



## Technical Note

# Determination of hexavalent chromium in plastic certified reference materials by X-ray absorption fine structure analysis

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## ABSTRACT

X-ray absorption fine structure (XAFS) analysis with transmission mode was used to determine the percentages of hexavalent chromium {Cr(VI)} in total Cr in plastic certified reference materials (CRMs). Cr-K edge X-ray absorption near-edge structure (XANES) spectra were observed and the normalized pre-edge peaks of the spectrum where absorption data was summed was acquired for the determination of Cr(VI). Examination of different number of data point and range of photon energy for summed absorption of the pre-edge peak resulted in reproducible absorption data, though the measurements were carried out at different beam time and beam line. The concentrations of Cr(VI) in the plastic CRMs were also estimated from both the certified value of total Cr and the determined percentage of Cr(VI). The analytical procedure and the estimated concentrations can be useful for the determination of Cr(VI) in plastics with respect to RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive.

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## 1. Introduction

EU (European Union) legislated the RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive since July, 2006 [1,2]. The directive restricted the concentration of such hazardous substances as Cd, Cr(VI), Hg, Pb, PBB (poly-brominated biphenyl) and PBDE (poly-brominated diphenyl ether) in electrical and electronics equipments produced in EU and transported from other areas. As well known, plastic resins are used widely in electrical and electronics equipment. It is also well recognized that hazardous substances mentioned above have been added into plastics purposely for the sake of noncombustibility and the coloring. In addition, new plastics without hazardous substances are concerned to be adulterated with used plastics with hazardous substances during recycling process. From these points of view, standard analytical procedures and certified reference materials (CRMs) of hazardous substances in plastics are still of great interest and are demanded to check the conformity to the RoHS directive [3–18]. Though several plastic CRMs with respect to the RoHS directive have been developed so far for both chemical analysis [3,4,6,11,14,18] and direct analysis [8,10,12,13,15–17], no CRMs were found to be certified the concentration of Cr(VI) in plastics even though the RoHS directive regulated. Several analytical methods were proposed to determine Cr(VI) in solid samples such as a high performance liquid chromatography (HPLC) couple with inductively coupled plasma mass

spectrometry (ICPMS) and UV–visible spectrophotometry using extraction procedures [19,20]. However, the extraction procedures of Cr(VI) from solid samples implies concern about the extraction efficiency as well as changing chemical form of Cr(VI) to e.g. Cr(III). X-ray absorption fine structure (XAFS) analysis should be the one to achieve the determination of Cr(VI) in solid samples directly without any concerns during extraction process [21–27].

In the present study, we determined the percentage of Cr(VI) in total Cr in plastic disk CRMs by XAFS analysis with transmission mode. The Cr–K edge X-ray absorption near-edge structure (XANES) spectra were observed and the normalized pre-edge peak of Cr–K edge XANES spectra where absorption data were summed were acquired to determine the percentage of Cr(VI) because the pre-edge peak was concluded to be suitable for quantitative analysis [21,23]. Different number of data point and range of photon energy for summed absorption of the pre-edge peak were examined to achieve accurate determination of the percentage of Cr(VI) in plastic disk CRMs and the variation of summed absorptions were also evaluated at different beam time and beam line. Moreover, the concentrations of Cr(VI) in the plastic disk CRMs were estimated from both the certified value of total Cr and the determined percentage of Cr(VI).

## 2. Experimental

## 2.1. Instrumentation

The Cr–K edge XANES spectra were observed by transmission mode with ionization chambers using a Si(111) double crystal

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**Table 1**  
Energy range, step, measurement time, and number of data for measured XAFS spectra.

Block	Initial energy (eV)	Final energy (eV)	Step (eV/step)	Measurement time (s)	Number of data
1	5659.30	5959.30	6.00	2.0	50
2	5959.30	6059.30	0.40	2.0	250
3	6059.30	6200.30	3.00	2.0	47

Total measurement time was 694 s for each spectrum.

**Table 2**  
Certified values of total Cr and their expanded uncertainties in plastic CRMs.

	Certified value (mg kg <sup>-1</sup> )	Expanded uncertainty <sup>a</sup> (mg kg <sup>-1</sup> )	Relative expanded uncertainty (%)
NMIJ CRM 8106-a	268.1	2.1	0.8
NMIJ CRM 8116-a(02)	912	46	5.0
NMIJ CRM 8136-a	890.6	10.7	1.2

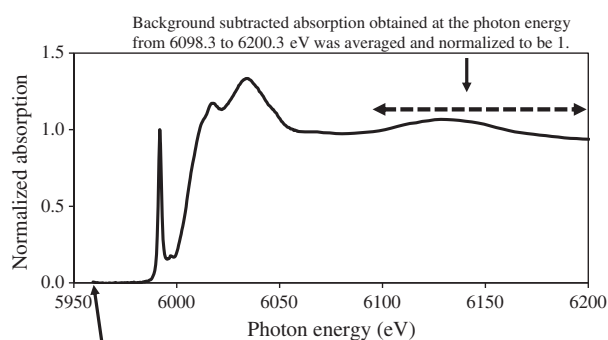
<sup>a</sup> Each expanded uncertainty was determined with the coverage factor  $k = 2$ ; it defines an interval estimated to have a level of confidence of approximately 95%.

monochromator of the XAFS beam lines of BL-7C, 9A, 9C, and 12C at KEK-PF (Tsukuba, Japan) [28]. The electron storage ring was operated with the energy of 2.5 GeV and a current of 300–450 mA. The photon energy of the Cr–K edge XANES spectrum between 5959.30 eV and 6200.30 eV was measured. A copper foil (6  $\mu\text{m}$  thickness) was used as a standard to calibrate photon energy for the Si(111) double crystal monochromator. The hump at the absorption edge of copper (8980.30 eV) was regarded as  $12.7185^\circ$ . The non-focused monochromated beam was collimated to 1 mm  $\times$  6 mm with respect to the sample surface by four slits. The measurement time for each energy range was listed in Table 1 and total measurement time was 694 s for one Cr–K edge XANES spectrum.

## 2.2. Samples and reagents

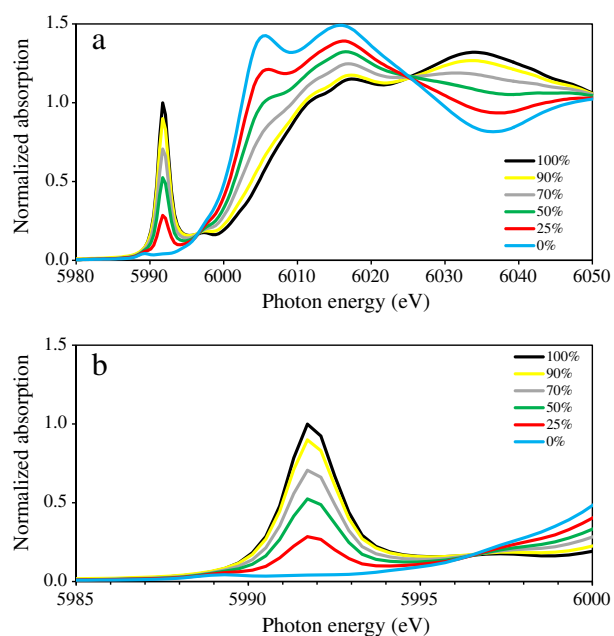
The plastic disk CRMs for heavy metal analysis with respect to RoHS directive such as NMIJ CRM 8106-a, 8116-a(02) and 8136-a as listed in Table 2 which were developed by National Metrology Institute of Japan (NMIJ) were used in the present study [14,16]. The plastic resins for NMIJ CRM 8106-a as well as 8116-a(02) and 8136-a are acrylonitrile-butadiene-styrene (ABS) and polypropylene (PP), respectively. The diameter and the thickness of these disks are 30 mm and 2 mm, respectively. The concentrations of total Cr in these plastic disk CRMs are certified as listed in Table 2 [14,16,29]. The percentages of Cr(VI) in total Cr was expected to be 100% in NMIJ CRM 8106-a because PbCrO<sub>4</sub> was only added. On the other hand, expected percentages of Cr(VI) were about 25% for NMIJ CRM 8116-a(02) and 8136-a because both

PbCrO<sub>4</sub> and Cr-acetylacetonate as Cr(VI) and Cr(III), respectively, were added with the Cr mass ratio of 1: 4. The blank plastic disks which did not contain any heavy metals were also used to correct XANES spectra for each disk CRM. In order to determine the percentage of Cr(VI) in the plastic disk CRMs, pellet form of calibration standards which consisted of both PbCrO<sub>4</sub> and Cr-acetylacetonate (Wako pure chemical industries Inc., Osaka, Japan) as Cr(VI) and Cr(III), respectively, were prepared by mixing with methyl cellulose (Wako pure chemical industries Inc., Osaka, Japan) as a binder, because PbCrO<sub>4</sub> and Cr-acetylacetonate were contained in the plastic disk CRMs as mentioned above. The percentages of Cr(VI) in plastic disk CRMs were determined by a calibration curve obtained from the calibration standards, which have different percentage of Cr(VI) in total Cr such as 0, 5, 10, 15, 20, 25, 30, 50, 75, 90, 95 and 100% prepared by pressing after mixing with three reagents by mass ratio. The addition amount of total Cr in each



Background subtracted absorption obtained at the photon energy of 5959.3 eV was set to be 0.

**Fig. 1.** Cr–K edge XANES spectra obtained for NMIJ CRM 8106-a.



**Fig. 2.** (a) and (b) Cr–K edge XANES spectra obtained for calibration standards of 0, 25, 50, 70, 90 and 100% Cr(VI) in total Cr prepared by mixing with PbCrO<sub>4</sub>, Cr-acetylacetonate and methyl cellulose observed for photon energy ranged (a) from 5980 eV to 6050 eV and (b) from 5985 eV to 6000 eV.

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