

Development of plastic certified reference materials (CRMs) to cope with restrictions on hazardous substances

— CRMs for analysis of heavy metals and brominated flame retardants regulated by RoHS directive —

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The RoHS directive had a significant impact on Japanese industry. Complying with this directive requires evaluating the raw materials, especially plastics, that are used in electrical and electronic equipment. However, few plastic reference materials (RMs) were appropriate for evaluation. In response to industry requests, we undertook rapid development of plastic RMs. First, we considered the development of RMs that were needed. To assign property values to candidate RMs, methods important for the homogeneity evaluation, digestion and determination were developed by various trials and errors. We aimed to register our calibration and measurement capabilities to the key comparison database in order to make our CRMs acceptable worldwide. In this paper we introduce our activities up until now including the distribution of CRMs inside and outside Japan.

Keywords : Restrictions of hazardous substances, RoHS Directive, plastics, certified reference materials (CRMs), analysis of heavy metals, analysis of brominated flame retardants

1 Introduction: Movement starting as response to the RoHS directive, a European regulation

The “RoHS directive” or the “Restrictions of the use of certain hazardous substances in electrical and electronic equipment”^[1] is one of the European Union (EU) directives which became effective in July 2006. In Japan, there was a great upheaval because the export of electrical/electronic equipment to EU would become impossible unless the requirements of the restrictions were met. Although this directive was for electrical/electronic equipment, the parts are made from raw materials and the final products are made by assembling the parts, and any parties of industries could not remain indifferent to the restrictions. The targeted hazardous substances were cadmium (Cd), mercury (Hg), lead (Pb), hexavalent chromium [Cr (VI)], polybrominated biphenyl (PBB), and polybrominated diphenyl ether (PBDE). The thresholds of restrictions (maximum values tolerated) were 100 mg/kg for Cd and 1000 mg/kg for the other substances. The PBB and PBDE belong to the group called brominated flame retardants, and their structural equations are shown in Fig. 1. There are many isomers depending on the number and position of bromine (Br). Since this was not a restriction on the total amount, a problem could develop even if a single part contained high concentration. It can be said that it is a rather unreasonable restriction on concentration.

The objectives of the RoHS directive are to remove the differences in legal regulations among the EU nations pertaining to the restriction of hazardous substances used in electrical/electronic equipment, as well as the protection of

health of users, the protection of health of workers involved in the processing of waste electrical/electronic equipment, the reduction of environmental and resource loads, and the promotion of resource recovery. Although the RoHS directive is just one of several restrictions, it should be considered as part of the movement for environmental protection. Moreover, not limited to electrical/electronic equipment, there are laws established for the restriction of use of hazardous substances, the quality labeling of products, and the recovery of waste products in many countries along the line of these objectives, and the basic principle is to stop using hazardous or specific substances considering the future. Therefore, the demand for measurement of hazardous or specific substances in products is expected to increase in the future.

The RoHS directive was revised in 2001 (commonly called RoHS2 or new RoHS; the new directive has replaced the old as of January 3, 2013).^[2] In the new directive, the restriction on the range of target increased, but the compounds under restriction and the concentration thresholds did not change. Other than the RoHS directive, there are the WEEE directive (directive on waste electrical and electronic equipment),^[3] the ELV directive (directive on end-of-life vehicles),^[4] and the REACH regulation (the EU regulation on the registration, evaluation, authorization and restriction of chemicals)^[5] which is a comprehensive regulation of chemical substances. Also, JIS C 0950:2008, which is commonly called the Japanese RoHS or J-Moss, was adopted to regulate the labeling of the content of specific substances. In the present paper, we discuss the development of RMs at the National Metrology Institute of Japan (NMIJ)

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which worked to support industry to satisfy the conditions for exporting electrical/electronic equipment to EU, particularly focusing on the parties involved in the RoHS directive. The early stage of the development was described in an interview article of the *Kankyo Shinbun* (The Environment News).^[6]

2 Setting of the research scenario

2.1 Impact of the RoHS directive and demand from industry

A representative event occurred in October 2001. The import of a product of a certain major Japanese company was banned by the Dutch authorities because it contained Cd surpassing the restricted quantity in the plastic parts. Immediately after this, many companies, not only the company involved, scrambled to figure out how they should respond. The response to the RoHS directive which was introduced as a unified restriction of EU, not just the Netherlands, rose as an urgent issue. Although the directive itself was for electrical/electronic equipment, it was recognized as a problem for all manufacturers of the final products and the industrial organization, Japan Electronics and Information Technology Industries Association (JEITA), as well as the entire supply chain (network of parts suppliers) including the parts and materials manufacturers on the upstream of the chain. Some companies worked on the management of the flow from design to shipment; for the purpose, they reorganized company sections, conducted questionnaire surveys of clients,

and introduced specialized analytical instruments needed. However, those companies were minorities and the ability to respond to the directive affected corporate survival. In such a situation, the adequacy to the regulation was unknown until the raw material or product was actually tested. This became a problem for the testing laboratories and analytical instrument companies involved, the Japanese industries were shaken, and all concerned bodies including the Japanese government had to cope with this historically significant problem. Against this background, in the early summer of 2003, NMIJ received an inquiry on whether we could develop plastic CRMs used in analyses which must be done to comply with the RoHS directive. Figure 2 shows the overview of the research scenario. The request matched the potentials in which the research groups excelled, and we launched the R&D to solve the problem.

At the time, the Inorganic Standards Section, Inorganic Analytical Chemistry Division, NMIJ had been working on the RMs for materials such as metals and ceramics, and had abundant experiences in inorganic analysis. In particular, we were studying atomic spectrometry such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), and were working on the methods for using ICP-MS with the isotope dilution method. Also our main mission was the development, maintenance, and supply of metrological

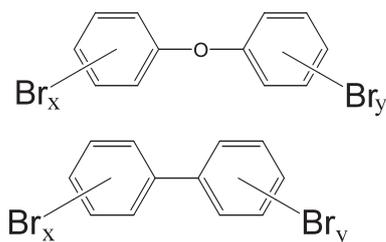


Fig. 1-a PBDE (polybrominated diphenyl ether: top) and PBB (polybrominated biphenyl: bottom)

x and y represents the number of Br. There are many isomers depending on the number and position of Br.

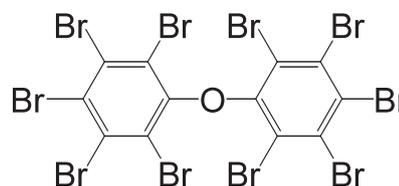


Fig. 1-b DBDE (decabrominated diphenyl ether) which is one of PBDE

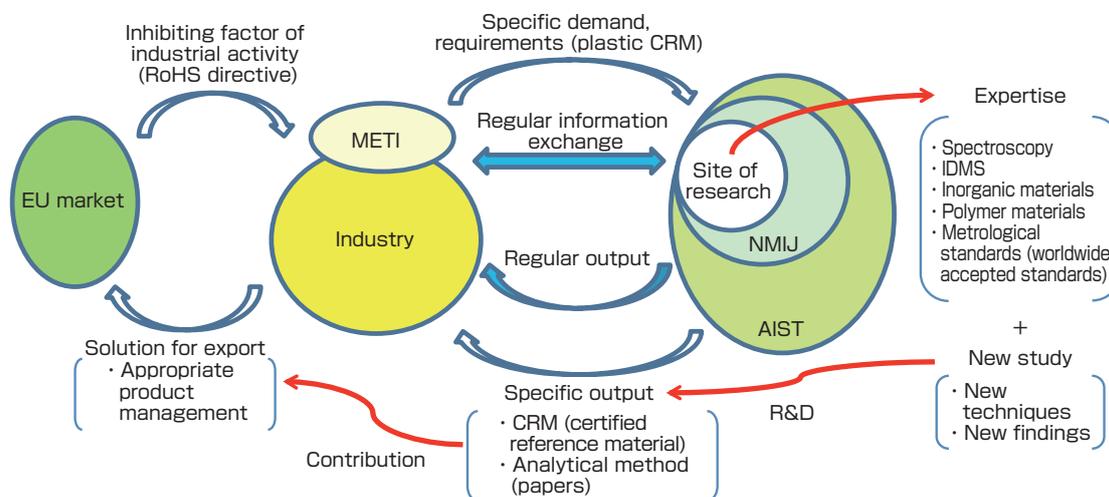


Fig. 2 Outline of the research scenario

standards, and therefore, we were engaging in research with priority on traceability to the international system of units (SI) which are necessary for international activities. "Traceability" is the property of a measurement result whereby the result can be related to a superior standard through a chain of assignments of property values, and when it is used as an adjective, the terminology "traceable" is used. To distinguish from traceability related to food origin recording, it is formally called metrological traceability. The Polymer Standards Section, Advanced Material Division (at the time) had abundant experiences in quantification of organic substances coexisting in plastic.

In the supply chain, the communication of data from the raw material stage was important, and the system construction for such communication was urgently required. However, considering that the final responsibility would lie on the direct supplier which supplied the products to EU, it was necessary for the supplier to ensure that the restricted substances in the final products were below threshold to respond properly to the RoHS directive, and therefore, precise analysis of them was needed for verification. To respond to these problems, an analytical method which was internationally accepted was particularly necessary. It is not easy to objectively show that one's own analytical method or result is appropriate and accurate. However, for a laboratory itself to analyze the CRM traceable to the appropriate reference and to show that the results are in agreement with the certified value (content or property value given in the certificate issued with the CRM) is one way of conducting general and effective internal-control of precision (to check whether the analytical value can be obtained appropriately by oneself).

For this issue, there were very few appropriate CRMs in 2003. It is said that the authorities who set forth the EU restrictions make decisions based on high ideals especially for the environment, and in fact, the RoHS directive was a restriction set forth with primary focus on ideals. That is, in the course of setting the directive, specific methods for investigating the compliance to the restriction were left behind, and the availability of appropriate CRMs was not considered at all. Meanwhile, it should be mentioned that there were two CRMs available [BCR-680 and BCR-681 from the Institute for Reference Materials and Measurements (IRMM)] which were given certified values for heavy metals and others in PE (polyethylene) resin. However, these CRMs were not created in consideration of the RoHS directive; therefore, the concentration levels for the restricted substances did not comply with the RoHS directive, and it did not comply at all with the restriction for brominated flame retardants which were ones of the six restricted substances.

There was no international standard method for analysis as a premise to use RMs, and the work of setting such a standard was pushed. Japan actively participated in this movement. The IEC 62321:2008^[7] was the first IEC standard for the quantification of six restricted substances, and NMIJ contributed by providing the candidate RMs (clearly written as NMIJ CRM 8112-a and

NMIJ CRM 8113-a in IEC 62321:2008) which were being developed, as samples for inter-laboratory comparisons in the early stages of the standard setting. This standard was revised as family type standards in the regular revision of 2013, where the contents were updated and the future diversification of RoHS regulations was considered. The updates were: IEC 62321-1:2013 (Introduction and overview); IEC 62321-2:2013 (Disassembly, disjunction and mechanical sample preparation); IEC 62321-3-1:2013 (Screening - Lead, mercury, cadmium, total chromium and total bromine using X-ray fluorescence spectrometry); IEC 62321-3-2:2013 (Screening - Total bromine in polymers and electronics by Combustion - Ion chromatography); IEC 62321-4:2013 (Mercury in polymers, metals and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS); and IEC 62321-5:2013 (Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS).

The awareness of the problem was high in the Ministry of Economy, Trade and Industry (METI) which held jurisdiction over issues related to the manufacture and export of electrical/electronic products. Therefore, with METI support, we were able to conduct the project "Research for Infrastructure Development on Environment-Conscious Design Promotion" of the New Energy and Industrial Technology Development Organization (NEDO) for two years (2005 to 2006), and NMIJ was able to develop several CRMs in a short period. For the movements for the new RoHS2, METI is engaging in activities such as holding seminars with the industrial associations.

2.2 Why plastics?

As mentioned earlier, the target substances of the RoHS directive were Cd, Hg, Pb, Cr (VI), PBB, and PBDE, and the thresholds of restrictions were 100 mg/kg for Cd and 1000 mg/kg for other substances. Most of the interests were focused on these substances in plastics, and the CRMs with a plastic matrix were in demand. The background for the demand of plastic CRMs was as follows: many plastic parts are used in electrical/electronic equipment; historically, restricted substances had been intentionally introduced to plastic for coloring and flame retardation; although intentional introduction of such substances is not done today, old plastics may become mixed in the recycling process; and there were hardly any CRMs with a plastic matrix at the time.

Due to the globalization and borderlessness of the market, the demand for traceability is increasing for chemical standards. When traceability is demanded, an analysis certificate in which the analytical values by testing laboratories can be internationally and mutually recognized is essential. Therefore, the provision of CRMs with traceability which complies with the international Mutual Recognition Arrangement (MRA) for the metrological standards of the International Committee for Weights and Measures (CIPM) under the Metre Convention is important. The developed RMs were of the following:

acrylonitrile butadiene styrene (ABS) resin, polypropylene (PP) resin, polyvinyl chloride (PVC) resin, and polystyrene (PS) resin which are plastics used widely today. Most of the plastics used in electrical/electronic equipment were one of these types of resin.

As the matrix for CRMs for heavy metal analysis, we considered PE or ABS resins which were frequently used in electrical/electronic equipment, and the ABS resin was selected for the first CRM because the CRMs of BCR which existed at that time were made of PE resin. CRMs of PP and PVC resins were produced later.^[8] Brominated flame retardants were mainly used in the body of TV sets, and they were mostly made of PS type plastic [ABS resin, high-impact polystyrene (HIPS) resin, and PS resin]; therefore, a candidate was selected among these for the brominated substances. For selecting which of the PS types would be used, we considered the ease of handling during analysis. For heavy metals, the sample could be digested completely since the analysis was for elements. On the other hand, for brominated flame retardants, complete digestion could not be applied since the analysis was for molecules; therefore, an appropriate extraction method was necessary. Since it was known that insoluble components were present when ABS and HIPS resins were dissolved in solvents, first, PS resin was selected because a homogenous solution could be made, and CRMs made of PVC resin were later produced.

2.3 Scenario from the international comparison to CMC registration

Since the impact of the RoHS to plastics was great, NMIJ focused on plastics and started the activities to develop and provide CRMs as soon as possible.^{[9][10]} At the same time, it was necessary that the CRMs be RMs which complied with CIPM MRA, and that the analysis results would be accepted worldwide. For the compliance of CRMs with CIPM MRA, the followings are needed : specifically, a management system of CRM production (management system based on standards or guides such as the ISO/IEC 17025 or ISO Guide 34) is constructed, and its technological capability is approved by several overseas experts in a so-called peer-review process. Furthermore, the ability to create the CRMs, a part of the calibration and measurement capability (CMC), must be claimed to the KCWG [one of the working groups (WGs) of the CCQM for Key Comparisons and CMC Quality] with available evidences from international comparisons (will be explained in subchapter 4.3), and then must be listed in the Key Comparison Database (KCDB)^[11] of the International Bureau of Weights and Measures (BIPM). When the CRM development was started, activities towards CMC registration were done alongside the development. The details will be discussed later.

2.4 Steps for deciding the RM matrices, target analytes, concentrations, and forms

Since the analytical methods for heavy metals and brominated

flame retardants are generally different, we decided to create different CRMs. However, for heavy metal analysis, the brominated flame retardants were included from the second series of NMIJ CRM 8112-a for heavy metal analysis, to leave possibilities for the future. The brominated flame retardants were restricted as compounds, and there should be no problem if total Br was measured and the value was sufficiently low. Since the minimum Br content in the case of 1000 mg/kg for compounds occurs in the case of monobrominated diphenyl ether (details will be explained later), the added compounds was set as decabromodiphenyl ether (DBDE or BDE-209) and its quantity added was determined. There were several candidates for the heavy metal compounds to be added to the CRM, and available compounds were sought thinking that fine powder would be desirable for mixing homogeneously with plastic. Considering the ease of handling of CRMs, lead chromate (PbCrO₄) and cadmium oxide (CdO) were selected since they were not restricted by the Poisonous and Deleterious Substances Control Law [chromium (III) acetylacetonate was also used from the second series for heavy metal analysis]. Mercury (II) sulfide (HgS) was selected as Hg compound to be added to the second series for heavy metal analysis from the same perspective.

There were two types of concentration: one around the restriction value (called high concentration); and the other about one-tenth of that value (called low concentration). In the first series for heavy metal analysis, the concentrations for Cd was set at slightly over 100 mg/kg and for Pb slightly over 1000 mg/kg, and the concentration for Cr(VI) was about 250 mg/kg (each concentration in the low concentration was one-tenth of such a value). For judging the adequacy to the restriction, we designed the concentration in CRM to be lower than the restriction value from the second series for heavy metal analysis, because determining whether analytical values were lower than the restriction value would be easier.

For the concentration of brominated flame retardants in RMs, we investigated how it should be chosen considering the threshold, and decided as follows. Of the target substances PBB and PBDE, the one with the lowest Br content (mass fraction) is monobrominated diphenyl ether (molecular weight 249.1) at 32 %. Therefore, when conducting simplified screening using Br measurement by non-destructive X-ray fluorescence (XRF) analysis, the 1000 mg/kg regulation for PBB and PBDE could be kept, if it was evaluated assuming that monobrominated diphenyl ether would be contained only as Br compounds. When DBDE was used as brominated flame retardants, the Br content (mass fraction) of 32 % would correspond to DBDE of 385 mg/kg. In the NMIJ CRM which contained DEDE only as Br compounds, it was designed at slightly lower concentration than this value. That is, we developed NMIJ CRM 8108- a (polystyrene) with DBDE certified value of 317 mg/kg, and as the following lots, developed NMIJ CRM 8108- b (polystyrene) with DBDE certified value of 312 mg/kg and

NMIJ CRM 8109-a (polyvinyl chloride) with DBDE certified value of 333 mg/kg. The reason for selecting the DBDE as the added brominated flame retardant was because DBDE was advantageous in accurately determining the certified value of CRM since pure DBDE was readily available. We further developed NMIJ CRM 8110-a (polystyrene, high concentration) with DBDE certified value of 886 mg/kg. This could be used for verifying linearity when drawing a calibration curve.

There were two RM forms for heavy metal analysis: pellet (small rods or round particles of about 0.01 g to 0.03 g) for wet analysis; and disk (diameter of 3 cm and thickness of 2 mm) due to strong demand for non-destructive XRF analysis. On the other hand, there was only the disk form for brominated flame retardant. The diameter of the disks was the size of a sample holder of an ordinary XRF analysis instrument. In case of plastics, since the result of the XRF analysis was dependent on thickness, we set the thin thickness of 2 mm considering the variation in thickness of samples to be analyzed, and more than one disk could be stacked together for thicker samples if necessary.^[12] For the manufacturing method, kneading and injection molding were done (hot press was used for the first series of NMIJ CRM 8105-a and 8106-a) (Fig. 3).

2.5 Cooperating institution and manufacturing method

It was necessary to find a cooperating institution which would help us manufacture the candidate RMs. We requested preliminary consideration to Y.K. Kobunshi Giken on December 2003. After visiting the actual plant and holding thorough meetings, we witnessed the kneading process, and the manufacturing was conducted while maintaining close communication. Later, after the second series for heavy metal analysis (NMIJ CRM 8102-a, 8103-a, 8105-a, and 8106-a), we searched for a different cooperating institution because

it was necessary to increase the size of the production lot. In September 2005, preliminary kneading was conducted with the Chemicals Evaluation and Research Institute, Japan. We went to the plant for each manufacturing to communicate with the workers to achieve better homogeneity.

While manufacturing was done by a universal method, kneading/extruding was done three times to ensure homogeneity. Preliminary kneading/extruding was conducted to check whether the homogeneity was sufficient after kneading/extruding three times. To avoid loss of homogeneity due to contamination from the kneading extruder or surrounding environment, optimum care was taken to meticulously cleanse the kneading extruder at a level not normally done.

Specifically, the details of manufacturing candidate RMs for heavy metal analysis are as follows. The commercially available raw resin pellets and powdered compounds (cadmium oxide, lead chromate, chromium (III) acetylacetonate, mercury (II) sulfide, DBDE, and others) were mixed, and the mixture was formed into pellets again using the kneading extruder. Furthermore, the reformation into pellets was repeated twice to manufacture the candidate RM of high concentration. The commercially available raw resin pellets were added again to this pellet, and the stirring, mixing, and pellet forming processes were repeated three times using the kneading extruder to manufacture the candidate RM of low concentration. The disk form candidate RMs were manufactured by hot press or injection molding methods using the aforementioned candidate RMs as the raw materials. For PVC resin, the base resin was made by adding the plasticizing agent diisononyl phthalate (DINP), stabilizer, etc. to the commercial PVC resin; then, powdered cadmium oxide, lead chromate, chromium (III) acetylacetonate, and mercury (II) sulfide were mixed with the base resin, and the mixture was

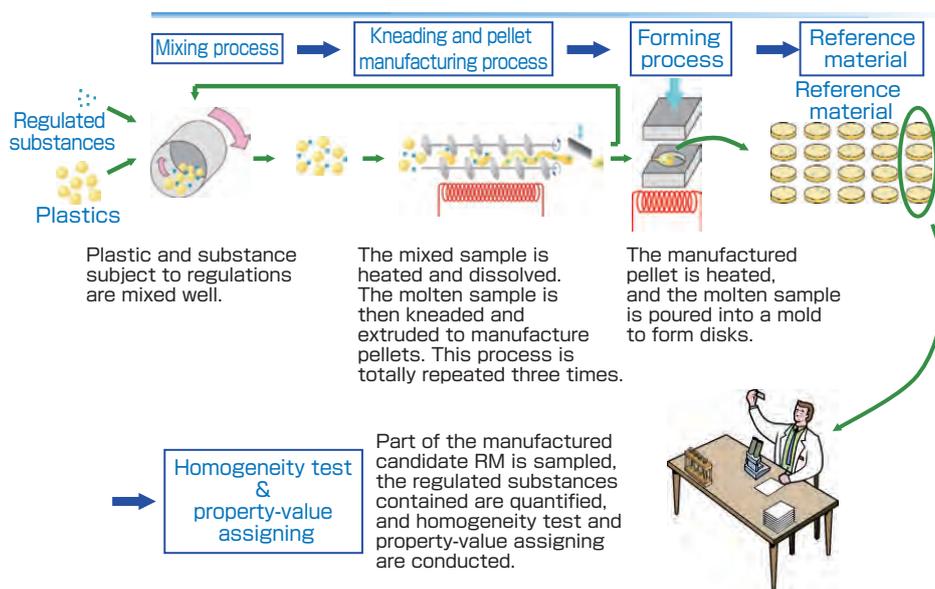


Fig. 3 Manufacturing process of plastic RMs (example)

Table 1. Performance in the acid and microwave digestion processes which were attempted^[13]

Acid used in digestion (number in parenthesis indicates the quantity used)	Degree of digestion achieved	Comment
95 % H ₂ SO ₄ (4 mL)	×	Turned into highly viscous blank solution
95 % H ₂ SO ₄ (4 mL) + 70 % HNO ₃ (4 mL)	◎	
95 % H ₂ SO ₄ (4 mL) + 60 % HNO ₃ (4 mL)	◎	
60 % HNO ₃ (8 mL)	×	
60 % HNO ₃ (5 mL) + 30 % H ₂ O ₂ (3 mL)	×	
60 % HNO ₃ (5 mL) + 60 % HClO ₄ (3 mL)	△	To achieve complete digestion, three microwave heating processes and two microwave heating processes were necessary.
60 % HNO ₃ (5 mL) + 60 % HClO ₄ (2 mL) + 48 % HF (1 mL)	△	
60 % HNO ₃ (5 mL) + 30 % H ₂ O ₂ (2 mL) + 48 % HF (1 mL)	×	
70 % HNO ₃ (8 mL)	○	To achieve complete digestion, the digestion containers used in a single operation had to be reduced to 5 instead of 10 used normally.

Sample: 0.1 g ABS resin pellet CRMs; Digestion device: ETHOS PLUS and ETHOS 1, Milestone

◎: Complete digestion was achieved with one microwave heating process.

○: Complete digestion was achieved with one microwave heating process (however, number of digestion containers which could be used in a single operation was limited).

△: Complete digestion was achieved by using both microwave-heating and microwave-drying processes.

×: Complete digestion could not be achieved by one microwave heating process.

formed into pellets using the kneading extruder. Using the pellets formed, the stirring, mixing, and pellet reforming processes were repeated two more times. For the RMs for brominated flame retardant analysis, disk-shaped candidate RMs were manufactured by the injection molding method using the pellets produced in the same way as those for the heavy metal analysis (for high concentration).

3 Development of the analytical method

Quick development of CRMs was demanded, and analysis was important after the manufacture of candidate CRMs. Although we had technological background which we accumulated over the years and minimum budget, those were not enough for analytical evaluation of the candidate CRMs. In particular, investigation of a digestion method was important, and we engaged in various trials-and-errors, as the situations differed according to individual samples (Table 1).^[13] For creating the CRM, multiple digestion methods and quantification ones had to be used, and it was necessary to develop alternative methods and to increase reliability, even if the best method was obtained. For Cr, the restriction was for hexavalent chromium, but there was no method for accurately analyzing the hexavalent chromium in plastics, and establishing such a method was considered difficult. Therefore, we conducted quantification of the total chromium. If the concentration of the total chromium was 1000 mg/kg or less, that of hexavalent chromium would, of course, be 1000 mg/kg or less.

3.1 Evaluation method for homogeneity

Homogeneity is extremely important for RM, and the evaluation method was considered from the stage of manufacture of the

candidate RMs. When filling the bottle with RM material after kneading/extruding, the order of filling the bottles was recorded, and the bottles from which the samples would be taken for homogeneity evaluation were selected from all bottles by stratified random sampling. We attempted homogeneity evaluation within a bottle and among the bottles assuming that sampling would be done once from one bottle purchased by the user (for disks, within disk surface and among disks). The homogeneity evaluation did not have to use quantitative values, and priority was given to making quick comparison among the samples, and it was sufficient as long as the values were proportional to the concentrations.

The homogeneity evaluation method is shown below using Cr of NMIJ CRM 8103-a (high concentration) as an example. For evaluation, 12 bottles were selected of about every 25th bottle among samples numbered by order of bottling. The measurement for homogeneity evaluation was done as follows. From the 12 bottles, 0.10 g each was sampled once, samples were digested according to an established method, and quantification was done by ICP-MS. The measurements were taken for the two isotopes of chromium (Cr-52 and Cr-53). The whole process starting with sampling was repeated again. To ensure accurate homogeneity, absolute values were not sought in the measurement.

The measurement results are shown in Table 2. The variance of measured value for the 12 samples of Cr-52 in the first round (0.74²) could be thought as a combination of variance among bottles, variance of measurement error, and variance within a bottle (non-repeated measurement). The standard deviation obtained from the combination of the variances would represent homogeneity, because the analytical value for one sampling

Table 2. Measurement example of Cr homogeneity test for NMIJ CRM 8103-a (high concentration) (the unit for each value is mg/kg)*1

Bottle	First round		Bottle	Second round	
	Concentration estimated from Cr-52 intensities	Concentration estimated from Cr-53 intensities		Concentration estimated from Cr-52 intensities	Concentration estimated from Cr-53 intensities
H001-1	273.18	272.06	H001-2	274.95	274.67
H027-1	272.65	272.22	H054-2	273.59	273.34
H054-1	272.89	271.62	H108-2	274.89	273.91
H081-1	273.33	272.87	H162-2	274.69	274.34
H108-1	273.07	271.53	H027-2	273.42	272.92
H135-1	271.91	271.50	H081-2	273.13	272.93
H162-1	272.29	271.96	H135-2	274.41	272.67
H189-1	274.62	273.12	H189-2	275.09	273.05
H216-1	273.29	273.82	H216-2	273.76	273.26
H270-1	272.54	273.26	H243-2	274.08	272.11
H243-1	272.42	273.37	H270-2	273.92	272.82
H275-1	273.91	273.04	H275-2	274.54	273.28
Average value	273.01	272.53	Average value	274.21	273.28
Experimental standard deviation	0.74	0.81	Experimental standard deviation	0.65	0.72

*1 Calibration curve was drawn using standard solutions, and the values in the table are different from the certified value due to the matrix effect of samples.

from a certain bottle will be given as the certified value. The homogeneity was calculated based on the average of four dispersions of two rounds and two isotopes, so the value would be as appropriate as possible. The relative standard uncertainty of homogeneity was 0.27 %, and it was confirmed that there was no problem in homogeneity.

For the homogeneity evaluation of the disks,^[14] for example, in the case of NMIJ CRM 8115-a (low concentration), 16 disks were selected at about equal intervals in the order of manufacture among all manufactured disks, Cd, Cr, Hg, and Pb were measured using the XRF analysis method, and the uncertainty arising from homogeneity was calculated from the variation in strength corresponding to each element. The homogeneity evaluation of Pb within disk surface was done using the XRF analysis method, and this was added to the uncertainty arising from homogeneity among disks for each element. These would be ultimately included in the uncertainty of each certified value of CRMs.

3.2 Investigation of the digestion method and the development and evaluation of the quantification method

For assigning the property values of CRMs, we decided to combine a method recognized as meeting the requirements of a primary method of measurement [only the isotope dilution mass spectrometry (IDMS) can be applied to this case] and one or more carefully evaluated methods. This policy would be generally employed to maintain reliability of NMIJ CRMs. Although the IDMS method cannot be applied in all cases, it is essential wherever it can be applied.

Specifically, the methods employed for heavy metals is as follows. For pellets and disks of all types, the quantification by isotope dilution ICP-MS was done after microwave digestion with sulfuric acid and nitric acid. In the case of pellets, two more methods were used: microwave digestion (one of the following three methods: method using sulfuric acid and nitric acid, one using nitric acid and perchloric acid, or one using 70 % nitric acid), and open-vessel dry-ashing (one of the following two methods: method using nitric acid and hydrogen peroxide or one using nitric acid). For instrumental analysis, ICP-MS and ICP-OES which have different principles were combined with either digestion method. As a result, the quantification values were calculated using multiple methods, which were mutually independent, to increase reliability. As a premise for deciding the methods, the digestion method mentioned before^[13] was investigated, as well as the effects of acid as matrix when measuring the digested solution by ICP-MS were investigated.^[15]

On the other hand, the quantification of brominated flame retardants as molecules was different from the quantification of heavy metals as elements: we had to ensure that the original molecule would not be broken. For such a purpose, the appropriate digestion, separation, and quantification methods were decided taking into consideration the chemical characteristics of both the analyte (component which is targeted for analysis) and the matrix.^[16]

For brominated flame retardants, tetrahydrofuran (THF), toluene, and chloroform etc. were considered as candidate solvents to dissolve PS. As a result of investigating the solubility of DBDE in these solvents, it was found that all dissolved at 1

mg/mL or more. Of these, when THF without any stabilizer was used, there was a possibility that DBDE would be decomposed due to minute amount of decomposed products of THF (using old solvents, decomposition actually occurred during gas chromatographic analysis). Therefore, PS was dissolved using toluene and chloroform.

The quantification of brominated flame retardants was done by the isotope dilution method and standard addition method. The isotope dilution method is a method which should be done as far as possible in principle, as mentioned before. With the standard addition method, PS was separated by adding a poor solvent (solvent with low solubility of target solute; methanol was selected) for PS into the solution prepared by dissolving RM, and the supernatant solution was collected and concentrated; finally the content of DBDE was measured. Here, the recovery should be considered, but pretreatment was carried out after adding several different amounts of DBDE to the RMs, and using these solutions, the contents were calculated using the standard addition method. Although this method is time consuming, it is a determination method where low recovery was not a concern.

Since there were many isomers of PBDE and PBB used as brominated flame retardants, it was difficult to determine the individual property values by adding all types of individual compounds. When the amount of Br per mass is high, the effect as flame retardant is high. Since such substances have been used, we selected the DBDE with the largest amount of Br per single molecule as the CRM additive. The effect of impurities during DBDE quantification was examined.^[17]

4 Metrological traceability, reliability of certified value, and others

4.1 Need for metrological traceability

Since voices were raised for the lack of RMs necessary for tests to respond to the RoHS derivative, some types of RMs were created by some private companies and the Japan Society for Analytical Chemistry. These were provided along with the CRMs developed by NMIJ, and it should be mentioned that they played a role different from the CRMs of NMIJ.

However, for the analytical value in response to the RoHS directive to be internationally accepted, it is important that the analysis is conducted by laboratories which obtained laboratory accreditation based on ISO/IEC 17025 etc. from accreditation bodies. The lab accredited for ISO/IEC 17025 did exist at the start of plastic CRM development at NMIJ, though smaller in number compared to now. Traceability is one of the requirements for lab accreditation, and the importance of CRMs was high for realization or verification of traceability at the lab. The CRM used there had to be accepted worldwide, and NMIJ CRMs were expected to play such a role, and this position has not changed even now.

Table 3-a. NMIJ CRM 8102-a: Case of ABS resin pellet for heavy metal analysis (Cd, Cr, Pb; low concentration)

	Certified value* ¹ Mass fraction (mg/kg)	Expanded uncertainty* ¹ Mass fraction (mg/kg)
Cd	10.77	0.20
Cr	27.87	0.35
Pb	108.9	0.90

*¹ Assigning done independently by NMIJ

	Median of collaborating analysis Mass fraction (mg/kg)	Estimated value of standard deviation for whole distribution Mass fraction (mg/kg)
Cd	10.31	0.53
Cr	26.64	1.64
Pb	106.6	5.5

Table 3-b. NMIJ CRM 8103-a: Case of ABS resin pellet for heavy metal analysis (Cd, Cr, Pb; high concentration)

	Certified value* ¹ Mass fraction (mg/kg)	Extended uncertainty* ¹ Mass fraction (mg/kg)
Cd	106.9	1.40
Cr	269.5	4.5
Pb	1084	9.6

*¹ Assigning done independently by NMIJ

	Median of collaborating analysis Mass fraction (mg/kg)	Estimated value of standard deviation for whole distribution Mass fraction (mg/kg)
Cd	105.4	4.4
Cr	267.4	13.0
Pb	1080	31

For metal standard solutions, the standard solutions supplied as the calibration standard solutions for Japan Calibration Service System (JCSS) based on the Measurement Law in Japan or its primary standards which NMIJ certified was directly used to maintain traceability. Since there were no JCSS standard solutions for brominated flame retardants, the purity of DBDE was originally determined using the HPLC method.

NMIJ constructed the management system based on ISO/IEC 17025 and ISO Guide 34, and has received the ASNITE accreditation from the International Accreditation Japan (IA Japan) of the National Institute of Technology and Evaluation (NITE). The NMIJ CRMs have been added to the accreditation scope as they are developed.

4.2 Analysis of interlaboratory comparison in Japan

With the participation of 19 testing labs and analytical institutes (18 institutes for Cr), analysis of interlaboratory comparison was conducted for Cd, Cr, and Pb in heavy-metal-containing ABS resin RMs [two materials for high level (NMIJ CRM 8103-a) and low level (NMIJ CRM 8102-a)] (from December 2004 to February 2005). Each median and the standard deviation of overall distribution estimated on the basis of the dispersion from the median were mentioned in the NMIJ CRM certificates as information. These values are shown in Table 3 along with the certified values. There were many acids used for sample digestion: nitric acid; nitric acid and hydrogen peroxide; nitric

acid and sulfuric acid; nitric acid and perchloric acid; nitric acid, sulfuric acid, and hydrogen peroxide; nitric acid, hydrofluoric acid, and boric acid; nitric acid, sulfuric acid, perchloric acid, and hydrochloric acid; fuming nitric acid, nitric acid, and perchloric acid; sulfuric acid; sulfuric acid/hydrogen peroxide; and sulfuric acid and nitric acid/hydrogen peroxide. There was also an institute which used the combination of dry ashing, alkali fusion, and hydrochloric acid extraction. The instrumental measurement methods were ICP-OES, ICP-MS, flame atomic absorption spectrometry, and electric thermal vaporization atomic absorption spectrometry. What distribution would the values obtained by different institutions using different acids and instrumental measurement methods have was useful information for knowing the reality of analysis for the users of the particular CRMs. For the testing labs and analytical institutes which participated, this exercise took a role much like a proficiency test. Of course, we were conducting determination of certified values with confidence, and agreement among the results by multiple methods were confirmed, but we had to be particularly careful since any apparent disagreement with the analytical value of labs might cause unnecessary confusion.

4.3 Proposal of international comparison to the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) under the Metre Convention

4.3.1 International comparisons under the Asian Collaboration on Reference Materials (ACRM) among Japan, China and Korea

The Asian Collaboration on Reference Materials (ACRM) is organized among three national metrology institutes (NMI) of Japan, China, and Korea, and the working groups (WGs) are set up for each technological field. WG3 specializes in the discussions about the RoHS directive, and Akiharu Hioki, one of the authors, was the convener, who is succeeded by Shigetomo Matsuyama. As activities under WG3, several comparisons were conducted when the samples of candidate RMs being developed in each country at the candidate RM stage were exchanged. In the field of RM for heavy metal analysis, WG3 has conducted interlaboratory comparisons for two types of ABS resin candidate RMs (later NMIJ CRM 8112-a and NMIJ CRM 8113-a) of NMIJ (2006), two types of PP resin candidate RMs of the National Institute of Metrology, China (NIM) (2007), and two types of PP resin candidate RMs of the Korea Research Institute of Standards and Science (KRISS) (2007). In the field of RM for brominated flame retardant analysis, three interlaboratory comparisons were planned of DBDE concentration in a toluene solution (2008), of DBDE concentration in PE (2009), and of DBDE concentration in HIPS (2010). Through such comparisons, the capability of each institute was confirmed, and sometimes they contributed to improving the skills.

4.3.2 International comparison of Consultative Committee for Amount of Substance: Metrology in Chemistry and

Biology (CCQM) under the Metre Convention

Under the Metre Convention, a technical consultative committee is organized for each metrology field, and CCQM is for the chemical metrology field. The Inorganic Analysis WG (IAWG) and the Organic Analysis WG (OAWG) are established as WGs in the CCQM. Through the comparisons and discussions at the ACRM meetings, enthusiasm for conducting a global level comparison increased, and pilot studies of CCQM/IAWG were proposed jointly by three countries, Japan (NMIJ), China (NIM), and Korea (KRISS): the proposal was adopted. This study CCQM-P106 (determination of the mass fractions of Cd, Cr, Hg, and Pb in PP) was given the position of benchmark in the IAWG as a result of active discussion proposed by NMIJ, and the results could be used as evidences to underpin CMC registration. It was, in fact, considered equivalent to a key comparison under the agreement of the participants of the study. The results are published in an international journal.^[18] An example of the results is shown in Fig. 4.

For the RM for brominated flame retardant analysis, although CMC claims were not aimed, equivalency was demonstrated in the CCQM-P114 (quantification of some of PBDE and PBB in PP) of CCQM/OAWG.^[19] The results are shown in Fig. 5 [Lab No. 4 indicates NMIJ, which participated only in the part of DBDE (BDE-209)].

4.4 Peer reviews based on CIPM MRA and CMC registration to the BIPM Key Comparison Database (KCDB)

NMIJ demonstrated the capability through (1) developing CRMs under the management system based on ISO, (2) receiving peer reviews, and (3) submitting good results for CCQM-P106, the international comparison of CCQM (in general, a key comparison is necessary, but as a

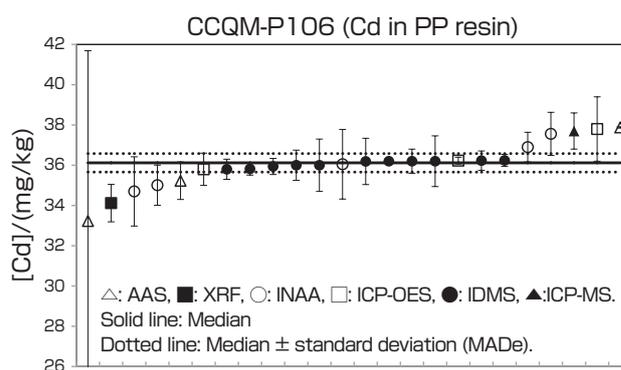


Fig. 4 Result of Cd in CCQM-P106, the international comparison for the quantification of four metals in PP resin

Horizontal axis shows the participating institutes, and NMIJ is ninth from the right. AAS: Atomic absorption spectrometry, XRF: X-ray fluorescence spectrometry, INAA: Instrumental neutron activation analysis, ICP-OES: Inductively coupled plasma optical emission spectrometry, IDMS: Isotope dilution mass spectrometry, ICP-MS: Inductively coupled plasma mass spectrometry. Half length of each bar indicates the expanded uncertainty (the coverage factor is 2 for almost all cases).^[18]

matter of fact this pilot study was considered equivalent to a key comparison). Three requirements from (1) to (3) were fulfilled, CMC registration to the BIPM KCDB was made, and CMCs for heavy metal analysis in plastics were registered. The registration of CMCs (Fig. 6) in the KCDB is one of the goals for CIPM MRA, and the corresponding metrological traceability of NMIJ is valid throughout the world through the standards entered therein.

5 Dissemination of the CRMs and following activities

5.1 State of dissemination

Some examples of packages of the developed NMIJ CRMs are shown in Fig. 7. The numbers per fiscal year of disseminated plastic CRMs for heavy metal analysis and brominated flame retardant analysis are shown in Fig. 8. The cumulative totals up to FY 2013 of the disseminated plastic CRMs were 1102 units for heavy metal analysis and 600 units for brominated flame retardant analysis. In general, since CRMs like the plastic CRM in response to the RoHS directive are not used daily, the dissemination number of each CRM is fairly close to the number of institutions which purchased it. The demand

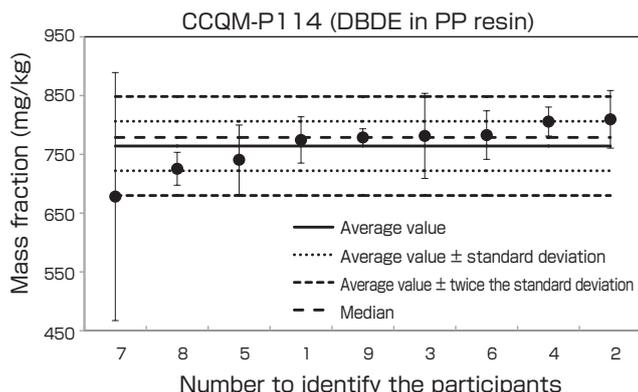


Fig. 5 Result of CCQM-P114, the international comparison for the quantification of DBDE in brominated flame retardant (institution number for NMIJ is 4) Half length of each bar indicates the expanded uncertainty (the coverage factor is 2 for almost all cases).^[19]

Calibration and measurement capability (CMC)

Amount of substance, Advanced materials, Japan, NMIJ (National Metrology Institute of Japan)

Expanded uncertainty is shown as the range from the uncertainty for value of minimum quantity to that for value of maximum quantity.

NMI Service Identifier	Measurement Service Sub-Category	Matrix	Measurand		Dissemination Range of Measurement Capability			Range of Expanded Uncertainties as Disseminated					
			Analyte or Component	Quantity	From	To	Unit	From	to	Unit	Coverage factor	Level of confidence	Is the expanded uncertainty a relative one?
8101-1	Polymers and plastics	ABS resin	cadmium	Mass fraction	1	10000	mg/kg	4	0.5	%	2	95 %	Yes
8101-2	Polymers and plastics	ABS resin	chromium	Mass fraction	1	10000	mg/kg	4	0.5	%	2	95 %	Yes
8101-3	Polymers and plastics	ABS resin	mercury	Mass fraction	1	10000	mg/kg	4	0.5	%	2	95 %	Yes
8101-4	Polymers and plastics	ABS resin	lead	Mass fraction	1	10000	mg/kg	4	0.5	%	2	95 %	Yes

Range of Certified Values in Reference Materials			Range of Expanded Uncertainties for Certified Values						Mechanism(s) for Measurement Service Delivery	Comments
From	To	Unit	From	To	Unit	Coverage factor	Level of confidence	Is the expanded uncertainty a relative one?		
1	10000	mg/kg	4	0.5	%	2	95 %	Yes	NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a	Pellet and disk forms Approved on 19 June 2014
1	10000	mg/kg	4	0.5	%	2	95 %	Yes	NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a	Pellet and disk forms Approved on 19 June 2014
1	10000	mg/kg	4	0.5	%	2	95 %	Yes	NMIJ CRM 8112-a, 8113-a, 8115-a, 8116-a	Pellet and disk forms Approved on 19 June 2014
1	10000	mg/kg	4	0.5	%	2	95 %	Yes	NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a	Pellet and disk forms Approved on 19 June 2014

Key Comparison Database (KCDB) of the International Bureau of Weights and Measures (BIPM) (July 2014)^[11]

Fig. 6 Example of the CMC registration to KCDB (plastics for heavy metal analysis)

from overseas as well as inside Japan is large, and 18 % of the number of the heavy metal analysis CRMs and 12 % of the number of the brominated flame retardant analysis CRMs have been disseminated to the customers overseas.

5.2 Monitoring of the stability and extension of the expiration date

For NMIJ's plastic CRMs, stability monitoring is conducted after the start of dissemination, following the stability test⁽²⁰⁾ during its development. Although in general, CRM is given an expiration date on its certificate, the expiration date may be extended based on the stability monitoring, and many have been extended as shown in Fig. 9. However, there is one example which unfortunately failed, and this must be reported here.

In the stability monitoring for NMIJ CRM 8113-a and NMIJ CRM 8116-a (four metals, high concentration, ABS), concentration changes were observed beyond the expanded uncertainties. First, measurement mistake was suspected, but it was finally found that there was increased oxygen in the ABS matrix. We had to correct the property values by sailing up the time, and this caused inconveniences to the users. The

drying condition was thoroughly considered and established during the development. The change in property value did not occur in the corresponding low concentration CRMs (NMIJ CRM 8112-a and NMIJ CRM 8115-a), was not seen in the other plastic CRMs, and was a phenomenon observed in the high concentration CRM containing Hg. It was concluded that the oxygen was taken in the matrix in some form, and the concentration of heavy metal decreased due to the increased mass of the matrix. It is assessed that this increase has been basically ceased at this moment. The details will be published elsewhere.

5.3 Prospect for the related CRM in the future

In the field of RM development in response to the hazardous substance regulation, other than the plastics presented in the present paper, there are CRM developments of lead-free solder (chip), phthalate-ester-containing plastics, bisphenol-A-containing plastics, and plastic (PP) for bromine analysis. Currently, consideration is being made for glass CRMs.

In the RoHS directive, there was no description on the addition of substances subject to regulations, but there is a possibility of addition in the new RoHS directive.



Fig. 7 Examples of the NMIJ CRMs in response to the RoHS directive

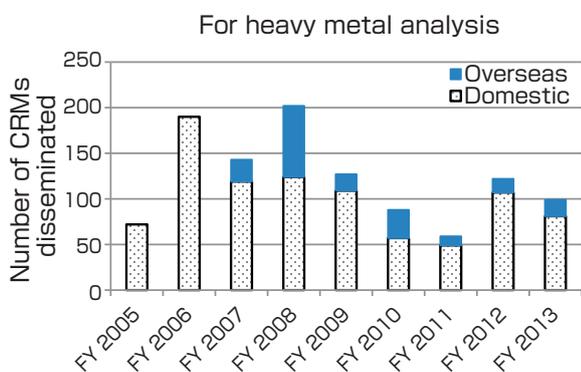


Fig. 8-a Annual change of the total dissemination number of CRMs for heavy metal analysis

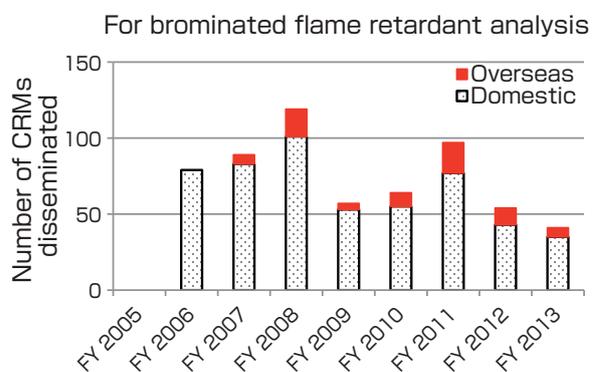


Fig. 8-b Annual change of the total dissemination number of CRMs for brominated flame retardant analysis

In the future, for brominated flame retardants, we will produce a PS CRMs containing 100 ppm each of DBDE, hexabromocyclododecane (HBCDD, a candidate for addition as target substance of the new RoHS directive), and tetrabromobisphenol-A (TBBPA). Other than those, we are in the process of producing CRMs of phthalate-ester-containing PVC and bisphenol-A-containing polycarbonate.

The development of plastic CRMs in response to the RoHS directive was started due to strong demand from industry. However, for the general demand of metrological standards including reference materials, daily information is obtained through various channels such as the NMIJ Metrology Club and NMIJ seminars. Systematic surveys are also conducted, as exemplified by the large-scale demand survey conducted by the Measurement and Intellectual Infrastructure Division, METI in the early 2013, and NMIJ participated to play a central role. The survey results and the developing plan for standards are presented as the “New developing plan of metrological standards and specific promotion of their use”^[21] on the METI website. NMIJ must engage in this plan with limited human and material resources; therefore, deciding what to focus on is extremely important. We hope NMIJ would be able to catch the social demand from the information including the above survey and be able to respond promptly.

6 Conclusion

For the NMIJ CRMs, the developments in the relatively

early stage and the current situation are described in detail in References [22] and [23]. How should the world respond to similar cases which may occur again some time in the future with the enforcement of the RoHS directive? Although the priority on ideal which tends to occur in the EU is understandable, discussions must include the CRMs which may become necessary in the enforcement of regulations. Ideally, someone who knows the actual manufacturing process should join the stages of regulation drafting and the document standards necessary to follow the regulation should be created concurrently. Japan was able to respond relatively quickly to the RoHS directive, but it is also a fact that much confusion occurred in industry. The RoHS directive is an EU directive and is just a domestic law, but it has major impact around the world. Therefore, it should be open to the world. For the perspective of the risk of brominated flame retardants, it is also necessary to pay attention to the differences in sense of values, such as whether one fears the bioaccumulation of substances or the fire which may occur because the flame retardant is not used.

When various regulations are issued in various countries, how NMIJ as a metrology institute should respond will be an issue in the future. Although not all issues can be dealt with, NMIJ must capture such actions as quickly as possible and start response activities if there are CRMs which must be newly developed, through collaboration with the stakeholders in industry and others.

CRM No.	Resin type	Level	Cd	Cr	Pb	Hg	DBDE	Form	04	05	06	07	08	09	10	11	12	13	14	15	16
8102-a	ABS	Low	◎	◎	◎			Pellet	■	→	→	→	→	●	→	→	→	→	●	→	→
8103-a	ABS	High	◎	◎	◎			Pellet	■	→	→	→	→	●	→	→	→	→	●	→	→
8105-a	ABS	Low	◎	◎	◎			Disk		■	→	→	→	●	→	→	→	→	●	→	→
8106-a	ABS	High	◎	◎	◎			Disk		■	→	→	→	●	→	→	→	→	×		
8112-a	ABS	Low	◎	◎	◎	◎		Pellet			■	→	→	→	→	●	→	→	→	→	→
8113-a(02)	ABS	High	◎	◎	◎	○		Pellet		■	→	→	→	→	△	□	●	→	→	→	→
8115-a	ABS	Low	◎	◎	◎	◎		Disk			■	→	→	→	→	●	→	→	→	→	→
8116-a(02)	ABS	High	◎	◎	◎	○		Disk			■	→	→	→	△	□	●	→	→	→	→
8123-a	PVC	High	◎	◎	◎	◎		Pellet					■	→	→	→	→	→	●	→	→
8133-a	PP	High	◎	◎	◎	◎		Pellet					■	→	→	→	→	→	●	→	→
8136-a	PP	High	◎	◎	◎	◎		Disk					■	→	→	→	→	→	●	→	→
8108-a	PS						◎	Disk			■	→	→	→	×						
8108-b	PS						◎	Disk						■	→	→	→	→	→	●	→
8109-a	PVC						◎	Disk						■	→	→	→	→	●	→	→
8110-a	PS						◎	Disk					■	→	→	→	→	→	●	→	→

◎: Certified value, ○: Indicative value

■: Development, ●: Extension of expiration date, △: Change of certified value, □: Recertification,

×: Sold out (Year of development is fiscal year in the western calendar; years of the others are western calendar years.)

Fig. 9 Year of development and status of extension, and so on

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Discussions with Reviewers

1 Overall

Comment (Koichi Chiba, AIST)

This paper provides an appropriate description of the social background where the plastic CRMs were demanded, the process from capturing the demand to developing the CRMs, the technological developments to satisfy the demand, and the current status of dissemination of certified reference materials as contribution to society. It has an interesting content which illustrates the course whereby the R&D at AIST becomes a fruit in society.

Comment (Shigeko Togashi, AIST)

This paper describes the strategy and process by which the internationally recognized CRMs for analysis of heavy metals and brominated flame retardants were developed, in prompt response to the strong demand from industry for immediate action coping with the RoHS directive. It is a theme appropriate for a paper in *Synthesiology*.

2 Addition of the research scenario diagram

Comment (Shigeko Togashi)

For the research scenario in chapter 2, please show a diagram of the scenario followed for the achievement of the objective, based on the research potential up to that point. To be of use as a reference to other R&Ds, please create a framework of the scenario which can be generalized, and describe the specific strategies for the issues you encountered.

Answer (Akiharu Hioki)

As you indicated, I created the diagram of the research scenario in chapter 2.

3 CRM

Question (Shigeko Togashi)

NMIJ distributes many CRMs other than the CRMs mentioned in the present study. What are the common and different points among the CRMs in the present paper and the other CRMs?

Answer (Akiharu Hioki)

The CRMs can be roughly divided into ones for calibration and the others for validation. The CRMs in the present study were mainly developed for the latter purpose. The NMIJ CRMs are produced based on NMIJ's management system in compliance with the ISO/IEC17025 and ISO Guide 34, and the basic idea for the manufacturing process and for determining the certified values for CRMs in the present study is the same as for the other NMIJ CRMs for validation. On the other hand, the CRMs in the present study were quickly designed and developed in response to the demand which arose around the world, although those were for extremely limited use (response to the RoHS directive). They are discriminated from the other CRMs by the fact that timely distribution was possible. Our CRMs became one of the global bestsellers, and are distributed widely around the world.