Technical Protocol

SIM.QM-S16 Supplementary Comparison for Metals in Drinking Water

1. Background

Due to the importance of water and its elemental composition to numerous activities and human health, most countries have regulations for water quality concerning elemental concentration. Laboratories make use of several techniques/methods suitable for this type of analysis, and reliability of these measurements is necessary for effective society protection. It is fundamental that National Metrology Institutes (NMI) and Designated Institutes (DI) provide metrological services such as CRM, PT schemes and calibration services to ensure proper regulatory enforcement and society protection on this field. In accordance with Section 3.3 of CIPM MRA-G-13, NMI/DI shall present technical evidence of the measurement competence and uncertainty levels, such as successful participation on a key or supplementary comparison, to publish CMCs in the KCDB and be able to assure SI-traceability of these metrological services.

In 2014, the CCQM-K124 (Trace Elements and Chromium Speciation in Drinking Water) key comparison was organized and the mass fraction of transition elements varied from 0.3 µg/kg to 6.0 µg/kg (As, Cd and Cr). Only three NMIs from SIM region participated in this comparison. NRCC piloted two supplemental comparisons for metals in water: SIM.QM-S7 (Cu, Sr, Pb, and Na) and SIM.QM-S8 (Ni, Zn, Mg, and Ca). In both comparisons, the mass fractions of transition elements were below 10 µg/kg. A new comparison (SIM.QM-S12) started in 2021, but only for elements with a mass fraction less than 20 µg/kg.

NMIs/DIs from SIM have demonstrated interest on a comparison that addresses a measurement range above 50 µg/kg. The Brazilian National Institute of Metrology, Quality and Technology (Inmetro) is making available a supplementary comparison of transition elements (Cu, Fe and Zn) in water in the range of interest within the SIM region. Despite it was conceived to be a regional comparison, it is open to other participants of the MRA throughout all RMOs.

The Supplementary Comparison SIM.QM-S16 will be able to provide NMIs and DIs, with successful participation, the necessary evidence for CMC claims for transition elements in freshwaters and similar matrices. The results of the supplementary comparison will be recorded in BIPM's key comparison database, the KCDB.

2. Proposed schedule

The expected schedule is presented in Table 1. If participants have specific problems or difficulties, please contact the organizers for evaluation of schedule modification.

Table 1 – Proposed schedule

February – April 2023	*Sample preparation, homogeneity and stability study*
IAWG meeting/Nov 2023	Further discussion of the protocol and results of the homogeneity and stability studies
22 Jan 2024	Call for participation
29 Feb 2024	Registration deadline
Apr 2024	Distribution of samples
30 Aug 2024	Deadline for receipt of data
Nov 2024	First discussion of results at IAWG meeting.

3. Measurands

The measurands and their expected mass fractions are listed in Table 2.

Table 2 – Proposed measurands and concentration range

Element	Target Concentration
Cu	(0.1 - 0.4) mg/kg
Fe	(0.1 - 0.4) mg/kg
Zn	(0.1 - 0.4) mg/kg

4. Study Material

The batch was prepared using purified water acidified to 2 % with sub-boiling distilled nitric acid and gravimetrically fortified with measurand calibration solutions. The batch was stirred for 24 hours with a magnetic stirrer covered with PTFE. The batch was bottled in pre-cleaned polyethylene bottles (250 mL). This material will be issued as a CRM after all the results of comparison are received from participants.

Ten bottles of sample were randomly selected for homogeneity study. Three subsamples were taken from each bottle for analysis. Determination of Cu and Zn was performed by ICP-MS and Fe was determined by ICP-OES. One way ANOVA at 95 % level of confidence was applied to assess the between-bottle homogeneity in accordance with ISO Guide

35:2017. The study material was found to be sufficiently homogeneous. The results are summarized in Table 3.

Table 3 - Results of the homogeneity assessment for the measurands.

Element	Anova test		Relative uncertainty (ubb) %
	F-statistics	Critical Value	
Cu	0.40	2.37	0.35
Fe	0.80	2.39	0.28
Zn	0.79	2.37	0.21

5. Test Sample Receipt / Handling

Samples will be distributed by courier to participants. Each laboratory will receive one bottle of the sample. If more sample is required, please inform us at the time of registration.

A Sample Receipt Form will be provided to the participating NMIs/DIs for completion. The completed form should be sent to Inmetro when participant receive the sample. Please inform the coordinator immediately if there is any incident during transportation of the sample.

6. Choice of Method / Procedure

Participants may use any method of their choice. In accordance with Section 3.1 of CIPM MRA-G-13, participants may establish the metrological traceability of their results to the SI using a direct realization via a primary method or using certified reference materials (CRMs) from an NMI/DI having the required CMC claims.

Participants are strongly encouraged to use quality control CRM to monitor the measurement quality.

7. Reporting

Results for each measurand should be reported in minimum triplicate as the element content mass fraction (mass/mass, µg/kg) on test aliquots drawn from the bottle.

Each laboratory shall provide a complete description of the method(s) used, including calibration technique(s) along with their metrological traceability and uncertainty assessment in accordance with the principles laid out in the Guide to the Expression of Uncertainty in Measurement.

Any participant that chooses to use multiple methods can decide only one composite result; e.g., an average value from different methods.

Results of all participating NMIs/DIs will be evaluated against the supplementary comparison reference value (SCRV). The SCRV and associated uncertainty will only be determined from results of NMIs/DIs that participate in the supplementary comparison using methods with

demonstrated metrological traceability. The document “CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence” shall be referenced for SCRV and Degree of Equivalence (DoE) calculations. The NIST decision tree will be applied to define the better statistical model to combine results and estimate SCRV.

8. Use of SIM.QM-S16 in support of calibration and measurement capability (CMC) claims

8.1 How Far the Light Shines

Successful participation in this supplementary comparison will help demonstrate capabilities for determination of transition elements in water matrix. Considering the IAWG Core Capability Matrix, this material falls into the matrix challenge called “water/aqueous”, and so will support CMCs for transition elements at mass fraction levels above 50 µg/kg, except mercury.

9. Contact details

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10. References

CIPM MRA-G-13 “Calibration and measurement capabilities in the context of the CIPM MRA, Guidelines for their review, acceptance and maintenance”, Version 1.1, 30/03/2021.

CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 12/04/2013

ISO/Guide 35:2017(en) Reference materials — Guidance for characterization and assessment of homogeneity and stability

CCQM-IAWG/GD-02 Core Capability Table

JCGM 100:2008 Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement.

JCGM 101:2008 Evaluation of Measurement Data — Supplement 1 to the “Guide to the Expression of Uncertainty in Measurement” — Propagation of Distributions Using a Monte Carlo Method

CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence

Registration Form

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Although this is a SIM comparison, the invitation to participate is extended to National Metrology Institutes (NMIs) and Designated Institutes (DIs) in all RMOs.

Indicate the element(s) for which you will be submitting results by filling **YES** or **NO** on the corresponding line.

Measurand	SIM.QM-S16 Supplementary Comparison
Cu	
Fe	
Zn	

Participant's Name	
Describe if it is a NMI or Designated Institute	
Name of the Institute	
Address	
Country	
E-Mail of contact	
Tel.-Number	

Shipping instructions:

Please indicate any special instructions (local customs/special permits) for importation and the full shipping address and telephone number of a contact.

Please send the completed form by before February 29, 2024 to:

Thiago Araujo and Marcelo Dominguez
toaraujo@inmetro.gov.br, mdalmeida@inmetro.gov.br

If you do not receive an acknowledgement of your registration from us within 5 working days, please send us an email.