

The Japan Society for Analytical Chemistry

Certificate of Analysis

Certified Reference Material

JSAC 0621

JSAC 0622

JSAC 0623

JSAC 0624

JSAC 0625

Plastics (disk form)

for Fluorescent X-ray Analysis of Trace Mercury

These certified reference materials (CRMs) consist of polyester disks whose concentrations of trace mercury were certified.

The CRMs are intended primarily for use in evaluating methods used in the determination of trace mercury 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 of Hg

CRM	Certified value \pm uncertainty* $\mu\text{g/g}$	Interlab. standard deviation	Number of data applied	Main methods of analyses**
JSAC 0621 (for blank test)	Reference value : Less than 1		6	(1), (2), (3), (4) (5), (6), (7)
JSAC 0622	10.0 ± 0.2	0.4	15	(1), (2), (3), (4) (5), (6), (7)
JSAC 0623	49.0 ± 1.0	1.7	14	(1), (2), (3), (4) (5), (6), (7)
JSAC 0624	121.1 ± 2.2	4.0	15	(1), (2), (3), (4) (5), (6), (7)
JSAC 0625	244.4 ± 6.3	11.3	15	(1), (2), (3), (4) (5), (6), (7)

* 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 X-ray intensity.

Notices for Fluorescent X-ray analysis

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

Full attention to following article 2 is necessary, otherwise it is possible to get result with very large errors.

1. On analysis line

Hg-L α line and Hg-L β line can be used for analysis of Hg. However, the energy of Hg-L β line is too close near to it of Br-K α line whose Br is contained in the resin as fire retardant. Then peaks will be overlapped. Therefore, it is recommended to use Hg-L α line (9.99 keV) in this case.

2. Primary X-ray output

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 is less than followings. Especially it is important when wavelength dispersion type 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

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, 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

Weighed necessary amount of organic complexes, 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, 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.

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, 220 disks for each level, were manufactured. 20 disks were extracted at random from every level, and analyzed concentrations of Hg with fluorescent X-ray analysis in order to confirm homogeneity of disks. As the results, between-bottle standard deviations including repeatability standard deviations were 0.6 ~ 1.1 % for JSAC 0623~0625 and was 2.6 % for JSAC 0622. Between-bottle standard deviations themselves for every

specimens were so small that cannot be calculated. From the results, it is proved that the polyester disks are homogeneous well.

Procedure for certification of the concentration

The certified values of mercury in these CRMs were obtained by statistical calculation of the results of an interlaboratory comparison study performed with 15 laboratories. Test samples in disk form were extracted at same intervals in casting order, and distributed to the laboratories. Laboratories crushed disks and then determined the concentrations of 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) Reflux cooling acid-decomposition – reductive vaporization atomic absorption spectrometry

Decompose the sample with nitric acid, sulfuric acid and K-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) Closed system acid-decomposition – reductive vaporization atomic absorption spectrometry

Decompose the sample with suitable reagent in a closed system, and determine Hg concentration applying the method (1) in above.

(3) Open system acid-decomposition – thermal vaporization – atomic absorption spectrometry

Decompose the sample with suitable reagents in an open system, heat obtained solution in an inert gas stream to vaporize Hg, heat obtained solution in an inert gas stream to vaporize Hg. Introduce the stream to atomic absorption spectrometer.

(4) Closed system acid decomposition – electrothermal heating – atomic absorption spectrometry

Decompose the sample with suitable reagents in a closed system, heat obtained solution using electric furnace in an inert gas stream to vaporize Hg. Introduce the stream to atomic absorption spectrometer.

(5) High temperature combustion – reductive vaporization atomic absorption spectrometry

Burn chips of the solid sample at high temperature, and treat the combustion product according to the method described in (1).

(6) Closed system acid-decomposition – high frequency (inductively coupled) plasma atomic emission spectrometry

Decompose the sample with suitable reagents in a closed system, spray the obtained solution into the inductively coupled plasma. Measure spectral intensity of Hg to determine the concentration.

(7) Closed system acid-decomposition – high frequency (inductively coupled) plasma-mass spectrometry

Decompose the sample with suitable reagents in a closed system, spray the obtained solution into the inductively coupled plasma. Measure amount of ion current at m/z of Hg to determine the concentration.

2. Operation of interlaboratory comparison study

The study was operated in the term, July through August, 2005.

3. Evaluation of results and their certification

z scores in robust method* for each reported analytical results from 15 laboratories 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, \pm U95% as its uncertainty.

* Submitted to ISO 5725-5:1998

** Submitted to ISO 5725-2:1994

Date of certification

December 1, 2005

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

Analysis Center Co.

Chemicals Evaluation and Research Institute, Japan

Environmental Giken Co.

Environmetal Technology Service Co.

Ibiden Engineering Co.

JFE Technoresearch Co

Kobelco Kaken Co.

Mitsui Kagaku Analysis Center Co.

Nihon Soken Co.

Nippon Steel Technoresearch Corp.

Nittech Research Corp.

Shimadzu Technoresearch Co.

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