CCQM K-129

Measurement of mole fractions of Cu, In, Ga and Se in $Cu(In,Ga)Se_2$ Films

Final Report

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Abstract

CCQM key comparison K-129 for the quantitative analysis of Cu(In,Ga)Se_2 (CIGS) films has been performed by the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM). The objective of this key comparison is to compare the equivalency of the National Metrology Institutes (NMIs) and Designated Institutes (DIs) for the measurement of mole fractions of Cu, In, Ga and Se in a thin CIGS film. The measurand of this key comparison is the average mole fractions of Cu, In, Ga and Se of a test CIGS alloy film in the unit of mole fraction (mol/mol). Mole fraction with the metrological unit of mol/mol can be practically converted to atomic fraction with the unit of at%.

In this key comparison, a CIGS film with certified mole fractions was supplied as a reference specimen to determine the relative sensitivity factors (RSFs) of Cu, In, Ga and Se. The mole fractions of the reference specimen were certified by isotope dilution - inductively coupled plasma/mass spectrometry (ID-ICP/MS) and are traceable to the SI. A total number counting (TNC) method was recommended as a method to determine the signal intensities of the constituent elements acquired in the depth profiles by Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). Seven NMIs and one DI participated in this key comparison. The mole fractions of the CIGS films were measured by depth profiling based-SIMS, AES and XPS. The mole fractions were also measured by non-destructive X-Ray Fluorescence (XRF) Analysis and Electron Probe Micro Analysis (EPMA) with Energy Dispersive X-ray Spectrometry (EDX).

In this key comparison, the average degrees of equivalence uncertainties for Cu, In, Ga and Se are 0.0093 mol/mol, 0.0123 mol/mol, 0.0047 mol/mol and 0.0228 mol/mol, respectively. These values are much smaller than that of Fe in a Fe-Ni alloy film in CCQM K-67 (0.0330 mol/mol). This means that the quantification of multi-element alloy films is possible by depth profiling analysis using the TNC method.

1. Introduction

CIGS thin film solar cells are one of the most promising next-generation solar cells with high conversion efficiency and low fabrication cost.[1,2] The relative mole fractions and in-depth distributions of the constituent elements should be well controlled for the formation of a chalcopyrite crystal structure because the conversion efficiency of the CIGS thin film solar cells depends on the crystalline structure.

Although the elemental depth profiling analysis of CIGS films has been studied by several conventional analytical techniques, none of these techniques could be identified without any restrictions as suitable for an unambiguous and quantitative elemental distribution analysis of a thin film with unknown compositional in-depth distribution while some of the techniques can be expected to meet those requirements when several appropriate reference depth profile samples can be provided.[3] In the conventional surface analysis methods such as SIMS, AES and XPS, the quantitative surface analysis of multi-element alloy films is difficult due to matrix effects and sputtering effects.

In the CCQM pilot study P-98 and key comparison K-67 for the quantitative analysis of Fe-Ni alloy films, the RSF method based on RSFs determined from a Fe-Ni alloy certified reference material was found to be more quantitative than from RSFs determined from pure Fe and Ni films.[4,5] The best method for the quantification of binary alloys is to use an alloy reference with a similar composition to the sample to be analyzed, and the next best approach is to use a calibration curve measured using a series of alloy reference materials with different compositions spanning the unknown composition.[6-9]

A CCQM pilot study P-140 for the measurement of mole fractions of CIGS films was performed to evaluate a protocol for a key comparison to demonstrate the equivalence of measurements by NMIs and DIs by various surface analysis methods such as SIMS, AES, XPS, X-ray Fluorescence (XRF) and Electron Probe Micro Analysis (EPMA) with Energy Dispersive X-ray Spectrometry (EDX). A certified CIGS film with non-uniform depth distributions was investigated as a reference film to determine the RSFs. A total number counting (TNC) method was used as a method to determine the signal intensities of the constituent elements in the CIGS films for SIMS, XPS and AES depth profiling analysis. XRF and EPMA were used as integral measurement techniques. For the latter two methods the mole fractions of the film were determined by measuring element-specific X-ray emission count-rates during a single excitation based experiment. 18 data sets collected from 15 laboratories showed that the relative expanded uncertainties of the pilot study are smaller than 5 % and the quantification of CIGS films is a suitable subject for key comparison.[10]

2. Outline of CCQM K-129

2.1. Objective

The objective of CCQM key comparison K-129 is to compare the mole fractions of Cu, In, Ga and Se in a thin CIGS alloy film. The measurands of this key comparison are the average mole fractions of Cu, In, Ga and Se of a test CIGS film in the unit of mol/mol.

2.2. Participation

Seven NMIs and one DI participated in CCQM K-129 key comparison as tabulated in Table 1. XPS, AES, SIMS, XRF and EPMA were used as the measurement methods.

Table 1. Participants in K-129

No.	Laboratory	Country	Participants	Method
1	BAM	Germany	T. WIRTH, V.-D. HODOROABA, W. E. S. UNGER	AES
2	INMETRO	Brazil	J. R. ARAUJO, B. S. ARCHANJO, C. E. GALHARDO J. DAMASCENO, C. A. ACHETE	XPS
3	KRISS	Korea	K. J. KIM, A. S. KIM, J. S. JANG, J. K. SUH	XPS
4	NIM	China	H. WANG, M. L. WANG	XPS
5	NIST	USA	J. BENNETT, D. SIMONS	SIMS
6	NMIJ	Japan	A. KUROKAWA, S. TERAUCHI, T. FUJIMOTO	AES
7	PTB	Germany	C. STREECK, B. BECKHOFF	XRF

3. The Specimens

3.1. Fabrication

The reference and test polycrystalline CIGS thin films were grown on 100 mm x 100 mm soda-lime glass substrates by 3-step thermal evaporation.[11] Before the growth of the CIGS layer, a Mo back contact layer of about 900 nm was deposited on a soda lime glass using a DC sputtering system. The mole fractions of the constituent elements (Cu, In, Ga, Se) are not homogeneous in depth, which are similar to those of a real solar cell. The thicknesses of the films are about 2 μm. The specimens were kept in vacuum packs to prevent a change of surface chemical state due to oxidation by exposure to the atmosphere

3.2. Certification of mole fractions by ID-ICP/MS

The relative mole fractions of Cu, In, Ga and Se in the reference CIGS film were certified by ID-ICP/MS and are traceable to the SI. The isotopic ratios of n(^{63}Cu)/n(^{65}Cu), n(^{113}In)/n(^{115}In), n(^{69}Ga)/n(^{71}Ga) and n(^{78}Se)/n(^{82}Se) were precisely measured for the quantification of metallic elements. The detailed method to certify can be found in previous literature.[10,12] The mole fractions and the measurement uncertainties of Cu, In, Ga and Se in the reference CIGS film are summarized in Table 2 and shown in the certificate (Appendix on page 16).

Table 2. The certified mole fractions (C_i^{AR}) and the expanded uncertainties of the mole fractions for the constituent elements in the reference CIGS film.

Element	Mole Fraction (mol/mol)	Relative Standard Uncertainty (%)	Degree of Freedom	Coverage Factor (k)	Relative Expanded Uncertainty (%)
Cu	0.2381	1.18	10	2.23	2.60
In	0.1948	1.23	11	2.20	2.72
Ga	0.0683	1.02	10	2.23	2.20
Se	0.4988	1.38	11	2.20	3.05

4. TNC Measurement Procedure

In the P-140 pilot study, the TNC method was confirmed to be a useful method to quantify multi-element alloy films by surface analysis methods using depth profiling analysis. The average mole fractions of the alloy films and the in-depth distributions of the constituent elements could be quantitatively determined using a reference material with similar compositions to those of the test specimen.[12,13]

4.1. Determination of signal intensity by the TNC method

Figure 1 shows an example for the determination of the signal intensities of Cu, In, Ga and Se in a raw SIMS and a raw AES depth profile of the reference CIGS film. The signal intensities (I_i^{AR}) of the constituent elements are determined from the summation of the individual intensities of element i ($i_{i,k}^{AR}$) of the constituent element i over all of the measurement cycles (k) by the TNC method after depth profiling of the reference CIGS film.

$$I_i^{AR} = \sum_{k=1}^{m} i_{i,k}^{AR} \quad \text{--} \quad (1)$$

The peak areas and the peak-to-peak heights can also be used as the signal intensities for the quantitative analysis by XPS and AES depth profiling analyses, respectively.

4.2. Determination of sensitivity factors

Alloy reference RSFs (ARRSFs) are recommended as the RSFs for the quantification of CIGS alloy films by surface analysis methods. The ARRSFs (S_i^{AR}) of the multi-element alloy films are determined by dividing the signal intensities (I_i^{AR}) of the constituent elements by the certified mole fractions (C_i^{AR}) from the following equation,

$$S_i^{AR} = (I_i^{AR} / C_i^{AR}) \text{ -- } (2)$$

The ARRSFs listed in Table 3 shows very large relative standard deviations due to the variations of the experimental conditions.

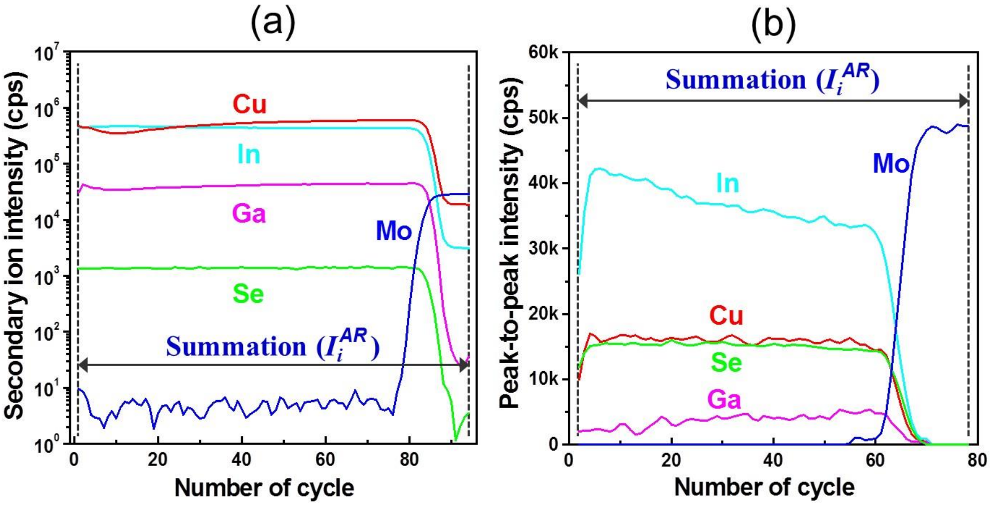

Figure 1. Method to determine the signal intensity using the total number counting method: (a) by summation of the secondary ion intensities in a SIMS depth profile, (b) by summation of the peak-to-peak heights in an AES depth profile.

Table 3. Example of the sensitivity factors (S_i^{AR}) of Cu, In, Ga and Se of the reference CIGS film measured by KRISS.

Element	1	2	3	4	Average	RSD(%)
Cu	966422	847484	669531	825024	827115	14.75
In	1398399	1237700	980187	1211430	1206929	14.27
Ga	1005936	873953	691202	868173	859816	15.02
Se	158589	140666	116621	143274	139788	12.41

4.3. Relative ratio of the sensitivity factors

In a practical quantitative analysis using an alloy reference film, the relative ratios (R_i^{AR}) of the ARRSFs (S_i^{AR}) divided by a representative ARRSF is more accurate than ARRSFs themselves. The relative ratios of the ARRSFs can be obtained by the following equation.

$$R_i^{AR} = (S_i^{AR} / S_{Cu}^{AR}) \text{ --- } (3)$$

$$R_{Cu}^{AR} = 1 \text{ -- } (4)$$

Table 4. Example of the relative ratios of the RSFs of Cu, In, Ga and Se of the reference CIGS film measured by KRISS.

Element	1	2	3	4	Average	RSD(%)
Cu	1.00	1.00	1.00	1.00	1.00	0.00
In	1.45	1.46	1.46	1.47	1.46	0.63
Ga	1.04	1.03	1.03	1.05	1.04	0.94
Se	0.16	0.17	0.17	0.17	0.17	3.06

The ARRSF of Cu ($S_{Cu}{}^{AR}$) is recommended as a representative ARRSF. Table 4 shows that the average relative standard deviations of the ARRSFs are highly improved from 14.1 % to 1.2% by using the relative ratios of the ARRSFs.

4.4. Average mole fractions of the constituent elements

The mole fractions ($X_i{}^{unk}$) of the constituent elements in the Test CIGS film are calculated from the relative ratios (R_i^{AR}) of the ARRSFs and the signal intensity (I_i) of element i in the depth profiles of the Test CIGS film by the following equation.

$$X_i^{unk} = \frac{(I_i / R_i^{AR})}{\sum_{j=1}^{n} (I_j / R_j^{AR})} \text{--} (5)$$

Table 5 shows an example of the measured average mole fractions of Cu, In, Ga and Se from the test CIGS film by KRISS using XPS. Figure 2 shows compositional XPS depth profiles of the reference CIGS film. The four individual profiles show reproducible results in the points of the quantity and the depth distribution of the constituent elements.

Table 5. Example of the measured average mole fractions of Cu, In, Ga and Se from the test CIGS film by KRISS using XPS.

Element	1	2	3	4	Average	RSD(%)
Cu	0.2483	0.2439	0.2440	0.2431	0.2448	0.97
In	0.1696	0.1725	0.1722	0.1727	0.1718	0.85
Ga	0.0850	0.0877	0.0875	0.0887	0.0872	1.79
Se	0.4971	0.4959	0.4963	0.4956	0.4962	0.13

4.5. Determination of Uncertainty

In the quantification of the CIGS films using ARRSFs, the combined relative standard uncertainty (u_c) is calculated from the following simple relation,

$$u_c^2 = u_{CRM}^2 + u_{RSF}^2 + u_{quant}^2 \text{---------------------------------------} (6)$$

where u_{CRM} is the combined relative standard uncertainty in the certification of the reference CIGS film as shown in Table 2. u_{RSF} and u_{quant} are the relative standard uncertainties of the means in the determination of the ARRSFs and the quantification of the CIGS films, respectively. The relative standard uncertainty in the determination of RSF (u_{RSF}) of $R_{Cu}{}^{AR}$ is fixed to be zero because Cu is the representative ARRSF in Eqn 4. An example of the determination of the combined relative standard uncertainty u_c and the expanded relative uncertainty $U = ku_c$, with 95 % confidence level is shown in Table 6. The effective degrees of freedom (ν_{eff}) were estimated from the standard uncertainties and the degrees of freedom by the Welch-Satterthwaite formula, as in the following equation.

$$\nu_{eff} = u_c^4 \Big/ \sum_{i=1}^{N} \frac{u_i^4}{\nu_i} \quad \text{--} \quad (7)$$

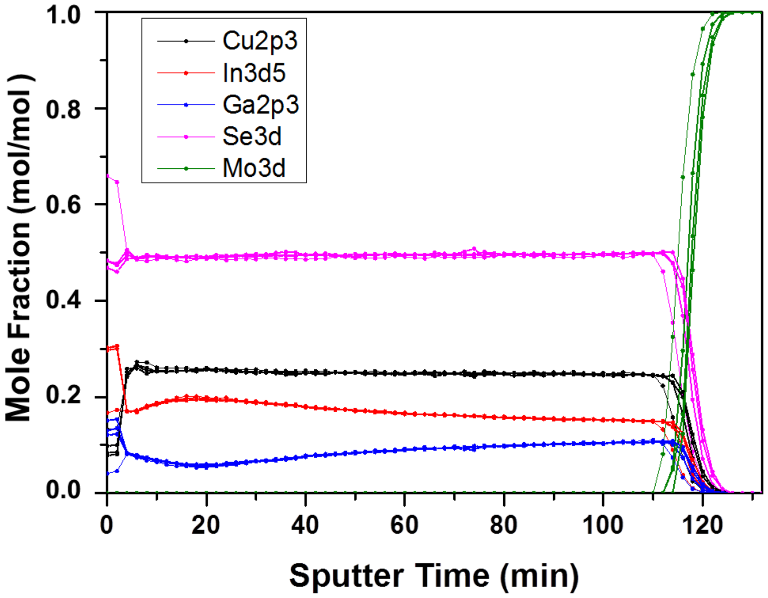

Figure 2. Four compositional depth profiles of the reference CIGS film by XPS from KRISS.

Table 6. An example of the uncertainty budget for the quantification of the test CIGS film by KRISS using XPS.

Uncertainty component	Element			
	Cu	In	Ga	Se
Relative standard uncertainty u_{CRM} (%)	1.18	1.23	1.02	1.38
Relative standard uncertainty u_{RSF} (%)	0	0.32	0.47	1.53
Relative standard uncertainty u_{quant} (%)	0.48	0.42	0.90	0.07
Combined rel. std. uncertainty u_{c} (%)	1.27	1.34	1.44	2.06
Degree of freedom, ν_{CRM}	10	11	10	11
Degree of freedom, ν_{RSF}	3	3	3	3
Degree of freedom, ν_{quant}	3	3	3	3
Effective degree of freedom, ν_{eff}	12	14	12	8
Coverage factor, k	2.18	2.14	2.18	2.31
$U = ku_{\mathrm{c}}$ (%)	2.78	2.86	3.14	4.76

5. Experimental Details

5-1. BAM (AES)

BAM used a PHI 700 Scanning Auger Probe (ULVAC-PHI Inc.) equipped with a cylindrical mirror analyzer. The Auger electrons were excited by a primary electron beam of 5 keV with a current of 20 nA. The primary electron beam hit the surface at 30° to the surface normal. Analyzing the CIGS film the Auger transitions Cu LMM (922 eV), In MNN (405 eV), Ga

LMM (1070 eV), Se LMM (1311 eV), Na KLL (996 eV), C KLL (275 eV) and O KLL (510 eV) were detected. The relative energy resolution of the analyzer ΔE/E was 0.5 %. Depth profiling was carried out by applying Ar^+ ion beam sputtering at 3 keV with a current of 2 µA. The ion beam was rastered across an area of 0.8 mm x 0.8 mm creating a flat crater bottom with little roughness. The incidence angle of the ion beam referred to the surface normal was 42^0. Depth profiles were performed by Auger signal detection and ion etching in alternating mode. In order to minimize surface roughening the primary electron beam was defocused to about 1 µm diameter.

5-2. INMETRO (XPS)

XPS was used in INMETRO for the quantification of CIGS films. The instrument used was an Escaplus P System, Omicron NanoScience-Oxford Instruments, with a non-monochromatic magnesium X-ray source (Kα=1253.6 eV) operated at 12.5 kV and 16 mA emission. The analysis area on the sample was approximately 2 mm in diameter. XPS spectra were acquired using an analyzer pass energy of 20 eV, 0.25 step, 0.4 s dwell per step, and the charge neutralizer was turned on during acquisition of XPS spectra (operated at 5 kV and 5 µA emission). The X-rays and charge neutralizer were switched off during sputtering. An Omicron NanoScience Fig-05 ion gun was used to sputter the samples with Ar^+ ions at beam energy of 4 KeV and at an angle of incidence of 40º from the surface normal, rastered over an area of approximately 4 mm x 3 mm on the sample. The beam current measured using a Fluke ammeter was approximately 7µA. The sputtering rate was ~ 0.12 nm/s. No sample rotation was used during sputtering. The peaks used for the quantification were Cu $2p_{3/2}$, In $3d_{5/2}$, Se 3d and Ga 3d. The peak intensities of CIGS alloy reference and CIGS test film were determined by measuring the raw peak area after Shirley background removal using CasaXPS software.

5-3. KRISS (XPS)

The mole fractions and depth distributions of the CIGS thin films were analyzed by a PHI 5000 VersaProbe II scanning XPS (ULVAC-PHI, Inc) using a monochromatic Al Kα radiation source with a pass energy of 20 eV. The CIGS films were sputtered by argon ion beam of 3 keV at an incidence angle of 40° with a rastered area of 2 mm x 2 mm. The samples were rotated during sputtering to minimize the development of surface topography. Depth profiles of Cu $2p_{3/2}$, In $3d_{5/2}$, Ga $2p_{3/2}$ and Se 3p peaks were obtained from the peak areas measured after removal of background. The intensities of Cu, In, Ga and Se were determined by summation of the peak intensities in the whole depth range including surface and substrate boundaries using a TNC method. The ARRSFs were determined from the depth profiles and the certified mole fractions of the reference CIGS film. The mole fractions of the test specimen were determined from the ARRSFs.

5-4. NIM (XPS)

The mole fractions and depth distributions of the CIGS thin films were analyzed using XPS (Escalab 250Xi, Thermo Fisher Scientific). An argon ion beam of 3 keV and medium current at an incidence angle of 40° was used as the sputtering source with the rastering area of 2 mm x 2 mm (the sample rotation was not used). Monochromatic Al Kα radiation source and a beam spot diameter of 400 µm were applied to the sample. Spectra were acquired using pass energy of 20 eV and the charge neutraliser was turned on during the whole process. The raw peak areas of Cu 2p3/2, In 3d5/2, Ga 2p3/2 and Se 3d were measured after removal of a Smart background using Avatagesystem software provided by the manufacturer. Using TNC method including surface and substrate boundaries, the mole fractions and depth distributions of the CIGS thin films were obtained by the peak areas of Cu 2p3/2, In 3d5/2, Ga 2p3/2 and Se 3d and the ARRSFs from the reference CIGS film.

5-5. NIST (SIMS)

The CIGS films were analyzed in a Cameca IMS-6f instrument*. Each sample was mounted behind the same hole in a multi-hole sample holder and held with a backing spring and pressure plate. The reference and test sample were both analyzed on the same day. An O_2^+ primary ion beam from the duoplasmatron ion source was accelerated to 12.5 keV and impacted the sample that was held at +4.5 kV for a net impact energy of 8 keV. The calculated angle of incidence from normal was 38°. The primary beam was rastered over a nominal 150 µm x 150 µm area. Positive secondary ions were accepted from a ~60 µm diameter area at the center of the raster, gated by a field aperture. The spectrometer entrance slit was set at 30 µm and the exit slit was set at 500 µm. The energy slit was set for a bandpass of 50 eV and was centered on the maximum in the energy distribution. The contrast aperture was 20 µm. Five depth profiles were collected from the reference sample and 6 depth profiles were collected from the test sample. The craters centers were separated by more than 300 µm and were located near the center of the mask hole.

The monitored species were ^{63}Cu (2 s), ^{71}Ga (1 s), ^{80}Se (3 s), and ^{113}In (1 s). The reference sample profiles were acquired with 120 cycles which took about 30 min to complete. The test sample profiles were acquired with 95 cycles which took about 16 min to complete. The data were processed in an Excel spreadsheet. The count rates for ^{63}Cu, ^{71}Ga, ^{80}Se, and ^{113}In were integrated up to a cycle where the signals began to decrease at the interface. Count rates were corrected for a detector dead-time of 25.1 ns. The effective dead-time was expanded to account for the gating of the signal during the raster. This factor was found to be about 6 by comparing the count rate of a static beam in the center of the raster with the count rate under raster conditions.

*Certain commercial equipment is identified in this report to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the equipment identified is necessarily the best available for the purpose.

5-6. NMIJ (AES)

NMIJ used a PHI SAM680 Scanning Auger Microprobe (ULVAC-PHI Inc.). For the depth profiling, an Ar ion beam with an impact energy of 3 keV and an incidence angle of 30° was rastered over an area of 1.0 mm ×1.0 mm on the sample surface. The electrons ejected from the central area of 0.1 x 0.1 mm^2 were analysed. The sample stage used Zalar rotation at a rate of 0.40 rotations per minute during the sputtering. The Zalar rotation was halted during the AES spectrum acquisition. The AES EN(E) spectra were obtained with an electron probe energy of 5 keV and with a current of 10 nA. For the depth-profile analysis over the entire film the spectrum acquisition followed by the ion sputtering were repeated 21 times. The AES signal intensity was derived from the peak-to-peak intensity in the derivative spectrum. The Cu-LMM, In-MNN, Ga-LMM and Se-LMM peaks were used.

5-7. PTB (XRF)

For this KC-129 reference-free X-Ray Fluorescence (XRF) measurement procedures as established at PTB were used.[10,14,15] These procedures are based on measurements using synchrotron radiation and, in particular, radiometrically calibrated instrumentation. For the reference-free quantification of the mole fractions no reference material or calibration sample is needed: Relevant experimental, instrumental and fundamental parameters are used.[14] For this KC-129 the samples were investigated with monochromatized synchrotron radiation at the FCM beamline in the PTB laboratory[16] at the electron storage ring BESSY II using excitation energy of 11 keV with different angles of incidence in the 0° to 45° range, with the 45° values used to derive the results presented. Here, the Cu-Kα, Ga-Kα and In-Lα fluorescence lines have been used for the reference-free XRF quantification. Detailed information is described in a published paper.[15]The determination of the expanded uncertainties (U) and relative expanded uncertainties (RU) of the reference-free XRF quantification results (see table 9) mainly involves the uncertainties of the fundamental atomic, experimental and instrumental parameters using standard propagation of uncertainty. Counting statistic contributions to the uncertainty are rather small. More detailed information can be found in a published literature.[17]

6. Reported Average Mole Fractions

The reported average mole fractions (x_i) of Cu, In, Ga and Se from the test CIGS specimen in this CCQM K-129 are listed in Table 7. The expanded uncertainties (U_i) were evaluated at 95% confidence level as shown in Table 8.

Table 7. Reported average mole fractions (unit: mol/mol) of Cu, In, Ga and Se in CCQM K-129.

Laboratory	BAM	INMETRO	KRISS	NIM	NIST	NMIJ	PTB
Method	AES	XPS	XPS	XPS	SIMS	AES	XRF
No of meas.	5	5	4	5	5	3	3
Cu	0.2464	0.2633	0.2448	0.2448	0.2544	0.2426	0.2380
In	0.1683	0.1656	0.1718	0.1734	0.1554	0.1745	0.1807
Ga	0.0855	0.0661	0.0872	0.0827	0.0824	0.0835	0.0765
Se	0.4998	0.5051	0.4962	0.4991	0.5078	0.4993	0.5048

Table 8. Reported expanded uncertainties (unit: mol/mol) of Cu, In, Ga and Se in CCQM K-129 at 95% confidence level.

Laboratory	BAM	INMETRO	KRISS	NIM	NIST	NMIJ	PTB
Method	AES	XPS	XPS	XPS	SIMS	AES	XRF
No of meas.	5	5	4	5	5	3	3
Cu	0.0069	0.0126	0.0068	0.0065	0.0069	0.0078	0.0083
In	0.0058	0.0067	0.0049	0.0058	0.0048	0.0063	0.0187
Ga	0.0081	0.0025	0.0027	0.0028	0.0020	0.0032	0.0047
Se	0.0176	0.0206	0.0236	0.0177	0.0162	0.0172	0.0209

7. Key Comparison Reference Value and Uncertainty

The reported results of K-129 are composed of two groups. Six data from BAM, INMETRO, KRISS, NIM, NIST and NMIJ were measured by sputter depth profiling (SDP) method and the mole fractions were based on the certified mole fractions of the KRISS CRM. However, the result of PTB was measured by the reference-free XRF method.

First, the arithmetic means (x_{SDP}) and the uncertainties (U_{S}) for the SDP results were determined from the data of BAM, KRISS, NIM, NIST and NMIJ by the following equations.

$$x_{SDP} = \sum_{i=1,m} x_i / m \quad \text{--} (8)$$

$$U_S = k u_S,\ u_S = s(x_i)/\sqrt{m} \quad \text{--} (9)$$

The uncertainty (U_{SDP}) of the reported SDP data was determined by combination of the uncertainties of the reported result (U_S) and the KRISS CRM (U_{CRM}) as shown in Table 2.

$$U_{SDP}^2 = (U_S^2 + U_{CRM}^2) \quad \text{---}(10)$$

Just after the presentation of the results in 2015 SAWG meeting, INMETRO has withdrawn their data because there was a mistake in the determination of Ga peak area. Therefore INMETRO's results have been not used for the calculation of the key comparison reference value (KCRV) and its uncertainty. Re-calculated INMETRO data and post-deadline reported NPL data are plotted in Appendix B and compared with the key comparison results.

Second, the key comparison reference values (KCRV: x_R) of K-129 were calculated by uncertainty-weighted mean method from the x_{SDP} and the reported mole fraction by reference-free XRF data (x_{XRF}) to recognize for the specific characters of the two groups.

$$U(x_R) = \sqrt{1 \Big/ \sum_{i=1,m} w_i}\ ,\quad w_i = \frac{u(x_i)^{-2}}{\sum_{j=1,m} u(x_j)^{-2}} \quad \text{------------------------} (11)$$

$$x_R = \sum_{i=1,m} w_i x_i \quad \text{--} (12)$$

The key comparison reference values and the uncertainties of Cu, In, Ga and Se in CCQM K-129 are shown in Table 9. Figure 3 shows the reported average mole fractions (x_i) and the expanded uncertainties (U_i) of Cu, In, Ga and Se in K-129. The solid blue lines and the broken red lines are the key comparison reference values and their standard uncertainties.

Table 9. Key comparison reference values and uncertainties of Cu, In, Ga and Se in CCQM K-129.

Element	Cu (mol/mol)		In (mol/mol)		Ga (mol/mol)		Se (mol/mol)	
	x_R^{Cu}	U_R^{Cu}	x_R^{In}	U_R^{In}	x_R^{Ga}	U_R^{Ga}	x_R^{Se}	U_R^{Se}
mean of SDP results (A)	0.2466	0.0081	0.1687	0.0104	0.0843	0.0028	0.5004	0.0160
reference-free XRF (B)	0.2380	0.0083	0.1807	0.0187	0.0765	0.0047	0.5048	0.0209
weighted mean of A and B	0.2424	0.0058	0.1715	0.0091	0.0823	0.0024	0.5021	0.0127

8. Equivalence Statements

The equivalence statements were calculated for each of the seven laboratories following BIPM guidelines. The degrees of equivalence (D_i) of the reported results, x_i, and the KCRV, x_R, were calculated using the following expression:

$$D_i = x_i - x_R \quad \text{--} (13)$$

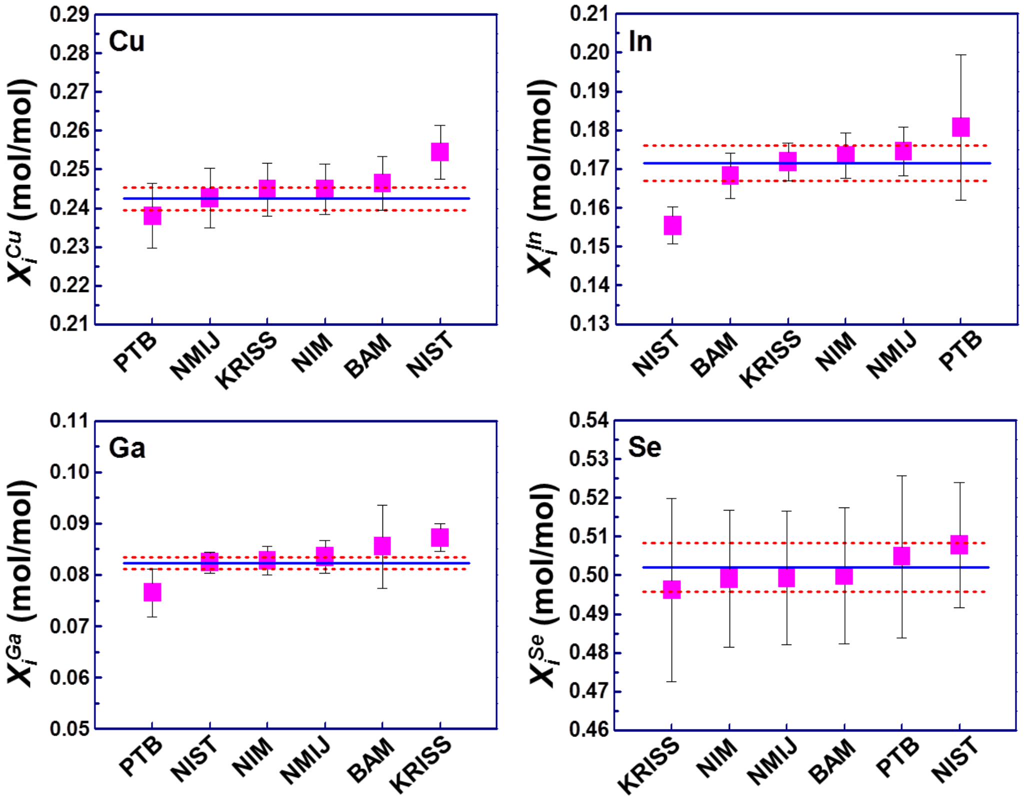

Figure 3. Key comparison reference values and their standard uncertainties in CCQM K-129.

The uncertainty for the degree of equivalence [$U(D_i)$] was calculated from the combination of the uncertainties of the individual data (U_i) and the uncertainty of the KCRV (U_R) from the following equation:

$$U^2(D_i) = U_i^2 + U_R^2 \qquad \text{--} \ (14)$$

Table 10 and Figure 4 show the degrees of equivalence (DoE) and their uncertainties for K-129.

Table 10. Degrees of equivalence (DoE) and their uncertainties for K-129.

Laboratory	Cu (mol/mol)		In (mol/mol)		Ga (mol/mol)		Se (mol/mol)	
	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$
BAM	0.0040	0.0090	-0.0032	0.0108	0.0032	0.0084	-0.0023	0.0217
KRISS	0.0024	0.0089	0.0003	0.0103	0.0049	0.0036	-0.0059	0.0268
NIM	0.0024	0.0087	0.0019	0.0108	0.0005	0.0037	-0.0030	0.0218
NIST	0.0120	0.0090	-0.0161	0.0103	0.0001	0.0031	0.0057	0.0206
NMIJ	0.0002	0.0097	0.0030	0.0111	0.0012	0.0040	-0.0028	0.0214
PTB	-0.0044	0.0101	0.0092	0.0208	-0.0058	0.0053	0.0027	0.0245

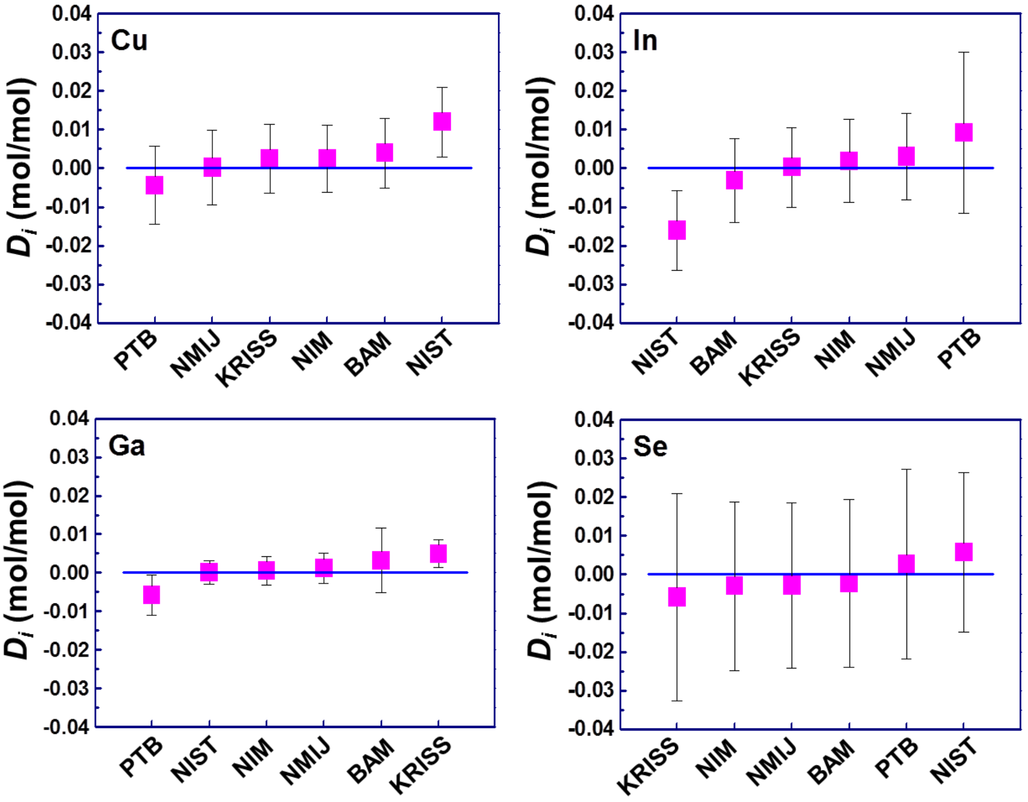

Figure 4. Degrees of equivalence for the mole fractions of Cu, In, Ga and Se in CCQM K-129.

9. Traceability for CMC

Although quantitative analysis by surface analytical methods such as XPS, AES and SIMS are not traceable, it can be made traceable if relative sensitivity factors (RSFs) of the constituent elements have been determined from a certified reference material (CRM) traceable to the SI unit Mol. In K-129, the reported mole fractions (mol/mol) of Cu, In, Ga and Se are traceable because they were determined using RSFs determined from the certified mole fractions of the KRISS CRM (see Certificate in Appendix A). NMIs which participated in K-129 may claim a CMC following these ways.

(1) Use of KRISS CRM
NMIs can claim CMCs by using the KRISS CRM because it was certified by ID-ICP/MS[10,12] traceable to the SI as shown in its Certificate in Appendix A. However, in this case, the CMCs are traceable to the KRISS CRM only. If the KRISS CRM used in K-129 is expired, KRISS will provide a new one.

(2) By own traceability

(a) Having established their own traceability under K-129, NMIs can claim CMCs as usual. PTB with their standard-free XRF protocol, which is traceable to the SI, is an example here.

(b) Traceability through KRISS can be replaced when a NMI certifies the KRISS CRM with traceability to the SI, e.g. by ID-ICP/MS[10,12]. For that purpose KRISS will provide another piece of the KRISS CRM on demand. By doing so the uncertainty claimed by a NMI in a CMC shall not be smaller than that delivered in K-129.

(c) Traceability through KRISS can be replaced when a NMI certifies its own CRM. By doing so the uncertainty claimed by a NMI in a CMC shall not be smaller than that delivered in K-129.

10. How far the light shines

This key comparison support the CMC claims for the mole fractions of Cu (0.20 ~ 0.30 mol/mol), In (0.12 ~ 0.22 mol/mol), Ga (0.03 ~ 0.13 mol/mol) and Se (0.45 ~ 0.55 mol/mol) in CIGS films in the thickness range from 500 nm to 3 μm. This comparison can be a representative example for the quantification of a multi-element alloy film by surface analysis methods.

11. Conclusion

CCQM key comparison K-129 for the quantitative analysis of $Cu(In,Ga)Se_2$ (CIGS) films was performed by the CCQM SAWG. The mole fractions of Cu, In, Ga and Se in a CIGS film were measured and reported by 7 NMIs and 1 DI using SIMS, AES, XPS and X-Ray Fluorescence (XRF) Analysis. Seven laboratories reported the mole fractions within the due date and their results were compared to each other.

The relative sensitivity factors of Cu, In, Ga and Se were recommended to be determined from a reference CIGS film with certified mole fractions by isotope dilution - inductively coupled plasma/mass spectrometry (ID-ICP/MS). A total number counting (TNC) method was also recommended as a method to determine the signal intensities of the constituent elements acquired in the depth profiles by SIMS, XPS and AES.

The average degrees of equivalence uncertainties for Cu, In, Ga and Se were 0.0093 mol/mol, 0.0123 mol/mol, 0.0047 mol/mol and 0.0228 mol/mol, respectively. The uncertainty of Se with a mole fraction of 0.5021 mol/mol is much smaller than that (0.0330 mol/mol) of Fe in a Fe-Ni alloy film with a mole fraction of 0.5002 mol/mol as shown in the report of CCQM K-67.

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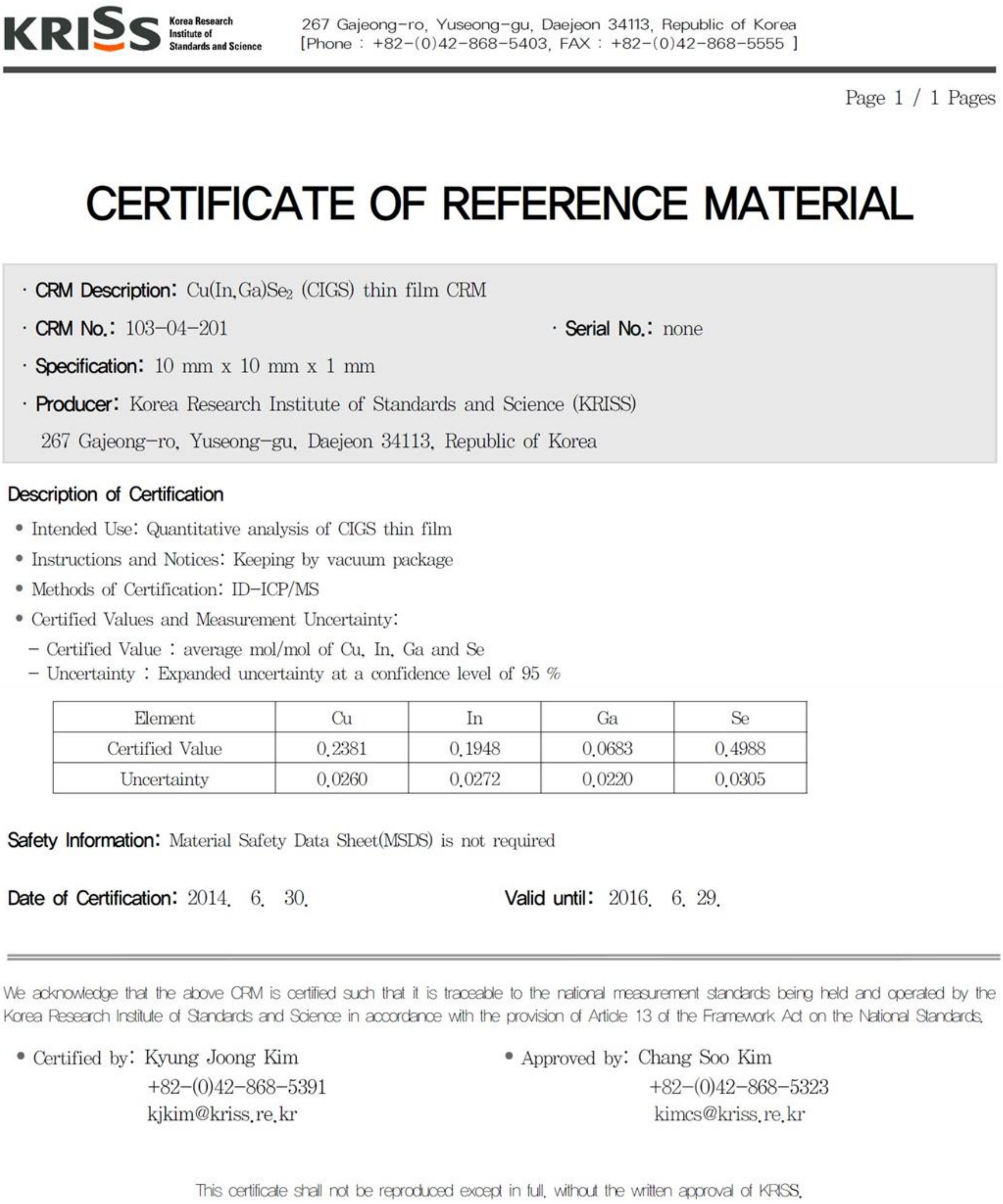
Appendix A: Certificate of the KRISS CRM



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CERTIFICATE OF REFERENCE MATERIAL

· **CRM Description:** $Cu(In,Ga)Se_2$ (CIGS) thin film CRM

· **CRM No.:** 103-04-201 · **Serial No.:** none

· **Specification:** 10 mm x 10 mm x 1 mm

· **Producer:** Korea Research Institute of Standards and Science (KRISS)
267 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

Description of Certification

- Intended Use: Quantitative analysis of CIGS thin film
- Instructions and Notices: Keeping by vacuum package
- Methods of Certification: ID-ICP/MS
- Certified Values and Measurement Uncertainty:
  - Certified Value : average mol/mol of Cu, In, Ga and Se
  - Uncertainty : Expanded uncertainty at a confidence level of 95 %

Element	Cu	In	Ga	Se
Certified Value	0.2381	0.1948	0.0683	0.4988
Uncertainty	0.0260	0.0272	0.0220	0.0305

Safety Information: Material Safety Data Sheet(MSDS) is not required

Date of Certification: 2014. 6. 30. **Valid until:** 2016. 6. 29.

We acknowledge that the above CRM is certified such that it is traceable to the national measurement standards being held and operated by the Korea Research Institute of Standards and Science in accordance with the provision of Article 13 of the Framework Act on the National Standards.

- Certified by: Kyung Joong Kim
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  kjkim@kriss.re.kr
- Approved by: Chang Soo Kim
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  kimcs@kriss.re.kr

This certificate shall not be reproduced except in full, without the written approval of KRISS.

Appendix B: Post-deadline (NPL) and Re-calculated Data (INMETRO)

There were post-deadline reported and re-calculated data sets as shown in Table A1. The exclusion of the post-deadline data from the key comparison was decided in the CCQM SAWG meeting in April, 2015. In the case of INMETRO they withdraw their first set of results because the peak area of Ga 3d (18 eV) was overestimated. The reason was that it is superimposed by the In 4d (16 eV) peak. The Ga $2_{p3/2}$ (~1116 eV) peak area is the better choice for Ga quantification, but using Mg K-alpha radiation source, the energy of transition in Ga 2p3/2 peak is close to the excitation energy of Mg source (1253.6 eV), increasing the signal close to this region due to the excitation of low kinetic energy electrons. Then, Al K-alpha radiation source is more appropriate to the Ga quantification. As Inmetro had only Mg K-alpha source available, the Ga 3d peak was deconvoluted and separated from the In 4d peak. As a result, the re-calculated mole fractions are much closer to the key comparison reference values.

NPL carried out the experiments using a Kratos Axis Ultra DLD with a monochromated aluminium X-ray source operated at 15 kV and 10 mA emission. The analysis area on the sample was approximately 220 μm in diameter. Spectra were acquired using a pass energy of 160 eV, 0.5 eV steps, 0.1 s dwell per step and the charge neutraliser was turned on during acquisition of XPS spectra. The X-rays and charge neutraliser were switched off during sputtering. A Kratos Minibeam IV ion gun was used to sputter the samples with Ar^+ ions at a beam energy of 4 keV and at an angle of incidence 45^o from the surface normal rastered over an area of approximately 4 mm x 4 mm on the sample. The sputtering rate was approximately 0.4 nm/s. No sample rotation was used during sputtering. The peaks used for quantification were Ga $2p_{3/2}$, Cu $2p_{3/2}$, O 1s, In $3d_{5/2}$ and Se 3p. The peak intensities were determined by measuring the raw peak area after removal of a Tougaard background using CasaXPS software. The surface and substrate boundaries were excluded from the quantification procedure.

The post-deadline data (NPL) and the re-calculated data (INMETRO) are given in Table A1 and plotted together with the key comparison results of K-129 in Figure A1. The equivalence statements for the post-deadline data (NPL) and the re-calculated data (INMETRO) were also calculated by the same method from the equations (13) and (14) using the key comparison reference values and uncertainties given in Table 9. The degrees of equivalence (DoE) and their uncertainties for the post-deadline data and the re-calculated data are given in Table A2 and plotted in Figure A2.

Table A1. A post-deadline and a re-calculated data with their expanded uncertainties.

Laboratory	Cu (mol/mol)		In (mol/mol)		Ga (mol/mol)		Se (mol/mol)	
	x_i^{Cu}	U_i^{Cu}	x_i^{In}	U_i^{In}	x_i^{Ga}	U_i^{Ga}	x_i^{Se}	U_i^{Se}
INMETRO	0.2595	0.0131	0.1619	0.0064	0.0829	0.0072	0.4958	0.0193
NPL	0.2446	0.0103	0.1650	0.0176	0.0862	0.0076	0.5042	0.0264

Table A2. Degrees of equivalence (DoE) and their uncertainties for the re-calculated and the post-deadline data.

Laboratory	Cu (mol/mol)		In (mol/mol)		Ga (mol/mol)		Se (mol/mol)	
	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$
INMETRO	0.0209	0.0139	-0.0059	0.0113	-0.0162	0.0035	0.0030	0.0242
NPL	0.0024	0.0089	0.0003	0.0103	0.0049	0.0036	-0.0059	0.0268

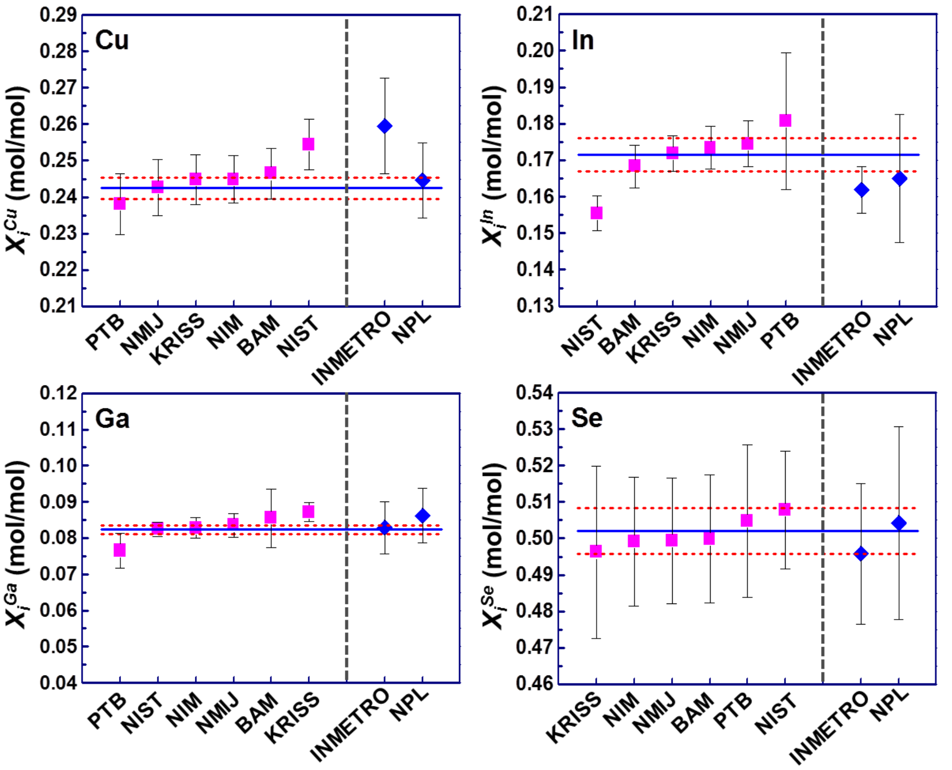

Figure A1. The key comparison results (pink square), the re-calculated and post-deadline data (blue diamond). The broken red lines are the standard uncertainties of the KCRVs.

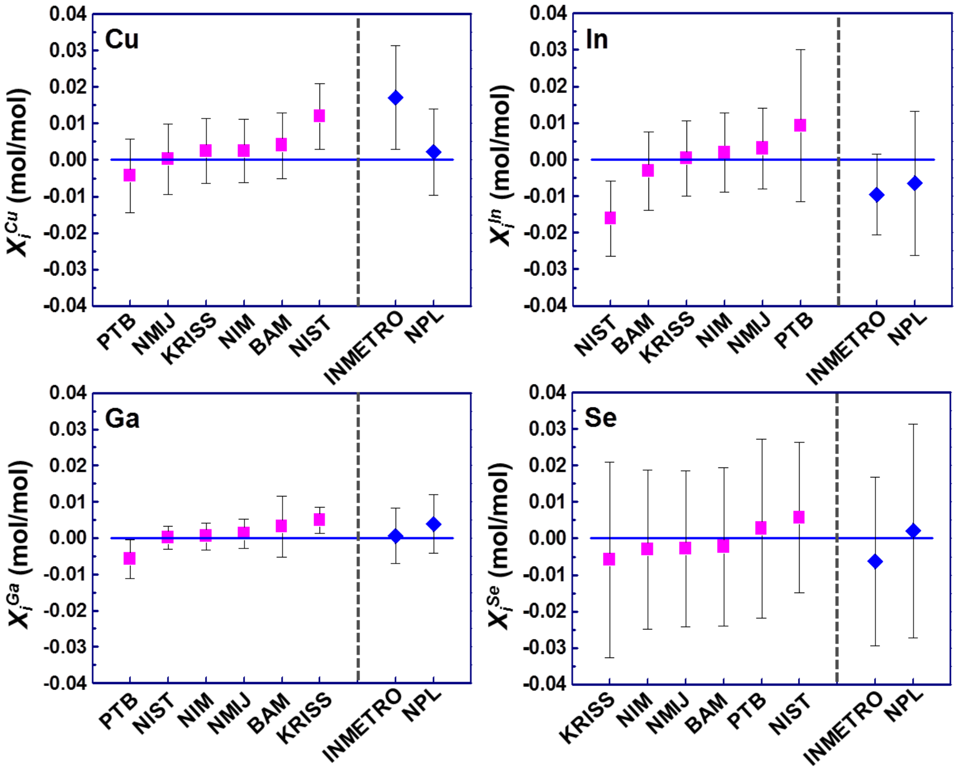

Figure A2. The degrees of equivalence (DoE) and their uncertainties for the post-deadline data and the re-calculated data.