

The Japan Society for Analytical Chemistry

Certificate of Analysis

Certified Reference Material

JSAC 0631

JSAC 0632

Plastics (disk form)

for Fluorescent X-ray Analysis of Hazardous Metals

These certified reference materials (CRMs) consist of polyester disks whose concentrations of lead, cadmium, chromium and mercury were certified. Certified values are shown in Table 1.

The CRMs are intended primarily for use in evaluating methods used in the determination of metals mentioned above in moldings or other products made of plastics with fluorescent X-ray analysis. It will be useful to analyze this CRM comparatively with the analytical samples in case of evaluating validity of analytical results of samples.

Each CRM is transparent polyester disk, 40 mm in radius and 4.00 ± 0.05 mm thick. Concentrations of metals in JSAC 0631 are different from JSAC 0632, and two disks, (JSAC 0631 and 0632 each), are packed in a carton case as a set.

Table 1 Certified concentration of metals

CRM	Metallic Element	Certified value \pm uncertainty* $\mu\text{g/g}$	Interlab. standard deviation (SD)	Number of data applied (N)	Main methods of analyses**
JSAC 0631	Pb	24.5 ± 0.5	1.4	24	(1)(2)(3)(4)(8)
	Cd	22.5 ± 0.4	0.9	23	(1)(2)(3)(4)(8)
	Cr	25.8 ± 0.6	1.8	23	(1)(2)(3)(4)(8)
	Hg	19.7 ± 0.5	1.3	21	(1)(5)(6)(7)(8)
JSAC 0632	Pb	92.9 ± 1.5	5.0	22	(1)(2)(3)(4)(8)
	Cd	46.1 ± 0.6	1.7	23	(1)(2)(3)(4)(8)
	Cr	93.3 ± 2.2	5.3	22	(1)(2)(3)(4)(8)
	Hg	59.4 ± 1.8	5.2	22	(1)(5)(6)(7)(8)

* Uncertainty was calculated by the following equation:
(Student's $t \times$ interlab standard deviation) \div (root of number of data applied)

** Refer the article "procedure for certification of the concentration" in this document.

Instructions for use

1. On handling the CRM disks, hold the disks at their edges, never touch their faces.
2. Keep the disks in the carton case immediately after use, and close the case with cover.
3. It is inhibited to use the CRMs in a place possible to contact the disks to organic solvents, because the disks will be damaged by organic solvents. Never place disks directly on a poly vinyl chloride

sheet or the like that contains plasticizers.

4. In case of comparing the analytical results of CRM disk to those of material to be measured, it is necessary to consider that differences in material, thickness or surface character will affect to fluorescence X-ray intensity.

Notices for Fluorescent X-ray analysis

Notices on X-ray fluorescent measurement of the certified reference materials are follows.

It is possible that a part of Hg in the CRM will be vaporized by irradiation of high power primary X-ray. In this reason, it is recommended that output of primary X-ray at irradiation should be less than followings. Especially it is important when wavelength dispersion type high power fluorescent X-ray analyzer is applied.

- 1) In case of vacuum or He atmosphere : less than 0.1 kW
- 2) In case of atmospheric air : less than 0.25 kW
- 3) In vacuum with Cu filter : less than 0.5 kW

Certified values of the CRM may not be guaranteed when the specimens are analyzed applying higher power than mentioned above in long time.

In case of fluorescent X-ray analysis of metallic contents in plastics or synthetic resins, it is very important to consider on selection of analysis line, peak overlapping caused by coexisting compounds, influence of thickness or sort of material of specimen to fluorescent X-ray intensity.

Storage of CRM and expiration of certification

1. The CRM should be kept in the carton case and stored at cool and dark place.
2. On the expiration of validity of certification for these CRMs, it is going the test at present. It will be reported on JSAC journal or the homepage after the test result have been obtained.

Preparation of CRM and confirmation of its homogeneity

1. Necessary amount of organic complexes, tetraphenyl lead, cadmium cyclohexane butyrate, chromium(III)acetylacetonate, and mercury cyclohexane butyrate were dissolved in toluene. The toluene solution was poured to necessary amount of the polyester oligomer (liquid) and mixed well. After addition of curing catalyst, the mixed solution was poured to molds, aluminum rings of 40 mm in radius and 5 mm depth that placed on a glass plate, and let them stand for 6 ~ 12 hours. In this way, 360 disks each of JSAC 0631 and 0632 candidates were obtained.

Hardened disks were planed both faces with milling machine to control the thickness in 4.00 ± 0.05 mm, and finished with buffing machine.

2. 20 disks each were sampled at random from two groups, and determined concentrations of Pb, Cd, Cr and Hg with fluorescent X-ray analysis. The analysis was executed two times independently ($n=2$) in order to confirm homogeneity of the plastic disks. As the results, the standard deviation between bottles was very small (impossible to calculate for some cases). It means the disks are homogeneous enough.

Procedure for certification of the concentration

The certified values of metal contents in these CRMs were obtained by statistical calculation of

the results of an interlaboratory comparison study performed with 24 laboratories. 24 disks were extracted at random, and distributed to the laboratories. Laboratories crushed disks into tips and then determined the concentrations of Pb, Cd, Cr and Hg by chemical analysis referring the manual#. The manual was sent to laboratories together with disks and requested to report data from two independent analyses. Analytical methods applied are shown in Table 1.

#: The manual is submitted to the official report of Japan Chemical Industry Association, "Standardization of analytical method for trace amount of certain metal elements in chemical products", 2003, funded from the Ministry of Economy, Trade and Industry.

1. Briefings of analytical methods applied in laboratories.

(1) Acid decomposition in closed system—Inductively coupled plasma mass spectrometry (ICP-MS)

After microwave digestion (in a closed vessel) of the sample with nitric acid or the like, the solution was sprayed into inductively coupled plasma of ICP-MS system. Ion currents of Pb, Cd, Cr and Hg at their m/z were measured to determine their quantities.

(2) Acid decomposition in closed system—Inductively coupled plasma-optical emission spectrometry (ICP-OES)

After microwave digestion (in a closed vessel) of the sample with suitable acid mixture that contained nitric acid, the solution was sprayed into inductively coupled plasma of ICP-emission spectrometer. Intensities of each spectral line of Pb, Cd and Cr were measured to determine their quantities.

(3) Acid decomposition in open system—Inductively coupled plasma-optical emission spectrometry (ICP-OES)

After acid decomposition of the sample with suitable acid mixture that contained nitric acid, the solution was sprayed into inductively coupled plasma of ICP-emission spectrometer. Intensities of each spectral line of Pb, Cd and Cr were measured to determine their quantities.

(4) Sulfuric acid carbonization·ashing·alkali fusion—Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Carbonization of the sample with conc. sulfuric acid at first, followed by ashing the product to oxidize metals, applied alkali fusion and then dissolved the fused material with suitable acid. The solution was sprayed into inductively coupled plasma of ICP-emission spectrometer. Intensities of each spectral line of Pb, Cd and Cr were measured to determine their quantities.

(5) Acid decomposition in closed system—Reduction airtation atomic absorption spectrometry

After microwave digestion (in a closed vessel) of the sample with suitable acid mixture that contained nitric acid, Hg component in the solution was reduced to metallic Hg by addition of Sn(II) solution. Hg vapor generated by airtation to the solution was led to atomic absorption spectrometer to determine its quantity.

(6) Reflux cooling acid decomposition—Reduction airtation atomic absorption spectrometry

The sample was decomposed with nitric acid, sulfuric acid and K-permanganate in a flask attached a reflux condenser. After decomposition of residual nitrous acid by addition of urea solution, excess K-permanganate was reduced by addition of hydroxyl ammonium chloride solution. Hg salts in the solution were reduced to metallic Hg by addition of SnCl_2 solution, and Hg vapor generated by airtation was introduced to atomic absorption spectrometer to determine Hg concentration.

(7) Thermal vaporization—Au amalgam atomic absorption spectrometry

Hg vapor generated by igniting the sample was collected by Au-amalgamation. Amalgam was heated again to vaporize Hg vapor at a time, and the vapor was introduced to atomic absorption spectrometer to determine Hg.

(8) Various methods of sample treatment other than above were applied by a few laboratories.

2. Operation of the interlaboratory comparison study

The study was operated in the term, April through May, 2006.

3. Evaluation of results and their certification

z scores in robust method* for every reported values of 24 laboratories were calculated, and the values providing absolute value of *z* scores more than 3 were rejected as outliers. Then, average, 95% confident interval (U95%) and standard deviation (SD) were calculated with the usual way**. These 3 kinds of values are shown in Table 1, average as certified value, \pm U95% as its uncertainty.

* Submitted to ISO 5725-5:1998

** Submitted to ISO 5725-2:1994

Date of certification

July 10, 2006

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

Analysis Center, Co., Ltd.

Chemicals Evaluation and Research Institute, Japan

Chugai Technos Corp.

Dia Analysis Service Inc.

Harison Toshiba Lighting Corp.

Ibiden Engineering Co., Ltd.

Japan Quality Assurance Organization

Japan Research Institute, Ltd.

Kankyo Giken Co., Ltd.

Kurita Analysis Services Co., Ltd.

Mitsui Chemical Analysis and Consulting Service Inc.

NEC Facilities, Ltd.

Nihon Environmental Services Co., Ltd.

Panasonic Electronic Devices Co., Ltd.

Shimadzu Techno-Research Inc.

Sumiko Techno-Research Co., Ltd.

Sumitomo Metal Technology, Inc.

The Knights of Environmental Science Co., Ltd.

Tohoku Ryokka Kankyo-Hozen Co., Ltd.

Tokai Techno Co.

Tomoegawa Corp.

Toray Research Center Inc.

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