XX IMEKO World Congress
Metrology for Green Growth
September 9–14, 2012, Busan, Republic of Korea

INTERLABORATROY COMPARISON FOR THE MEASUREMENT OF BROMINE CONTENTS IN PLASTIC SAMPLES USING COMBUSTION ION CHROMATOGRAPHY

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Abstract: An interlaboratory comparison study was performed. It was on the determination of bromine contents in plastic samples by using electric furnace combustion ion chromatography (C-IC) method, which had been proposed a new Korean standard procedure for the measurement of halogen (bromine, chlorine, fluorine). Two candidate reference materials were used as test materials. Range of bromine contents in the materials was 100 – 1 000 mg/kg. Instrumental neutron activation analysis was applied to determine the bromine contents in the materials, which were used as the reference values of thhis study. 14 voluntary laboratories from electronics manufacturing companies, testing companies, governmental bodies participated in the study.

Keywords: Interlaboratory comparison study, electric furnace combustion ion chromatography, bromine, certified reference material, instrumental neutron activation analysis

1. INTRODUCTION

Bromine compounds were used as flame retardants in thermoplastics, thermosets, textiles, etc. But environmental issues were raised on their toxicity. [1-2], and usage of two classes of them - polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) in electric and electronic devices is now banned by RoHS directive [3] in European Union. The maximum allowed level of the substances is 1 000 mg/kg as mass fraction.

Regulation requires measurement. But measurement of PBBs and PBDEs takes much cost, since they have many congeners. The cost can be reduced by screening bromine contents.

Measurement of bromine contents with high accuracy can be made by the instrumental neutron activation analysis (INAA). It requires no sample pre-treatment (digestion), and volatile loss of bromine during sample preparation is not a matter of concern. Detection limit can be as low as 0.1 μg/kg, which depends on the property of neutron source. However, it requires long turn-around time. So, it is not feasible for the purpose of screening bromine contents. XRF is another non-destructive method. It is very simple and fast. And an international standard procedure is already established [4]. However, it can be affected by the condition of sample surface or matrix. Combustion methods can be applied for bromine measurement, too. Classically, oxygen bomb and oxygen flask methods have been available. Recently, fully automated electric furnace combustion ion chromatography (C-IC) has become available. The C-IC was suggested as a new Korean standard procedure for the measurement of halogen (bromine, chlorine, fluorine) and sulfur. This study was performed for the verification of the C-IC method for the measurement of bromine contents.

2. EXPERIMENTAL

- *Test materials*

ABS (Acrylonitrile Butadiene Styrene) materials which had been prepared as candidate material for CRMs (certified reference materials) were used as test material for this study. The materials had been prepared so that they might cover the range of from blank to 1 000 mg/kg of bromine (Br) and other elements (Cd, Cr, Hg, Pb, etc.). They are in granule form (10 mg/each) and kept in glass amber bottles (net weight 50 g). Their model numbers are KRISS 113-01-011, 113-01-012, 113-01-013, 113-01-014, 113-01-014 [5]. In this study, KRISS 113-01-013, 113-01-015 were used as the test materials.

- *Determination of Bromine*

Bromine content in the test materials was determined by INAA. Standard comparators were prepared by transferring bromine standard solution on to cellulose filter papers. It was found that the background level of bromine content in the filter papers was as much as 0.6 mg/kg. So it was corrected.

Samples were irradiated to neutron in a NAA irradiation hole (NAA #2) at HANARO [6]. Thermal neutron flux in the hole is 3.3×10^{13} $cm^{-2}\cdot s^{-1}$ and the Cd-ratio (Au) is 100. Samples were irradiated together with standard comparators in a rabbit for 10 minutes to 3 hours. Irradiation time was determined considering the mass fraction of bromine and other elements.

Gamma-ray was counted on a HPGe detector (FWHM 1.8 keV at 1.3 MeV). It was performed after five to six days

in order to eliminate short half life radio isotopes. Bromine content was determined at 776.5 keV energy gamma-ray peak of ^{82}Br. It was (124 ± 6) mg/kg, (890 ± 30) mg/kg for the KRISS 113-01-013 and 113-01-015, respectively.

3. INTERLABORATORY COMPARISON STUDY

The interlaboratory comparison study was organized by KRISS (Korea Research Institute of Standards and Science) and KATS (Korean Agency for Technology and Standards), together. Purpose of the study was for the verification of the C-IC as a new standard procedure for the measurement of bromine contents. Hence, only the C-IC according to the proposal of KS M 0180:2009 [7] was allowed for the participants.

It was performed in February 2009. 14 voluntary laboratories from electronics manufacturing companies, testing companies, governmental bodies participated in. Four sample bottles were provided to each participant together with technical protocol. Two bottles contained 15 g of unknown test materials of KRISS 113-01-013, 113-01-015. The other bottles contained 3 g of well known PE (polyethylene) CRMs of ERM EC681k, EC680k [8]. In the technical protocol, it was required that the participants should take more than 0.1 g of sample and repeat the measurement at least five times.

4. RESULTS AND DISCUSSION

The results are as shown in the table 1 and figure 1. In the figure 1, "Mean" and "SD" mean values of mean and standard deviation of the participants evaluated according to a robust statistical algorism A of Annex C (ISO 13528-2005) [9], respectively. Solid lines indicate the reference values. Error bar is standard deviation.

Since ERM EC680k and EC681k were well known materials to the participants, excellent data set was produced on them. Their mean agreed to the reference values within 2 % and the relative standard deviation was less than 5 %. The participants must had tried these materials many times to optimize their own C-IC systems and measurement procedure. Therefore, it is thought that this would be the limit of reproducibility of C-IC on bromine content in plastic samples.

Also the result of KRISS 113-01-013 showed good consistency to the reference value. The mean value differed from the reference value by only 2.7 %, while standard deviation among the participants was 10 %. However, the mean value of participants on KRISS 113-01-015 differed from the reference value by 9 %. The content of bromine in

Table 1. Result of the interlaboratory comparison study

Sample	Mean,[1] mg/kg	SD,[2] mg/kg	Reference, mg/kg	
			Value	U[3]
113-01-013	121	12 (10 %)	124	6
113-01-015	812	71 (9 %)	890	30
EC680k	94	5 (5 %)	96	4
EC681k	782	13 (2 %)	770	40

[1] Mean of participants evaluated by a robust statistics [9]
[2] Standard deviation of participants evaluated by a robust statistics [9], the value in the parenthesis is the relative standard deviation
[3] Expanded uncertainty at approximately 95 % level of confidence

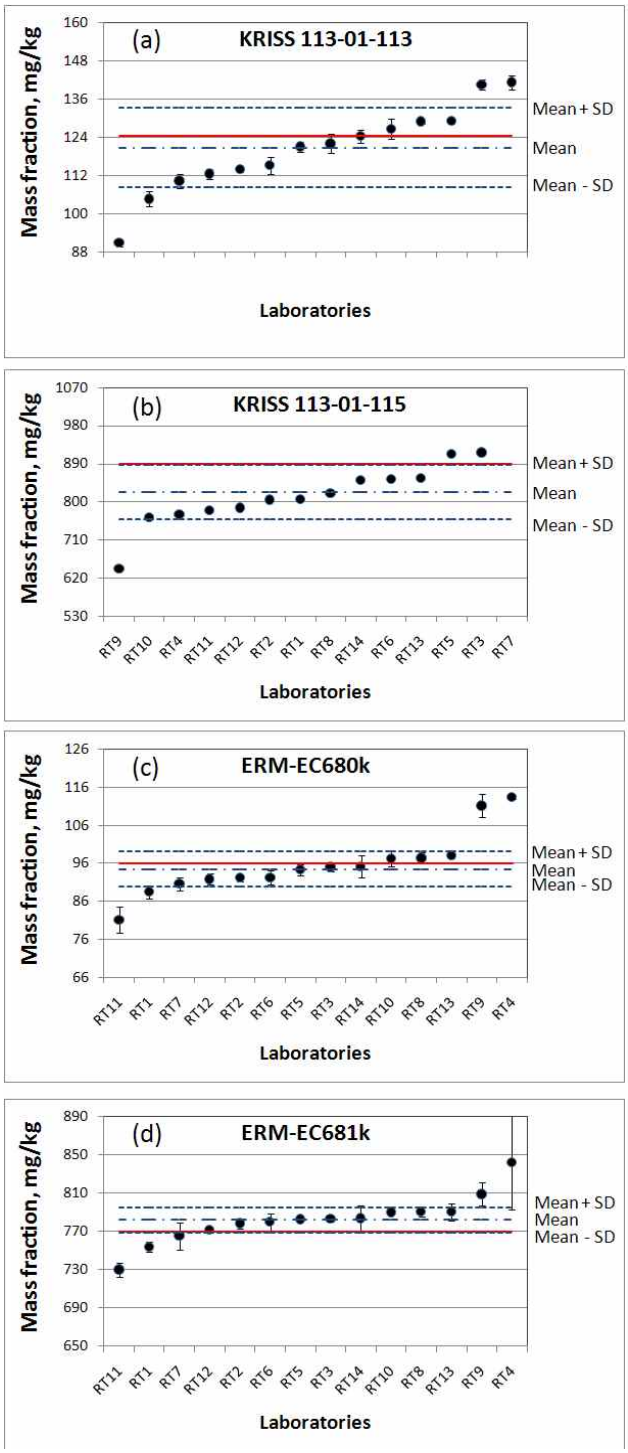

Fig. 1. Results of the interlaboratory study on KRISS 113-01-013 (a), 113-01-015 (b), ERM EC680k (c) and EC681k (d). Solid line indicates reference value.

KRISS 113-01-015 is not so much bigger than that of ERM EC681k. So it was thought that the bromine content of KRISS 113-01-015 did not exceed the upper limit of measurement range of the C-IC. But it might be affected by the coexistent elements. In the KRISS 113-01-015, there are many elements; As, Cr, Hg, Pb, S, Zn, Ni, Sb, Se, Cl in 1 000 mg/kg, Ba 2 000 mg/kg, Cd 100 mg/kg. In the KRISS 113-01-013, the concentration of those elements is less than 300 mg/kg. In the ERM EC681k, the concentration exceeds 500 mg/kg only for of Cl, S, Zn [8].

5. CONCLUSION

For the ABS samples (KRISS 113-01-013, 113-01-015), within a range of bromine content from 100 mg/kg to 1 000 mg/kg, the mean of participants consist to the reference value within 9 % and the standard deviation was not bigger than 10 %. For the ERM samples (EC680k, EC681k), result of the interlaboratory study was excellent. Standard deviation among the participants was small ($\leq$ 5 %) and their mean agreed to the reference values within 2 %. This shows a vivid example for the usefulness of CRMs. If ABS CRMs for the measurement of bromine contents had been available before this study, the results of the KRISS 113-01-013, 113-01-015 would have been as good as that of ERMs. It is thought that the result of ERM samples in this study would be the limit of reproducibility of C-IC on bromine content in plastic samples.

The KRISS 113-01-011, 113-01-012, 113-01-013, 113-01-014, 113-01-014 are now available since January 2012. They provide certified values on eight elements of As, Br, Cd, Cr, Hg, Ni, Pb, Sb within 10 mg/kg to 1 000 mg/kg (1 mg/kg to 100 mg/kg for Cd). We authors wishes that these materials would be helpful not only for the bromine analysis by C-IC but also for the other measurement related to the international environmental regulations such as RoHS directive[1]. And also wish that more various CRMs would be available for those application fields.

5. REFERENCES

[1] P. Eriksson, E. Jakobsson, and A. Fredriksson, “Brominated flame retardants: A novel class of developmental neutrotoxicants in our environment?”, Environ. Health Perspect. vol. 109(9), pp. 903–908, 2001

[2] EPA/635/R-07/008F, “Toxicological review of Decabromodiphenyl Ether (BDE-209)”, EPA, 2008

[3] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment

[4] IEC ACEA. IEC 62321: Procedures for the determination of levels of regulated substances in electrotechnical products. Version 1.0, 12 June 2004.

[5] Certificate of Reference Material; KRISS CRM 113-01-011~113-01-015, ABS (Acrylonitrile Butadiene Styrene) for analysis of hazardous elements, KRISS, 2012.

[6] Y.-S. Chung, S.-H. Kim, J.-H. Moon, S.-Y. Baek, H.-R. Kim and Y.-J. Kim, “Characteristics of a new pneumatic transfer system for a neutron activation analysis at the HANARO research reactor”, Nucl. Eng. & Tec. 41 (6), pp. 813-820, 2009.

[7] KS M 0180:2009; Standard test method of halogen (F, Cl, Br) and sulfur content by oxidative pyrohydrolytic combustion followed by ion chromatography detection (Combustion ion chromatography, CIC)

[8] Report EUR 22784 EN; Certificate report, The certification of the mass fractions of As, Br, Cd, Cl, Hg, Pb, S and Sb and the assignment of indicative values for Sn and Zn in two polyethylene reference materials, Certified Reference Materials ERM®-EC680k and ERM®-EC681k, IRMM, 2007.

[9] ISO 13528 (2005); Statistical Methods for use in proficiency testing by inter laboratory comparisons. International Organization for standardization, Geneva