

*The Japan Society for Analytical Chemistry*

## Certificate of Analysis

### Certified Reference Materials JSAC 0641 and JSAC 0642

#### Plastics (powder)

#### for Chemical Analysis of Polybrominated Diphenyl Ethers

This certified reference material (CRM) consists of polyester resin powder whose concentration of polybrominated diphenyl ethers were certified.

This CRM is intended primarily for use in evaluating methods used in the determination of polybromodiphenyl ether in moldings or other products made of plastics. It will be useful to analyze this CRM comparatively with the analytical samples in case of evaluating validity of analytical results of samples.

This CRM is polyester resin powder, less than 0.15 mm in particle size. 25 g of CRM is bottled in an amber glass bottle and the bottle is packed in a carton box.

Table 1 Certified concentration

JSAC	Elements	Certified value $\pm$ uncertainty* $\mu\text{g/g}$	Interlab. standard deviation	Number of data applied	Main methods of analyses**
JSAC 0641	Deca-BDE	27.2 $\pm$ 2.6	4.7	15	①、②
	Nona-BDE	21.1 $\pm$ 2.7	4.8	15	①、②
	Octa-BDE	46.9 $\pm$ 6.6	11.3	14	①、②
	Hepta-BDE	60.0 $\pm$ 4.7	7.8	13	①、②
	Hexa-BDE	16.4 $\pm$ 2.0	3.6	15	①、②
	Penta-BDE	28.2 $\pm$ 3.8	6.8	15	①、②
	Tetra-BDE	18.7 $\pm$ 2.5	4.1	13	①、②
	Bromine	170 $\pm$ 5	9	15	③、④、⑤
JSAC 0642	Deca-BDE	137 $\pm$ 13	22	13	①、②
	Nona-BDE	113 $\pm$ 15	25	13	①、②
	Octa-BDE	287 $\pm$ 42	73	14	①、②
	Hepta-BDE	361 $\pm$ 30	47	12	①、②
	Hexa-BDE	75 $\pm$ 13	24	15	①、②
	Bromine	792 $\pm$ 12	20	14	③、④、⑤

- \* Uncertainty was calculated by the following equation:  
(Student's  $t \times$  interlab standard deviation)  $\div$  (root of number of data applied)
- \*\* For (No.), refer to "Procedure for certification of concentration" 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.

### 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 film bag in order to avoid the CRM from environmental contamination.
2. On the expiration of validity of certification for this CRM, see the homepage of JSAC (<http://www.jsac.or.jp/srm.html>).

### Preparation of CRM and confirmation of its homogeneity

Weighed necessary amount of TOKYO CHEMICAL Decabromodiphenyl ether (CAS number 1163-19-5, purity of  $C_{12}Br_{10}O$  is 95.917 %) and Great Lakes DE-79<sup>TM</sup>(Octabromodiphenyl Oxide, CAS number 32536-52-0,  $C_{12}H_{10-n}Br_nO$ ( $n=5-10$ )) were dissolved in toluene. For JSAC 0641, Great Lakes DE-71<sup>TM</sup>(Pentabromodiphenyl Oxide, CAS number 32534-81-9,  $C_{12}H_{10-n}Br_nO$ ( $n=3-7$ )) was also used. The toluene solution was poured to the polyester oligomer (liquid) and mixed sufficiently. After addition of curing catalyst, the mixed solution was poured to molds in order to make polyester plates, approximately 520 mm square and 3 mm thick.

Hardened plates were broken to 1.5 mm size pieces by a cutter mill whose components were made of high speed steel and powdered by ball mill whose components were made of alumina ceramic. Polyester powder discharged from exit screen of the mill were sieved to get less than 0.15 mm size particles.

Each 25 g of homogenized polyester powders were kept into 340 amber glass bottles as candidate CRMs of JSAC 0641 and JSAC 0642 respectively.

For each candidate CRM, two portions of 1.50 g of powder were sampled from 10 bottles extracted in same intervals in casting for homogeneity test of bromine(Br) by fluorescent X-ray analysis. A test portion was put in a vinyl chloride ring(30 mm diameter and 5 mm height cylinder) on the flat table and pressed by 100 kg/cm<sup>2</sup> pressure into briquette shape test sample. Bromine of each sample was determined two times in repeatability condition. Relative combined standard deviation of within- and between-bottles was 1.3 % to 2.0 % for JSAC 0641 and 1.5 % to 1.6 % for JSAC 0642.

For each candidate CRM, two portions of powder were also sampled from 10 bottles for

homogeneity test of bromine(Br) by combustion in silica glass tube—ion chromatography. Relative combined standard deviation of within- and between-bottles was 2.9 % to 5.9 % for JSAC 0641 and 3.6 % to 4.7 % for JSAC 0642.

From the results it is proved that the polyester powders are homogeneous well.

### **Procedure for certification of the concentration**

For each candidate CRM, 17 bottles were extracted in same intervals in casting for interlaboratory cooperative study and distributed to the 17 laboratories. Analytical methods depended on IEC 62321, 7. Determination of PBB and PBDE in Polymers by GC-MS. The certified values were obtained by statistical calculation of the results of all laboratories according to Quality Manual JSAC CRM QM 002.

#### **1. Briefings of analytical methods in interlaboratory cooperative study.**

##### **(1) PBDEs**

- ① Soxhlet extraction—clean up through silica gel column — Gas chromatograph-mass spectrometry(GC-MS)
- ② Solvent extraction — Gas chromatograph-mass spectrometry(GC-MS)

##### **(2) Bromine**

- ③ Combustion in silica glass tube—ion chromatography
- ④ Combustion in flask—ion chromatography
- ⑤ Conversion to ash by heating— Gas chromatography

#### **2. Operation of interlaboratory comparison study**

The study was operated in the term, October, 2008 through January, 2009.

#### **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.

\*\* Submitted to ISO 5725-5:1998

\*\*\* Submitted to ISO 5725-2:1994

### **Date of certification**

June 8, 2009

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

Chugai Technos Co., Ltd.

Institute for Industrial Pollution and Medicals

Japan Food Research Laboratories

Kankyo Asist Co.

Kankyo Giken Co.  
Kobelco Kaken Co.  
Mitsubishi Chemical Analytech. Co., Ltd  
Mitsui Kagaku Analysis Center Co.  
Nissan Arc Co.  
Nitto Analysis Center Co.  
Nittech Research Corp.  
Shimadzu Technoresearch Co.  
Sumika Chemical Analysis Service Ltd.  
Toray Research Center Corp.  
Toshiba Environmental Solutions Corp.  
Toshiba Nanoanalysis Corp.  
Towa Environment Science Co., Ltd.

17 laboratories

**Distributor**

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