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Comparative analysis on homogeneity of Pb and Cd in epoxy molding compounds

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Abstract: Reference materials for quantitative determination of regulated heavy metals, such as Pb and Cd in electronic components, were designed and investigated in terms of stability and homogeneity. Reference materials with two concentration levels of heavy metals were prepared by spiking Pb and Cd compounds to epoxy molding compounds made by mixing silica powders and epoxy resin. The concentration changes of the reference materials during stability test for 1 a were not observed. In the homogeneity assessment, the as-prepared reference materials were studied by using three different analytical tools, inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluoroescence spectrometry (XRF) and laser ablation ICP mass. The results show different homogeneities by the characteristics of analytical tools and the materials.

Key words: epoxy molding compound; Pb; Cd; reference materials; homogeneity

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1 Introduction

In recent years the hazardousness of heavy metal in various places has become an important factor for the electrical and electronic industries. EU directive[1] has banned uses of four metals (Pb, Cd, Hg and Cr^{6+}) and brominated flame retardants such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) for electrical and electronic devices and products since July 2006. To control and monitor restricted substances, an international standard testing method (IEC 62321) was released in 2008[2].

Also to validate the analytical results, many types of reference materials (RMs) have been developed[3], but such RMs for composite materials are few because it is difficult to define and generate homogeneity for composite materials, while it is also challenging to access the homogeneities of the materials. The homogeneity is an important factor in the preparation of RMs. To extract a usable RM all analysts participating in using the materials will obtain the same property values from the materials. This implies that replicate subsamples, within and between lots of RMs, show no significant difference within the boundaries of the precision of the testing methods.

For the purpose of extracting such RMs, the testing methods to define homogeneity for composite materials were used. Generally, inductively coupled plasma atomic emission spectrometry (ICP-AES) and X-ray fluoroescence spectrometry (XRF), which are considered to be the most popular analytical methods, were used to analyze heavy metals. In this work, more precise analytical tools than ICP-AES or XRF for the purpose of reaching the homogeneity for RMs were strived to be developed. For example, laser ablation ICP mass is also currently used as another option for an analytical tool for extracting the homogeneity because it gives micro sampling and shows micro heterogeneity of the samples. Moreover, ICP mass provides the highest sensitivity for heavy metals among the inorganic testing instruments.

Nowadays, different types of plastic epoxy molding compounds (CRMs) containing heavy metals, such as VDA001−004[4] and BCR 680−681 (IRMM, Belgium)[5] for polyethylene (PE) containing heavy metals, JASC 0601−0602[6] for polyester or ABS as a matrix, JSAC 0611−0615[7] for polyesters containing Pb, Cd and Cr, and JSAC 0621−0625[8] for polyesters

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containing Hg, are available, where there are also two types of CRMs for glass and powder types of paints available. However, no CRMs are reported for Pb and Cd in EMCs, which is commonly found in electrical and electronic components to determine the amount in quantitative ways. Epoxy molding compounds are known as a kind of material composed of a composite material and used in representative semiconductor packaging. They are composed of silica, epoxy plastics and other additives. In this work, the preparation of RMs and the homogeneity of Pb and Cd were investigated through analytical tools. Also the comparative methods were performed to investigate the effect of the composite material on the result of the each analytical tool.

2 Experimental

The composition of EMCs as a starting material is listed in Table 1 with the total mass of 1 kg. The additives were of reagent grade. Pb was $Pb(C_{18}H_{35}O_2)_2$ from WAKO Pure Chemical Industries, Ltd. Cd was in CdO from KANTO Chemical Co., Inc.

Table 1 Components of candidate EMC CRMs

Material	No.	Item	Formulation		
			High level/g	Low level/g	Mark
EMC (Epoxy molding compound)	1	Filler (SS-0300)	833	833.99	Fused spherical silica
	2	Coupling agent (s-510)	5	5	Epoxysilane
	3	Epoxy resin (YDCN-500-5p)	103.7	103.7	Epoxy resin, mp: 62 °C
	4	Hardener (KPH-F2001)	52.8	52.8	Hardener, mp: 85 °C
	5	Catalyst (TPP)	1.4	1.4	Triphenol phosphorous
	6	Wax(C.W)	3	3	Carnaubar wax
Heavy metals	7	Lead stearate	1	0.1	WAKO Pure Chemical Industries Ltd
	8	CdO	0.1	0.01	KANTO Chemical Co., Inc
	Total		1000	1000	

EMCs were prepared by mixing with blended filler and coupling agent (No.1+No.2) and blended epoxy resin, hardener, catalyst, and wax (No.3+No.4+No.5+No.6) twice for 1 min in a stainless-steel mixer. $Pb(C_{18}H_{35}O_2)_2$ and CdO were weighed and spiked in the prepared EMCs and mixed 10 times for 1 min. The EMCs with hazardous metals passed through a kneader machine at 121 °C and then cooled down. The cooled EMC CRMs were crushed into powder less than 3 mm and post-cured at 175 °C for 4 h. Finally, the EMC CRMs had the particle size of less than 1 mm after the second crushing. 40 g homogeneously-made EMC CRMs powders were put into a brown bottle.

The homogeneity, stability and certified values are very important factors in the candidate CRM. They were investigated by non-destructive and destructive methods. For a non-destructive method that reduces the time-consuming for sample pretreatment, prepared EMC CRMs powders were pressed in a form of a disk with 40 mm in diameter and 3 mm in thickness using uni-axial pressure at 100 MPa. The homogeneity of prepared disks was examined by checking the intensity of Pb and Cd using wavelength dispersive X-ray fluorescence (WD-XRF, Rigaku, ZSX 100E) and inductively coupled plasma-mass spectrometer (ICP-MS, Perkin-Elmer, Elan DRC) laser ablation. For the destructive analytic method, test samples of 0.5 g at high level and 1.0 g at low level within 1 mg error range were transferred into a polytetrafluoro ethylene (PTFE, Teflon) beaker. H_2SO_4 and HNO_3 solutions were added to the beaker for the decomposition of organic compounds, and HF solution was added to the beaker for the decomposition and the removal of sample matrix Si. The test procedure is shown in Fig.1. Concentrations of Pb and Cd were measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES, PERKIN-ELMER Optima 4300). The inductively coupled plasma-mass spectrometer (ICP-MS, Perkin-Elmer Elan DRCⅡ) was used to determine the certified values of candidate EMC CRMs.

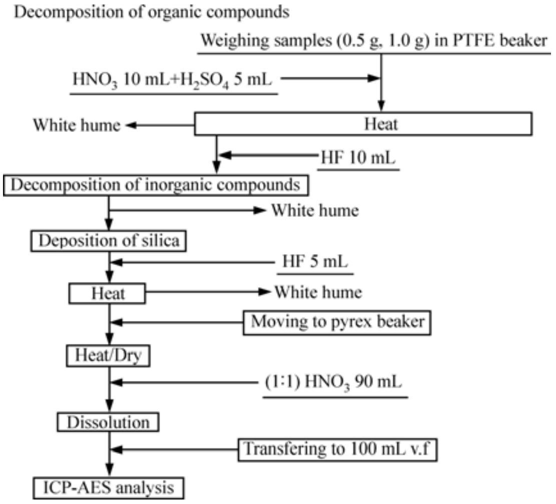

Fig.1 Flow chart of chemical analysis for candidate EMC CRMs

3 Results and discussion

3.1 Homogeneity

Extracting and defining the homogeneity is one of the most important factors to prepare CRMs for EMC. Firstly, the homogeneity tests should enable the estimation of the variation of average concentrations between bottles. Secondly, it should establish the inhomogeneity within a bottle to establish the minimum sample intake, thus a stability test and determination of certified value can progress only for the homogeneously-prepared CRMs.

X-ray is widely irradiated to a sample surface, which is 20 mm in diameter while the surface irradiated by laser is approximately 4. It was measured with three times intensities of Pb and Cd repeatedly under conditions of 25 samples with 40 mm in diameter and 3 mm in thickness. The results obtained from both homogeneity studies are shown in Table 2. Relative standard deviations for high level are 3.78% and 4.82% for Pb, whereas 5.23% and 2.84% for Cd. The relative standard deviations for low level are 1.66% and 3.57% for Pb, while 8.63% and 9.29% for Cd. As a result, there is no significant difference in the relative standard deviations found. It is found that the EMC CRMs are homogenously made in terms of measuring mechanism without considering the surface roughness or the particle size that affects the measurement.

Table 2 Homogeneity intensities of Pb and Cd by XRF and ICP-MS laser ablation (Unit : cps)

Instrument	Level	Pb	Cd
WD-XRF	Low	572(1.66%)	3 327(8.63%)
	High	2 548(3.78%)	8 114(5.23%)
ICP-MS laser ablation	Low	28 189(3.57%)	762(9.29%)
	High	335 246(4.82%)	4 886(2.84%)

Figures in parakets represent relative standard deviation, n=25

The between-bottles and within-bottle homogeneity tests were performed according to the layout of Guide 35[9]. Twenty bottles were selected from the batch and the destructive analysis was carried out three times for each sample. Although Pb is precipitated into $PbSO_4$, it can be all dissolved in 15% HNO_3 solution. The analytical results are given in Table 3 and Fig.2. Relative standard deviations of two EMC CRMs are ranged from 0.78 % to 1.43 % for Pb and Cd. The analysis of variance test, ANOVA, was applied to the analytical results for a between-bottle and within-bottle homogeneity evaluation of the batch. F value is 1.42 for Pb and 0.88 for Cd at high level, and 1.25 for Pb and 1.11 for Cd at low level. These results are smaller than 1.85, which is F critical value (F_c). Since F values of two EMC CRMs are smaller than F critical value ($F<F_c$), the sample can be demonstrated to be homogeneous in between-bottles. From the results of analysis of variance, the standard deviations for repeatability of within-bottle (S_r) and between-bottles (S_{bb}) were calculated. The S_r and S_{bb} values are ranged from 0.02 to 0.48 mg/kg for Pb and Cd, respectively. These values exhibit that the repeatability standard deviation of the measurement method is considerably smaller than the combined standard uncertainty

Table 3 Homogeneity results of candidate EMC CRMs by ICP-AES: ANOVA calculations

Parameter	High level		Low level	
	Pb	Cd	Pb	Cd
A_{ve}/(mg·kg^{-1})	188.06	74.41	23.46	17.37
S_D/(mg·kg^{-1})	0.410	0.238	0.148	0.112
R_{SD}/%	0.22	0.32	0.63	0.64
N	20	20	20	20
F	1.42	0.88	1.25	1.11
S_r/(mg·kg^{-1})	0.484	0.257	0.160	0.112
S_{bb}/(mg·kg^{-1})	0.182	0.685	0.046	0.021

A_{ve}: Average; S_D: Standard deviation; R_{SD}: Relative standard deviation; N: Number of analyses; F: F value; S_r: Repeatibility standard deviation of within-bottle; S_{bb}: Between-bottle standard deviation.

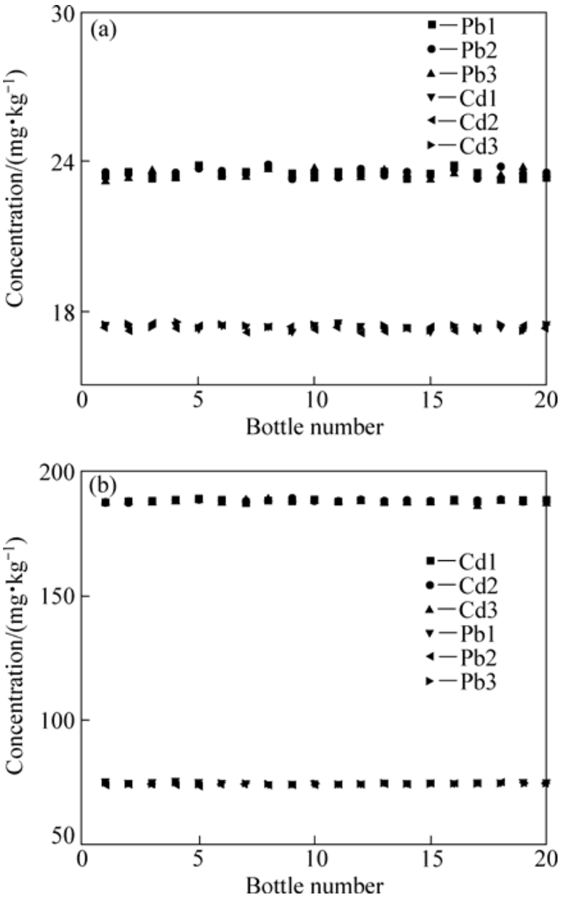

Fig.2 Graphical illustrations of homogeneity for candidate EMC CRMs by ICP-AES: (a) Low level; (b) High level

from the determination of the property value. As a consequence, within-bottle and between-bottles homogeneity of candidate EMC CRMs should be established.

3.2 Stability

Since candidate CRMs with a certified value should not change during storage and transport, a short term and long-term safety tests must be carried out. In an early stage, they were stored at room temperature, and after 60 d stored below 25 °C. The test method was exactly the same as the evaluation of between-bottles and within-bottle homogeneity tests, and its stability for 1 a was studied during the research. The tendency of concentration change with time is listed in Table 4. Since the F-table can be used for evaluating the significance of regression. It becomes significant for $p<0.05$ at 95% confidence level[10].

Table 4 Test results on stability of candidate EMC CRMs by ICP-AES: *F*-test calculation of regression analysis

Parameter	High level		Low level	
	Pb	Cd	Pb	Cd
$A_{ve}/(mg\cdot kg^{-1})$	188.1	74.4	23.5	17.4
$S_D/(mg\cdot kg^{-1})$	0.125	0.102	0.044	0.060
p	0.15	0.49	0.58	0.95
s_{b1}	0.008	0.011	0.005	0.008

p: p value; s_{b1}: Uncertainty of slope.

F-test and linear regression analysis by software (Microsoft, Excel) was applied to the analytical results of the candidate EMC CRMs. The *p*-values and uncertainty of slope (s_{b1}) were calculated. The *p*-values were ranged from 0.15 to 0.95 for Pb and Cd of two difference level for EMC CRMs. Since the *p*-values are bigger than 0.05 at 95% confidence level, regression is insignificant. The uncertainty of slope (s_{b1}) due to long-term stability is very small. Therefore, the candidate EMC CRMs are no trend of concentration change. The good stabilities during the research (1 a) were obtained.

3.3 Certification by isotope dilution mass spectrometry (IDMS)

The property values of candidate EMC CRMs were certified by IDMS[11−13] according to ISO Guide 35. The isotopes, 99.97% ^{206}Pb and 96.31% ^{111}Cd were used, ^{112}Cd/^{111}Cd and ^{208}Pb/^{206}Pb mass spectrometric measurements were measured by ICP-MS.

IDMS results were calculated by Eq.(1):

$$c=\frac{m_s K(A_s-B_s R)}{m(BR-A)} \tag{1}$$

where c is the concentration of analyte in sample; m_s is the mass of the spike; m is the mass of the sample; K is the ratio of the natural atomic mass and the atomic mass of ^{111}Cd-enriched material; A is the natural abundance of ^{112}Cd (the reference isotope); B is the natural abundance of ^{111}Cd (the spike isotope); A_s is the natural abundance of ^{112}Cd in the ^{111}Cd -enriched spike; B_s is the natural abundance of ^{111}Cd in the ^{111}Cd -enriched spike and R is the measured mass ratio of ^{112}Cd to ^{111}Cd.

The combined standard uncertainty associated with the property value can be computed by Eq.(2):

$$u_{char}=\sqrt{u_{m_s}^{2}+u_{m}^{2}+u_{A_s}^{2}+u_{B_s}^{2}+u_{R}^{2}} \tag{2}$$

3.4 Certified values and uncertainties

The final uncertainty (U_{CRM}) of a certified value includes the uncertainty of the sample measurement (u_{char}), the uncertainty of between-bottle homogeneity (u_{bb}) , and the uncertainty of long-term stability (u_{lts}):

$$U_{CRM}=k\sqrt{u_{char}^{2}+u_{bb}^{2}+u_{lts}^{2}} \tag{3}$$

According to Eq.(3), expanded uncertainties can be computed.

The uncertainty values and expanded uncertainties are summarized in Table 5. Since the degree of freedom is bigger than 10, coverage factor k=2 was used in these results at 95% level of confidence[9]. The results were obtained to be 3%−5%. Consequently, the certified value of EMC CRMs has a shelf life time of 1 a, showing (188.0±2.5) mg/kg for Pb and (74.5±1.4) mg/kg for Cd at the high level, while (23.4±0.5) mg/kg for Pb and (17.3±0.4) mg/kg for Cd at the low level.

Table 5 Certified values and uncertainties of EMC CRMs by ICP-MS

Parameter	High level		Low level	
	Pb	Cd	Pb	Cd
$A_{ve}/(mg\cdot kg^{-1})$	188.05	74.40	23.48	17.41
u_{char}/%	2.45	1.65	2.0	1.82
u_{bb}/%	0.51	0.46	1.71	0.78
u_{lts}/%	0.06	0.14	0.19	0.34
k (95%)	2	2	2	2
$u/(mg\cdot kg^{-1})$	9.4	2.5	1.2	0.7
U/%	5.0	3.4	5.3	4.0

U: Expanded uncertainty.

4 Conclusions

1) The overall results demonstrate that the CRMs developed are very useful for the quantitative determination of Pb and Cd in epoxy molding compounds.

2) CRMs prepared in the form of powder show good homogeneity and stability characteristics.

3) The certified values of the EMC CRMs have a shelf life time of 1 a and the uncertainties of the 95%

confidence interval are ranged from 3% to 5% for the two concentration levels.

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