeneity test. The produced disks after polishing had good homogeneity. This CRMs is great useful for the hazardous metal analysis in plastics. The produced CRMs are already commercially available from the Japan Society for Analytical Chemistry (Phone: +81-3-3490-3351, FAX: +81-3-3490-3572, E-mail address: shomu@jsac.or.jp), with a certification report describing in detail the prepared method and statistical results\textsuperscript{16)).

REFERENCES

[13] Lambert A.; Borm WV.; Quevauviller P.;: EUR 19450 – The certification of the mass fractions of As, Br, Cd, Cl, Cr, Hg, Pb and S.