The Japan Society for Analytical Chemistry

Certificate of Analysis

Certified Reference Material JSAC 0602-3
Plastics (tip form)
for Chemical Analysis of Hazardous Metals

This certified reference material (CRM) consists of polyester resin tips whose trace concentrations of lead (Pb), cadmium (Cd), chromium (Cr) and mercury (Hg) were certified. Certified values are shown in Table 1 together with their uncertainties.

This CRM is intended primarily for use in evaluating methods of analyses used in the determination of trace metallic elements in polymer moldings or other products made of plastics by comparing the certified values with the analytical results of the CRM obtained from the analysis executed in parallel with the sample to be analyzed.

This CRM is crushed polyester resin tips, 0.5 ~ 1 mm in tip size. 50 g of CRM is filled in an amber glass bottle and the bottle is packed in a carton box.

Table 1 Certified values

Elements	Certified value ± uncertainty[1] μg/g	Interlaboratory standard deviation[2] (*SD*) μg/g	Number of data applied (*N*)	Main methods of analyses[3]
Pb	112.0 ± 1.4	2.9	19	(1),(2),(3),(4),(5),(6),(8)
Cd	50.4 ± 0.5	1.1	18	(1),(2),(3),(4),(6),(8)
Cr	112.6 ± 1.8	3.8	20	(1),(2),(3),(4),(6),(8)
Hg	12.1 ± 0.6	1.1	17	(1),(6),(7),(8)

Note

1) Uncertainties were 95% confident limit of each medians ($U_{95\%}$). They were calculated with the following equation.

$$U_{95\%} = (t \times SD) \div \sqrt{N}$$

t : in the Student t distribution table

2) In case of evaluation of analytical results by the user of the CRM, it is recommended to consider not only uncertainties but also *SD*s.

3) For method No., refer "**Procedure for certification**, 1 in next page.

Instructions for use

1. Be careful of contamination from environment in handling the CRM.
2. Plug the bottle immediately after putting out the contents except when the bottle had been made empty.

3. The CRM once taken out from the bottle should not be return to the bottle.
4. Notice related to the safety data sheet for chemical product: this CRM contains slight amount of compounds of Hg that is indicated legally as poisonous/deleterious materials. Be careful at handling.

Storage of CRM and expiration of certification

1. The CRM should be stored in the dark and cool place. It is a safe way to keep the CRM in a box or in a plastic film bag in order to avoid the CRM from environmental contamination.
2. There will be no change on certified values if the CRM stored in dark and cool place. It is planned the periodical stability test for this CRM. It will be reported on JSAC journal or the homepage after test result will be obtained.

Preparation of CRM and confirmation of its homogeneity

1. Weighed necessary amount of organic complexes, Cr(Ⅲ)-acetyl acetonate, Cd-cyclohexane butyrate, tetraphenyl-Pb and Hg-cyclohexane butyrate were dissolved in toluene. The toluene solution was poured to the polyester oligomer (liquid) and mixed well. After addition of curing catalyst, the mixed solution was poured to molds in order to make polyester plates, approximately 50 cm square and 3 mm thick.

   Hardened plates were broken in small pieces by hand, and then crushed with a cutter mill (steel body, rotor edge and stator edge are made of high speed steel). Polyester fragments discharged from exit screen of the mill were sieved to get fragments, passing 1 mm screen and stopped on 0.5 mm screen. Obtained fragments were put in a polypropylene bottle, 17 L of capacity. Then the bottle was rotated using a roll mill to homogenize the contents.
2. Homogenized polyester tips were packed 50 g each in 243 amber glass bottles (cap:110 mL). Small amount of tips were sampled in 2 times from 10 bottles, and applied acid decomposition. Concentrations of Cd, Pb and Cr in the solutions were measured by ICP atomic emission spectrometric analysis.

   The standard deviations between bottles were so small that they cannot be calculated. From the results it is proved that the polyester tips are homogeneous well.

Procedure for certification of the concentration

The certified values of metals in this CRM were obtained by statistical calculation of the results of an interlaboratory comparison study performed with 20 laboratories. In the study, numbers of elements to be measured were four as shown in Table 1, and analytical methods were limited as shown in “Manual for analysis” sent to laboratories from JSAC.

1. Briefings of analytical methods in the manual.

(1) Closed system acid decomposition－inductively coupled plasma mass spectrometry

The sample was digested with suitable reagents such as nitric acid using microwave digester and the digested solution was sprayed into inductively coupled plasma. Intensities of ion

currents of Cd, Cr, Pb were measured at their m/z. Cd, Cr and Pb are quantified from their intensity ratios of ion current to internal standard.

(2) Closed system acid decomposition－inductively coupled plasma atomic emission spectrometry
The sample was digested with suitable mixed acids including nitric acid using microwave digester and the digested solution was sprayed into inductively coupled plasma. Cd, Cr and Pb are quantified from their intensities of emission spectra.

(3) Open system acid decomposition－inductively coupled plasma atomic emission spectrometry
The sample was digested with suitable mixed acids including nitric acid, and the digested solution was sprayed into inductively coupled plasma. Cd, Cr and Pb were quantified from their intensities of emission spectra.

(4) Sulfuric acid carbonization-ashing-fusion－high frequency plasma atomic emission spectrometry
The sample was carbonized by sulfuric acid at first, ashed at low temperature, and then fused. Metallic constituents in fused material were extracted by acid. Pb, Cd and Cr in the extract were analyzed by inductively coupled plasma atomic emission spectrometry

(5) Closed system acid decomposition－reduction airlation atomic absorption spectrometry
The sample was digested with suitable reagent including nitric acid using microwave digester. To the digested solution, $SnCl_2$ solution was added to reduce mercury compounds to elemental Hg. The product solution was made for airlation to evaporate mercury vapor. The vapor was introduced to the cold vapor atomic absorption spectrometer to quantify Hg.

(6) Reflux cooling acid decomposition－reduction airlation atomic absorption spectrometry
The sample was decomposed with nitric acid, sulfuric acid and potassium permanganate. After decomposition of residual nitrous acid by addition of urea solution, potassium permanganate in excess was reduced by addition of hydroxylammonium chloride solution. Hg compound in the solution was reduced by addition of $SnCl_2$ solution. Generated Hg vapor by airlation into this solution was introduced to cold vapor atomic absorption spectrometer.

(7) Thermal vaporization-gold amalgam－atomic absorption spectrometry
The sample was heated to produce mercury vapor from mercury compounds. The vapor is introduced to the surface of golden plate. After mercury in vapor was caught as gold amalgam, the amalgam was heated to release concentrated mercury vapor. Mercury vapor was introduced to atomic absorption spectrometer.

(8) Other methods

2. Operation of interlaboratory comparison study
The study was operated in the term, December, 2007 through January, 2008

3. Evaluation of results and their certification
z scores in robust method# for each reported analytical results were calculated, and the values providing absolute value of z score more than 3 were rejected as outliers. Then, Average, 95 % confident interval($U_{95\%}$) and standard deviation(SD) were calculated with the usual way . These

values are shown in Table 1, average as certified value, $\pm U_{95\%}$ as uncertainty.

Date of certification

March 27, 2008

Laboratories cooperated for the certification (members of the interlaboratory comparison study)

Analysis Center Co.
Canon Corp., Torite Factory
Chemicals Evaluation and Research Institute, Japan
Environmental Giken Co., Dept. of Technology
Environmental Technology Service Co., Hibiki Research Laboratory
Harison Toshiba Lighting Corp., Development Technology Management Div.
Horiba Ltd., Analysis Center
Jo-etsu Environmental Science Center, Dept. of Inspection
Kobelco Kaken Co., Applied Chemistry Div.
Konika-Minolta Technology Center Inc., Material Technology Laboratory
Mitsui Kagaku Analysis Center Co., Structural Analysis Lab.
Nissan Arc Co., Research Div.
Nittech Research Corp., Material Technology Div.
Nitto Analysis Center Co., Trace Analysis Lab.
Shimadzu Technoresearch Corp., Quality Assurance Div.
SII Nanotechnology Co., Dept. of Applied Technology
Sumika Chemical Analysis Service Ltd., Ehime Branch
Sumitomo Metal Technology Inc., Wakayama Branch
Tokai Techno Co., Environment Div.
Toray Research Center Co., Inorganic Chemical Analysis Lab.

20 laboratories

Distributor

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Laboratory of preparation

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Information Service

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