The Japan Society for Analytical Chemistry

Certificate of Analysis

Certified Reference Material
JSAC 0611-2
JSAC 0612-2
JSAC 0613-2
JSAC 0614-2
JSAC 0615-2
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 and chromium were certified.

The CRMs are intended primarily for use in evaluating methods used in the determination of trace metallic elements 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 4.0 mm thick. 5 disks in different concentration (including a disk for blank test) are packed in a carton case as a set.

Table 1 Certified concentration

CRM	Elements	Certified value ± uncertainty* μg/g	Interlab. standard deviation, *(SD)* μg/g	Number of data applied, *(N)*	Main methods of analyses**
JSAC 0611-2 (for blank test)	Pb	0.00 ± 0.06	0.11	16	(2), (3), (4), (5)
	Cd	0.00 ± 0.01	0.01	14	(2), (3), (4), (5)
	Cr	0.00 ± 0.04	0.08	15	(2), (3), (4), (5)
JSAC 0612-2	Pb	24.2 ± 0.3	0.5	16	(2), (3), (4)
	Cd	8.6 ± 0.2	0.4	17	(2), (3), (4)
	Cr	24.3 ± 0.4	0.8	18	(2), (3), (4)
JSAC 0613-2	Pb	48.5 ± 0.7	1.3	17	(2), (3), (4)
	Cd	21.9 ± 0.6	1.2	18	(2), (3), (4)
	Cr	48.8 ± 0.5	1.0	17	(2), (3), (4)
JSAC 0614-2	Pb	95.9 ± 1.8	3.5	18	(2), (3), (4)
	Cd	43.0 ± 1.3	2.6	19	(2), (3), (4)
	Cr	96.6 ± 1.3	2.5	17	(2), (3), (4)
JSAC 0615-2	Pb	192.9 ± 3.0	5.7	17	(2), (3), (4)
	Cd	86.6 ± 2.4	4.9	19	(2), (3), (4)
	Cr	194.1 ± 2.1	4.1	17	(2), (3), (4)

* Uncertainty was calculated by the following equation; (Student's t $\times$SD)$\div\sqrt{N}$

** 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 X-ray intensity.
5. This CRM contains compounds of Pb, Cd and Cr. Be careful at handling.

Storage of CRM and expiration of certification

The CRM should be stored in the carton case at room temperature and no exposure to direct sun light.

On the expiration of validity of certification for these CRMs, the sample is periodically tested the stability and it will be reported on JSAC journal or the web-site from the test result.

Preparation of CRMs and confirmation of their homogeneity

Weighed necessary amount of organic complexes, Cr(Ⅲ)-acetyl acetonate, Cd-cyclohexane butyrate and tetraphenyl-Pb 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, aluminum rings of 40 mm in radius and 5 mm depth were placed on a glass plate, and let them stand for 6 ~ 12 hours.

Hardened disks were planed both faces with milling machine to control the thickness in 4.00± 0.02 mm, and finished with buffing machine.

Disks in 5 concentration levels, 125 disks for each level, were manufactured. 10 disks were extracted at random from every level, and determined concentrations of Pb, Cd and Cr with fluorescent X-ray analysis in order to confirm homogeneity of disks. Relative standard deviations of fluorescent X-ray intensity were less than 3% for Pb, less than 1% for Cd and less than 2% for Cr. From the results, it is proved that the polyester disks are homogeneous well.

Procedure for certification of the concentration

The certified values of metals in these CRMs were obtained by statistical calculation of the results of an interlaboratory comparison study performed with 19 laboratories. In the study, number of elements to be measured were indicated 3 shown in Table 1, and analytical methods were limited as shown in "Manual for analysis" sent to laboratories from JSAC. The details of the manual are 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 and industry.

1. Briefings of analytical methods in the manual.

(1) Reflux cooling acid-decomposition—reductive vaporization atomic absorption spectrometry

Decompose the sample with nitric acid, sulfuric acid and potassium permanganate. After decomposition of residual nitrous acid by addition of urea, reduce excess K-permanganate by addition of hydroxylammonium chloride. Reduce Hg salt in Hg by addition of tin(II) chloride reagent and pass air stream into this solution to generate Hg vapor. Introduce the stream to atomic absorption spectrometer.

(2) Open system acid-decomposition—high frequency (inductively coupled) plasma atomic emission spectrometry

Decompose the sample with sulfuric acid, nitric acid and hydrogen peroxide solution. Spray the decomposed solution into inductively coupled plasma torch and measure the intensities of atomic spectra of Cd and Cr.

(3) Closed system acid-decomposition—high frequency (inductively coupled) plasma mass-spectrometry

Decompose the sample with suitable reagents* using microwave heater and spray the decomposed solution into inductively coupled plasma torch. Measure intensities of ion currents of Cd, Cr, Pb and internal standard at their m/z. Cd, Cr and Pb are quantified from their intensity ratios of ion current to internal standard. For Hg, spray the microwave-decomposed solution after addition of K- permanganate and sulfuric acid and measure ion current at m/z of Hg.

* There are 3 kinds of acid composition used in microwave decomposition.

(4) Closed system acid decomposition—high frequency (inductively coupled) plasma atomic emission spectrometry

Decompose the sample with suitable reagents* using microwave heater and spray the decomposed solution into inductively coupled plasma torch. Measure intensities of atomic spectra of Cd, Cr and Pb.

(5) Closed system acid decomposition—electrothermal atomic absorption spectrometry

Decompose the sample with suitable reagents* using microwave heater and apply the decomposed solution to electrothermal atomic absorption spectrometer to measure the atomic absorption of Pb. Standard addition method may be used in necessity.

(6) 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.

(7) Quartz glass tube combustion—ion chromatography

(8) Flask combustion—ion chromatography

2. Operation of interlaboratory comparison study

The study was operated in the term, May through July, 2011.

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 not accepted as they are 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, ±U95%

as uncertainty.

** Submitted to ISO 5725-5:1998

*** Submitted to ISO 5725-2:1994

4. Traceability

The certified value of this CRM is determined in accordance with the analysis procedure, IEC 62321 and JSAC-D1001.

Please refer to ISO/IEC Guide99:2007, item 2.41 and ISO Guide35:2006.

Date of certification

March 1, 2012

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

SGS Japan Inc.
Chemicals Evaluation and Research Institute, Japan
KOA Corporation
Konica Minolta, Inc.
Toho Kaken Incorporated.
Shimadzu Technoresearch Co.
Sumitomo Metal Technology Inc.
TDK Corporation.
DJK Corporation CO,.LTD.
Toray Research Center Co.
NIDEC CORPORATION
NGK INSULATORS, LTD.
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