**EURAMET.QM-S11 / EURAMET pilot**

**Supplementary comparison & pilot study on**

**determination of**

**Elements in River Water**

**Technical protocol**

1. **Introduction**

The need for quality assessment of anthropogenic impact on environmental pollution is increasing due to discharge from various industries, the use of chemicals in agriculture and the consumption of fossil fuels. Diminishing resources such as natural waters used for the cultivation of agricultural products, plant and animal habitats are under severe pollution pressure and are at constant risk. The EU has stipulated the maximum allowable concentration of priority pollutants in different classes of surface water under the Water Framework Directive in Directive 2008/105/EC Annex I “Environmental quality standards for priority substances and certain other pollutants”, and Annex II “List of priority substances in the field of water policy”. Several parameters, such as Pb, Cd, Ni, Hg were listed in the priority substances and Cd and Hg were further identified as priority hazardous substances. Arsenic is also an important contaminant for its potential toxicological and carcinogenic effects.

The study is organized as part of the Matrix Reference Materials for Environmental Analysis (EnvCRM) project ([www.envcrm.com](http://www.envcrm.com/)) funded by Environmental European Metrology Programme for Innovation and Research (EMPIR). The candidate ‘Elements in River Water’ certified reference material (CRM) is one of the three reference materials targeted in the project, and serves as the test material for this study.

The aim of the study is to test the capabilities of participants in measuring the elements As, Cd, Ni, Pb and Se in river water. While the elements As, Cd, Ni and Pb are mandatory measurands, Se is optional. Although it was targeted first, Hg has been excluded from the list due to the stability issues.

The participants of supplementary comparison will be able to use the comparison results to support their CMC claims for the elements of interest. Along with the Core Capability Tables, it may be possible to claim CMCs in related matrices as well.

1. **Test material**

River water, candidate certified reference material, was collected from a creek feeding Darlık dam reservoir providing city water to Istanbul. The material was acidified to have a final concentration of 2% (v/v) HNO3, and stored in +4 °C refrigerated room for 2 months until further processing. All the water was filtered through a coarse filter and a 0.45 um-pore size filter, respectively. After adding the elements to reach in appropriate concentrations, the whole batch (about 140 L) was homogenized for 6 hours. After this step, the water sample was filled in HDPE bottles to have a volume of 100 mL. Capped bottles were gamma irradiated for sterilization.

The homogeneity of the test material was performed by selecting 12 bottles among a batch of 1200 with random stratified sampling approach. The measurements were conducted with HR-ICPMS, and the data were evaluated with ANOVA. Between bottle homogeneity values for As, Cd, Ni, Pb and Se were determined as 0.34%, 0.43%, 0.90%, 0.30% and 0.79%, respectively.

The stability of the material was tested for 4 weeks at 40 °C and 60 °C to check the stability during the transport. The results revealed no sign of significant change for any measurand for the test period. Long term stability tests are in progress, and the tests will be continued until result submission date.

Each participant will receive two sample bottles containing approximately 100 mL of the river water. The sample receipt form is expected to be filled and returned to TUBITAK UME via e-mail once they are received. It is recommended that the bottles are kept +4 °C until the sample preparations for measurements.

1. **Coordinating laboratories**

The comparison is co-organized by TUBITAK UME and IMBIH. TUBITAK UME, as the pilot laboratory, will conduct the preparation of samples, and homogeneity and stability tests. Distribution of samples will be performed by TUBITAK UME. IMBIH and TUBITAK UME will evaluate the participant results, and will draft the measurement reports.

1. **Measurands and methods**

The participants are required to measure and report the mass fractions of the 4 mandatory and 1 optional measurands. The measurands and their expected mass fractions are listed in Table 1.

Table 1. Measurands and respective mass fraction ranges

|  |  |
| --- | --- |
| Measurand | Expected mass fraction (µg/kg) |
| Arsenic | 2 – 20 |
| Cadmium | 0.1 – 5 |
| Nickel | 2 – 20 |
| Lead | 2 – 20 |
| *Selenium\** | *2 – 20* |

*\**Optional

The participants can use the method of their choice.

1. **Reporting and submission of results**

A reporting form will be provided to participants after test materials are distributed. Each participant will be expected to report individual results, detailed uncertainty budget, details about the method used, etc. At least 3 results from each of the two bottles will be expected for each measurand. All analytical calibrations should be performed using metrologically traceable standards.

Reference value for each measurand will be either the mean or the median of the submitted Supplementary comparison data. If any participant submits results by multiple methods, the result with the smallest uncertainty will be chosen for the calculation of the reference value. Results from participants of pilot study will not be used for reference value determination.

All participants in EURAMET.QM-S11 are required to submit a Core Capability Table for the measurement technique they use. Forms of appropriate Core Capability Table are available at CCQM-IAWG website.

1. **Schedule**

June 15, 2017 Registration deadline

June/July 2017 Distribution of samples

November 30, 2017 Results submission deadline

February 2018 Presentation of results at the EURAMET TC-MC SCIA Meeting

April 2018 Presentation of results at the CCQM-IAWG Meeting

1. **Participants**

Participation to EURAMET Supplementary comparison is open to all interested NMIs or DIs. Any other institutions or laboratories may participate in the pilot study with approval.

1. **Registration**

Please complete and return the enclosed registration forms to Süleyman Z. Can ([suleyman.can@tubitak.gov.tr](mailto:suleyman.can@tubitak.gov.tr)) and Alper Isleyen ([alper.isleyen@tubitak.gov.tr](mailto:alper.isleyen@tubitak.gov.tr)) no later than the registration deadline, 12 June 2017.

For enquiries, participants may contact the coordinating laboratories as follows:

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