Chemistry

7C, 9A/2008G625

Quantitative XAFS analysis of hexavalent chromium in ABS resin certified reference materials for heavy metal analysis

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Introduction

EU (European Union) legislated the RoHS (restriction of the use of hazardous substances in electrical and electronic equipment) directive and it became effective on July, 2006 [1]. According to the directive, concentration values of hazardous substances such as Cd, Cr(VI) (hexavalent chromium), Hg, Pb, PBB (polybrominated biphenyl) and PBDE (polybrominated diphenyl ether) in electrical and electronic equipment produced in EU and transported from other areas should be restricted.

It is well kown that plastic materials are widely used in electrical and electronic equipment. Therefore, standard analytical methods and certified reference materials (CRMs) for the determination of the hazardous substances in plastics are of great interest and demanded to check whether the concentration values of these hazardous substances in electrical and electronic equipment conform to the RoHS directive or not.

National Metrology Institute of Japan (NMIJ) has been developing the plastic CRMs with respect to the RoHS directive. The concentrations of Cd, total Cr, Hg and Pb were certified in the CRMs [2]; however, the concentration of hexavalent chromium (Cr(VI)) was not certified. In addition, no CRMs are available for the determination of Cr(VI) in plastics all over the world.

It is well known that XAFS analysis can be applied to Cr(VI) measurements in solid samples; therefore, quantitative XAFS analysis of Cr(VI) in plastic was examined in the present study.

Experimental

The ABS resin disk CRM (NMIJ CRM 8106-a) was used as a plastic sample in the present study. The diameter and thickness of the ABS reisn disk CRM are 30 mm and 2 mm, respectively. The concentration of total Cr in the ABS resin disk CRM is certified as 269.5 mg/kg. The chemicals added for Cr in the ABS resin disk was $PbCrO_4$ [2]; therefore, it can be expected that the oxidation state of Cr in the ABS resin disk is hexavalent (Cr(VI)). The blank ABS resin disk which does not contain any heavy metals was also used to correct XAFS spectrum of the ABS resin disk CRM. In order to evaluate the concentration of Cr(VI) in the ABS resin disk CRM, two pellets which were made from $PbCrO_4$ (100 % Cr(VI)) and from Cr-acetylacetonate (0 % Cr(VI)) were prepared, and the concentration of Cr(VI) in the ABS resin disk CRM was estimated using the linear calibration curve calculated from XANES spectra observed from both pellets. The Cr K-edge spectra were measured using the station of BL-7C at KEK-PF.

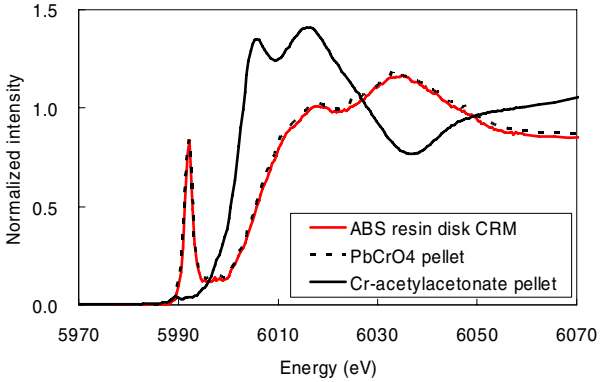

Fig. 1 Normalized XANES spectra observed for ABS resin deisk CRM, $PbCrO_4$ pellet and Cr-acethylacetonato pellet.

Results and Discussion

Figure 1 shows the XANES spectra observed for the ABS resin disk CRM, $PbCrO_4$ pellet, and Cr-acethylacetonate one. Similar XANES spectra were observed for both the ABS resin disk CRM and the $PbCrO_4$ pellet. On the other hand, different XANES spectrum was observed for the Cr-acetylacetonate pellet. From these results, it was expected that most Cr in the ABS resin disk CRM was Cr(VI); however, the concentration ratio of Cr(VI) to total Cr could never be evaluated from the Fig. 1 only. Therefore, the concentration ratio of Cr(VI) to total Cr in the ABS resin disk CRM was estimated using the linear calibration curve calculated from the XANES spectra observed for both the $PbCrO_4$ pellet and Cr-acetylacetonate one. The concentration ratio of Cr(VI) to total Cr in the ABS resin disk CRM was estimated as more than 95 %.

References

[1] Directive 2002/95/EC of the european parliament and of the council of 27 January 2003, on the restriction of the use of certain hazardous substances in electrical and electronic equipment, *Official Journal of European Union*, 13. 2. (2003).
[2] Masaki Ohata, Masayasu Kurahashi, Akiharu Hioki, BUNSEKI KAGAKU, 57, 417 (2008).

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