Development of PVC and PP Resin Pellet Certified Reference Materials for Heavy Metal Analysis with Respect to the RoHS Directive

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The PVC (polyvinyl chloride) and the PP (polypropylene) resin pellet certified reference materials (CRMs, NMIJ CRM 8123-a and 8133-a) with respect to the RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive were developed in the present study. Both the sample pretreatment and the measurement procedures for the determination of Cd, Cr, Hg and Pb in the PVC and the PP resin pellets were examined, and several analytical methods were developed. Microwave acid digestion and dry-ashing followed by acid digestion procedures were examined as sample pretreatment procedures. In the case of measurement procedures, an inductively coupled plasma mass spectrometry (ICPMS) including an isotope dilution mass spectrometry (IDMS) and an ICP optical emission spectrometry (ICPOES) were used. Since the analytical results obtained by different analytical methods showed good agreement within their uncertainties estimated, it was concluded that the analytical methods established in this study were reliable with high accuracy. The homogeneity and the stability of Cd, Cr, Hg and Pb in these plastic CRMs were also evaluated, and the results revealed sufficient homogeneity of 0.3 – 0.7% and stability for more than 5 years. From these results, it is considered that these CRMs are useful CRM for the determination of Cd, Cr, Hg and Pb in plastics with respect to the RoHS directive.

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Introduction

The EU (European Union) legislated the RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive, which became effective in July, 2006.^{1,2} According to the directive, the concentration values of hazardous substances, such as Cd, Cr(VI), Hg, Pb, PBB (poly-brominated biphenyl) and PBDE (poly-brominated diphenyl ether), in electrical and electronics equipment produced in the EU, as well as transported from other areas, should be restricted. Plastic materials are well known to be widespread used in electrical and electronics equipment. It is also well recognized that the hazardous substances mentioned above have been added into plastics to improve the noncombustible character as well as the coloring. In addition, new plastics without hazardous substances are considered to be adulterated with used plastics during the recycling process. Consequently, standard analytical procedures and certified reference materials (CRMs) of hazardous substances in plastics are of great interest, and demanded to check the concentration values of these hazardous substances in electrical and electronics equipment regulated in the RoHS directive.³⁻¹⁷

Several plastic CRMs with respect to the RoHS directive have been developed so far for both chemical analysis^{3,4,6,11,14} and

direct analysis^{8,10,12,13,15-17} that request the sample pretreatment procedure to dissolve plastics, and can measure hazardous substances directly using such techniques as X-ray fluorescence spectrometry (XRF), respectively. In the case of CRM development, reliable analytical methods with high accuracy that comprise the sample pretreatment and the measurement procedures are required. Generally, plastic is dissolved by an acids digestion procedure, and the solution obtained is measured by such measurement procedures as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICPOES) and inductively coupled plasma mass spectrometry (ICPMS). The most crucial point is the sample pretreatment procedure, which has an effect on an accurate determination, because the loss and the contamination of hazardous substances are of concern if it is not appropriate and is not appropriately conducted. Both the open and the close systems used for the sample pretreatment procedure are well known, and are still applied for element analysis such as hazardous substances regulated in the RoHS directive combined with the measurement procedures mentioned above. From this point of view, both the sample pretreatment and the measurement procedures are worthwhile to examine for the development of CRM as well as the establishment of standard analytical procedures.

In this study, the PVC (polyvinyl chloride) and the PP (polypropylene) resin pellet CRMs for the determination of Cd, Cr, Hg and Pb with respect to the RoHS directive were developed. Both the sample pretreatment and the measurement procedures

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were examined, and several analytical methods were developed. Microwave acid digestion and dry-ashing followed by acid digestion procedures were examined as sample pretreatment procedures. In the case of measurement procedures, an ICPMS including an isotope dilution mass spectrometry (IDMS) and an ICPOES were used. The analytical results obtained for different analytical methods as well as the results concerning the homogeneity and the stability of elements were discussed in this study.

Experimental

Instrumentation

The instruments used were Agilent 7500cs ICPMS (Agilent, Tokyo, Japan) and Optima 4300DV ICPOES (PerkinElmer, USA). The typical operating conditions of these analytical instruments are described in Ref. 14. For the sample pretreatment procedures, a microwave digestion system (Ethos 1, Milestone, Italy) and an electric furnace (Fujiwara Seisakusyo, Ibaraki, Japan) for the dry-ashing procedure were used. A heating program of the microwave digestion system, described in Ref. 14, was used with a minor amendment (a maximum temperature of 230°C was programmed in this study). Cleaning of the polytetrafluoroethylene (PTFE) vessel for the microwave digestion system was performed using 8 mL of 70% HNO₃ by the same microwave heating. The PTFE vessel was rinsed more than three times by Milli-Q purified water (Milli-Q Element, Millipore, Tokyo, Japan) after microwave heating, and the dry one was used for microwave digestion. The operating condition of the electric furnace for the dry-ashing procedure is described in the Results and Discussion section. The quartz beaker used was cleaned by soaking in *ca.* 1 M HNO₃ bath for more than two days and dried prior to the dry-ashing procedure.

Reagents

The reagents of CdO (99.5%, < 1 µm, Sigma-Aldrich Co. LLC, USA), HgS (99%, Wako Pure Chemical Industries, Ltd., Japan), PbCrO₄ (>90%, Wako Pure Chemical Industries, Ltd., Japan), and Cr-acetylacetonate (97%, Acros Organics, Belgium) were used to prepare candidate CRMs of the PVC and the PP resin pellets. The acids used for sample digestion were 60% and 70% HNO₃ (EL grade, Kanto Chemical Co. Inc., Japan), 95% H₂SO₄ (reagent grade, Wako Pure Chemical Industries, Ltd., Japan), 30% H₂O₂ (reagent grade, Wako Pure Chemical Industries, Ltd., Japan), and 36% HCl (EL grade, Kanto Chemical Co. Inc., Japan). The standard solutions (*ca.* 1000 mg kg⁻¹) of Cd, Cr, Hg and Pb used were primary standard solutions prepared at National Metrology Institute of Japan (NMIJ, Tsukuba, Ibaraki, Japan). The standard solutions were well characterized, and their standard uncertainty was 0.05% (*k* = 1). Enriched spike solutions for IDMS were prepared from enriched isotope materials of ¹¹¹Cd enriched metal (plate form), ⁵³Cr enriched metal (powder form), ²⁰¹Hg enriched oxide (HgO, powder form) and ²⁰⁶Pb enriched carbonate (PbCO₃, powder form), which were purchased from Oak Ridge National Laboratory (Oak Ridge, TN), by dissolving with appropriate concentrations of acids. A mixed spike solution was prepared from each enriched spike solution, and the concentrations of enriched isotopes of elements were determined accurately by reverse IDMS. In this study, we adopted the values of the isotopic abundances for Cd, Cr and Hg listed in IUPAC,¹⁸ because these values could be accepted generally. On the other hand, a Pb isotopic standard solution prepared from NIST SRM 981 (metal wire form) was used to determine the Pb isotopic

Table 1 Examined acids and their performances on microwave acid digestion procedure (Ethos 1, Milestone) with respect to *ca.* 0.1 g of the PVC and the PP resin pellet CRMs

Acids (amount)	Performance	
	PVC	PP
95% H ₂ SO ₄ (4 mL)	×	×
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 (2 mL) + 36% HCl (6 mL)	△	◎
60% HNO ₃ (6 mL) + 36% HCl (2 mL)	△	◎
70% HNO ₃ (8 mL)	○	◎
70% HNO ₃ (8 mL)	△	◎

◎: Complete digestion can be achieved by a single microwave heating procedure.

○: Complete digestion can be achieved by a single microwave heating procedure with reduced number of vessels (from 10 to 5).

△: Complete digestion can be achieved if the microwave heating procedure is repeated for two or three times (number of vessels is 10).

×: Complete digestion can not be achieved by a single microwave heating procedure (black solution with high viscosity is obtained).

abundance for both the Pb primary standard solution and the Pb in the plastic pellets, because different Pb isotopic abundances were observed obviously between the IUPAC value and the Pb standard solution as well as the Pb in the plastic pellets. Milli-Q purified water was used to prepare acids with appropriate concentrations which were used to prepare mixed standard solutions as well as the sample solutions for measurements.

Samples

In order to prepare candidate PVC and PP resin pellet CRMs that contain *ca.* 100 mg kg⁻¹ of Cd and *ca.* 1000 mg kg⁻¹ of Cr, Hg and Pb, certain amounts of reagents of CdO, HgS, PbCrO₄ and Cr-acetylacetonate were mixed by dry blend with base resin pellets of PVC or PP in a plastic bag. The mixed materials were extruded by an extruder at 200°C; then, the extruded plastics were pelletized by a pelletizer and homogenized. The preparation procedure from extrusion to homogenization was carried out for a total of three times to achieve sufficient homogeneity of elements in the candidate PVC and PP resin pellet CRMs. The preparation procedures mentioned above were similar to that of our previous work.¹⁴ The final PVC and PP resin pellets obtained were *ca.* 30 mg and *ca.* 10 mg for each one pellet, respectively. The measured densities of the PVC and the PP resin pellets were 1.280 ± 0.026 g cm⁻³ (*k* = 2) and 0.8990 ± 0.0103 g cm⁻³ (*k* = 2), respectively. Before weighing these pellets, they were dried at 80°C for 1 h in an electric oven and cooled in a desiccator with silica gel for 1 h to remove any moisture.¹⁴

Results and Discussion

Examination of the microwave acid digestion procedure

The acid combinations were examined to achieve complete digestion of the PVC and the PP resin pellets by the microwave digestion procedure. Table 1 lists the examined acid combinations as well as their performances using the microwave digestion system with respect to *ca.* 0.1 g for both the PVC and the PP resin pellets. The mixed acid of HNO₃ and H₂SO₄ achieved complete digestion for both plastic pellets in a single microwave heating program; however, a few amounts of Pb

Fig. 1 Analytical results obtained for each analytical method (●), mean value calculated from different analytical results (○), homogeneities (—) and certified values (□) of (a) Cd, (b) Cr, (c) Hg and (d) Pb in the PVC resin pellet. The analytical methods are (A) isotope dilution ICPMS with the HNO₃-H₂SO₄ microwave digestion procedure, (B) standard addition ICPOES with the 70% HNO₃ microwave digestion procedure and (C) standard addition ICPOES with dry-ashing followed by the HNO₃-H₂O₂ digestion procedure. The certified values were the mean values calculated from 2 (Hg) or 3 analytical results. The values of the homogeneity for each element are indicated as being the same as those of the mean and the certified values. The bar indicated is the combined standard uncertainty ($k = 1$) estimated for each analytical method, the mean value and the certified value. The bar of the homogeneity is the standard deviation (SD) obtained by evaluating the homogeneity. The combined standard uncertainty of the certified value was calculated by the square root of the sum of the squares of the combined standard uncertainty of the mean value, the SD of the homogeneity and the standard uncertainty of the standard solution (0.05%, $k = 1$). The value in parentheses is the relative value (%).

Fig. 2 Analytical results obtained for each analytical method (●), mean value calculated from different analytical results (○), homogeneities (—) and certified values (□) of (a) Cd, (b) Cr, (c) Hg and (d) Pb in the PP resin pellet. The analytical methods are (A) isotope dilution ICPMS with the HNO₃-H₂SO₄ microwave digestion procedure, (B) standard addition ICPOES with the 70% HNO₃ microwave digestion procedure and (C) standard addition ICPOES with dry-ashing followed by the HNO₃-H₂O₂ digestion procedure. The certified values were the mean values calculated from 2 (Cr and Hg) or 3 analytical results. The values of the homogeneity for each element are indicated as being the same as those of the mean and the certified values. The bar indicated is the combined standard uncertainty ($k = 1$) estimated for each analytical method, the mean value and the certified value. The bar of the homogeneity is the standard deviation (SD) obtained by the homogeneity evaluation. The combined standard uncertainty of the certified value was calculated by the square root of the sum of the squares of the combined standard uncertainty of the mean value, the SD of the homogeneity and the standard uncertainty of the standard solution (0.05%, $k = 1$). The value in parentheses is the relative value (%).

were concerned to be precipitated with SO₄²⁻ after microwave heating. Although precipitation may disturb accurate Pb determination by the calibration curve and the standard addition methods, IDMS achieves an accurate determination because the

final Pb isotope ratio obtained after achieving isotopic equilibrium during the sample digestion procedure, which has an effect on the determination of Pb, does not change even if a few amounts of Pb are precipitated. Therefore, the mixed acid

of HNO_3 and H_2SO_4 was used for the microwave digestion procedure with respect to the IDMS. The analytical results obtained by the IDMS for the PVC and PP resin pellets are shown in Figs. 1 and 2, respectively. The maximum concentrations evaluated for Cd, Cr, Hg and Pb in a blank solution of the mixed acid of HNO_3 and H_2SO_4 were enough low with respect to the analytical results (0.1, 1.2, 0.1 and 0.002 mg kg^{-1} for the PVC and the PP resin pellets). The alternative acid combinations were examined to avoid any inaccuracy in the Pb determination by the calibration curve and the standard addition methods. As can be found in Table 1, 70% HNO_3 can be used as an alternative acid for both the PVC and the PP resin pellets. In the case of the PVC resin pellet, complete digestion could be achieved by 70% HNO_3 if number of vessels of the microwave digestion system reduced or the microwave heating program was repeated for 2 or 3 times. An aquaregia and a reverse-aquaregia could also achieve complete digestion of the PVC resin pellet, if the microwave heating program was repeated for 2 or 3 times. From these results, 70% HNO_3 was chosen for the microwave digestion procedure, even though the number of vessels should be reduced from 10 to 5 to achieve complete digestion of the PVC resin pellet in a single microwave heating program. In order to establish a second analytical method beyond the IDMS, we chose the standard addition method using ICPOES. Several analytical methods consisting of different sample pretreatment and measurement procedures are recommended and required for CRM development, because the certified value determined by several analytical methods are more reliable than that determined by a single analytical method. From the theoretical point of view, the IDMS and the standard addition method are different measurement procedures because they measure the isotope ratio and the signal intensity of elements, respectively. Moreover, since ICPMS and ICPOES detect ions and emission of elements, respectively; it can be considered that they are different measurement procedures. Therefore, we decided to use ICPOES rather than ICPMS for the standard addition method in this study. Since 70% HNO_3 for the microwave digestion procedure was diluted due to the addition of mixed standard solutions for the standard addition method, the amount of the PVC resin pellet was also reduced to 2 pellets (*ca.* 0.06 g) from 3 pellets (*ca.* 0.09 – 0.1 g) to achieve complete digestion in a single microwave heating program. The analytical results obtained by the standard addition ICPOES with the 70% HNO_3 microwave digestion procedure for the PVC and the PP resin pellets are shown in Figs. 1 and 2, respectively. The maximum concentrations estimated for Cd, Cr, Hg and Pb in a blank solution were sufficiently low with respect to the analytical results (0.05, 0.5, 1.6 and 1.3 mg kg^{-1} for the PVC and the PP resin pellets).

Examination on dry-ashing followed by the HNO_3 - H_2O_2 digestion procedure

Dry-ashing followed by acid digestion procedure was applied as a different sample pretreatment procedure compared to that of the microwave acid digestion procedure. Unfortunately, this sample pretreatment procedure does not fit to Hg analysis because it is not a closed system, which can not keep volatile elements, such as Hg. About 0.5 g of the PVC or the PP resin pellets was weighed accurately and put them into a quartz beaker without any reagents. The beaker was put inside an electric furnace for dry-ashing. Although H_2SO_4 is used generally for dry-ashing, we do not use it to avoid the risk of Pb precipitation. A lower temperature can be considered to avoid the loss of elements. In our previous work,¹⁴ we chose a

dry-ashing temperature of 350°C which was hold for 6 h for dry-ashing on ABS (acrylonitrile-butadiene-styrene) resin pellets. After the dry-ashing procedure, the obtained ash (residue) of the ABS resin pellets was dissolved successfully by a hot-plate heating procedure with HNO_3 and H_2O_2 . Figures 3(a) – 3(d) show the obtained residues after the dry-ashing procedure for the PVC and the PP resin pellets. The ash obtained for the PVC resin pellet (Fig. 3(a)) was similar to that of the ABS resin pellet under a dry-ashing condition of 350°C for 6 h. We examined dry-ashing at 300°C for 1, 3 and 6 h concerning the PVC resin pellet; however, the ashes obtained could not be dissolved by the hot-plate heating procedure. The dry-ashing procedures at 350°C for 1, 3 and 6 h were also examined on the PVC resin pellet. Although the obtained ashes could be dissolved by the hot-plate heating procedure, the dissolution of ash obtained for 6 h was easier than those of the others. The ashing temperature at 400°C resulted in a yellow residue of the PVC resin pellet, as shown in Fig. 3(b) which was concerned a loss of elements, even though dissolution of the residue was easy. Therefore, the dry-ashing condition of 350°C for 6 h was adopted for the PVC resin pellet. In the case of the PP resin pellet, different residues from those of the PVC resin pellet were obtained, as shown in Figs. 3(c) and 3(d). Although the dry-ashing temperatures at 250, 300 and 325°C as well as the ashing times of 1, 3 and 6 h were examined for the PP resin pellet, a similar residue like coal tar as shown in Fig. 3(c) was obtained. The residue could be dissolved by the hot-plate heating procedure, but it was very difficult. A similar residue to that of Fig. 3(c) was also observed when the dry-ashing procedures at 350°C for 1 and 3 h were carried out. However, if the ashing time at 350°C was increased to 6 h, a different residue, as shown in Fig. 3(d), was obtained that concerned the loss of elements, even though the residue could be dissolved easily. Because the residue shown in Fig. 3(c) was absolutely difficult to decompose by the hot-plate heating procedure, the dry-ashing condition at 350°C for 6 h was chosen on the PP resin pellet. The analytical results obtained by the standard addition ICPOES with dry-ashing followed by the HNO_3 - H_2O_2 digestion procedure for the PVC and the PP resin pellets are shown in Figs. 1 and 2, respectively. The maximum concentrations estimated for Cd, Cr and Pb in a blank solution were enough low with respect to the analytical results (0.1, 0.5 and 1.1 mg kg^{-1} for the PVC and the PP resin pellets).

Evaluation of the homogeneity of elements

The homogeneity of elements in both the PVC and the PP resin pellets was evaluated. The relative standard deviation (RSD, %) obtained for analytical results of 28 samples from 14 bottles (2 samples from each bottle) was evaluated as the homogeneity of elements in both the PVC and the PP resin pellets. A calibration curve method using ICPMS as well as the microwave digestion procedure with 70% HNO_3 was used to evaluate the homogeneity. About 0.1 g of the PVC and the PP resin pellets was used for the microwave digestion procedure. The results are indicated in Figs. 1 and 2. Relative values ranging from 0.3 to 0.7% were obtained as the homogeneity of elements in both plastic pellets. It was concluded that the homogeneity obtained was sufficiently small for the development of the CRMs and the values obtained were similar to those of our previous work.¹⁴

Comparison of analytical results from different analytical methods

Figures 1 and 2 show the analytical results obtained by different analytical methods established in this study. The mean

Fig. 3 Residues obtained after the dry-ashing procedure at different temperatures for 6 h: (a) at 350°C and (b) at 400°C for the PVC resin pellet, (c) at 325°C and (d) at 350°C for the PP resin pellet.

values calculated from different analytical results, the results of homogeneity as well as the certified values are also indicated. The combined standard uncertainties for each analytical method, the mean value as well as the certified value were estimated in accordance with references^{4,14,19} as well as GUM (Guide to the expression of Uncertainty in Measurement).²⁰ Because the analytical results obtained agreed well within their combined standard uncertainties and the combined standard uncertainties were also at a similar level to each other, the mean value was adopted to determine the certified value. The analytical result of Cr for the PP resin pellet obtained by the dry-ashing procedure (350°C for 6 h) was excluded from the calculation because the loss of Cr was considered. If a dry-ashing temperature of 300°C is adopted, the loss of Cr might be prevented. Even though the dry-ashing procedure (350°C for 6 h) lost Cr from the PP resin pellet, it could keep Cd and Pb quantitatively. The analytical results obtained by the standard addition ICPOES with dry-ashing followed by the $\text{HNO}_3\text{-H}_2\text{O}_2$ digestion procedure could be used for the determination of Cd, Cr and Pb in the PVC resin pellet as well as Cd and Pb in the PP resin pellet, even though the sample pretreatment procedure was an open system, complicated and time consuming.¹⁴ The combined standard uncertainty estimated for each element (0.4 – 0.5%) originated from the uncertainty estimated from the regression

curve obtained by the standard addition method including the sample pretreatment procedure. The analytical results obtained by the isotope dilution ICPMS with the $\text{HNO}_3\text{-H}_2\text{SO}_4$ microwave digestion procedure are reliable because the analytical method is accepted as a primary method of measurement; however, the method is not under widespread use because enriched isotopes of elements are necessary and a single element measurement (non multi-element analysis) is recommended to achieve a high precision of the measurement which leads to a lower sample throughput. The combined standard uncertainties estimated for Cd and Hg (1.4 – 1.7%) were relatively larger than those of Cr and Pb (0.2 – 0.4%), which were attributed to the large uncertainties of the isotope ratios estimated from the uncertainties of the isotopic abundances of Cd and Hg listed in IUPAC.^{14,18} The standard addition ICPOES with the 70% HNO_3 microwave digestion procedure was also a useful analytical method for Cd, Cr, Hg and Pb in both the PVC and the PP resin pellets, because the analytical results obtained agreed with those of other analytical methods within their combined standard uncertainties estimated. The combined standard uncertainty estimated for each element (0.4 – 0.8%) originated from the same source for the standard addition method including the sample pretreatment procedure. According to the purpose for the development of CRMs, ICPOES was chosen in this study;

Table 2 Certified values for both the PVC and the PP resin pellet CRMs

	PVC resin pellet CRM (NMIJ CRM 8123-a)	PP resin pellet CRM (NMIJ CRM 8133-a)
Cd	95.62 ± 1.39	94.26 ± 1.39
Cr	949.0 ± 9.7	895.2 ± 9.6
Hg	937.0 ± 19.4	941.5 ± 19.6
Pb	965.5 ± 6.6	949.2 ± 7.5

The numeric value after the symbol ± of each certified value indicates an expanded uncertainty, determined with the coverage factor $k = 2$; it defines an interval estimated to have a level of confidence of approximately 95%.

however, ICPMS can be applied instead of ICPOES. The combined standard uncertainty of the certified value was calculated from the combined standard uncertainties of the mean value (0.3 – 0.9%), the standard deviation of the element obtained by the evaluation of homogeneity (0.3 – 0.7%) and the standard uncertainty of the standard solution (0.05%, $k = 1$). As can be seen in Figs. 1 and 2, the uncertainties between the mean value and the homogeneity had similar level of amount and it was concluded that they were the main source of the final uncertainty of the certified value. Table 2 gives the certified values as well as expanded uncertainties estimated ($k = 2$) for Cd, Cr, Hg and Pb in both the PVC and the PP resin pellets as NMIJ CRM 8123-a and 8133-a, respectively. The expanded uncertainties estimated for Hg were relatively larger than those of other elements, because they were calculated from only two analytical methods including the IDMS which resulted in the large combined standard uncertainty on Hg, as can be seen in Figs. 1 and 2. As mentioned above, since the analytical results obtained were consistent with each other within their similar combined standard uncertainties and the certified value was determined from those obtained by different analytical methods, including the IDMS which was accepted as a primary method of measurement, it was evaluated that the analytical methods established in this study were reliable with high accuracy and the CRMs developed have international consistency.

Evaluation of the stability of elements

Figures 4 and 5 show the results concerning the stability of elements for both the PVC and the PP resin pellets, respectively. The consistency between the certified value and the analytical results was judged by the following:

$$|C_{\text{stab},i} - C_{\text{CRM}}| < \sqrt{((2u_{\text{stab},i})^2 + U_{\text{CRM}}^2)}. \quad (1)$$

$C_{\text{stab},i}$ and C_{CRM} are the analytical results for the stability of elements and the certified values (mg kg^{-1}), respectively. The $u_{\text{stab},i}$ is the standard uncertainty of the analytical results (mg kg^{-1}) for the stability of elements and U_{CRM} is the expanded uncertainty of the certified value (mg kg^{-1}). The values for both $2u_{\text{stab},i}$ and U_{CRM} should be similar, if the judgement is conducted. Since the IDMS was a reliable analytical method, it was applied to evaluating the stability of elements after certification even though it resulted in larger combined standard uncertainties for both Cd and Hg, as can be seen in Figs. 4 and 5. According to the judgement, it was evaluated that the analytical results obtained before and after the certification were consistent with the certified values. From these results, it was concluded that both the PVC and the PP resin pellet CRMs were stable for a monitoring period of more than 5 years. Consequently, the

Fig. 4 Results of stability for (a) Cd, (b) Cr, (c) Hg and (d) Pb in the PVC resin pellet; analytical result obtained by standard addition ICPOES with the 70% HNO_3 microwave digestion procedure before certification ($\blacktriangle$), analytical result obtained by isotope dilution ICPMS with the HNO_3 - H_2SO_4 microwave digestion procedure before certification ($\bullet$), certified value certified on March 2009 ($\times$), analytical results obtained by isotope dilution ICPMS with the HNO_3 - H_2SO_4 microwave digestion procedure after the certification ($\square$). The bars indicated are the combined standard uncertainty ($k = 1$) and the expanded uncertainty ($k = 2$) estimated for each analytical result and the certified value, respectively.

CRMs are expected to be stable for a long time if they are stored in an appropriate space in accordance with the certification.²¹

Conclusions

The PVC and the PP resin pellet CRMs of NMIJ CRM 8123-a and 8133-a, respectively, with respect to the RoHS directive were developed in this study. Both the sample pretreatment and the measurement procedures for the determination of Cd, Cr, Hg and Pb in the PVC and the PP resin pellets were examined and these analytical methods such as the isotope dilution ICPMS

Fig. 5 Results of stability for (a) Cd, (b) Cr, (c) Hg and (d) Pb in the PP resin pellet; analytical result obtained by isotope dilution ICPMS with the $\text{HNO}_3\text{-H}_2\text{SO}_4$ microwave digestion procedure before certification (●), certified value certified on January 2008 (×), analytical results obtained by isotope dilution ICPMS with the $\text{HNO}_3\text{-H}_2\text{SO}_4$ microwave digestion procedure after the certification (□). The bars indicated are the combined standard uncertainty ($k = 1$) and the expanded uncertainty ($k = 2$) estimated for each analytical result and the certified value, respectively.

with $\text{HNO}_3\text{-H}_2\text{SO}_4$ microwave digestion, the standard addition ICPOES with 70% HNO_3 microwave digestion and the standard addition ICPOES with dry-ashing followed by $\text{HNO}_3\text{-H}_2\text{O}_2$ digestion procedures were developed. Since the analytical results obtained by different analytical methods, including IDMS which was accepted as a primary method of measurement, showed good agreement within their uncertainties estimated, it was concluded that the analytical methods established in this study were reliable with high accuracy and the CRMs developed have international consistency. The homogeneity and the stability of Cd, Cr, Hg and Pb in these plastic pellet CRMs were also evaluated, and the results revealed sufficient homogeneity of 0.3 – 0.7% and stability for more than 5 years, which satisfied the requirement of CRM. The uncertainties estimated for both the analytical methods and the homogeneity were the main

sources of the final uncertainty of the certified value and the final uncertainty was also sufficiently small with respect to the requirement of the CRM. From these results, it is considered that these CRMs are useful CRM for the determination of Cd, Cr, Hg and Pb in plastics with respect to the RoHS directive.

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