

CCQM-K143 Comparison of Copper Calibration Solutions Prepared by NMIs/DIs

Final Report

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Abstract

CCQM-K143 is a key comparison that assesses participants' ability to prepare single element calibration solutions. Preparing calibration solutions properly is the cornerstone of establishing a traceability link to the International System of Units (SI), and therefore should be tested in order to confirm the validity of CCQM comparisons of more complex materials. CCQM-K143 consisted of participants each preparing a single copper calibration solution at 10 g/kg copper mass fraction and shipping 10 bottled aliquots of that solution to the coordinating laboratory, the National Institute of Standards and Technology (NIST). The masses and mass fraction for the prepared solutions were documented with the submitted samples. The solutions prepared by all participants were measured at NIST by high performance inductively coupled plasma optical emission spectroscopy (HP-ICP-OES). The intensity measurements for copper were not mapped onto values of mass fraction via calibration. Instead, ratios were computed between the measurements for copper and simultaneous measurements for manganese, the internal standard, and all subsequent data reductions, including the computation of the KCRV and the degrees of equivalence, were based on these ratios. Other than for two participants whose measurement results appeared to suffer from calculation or preparation errors, all unilateral degrees of equivalence showed that the measured values did not differ significantly from the KCRV. These results were confirmed by a second set of ICP-OES measurements performed by the Physikalisch-Technische Bundesanstalt (PTB). CCQM-K143 showed that participants are capable of preparing calibration solutions starting from high purity, assayed copper metal. Similar steps are involved when preparing solutions for other elements, so it seems safe to infer that similar capabilities should prevail when preparing many different, single-element solutions.

Introduction

For inorganic chemical analysis, metrological traceability to the International System of Units (SI) is most often established through calibration with high-purity, assayed materials. These calibration materials are usually composed of solutions made by dissolving high-purity, assayed solids into high-purity solvents, such that the composition of the solution in terms of the analyte is well-known. For reliability, the analyte composition of the solution must have a metrologically rigorous assigned value and uncertainty estimate.

In the past, the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) Inorganic Analysis Working Group (IAWG) has performed many key comparisons and pilot studies consisting of inorganic chemical analyses for which participants have relied upon solution calibration materials. These studies assumed the participants could prepare or procure solution calibrants because unbiased analysis results cannot be obtained when the analyte value assigned to the calibrant is itself biased. However, the IAWG has not directly tested the capabilities of its members for preparing calibrants, except in relatively rare instances.

The first IAWG activity to directly evaluate the capabilities of IAWG members for making their own calibration solutions was CCQM-K8 Monoelemental Calibration Solutions [1]. In CCQM-K8, as well as in the later CCQM-K87 Monoelemental Calibration Solutions [2], participants were provided with solutions to analyze and some participants prepared their own calibration solutions to perform their analyses. Because the samples were neat solutions, the CCQM-K8 and CCQM-K87 results might be viewed as providing a more direct evaluation of the calibration solutions prepared by the participants than is provided when participant-prepared calibration solutions are utilized to analyze a sample with a complicated matrix. More recently, CCQM-K72 Purity of Zinc with Respect to Six Defined Metallic Analytes [3], as well as CCQM-P149 Estimation of Impurities for the Overall Purity Evaluation of Zinc [4], have focused attention on the capabilities of IAWG members for performing the purity assays of high-purity solid materials. Consequently, there exists a gap in the traceability chain between the SI and the final measurements which has not been sufficiently assessed.

The past IAWG activity that is most like CCQM-K143 is the unpublished CCQM-P46 Preparation of Elemental Solutions, conducted in 2004-2005. In this pilot study, participants prepared and shipped to the National Institute of Standards and Technology (NIST) single-element calibration solutions composed of copper, magnesium, and rhodium. These three elements were selected on the perception of the ease with which reliable calibration solutions could be prepared: relatively easy (copper), more difficult (magnesium), and very difficult (rhodium). Not all participants provided solutions for all three elements. CCQM-P46 participants shipped their solutions to NIST using their own shipping bottles and packaging materials. NIST then compared all the solutions for each element, reporting the relative amounts (referred to as relative sensitivities) rather than an absolute calibration, using inductively coupled plasma optical emission spectrometry (ICP-OES). CCQM-K143 will similarly present results on a relative scale, focusing on the ratio of the ICP-OES response for Cu and the internal standard (Mn), which will be referred to in this report as “sensitivities”.

Given the similar nature of the CCQM-P46 comparison, it was recognized that parts of its protocol could be improved to increase the confidence of the CCQM-K143 results. The largest unknown in CCQM-P46 came from the shipment of each participant’s samples to NIST: each sample set experienced unique conditions during shipment. This variability was assumed to have an insignificant effect on the solutions. However, while most bottles were uncompromised, some had leaked or had otherwise questionable

seals, and others were difficult to open. Temperature and pressure exposure were unknown during transit, and the amount of solution transpiration may have varied considerably.

It was also recognized that participants in studies of this design would benefit from knowing the choice of internal standard used for the ICP-OES analysis so that any impurities in solvents or the Cu source material could be considered. Further, given the foundational character of calibration solutions to inorganic chemical analysis, confirmation measurements by a second NMI would provide greater trust in the comparison results.

Participation requirements for CCQM-K143 and CCQM-P181

CCQM-K143 was performed in parallel with a pilot study, CCQM-P181. No guidance was given to the national metrology institutes and designated institutes (NMIs/DIs) interested in participating in CCQM-K143/P181 as to which exercise would be appropriate. Nearly all laboratories chose to participate in CCQM-K143.

CCQM-K143 was structured as follows, as agreed upon at the April 2016 IAWG meeting in Sèvres, France:

1. Participants in CCQM-K143 were required to use high-purity copper metal as the source material for the submitted solutions. Participants using high-purity copper compounds could only participate in CCQM-P181.
2. Participants in CCQM-K143 must have evaluated their own assay value for the copper metal, using results of their own measurements and/or those provided by trusted subcontractors. (It should be noted that this requirement should be specified more clearly in any future exercises as some participants used source materials and associated assays directly provided by third parties, in most cases another NMI.)
3. The target mass fraction value for copper in the calibration solution was 10.0 g/kg. Participants were instructed to prepare solutions within 1 % of this target value; i.e., (9.9 to 10.1) g/kg.
4. The target relative expanded uncertainty, expressed at a 95 % confidence level, was 0.3 % or less.
5. Participants in CCQM-K143 provided their own digestion/solution preparation protocol. This protocol was to be documented and submitted along with the solutions.
6. Participants in CCQM-K143 provided their own acids and any other required reagents.
7. The final matrix of the prepared copper solutions consisted of nitric acid, at mass fractions between 6 % to 8 %.
8. After preparation of the copper solution, it was aliquoted into ten 60 mL HDPE bottles, with $25 \text{ g} \pm 0.3 \text{ g}$ of solution in each bottle. The amount of solution present was determined using weighing by difference, using any correction factors the participant felt necessary. After shipment the mass fraction calculated by the participant could be combined with the solution mass measured by the participant to determine the mass of copper present in each bottle upon preparation. This amount of copper would be constant independent of transpiration but would be sensitive to sample loss such as by leakage during transport.

9. NIST provided the bottling and packaging materials and equipment necessary to help ensure the integrity of the solutions during shipment to NIST. The packaged solution aliquots were contained within bottles sealed inside aluminized polyester pouches. NIST provided materials intended to minimize sample loss during transportation. A list of items and their intended use are provided in Table 1. Instructions for using these materials were provided to participants in written and video format.
10. Each participant was required to arrange and pay for transport of solutions back to NIST. NIST provided safety labels which were compliant with the Globally Harmonized System for bottles as well as supplying a Safety Data Sheet. Participants were responsible for safely shipping samples or contracting another organization to do so.

An invitation to participate in CCQM-K143 was published in 21 September 2016. The invitation contained participation requirements, a draft preparation protocol and sample results reporting form. Registrations to participate were submitted until 9 May 2017.

Packaging materials provided

The packaging materials were shipped to participants starting 23 March 2017 with the last set sent 18 May 2017. A preparation protocol, results reporting form and packaging instructions were provided to participants at this time (Appendix A). The range in shipment times encompassed late registrations as well as some import restrictions which necessitated the removal of items from the list in Table 1, and reshipment. This would not invalidate participation as institutes were not required to use the materials provided, especially if onsite equipment existed which was more advanced (such as with a more advanced impulse sealer) or with which participants were more experienced. The provided packaging materials were supplied as a minimal safeguard to ensure solutions arrived at NIST in a state most like the state of initial preparation. Participants could and did augment the provided packaging with items such as more insulation or nested boxes.

Condition of received samples

A list of all registered participants can be found in Table 2. Solutions submitted by participants arrived between 16 May 2017 and 3 August 2017. The initial deadline for sample submission was extended from 30 June 2017 to 7 July 2017 after requests from multiple participants. Some leeway was given to participants on these deadlines as some participants encountered shipping issues depending on country of origin, and past experience with shipping similar materials. In all cases (except those noted in Table 2) participants digitally submitted their results reports detailing solution masses, uncertainties and overall mass fraction by the 7 July 2017 deadline. One institute registered to participate in CCQM-K143 did not receive the packaging materials with time to participate and another institute registered for CCQM-K143 but did not ship samples by 17 August 2017 when submissions were closed.

Each participant's solutions were inspected immediately upon receipt. In general, the solutions were received in good condition. Each participant submitted the appropriate number of bottles, and no bottles were found to be leaking solution. The bottles themselves were not visually inspected as they remained sealed in aluminized polyester bags until shortly before sample preparation and measurement. Instead, the polyester bags were inspected for intact seals, counted, and sealed in a larger polyester bag for storage until all solutions were measured. For received sample sets of ten bottles, participants ranged from having no polyester bags with compromised seals up to 7 bags with compromised seals. Bags with compromised seals were marked externally and resealed with an onsite impulse sealer. Bags which were

marked with compromised or questionable seals were used last or not at all during analysis of all participants' solutions.

Temperature stickers were examined and activation of either the heat sensitive or cold sensitive sticker was noted. Activation of these stickers was not used to disqualify samples but rather as a tool when looking for explanations of differences between participants' results. Fifteen participants included the temperature sensitive stickers. Four heat sensitive stickers had activated, with temperatures of 43 °C to 54 °C.

In general, the packaging materials and protocol put in place allowed participants' samples to reach NIST in good condition. Some participants were required to use third party hazardous material shippers which added a degree of variability to the shipment of material as some shippers removed the temperature stickers or used boxes which were not insulated. Ideally for any similar studies in the future, more instruction should be provided on the use of the impulse sealer as some participants appeared to have difficulty achieving a robust seal.

HP-ICP-OES measurement

Instrumentation

All analyses at NIST were performed on a Perkin Elmer Optima 8300DV ICP-OES¹ equipped with a crossflow nebulizer, a Scott double-pass spray chamber, an alumina injector with an inner diameter of 2.0 mm, and a quartz torch. The plasma was operated using standard settings of 1500 W rf power, and plasma, auxiliary, and nebulizer gas flow rates of 12 L/min, 2 L/min, and 0.70 L/min, respectively. Solutions were delivered to the nebulizer by a peristaltic pump at a flow rate of 1.00 mL/min. Spectra were acquired in axial viewing mode and quantified as peak areas with two-point background correction. A temperature monitor (Inkbird THC-4 Temperature and Humidity Data Logger)¹ was used to monitor the temperature and relative humidity near the spray chamber after starting the ICP-OES instrument.

Wavelength selection

Emission peaks were monitored for Cu and Mn as well as several elements that could cause spectral interferences. The emissions lines measured are shown in Table 3 with the two lines used for the CCQM-K143 comparison shown in bold. The emission lines used for analysis of participants' solutions were carefully chosen based upon sufficient signal intensity and linearity of instrument response at the expected mass fractions of the prepared working solutions.

A simulated CCQM-K143 sample was measured repeatedly over several hours to characterize the effects of temperature changes. The instrumental response changed with changing temperature, with the relationship being dependent on the Cu and Mn emission lines used. The fluctuation of instrumental response was not eliminated using the Mn internal standard and was most pronounced immediately after turning on the ICP-OES instrument. The Cu (I) 327.396 nm and Mn (I) 279.482 nm emission line combination was the least sensitive to temperature fluctuations, but the Mn (I) 279.482 nm was more susceptible to spectral interference and lower intensity than the Mn (II) 293.305 nm line. It was found that the temperature fluctuations could be minimized by waiting a minimum of 70 minutes after turning on the ICP-OES before starting an analysis.

¹ The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

Analysis procedure

Each participant submitted 10 bottles. From each set a random selection of:

- Five bottles were analyzed by NIST using ICP-OES. This set of bottles gave five measurements which were combined for a single result for each participant in a manner described later in this report.
- The density of the solution prepared by each participant was determined by NIST using the contents of one of the bottles each participant provided. This bottle was not used for other measurements.
- Two bottles of a subset of participants were sent to PTB for independent, confirmatory measurements. This subset of participants was not random. Samples were chosen after initial measurements at NIST from a selection of participants that appeared close to the mean and at the extremes of the set. PTB measured two aliquots out of each bottle resulting in four measurements total. These measurements did not contribute to the KCRV.
- One unused bottle was weighed after conclusion of all measurements to assess mass loss after preparation.
- One bottle was reserved for the case that a measurement needed additional confirmation, or if a measured bottle was unusable.

Sample preparation and measurement at NIST

The following procedure was used to prepare each bottle to be measured by the High Performance Inductively Coupled Plasma Optical Emission Spectroscopy (HP-ICP-OES) methodology described elsewhere [5-8]. Each step was done for an entire set of bottles (*i.e.* one bottle per participant) before moving on to the next step:

1. Seal was broken on polyester bag and bottle was removed. Identification tag was removed, and bottle was weighed on a four-place balance (*Mettler-Toledo AB304-S/FACT*). Heat shrink seal was removed and bottle was reweighed. Initially bottles were weighed before and after removal of heat shrink in the case that participants' submitted masses included the mass of the heat shrink. No participants appeared to have included the mass of the heat shrink, so all bottles after the first bottle only were weighed after removal of heat shrink. Only one bottle was removed from polyester bag at a time so that unlabeled, untagged bottles could not be misidentified. Approximately 10 g of Mn internal standard was added to each bottle. The Mn stock solution used was made from high-purity manganese metal assayed by NIST. The HP-ICP-OES method uses sample preparation to match all samples being run to each other. Typically, this involves matching well characterized calibration solutions to samples being analyzed. In this case, since no calibrants are used, samples are matched to each other based on the mass of copper present in each bottle, which has been derived from the solution masses and mass fractions submitted by the participants. The amount of Mn added varied slightly from bottle to bottle because of the eventual goal of having an identical Cu/Mn signal ratio across all samples, indicating solutions were measured to have the amount of copper present claimed by each participant. This will be discussed in more detail in later sections. After weighing, bottle was labeled using a permanent marker.
2. The resulting solutions were diluted twice with 2 % volume fraction of nitric acid (HNO_3), made from concentrated HNO_3 (Fisher Scientific Trace Metal Grade) diluted 1:50 by volume with high-purity water [CAP (College of American Pathologists) Type III grade or better, generated onsite].

The dilution factor varied slightly from sample to sample to generate solutions with identical Cu and Mn mass fractions of approximately 11 µg/g and 12 µg/g, respectively.

3. An additional sample was prepared along with the set of samples from NIST SRM 3114 Copper (Cu) Standard Solution, Lot Number 121207. This sample was prepared in a larger quantity to roughly match the sample set and be run during HP-ICP-OES analysis to monitor instrumental drift.

Sample analysis

During a run, the set of samples being tested consisted of one bottle from each participant in CCQM-K143. These were run as a set, in random order, along with a drift sample (see step 3 above) inserted every 10 min to 12 min as a real-time diagnostic. (Note that when data reduction was undertaken later, drift correction was accomplished using a published approach not based on this diagnostic drift sample) [5]. For the remainder of the run, the set of CCQM-K143 samples was repeated in a different random order for each replicate, for a total of six replicates. During the last replicate set, a blank (2 % volume fraction of concentrated nitric acid) was run between every sample to detect any memory effects or analyte carryover. The total analysis time for all six replicates was 10 hours. Four additional runs were performed in this way, using a single bottle from each CCQM-K143 participant per run. In this way, the complete analysis involved a total of five bottles from each participant, with the runs occurring between 26 March 2018 and 24 July 2018.

The claimed mass fraction of each solution submitted is shown in Figure 1 and Table 4. These values were drawn directly from the results reports submitted by each participant, and it is important to note that the purpose of the preparation was to prepare a solution which had a copper content that matched the assigned value and uncertainty rather than attempting to prepare a solution which was exactly 10 g/kg. It was apparent that the samples submitted by KEBS did not comply with the preparation protocol which stipulated a mass fraction between 9.9 g/kg and 10.1 g/kg and relative expanded uncertainty of less than 0.3 %. The KEBS samples were treated identical to all other CCQM-K143 samples during sample preparation, analysis, and data reduction except that the results were removed from the drift correction procedure, normalization of the data (discussed below), and eventual calculation of the KCRV. Each mass fraction claimed by each j participant was converted to mass of copper (m_{ij}^{Cu}) present in a given aliquot, i , using the equation:

$$m_{ij}^{Cu} = (w_{Cu}) (m_{ij}) \quad \text{Eq. 1}$$

where w_{Cu} is the mass fraction reported by each participant for the set of bottles submitted and m_{ij} is the aliquot mass reported by each participant. The associated uncertainty, $u(m_{ij}^{Cu})$ was calculated by:

$$u(m_{ij}^{Cu}) = m_{Cu} \times \sqrt{\left(\frac{u(w_{Cu})}{w_{Cu}}\right)^2 + \left(\frac{u(m_{ij})}{m_{ij}}\right)^2} \quad \text{Eq. 2}$$

where $u(w_{Cu})$ is the standard combined uncertainty of mass fraction reported by the participant, and $u(m_{ij})$ is the standard combined uncertainty of aliquot mass in bottle i for participant j as reported by that participant.

Data reduction

All data were exported to Microsoft Excel 2016 and samples were labeled with a two-letter identifying code to anonymize the data until the results were finalized. The net intensities for the chosen Cu and Mn lines were used and manipulated in a manner described previously [5-8]. In summary, a drift correction routine was used based upon the variation of 5 replicate measurements of each sample during the analysis run. A measure of the instrument's response, or sensitivity, S is calculated for each of the i working solutions prepared from the submitted aliquots of participant j , according to the equation:

$$S_{ij} = \frac{(R_{ij})(m_{ij}^{IS})}{m_{ij}^{Cu}} \quad \text{Eq. 3}$$

where R_{ij} is the observed Cu to Mn emission intensity ratio, m_{ij}^{IS} is the mass of internal standard stock solution added, and m_{ij}^{Cu} is the mass of Cu believed to be present based upon Eq. 1. The uncertainty for the sensitivity is given by:

$$u(S_{ij}) = \sqrt{\left(\frac{(R_{ij})u(m_{ij}^{IS})}{m_{ij}^{Cu}}\right)^2 + \left(\frac{(m_{ij}^{IS})u(R_{ij})}{m_{ij}^{Cu}}\right)^2 + \left(\frac{(R_{ij})(m_{ij}^{IS})u(m_{ij}^{Cu})}{(m_{ij}^{Cu})^2}\right)^2} \quad \text{Eq. 4}$$

where $u(m_{ij}^{Cu})$ is from Eq. 2, $u(m_{ij}^{IS})$ is the uncertainty of mass of internal standard used, and $u(R_{ij})$ is the uncertainty of signal ratio of Cu to Mn (the standard deviation of 5 measurements of a given solution during an analysis run divided by square root of 5). The sensitivity value from Eq. 3 was normalized by dividing S_{ij} by the average of all sensitivity values for CCQM-K143 samples in the run (\bar{S}_i). The resulting value was a relative sensitivity value, because no suitable, independent calibrant for this measurement exists. Additionally, the instrument response was not consistent from run to run partially due to several months passing between the analysis of all five bottles. Using the ratio of the sensitivity for a participant over the mean of all participants for a given run minimized the effects of the difference in instrument response over this time period.

Sample preparation and measurement at PTB

PTB received a subset of samples consisting of duplicate bottles from ten CCQM-K143 participants. Bottles were received in their original state (sealed, wrapped, etc.) from NIST on 18 June 2018. On 20 August 2018, one sample per participant was unwrapped, its sealing and label was removed, and the bottles were weighed after briefly opening and closing each bottle (necessary to equilibrate the inner and outer pressure). The ambient conditions (air temperature, pressure, and relative humidity) were recorded to correct for air buoyancy. From the corrected masses (m_x) of the Cu solutions in the bottles, their original mass fraction and original mass, their evaporation corrected Cu mass fraction was determined.

To each bottle approximately 15.6 g of a 10 mg/g Mn solution in 7 % HNO₃ was added. The bottles were given time to equilibrate overnight, then 8 g of each sample was diluted in 100 g using 0.15 mol/kg HNO₃. Between 24 August 2018 and 11 September 2018, 4 g of these solutions were further diluted in 500 g of 0.15 mol/kg HNO₃ for measurement. This preparation yielded solutions with Cu and Mn mass fractions of approximately 4 µg/g and 2.5 µg/g, respectively. A diagram of the sample preparation protocol can be found in Figure 2a. The bracketing standards for the ICP-OES measurements were prepared starting from BAM-Y001 high-purity copper CRM and a Mn standard solution with a mass fraction of 500 µg/g. The final measurement solutions 1 and 2 of the standards had approximately the

same Mn mass fraction and a slightly lower or, respectively, higher Cu mass fraction. A diagram of the preparation of the bracketing standards can be found in Figure 2b.

Sample Analysis

The ICP-OES measurements ($\lambda(\text{Cu}) = 224 \text{ nm}$, $\lambda(\text{Mn}) = 257 \text{ nm}$) were performed between 27 August 2018 and 17 September 2018 using a Spectro ARCOS (SPECTRO Analytical Instruments GmbH, Germany) equipped with a Scott type quartz spray chamber, a Pt-Ir cross-flow nebulizer, and a standard quartz torch (0.8 mm injector). The plasma was operated at 1400 W with 12 L/min coolant, 1 L/min auxiliary, and 0.85 L/min nebulizer gas flow. A bracketing scheme was applied as described in previous work [9]. Within a 4 h sequence consisting of 11 measurements of the standard 1, 20 measurements of the according K143 sample, and 10 measurements of the standard 2, 20 results of the Cu mass fraction were gathered. Each sequence was run on two different nights. Two independent preparations were done per bottle, giving four results per bottle (participant) over a 16 h measurement time in total. The typical uncertainty of these values (including the spread of the individual results) was $U_{\text{rel}}(w_x) \leq 0.074 \%$. Since the Mn mass fraction of the solution added to the samples and to the standards was different, the measurements were evaluated with an equation slightly modified compared to the one from [9]:

$$w_x = w_z \times \frac{w_{yx}}{w_{yz}} \times \frac{\frac{m_{yx}}{m_x} \times (R_1 - R_2)}{\frac{m_{y1}}{m_{z1}} \times (R_{\text{bx}} - R_2) + \frac{m_{y2}}{m_{z2}} \times (R_1 - R_{\text{bx}})} \quad \text{Eq. 5}$$

m_x	mass of solution in bottle received by PTB and used for correction of mass fraction for evaporative loss	g
m_{yx}	mass of Mn internal standard solution (Mn-1-3.2) added to submitted samples	g
m_{y1}	mass of Mn internal standard solution (Mn-1-3.1) added to bracket standard 1	g
m_{z1}	mass of Cu solution (Cu-1-20.1) added to bracket standard 1	g
m_{y2}	mass of Mn internal standard solution (Mn-1-3.1) added to bracket standard 2	g
m_{z2}	mass of Cu solution (Cu-1-20.1) added to bracket standard 2	g
w_x	mass fraction of Cu solution in K143 sample	$\mu\text{g/g}$
w_{yx}	mass fraction of Mn in internal standard solution (Mn-1-3.2) added to samples	$\mu\text{g/g}$
w_{yz}	mass fraction of Mn in internal standard solution (Mn-1-3.1) added to standards	$\mu\text{g/g}$
w_z	mass fraction of Cu solution (Cu-1-20.1) added to standards	$\mu\text{g/g}$
R_1	Mn/Cu signal intensity ratio for bracket standard 1	$\text{s}^{-1}/\text{s}^{-1}$
R_2	Mn/Cu signal intensity ratio for bracket standard 2	$\text{s}^{-1}/\text{s}^{-1}$
R_{bx}	Mn/Cu signal intensity ratio for K143 sample	$\text{s}^{-1}/\text{s}^{-1}$
m_{grav}	mass of K143 solution as reported from gravimetric preparation by participant	g
w_{grav}	mass fraction of K143 solution as reported from gravimetric preparation by participant	$\mu\text{g/g}$

Mass change during transport and storage

The mass of a given bottle could be compared to the mass at preparation based on the mass submitted by each participant. Ideally the mass difference would be near zero indicating minimal transpiration or change in mass due to other processes. However, this is not the case as shown by the differences in mass in Figure 3a. All participants experienced a loss of mass to varying amounts. Additionally, as detailed above, the bottle masses were measured just before sample preparation for ICP-OES measurement, over a period of 4 months with the exception of bottle 6 which was weighed 5 March

2019, nearly a year after bottle 1. In general, there appears to be a trend where the mass loss is increasing over time. The exception appears to be the NIST bottles which show no mass loss initially, but after enough time has passed (approximately 21 months since preparation) the loss appears to be similar to all other samples.

The magnitude of the mass losses shown was confirmed by PTB, measuring bottles 20 August 2018 and 4 December 2018. Figure 3b shows the set of bottles measured by NIST and PTB with the number of days from the sample submission deadline denoted. Once again, the loss in sample appears to be increasing with time. Copper would not be lost during transpiration, only solvent, so aliquot changes affecting the results would be limited to total sample loss through mechanisms such as bottle leakage which is more easily controlled and monitored. Measurements from PTB illustrated the effect of evaporative loss in Figure 3c, showing the change in solution mass rather than bottle mass and subsequent adjusted copper mass fraction based on participants submitted bottles masses and mass fractions. The largest apparent loss of copper mass fraction, from an increase in solution mass, was 0.14 % relative to the mass fraction as reported during preparation and the largest apparent gain in copper mass fraction due to evaporative loss is 0.24 % relative to the mass fraction as reported during preparation. Perhaps more significant is the calculated mass fraction change compared to the claimed mass fraction uncertainty upon gravimetric preparation. In most cases, the change in mass fraction was not significant compared to the claimed mass fraction uncertainty. For CODELCO, NIST, NMIJ, and PTB the change was much larger than could be explained simply by the uncertainty on the assigned mass fraction value, however this is due partly to small uncertainties for the assigned mass fraction values compared to other participants. While the design of CCQM-K143 is insensitive to this type of change, it should be a concern for the stability of the mass fraction during shipment of any solutions with assigned mass fraction values.

Results and Discussion

The results of the analyses of five bottles submitted by each CCQM-K143 participant are shown in Figure 4. The data have been ordered by the mean of all five bottles from smallest to largest, with KEBS off scale in the negative direction. Data have also been included from the ICP-OES analysis of CCQM-K143 samples by PTB. For the PTB data to be compared, each participant's measured mass fraction (w_x from Eq. 2) was ratioed to the reported mass fractions w_{grav} after an evaporation correction. Each ratio was then normalized with the arithmetic mean of all ratios in a manner similar to the NIST dataset. The NIST and PTB results for the samples measured are nearly identical, giving a greater degree of confidence in the results.

Figure 4 shows an outlier in the positive direction, for the bottles submitted by JRC. The results for JRC are consistently high across all five bottles measured by NIST and the bottle measured by PTB, suggesting either a sample preparation or calculation error. Consultation with JRC revealed a small calculation error resulting in this positive bias [10]. If this error had not been present in the submitted results report, the results from JRC would have been in the middle of participants' results in Figure 4. Given this positive bias and its known source, the data for JRC samples were not used for drift correction, normalization of the dataset, or calculation of the KCRV.

Figure 4 gives some idea of the homogeneity of the prepared solutions for a given participant. All bottles are simply aliquots of a single solution prepared, so any variation would arise from aliquoting errors (weighing errors or sample loss), loss of copper during transport and storage, or the preparation of working solutions from the submitted samples not being repeatable. A closer look at the data for each participant indicates that there may be some component of uncertainty which is unaccounted for due to

the mutual inconsistency of the results across the five bottles for some participants. This is shown in Figure 5. Cochran's Q test of homogeneity was applied to the set of 5 measurement results (one per bottle) for each participant. The test revealed that, for some participants, there was some "extra" uncertainty component (dark uncertainty) unaccounted for in the original measurement results [11,12]. This dark uncertainty could have a variety of sources including but not limited to: an unaccounted for or underestimation of $u(S_{ij})$ using Eq. 1 through Eq. 4 above, an underestimation of preparation uncertainty by participants, or a small preparation uncertainty submitted by participants which became inflated by a larger additional uncertainty added by the sample preparation conducted by NIST.

Figure 5 and the corresponding tests of mutual consistency reveal the presence of dark uncertainty, unaccounted for in the bottle-specific uncertainty budgets, for several participants. Therefore, to combine the bottle-specific sensitivities into a participant's sensitivity, a consensus building procedure was used that estimates and recognizes the dark uncertainty in the weights used in a weighted average of the bottle-specific sensitivities. A suitable choice is the widely used DerSimonian-Laird procedure reviewed by Koepke et al. [13] and implemented in the NIST Consensus Builder [18]. This procedure produces an adaptive weighted average, in the sense that it tunes itself automatically according to whether it detects, or not, the presence of dark uncertainty. The resulting mean sensitivities (\bar{S}_j), standard uncertainties ($u(\bar{S}_j)$), and calculated dark uncertainty (τ_j) for each participant are shown in Table 5 and Figure 6.

The dataset does not appear to have any outliers other than ones already discussed with known causes. When comparing Figure 4, Figure 5, and Figure 6, it is immediately obvious that for NPLI the largest source of uncertainty is the bottle to bottle variability, reflected by the value for τ_j in Table 5. Several other participants such as INM, INMETRO, and NMISA have uncertainties of similar magnitude in Figure 6, but this appears to be caused by a submitted mass fraction which has a higher uncertainty ($u(x_{Cu})$ from Eq. 2) than most other participants (Figure 1), due presumably to weighing or source material assay uncertainty. Accordingly, the value for τ_j in Table 5 is zero for these participants because no additional dark uncertainty can be discerned above the conservative uncertainty estimate the participants had submitted.

The overall spread of sensitivity values in Table 5 is 0.2 % relative to the mean of all sensitivities of CCQM-K143 participants not removed from the dataset (JRC and KEBS). While this range is small, it is important to consider the contributions made to this spread by the experimental setup. One obvious environmental effect would be temperature fluctuations during analysis. Temperature fluctuations could cause changes in viscosity and delivery of copper to the plasma. Sufficient warm up time after instrument start minimized temperature fluctuations, and temperature monitoring during analysis runs revealed a range of 23.2 °C to 24.2 °C over the course of the runs. The temperature fluctuations did not show any trend correlated with the Cu/Mn signal intensity. However, if fluctuations in signal were present due to temperature changes, any long-term shift would be mitigated by the drift correction procedure and short-term changes would be mitigated by replicate measurements. At worst, temperature changes would present as additional measurement uncertainty such as that shown by the error bars in Figure 4. Drift from other unknown sources would also present in this manner. If the drift were a determining factor in the overall measurement uncertainty, one would expect expanded uncertainties in Figure 4 to be of the same magnitude for all participants in a given run. This does not appear to be the case as other sources (source material assay, weighing uncertainty, bottle to bottle repeatability) appear to dominate the overall uncertainty.

Related to temperature changes, changes in density from one participant's sample to the next could bias the measured relative sensitivity. To that end, the density of solution in one freshly opened bottle was measured for each participant using a density meter (Mettler/Par DMA 35). The results of these measurements are shown in Figure 7a. Measurements were made over 2 days with half the sample set measured each day. The NIST sample was run both days to detect any measurement drift. The average temperature of solutions was 20.04 °C both days and the change in the NIST sample density was only 0.00003 g/cm³. The overall range in densities measured was 3 % relative to the mean value for all densities in the set. Given that the preparation protocol mandated a nitric acid mass fraction between 6 % and 8 % and calculated densities for those mass fractions [14] predict a range of 1 %, it appears that some samples fall outside this range of acid composition. There appears to be a discontinuity present in Figure 7a which is unexplained, not varying by time/day of measurements, and most likely related to the method of sample preparation in some way. However, the capability of an institute to prepare solutions of an exact amount of acid was not being tested in this exercise, so no further investigation was pursued. More pertinent to the larger discussion is the measurement of densities of the working solutions measured affecting the efficiency of sample introduction into the ICP-OES. The measured densities are shown in Figure 7b for the fifth bottle measured in Figure 4. In this case the range of solution densities was only 0.009 % relative, indicating that density changes between participant's samples did not contribute significantly to the overall variation between samples. The diluent (2 % volume fraction of concentrated nitric acid) density dominates any variation due to sample density.

Part of the experimental design for CCQM-K143 assumed that transpiration of solvent from prepared samples could not be completely eliminated between initial preparation and the measurement of the copper present. This assumption was supported by the change in mass and presumably mass fraction observed by PTB as shown in Figure 3c. The exercise was designed to use the mass of copper present in each submitted aliquot rather than the mass fraction in any calculations. To determine the mass of copper in each aliquot, NIST used the mass of solution present in each bottle and the calculated mass fraction of the overall solution prepared. While this experimental design had the benefit of making the comparison more robust, it did have an unintended consequence which was not obvious until after measurement of the samples. That consequence was the diminishing of institutes' ability to weigh properly during sample preparation. Specifically, masses during sample preparation should have been corrected for buoyancy in air according to the equation [15]:

$$m_{\text{corr}} = m_{\text{air}} \left(\frac{1 - \frac{\rho_{\text{air}}}{\rho_{\text{ref}}}}{1 - \frac{\rho_{\text{air}}}{\rho_{\text{sample}}}} \right) \quad \text{Eq. 6}$$

m_{corr}	buoyancy corrected mass	g
m_{air}	aliquot mass in air	g
ρ_{air}	density of air (at ambient conditions during preparation)	g/cm ³
ρ_{ref}	density of the calibration weights used for the balance	g/cm ³
ρ_{sample}	measured or calculated source material/solution density	g/cm ³

Equation 6 should have been used for 3 measurements during sample preparation: source material (high-purity copper) mass, total solution mass, and for each aliquot mass. For the first instance it is important to note that typically $\rho_{\text{ref}} \approx 8 \text{ g/cm}^3$ and ρ_{sample} is 8.96 g/cm³. Because the two densities are similar the

correction factor is nearly unity at typical laboratory conditions ($\rho_{\text{air}} \approx 0.0012 \text{ g/cm}^3$), minimizing the effects of including the correction. This would not be the case for weighing samples having densities much different from 8 g/cm^3 . Buoyancy corrections should have been included for measurement of the total solution mass and the mass of each aliquot. However, the use of mass of copper in each aliquot used the submitted mass fraction multiplied by the submitted aliquot mass. The former is simply the source material mass divided by the total solution mass meaning that air buoyancy correction canceled out if it was applied (or not) consistently throughout the procedure.

Calculation of KCRV and Degrees of Equivalence

The end goal of this exercise is to transform the data shown in Figure 6 into a format that can support Calibration and Measurement Capability (CMC) claims. The CCQM has a guidance note which provides a pathway to establishing a Key Comparison Reference Value (KCRV) and degrees of equivalence (DOEs) [16]. The calculation of the KCRV is simple as it is approximately 1 as dictated by experimental design and data reduction. However, following the guidance document stipulates “qualified participants” must be determined, as outliers could shift the entire dataset away from this KCRV value. Therefore, the participants which were not considered qualified participants are shown in Table 6.

For the dataset containing only qualified participants, statistical treatment of the data can be determined by looking for the presence of excess variance and for the presence of outliers. The latter is straightforward as there are no outliers in the dataset (Figure 6). Excess variance is more difficult to quantify, but Cochran’s Q test of homogeneity (which is the same as the chi-squared test described in Appendix 1 of the CCQM guidance document) was applied to the set of measurement results from all participants. The test revealed that, for some participants, there was some “extra” uncertainty component (dark uncertainty) unaccounted for in the original measurement results. This test for mutual consistency serves as one indicator but is supported by the data in Figure 6. All qualified participants are closely bunched together, but many do not have overlapping uncertainties indicative of some excess variance or dark uncertainty being present but unaccounted for. Possibilities include under representation of the uncertainty in the copper source material, such as due to heterogeneity, or some unknown factor affecting samples to varying degrees during transport to NIST. Given the lack of outliers and degree of mutual inconsistency, a DerSimonian-Laird estimator [17] was chosen for determination of the KCRV and associated uncertainty as described in the CCQM guidance document [16] in the form implemented by Koepke et. al [13]. The degree of equivalence, d_j for a given participant is calculated by:

$$d_j = \bar{S}_j - S_{KCRV} \quad \text{Eq. 7}$$

where S_{KCRV} is the KCRV. Table 7 and Figure 8 detail the DOEs along with associated uncertainties for each participant. The calculation of d_j and associated uncertainties for each participant can be examined more closely at will by using the NIST Consensus Builder (<http://consensus.nist.gov/>), along with a lengthier explanation of the use of the DerSimonian-Laird estimator [13, 18]. All CCQM-K143 participants which were considered qualified demonstrated equivalence. Uncertainties obtained using HP-ICP-OES method are typically near 0.1 % [8]. In the case of CCQM-K143, the measurement uncertainty from the coordination laboratory is considerably smaller due to the measurement on a relative scale. No uncertainty contribution was made for calibration of the method resulting in a measurement uncertainty of 0.02 %. Most participants submitted samples with assigned mass fraction uncertainties large enough

that this uncertainty contribution was not the dominating factor in the overall uncertainty of the measurements.

Measurement capability claims (CMCs)- How far the light shines

This comparison tested measurement capabilities directly and indirectly. Arguably every CCQM comparison directly assesses the measurand of interest as well as indirectly tests the quality of the traceability chain back to the SI. The purpose of CCQM-K143 was to assess measurement capability claims with a relatively short chain of traceability, with the purity assessment of the copper source material indirectly tested and inexplicably linked to any result contained herein. However, it is difficult to determine measurement capabilities for copper purity assay based on these results, especially considering several participants used copper from similar or identical sources. More discussion of these types of measurement capabilities can be found in CCQM-P149 Estimation of Impurities for the Overall Purity Evaluation of Zinc [4]. CCQM-K143 can provide very limited evidence of capabilities and competence in assessing purity of highly pure metal source materials only for those institutes that performed their own purity assessments and showed equivalence in CCQM-K143. CCQM-K143 is not sufficient alone in supporting such claims, and must be combined with other evidence to support such claims.

Measurement capabilities more directly tested are more easily described in two parts:

- Dissolution: The participants demonstrated the ability to dissolve high purity metal in acid without significant sample loss and transfer the resulting solution to containers for use.
- Weighing: The participants demonstrated the ability to measure the amount of source material and final solution. While buoyancy correction is typically an integral part of this process, it was not tested in this study in favor of a protocol that is more tolerant of solution loss to transpiration during transport to NIST.

“How far does the light shine?” In this case, the comparison is readily applicable to preparation of calibration solutions for high-purity metals which are easily dissolved. All participants showed the ability to do this in a relatively repeatable manner although the set of 5 bottles measured for some participants appeared to have a heterogeneity component which added to the overall uncertainty. However, it is impossible to attribute this bottle to bottle heterogeneity component to preparation problems or an underestimation of mass fraction uncertainty by an NMI/DI, since the heterogeneity could have occurred due to transport or sample preparation by the coordinating laboratory. It is important to note that CCQM-K143 tested the ability of NMIs/DIs to prepare solutions on a relative scale only. Preparation of solutions with a specific absolute mass fraction value was not tested due to the absence of an independent, high quality material for calibration.

Due to the nature of CCQM-K143 it would be useful to suggest how CMC claims should be applied. Typically, once equivalence is shown, claims can be based on measurements submitted by participants which were compared to some reference value or KCRV. For CCQM-K143, participants submitted claimed mass fractions at the beginning of the exercise upon submission of samples. These claimed mass fractions and their uncertainties (Table 4 and Figure 1) provide guidance for making a CMC claim. CCQM-K143 only confirmed that participants were able to make the solution that they claimed, not make an equivalent solution. The coordinating laboratory prepared equivalent working solutions from the solutions submitted by the participants, and these working solutions were measured based on the mass fractions and uncertainties claimed by the participants for their submitted solutions. In essence, each participant

drew its own target, the size of which was determined by the claimed mass fraction uncertainty, and Figure 8 shows that all qualified participants were able to hit their individualized targets.

It would also be prudent to suggest where the results of this exercise are of limited applicability; that is to say, “Where is there still darkness?” This question should be asked to see where to go next, how to improve future comparisons, and minimize the chance results could be misapplied to a CMC claim. CCQM-K143 would not be applicable for materials which are compounds or have large impurities, especially impurities forming insoluble species in the final solution. Applicability would also be limited in instances where the source material required more complex solvents, such as oxidizing or reducing agents, or are difficult to dissolve or keep in solution (for example Rh). A source material with a density much different from copper would also be more effective at assessing participants’ ability to weigh with a proper correction for air buoyancy but should not limit applicability of CCQM-K143 to elements beyond copper.

Conclusions

CCQM-K143 allowed participants to demonstrate the ability to correctly prepare calibration solutions from a high purity source material. For the subset of institutes considered “qualified participants” this was demonstrated in a manner that showed equivalence on a relative scale among all participants as well as the ability to produce homogenous solutions. HP-ICP-OES was an appropriate technique for performing these measurements, as relatively low measurement uncertainties allowed sources of uncertainty from other sources to be evident. Many of the logistical problems related to getting prepared solutions to a coordinating laboratory without changing were addressed, although there is room for improvement in any future studies.

Lastly, it is important to note the place CCQM K143 holds with two other comparisons: CCQM P149 Estimation of Impurities for the Overall Purity Evaluation of Zinc [4] and CCQM K87 Mono-elemental Calibration Solutions [2]. The former provides evidence of capabilities when assaying high purity primary materials for direct linkage to the SI while the latter is a demonstration of capabilities to measure and assign a mass fraction of a given element to a prepared single element solution. CCQM K143 provides a linkage between these two studies, enabling a demonstration of measurement capabilities from the SI along the entire traceability chain to any specific elemental analysis measurement

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K143 Draft B tables and figures

Table 1. Listing of materials provide to all participants for packing and shipment of prepared samples

Item	Description/Use
insulated return box	contained submitted samples during shipment and minimized the effects of exterior temperature fluctuations. Polystyrene foam walls with a thickness of 3.18 cm.
HDPE 60 mL bottles	fifteen bottles were cleaned with nitric acid and dried. Bottles were to be used for participants' submitted samples
torque wrench	closure of HDPE bottles to a tightness which would minimize transpiration and to homogenize sealing between participants
torque wrench adapter	used to attach torque wrench to HDPE bottle cap
heat shrink for cap seal	minimized transpiration and ensured bottle was not opened during transport
small heat gun	facilitated sealing of bottles with heat shrink
identification tags	bottle mass was used to monitor transpiration and amount of copper present so adhesive labels could not be attached to bottles. Hanging tags were used to prevent misidentification of submitted bottles.
aluminized polyester bags	minimized transpiration, bags could be sealed with impulse sealer to isolate each sample bottle from surrounding environment.
impulse sealer	sealed aluminized polyester bag to minimize transpiration
heat sensitive sticker	indicated temperature extreme inside shipping box during shipment. An irreversible color change indicated exposure to a temperature above 37 °C with an indicator scale up to 65 °C.
cold sensitive sticker	monitored temperature inside shipping box during shipment. An irreversible color change indicated exposure to a temperature below 0 °C
2000 W voltage converter	allowed operation of provided impulse sealer and heat gun independent of plug type for all participants
international plug adapter	allowed operation of provided impulse sealer and heat gun independent of plug type for all participants

Table 2. Listing of participants

NMI/DI		Country	Contact
Instituto Nacional De Metrologia, Qualidade E Tecnologia	INMETRO	Brazil	Rodrigo Caciano de Sena
National Research Council	NRC	Canada	Lu Yang
National Copper Corporation of Chile	CODELCO	Chile	Patricia Romero Arancibia
National Institute of Metrology	NIM	P. R. China	Wu Bing, Zhou Tao
European Commission Joint Research Center	JRC	EU	James Snell
Physikalisch-Technische Bundesanstalt	PTB	Germany	Olaf Rienitz
Bundesanstalt für Materialforschung und -prüfung	BAM	Germany	Jochen Vogl
National Physical Laboratory, India	NPLI	India	R. K. Kotnala, S. Swarupa Tripathy
Research Center for Metrology, Indonesian Institute of Sciences	LIPI	Indonesia	Christine Elishian, Rosi Ketrin
National Metrology Institute of Japan	NMIJ	Japan	Toshihiro Suzuki
Kenya Bureau of Standards	KEBS	Kenya	Tom Oduor Okumu
Korea Research Institute of Standards and Science	KRISS	Republic of Korea	Yong-Hyeon Yim
Centro Nacional de Metrología	CENAM	Mexico	Judith Velina Lara Manzano
National Institute of Metrology	INM	Romania	Mirella Buzoianu
Ural Scientific Research Institute for Metrology	UNIIM	Russia	Alena Sobina
National Metrology Institute of South Africa	NMISA	South Africa	S. M. Linsky
Ulusal Metroloji Enstitüsü, National Metrology Institute of Turkey	UME	Turkey	Süleyman Z. Can
LGC Group	LGC	UK	Heidi Goenaga Infante
National Institute of Standards and Technology	NIST	USA	John Molloy, Michael Winchester
Instituto Nacional de Calidad	INACAL*	Peru	Christian Uribe
Institut National de Recherche et d'Analyse Physico-Chimique	INRAP**	Tunisia	Jebali Raouf, Hanen Klich

* This participant did not send prepared solutions before exercise was closed to submissions.

**This participant did not receive shipping materials with time to complete material preparation.

Table 3. Emission lines monitored during HP-ICP-OES analysis

Emission line (nm)	Possible interfering lines
Cu (I) 327.396	V
Cu (I) 324.754	V, Fe
Mn (II) 294.920	V, Fe
Mn (II) 293.305	Ag
Mn (I) 279.482	V
Fe (II) 259.939	monitor for presence of interference
V (II) 292.402	monitor for presence of interference
Ag (I) 328.068	monitor for presence of interference

Table 4. Claimed mass fraction and uncertainty submitted by participants

NMI/DI	mass fraction (g/kg)	expanded uncertainty (g/kg)^a
BAM	9.999495	0.000140
CENAM	9.9997	0.0150
CODELCO	9.9897	0.0019
INM	9.993	0.026
INMETRO	9.998	0.027
JRC	9.99136	0.00010
KEBS	10.40	0.91
KRISS	10.0007	0.0061
LGC	9.9915	0.0048
LIPI	9.9836	0.0018
NIM	9.999	0.008
NIST	9.96438	0.00013
NMIJ	9.9999	0.0050
NMISA	9.991	0.028
NPLI	9.965	0.026
NRC	10.0040	0.0071
PTB	10.00103	0.00022
UME	9.989	0.016
UNIIM	9.991	0.018

^a Expanded uncertainty at a level of confidence of approximately 95 %.

Table 5. Mean sensitivity values determined using DerSimonian-Laird procedure

Participant ^a	mean sensitivity, \bar{S}_j	combined uncertainty, $u(\bar{S}_j)$	dark uncertainty, τ_j
<i>KEBS</i>	<i>0.95432</i>	<i>0.01559</i>	<i>0</i>
NIST	0.99905	0.00013	0.00024
PTB	0.99915	0.00028	0.00058
KRISS	0.99916	0.00041	0.00084
NMIJ	0.99946	0.00018	0.00021
NMISA	0.99949	0.00068	0
UME	0.99957	0.00034	0
UNIIM	0.99972	0.0004	0
CENAM	0.99976	0.00036	0
NPLI	0.99976	0.00072	0.00091
INMETRO	1.00011	0.00055	0
LIPI	1.00014	0.00012	0
LGC	1.00015	0.00017	0.00027
NIM	1.00059	0.00022	0.00013
CODELCO	1.00072	0.00029	0.00060
INM	1.00088	0.0005	0
NRC	1.0009	0.00023	0.00029
BAM	1.00125	0.00016	0.00023
<i>JRC</i>	<i>1.00993</i>	<i>0.00024</i>	<i>0.00048</i>

^a Italics indicates participant was removed from dataset for reasons outlined in Results and Discussion section and Table 6.

Table 6. Participants removed from set of “qualified participants”

participant removed	reason for removal
KEBS	Preparation protocol was not followed resulting in sample different from others
JRC	Calculation error resulted in incorrect claimed mass fraction

Table 7. Determined degrees of equivalence with associated uncertainty values using DerSimonian-Laird estimation of KCRV

Participant	qualified participant?	d_j	$U(d_j)$
KEBS	no	-0.04569	0.03123
NIST	yes	-0.00096	0.00144
KRISS	yes	-0.00086	0.00151
PTB	yes	-0.00085	0.00162
NMISA	yes	-0.00055	0.00145
NMIJ	yes	-0.00052	0.00193
UME	yes	-0.00044	0.00156
UNIIM	yes	-0.00029	0.00161
CENAM	yes	-0.00025	0.00158
NPLI	yes	-0.00025	0.00199
INMETRO	yes	0.00010	0.00176
LGC	yes	0.00013	0.00143
LIPI	yes	0.00014	0.00146
NIM	yes	0.00058	0.00148
CODELCO	yes	0.00071	0.00152
INM	yes	0.00087	0.00169
NRC	yes	0.00089	0.00148
BAM	yes	0.00124	0.00147
JRC	no	0.00992	0.00158
	S_{KCRV}	$u(S_{KCRV})$	
KCRV	1.00001	0.00020	

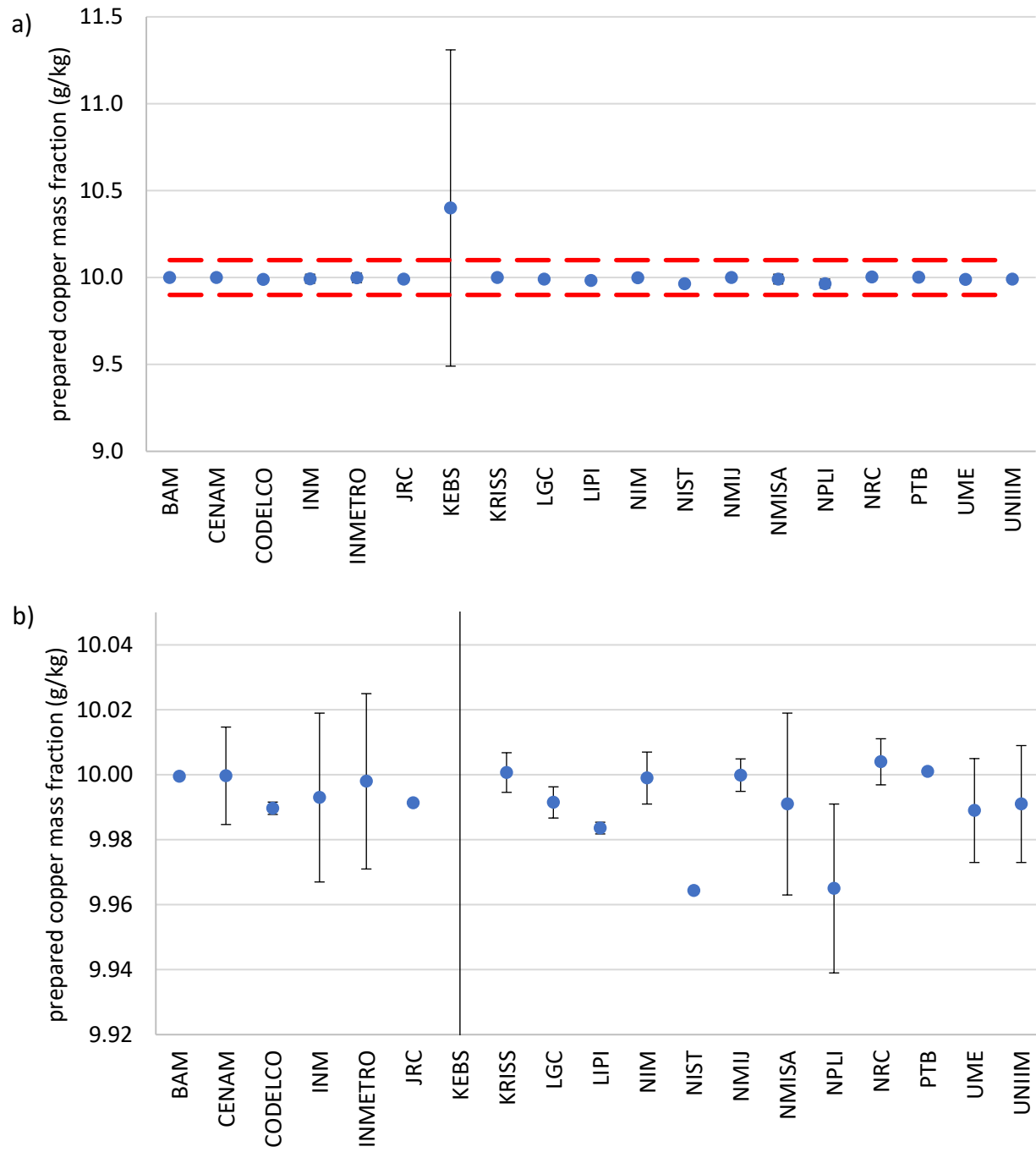
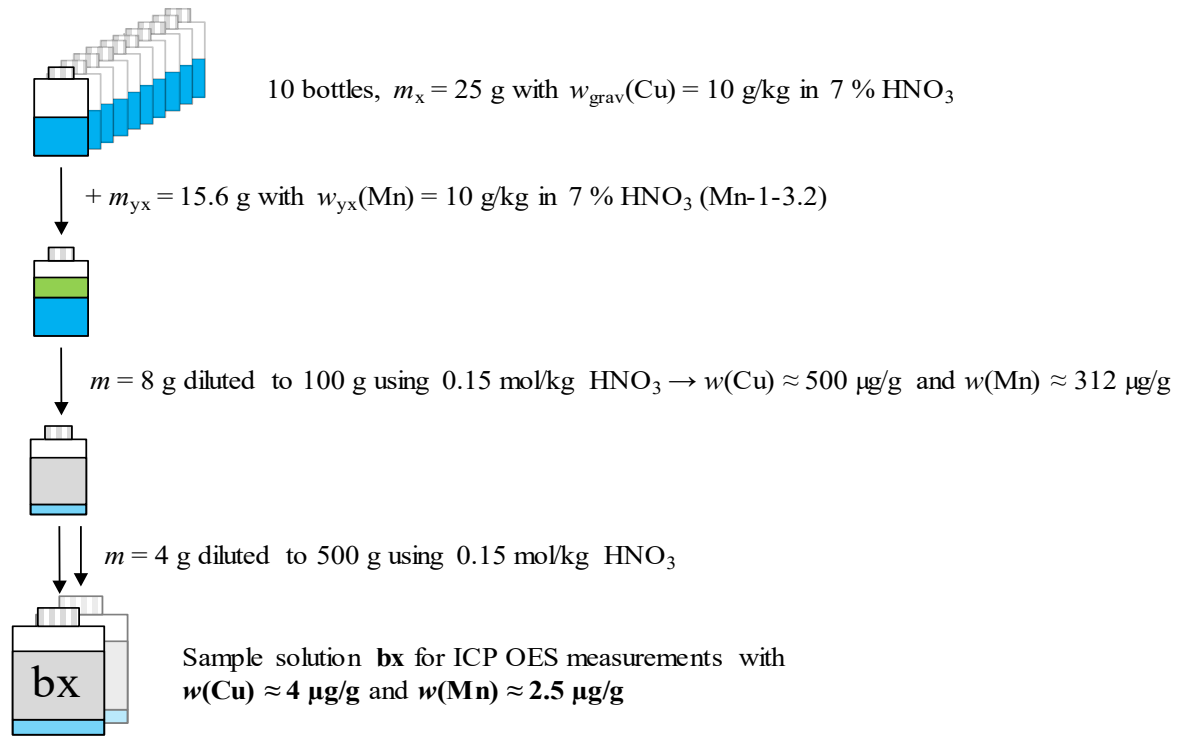


Figure 1: Prepared mass fractions of copper present in submitted solutions for CCQM-K143 a) overall and b) zoomed in. Dashed lines indicate limits of mass fraction allowed by comparison invitation and preparation protocol. Error bars indicate expanded uncertainties.

a)



b)

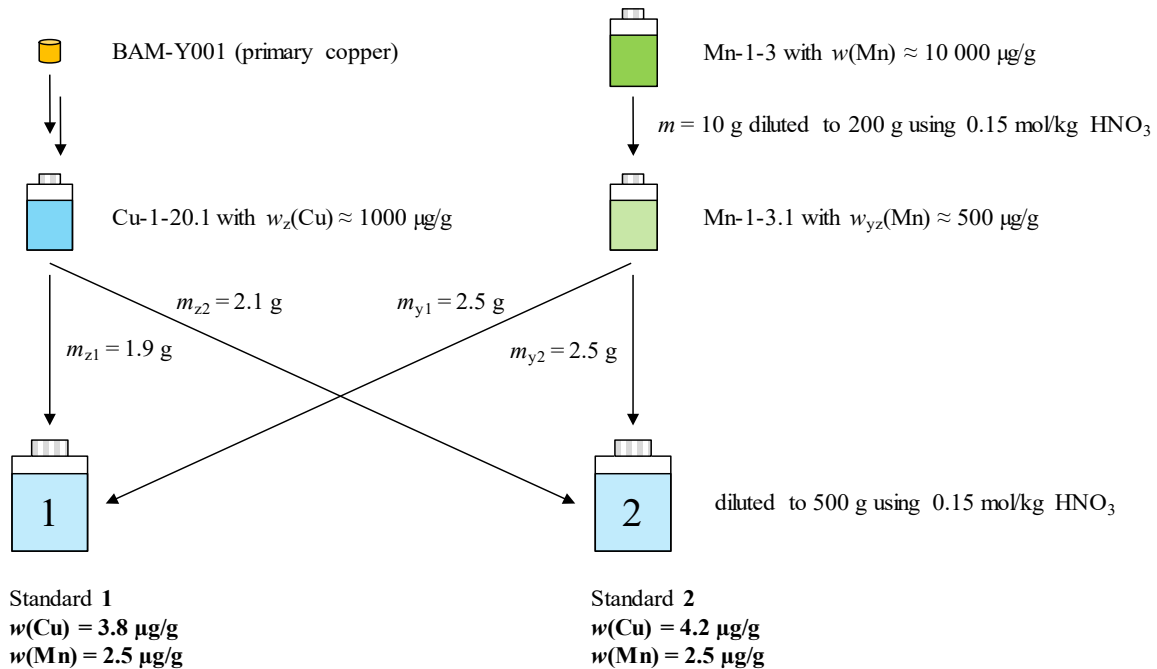


Figure 2: Diagram showing sample preparation protocol used by PTB for a) CCQM-K143 samples and b) bracketing standards. The identity and usage of the variable shown is given in the text by Equation 5.

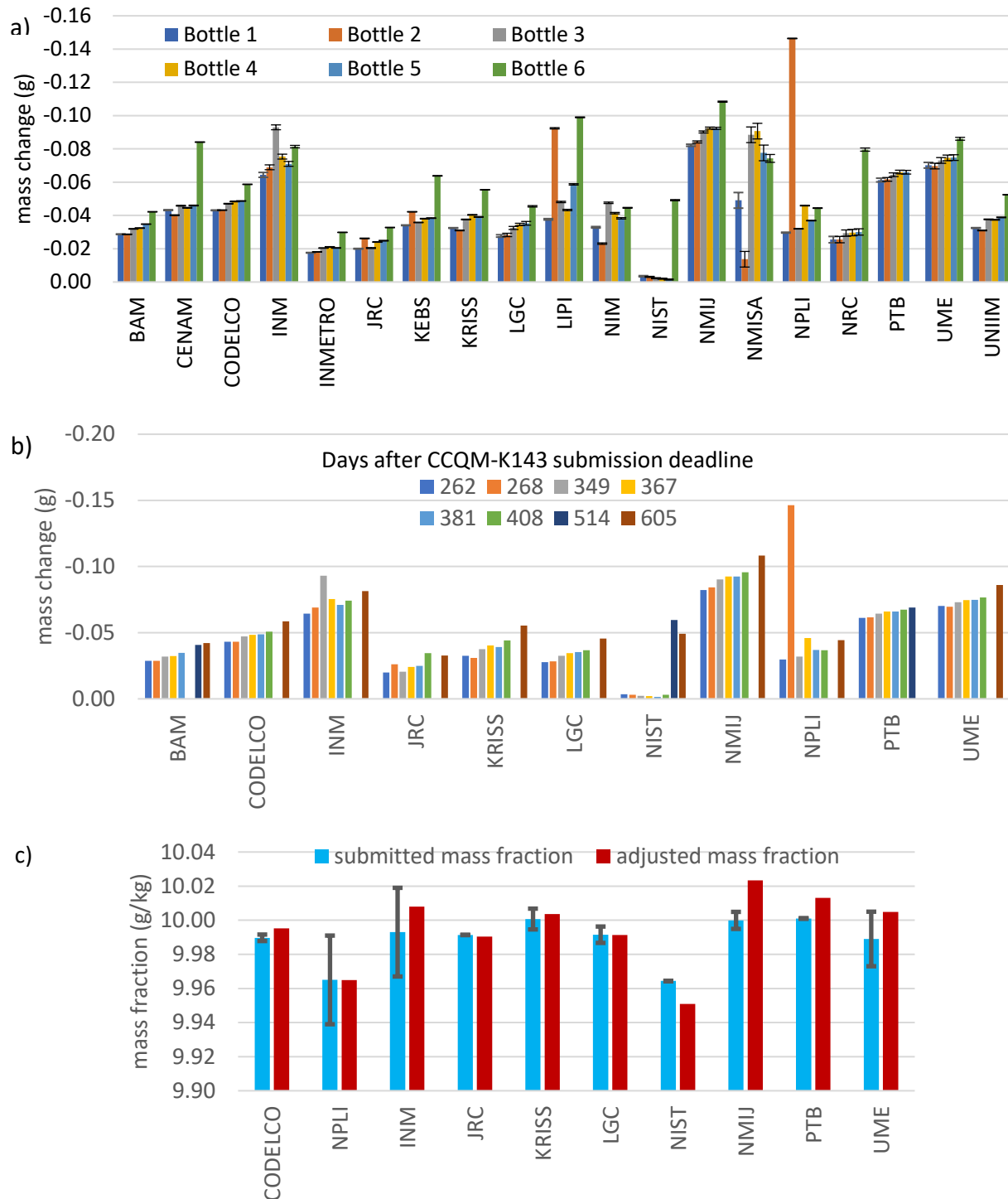


Figure 3: Mass loss after preparation for a) bottles from all participants, b) bottles measured by NIST and PTB organized by days since the CCQM-K143 sample submission deadline, and c) corrected Cu mass fraction based on evaporative loss calculated by PTB before measurement. All mass changes and mass fractions were compared to claimed mass fraction values and uncertainties calculated upon gravimetric preparation. Error bars in 3a are based only on calculated weighing uncertainty and in 3c are based on reported mass fraction uncertainties by participants.

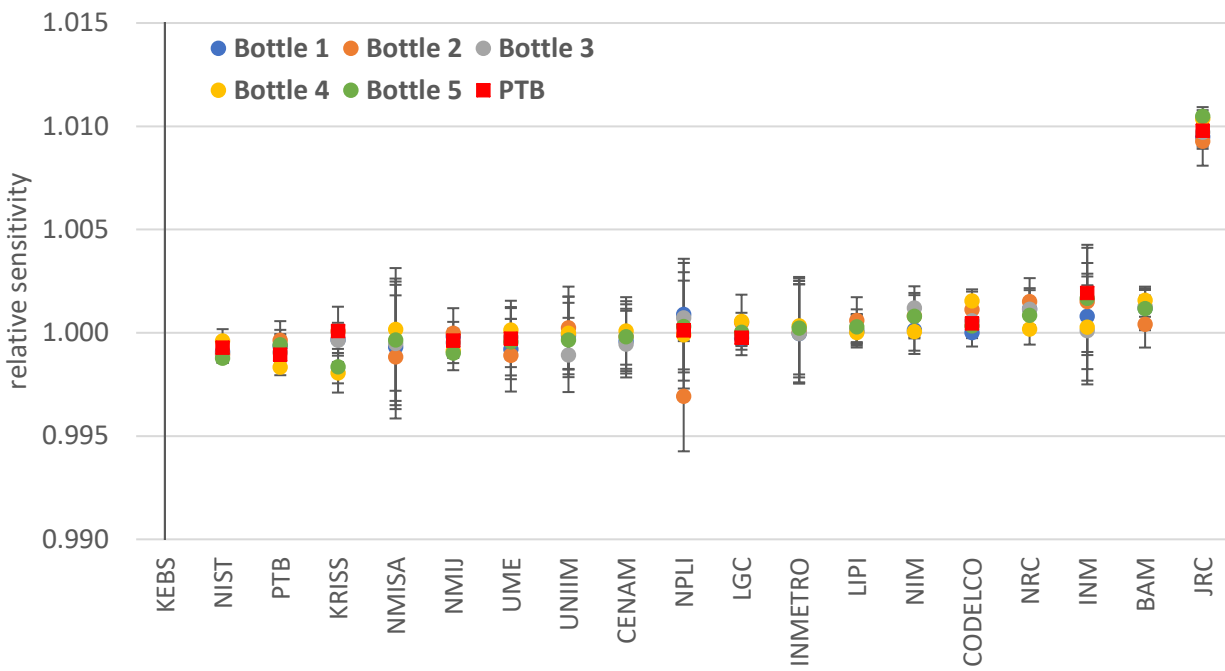


Figure 4: Results of analysis of five bottles measured by NIST from each participant of CCQM-K143 and one bottle measured by PTB for a subset of participants. Error bars indicate expanded uncertainties at a level of confidence of approximately 95 %.

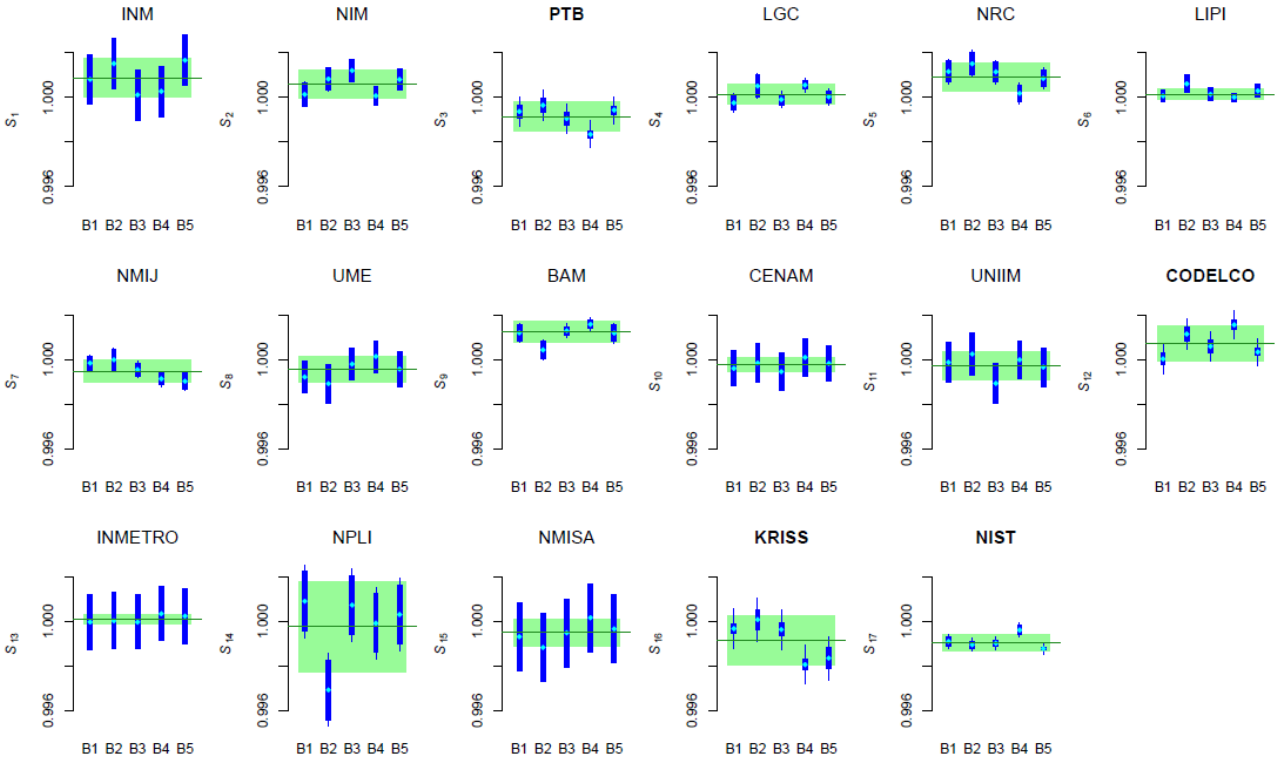


Figure 5: Measurement results for the groups of 5 bottles submitted by each participant $j = 1 \dots 17$ that qualified for inclusion in the KCRV. The value of the sensitivity S_{ij} for each bottle $i = 1 \dots 5$ from participant j , is indicated by a light blue diamond. The S_{ij} come from the individual bottle results shown in Figure 4. The thick, vertical, blue bars represent $\{S_{ij} \pm u(S_{ij})\}$, where $u(S_{ij})$ is the reported standard uncertainties shown as error bars for each bottle in Figure 4. The thin lines represent effective standard uncertainties including the contributions, τ_j , from dark uncertainty. The thin, horizontal, dark green lines represent weighted averages \bar{S}_j computed for each group of 5 measurement results. The light green bands represent $\{\bar{S}_j \pm U_{95\%}(\bar{S}_j)\}$.

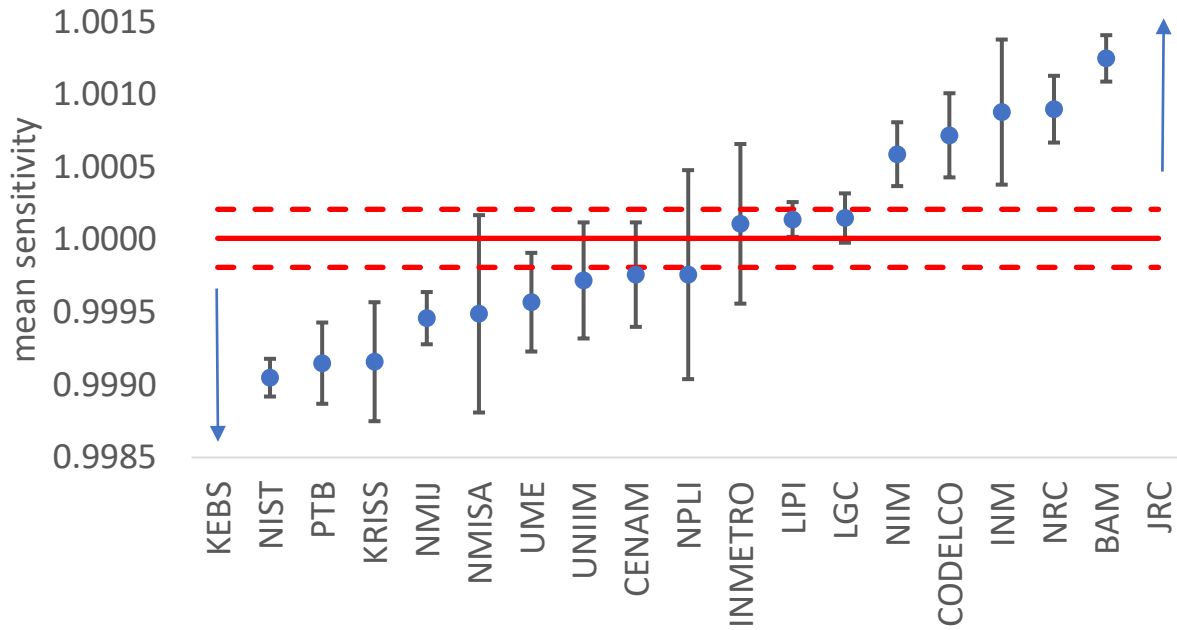


Figure 6: Mean sensitivity values for participants of CCQM K143 for measurements by NIST. Error bars are standard uncertainties calculated for each participant calculated using DerSimonian Laird procedure as described by Koepke et. al [13].

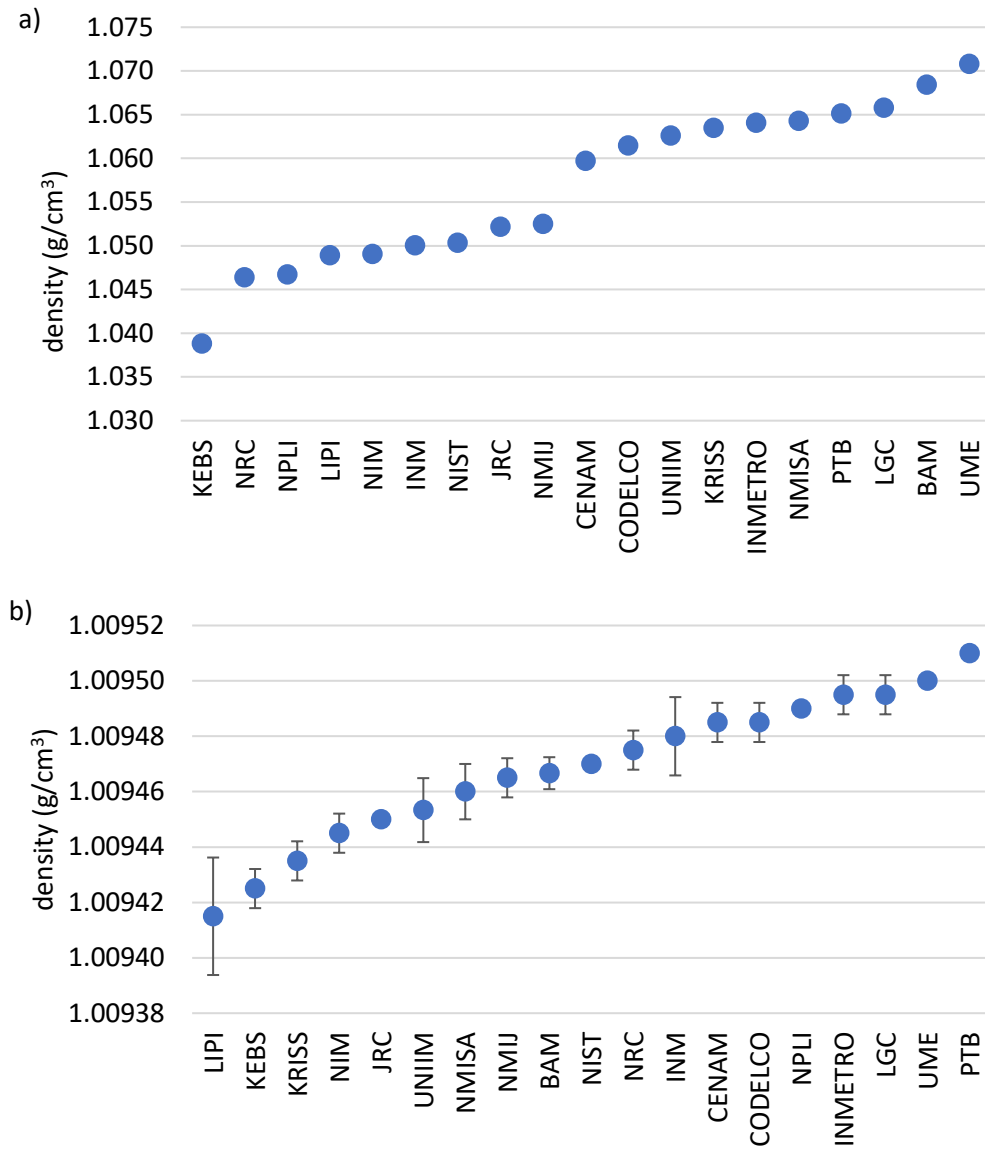


Figure 7. Density measurements of a) submitted solutions and b) working solutions measured for each participant. Error bars indicating standard deviation of three replicate measurements are present but too small to see in Figure 7a.

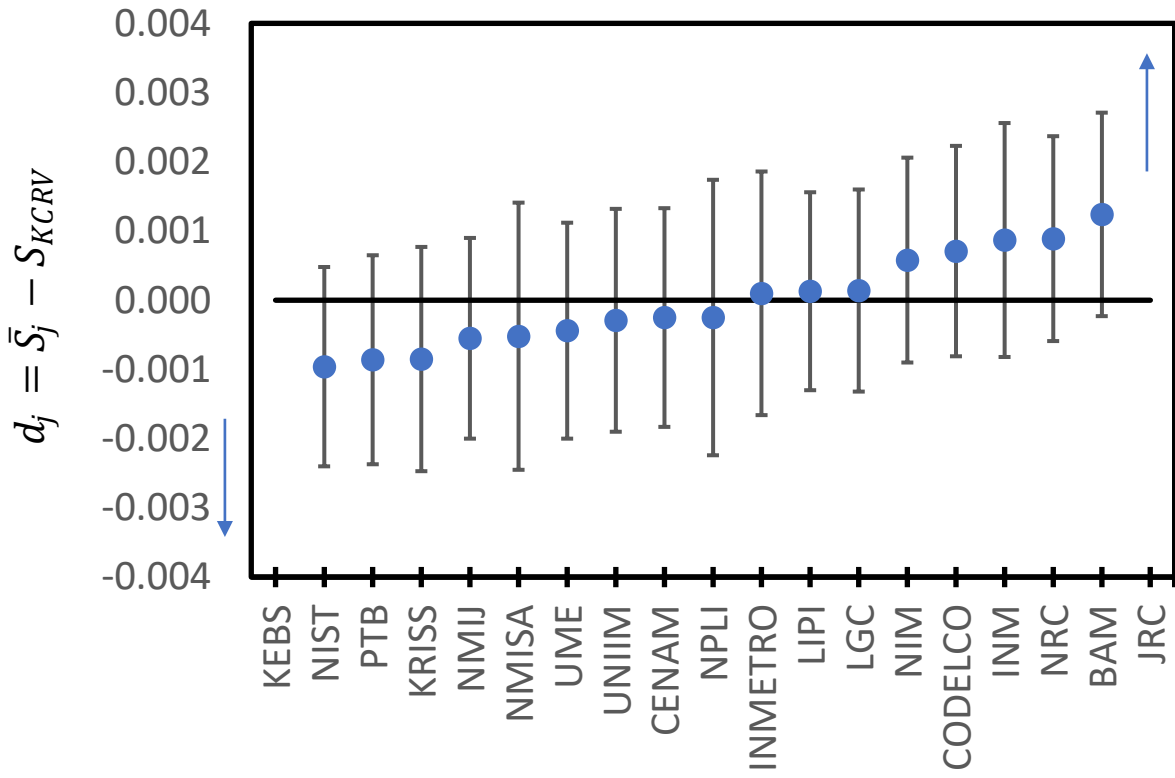


Figure 8: Degrees of Equivalence. Error bars represent 95 % Confidence Interval

Appendix A: Technical protocol, reporting form and packaging instructions for CCQM-K143 and CCQM P181

TECHNICAL PROTOCOL

Detailed Protocol Steps

Step 1: The participant laboratory will prepare one (1) copper calibration solution using their own materials, including high-purity copper metal (or other starting material in the case of some P181 participants) and any required acids and other reagents, and their own preparation protocol. The target copper mass fraction is 10.0 g/kg (values ranging from 9.9 g/kg to 10.1 g/kg will be acceptable), and the target mass fraction of HNO₃ is 7 % (values ranging from 6 % to 8 % will be acceptable; remember to account for the HNO₃ that is consumed during digestion). The total mass of copper solution to be shipped to NIST in Step 3 is 250 g. Therefore, the total mass of copper solution prepared in this step must be in excess of 250 g, but is left to the discretion of the participant. The participant must calculate the copper mass fraction of the solution, along with an estimate of its uncertainty, to be reported to NIST.

Step 2: Ten aliquots of the copper solution prepared in Step 1 will be placed into ten bottles by the participant. Each aliquot must have a mass of (25.0 ± 0.3) g, and there is to be only one aliquot per bottle. The mass of each bottle, cap, and aliquot, as well as the mass of each aliquot, must be weighed to the nearest 0.1 mg. All mass values, along with uncertainty estimates, are to be reported to NIST. Pre-cleaned 60 mL high density polyethylene bottles and caps will be provided by NIST. The participant will package the bottles containing the aliquots as directed by NIST. All packaging materials, equipment and instructions needed to result in sealed bottles inside sealed aluminized polyester pouches will be provided by NIST. An individual aliquot will appear as in the photo; the participant will have ten such pouches to ship to NIST.



Step 3: The packaged bottles will then be shipped to NIST with clear marking whether the set of bottles is part of CCQM-K143 or CCQM-P181. The copper mass fraction and uncertainty from Step 1 and the mass values and uncertainties from Step 2 will be reported to NIST, along with a description of the preparation protocol used and the assay value and associated uncertainty for copper in the starting material. In the event that a participant is submitting a set of bottles for CCQM-K143 and one or more additional sets of bottles for CCQM-P181, the sets must be clearly distinguishable, and individual sets of data and protocols must be provided accordingly.

NOTE: At this point, the laboratories participating in CCQM-K143/P181 will have completed their primary responsibilities. Nevertheless, for information, the remaining protocol steps are briefly stated:

Step 4: NIST will run one of the aliquots of each received solution using semi-quantitative ICP-MS or another suitable technique to check for contaminants and any significant concentration of the internal standard element to be used in the ICP-OES comparison (Step 5).

Step 5: NIST will gravimetrically add an internal standard solution and a diluent to each bottle received from the participants. Note that the internal standard element will be manganese. Further dilutions will be performed, and the set of diluted solutions will then be compared using ICP-OES.

Step 6: NIST will measure the density of each diluted solution to a readability of 0.000001 mg/L, as a way to check for small differences in matrix that might cause biases in the comparison results. If matrix differences are suspected, correction factors, with appropriate uncertainty estimates, will be investigated.

Step 7: NIST will ship to PTB a subset of the original solutions received from the participants, along with the internal standard stock, so that the NIST comparison results can be checked experimentally and independently by a second NMI. NIST gratefully acknowledges the willingness of PTB to serve in this capacity.

Step 8: NIST will generate the comparison results for discussion at IAWG meetings and eventual preparation of the required Draft A and Draft B reports. Copper mass fraction values measured for each set of calibration solutions will be compared on a relative scale only.

Deliverables Due from Participants

The deliverables for participants in either CCQM-K143 or CCQM-P181 are the same:

Ten 25.0 g aliquots of one preparation of a copper calibration solution.

Assigned copper mass fraction and uncertainty for the calibration solution, along with the mass fraction and associated uncertainty of copper in the starting material, a full uncertainty budget and complete description of preparation protocol.

Mass values of each of the ten (bottles + caps + aliquots) and each of the ten aliquots, along with estimates of uncertainty.

Planned (and admittedly optimistic) Time Schedule

Call for participation	21 September 2016
Registrations returned to NIST	15 December 2016
Packaging materials sent to participants	31 March 2017
Solutions shipped, and data sent, to NIST	30 June 2017
Draft A report	January 2019
Draft B report	August 2019

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RESULTS REPORT FORM (Page 1 of 2)

CCQM-K143 and CCQM-P181 Comparison of Copper Calibration Solutions Prepared by NMIs/DIs

Contact Name: _____

Institute: _____

Address: _____

Telephone: _____

Email: _____

Instructions:

The tables for reporting data are found on the second page of this form.

In addition to reporting the data in the tables, please provide in a separate document a complete uncertainty budget for the copper mass fraction assigned to your copper solution, including descriptions of methods used to estimate components of uncertainty.

Also, please provide in a separate document a complete description of the protocol used to prepare the copper solution, identifying starting materials, assay value and uncertainty of the source of copper, and other pertinent experimental details.

RESULTS REPORT FORM (Page 2 of 2)

CCQM-K143 and CCQM-P181 Comparison of Copper Calibration Solutions Prepared by NMIs/DIs

Your Copper Solution

Copper mass fraction		g/kg
Combined standard uncertainty, u_c		g/kg
Effective degrees of freedom, ν_{eff}		
Coverage factor, k^a		
Expanded uncertainty, U^b		g/kg

^a Coverage factor for a level of confidence of approximately 95 %.

^b Expanded uncertainty at a level of confidence of approximately 95 %.

Your Bottles and Aliquots Shipped to NIST

Bottle ID	Bottle + Cap + Aliquot ^a		Aliquot				
	Mass, g	U , g ^b	Mass, g	u_c , g	ν_{eff}	k^c	U , g ^b
A							
B							
C							
D							
E							

F							
G							
H							
I							
J							

- ^a Will only be used to check the integrity of the bottle after it has been received at NIST.
- ^b Expanded uncertainty at a level of confidence of approximately 95 %.
- ^c Coverage factor for a level of confidence of approximately 95 %.

Packaging instructions for CCQM K143/P181

Note: These instructions are only intended to ensure the integrity of the test samples during transport back to NIST. This document is not part of the Technical Protocol of CCQM K143/P181 but is the coordinating laboratory's recommendation for shipment. Local and international shipping regulations may require changes in packaging and safe shipment of test samples are the responsibility of each participant.

1. Complete Steps 1 and 2 of technical protocol for CCQM K143/P181. Bottles will be filled with prepared solution and all weighing will have been performed before any packaging activities occur.
2. For each bottle, close cap by hand and then tighten cap using provided torque wrench and adapter to 1 N·m. Put heat shrink over cap in such a way that it covers the gap where bottle and cap meet. Use provided heat gun to activate heat shrink, taking care to direct heat away from body of the bottle, minimizing heating of prepared solution.
3. Write identifying information and preparation date on provided tag and affix tag to bottle with elastic band. Do not apply any sort of adhesive labels, stickers or tape to bottles as such items may leave residue and change the bottle mass. It is possible that hazardous material shipper may require a safety label with each bottle. If that is the case, print hazard label on thick paper, make a small hole in the label and thread the elastic band through the hole before attaching the identification label and safety label to each bottle.
4. Insert bottle and tag(s) into provided polyester bag. Use provided heat sealer to seal polyester bag. This step can be very difficult as the seal should not have any wrinkles, and seal should not allow passage of air. It may be easier to achieve a proper seal by having one person hold the polyester bag tightly as to present an unwrinkled surface to the heat sealer while a second person operates the heat sealer. Extra polyester bags are provided if a proper seal is not achieved on the first attempt.
5. After all bottles are sealed in polyester bags, attach hazard information to each sealed bag.
6. Put sealed polyester bags into provided insulated return box. Depending on shipping requirements, it is likely that all pouches will need to be put in an additional bag to contain possible spills and absorbent material will need to be added. Hazardous material shippers may require a different return box, use of the provided box is not required but was provided to assist participants.
7. Peel heat sensitive sticker from paper and apply to the inside of the return box. Pull activation tab for cold sensitive sticker, peel from paper and apply to the inside of the return box.
8. Prepare return box in any other manner required for shipping. Close and seal return box.
9. Mail samples to:
John Molloy
NIST
100 Bureau Drive, Stop 8391
Gaithersburg, MD, USA 20899-8391
1-301-975-4114