CENAM
CENTRO NACIONAL DE METROLOGÍA

Jožef Stefan Institute

# Key Comparison CCQM-K127 “Contaminant and other elements in soil”

## Final Report

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**CCQM-K127 Participants:**

[1] Centro Nacional de Metrologia (CENAM), Mexico
[2] Jožef Stefan Institute (JSI), Slovenia
[3] Instituto Nacional de Tecnología Industrial (INTI), Argentina
[4] Australian Nuclear Science and Technology Organisation (ANSTO), Australia
[5] Institute for Reference Materials and Measurements (IRMM), Belgium
[6] Instituto Nacional de Metrologia. Qualidade e Tecnologia (INMETRO), Brazil
[7] National Research Council Canada (NRC), Canada
[8] National Institute of Metrology (NIM), P.R. China
[9] Laboratoire National de Métrologie et D'essais (LNE), France
[10] Government Laboratory (GLHK), Hong Kong, China
[11] National Physical Laboratory (CSIR-NPLI), India
[12] National Metrology Institute of Japan (NMIJ), Japan
[13] Instituto Nacional de Calidad (INACAL), Peru
[14] National Metrology Institute (INM), Romania
[15] Mendeleyev Institute for Metrology (VNIIM), Russia
[16] National Metrology Institute of South Africa (NMISA), South Africa
[17] TUBITAK Ulusal Metroloji Enstitisu (TUBITAK UME), Turkey
[18] National Institute of Standards and Technology (NIST), USA
[19] Kenya Bureau of Standards (KEBS), Kenia

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## 1. Introduction

Non-contaminated soils contain trace and major elements at levels representing geochemical background of the region. The main sources of elements as contaminants/pollutants in soils are mining and smelting activities, fossil fuel combustion, agricultural practices, industrial activities and waste disposal. Contaminated/polluted sites are of great concern and represent serious environmental, health and economic problems. Characterization and identification of contaminated land is the first step in risk assessment and remediation activities. It is well known that soil is a complex matrix with huge variation locally and worldwide. Consequently, despite the available reference materials (RM) certified for trace and major elements in soils, there is still a lack of concentration and matrix-matched soils RM at testing and calibration levels.
According to the IAWG´s five year plan, it is recommended to have a key comparison under the measurement service category of soils and sediments for the year 2015. Currently 13 NMI has claimed CMCs in Category 13: 29 CMCs in soil and 96 CMCs in sediments. In this regard this is a follow-up comparison in the category 13; wherein three key comparisons have been carried out during the years 2000 (CCQM-K13), 2003 (CCQM-K28) and 2004 (CCQM-K44).

Since it is important to update the capabilities of NMIs in this category, at the CCQM-IAWG meeting held in April 2014, CENAM and JSI proposed a key comparison in this category and a pilot study in parallel. The proposed study was agreed by IAWG members, where two soils samples were used in both CCQM-K127 and CCQM-P162 representing a non-contaminated soil with low concentrations of elements (Arsenic, Cadmium, Iron, Lead and Manganese), and a contaminated soil with much higher concentration of selected elements (Arsenic, Cadmium, Iron and Lead). This broadens the scope and a degree of complexity of earlier measurements in this field. National metrology institutes (NMIs)/designate institutes (DIs) should, therefore, demonstrate their measurement capabilities of trace and major elements in a wide concentration ranges, representing background/reference sites as well as highly contaminated soils by their available analytical methods. This facilitate to investigate the core capabilities of participants to measure the mass fraction of tested elements in soil and therefore to claim their Calibration and Measurement Capabilities as listed in Appendix C of the Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA). Participants are requested to complete the Inorganic Core Capabilities Tables as a means of providing evidence for their CMC claims.

## 2. Participating Institutes

Totally 19 institutes registered in the Key Comparison CCQM-K127. Table 1 lists the participating NMIs in alphabetic order of the countries' names of participating NMIs/DIs.

**Table 1.** List of participating NMIs/DIs for CCQM-K127.

| No. | NMI | Country | Contact person | Measurand | |
|---|---|---|---|---|---|
| | | | | Non-Contaminated Soil | Contaminated Soil |
| 1 | INTI<br>Instituto Nacional de Tecnología Industrial | Argentina | Lic. Osvaldo Acosta | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 2 | ANSTO<br>Australian Nuclear Science and Technology Organisation | Australia | Dr. John Bennet | As, Fe, Mn | As, Cd, Fe |
| 3 | IRMM<br>Institute for Reference Materials and Measurements | Belgium | Dr. James Snell | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 4 | INMETRO<br>Instituto Nacional de Metrologia. Qualidade e Tecnologia | Brazil | Dr. Marcelo D. Almeida, Dr. Thiago O. Araujo | As, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 5 | NRC-CNRC<br>National Research Council Canada | Canada | Dr. Lu Yang | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 6 | LNE<br>Laboratoire national de métrologie et d'essais | France | Dr. Labarraque Guillaume | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 7 | GLHK<br>Government Laboratory Hong Kong | Hong Kong, China | Dr. Michael H.P. Yau, Dr. Wai-hong Fung | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 8 | CSIR-NPLI<br>National Physical Laboratory | India | Dr. Shankar G. Aggarwal,<br>Dr. Daya Soni | - | As, Cd, Fe, Pb |
| 9 | NMIJ<br>National Metrology Institute of Japan | Japan | Dr. Shin-ichi Miyashita | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 10 | KEBS<br>Kenya Bureau of Standards | Kenya | Mr. Tom Oduor Okumu | - | - |
| 11 | CENAM<br>Centro Nacional de Metrologia | Mexico | Mrs. J. Velina Lara Manzano<br>M. Sc. M. Rocio Arvizu Torres | As, Cd, Fe Pb, Mn | As, Cd, Fe, Pb |
| 12 | INACAL<br>Instituto Nacional de Calidad | Peru | Christian Uribe | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 13 | NIM National Institute of Metrology | P.R. China | Dr. Haifeng Li, Dr. Jingbo Chao | As, Cd, Mn | As, Cd, Fe, Pb |
| 14 | INM<br>National Metrology Institute | Romania | Dr. Mirella Buzoianu | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |

| No. | NMI | Country | Contact person | Measurand | |
|---|---|---|---|---|---|
| | | | | Non-Contaminated Soil | Contaminated Soil |
| 15 | VNIIM<br>D.I. Mendeleyev Institute for Metrology | Russia | Prof. Leonid Konopelko | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 16 | JSI<br>Jožef Stefan Institute | Slovenia | Prof. Dr. Milena Horvat | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 17 | NMISA<br>National Metrology Institute of South Africa | South Africa | Dr. Maré Linsky | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 18 | TUBITAK UME<br>TUBITAK Ulusal Metroloji Enstitisu | Turkey | Dr. Suleyman Z. Can | As, Cd, Fe, Pb, Mn | As, Cd, Fe, Pb |
| 19 | NIST<br>National Institute of Standards and Technology | United States | Dr. Michael Winchester | Cd, Fe, Pb, Mn | Cd, Fe, Pb |

**Remarks:** KEBS was not able to submit their results because of transfer of laboratory equipment. CSIR-NPLI did not submit results because of instrumental problem. Also some institutes did not sent results for non-contaminated soil, and for As, Cd, Fe.

## 3. Samples and Instruction to Participants

### 3.1. Soil samples

Two soils samples were used in both CCQM-K127 and CCQM-P162, representing a non-contaminated soil with low concentrations of elements (Arsenic, Cadmium, Iron, Lead and Manganese), and a contaminated soil with much higher concentration of selected elements (Arsenic, Cadmium, Iron and Lead).

Non-contaminated soil sample was prepared by JSI. Soil was collected from a natural grassland and is characterized as eutric cambisol on gravel and sand. The sample was prepared according to ISO 11464:2006, Soil quality - Pretreatment of samples for physic-chemical analysis. A fraction bellow 250 µm was finally homogenized for 60 h in ball drum. After homogeneity testing for 5 elements, the soils were bottled into 40 mL amber vials containing 20 g of soil each. The samples are stored at room temperature (20 ± 2) ºC before shipment.

Contaminated soil sample was prepared by CENAM. The contaminated sandy soil of rhyolitic origin was collected from an industrial area, near to an abandoned mining industry, just before their remediation process. It was characterized for total contents of the metals proposed. The soil batch was processed according to the ISO Guide 34:2009 General requirements for the competence of reference material producers. The soil was homogenized using a homogenizer drum with three dimensions for 3 hours, and also in a sampler splitter of 10 positions, and then packaged with 60 g of soil with a particle size in the range between (75 - 90) µm, contained in an amber borosilicate glass bottle and packed in a vacuum double bag, the first was striated polyethylene bag and the second (outer) in a polyethylene terephthalate bag (Maylar®). The samples are stored at room temperature (20 to 25) ºC before shipment.

### 3.2. Homogeneity and stability study

The homogeneity study for non-contaminated soil sample was conducted after the testing material was bottled and irradiated. The study was carried out with sample size of 0.25 g and 10 bottles which were analysed in triplicate. For this purpose, ICP-QMS was applied for the determination of Mn, Fe, As and Pb, while ET-AAS was applied for the determination of Cd, as shown in Table 2 after microwave assisted digestion. In addition, $k_0$-INAA was applied for the determination of Fe and As, where 10 bottles were analysed in duplicate.

The homogeneity study for contaminated soil sample was conducted after the testing material was bottled and irradiated. Stratified random sampling of 20 bottles was done, and three test portions of 0.5 g were taken from each bottle for analysis. The test portions were digested using microwave assisted digestion method. The digested samples and reagent blanks were analysed using internal standard and standard addition method with ICP-AES for Cd and Fe, and using internal standard and standard addition method with ICP-QQQMS using the reaction cell for As and Pb, as is shown in Table 3.

The statistical technique analysis of variance was applied to assess the between-bottle heterogeneity. The standard uncertainty originated from between bottles heterogeneity $u_{bb}$ was calculated using the equation (1) in accordance with ISO Guide 35:2006 [1]

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MS_{within}}}} \tag{1}$$

where

| | |
|---|---|
| $u_{bb}$ | Uncertainty originated from between bottles heterogeneity. |
| $MS_{\mathrm{within}}$ | Mean square (ANOVA) of within bottles. |
| $\nu_{MS_{\mathrm{within}}}$ | Degree of freedom of mean square of within bottles. |
| $n$ | Number of replicates (samples per bottle). |

**Table 2.** Summary of homogeneity study results for non-contaminated soil.

| Element | ANOVA test on heterogeneity | | Between-bottle heterogeneity $u_{\mathrm{bb}}$ (%) | Analytical method Internal standard |
|---|---|---|---|---|
| | $F$ | $F_{\mathrm{critical\ value}}$ | | |
| Mn | 1.00 | 2.46 | 0.50 | ICP-QMS |
| Fe | 2.24 | 2.46 | 0.60 | ICP-QMS |
| As | 1.54 | 2.46 | 0.85 | ICP-QMS |
| Pb | 2.44 | 2.46 | 0.50 | ICP-QMS |
| Cd | 1.73 | 2.46 | 0.80 | ET-AAS |

Note: ANOVA single factor test was applied for Fe and As results obtained by $k_0$-INAA (10 bottles were analysed in duplicate) and uncertainty originated from between bottles heterogeneity ($u_{\mathrm{bb}}$) for Fe = 0.18 % and As = 0.22 % was obtained.

**Table 3.** Summary of homogeneity study results for contaminated soil.

| Element | ANOVA test on heterogeneity | | Between-bottle heterogeneity $u_{bb}$ (%) | Analytical method Internal standard |
|---|---|---|---|---|
| | $F$ | $F_{\text{critical value}}$ | | |
| Cd | 0.44 | 1.85 | 0.37 | ICP-OES |
| Fe | 0.74 | 1.85 | 0.43 | ICP-OES |
| As | 1.27 | 1.85 | 0.82 | ICP-QQQMS mode $O_2$ ($^{75}As^{16}O^+/^{71}Ga^+$) |
| As | 0.86 | 1.85 | 0.29 | ICP-QQQMS mode $H_2$ ($^{75}As^+/Ga^+$) |
| Pb | 1.23 | 1.85 | 0.78 | ICP-QQQMS mode No gas ($^{208}Pb^+/^{209}Bi^+$) |
| Pb | 1.47 | 1.85 | 0.77 | ICP-QQQMS mode No gas ($^{206}Pb^+/^{209}Bi^+$) |

The homogeneity study results reported in Tables 2 and 3 show that no significant heterogeneity was observed in the non-contaminated and contaminated soil. The test material was considered fit for purpose of this comparison.

For stability study of non-contaminated soil, the samples were sterilized by Co-60 irradiation at a dose between (18 – 24) kGy. The samples are stored at room temperature (20 ± 2) ºC before shipment.

For stability purposes of contaminated soil, the batch was irradiated with Co-60 at a dose between (17 - 22) kGy for microbiological control and bottled. A microbiological study was conducted and non-significant presence of microorganisms was observed. The samples are stored at room temperature (20 to 25) ºC before shipment.

Long-term and short-term stability studies were conducted. The long-term stability is associated with the behaviour of the test material under storage in participating laboratories while the short-term stability studies aimed to show the stability of the material during its transport. The long-term stability was conducted at 20 ºC covering the period from the distribution of test material to the deadline for submission of results. The short-term stability was conducted at 40 ºC and 50 ºC over a 4-week period (sampling points: 1 week, 2 weeks and 4 weeks). All samples of contaminated soil were digested using the microwave assisted digestion method, then the digested samples and reagent blanks were analysed using internal standard and standard addition method with ICP-SFMS. For Cd, Fe and Pb medium resolution mode was applied; for As high resolution mode was used. For samples of non-contaminated soil, the samples were also digested using the microwave assisted digestion method and then ICP-QMS (As, Fe, Mn and Pb) and ET-AAS (Cd) were applied.
The trend-analysis technique proposed by ISO Guide 35:2006 [1] was used to assess the stability of the test material at 20 ºC, 40 ºC and 50 ºC. The basic model for the stability study is expressed as the equation (2).

$$Y = \beta_0 + \beta_1 X + \varepsilon \qquad (2)$$

Where $\beta_0$ and $\beta_1$ are the regression coefficients, and $\varepsilon$ denotes the random error component. With appropriate $t$-factors, $\beta_1$ can be tested for significance of deviation from zero. The Tables 4 and 5 summarize the results for each element of the stability studies tested at 20 ºC, 40 ºC and 50 ºC respectively.

**Table 4.** Summary of stability study results for contaminated soil.

| Element | $p$ value for significance test for $\beta_1$ | | | $\lvert b_1 \rvert < t_{0.95,n-2} \cdot s(b_1)$ | | | Analytical method Internal standard |
|---|---|---|---|---|---|---|---|
| | 20 °C | 40 °C | 50 °C | 20 °C | 40 °C | 50 °C | |
| Cd | 0.449 | 0.470 | 0.662 | $\lvert 4.2 \rvert < 45$ | $\lvert 2.6 \rvert < 30$ | $\lvert 1.6 \rvert < 34$ | ICP-SFMS MR<br>($^{114}$Cd/$^{103}$Rh) |
| Fe | 0.363 | 0.859 | 0.967 | $\lvert 157 \rvert < 1285$ | $\lvert 46 \rvert < 2599$ | $\lvert 14 \rvert < 3522$ | ICP-SFMS MR<br>($^{56}$Fe/$^{45}$Sc) |
| As | 0.899 | 0.951 | 0.899 | $\lvert 0.05 \rvert < 4.2$ | $\lvert 0.03 \rvert < 4.8$ | $\lvert 0.05 \rvert < 4.0$ | ICP-SFMS HR<br>($^{75}$As/$^{71}$Ga) |
| Pb | 0.815 | 0.789 | 0.725 | $\lvert 0.53 \rvert < 22$ | $\lvert 0.60 \rvert < 22$ | $\lvert 0.52 \rvert < 14$ | ICP-SFMS MR<br>($^{208}$Pb/$^{209}$Bi) |

**Table 5.** Summary of stability study results for non-contaminated soil.

| Element | $p$ value for significance test for $\beta_1$ | | | $\lvert b_1 \rvert < t_{0.95,n-2} \cdot s(b_1)$ | | | Analytical method Internal standard |
|---|---|---|---|---|---|---|---|
| | 20 °C | 40 °C | 50 °C | 20 °C | 40 °C | 50 °C | |
| Cd | 0.230 | 0.524 | 0.887 | $\lvert 0.00015 \rvert < 0.00039$ | $\lvert 0.0006 \rvert < 0.0083$ | $\lvert 0.0002 \rvert < 0.0137$ | ET-AAS |
| Fe | 0.525 | 0.627 | 0.772 | $\lvert 0.0036 \rvert < 0.0205$ | $\lvert 0.033 \rvert < 0.629$ | $\lvert 0.026 \rvert < 0.896$ | ICP-QMS |
| As | 0.067 | 0.731 | 0.265 | $\lvert 0.00095 \rvert < 0.00111$ | $\lvert 0.035 \rvert < 0.990$ | $\lvert 0.073 \rvert < 0.409$ | ICP-QMS |
| Pb | 0.834 | 0.906 | 0.212 | $\lvert 0.0012 \rvert < 0.0216$ | $\lvert 0.011 \rvert < 0.975$ | $\lvert 0.107 \rvert < 0.472$ | ICP-QMS |
| Mn | 0.898 | 0.596 | 0.546 | $\lvert 0.073 \rvert < 2.175$ | $\lvert 2.6 \rvert < 45.6$ | $\lvert 0.43 \rvert < 6.29$ | ICP-QMS |

All $p$-values were found greater than 0.05, then it was concluded that the corresponding $\beta_1$ value was not significantly deviated from zero at 95% level of confidence; then, no instability was observed for the test material at 20 ºC, 40 ºC and 50 ºC during the testing period. The test material was considered fit for the purpose of this comparison.

In addition, JSI repeated determination of As, Fe, Mn and Cd using $k_0$-INAA and TRIGA Mark II (250 kW) research reactor in the studied bottles of non-contaminated soil (bottle No. 28) and contaminated soil (bottle No. 75) in August 2016. JSI reported for CCQM-K127 dry mass factor for non-contaminated soil 1.0358 and for contaminated soil 1.0294 (both measured in April 2015). Determination of dry mass factor in August 2016 shows the results as follows: 1.0324 for non-contaminated soil and 1.0273 for contaminated soil. From the data can be concluded that the sample has good stability. The results obtained by $k_0$-INAA for As, Fe, Mn and Cd are given in Tables 6 and 7. Good agreement between the reported and recently obtained data can be observed.

**Table 6.** Comparison of CCQM-K127 data for <u>non-contaminated soil</u> obtained by $k_0$-INAA

| El | Measured in October 2015 | | | | Measured in August 2016 | | | | Diff. | Note |
|---|---|---|---|---|---|---|---|---|---|---|
| | $x_i$ | $u_c$ | $u_c$, % | $n$ | $x_i$ | $u_c$ | $u_c$, % | $n$ | | |
| As (mg/kg) | 14.18 | 0.43 | 3.03 | 7 | 14.05 | 0.43 | 3.08 | 3 | -0.91% | HPGe: CA5* |
| Fe (g/kg) | 34.25 | 0.86 | 2.51 | 7 | 33.78 | 0.85 | 2.50 | 3 | -1.37% | HPGe: CA5* |
| Mn (mg/kg) | 1194 | 36 | 3.02 | 7 | 1198 | 36 | 3.03 | 3 | 0.33% | HPGe: CA5* |

Note: * - HPGe detector CA5 (45%) with CA5B absolute calibration was used in both studies

**Table 7.** Comparison of CCQM-K127 data for <u>contaminated soil</u> obtained by $k_0$-INAA

| El | Measured in October 2015 | | | | Measured in August 2016 | | | | Diff. | Note |
|---|---|---|---|---|---|---|---|---|---|---|
| | $x_i$ | $u_c$ | $u_c$, % | $n$ | $x_i$ | $u_c$ | $u_c$, % | $n$ | | |
| As (mg/kg) | 79.5 | 2.4 | 3.02 | 7 | 78.8 | 2.4 | 3.06 | 3 | -0.88% | HPGe: CA6* |
| Cd (mg/kg) | 446 | 16 | 3.59 | 7 | 452 | 16 | 3.51 | 3 | 1.34% | HPGe: CA6* |
| Fe (g/kg) | 21.14 | 0.53 | 2.51 | 7 | 20.85 | 0.52 | 2.50 | 3 | -1.36% | HPGe: CA6* |

Note: * - HPGe detector CA6 (40%) with CA6B absolute calibration was used to obtain results in October 2015, while recently absolute calibration of the same detector (CA6C, August 2016) was used in this work

### 3.3. Instruction to participants

The participants were encouraged to use any method of their choice for the measurement of total contents of elements in soil samples. It was suggested to mix the sample thoroughly before processing and to analyse the soil samples with a minimum portion of 0.5 g for contaminated soil and 0.25 g for non-contaminated soil. The technical protocol and example of the reporting forms used in this study are shown in Appendix I.

Participants were requested to perform independent measurements on at least five separate portions of the sample and to determine the total mass fractions of the analytes of interest. It was recommended that the preparation and dilution of solutions be carried out by weighing. Measurement results of elements in the soil samples should be dry mass corrected.

For both soil samples, and for the determination of dry mass correction factor a minimum of three separate portions with size of about 1 g each was recommended. Also, it was recommended to dry the soil in a ventilated oven at a temperature of (105 ± 2) °C for minimum 2 hours. Then weight and repeat drying until constant mass is attained (as recommendation: successive weights should not different more than 1 mg). The loss of mass corresponded to the correction that should be applied as dry mass correction. It was advisable to perform this procedure at the same time when weighing the soil samples for the measurements of the measurands.

The participants were requested to provide values for each subsample and the mean value of at least five independent separate portions of sample (subsamples) and its associated measurement uncertainty shall be reported on a dry mass basis. Also, if any participant that chooses to use multiple methods, all results from different methods could be reported, but it was required to report only one composite result (e.g., an average value from different methods).

Participants were asked to provide all the necessary information about their analytical methods, including the sample dissolution, calibration methods and certified reference materials used for calibration purpose and their source of traceability. In addition, complete specification of the measurement equations, details of the uncertainty estimation including the individual sources of uncertainty; the core capability tables, which form part of the key comparison report, in Appendix II is shown the summary of the core capability tables reported.

## 4. Methods of Measurement

The measurement methods were left free to be selected by the participant institutes. The analytical techniques ICP-MS, ICP-OES, FAAS, ET-AAS and INAA were widely used by the participants. The sample preparation methods used were based on microwave assisted digestion, except when it was used INAA. Two institutes (JSI and NIM) submitted results by two methods for several measurands. The principle method (used in the KCRV calculation) for these analytes was identified as ICP-MS by JSI except for Fe in contaminated soil and as ICP-MS or ID-ICP-MS by NIM. The alternative methods were $k_0$-INAA (JSI) and ICP-OES (NIM). These alternative methods are indicated as such in Table 8. The results obtained by the alternative methods were provided as information values and this is indicated in the relevant tables of results.

**Table 8.** Summary of methods of measurement used by the participants

| Institute | Sample | Analyte | Sample preparation/Digestion procedure | Calibration method | Analytical instrument | Reference material used for calibration (Traceability) |
|---|---|---|---|---|---|---|
| ANSTO | Non-contaminated soil | As, Fe, Mn | Weighing into polyethylene capsules only | $k_0$ method | As, Cd, Fe, Mn: $k_0$-NAA | As, Fe: Au (IRMM-530RC)<br>Mn: Au (NIST SRM 3121) |
|  | Contaminated soil | As, Cd, Fe |  |  |  |  |
| CENAM | Non-contaminated soil | As, Cd, Fe, Mn, Pb | Microwave-assisted digestion:<br>As, Cd, Fe, Pb for ICP-SFMS ($HCl/HNO_3/HF/H_2O_2/H_3BO_3$)<br>As, Pb for ICP-AES and EAA-HG | As, Mn: Internal standard with single point standard addition<br>Cd, Fe, Pb: Exact matching double ID-ICP-SFMS | As, Mn: High resolution ICP-SFMS<br>Cd: Low resolution ICP-SFMS<br>Fe, Pb: Medium resolution ICP-SFMS | As: Reference material used for calibration SRM 3103 arsenic; for internal standard SRM-3119 Gallium<br>Cd: Reference material used for calibration DMR-461a cadmium; the enriched isotope used was the $^{111}$Cd<br>Fe: Reference material used for calibration CAL-620-67 iron; the enriched isotope used was the |

| Institute | Sample | Analyte | Sample preparation/Digestion procedure | Calibration method | Analytical instrument | Reference material used for calibration (Traceability) |
|---|---|---|---|---|---|---|
| | Contaminated soil | As, Cd, Fe, Pb | (HCl/HNO$_3$/HF/H$_2$O$_2$)<br>Cd, Fe, Pb: anion exchange separation method | As, Pb: Internal standard with single point standard addition<br>As: External calibration with single point standard addition<br>Cd, Fe, Pb: Exact matching double ID-ICP-SFMS | As: High resolution ICP-SFMS; HG-EAA/ICP-AES<br>Cd: Low resolution ICP-SFMS<br>Fe, Pb: Medium resolution ICP-SFMS<br>Pb: ICP-AES | $^{57}$Fe<br>Pb: Reference material used for calibration DMR-463a lead; the enriched isotope used was the SRM-991 $^{206}$Pb<br>Mn: Reference material used for calibration DMR-123 manganese; for internal standard High Purity (HP) Germanium |
| CSIR-NPLI | Non-contaminated soil | N/A | N/A | N/A | N/A | N/A |
| | Contaminated soil | As, Cd, Fe, Pb | Microwave-assisted digestion (HCl/HNO$_3$/HF) | As, Cd, Pb: External Calibration<br>Fe: External Calibration (Bracketing) | ICP-OES | As: NPLI traceable CRM; BND 33.100.01<br>Pb: NPLI traceable CRM; BND 82.100.01<br>Cd, Pb: NIST traceable CRM |
| GLHK | Non-contaminated soil | As, Cd, Fe, Mn, Pb | Microwave-assisted digestion (HNO$_3$/H$_2$O$_2$/HF) | Gravimetric Standard Addition | As, Cd, Pb: ICP-MS<br>Fe, Mn: ICP-OES | As: NIST SRM 3103a; NIST SRM 2709a; NRCC PACS-3<br>Cd: NIST SRM 3108; NIST SRM 2709a; NRCC PACS-3<br>Fe: NIST SRM 3126a; NIST SRM 2709a; NRCC PACS-3<br>Pb: NIST SRM 3128; NIST SRM 2709a; NRCC PACS-3<br>Mn: NIST SRM 3132; NIST SRM 2709a; NRCC PACS-3 |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |
| INACAL | Non-contaminated soil | As, Cd, Fe, Mn, Pb | EPA Method 3052: Microwave assisted acid digestion of siliceous and organically based matrices | Standard addition | As, Cd, Pb: ET-AAS<br>Fe, Mn: FAAS | As: SRM 3103a, SRM 2711a<br>Cd: SRM 3108, SRM 2711a<br>Fe: SRM 3126a, SRM 2711a<br>Pb: SRM 3128, SRM 2711a<br>Mn: SRM 3132, SRM 2711a |
| | Contaminated soil | As, Cd, Fe, Pb | | | As, Pb: ET-AAS<br>Cd, Fe: FAAS | |
| INTI | Non-contaminated soil | As, Cd, Fe, Mn, Pb | Microwave oven digestion (HNO$_3$/HF) | Standard addition | As, Cd, Pb: ICP-MS<br>Fe, Mn: ICP-OES | NIST, Fluka, SRM-2781 Domestic sludge. |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |
| INM | Non-contaminated soil | As, Cd, Fe, Mn, Pb | Microwave digestion (HNO$_3$/HCl/HF) | bracketing method | As, Cd, Pb: ICP-MS<br>Fe, Mn: FAAS | Fe: ERMÒ-CC141 Loam Soil, Valid until 15.05.2016; SRM NIST 3126a, lot 051031<br>Pb: SRM NIST 3128, lot 030721<br>Mn: SRM NIST 3132, lot 030721<br>Cd: SRM NIST 3108, lot 130116<br>As: Arsenic Standard for AAS, TraceCERT, Lot BCBL3830V |
| | Contaminated soil | As, Cd, Fe, Pb | | | As, Cd, Fe, Pb: FAAS | |
| INMETRO | Non-contaminated soil | As, Fe, Mn, Pb | Microwave digestion (HF/HNO$_3$/H$_2$O$_2$) | External Standard Calibration | As: ICP-MS<br>Fe, Pb, Mn: ICP-OES (Plasma operated under | As: Calibration: SRM 3103a (NIST); Quality Control: SRM 2782 (NIST) and SRM 2586 (NIST) |

| Institute | Sample | Analyte | Sample preparation/Digestion procedure | Calibration method | Analytical instrument | Reference material used for calibration (Traceability) |
|---|---|---|---|---|---|---|
|  |  |  |  |  | robust conditions) | Fe: Calibration: SRM 3126a (NIST); Quality Control: SRM 2586 (NIST)<br>Pb: Calibration: SRM 3128 (NIST); Quality Control: SRM 2782 (NIST) and SRM 2586 (NIST)<br>Mn: Calibration: SRM 3132 (NIST); Quality Control: SRM 2782 (NIST) and SRM 2586 (NIST)<br>Cd: Calibration: SRM 3108 (NIST) |
|  | Contaminated soil | As, Cd, Fe, Pb |  |  | As, Cd, Fe, Pb: CP-OES (Plasma operated under robust conditions) |  |
| IRMM | Non-contaminated soil | As, Cd, Fe, Mn, Pb | Digested in a Milestone Ultraclave ($HNO_3$/HF) | As: External with 2 bracketing standards, linear calibration<br>Cd, Pb: ID<br>Fe, Mn: External with 6 standards | As, Fe, Mn: ICP-OES<br>Cd, Pb: ICP-MS | As: Merck Certipur 1000 mg/L As standard<br>Cd: IRMM-622<br>Fe: Merck Certipur 1000 mg/L Fe standard<br>Pb: Inorganic Ventures 10 mg/L $^{206}$Pb, NIST997<br>Mn: Merck Certipur 1000 mg/L Mn standard |
|  | Contaminated soil | As, Cd, Fe, Pb |  |  |  |  |
| JSI | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave-assisted digestion ($HNO_3$/HCl/HF/$H_3BO_3$)<br>For $k_0$-INAA: Weighing into polyethylene capsules only | As, Cd, Fe, Pb, Mn: External Calibration<br>As, Fe, Mn: $k_0$-standardization method of INAA. | As, Fe, Pb, Mn: ICP-MS<br>Cd: ET-AAS<br>As*, Fe*, Mn*: $k_0$-INAA | As, Fe, Mn: ERM-CC141 Loam soil<br>BCR-320R Channel sediment<br>IRMM-530R (Al-0.1%Au alloy) |
|  | Contaminated soil | As, Cd, Pb |  | As, Cd, Pb: External Calibration<br>As, Cd, Fe: $k_0$-standardization method of INAA. | As, Cd, Pb: ICP-MS<br>As*, Cd*, Fe: $k_0$-INAA |  |
| LNE | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Digestion in a closed micro wave oven with $HNO_3$/HF/$H_2O_2$ | As, Mn: Standard addition method with internal standard ($^{75}$As/$^{89}$Y) and ($^{55}$Mn/$^{54}$Fe).<br>Cd, Pb: Double isotope dilution ($^{113}$Cd/$^{111}$Cd), ($^{112}$Cd/$^{111}$Cd), ($^{208}$Pb/$^{206}$Pb)<br>Fe: external calibration monitoring $^{54}$Fe, $^{56}$Fe, $^{57}$Fe | As, Fe, Mn: ICP-QMS with collision cell<br>Cd, Pb: ID-ICP-QMS | As: calibrant solution for standard addition is in house prepared based on high-purity As, 99.9 %, previously checked for impurities<br>Cd: calibrant (reverse ID) is in house prepared primary calibration solution based on high-purity Cadmium 99.999 %, previously checked for impurities; Spike $^{111}$Cd (97.23 %)<br>Fe: calibrant solution for external calibration is in house prepared based on high-purity Fe, 99.995 %, previously checked for impurities<br>Pb: calibrant (reverse ID) is in house prepared primary calibration solution based on high-purity Lead 99.9999 %, previously checked for impurities; Spike $^{206}$Pb (99.302%)<br>Mn: calibrant solution for standard addition is in house prepared based on high-purity |
|  | contaminated soil | As, Cd, Pb |  |  |  |  |

| Institute | Sample | Analyte | Sample preparation/Digestion procedure | Calibration method | Analytical instrument | Reference material used for calibration (Traceability) |
|---|---|---|---|---|---|---|
| | | | | | | Mn, 99.995 %, previously checked for impurities |
| NIM | Non-contaminated soil | As, Cd, Mn | Thermal digestion of 150 ℃-170 ℃ ($HNO_3$/HF/$HClO_4$) | As, Fe, Mn: External calibration method<br>Cd: $^{111}$Cd spike (GBW 04441) CRM used as calibrant. | As: ICP-MS<br>Cd: ID-ICP-MS<br>Mn: ICP-OES | As: GBW 08611 As standard solution<br>Cd: GBW 04441 $^{111}$Cd spike CRM; GBW 08612 Cd standard solution<br>Mn: GBW(E) 080157 Mn standard solution<br>Fe: GBW 08616 Fe standard solution<br>Pb: GBW 08619 Pb standard solution as primary standard |
| | Contaminated soil | As, Cd, Fe, Pb | | As, Cd, Fe: External calibration method<br>Cd: GBW 08612 Cd standard as calibrant<br>Pb: NIST 981 CRM used as calibrant. | As: ICP-MS/ICP-OES*<br>Cd: ID-ICP-MS/ ICP-OES*<br>Fe: ICP-OES<br>Pb: ID-ICP-MS | |
| NIST | Non-contaminated soil | Cd, Fe, Pb, Mn | Microwave-assisted digestion:<br>Cd, Pb: $HNO_3$/$HClO_4$/HF<br>Fe, Mn: $HNO_3$/HCl/HF | Cd, Pb: reverse isotope dilution mass spectrometry<br>Fe, Mn: Single point standard addition | Cd, Pb: ID-ICP-QMS<br>Fe, Mn: ICP-OES | Cd: SRM 3108 Cadmium Standard Solution (lot # 130116) and SRM 746 Cadmium-Vapor Pressure<br>Fe, Mn: SRMs 2709a San Joaquin Soil and 2711a Montana II Soil<br>Pb: SRM 3128 Lead Standard Solution (lot # 101026) |
| | Contaminated soil | Cd, Fe, Pb | Microwave-assisted digestion:<br>Cd, Pb: $HNO_3$/HF<br>Fe: $HNO_3$/HCl/HF | | | |
| NMIJ | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave-assisted digestion ($HNO_3$/$HClO_4$/HF)<br>For non-contaminated soil: chemical coprecipitation as Cd separation method | As, Mn: External calibration<br>Cd, Fe, Pb: Double IDMS | As: High resolution ICP-MS<br>As, Cd, Fe, Pb, Mn: ICP-MS | As, Cd, Fe, Mn: JCSS standard solution<br>Pb: JCSS standard solution; NIST SRM 981 and 982 (used for mass bias correction) |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |
| NMISA | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave digestion ($HNO_3$/HCl/HF/ $H_3BO_3$) | As, Mn: External calibration, 6 calibration points<br>Cd, Fe, Pb: Double Isotope Dilution-ICPMS | As, Mn: ICP-SFMS<br>Cd, Fe, Pb: ID-ICP-SFMS | NCS DC 73319 (GBW 07401)<br>NCS DC 73323 (GBW 07405) |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |
| NRC | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave digestion ($HNO_3$/HF/ $HClO_4$) | Fe, As, Pb, Mn: Standard additions<br>Cd: Isotope dilution | Fe, As, Pb, Mn ICP-OES<br>Cd : ICP-MS | Fe-28966<br>Mn-32456a<br>Pb-27668<br>As-28858<br>Cd-32862 |
| | Contaminated soil | As, Cd, Fe, Pb | | As, Cd, Fe, Pb: Standard additions ICP-OES | Fe, As, Pb: ICP-OES<br>Cd : ICP-MS | |

| Institute | Sample | Analyte | Sample preparation/Digestion procedure | Calibration method | Analytical instrument | Reference material used for calibration (Traceability) |
|---|---|---|---|---|---|---|
| TUBITAK UME | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave digestion ($HNO_3$/HCl/HF) | As, Mn: Matrix matched standard additions method<br>Cd, Fe: Isotope dilution mass spectrometry<br>Pb: Isotope dilution mass spectrometry (Reverse IDMS) | As, Mn: High resolution ICP-MS<br>Cd, Fe, Pb: ID-ICP-MS | As: NIST SRM 3103a<br>Cd: IRMM 621<br>Fe: IRMM 640<br>Pb: NIST SRM 991; NIST SRM 981; NIST SRM 982<br>Mn: NIST SRM 3132 |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |
| VNIIM | Non-contaminated soil | As, Cd, Fe, Pb, Mn | Microwave digestion ($HNO_3$/HCl) | External calibration, linear 5 points | ICP-MS | ICP multi-element standard solution IV (Merck)<br>Environmental calibration standard (Agilent Technologies) |
| | Contaminated soil | As, Cd, Fe, Pb | | | | |

* Methods of measurement that provide information values from JSI and NIM.

## 5. Results and Discussion

### 5.1 General

The total registered institutes were 19 for CCQM-K127 and only 18 institutes sent report results. In Table 9 is shown the reported analytes by each institute and by sample.

**Table 9.** List of reported results for each analyte in both soils by each institute.

| NMI | | Non-Contaminated Soil | | | | | Contaminated Soil | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | As | Cd | Fe | Pb | Mn | As | Cd | Fe | Pb |
| 1 | ANSTO | X | | X | | X | X | X | X | |
| 2 | CENAM | X | X | X | X | X | X | X | X | X |
| 3 | CSIR-NPLI | | | | | | X | X | X | X |
| 4 | GLHK | X | X | X | X | X | X | X | X | X |
| 5 | INACAL | X | X | X | X | X | X | X | X | X |
| 6 | INM | X | X | X | X | X | X | X | X | X |
| 7 | INMETRO | X | | X | X | X | X | X | X | X |
| 8 | INTI | X | X | X | X | X | X | X | X | X |
| 9 | IRMM | X | X | X | X | X | X | X | X | X |
| 10 | JSI | XX | X | XX | X | XX | XX | XX | X | X |
| 11 | KEBS | | | | | | | | | |
| 12 | LNE | X | X | X | X | X | X | X | X | X |
| 13 | NIM | X | X | | | X | XX | XX | X | X |
| 14 | NIST | | X | X | X | X | | X | X | X |
| 15 | NMIJ | X | X | X | X | X | X | X | X | X |
| 16 | NMISA | X | X | X | X | X | X | X | X | X |
| 17 | NRC | X | X | X | X | X | X | X | X | X |
| 18 | TUBITAK | X | X | X | X | X | X | X | X | X |
| 19 | VNIIM | X | X | X | X | X | X | X | X | X |

It is important to mention, that the original programmed schedule suffer some changes in the deadline for delivery results. It happens due the requested participation of 4 new institutes (IRMM, ANSTO, CSIR-NPLI and KEBS) which was approved during the IAWG meeting in April 2015, then the deadline was change from August 31st to October 15th. Later on, due some institutes had some problems with the process of customs, in order to obtain the soils samples, it was required a new dead line for delivery results, which finally was set on November 1st 2015.

## 5.2 Reported results

The reported results of the key comparison were from 18 institutes (NMIs/DIs), 151 measurements were reported for CCQM-K127. KEBS does not report results due to some problems in their institute. As specified in the protocol, participants were required to report their results on dry mass basis for comparability purposes. The Tables 10 to 18 shown the reported results, which identify the results with the names of the participating institutes and it is sorted in ascending order.

**Table 10.** Reported results of mass fraction of As in non-contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 9.41 | 0.39 | 2 | 0.77 | EC-ICP-MS | 0.9712 |
| IRMM* | 10.4 | 2.4 | 2 | 4.8 | ECB-ICP-OES | 0.9730 |
| LNE | 12.25 | 0.28 | 2 | 0.56 | IE+SA-ICP-QMS-CC | 0.9910 |
| NIM | 12.7 | 0.3 | 2 | 0.6 | EC-ICP-MS | 0.978 |
| INM | 12.8 | 0.9 | 2 | 1.8 | B-ICP-MS | 0.9774 |
| GLHK | 12.9 | 0.6 | 2 | 1.2 | SA-ICP-MS | 0.9866 |
| ANSTO | 13.1 | 0.5 | 2 | 1 | INAA | 0.9690 |
| INMETRO | 13.35 | 0.22 | 2 | 0.44 | EC-ICP-MS | 0.9696 |
| NMIJ | 13.48 | 0.09 | 2 | 0.18 | EC-ICP-SFMS | 0.9698 |
| CENAM | 13.53 | 0.46 | 2 | 0.93 | IE+SA-ICP-SFMS | 0.9775 |
| NMISA | 13.78 | 0.55 | 2 | 1.1 | EC-ICP-SFMS | 0.971938 |
| INTI | 13.79 | 0.26 | 2 | 0.52 | SA-ICP-MS | 0.9807 |
| NRC | 14.2 | 0.57 | 2 | 1.1 | SA-ICP-OES | 0.9698 |
| JSI | 14.2 | 0.4 | 2 | 0.8 | EC-ICP-MS | 0.9654 |
| TUBITAK | 14.4 | 0.44 | 2 | 0.88 | SA-HR-ICP-MS | 0.9737 |
| INACAL | 19.88 | 0.80 | 2 | 1.6 | EC-HG-AAS | 0.9709 |
| JSI** | 14.18 | 0.43 | 2 | 0.86 | INAA | 0.9654 |

* The IRMM suggested their result of As in non-contaminated soil should not be included in the KCRV as they knew it to be erroneous. Also, the IRMM advised that the standard uncertainty for calculation was in error because they reported the expanded uncertainty, the IRMM result will be evaluated with the original reported standard uncertainty.

** Information value.

**Table 11.** Reported results of mass fraction of As in contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 60.56 | 2.79 | 2 | 5.6 | EC-ICP-MS | 0.9782 |
| LNE | 68 | 3 | 2 | 6 | IE+SA-ICP-QMS-CC | 0.9800 |
| NMISA | 71.2 | 3.2 | 2 | 6.4 | EC-ICP-SFMS | 0.97892 |
| IRMM* | 72 | 17 | 2 | 34 | ECB-ICP-OES | 0.9762 |
| INTI | 74.46 | 0.75 | 2 | 1.5 | SA-ICP-MS | 0.9852 |
| NRC | 75.0 | 2.9 | 2 | 5.8 | SA-ICP-OES | 0.9751 |
| ANSTO | 75.7 | 3.0 | 2 | 6 | INAA | 0.9756 |
| GLHK | 76.2 | 3.2 | 2 | 6.4 | SA-ICP-MS | 0.9908 |
| NMIJ | 76.24 | 0.58 | 2 | 1.2 | EC-ICP-MS | 0.9762 |
| INM | 76.6 | 5.15 | 2 | 10 | B-FAAS | 0.9954 |
| CENAM | 77.7 | 1.4 | 2 | 2.8 | IE+SA-ICP-SFMS | 0.97753 |
| JSI | 78.5 | 1.9 | 2 | 3.8 | EC-ICP-MS | 0.9714 |
| INMETRO | 78.6 | 1.2 | 2 | 2.4 | EC-ICP-OES | 0.9732 |
| INACAL | 79.66 | 3.21 | 2 | 6.4 | SA-ETAAS | 0.9804 |
| TUBITAK | 79.7 | 2.7 | 2 | 5.4 | SA-HR-ICP-MS | 0.9799 |
| NIM | 80.2 | 1.3 | 2 | 2.6 | EC-ICP-MS | 0.972 |
| CSIR-NPLI | 92.18 | 4.22 | 2 | 8.4 | EC-ICP-OES | 0.9903 |
| NIM** | 78.0 | 1.4 | 2 | 2.8 | EC-ICP-OES | 0.972 |
| JSI** | 79.5 | 2.4 | 2 | 4.8 | INAA | 0.9714 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

** Information values.

**Table 12.** Reported results of mass fraction of Cd in non-contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| INM | 0.37 | 0.03 | 2 | 0.06 | B-ICP-MS | 0.9774 |
| VNIIM | 0.385 | 0.026 | 2 | 0.052 | EC-ICP-MS | 0.9712 |
| LNE | 0.481 | 0.005 | 2 | 0.01 | ID-ICP-QMS | 0.9820 |
| CENAM | 0.5121 | 0.0042 | 2 | 0.0084 | ID-ICP-SFMS | 0.9707 |
| GLHK | 0.513 | 0.024 | 2 | 0.048 | SA-ICP-MS | 0.9866 |
| NIST | 0.5146 | 0.0044 | 2.18 | 0.0096 | ID-ICP-QMS | 0.9713 |
| NMIJ | 0.518 | 0.011 | 2 | 0.022 | ID-ICP-MS | 0.9692 |
| INACAL | 0.52 | 0.02 | 2 | 0.04 | SA-ETAAS | 0.9709 |
| NIM | 0.531 | 0.008 | 2 | 0.016 | ID-ICP-MS | 0.978 |
| NMISA | 0.534 | 0.011 | 2 | 0.022 | ID-ICP-SFMS | 0.971938 |
| TUBITAK | 0.550 | 0.008 | 2 | 0.016 | ID-ICP-MS | 0.9737 |
| NRC | 0.551 | 0.022 | 2 | 0.044 | ID-ICP-QMS | 0.9698 |
| JSI | 0.557 | 0.012 | 2 | 0.024 | EC-ETAAS | 0.9654 |
| IRMM* | 0.571 | 0.012 | 2 | 0.024 | ID-ICP-MS | 0.9730 |
| INTI | 0.619 | 0.015 | 2 | 0.03 | SA-ICP-MS | 0.9807 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

**Table 13.** Reported results of mass fraction of Cd in contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 395.3 | 11.6 | 2 | 23 | EC-ICP-MS | 0.9782 |
| ANSTO | 416 | 15 | 2 | 30 | INAA | 0.9756 |
| NMISA | 422.7 | 7.8 | 2 | 16 | ID-ICP-SFMS | 0.97892 |
| CSIR-NPLI | 424.12 | 18.29 | 2 | 37 | EC-ICP-OES | 0.9903 |
| INTI | 426.8 | 3.1 | 2 | 6.2 | SA-ICP-MS | 0.9852 |
| NRC | 427 | 14.4 | 2 | 29 | SA-ICP-OES | 0.9751 |
| INMETRO | 432.0 | 4.7 | 2 | 9.4 | EC-ICP-OES | 0.9732 |
| NMIJ | 436.2 | 5.1 | 2 | 10 | ID-ICP-MS | 0.976 |
| LNE | 438 | 3 | 2 | 6 | ID-ICP-QMS | 0.9860 |
| IRMM* | 438.1 | 8.2 | 2 | 16 | ID-ICP-MS | 0.9762 |
| NIST | 440.7 | 3.4 | 2.13 | 7.2 | ID-ICP-QMS | 0.9769 |
| TUBITAK | 442 | 6 | 2 | 12 | ID-ICP-MS | 0.9799 |
| NIM | 443.0 | 3.7 | 2 | 7.4 | ID-ICP-MS | 0.972 |
| CENAM | 443.3 | 2.8 | 2 | 5.6 | ID-ICP-SFMS | 0.9765 |
| INACAL | 452.47 | 11.32 | 2 | 23 | SA-FAAS | 0.9804 |
| GLHK | 455 | 16 | 2 | 32 | SA-ICP-MS | 0.9908 |
| JSI | 458 | 9 | 2 | 18 | EC-ICP-MS | 0.9714 |
| INM | 461 | 12 | 2 | 24 | B-FAAS | 0.9954 |
| NIM** | 445.2 | 7.2 | 2 | 14 | EC-ICP-OES | 0.972 |
| JSI** | 446 | 16 | 2 | 32 | INAA | 0.9714 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

** Information values.

**Table 14.** Reported results of mass fraction of Fe in non-contaminated soil.

| Institute | Reported value (mg/g) | Standard uncertainty (mg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (mg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 24.27 | 0.52 | 2 | 1 | EC-ICP-MS | 0.9712 |
| INTI | 28.27 | 0.40 | 2 | 0.8 | SA-ICP-OES | 0.9807 |
| INM | 31.4 | 0.3 | 2 | 0.6 | B-FAAS | 0.9774 |
| LNE | 31.59 | 0.68 | 2 | 1.4 | EC-ICP-QMS-CC | 0.991 |
| IRMM* | 31.9 | 4.3 | 2 | 8.6 | EC-ICP-OES | 0.9730 |
| NRC | 31.9 | 0.77 | 2 | 1.5 | SA-ICP-OES | 0.9698 |
| GLHK | 32.1 | 0.8 | 2 | 1.6 | SA-ICP-OES | 0.9866 |
| ANSTO | 32.3 | 1.2 | 2 | 2.4 | INAA | 0.9690 |
| INMETRO | 32.36 | 0.30 | 2 | 0.6 | EC-ICP-OES | 0.9696 |
| NMISA | 32.5 | 0.45 | 2 | 0.9 | ID-ICP-SFMS | 0.971938 |
| NIST | 32.654 | 0.087 | 2.2 | 0.19 | SA-ICP-OES | 0.9713 |
| CENAM | 32.66 | 0.28 | 2 | 0.56 | ID-ICP-SFMS | 0.9707 |
| NMIJ | 32.85 | 0.64 | 2 | 1.3 | ID-ICP-MS | 0.9692 |
| TUBITAK | 33.2 | 0.3 | 2 | 0.6 | ID-ICP-MS | 0.9737 |
| INACAL | 34.20 | 0.84 | 2 | 1.7 | SA-FAAS | 0.9709 |
| JSI | 34.3 | 0.7 | 2 | 1.4 | EC-ICP-MS | 0.9654 |
| JSI** | 34.25 | 0.86 | 2 | 1.7 | INAA | 0.9654 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

** Information value.

**Table 15.** Reported results of mass fraction of Fe in contaminated soil.

| Institute | Reported value (mg/g) | Standard uncertainty (mg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (mg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 17.55 | 0.39 | 2 | 0.78 | EC-ICP-MS | 0.9782 |
| INTI | 18.02 | 0.50 | 2 | 1 | SA-ICP-OES | 0.9852 |
| LNE | 19.1 | 0.3 | 2 | 0.6 | EC-ICP-QMS-CC | 0.9800 |
| NRC | 19.4 | 0.77 | 2 | 1.5 | SA-ICP-OES | 0.9751 |
| NIM | 19.5 | 0.4 | 2 | 0.8 | EC-ICP-OES | 0.972 |
| INMETRO | 19.5 | 0.19 | 2 | 0.38 | EC-ICP-OES | 0.9732 |
| NMISA | 19.72 | 0.33 | 2 | 0.66 | ID-ICP-SFMS | 0.97892 |
| GLHK | 20.1 | 0.5 | 2 | 1 | SA-ICP-OES | 0.9908 |
| INM | 20.2 | 0.3 | 2 | 0.6 | B-FAAS | 0.9954 |
| NIST | 20.42 | 0.34 | 2.8 | 0.95 | SA-ICP-OES | 0.9769 |
| TUBITAK | 20.6 | 0.2 | 2 | 0.4 | ID-ICP-MS | 0.9799 |
| NMIJ | 20.65 | 0.58 | 2 | 1.2 | ID-ICP-MS | 0.976 |
| CENAM | 20.66 | 0.28 | 2 | 0.56 | ID-ICP-SFMS | 0.9765 |
| ANSTO | 20.7 | 0.8 | 2 | 1.6 | INAA | 0.9756 |
| IRMM* | 21.1 | 2.9 | 2 | 5.8 | EC-ICP-OES | 0.9762 |
| JSI | 21.14 | 0.53 | 2 | 1.1 | INAA | 0.9714 |
| INACAL | 21.30 | 0.52 | 2 | 1 | SA-FAAS | 0.9804 |
| CSIR-NPLI | 22.64 | 0.21 | 2 | 0.42 | ECB-ICP-OES | 0.9903 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

**Table 16.** Reported results of mass fraction of Pb in non-contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 35.34 | 1.05 | 2 | 2.1 | EC-ICP-MS | 0.9712 |
| JSI | 36.9 | 0.7 | 2 | 1.4 | EC-ICP-MS | 0.9654 |
| NRC | 37.22 | 1.2 | 2 | 2.4 | SA-ICP-OES | 0.9698 |
| NMIJ | 38.56 | 1.01 | 2 | 2 | ID-ICP-MS | 0.9692 |
| INACAL | 38.9 | 1.6 | 2 | 3.2 | SA-ETAAS | 0.9709 |
| GLHK | 39.2 | 1.0 | 2 | 2 | SA-ICP-MS | 0.9866 |
| INTI | 39.29 | 0.91 | 2 | 1.8 | SA-ICP-MS | 0.9807 |
| INM | 39.4 | 2.3 | 2 | 4.6 | B-ICP-MS | 0.9774 |
| CENAM | 39.48 | 0.18 | 2 | 0.36 | ID-ICP-SFMS | 0.9775 |
| NMISA | 39.65 | 0.41 | 2 | 0.82 | ID-ICP-SFMS | 0.971938 |
| IRMM* | 39.72 | 0.85 | 2 | 1.7 | ID-ICP-MS | 0.9730 |
| LNE | 40.0 | 0.75 | 2 | 1.5 | ID-ICP-QMS | 0.9710 |
| NIST | 40.34 | 0.50 | 2.03 | 1 | ID-ICP-QMS | 0.9713 |
| TUBITAK | 41.3 | 1.4 | 2 | 2.8 | ID-ICP-MS | 0.9737 |
| INMETRO | 54.74 | 0.94 | 2 | 1.9 | EC-ICP-OES | 0.9696 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

**Table 17.** Reported results of mass fraction of Pb in contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| INTI | 214.4 | 4.6 | 2 | 9.2 | SA-ICP-MS | 0.9852 |
| JSI | 215 | 4 | 2 | 8 | EC-ICP-MS | 0.9714 |
| VNIIM | 219.6 | 10.6 | 2 | 21 | EC-ICP-MS | 0.9782 |
| INM | 225 | 5 | 2 | 10 | B-FAAS | 0.9954 |
| NMISA | 225.1 | 3.3 | 2 | 6.6 | ID-ICP-SFMS | 0.97892 |
| INACAL | 227.62 | 9.56 | 2 | 19 | SA-ETAAS | 0.9804 |
| LNE | 229 | 2.5 | 2 | 5 | ID-ICP-QMS | 0.98 |
| IRMM* | 229.9 | 4.2 | 2 | 8.4 | ID-ICP-MS | 0.9762 |
| INMETRO | 230.4 | 2.2 | 2 | 4.4 | EC-ICP-OES | 0.9732 |
| NIST | 230.6 | 2.1 | 1.97 | 4.1 | ID-ICP-QMS | 0.9769 |
| CENAM | 231.0 | 1.4 | 2 | 2.8 | ID-ICP-SFMS | 0.9775 |
| NRC | 232 | 8.7 | 2 | 17 | SA-ICP-OES | 0.9751 |
| NMIJ | 232.3 | 1.9 | 2 | 3.8 | ID-ICP-MS | 0.976 |
| GLHK | 234 | 5.5 | 2 | 11 | SA-ICP-MS | 0.9908 |
| NIM | 234.0 | 1.9 | 2 | 3.8 | ID-ICP-MS | 0.972 |
| TUBITAK | 235 | 8 | 2 | 16 | ID-ICP-MS | 0.9799 |
| CSIR-NPLI | 237.9 | 10.42 | 2 | 21 | EC-ICP-OES | 0.9903 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

**Table 18.** Reported results of mass fraction of Mn in non-contaminated soil.

| Institute | Reported value (µg/g) | Standard uncertainty (µg/g) | Coverage factor *k* (95% level of confidence) | Expanded uncertainty (µg/g) | Analytical instrument / Method | Dry mass correction factor (g/g) |
|---|---|---|---|---|---|---|
| VNIIM | 830.2 | 29.9 | 2 | 60 | EC-ICP-MS | 0.9712 |
| INTI | 848.7 | 17.4 | 2 | 35 | SA-ICP-OES | 0.9807 |
| NIM | 1033 | 23 | 2 | 46 | EC-ICP-OES | 0.978 |
| INM | 1052 | 21 | 2 | 42 | B-FAAS | 0.9774 |
| LNE | 1071 | 32 | 2 | 64 | IE+SA-ICP-QMS-CC | 0.991 |
| NMISA | 1122 | 12 | 2 | 24 | EC-ICP-SFMS | 0.971938 |
| INMETRO | 1131.14 | 8.65 | 2 | 17 | EC-ICP-OES | 0.9696 |
| GLHK | 1150 | 48 | 2 | 96 | SA-ICP-OES | 0.9866 |
| NRC | 1150 | 18 | 2 | 36 | SA-ICP-OES | 0.9698 |
| CENAM | 1150 | 49 | 2 | 98 | IE+SA-ICP-SFMS | 0.9775 |
| NMIJ | 1156.5 | 5.5 | 2 | 11 | EC-ICP-MS | 0.9698 |
| ANSTO | 1157 | 45 | 2 | 90 | INAA | 0.9690 |
| JSI | 1167 | 32 | 2 | 64 | EC-ICP-MS | 0.9654 |
| TUBITAK | 1172 | 38 | 2 | 76 | SA-HR-ICP-MS | 0.9737 |
| NIST | 1175.4 | 6.2 | 2.3 | 14 | SA-ICP-OES | 0.9713 |
| IRMM* | 1180 | 170 | 2 | 340 | EC-ICP-OES | 0.9730 |
| INACAL | 1214.26 | 25.50 | 2 | 51 | SA-FAAS | 0.9709 |
| JSI** | 1194 | 36 | 2 | 72 | INAA | 0.9654 |

* The IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

** Information value.

### 5.3 Estimation of the key comparison mass fraction reference values and associated uncertainties

During the IAWG meeting on 17 to 19 November of 2015 in Teddington, the preliminary results of the comparison using all reported data were presented. The presentation summarized the calculated consensus values and their respective standard uncertainties using different location estimators including arithmetic mean, median, robust mean and mixture-model median (MM-median); all data were included in the calculation. The proposed statistics used for analyse the evaluation [2] using all data were:

- Simple arithmetic mean (Eq. 3), and the standard deviation of the mean augmented with the mean of the reported within variance of the participants $u^2(x_i)$ (Eq. 4). This is named S+ in the CCQM-04-15 [3].

$$x_{\mathrm{KCRV}} = \frac{1}{n}\sum_{i=1}^{n} x_i, \qquad (3)$$

$$u[x_{\mathrm{KCRV}}] = \sqrt{\frac{1}{n}\left(\frac{1}{n-1}\sum_{i=1}^{n}(x_i - x_{\mathrm{KCRV}})^2 + \frac{1}{n}\sum_{i=1}^{n} u^2(x_i)\right)} \qquad (4)$$

- Median for location (Eq. 5) and the Modified Median Absolute Deviation About the Median (MMADe) uncertainty estimation (Eq. 6), which appears as MADe in the pdf-Maker software [median absolute deviation (MAD) multiplied by 1.483] augmented with the median of the reported within variance of the participants $u^2(x_i)$. This is named MADe+ in the CCQM-04-15 [3].

$$x_{\mathrm{KCRV}} = median(x_i) \qquad (5)$$

$$MMADe(x_1, \ldots, x_n) = \sqrt{\frac{\pi}{2n}\left(\left(MADe(x_i)\right)^2 + median\left(u^2(x_i)\right)\right)} \qquad (6)$$

Where,

$$MADe(x_1, \ldots, x_n) = 1.483 \cdot median(|x_i - x_{\mathrm{KCRV}}|) \qquad (7)$$

- MMmedian statistics for location and the Modified MADe (MMADe) uncertainty estimation. MMmedian statistics is based on the mixture of the probability density functions (pdf) of the participants. The mixture pdf is called MM-PDF in the CCQM-04-15 [3]. The analytic solution to this mixture of pdf becomes increasingly complex with the number of participants, so the way to proceed is by computing a numerical solution, often an iteratively method is applied. In this sense an estimate using Monte Carlo Simulation converges to the same numerical solution. As a double check, it was conducted an independent estimation validation process, which uses Monte Carlo simulation, for the MMmedian-MMADe estimates. Once the pdf-Maker estimations were validated, the estimates were produced thereafter by using the Monte Carlo method.

**5.3.1** During the IAWG meeting in Teddington, it was presented the preliminary results, and during the IAWG meeting carried out in April 2016, it was agreed after discussion to use the Median as KCRV and the MMADe as $u(x_{\mathrm{KCRV}})$. The tables 19 and 20 show the results.

For those institutes, which submitted more than one result for a measurand, the value obtained with their principle method was used for the KCRV as this represents their best measurement capability. IRMM suggested their result of As in non-contaminated soil should not be included in the KCRV as they knew it to be erroneous and it was accepted by the IAWG. Also, IRMM advised that their standard uncertainty was in error because they had reported the expanded uncertainty. It was approved to use the corrected standard uncertainty for the calculation of KCRV, but the IRMM result will be evaluated with the original reported standard uncertainty.

**Table 19.** Values of the KCRV and respective standard uncertainties, with no multiple methods and with all data reported by NMIs/DIs for Non-contaminated soil.

| Measurand | Median | MMADe | *n* |
|---|---|---|---|
| As (µg/g) | 13.48 | 0.36 | 15 |
| Cd (µg/g) | 0.520 | 0.015 | 15 |
| Fe (mg/g) | 32.33 | 0.29 | 16 |
| Pb (µg/g) | 39.40 | 0.42 | 15 |
| Mn (µg/g) | 1150 | 14 | 17 |

**Table 20.** Values of the KCRV and respective standard uncertainties, with no multiple methods and with all data reported by NMIs/DIs for Contaminated soil.

| Measurand | Median | MMADe | *n* |
|---|---|---|---|
| As (µg/g) | 76.2 | 1.4 | 17 |
| Cd (µg/g) | 438.1 | 5.3 | 18 |
| Fe (mg/g) | 20.31 | 0.37 | 18 |
| Pb (µg/g) | 230.4 | 2.0 | 17 |

The results of the CCQM-K127 are presented in Figures 1 to 9 with the respective Median as KCRV and MMADe as $u$(KCRV).

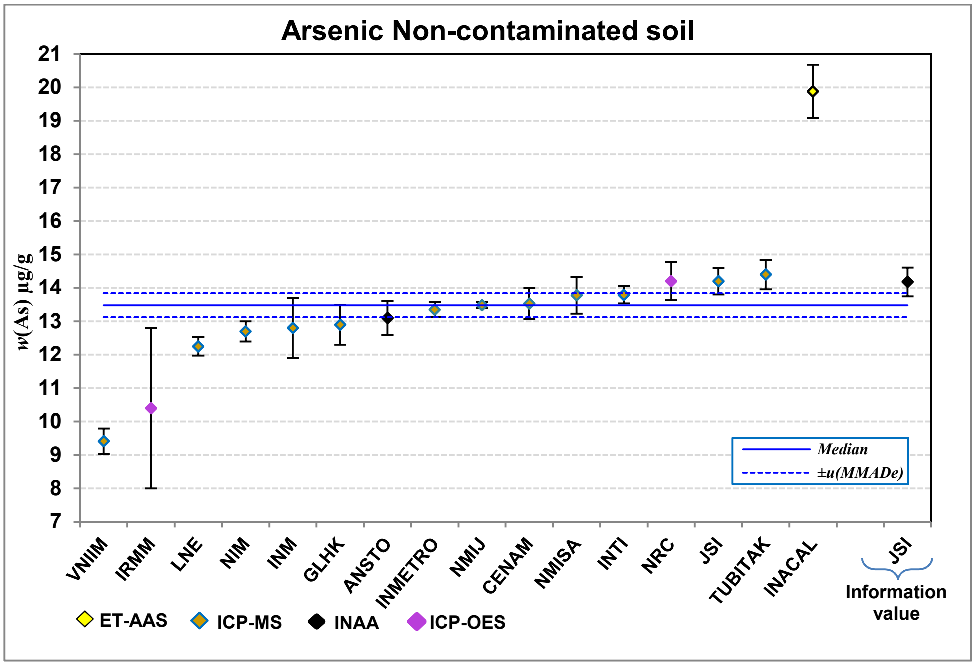

**Figure 1.** Arsenic in non-contaminated soil and standard uncertainties.
IRMM suggested their result of As in non-contaminated soil should not be included in the KCRV as they knew it to be erroneous.

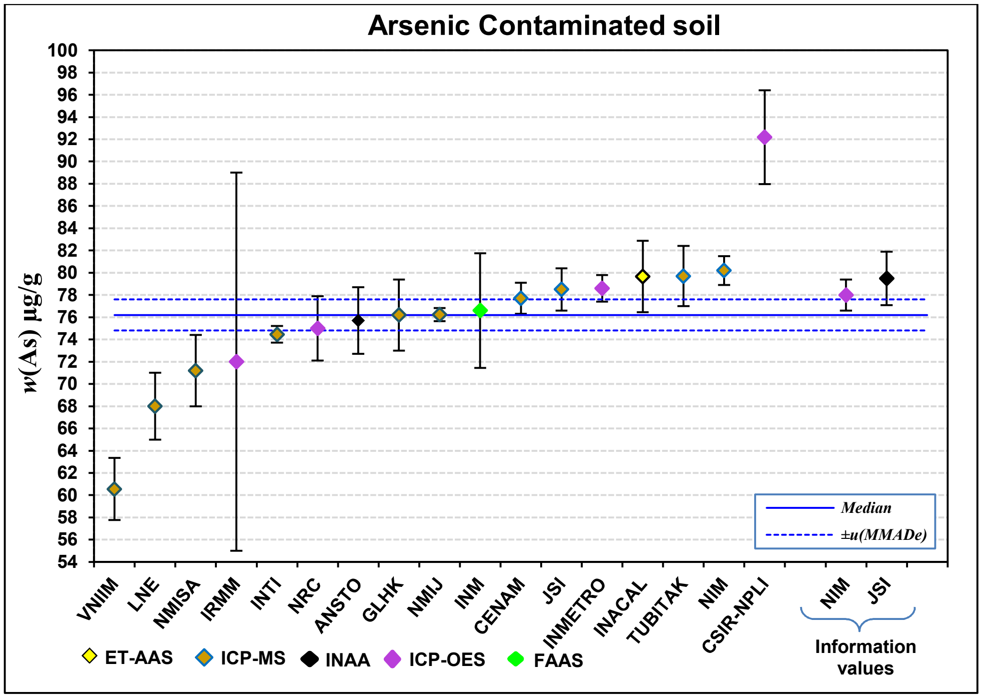

**Figure 2.** Arsenic in contaminated soil and standard uncertainties.

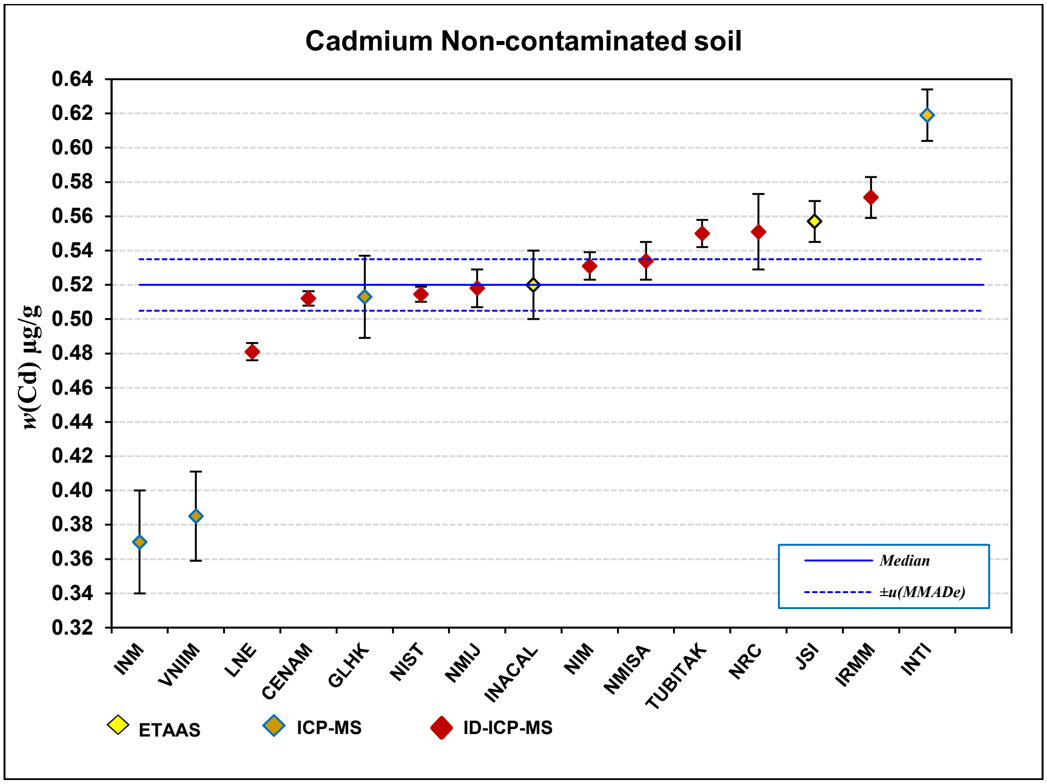

**Figure 3.** Cadmium in non-contaminated soil and standard uncertainties.

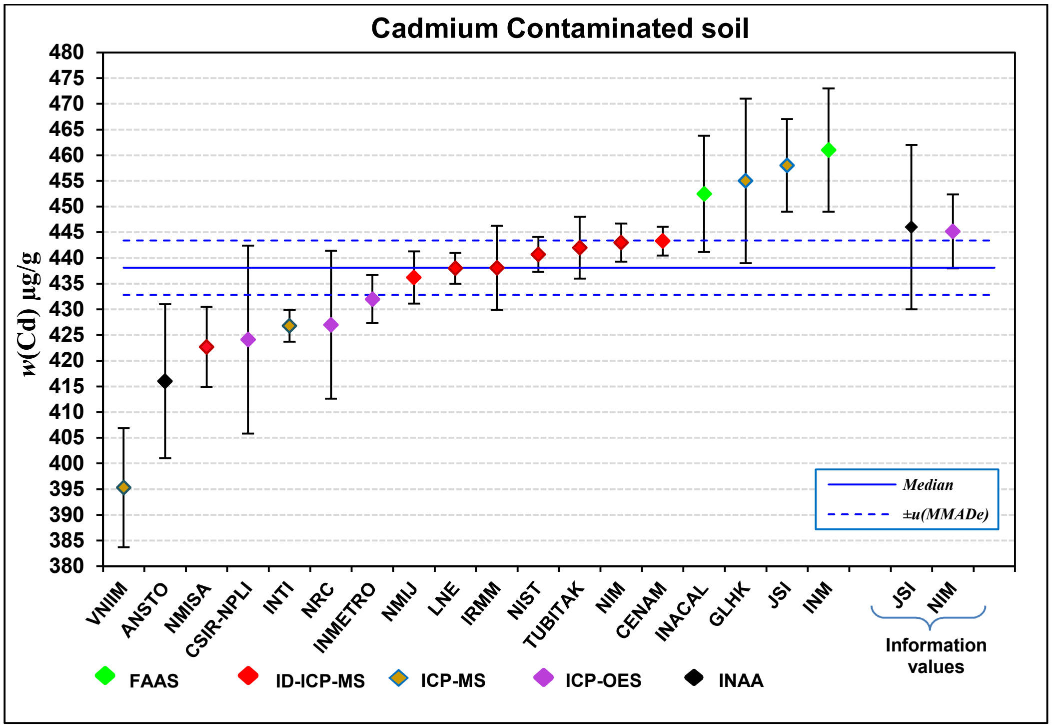

**Figure 4.** Cadmium in contaminated soil and standard uncertainties.

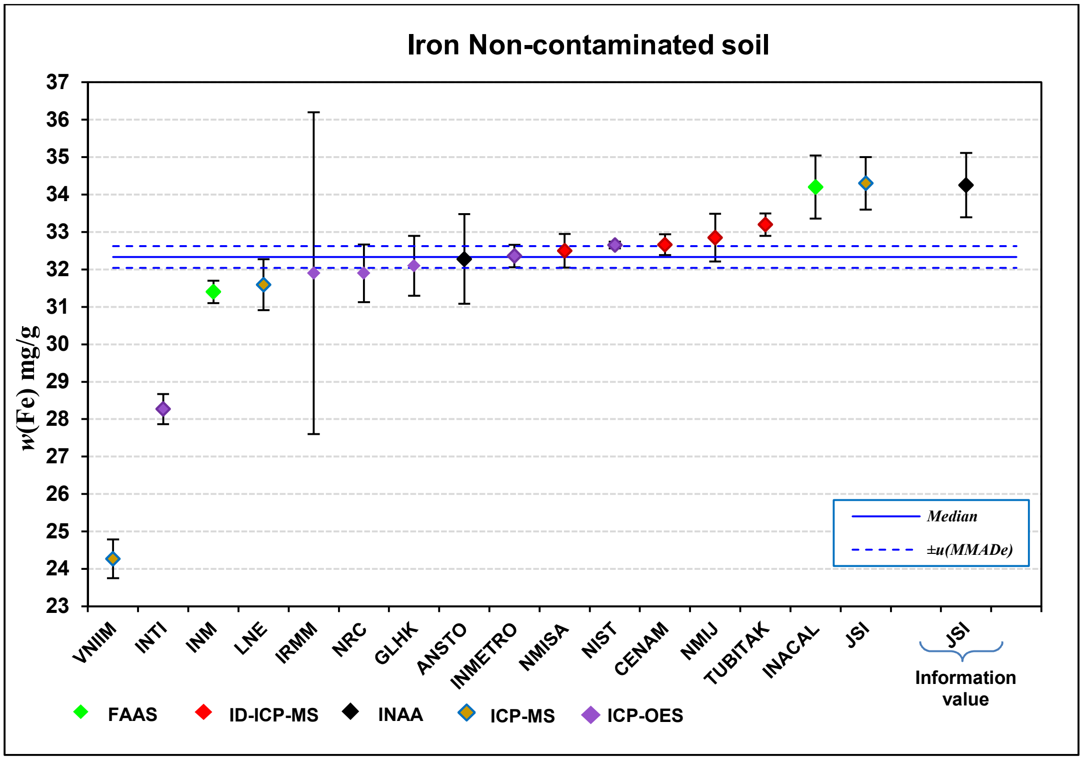

**Figure 5.** Iron in non-contaminated soil and standard uncertainties.

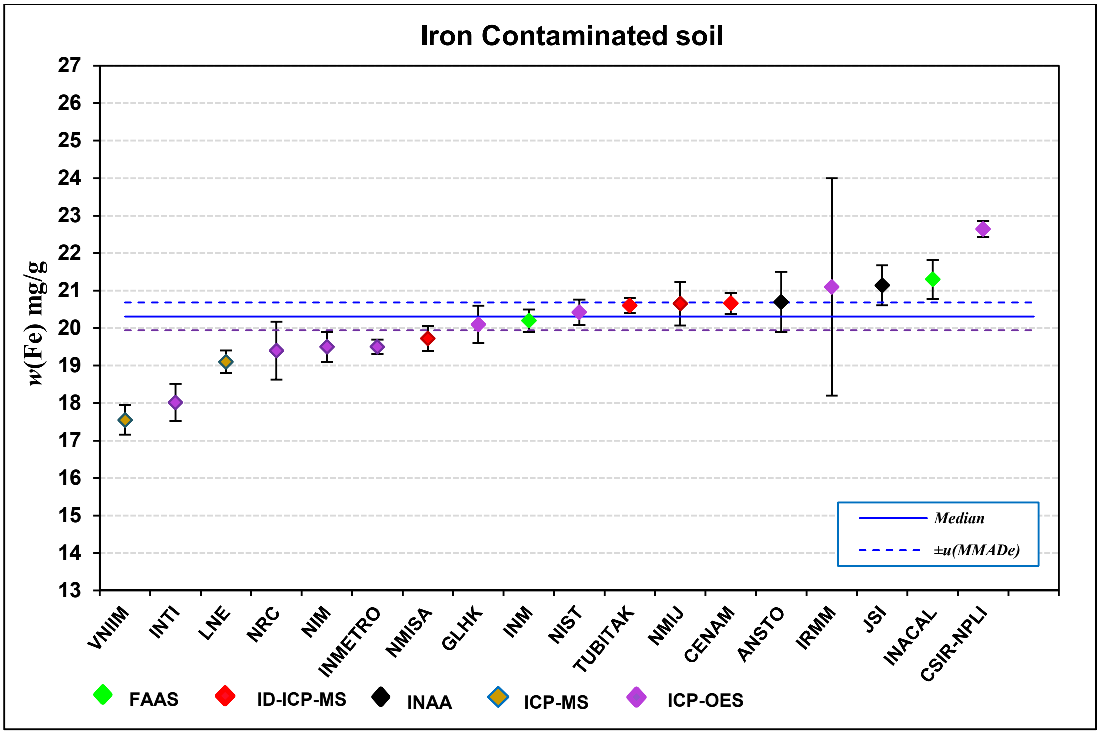

**Figure 6.** Iron in contaminated soil and standard uncertainties.

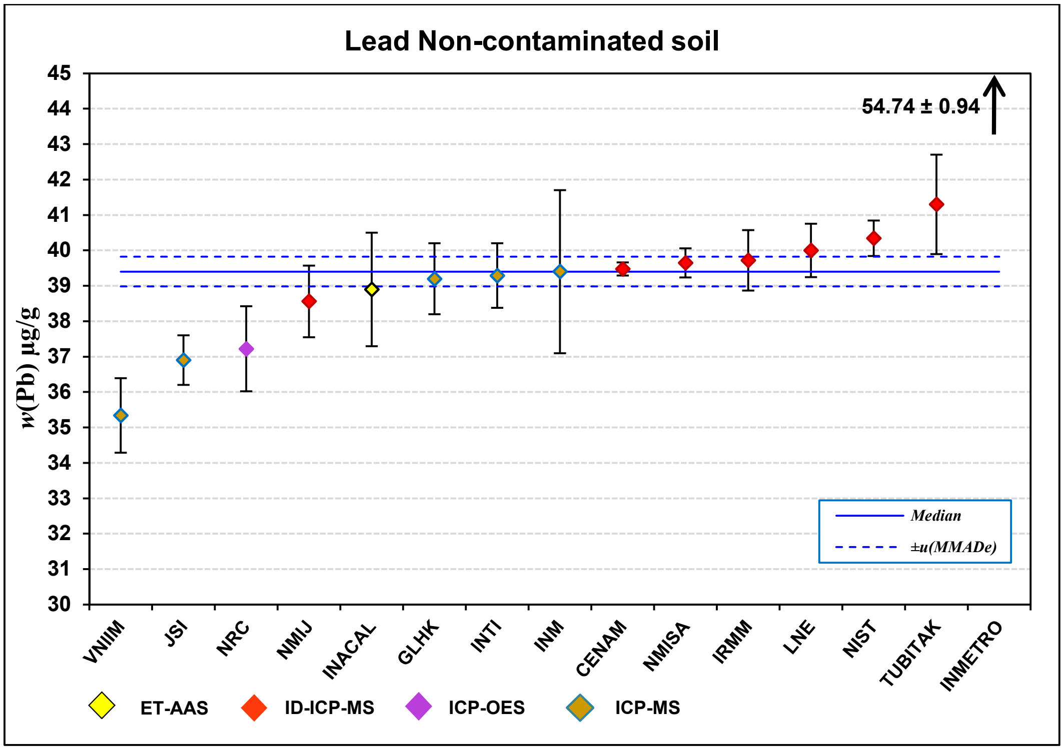

**Figure 7.** Lead in non-contaminated soil and standard uncertainties.

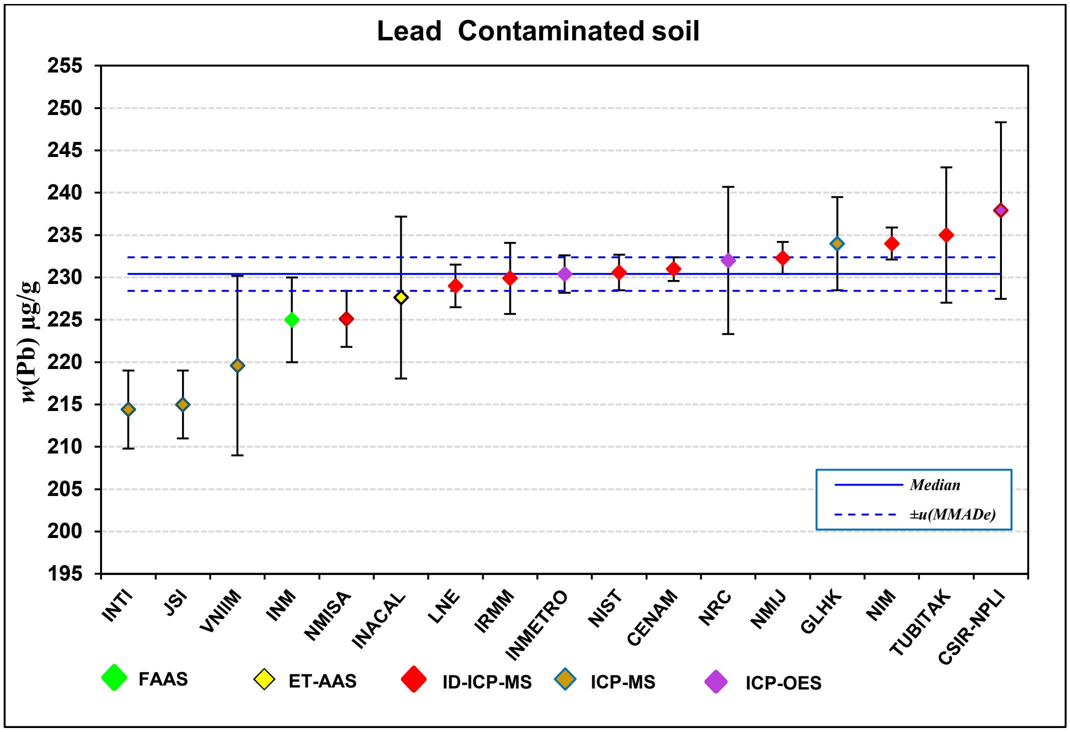

**Figure 8.** Lead in contaminated soil and standard uncertainties.

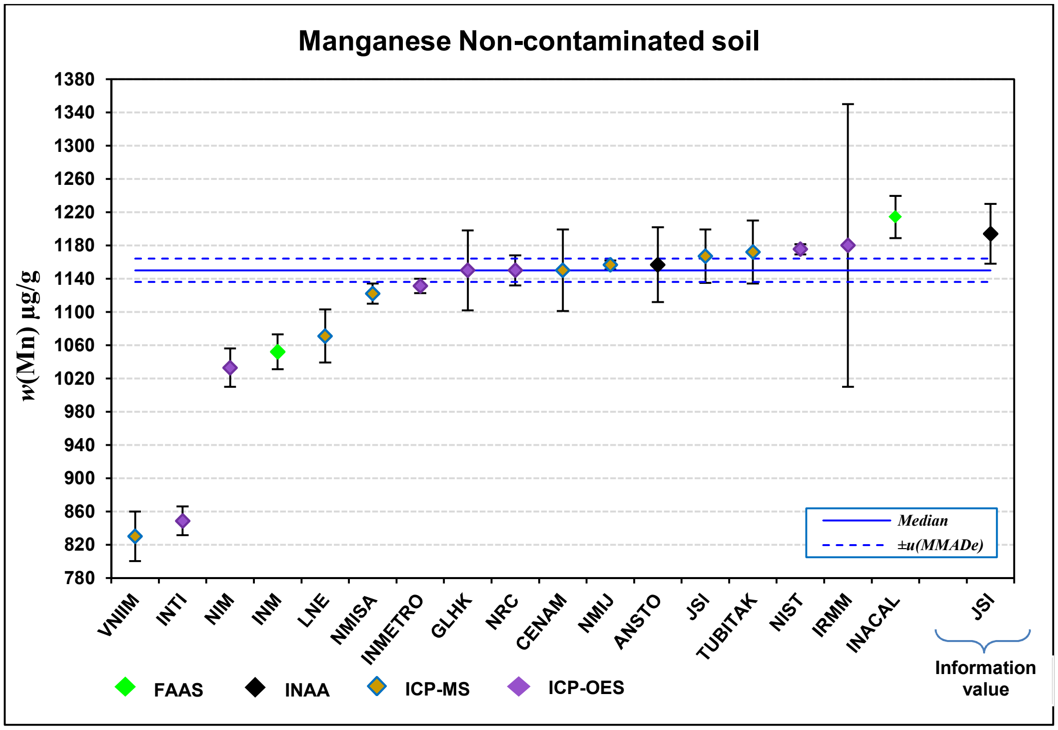

**Figure 9.** Manganese in non-contaminated soil and standard uncertainties.

### 5.4 The equivalence statements

The degree of equivalence (DoE), $d_i$, between an individual NMI/DI result, $x_i$, and the KCRV, $x_{\mathrm{KCRV}}$, and its standard uncertainty $u(d_i)$ was calculated using equations 8, 9, and 10, in accordance with the CCQM guidance note 2013 in Appendix 2, Section 2.3, where the uncertainty of the degrees of equivalence include covariance terms [2]. The calculations used the KCRV and associated standard uncertainty for each measurand presented in section 5.3 (Tables 19 and 20). The DoE was not calculated for information values reported by NMIs/DIs which used multiple methods for the same measurand.

$$d_i = x_i - x_{\mathrm{KCRV}} \tag{8}$$

$$u(d_i) = \sqrt{u^2(x_i) + u^2(x_{\mathrm{KCRV}}) - 2 \cdot \mathrm{cov}(x_i, x_{\mathrm{KCRV}})} \tag{9}$$

where the covariance $cov(x_i, x_{\mathrm{KCRV}})$ and the expanded uncertainty $U(d_i)$ are calculated as follows:

$$cov(x_i, x_{\mathrm{KCRV}}) = \begin{cases} 0, \; if \; x_i \; is \; not \; used \; to \; estimate \; x_{\mathrm{KCRV}} \\ u^2(x_i)/n, \; if \; x_i \; is \; used \; to \; estimate \; x_{\mathrm{KCRV}} \end{cases} \tag{10}$$

Where values for $n$ are shown in tables 19 and 20.

Explanation of the evaluation of IRMM:

From section 2.3 in CCQM13-22 (special cases, page 26) and the fact that we are using corrected uncertainty $u(x_i)$ for the KCRV, but the uncorrected uncertainty $k_i u(x_i)$ for DOE evaluation, where $k_i$ is the expansion factor used by the participating laboratory, we have,

$$u^2(d_i) = u^2\left[x_{i,\mathrm{uncorrected}} - X_{\mathrm{KCRV}}\right] = u^2\left[x_{i,\mathrm{uncorrected}}\right] + u^2[X_{\mathrm{KCRV}}] - 2Cov\left[x_{i,\mathrm{uncorrected}}, X_{\mathrm{KCRV}}\right] = \left(k_i u(x_i)\right)^2 + u^2(X_{\mathrm{KCRV}}) - 2k_i Cov\left[x_{i,\mathrm{corrected}}, X_{\mathrm{KCRV}}\right] = \left(k_i^2 - \frac{2k_i}{m}\right) u^2(x_i) + u^2(X_{\mathrm{KCRV}}) \tag{11}$$

And $u^2(X_{\mathrm{KCRV}}) = MMADe(x_1, \ldots, x_n)$ as stated in equation (6). This new solution approaches to the known result as $k_i$ converges to 1.

The $U(d_i)$ is calculated as follows:

$$U(d_i) = k \cdot u(d_i) \tag{12}$$

The result DoEs are listed together with their associated uncertainties for each measurand in Table 21 through 29 and graphically displayed in Figures 10 to 18. The normalized error $E_n$ (equation 13) is also added to these tables.

$$E_n = \frac{|d_i|}{U(d_i)} \qquad (13)$$

The $u(di)$ for each reported measurand of IRMM (Belgium) is calculated using the original reported standard uncertainty.

**Table 21.** Equivalence statement of Arsenic in non-contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{\mathrm{KCRV}}$ % | $U(d_i)/x_{\mathrm{KCRV}}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 9.41 | 0.39 | -4.1 | 1 | -4.0 | -30% | 7.6% |
| IRMM | 10.4 | 2.4 | -3.1 | 4.9 | -0.63 | -23% | 36% |
| LNE | 12.25 | 0.28 | -1.2 | 0.89 | -1.4 | -9.1% | 6.6% |
| NIM | 12.7 | 0.3 | -0.78 | 0.91 | -0.86 | -5.8% | 6.8% |
| INM | 12.8 | 0.9 | -0.68 | 1.8 | -0.37 | -5.0% | 13.5% |
| GLHK | 12.9 | 0.6 | -0.58 | 1.3 | -0.44 | -4.3% | 9.9% |
| ANSTO | 13.1 | 0.5 | -0.38 | 1.2 | -0.32 | -2.8% | 8.7% |
| INMETRO | 13.35 | 0.22 | -0.13 | 0.83 | -0.16 | -1.0% | 6.1% |
| NMIJ | 13.48 | 0.09 | 0.0 | 0.74 | 0.0 | 0.0% | 5.5% |
| CENAM | 13.53 | 0.46 | 0.050 | 1.1 | 0.045 | 0.37% | 8.3% |
| NMISA | 13.78 | 0.55 | 0.30 | 1.3 | 0.24 | 2.2% | 9.3% |
| INTI | 13.79 | 0.26 | 0.31 | 0.87 | 0.36 | 2.3% | 6.4% |
| JSI | 14.2 | 0.4 | 0.72 | 1 | 0.70 | 5.3% | 7.7% |
| NRC | 14.2 | 0.57 | 0.72 | 1.3 | 0.56 | 5.3% | 9.5% |
| TUBITAK | 14.4 | 0.44 | 0.92 | 1.1 | 0.84 | 6.8% | 8.1% |
| INACAL | 19.88 | 0.80 | 6.4 | 1.7 | 3.9 | 47% | 12% |

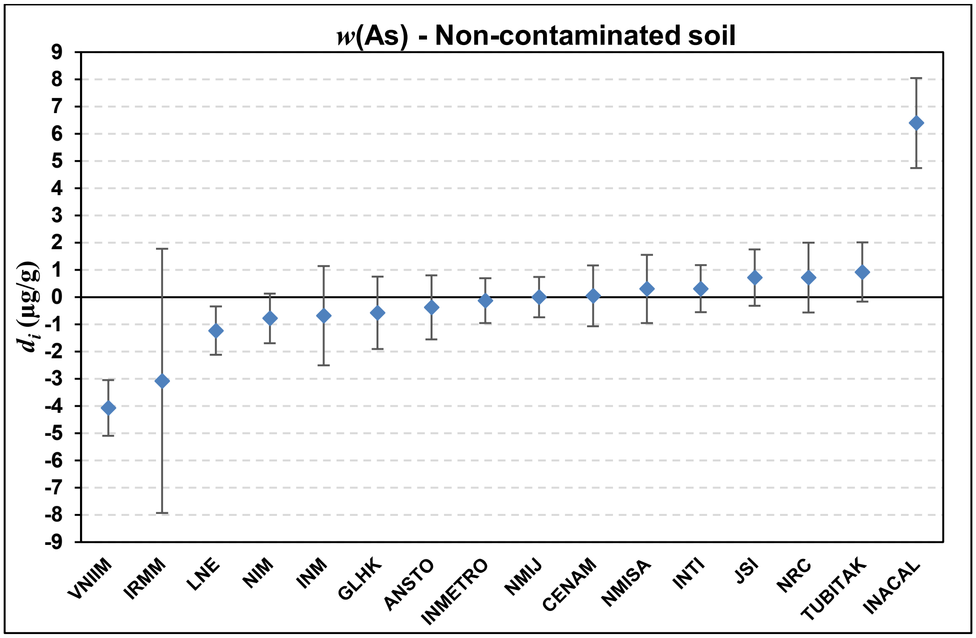

**Figure 10.** Graph of equivalence statements for CCQM-K127 As in non-contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 22.** Equivalence statement of Arsenic in contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_{i,}$ (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{\mathrm{KCRV}}$ % | $U(d_i)/x_{\mathrm{KCRV}}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 60.56 | 2.79 | -16 | 5.9 | -2.6 | -21% | 7.8% |
| LNE | 68 | 3 | -8.2 | 6.3 | -1.3 | -11% | 8.3% |
| NMISA | 71.2 | 3.2 | -5.0 | 6.6 | -0.75 | -6.6% | 8.7% |
| IRMM | 72 | 17 | -4.2 | 32 | -0.13 | -5.5% | 42% |
| INTI | 74.46 | 0.75 | -1.7 | 3.1 | -0.56 | -2.3% | 4.1% |
| NRC | 75.0 | 2.9 | -1.2 | 6.1 | -0.20 | -1.6% | 8.0% |
| ANSTO | 75.7 | 3.0 | -0.50 | 6.3 | -0.079 | -0.66% | 8.3% |
| GLHK | 76.2 | 3.2 | 0.0 | 6.6 | 0.0 | 0.0% | 8.7% |
| NMIJ | 76.24 | 0.58 | 0.04 | 3 | 0.0 | 0.1% | 3.9% |
| INM | 76.6 | 5.15 | 0.4 | 10 | 0.04 | 0.52% | 13% |
| CENAM | 77.7 | 1.4 | 1.5 | 3.8 | 0.39 | 2.0% | 5.0% |
| JSI | 78.5 | 1.9 | 2.3 | 4.5 | 0.51 | 3.0% | 6.0% |
| INMETRO | 78.6 | 1.2 | 2.4 | 3.6 | 0.67 | 3.1% | 4.7% |
| INACAL | 79.66 | 3.21 | 3.5 | 6.6 | 0.52 | 4.5% | 8.7% |
| TUBITAK | 79.7 | 2.7 | 3.5 | 5.8 | 0.60 | 4.6% | 7.6% |
| NIM | 80.2 | 1.3 | 4.0 | 3.7 | 1.1 | 5.2% | 4.9% |
| CSIR-NPLI | 92.18 | 4.22 | 16 | 8.4 | 1.9 | 21% | 11% |

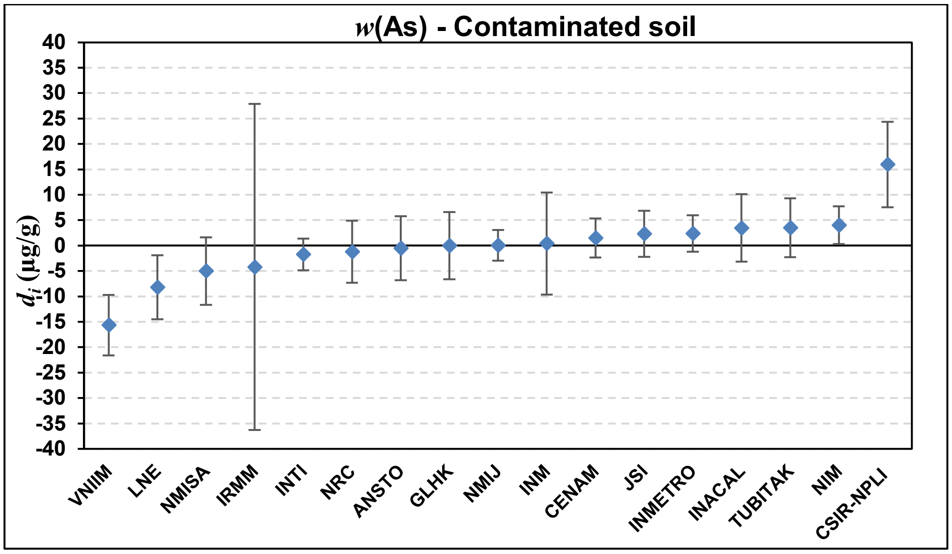

**Figure 11.** Graph of equivalence statements for CCQM-K127 As in contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 23.** Equivalence statement of Cadmium in non-contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{KCRV}$ % | $U(d_i)/x_{KCRV}$ % |
|---|---|---|---|---|---|---|---|
| INM | 0.37 | 0.03 | -0.15 | 0.063 | -2.4 | -29% | 12% |
| VNIIM | 0.385 | 0.026 | -0.14 | 0.057 | -2.4 | -26% | 11% |
| LNE | 0.481 | 0.005 | -0.039 | 0.031 | -1.2 | -7.5% | 6.0% |
| CENAM | 0.5121 | 0.0042 | -0.0079 | 0.031 | -0.25 | -1.5% | 6.0% |
| GLHK | 0.513 | 0.024 | -0.0070 | 0.054 | -0.13 | -1.3% | 10% |
| NIST | 0.5146 | 0.0044 | -0.0054 | 0.031 | -0.17 | -1.0% | 6.0% |
| NMIJ | 0.518 | 0.011 | -0.0020 | 0.036 | -0.055 | -0.38% | 7.0% |
| INACAL | 0.52 | 0.02 | 0.0 | 0.048 | 0.0 | 0.0% | 9.2% |
| NIM | 0.531 | 0.008 | 0.011 | 0.033 | 0.33 | 2.1% | 6.4% |
| NMISA | 0.534 | 0.011 | 0.014 | 0.036 | 0.39 | 2.7% | 7.0% |
| TUBITAK | 0.55 | 0.008 | 0.030 | 0.033 | 0.90 | 5.8% | 6.4% |
| NRC | 0.551 | 0.022 | 0.031 | 0.051 | 0.61 | 6.0% | 9.8% |
| JSI | 0.557 | 0.012 | 0.0370 | 0.037 | 0.99 | 7.1% | 7.2% |
| IRMM | 0.571 | 0.012 | 0.051 | 0.037 | 1.4 | 9.8% | 7.2% |
| INTI | 0.619 | 0.015 | 0.099 | 0.041 | 2.4 | 19% | 7.9% |

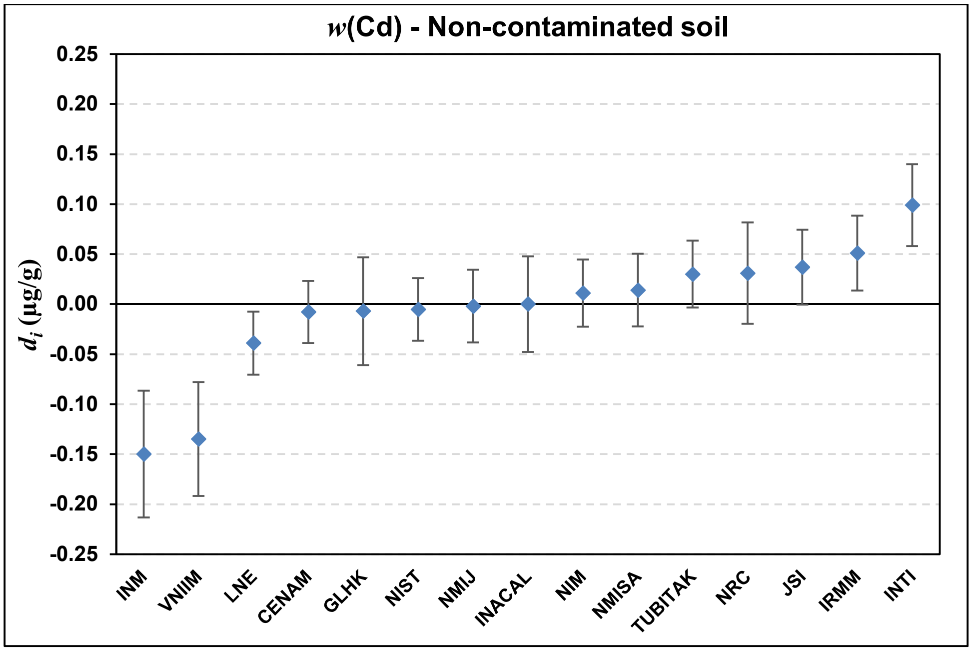

**Figure 12.** Graph of equivalence statements for CCQM-K127 Cd in non-contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 24.** Equivalence statement of Cadmium in contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{KCRV}$ % | $U(d_i)/x_{KCRV}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 395.3 | 11.6 | -43 | 24 | -1.8 | -9.8% | 5.5% |
| ANSTO | 416 | 15 | -22 | 30 | -0.73 | -5.0% | 6.9% |
| NMISA | 422.7 | 7.8 | -15 | 18 | -0.85 | -3.5% | 4.1% |
| CSIR-NPLI | 424.12 | 18.29 | -14 | 36 | -0.39 | -3.2% | 8.2% |
| INTI | 426.8 | 3.1 | -11 | 12 | -0.93 | -2.6% | 2.8% |
| NRC | 427 | 14.4 | -11 | 29 | -0.38 | -2.5% | 6.7% |
| INMETRO | 432 | 4.7 | -6.1 | 14 | -0.44 | -1.4% | 3.2% |
| NMIJ | 436.2 | 5.1 | -1.9 | 14 | -0.13 | -0.43% | 3.3% |
| LNE | 438 | 3 | -0.10 | 12 | -0.0083 | -0.023% | 2.7% |
| IRMM | 438.1 | 8.2 | 0.0 | 19 | 0.0 | 0.0% | 4.3% |
| NIST | 440.7 | 3.4 | 2.6 | 13 | 0.21 | 0.59% | 2.9% |
| TUBITAK | 442 | 6 | 3.9 | 16 | 0.25 | 0.89% | 3.5% |
| NIM | 443 | 3.7 | 4.9 | 13 | 0.39 | 1.1% | 2.9% |
| CENAM | 443.3 | 2.8 | 5.2 | 12 | 0.44 | 1.2% | 2.7% |
| INACAL | 452.47 | 11.32 | 14 | 24 | 0.60 | 3.3% | 5.4% |
| GLHK | 455 | 16 | 17 | 32 | 0.53 | 3.9% | 7.3% |
| JSI | 458 | 9 | 19.9 | 20 | 0.99 | 4.5% | 4.6% |
| INM | 461 | 12 | 23 | 25 | 0.92 | 5.2% | 5.7% |

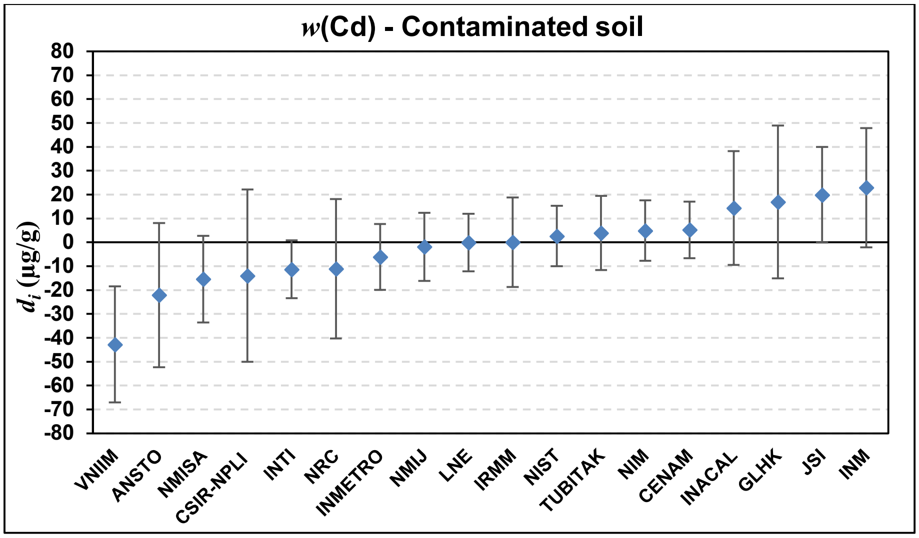

**Figure 13.** Graph of equivalence statements for CCQM-K127 Cd in contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 25.** Equivalence statement of Iron in non-contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (mg/g) | $u(x_i)$ (mg/g) | $d_i$ mg/g | $U(d_i)$ mg/g | $d_i/U(d_i)$ | $d_i/x_{KCRV}$ % | $U(d_i)/x_{KCRV}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 24.27 | 0.52 | -8.1 | 1.1 | -7.1 | -25% | 3.5% |
| INTI | 28.27 | 0.40 | -4.1 | 0.95 | -4.3 | -13% | 2.9% |
| INM | 31.4 | 0.3 | -0.93 | 0.81 | -1.2 | -2.9% | 2.5% |
| LNE | 31.59 | 0.68 | -0.74 | 1.4 | -0.53 | -2.3% | 4.3% |
| IRMM | 31.9 | 4.3 | -0.43 | 8.1 | -0.053 | -1.3% | 25% |
| NRC | 31.9 | 0.77 | -0.43 | 1.6 | -0.28 | -1.3% | 4.8% |
| GLHK | 32.1 | 0.80 | -0.23 | 1.6 | -0.14 | -0.71% | 5.0% |
| ANSTO | 32.3 | 1.2 | 0.0 | 2.3 | -0.013 | -0.093% | 7.2% |
| INMETRO | 32.36 | 0.30 | 0.03 | 0.81 | 0.037 | 0.09% | 2.5% |
| NMISA | 32.5 | 0.45 | 0.17 | 1 | 0.17 | 0.53% | 3.2% |
| NIST | 32.654 | 0.087 | 0.32 | 0.61 | 0.53 | 1.0% | 1.9% |
| CENAM | 32.66 | 0.28 | 0.33 | 0.78 | 0.42 | 1.0% | 2.4% |
| NMIJ | 32.85 | 0.64 | 0.52 | 1.3 | 0.39 | 1.6% | 4.1% |
| TUBITAK | 33.2 | 0.30 | 0.87 | 0.81 | 1.1 | 2.7% | 2.5% |
| INACAL | 34.20 | 0.84 | 1.9 | 1.7 | 1.1 | 5.8% | 5.2% |
| JSI | 34.3 | 0.7 | 2.0 | 1.4 | 1.4 | 6.1% | 4.4% |

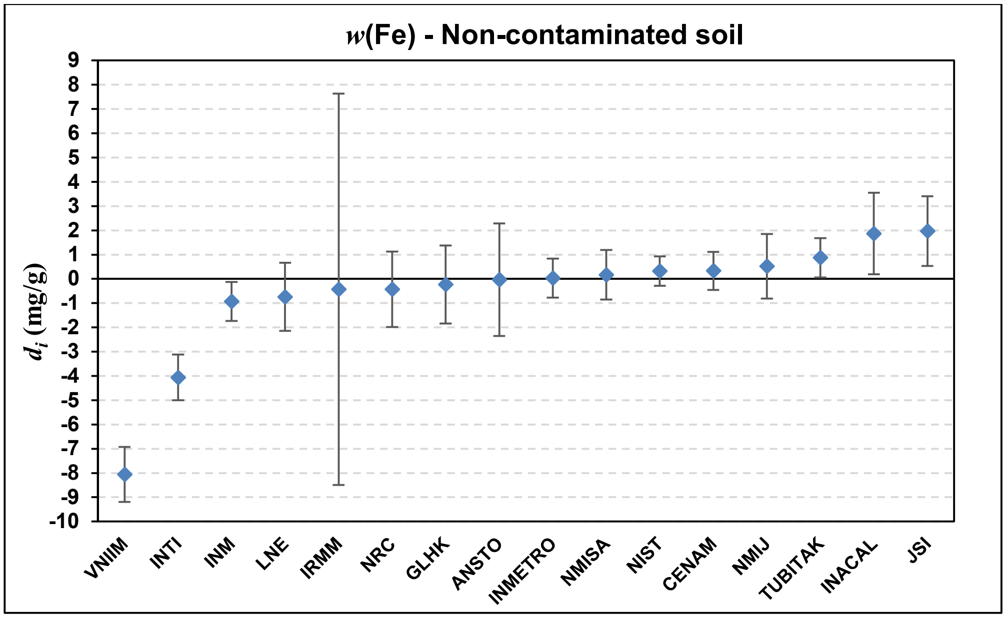

**Figure 14.** Graph of equivalence statements for CCQM-K127 Fe in non-contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI

**Table 26.** Equivalence statement of Iron in contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (mg/g) | $u(x_i)$ (mg/g) | $d_i$ mg/g | $U(d_i)$ mg/g | $d_i/U(d_i)$ | $d_i/x_{KCRV}$ % | $U(d_i)/x_{KCRV}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 17.55 | 0.39 | -2.8 | 1 | -2.6 | -14% | 5.1% |
| INTI | 18.02 | 0.5 | -2.3 | 1.2 | -1.9 | -11% | 5.9% |
| LNE | 19.1 | 0.3 | -1.2 | 0.93 | -1.3 | -6.0% | 4.6% |
| NRC | 19.4 | 0.77 | -0.91 | 1.6 | -0.56 | -4.5% | 8.0% |
| NIM | 19.5 | 0.4 | -0.81 | 1.1 | -0.77 | -4.0% | 5.2% |
| INMETRO | 19.5 | 0.19 | -0.81 | 0.82 | -0.99 | -4.0% | 4.0% |
| NMISA | 19.72 | 0.33 | -0.59 | 0.97 | -0.61 | -2.9% | 4.8% |
| GLHK | 20.1 | 0.5 | -0.21 | 1.2 | -0.18 | -1.0% | 5.9% |
| INM | 20.2 | 0.3 | -0.11 | 0.93 | -0.12 | -0.54% | 4.6% |
| NIST | 20.42 | 0.34 | 0.11 | 1.2 | 0.094 | 0.54% | 5.8% |
| TUBITAK | 20.6 | 0.2 | 0.29 | 0.83 | 0.35 | 1.4% | 4.1% |
| NMIJ | 20.65 | 0.58 | 0.340 | 1.3 | 0.26 | 1.7% | 6.5% |
| CENAM | 20.66 | 0.28 | 0.35 | 0.91 | 0.39 | 1.7% | 4.5% |
| ANSTO | 20.7 | 0.8 | 0.39 | 1.7 | 0.23 | 1.9% | 8.3% |
| IRMM | 21.1 | 2.9 | 0.79 | 5.5 | 0.14 | 3.9% | 27% |
| JSI | 21.14 | 0.53 | 0.83 | 1.2 | 0.67 | 4.1% | 6.1% |
| INACAL | 21.3 | 0.52 | 0.99 | 1.2 | 0.81 | 4.9% | 6.0% |
| CSIR-NPLI | 22.64 | 0.21 | 2.3 | 0.84 | 2.8 | 11% | 4.1% |

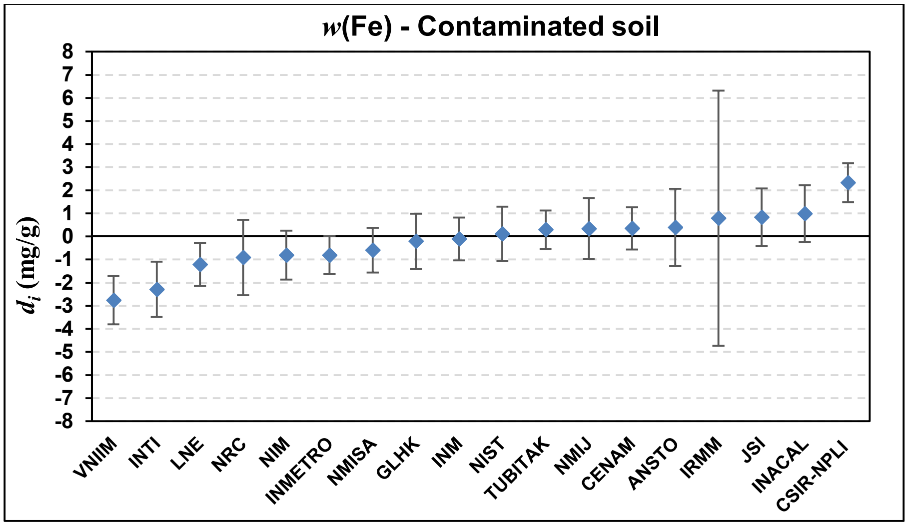

**Figure 15.** Graph of equivalence statements for CCQM-K127 Fe in contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 27.** Equivalence statement of Lead in non-contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{\mathrm{KCRV}}$ % | $U(d_i)/x_{\mathrm{KCRV}}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 35.34 | 1.05 | -4.1 | 2.1 | -1.9 | -10% | 5.4% |
| JSI | 36.9 | 0.7 | -2.5 | 1.6 | -1.6 | -6.3% | 3.9% |
| NRC | 37.22 | 1.2 | -2.2 | 2.4 | -0.91 | -5.5% | 6.1% |
| NMIJ | 38.56 | 1.01 | -0.84 | 2.1 | -0.41 | -2.1% | 5.2% |
| INACAL | 38.9 | 1.6 | -0.50 | 3.1 | -0.16 | -1.3% | 7.9% |
| GLHK | 39.2 | 1.0 | -0.20 | 2 | -0.10 | -0.51% | 5.2% |
| INTI | 39.29 | 0.91 | -0.11 | 1.9 | -0.058 | -0.28% | 4.8% |
| INM | 39.4 | 2.3 | 0.0 | 4.4 | 0.0 | 0.0% | 11% |
| CENAM | 39.48 | 0.18 | 0.080 | 0.9 | 0.088 | 0.20% | 2.3% |
| NMISA | 39.65 | 0.41 | 0.25 | 1.1 | 0.22 | 0.63% | 2.9% |
| IRMM | 39.72 | 0.85 | 0.32 | 1.8 | 0.18 | 0.81% | 4.5% |
| LNE | 40.0 | 0.75 | 0.60 | 1.6 | 0.37 | 1.5% | 4.1% |
| NIST | 40.34 | 0.50 | 0.94 | 1.27 | 0.74 | 2.4% | 3.2% |
| TUBITAK | 41.3 | 1.4 | 1.9 | 2.7 | 0.69 | 4.8% | 7.0% |
| INMETRO | 54.74 | 0.94 | 15 | 1.9 | 7.9 | 39% | 4.9% |

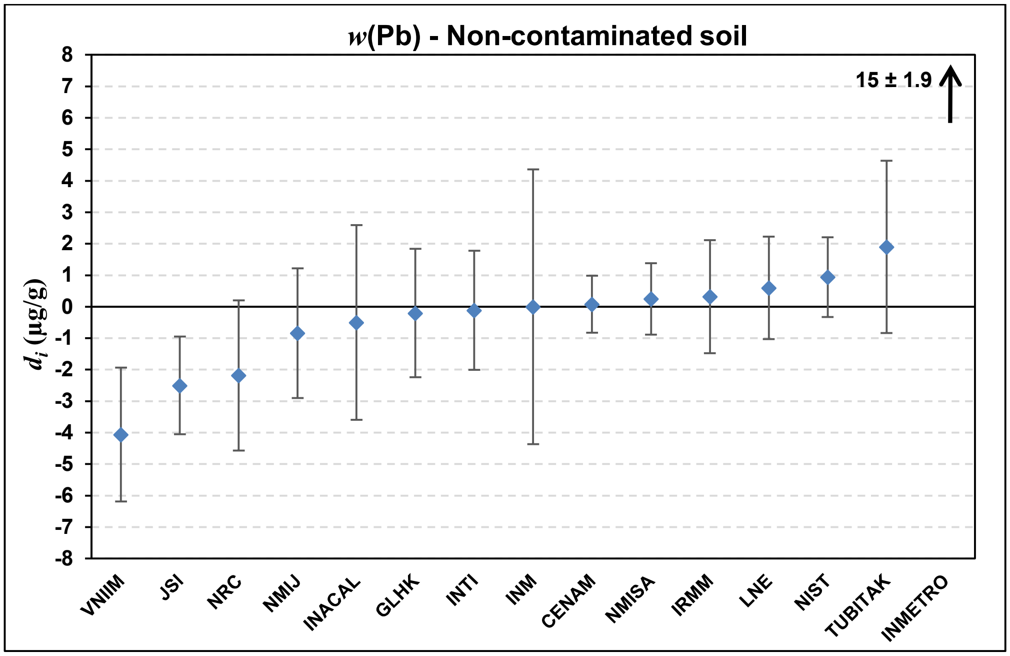

**Figure 16.** Graph of equivalence statements for CCQM-K127 Pb in non-contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 28.** Equivalence statement of Lead in contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{KCRV}$ % | $U(d_i)/x_{KCRV}$ % |
|---|---|---|---|---|---|---|---|
| INTI | 214.4 | 4.6 | -16 | 9.5 | -1.7 | -6.9% | 4.1% |
| JSI | 215 | 4 | -15 | 8.5 | -1.8 | -6.7% | 3.7% |
| VNIIM | 220 | 10.6 | -11 | 20 | -0.53 | -4.7% | 8.8% |
| INM | 225 | 5 | -5.4 | 10 | -0.53 | -2.3% | 4.4% |
| NMISA | 225.1 | 3.3 | -5.3 | 7.4 | -0.72 | -2.3% | 3.2% |
| INACAL | 227.62 | 9.56 | -2.8 | 18 | -0.15 | -1.2% | 8.0% |
| LNE | 229 | 2.5 | -1.4 | 6.2 | -0.23 | -0.61% | 2.7% |
| IRMM | 229.9 | 4.2 | -0.50 | 8.8 | -0.057 | -0.22% | 3.8% |
| INMETRO | 230.4 | 2.2 | 0.00 | 5.8 | 0.00 | 0.0% | 2.5% |
| NIST | 230.6 | 2.1 | 0.20 | 5.6 | 0.036 | 0.087% | 2.4% |
| CENAM | 231.0 | 1.4 | 0.60 | 4.8 | 0.13 | 0.26% | 2.1% |
| NRC | 232 | 8.7 | 1.6 | 17 | 0.095 | 0.69% | 7.3% |
| NMIJ | 232.3 | 1.9 | 1.9 | 5.4 | 0.35 | 0.82% | 2.3% |
| GLHK | 234 | 5.5 | 3.6 | 11 | 0.32 | 1.6% | 4.8% |
| NIM | 234.0 | 1.9 | 3.6 | 5.4 | 0.67 | 1.6% | 2.3% |
| TUBITAK | 235 | 8 | 4.6 | 16 | 0.30 | 2.0% | 6.8% |
| CSIR-NPLI | 237.9 | 10.42 | 7.5 | 20 | 0.38 | 3.3% | 8.7% |

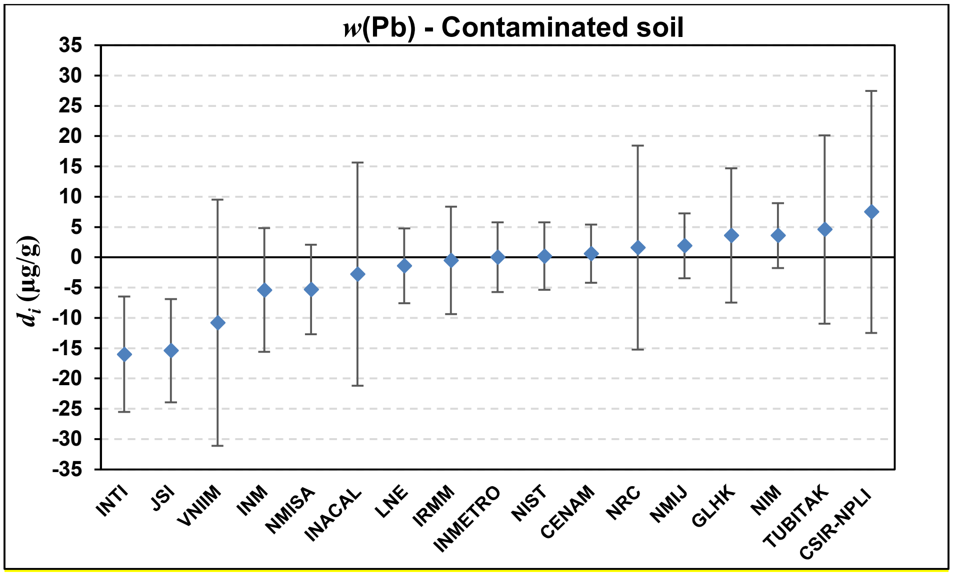

**Figure 17.** Graph of equivalence statements for CCQM-K127 Pb in contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

**Table 29.** Equivalence statement of Manganese in non-contaminated soil for CCQM-K127.

| NMI/DI | Reported value $x_i$, (µg/g) | $u(x_i)$ (µg/g) | $d_i$ µg/g | $U(d_i)$ µg/g | $d_i/U(d_i)$ | $d_i/x_{\mathrm{KCRV}}$ % | $U(d_i)/x_{\mathrm{KCRV}}$ % |
|---|---|---|---|---|---|---|---|
| VNIIM | 830.2 | 29.9 | -320 | 63 | -5.1 | -28% | 5.5% |
| INTI | 848.7 | 17.4 | -301 | 43 | -7.0 | -26% | 3.7% |
| NIM | 1033 | 23 | -117 | 51 | -2.3 | -10% | 4.5% |
| INM | 1052 | 21 | -98 | 48 | -2.0 | -8.5% | 4.2% |
| LNE | 1071 | 32 | -79 | 66 | -1.2 | -6.9% | 5.8% |
| NMISA | 1122 | 12 | -28 | 36 | -0.78 | -2.4% | 3.1% |
| INMETRO | 1131.14 | 8.65 | -19 | 32 | -0.58 | -1.6% | 2.8% |
| GLHK | 1150 | 48 | 0.0 | 94 | 0.0 | 0.0% | 8.2% |
| NRC | 1150 | 18 | 0.0 | 44 | 0.0 | 0.0% | 3.8% |
| CENAM | 1150 | 49 | 0.0 | 96 | 0.0 | 0.0% | 8.4% |
| NMIJ | 1156.5 | 5.5 | 6.5 | 30 | 0.22 | 0.57% | 2.6% |
| ANSTO | 1157 | 45 | 7.0 | 89 | 0.079 | 0.61% | 7.7% |
| JSI | 1167 | 32 | 17 | 66 | 0.26 | 1.5% | 5.8% |
| TUBITAK | 1172 | 38 | 22 | 77 | 0.29 | 1.9% | 6.7% |
| NIST | 1175.4 | 6.2 | 25 | 31 | 0.82 | 2.2% | 2.7% |
| IRMM | 1180 | 170 | 30 | 321 | 0.094 | 2.6% | 28% |
| INACAL | 1214.26 | 25.50 | 64 | 55 | 1.2 | 5.6% | 4.8% |

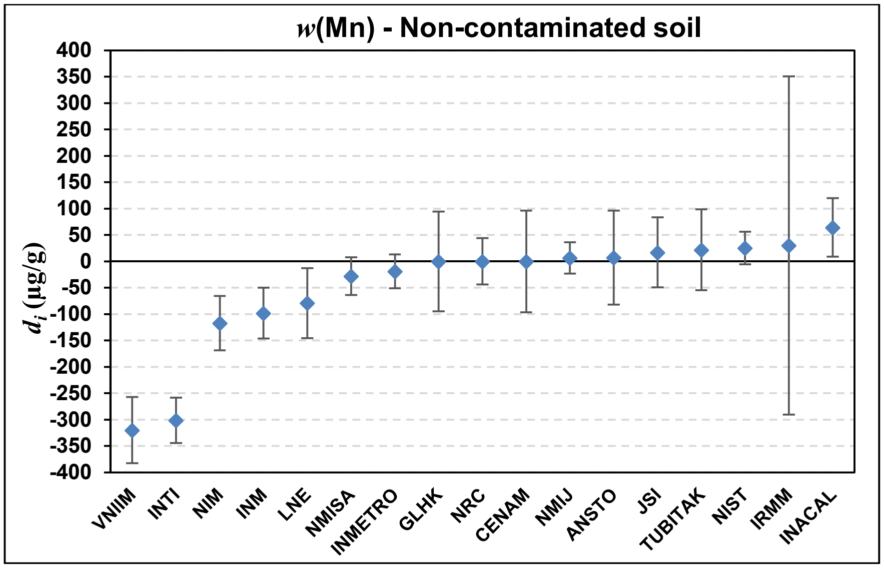

**Figure 18.** Graph of equivalence statements for CCQM-K127 Mn in contaminated soil. Error bars represent the interval calculated by the expanded uncertainties with the corresponding coverage factor reported by each NMI/DI.

## 6. Conclusions

Generally most of the results of the participants were found consistent for all measurements according to their equivalence statements, excepting some extreme values, which were identified with value of $d_i/U(d_i)$ higher than 1.

Regarding to the methodology of sample preparation, most of the participants used microwave acid digestion methods for sample treatment, except those participants using INAA as measurement technique. For soil samples, it is critical to use mixture of acids and the period of digestion time to obtain total digestion. Technically, it seemed appropriate to use a mix of acids with $HNO_3$, HCl and HF and in some cases $H_3BO_3$ to control the excess of HF used for the high content of silicon present in the sample. For Mn and Fe it is observed that some results had high negative bias, in some cases for these elements, a few participants did not use HCl, others used $H_2O_2$. For Cd in non-contaminated soil some variation was observed, it could be due to presence of interferences.
With respect to the analytical techniques, a great variety was used, it is observed that for those who use external calibration, greater variability in results was obtained, and for the participants who used isotope dilution with mass spectrometry, better consistency in results are observed.

This key comparison is a mean of providing evidence for practical demonstration of a CCQM comparison Calibration and Measurement Capabilities (CMC) claims for contaminant and others elements, in low and medium content levels in non-contaminated and contaminated matrixes described in category 13.

## 7. Coordinating laboratories

The CCQM-K127 are coordinated by CENAM (Maria-del-Rocio Arvizu-Torres and J. Velina Lara Manzano) and JSI (Milena Horvat and Radojko Jaćimović).

## 8. Acknowledgement

The coordinate laboratories would like to thank Dr. M. Sargent, the Chairman of the IAWG/CCQM for his encouragement and guidance through the study. Also, to Dr. Yoshito Mitani N. for their support in the development of this study, Dr. Hugo Gasca for their collaboration in the statistical evaluation of the KCRV and all the staff involved in this project of the Dirección de Análisis Inorgánico of CENAM. The JSI would like to thank Dr. Branka Mihaljević from Rudjer Bošković Institute (RBI), Zagreb, Croatia for irradiation of non-contaminated soil by Co-60 in November 2014.

The contributions from the analysts of participating NMIs/Dis as listed below, are highly appreciated and acknowledged.

| Institute | Analysts |
|---|---|
| ANSTO | Attila Stopic, John Bennett |
| CENAM | Edith Valle Moya, Francisco Segoviano Regalado, Faviola A. Solís González, Griselda Rivera Sánchez, Itzel Santiago Castellanos, M. Rocio Arvizu Torres |
| CSIR-NPLI | Daya Soni, Shankar Gopala Aggarwal |
| INACAL | Elmer Carrasco, Christian Uribe |
| INM | Steluța Duță, Mirella Buzoianu |
| INMETRO | Ana Catalina Palacios Osorio, Emily Silva Dutra, Marcelo Dominguez de Almeida, Rodrigo Caciano de Sena |
| INTI | Gisela Mazzitello, Osvaldo Acosta |
| IRMM | James Snell, Geert Van Britsom |
| JSI | Tea Zuliani, Radojko Jacimovic |
| LNE | Anaïs Rincel |
| NIM | Haifeng Li, Jingbo Chao |
| NIST | Savelas A. Rabb, Karen E. Murphy, George C. Caceras |
| NMIJ | Shin-ichi Miyashita |
| NMISA | Alex Barzev, Angelique Botha, Maré Linsky |
| NRC | Indu Gedara Pihillagawa, Lu Yang |
| TUBITAK | Oktay Cankur, Zehra Çakılbahçe, Süleyman Z. Can |
| VNIIM | Smirnov Vadim |

## 10. References

[1] International Standards Organization, ISO Guide 35: Reference materials – General and statistical principles for certification, Geneva, Switzerland, 2006.
[2] CCQM/13-22: CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 2013-04-12.
[3] D. Duewer: A Robust Approach for the Determination of CCQM Key Comparison Reference Values and Uncertainties.

## Annex I: Tables of demonstrated core capabilities

## Inorganic Core Capabilities
## Summary Table

**CCQM Study: ✓ CCQM-K127 □ CCQM-P162**

**Institute(s): NRC-CNRC, LNE, NIST, NIM, TUBİTAK UME, NMISA, NMIJ, CENAM, IRMM**

**Method:** ***ID-ICP-MS (NRC-CNRC, LNE, NIST, NIM, TUBİTAK UME, NMISA, NMIJ, CENAM, IRMM)***
**Analyte(s): Cd (NRC-CNRC, LNE, NIST, NIM, TUBİTAK UME, NMISA, NMIJ, CENAM, IRMM), Fe (TUBİTAK UME, NMISA, NMIJ, CENAM), Pb (LNE, NIST, NIM, TUBİTAK UME, NMISA, NMIJ, CENAM, IRMM)**

### Instructions:

*List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.*

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Contamination control and correction<br>*All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.* | NMIJ (Fe, Cd, Pb) | NRC-CNRC<br>LNE (Cd, Pb)<br>NIST (Cd, Pb)<br>NIM (Cd, Pb)<br>TUBİTAK UME<br>NMISA (Cd, Fe, Pb)<br>CENAM (Cd, Fe and Pb) | Contamination is controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents (NRC-CNRC).<br>Contamination control was not a challenge for these materials as the mass fraction levels, even for the non-contaminated soil, were sufficiently high. Mean blank corrections did not exceed 0.05 % (NIST).<br>Blank correction and selected high quality of HF and $HNO_3$ (NIM).<br>All sample preparations were performed using ultrapure grade $HNO_3$ (TUBİTAK UME).<br>The contamination was not significant; however, it was controlled by preparing samples and isotopes in class-10/100 clean room and use of high purity reagents (CENAM). |
| Digestion/dissolution of organic matrices<br>*All techniques and procedures used to bring a sample that is primarily* | LNE (Cd, Pb)<br>NIM (Cd, Pb)<br>TUBİTAK UME | IRMM | |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *organic in nature into solution suitable for liquid sample introduction to the ICP.* | NMISA<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb) | | |
| Digestion/dissolution of inorganic matrices<br>*All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.* | NIM (Cd, Pb) | LNE (Cd, Pb)<br>NIST (Cd, Pb)<br>TUBÍTAK UME<br>NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb) | Some residues ($SiO_2$) remaining after digestion of the samples (LNE).<br>Colourless residue remained after sample digestion (IRMM).<br>The non-contaminated soil required a perchloric acid digest to bring it completely into solution (NIST).<br>Microwave sample decomposition procedure was applied (TUBÍTAK UME).<br>Closed vessel microwave digestion with a mixture of nitric acid, perchloric acid and hydrofluoric acid was employed. After digestion, the digest was evaporated to remove the silicon as $SiF_6$ (NMIJ).<br>The both soils required a microwave acid digestion using a mixture of HCl, $HNO_3$, HF, $H_2O_2$ and a second step of microwave digestion, where additional $H_2O_2$ and $H_3BO_3$ was required to bring it completely into solution with quick redissolved process of the samples in 7 % HCl to avoid precipitation (CENAM), then to re-dissolved. |
| Volatile element containment<br>*All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.* | LNE (Cd, Pb)<br>NIM (Cd)<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb)<br>IRMM | NIM (Pb) | Compared wet digestion and microwave assisted digestion method for Pb (NIM). |
| Pre-concentration<br>*Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | LNE (Cd, Pb)<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb) | NIST (Cd) | See matrix separation (NIST). |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Vapor generation<br>*Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.* | TUBÍTAK UME<br>NMISA<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb)<br>IRMM | | |
| Matrix separation<br>*Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | LNE (Cd, Pb),<br>NIM (Pb),<br>TUBÍTAK UME, NMISA,<br>NMIJ (Fe, Pb)<br>IRMM | NIST (Cd)<br>NIM(Cd)<br>NMIJ (Cd)<br>CENAM (Cd, Fe and Pb) | The non-contaminated soil required matrix separation to reduce spectral interference on Cd from matrix elements, particularly 8888Zr and Sn (NIST).<br>Adopted different collision gas and membrane desolvation technique to reduce polyatomic and oxide interference to Cd (NIM).<br>Co-precipitate separation was performed for sample matrix such as Al and Fe compounds. The method has been published in a journal (Inagaki et al., J. Anal. At. Spectrum. 2001, 16, 1370) (NMIJ).<br>Anion exchange separation for Cd, Fe and Pb, to minimized spectral interferences from matrix elements, for Cd: Zr, Sn, Nb, Mo, Zn; for Fe: Ni and Cr; and for all elements to avoid matrix effects, which provide a high dissolved solid in the sample introduction system (CENAM). |
| Spike equilibration with sample<br>*The mixing and equilibration of the enriched isotopic spike with the sample.* | | NRC-CNRC (Cd)<br>LNE (Cd, Pb)<br>NIST (Cd, Pb)<br>NIM (Cd, Pb)<br>TUBÍTAK UME<br>NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb)<br>IRMM | Enriched isotope was spiked before the microwave digestion. Samples were subject to rigorous digestion procedures (microwave) to ensure complete dissolution of the sample enabling equilibration of the enriched isotope spike with the sample (NIST, NRC-CNRC, LNE, TUBÍTAK UME, NMIJ, CENAM).<br>The contaminated sample was digested and diluted before spiking, as the level was too high for our spike materials. Two CRMs (ERM-CC141 and BCR-320R) were measured together with the samples (IRMM). |
| Signal detection<br>*The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.* | LNE (Cd, Pb)<br>TUBÍTAK UME, NMISA (Fe)<br>NMIJ (Fe, Cd, Pb) | NRC-CNRC (Cd)<br>NIST (Cd, Pb)<br>NIM (Cd, Pb)<br>NMISA (Cd, Pb)<br>CENAM (Cd, | Adequate sensitivity (NRC-CNRC).<br>Samples were analyzed in both standard mode and collision cell kinetic energy discrimination mode (CC/KED mode) for Cd. In comparison to standard mode, CC/KED mode has the advantage |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | Fe and Pb) | of lower molecular ion formation, but the disadvantage of lower sensitivity. For both modes, parameters were optimized using a tune solution containing indium (In) and cerium (Ce). The operating parameters were first adjusted to obtain maximum sensitivity for $^{115}$In and then further adjusted until the minimum achievable $^{156}$CeO$^{+}$/$^{140}$Ce$^{+}$ ratio was obtained (NIST).<br>Adequate sensitivity with the operating parameters, which first adjusted to obtain maximum sensitivity for $^{115}$In and then further adjusted until the minimum achievable $^{137}$Ba$^{16}$O/$^{137}$Ba and $^{137}$Ba$^{++}$/$^{137}$Ba ratio was obtained (CENAM). |
| Memory effect<br>*Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.* | LNE (Cd, Pb)<br>NIM (Cd, Pb)<br>NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd) | NRC-CNRC (Cd)<br>NIST (Cd, Pb)<br>TUBİTAK UME<br>NMIJ (Pb)<br>CENAM (Cd, Fe and Pb) | Rigorous rinsed between each measurement of samples with 2 % HNO$_3$ solution (CENAM, NRC-CNRC).<br>Before analysis, a washing time was optimized for minimizing memory effect. Consequently, three minutes washing was performed (NMIJ).<br>Cones were cleaned and new sample introduction tubing was used to mitigate element carryover and reduce Cd and Pb background coming from the instrument (NIST).<br>For all isotopic measurements, background checks were performed between each run. No significant memory effect was observed for the elements (TUBİTAK UME).<br>Normal rinse delays employed (NMISA). |
| Correction or removal of isobaric/polyatomic interferences<br>*Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.* | NIM (Pb) | NRC-CNRC (Cd)<br>LNE (Cd, Pb)<br>NIM (Cd)<br>TUBİTAK, UME,<br>NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb)<br>IRMM | Selected ratio $^{113}$Cd/ $^{111}$Cd was measured in the unspiked sample is in agreement with IUPAC value, confirming no significant interferences present (NRC-CNRC).<br>Choice of the isotope free of interferences specially for Cd. Subtraction of a closed matrix matching blank (LNE).<br><br>For removal see 'Matrix separation'. Correction algorithms and instrumental methods of interference reduction (collision |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | cell/kinetic energy discrimination mode) were employed for Cd. Corrections for spectral inferences stemming from Zr, Mo, In, and Sn were applied<br>For Pb isotopic composition measurements correction for isobaric interface from $^{204}$Hg on $^{204}$Pb was applied (NIST).<br>Adopted He as collision gas and membrane desolvation technique to reduce $^{95}$Mo$^{16}$O, $^{94}$Mo$^{16}$O $^{95}$Zr$^{16}$O interference to $^{111}$Cd and $^{110}$Cd (NIM).<br>Iron measurements were performed at medium resolution mode of HR-ICP-MS. Polyatomic interferences of Zr and Mo oxides on Cd signals were checked and corrected whenever necessary by measuring the oxide formation rates. Isobaric interferences on Cd were also corrected by mathematical equations (TUBİTAK UME).<br>Cd: minimum correction for molybdenum oxide and tin isobaric interferences on $^{111}$Cd and $^{114}$Cd; Fe: Analysis in medium resolution, to avoid Ar-molecular interferences. Pb: Correction for potential Hg interferences (NMISA).<br>Before analysis, the presence of potential interferences was cross-checked using high resolution ICP-MS and quadrupole ICP-MS with a collision/reaction cell. For Fe, collision/reaction cell technique was used for removal of interferences. For Cd, interferences were removed by the co-precipitation separation method. For Pb, interference of $^{204}$Hg with $^{204}$Pb was removed during the evaporation process in the digestion (NMIJ).<br>For Cd, Fe and Pb it was applied a removal of matrix separation (see matrix separation) and verify the following interferences: Cadmium measured ratio |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | $^{111}$Cd/$^{114}$Cd in low resolution mode required a minimum correction for:<br>$^{114}$Cd: molybdenum oxide and $^{114}$Sn isobaric interferences.<br>$^{111}$Cd: Mo and Zr oxides.<br>Measure ratio $^{57}$Fe/$^{56}$Fe in medium resolution mode was required, to avoid the molecular interference of $^{40}$Ar$^{16}$O in $^{56}$Fe.<br>Lead required the correction for potential Hg interferences of $^{204}$Hg in $^{204}$Pb (CENAM).<br><br>For Cd measurement the ICP MS was optimised to minimise MoO$^{+}$ formation. Cd signal correction not found to be necessary as the potential level of interference would not influence the uncertainty budget. Levels of In were also measured and found to be insignificant.<br>For Pb molar mass determination, $^{202}$Hg was measured and used to correct the overlap of $^{204}$Hg on the m/z 204 signal (IRMM). |
| Detector deadtime correction<br>*Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.* | LNE (Cd, Pb)<br>NIM (Cd, Pb) | NRC-CNRC (yes)<br>NIST (Cd, Pb)<br>TUBİTAK UME<br>NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb) | Use of the calculated value by the producer of the ICP/MS (LNE).<br>Detector dead-time was experimentally determined using natural gadolinium solutions with mass fractions that resulted in count rates spanning the count rate range from 1 x 105 counts per second (cps) to 9 x 105 cps. The measured dead-time was 37 ns (NIST).<br>Deadtime for the detector was determined before measurements. The deadtime correction was activated during measurements (TUBİTAK UME).<br>Double IDMS with matching of sample and standard concentrations (NMISA).<br>Counting rate was controlled for minimizing the effect of detector deadtime, typically under 1000000 cps (NMIJ).<br>It was controlled by using the ion count rates countered (CENAM). |
| Mass bias/fractionation control and correction<br>*Techniques used to determine, monitor, and correct for mass bias/fractionation.* | CENAM (Cd, Fe) | NRC-CNRC (yes)<br>LNE (Cd, Pb)<br>NIST (Cd, Pb)<br>NIM (Cd, Pb)<br>TUBİTAK UME | Use of high purity standard solution for Cd and CRM 982 for Pb (LNE).<br>A solution of pure Cd with natural isotopic composition and a solution of SRM 982 Equal-Atom |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | NMISA (Cd, Fe, Pb)<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Pb)<br>IRMM | Lead (Isotopic) Standard was used to measure the mass bias correction factor. The mass bias correction factor was measured at the beginning of the analysis sequence and then used to correct the ratio of a spike calibration sample measured immediately afterward. The spike calibration sample had an isotopic ratio similar to the spiked test portions and was re-measured throughout the analysis. It was used to correct the blanks, remaining calibration samples, test portions and controls for mass bias and any subsequent instrument drift. Drift was assessed every three samples and a correction applied by assuming it to be linear with time. A solution of SRM 981 Common Lead Isotopic Standard was used to measure the mass bias correction factor for composition samples (NIST).<br>Mass bias correction factors were determined between runs and included in the calculations.<br>Bracketing technique was used for mass bias correction (TUBİTAK UME).<br>Mass bias standards measured throughout sequence and correction applied (NMISA).<br>For Fe and Cd, natural abundance solutions were used for correcting mass bias. For Pb, NIST SRM 981 and 982 were used for correcting mass bias (NMIJ).<br>SRM-981 lead natural isotopic standard used to measure the mass bias correction factor for isotopic composition of Pb in the samples. SRM-982 equa- atom lead isotopic standard, from NIST used for determining the mass bias correction factors for Pb ratios in the blends ($R_{bx}$ and $R_{bz}$) (CENAM).<br>For Cd, sample blend measurements were bracketed within the measurement sequence with measurements of unspiked samples. These were used to correct for mass bias. For Pb an internal standard of NIST997 (Tl) |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | was used to correct for mass bias, using a linear model (IRMM). |
| Spike calibration<br>*Techniques used to determine the analyte concentration in the enriched isotopic spike solution.* | NMISA (Cd, Fe, Pb)<br>IRMM | NRC-CNRC (yes)<br>LNE (Cd, Pb)<br>NIST (Cd, Pb)<br>NIM (Cd, Pb)<br>TUBİTAK UME<br>NMIJ (Fe, Cd, Pb)<br>CENAM (Cd, Fe and Pb) | In house accurate preparation of the high purity standard solutions for reverse ID (LNE).<br>Reverse IDMS was used, employing two calibration solutions, which for Cd were SRM 3108 Cadmium (Cd) Standard Solution, Lot No. 130116, and a solution prepared in-house from SRM 746 Cadmium-Vapor Pressure and for Pb were SRM 3128 Lead (Pb) Standard Solution (Lot # 101026) and a solution prepared in-house from high purity (99.999, vendor assay) Pb metal (NIST).<br>Lead measurements were performed using double IDMS technique. Concentration of enriched isotopic solution was calibrated via primary certified reference material (TUBİTAK UME).<br>Double Isotope Dilution used (NMISA).<br>Double ID procedure was employed (NMIJ).<br>Measurements were performed by exact matching double ID-ICPMS, with correction of Pb and not ratio correction for Cd and Fe due the matching of sample and standard. The analytical challenge is to match the isotope ratio in the blends (sample and the primary standard) (CENAM). |

## Inorganic Core Capabilities
## Summary Table

**CCQM Study: ✓ CCQM-K127 ☐ CCQM-P162**

**Institute(s): LNE, GLHK, NIM, TUBÍTAK UME, NMISA, NMIJ, CENAM, INMETRO, INTI, VNIIM, JSI, INM.**

**Method: ICP-MS (without isotope dilution) LNE, GLHK, NIM, TUBÍTAK UME, NMISA, NMIJ, CENAM (IE-ICP-MS), INMETRO, INTI, VNIIM, JSI, INM.**

**Analyte(s): As (LNE, GLHK, NIM, TUBÍTAK UME, NMISA, NMIJ, CENAM, INMETRO, INTI, VNIIM, JSI, INM), Cd (GLHK, INTI, VNIIM, JSI, INM), Fe (LNE, VNIIM, JSI), Mn (LNE, TUBÍTAK UME, NMISA, NMIJ, CENAM, VNIIM, JSI), Pb (GLHK, INTI, VNIIM, JSI, INM).**

### Instructions:

*List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.*

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Contamination control and correction<br>*All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.* | NMISA (Mn)<br>NMIJ (Mn, As)<br>VNIIM | LNE (As, Fe, Mn)<br>GLHK, NIM<br>TUBÍTAK UME (As)<br>CENAM (As and Mn)<br>INMETRO (As)<br>INTI, JSI (As, Cd, Fe, Pb, Mn)<br>INM (Cd, As) | High purity reagents needed for As and Mn (LNE).<br>Blank correction and selected high quality of HF and $HNO_3$ (NIM).<br>In order to minimize the possible contamination of sample, suprapure grade reagents and pre-cleaned PFA labwares were used during the analysis (TUBÍTAK UME).<br>The contamination was not significant, however it was controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents (CENAM).<br>Adopted procedures to avoid contamination included: in-house distilled acid for purification and blank control (INMETRO).<br>The blank values were under the limits of detection (JSI).<br>For each digestion, a separate blank sample was included. The blank samples containing all acids, without the sample itself, went through all analytical procedure stages and measured. |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | Contamination of blanks/samples is critical for Cd and As at low concentration (INM). |
| Digestion/dissolution of organic matrices<br>*All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.* | LNE (As, Fe, Mn)<br>NIM<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Mn, As)<br>CENAM (As and Mn)<br>INMETRO (As)<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | | Strong control of environment to avoid Fe contamination (LNE). |
| Digestion/dissolution of inorganic matrices<br>*All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.* | JSI (As, Cd, Fe, Pb, Mn) | LNE (As, Fe, Mn)<br>GLHK<br>NIM<br>TUBÍTAK UME<br>NMISA (As, Mn)<br>NMIJ (As, Mn)<br>CENAM (As, Mn)<br>INMETRO (As)<br>INTI<br>VNIIM<br>INM | Some residues ($SiO_2$) remaining after digestion of the samples (LNE).<br>Compared different mixture of acids and digestion temperature (NIM).<br>Microwave sample decomposition procedure was applied (TUBÍTAK UME).<br>Closed vessel microwave digestion with a mixture of nitric acid, perchloric acid and hydrofluoric acid was performed. After digestion, the digest was evaporated to remove the silicon as $SiF_6$ (NMIJ).<br>The both soils required a microwave acid digestion using HCl, $HNO_3$, HF, $H_2O_2$ and a second step of microwave digestion, where additional $H_2O_2$ and $H_3BO_3$ were required to bring it completely into solution with quick redissolved process of the samples in 5 % HCl to avoid precipitation (CENAM).<br>HF acid was added in the microwave digestion procedure, but in the digested samples was observed a small amount of residue. This residue was not dissolved by adding more HF (INMETRO).<br>Close vessel microwave acid digestion (MARS-5). After microwave acid digestion and dilution by deionized water up to 50 ml, used ashless filter, to separate the insoluble residue<br>Approx.0.5 g of soil samples taken. Microwave digestion. Samples completed digested with $HNO_3$ (5 mL)+HCl(2 mL) +HF(3 mL) (INM).<br>Digestion program and conditions validated against ERM CC141 (VNIIM). |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Volatile element containment<br>*All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.* | LNE (As, Fe, Mn)<br>GLHK<br>TUBÍTAK UME<br>NMISA (Mn)<br>NMIJ (Mn)<br>CENAM (Mn) | NIM<br>NMISA (As)<br>NMIJ ( As)<br>INMETRO (As)<br>CENAM (As)<br>INTI<br>VNIIM<br>INM | Compared wet digestion and microwave assisted digestion method (NIM).<br>Closed vessel microwave digestion was performed to prevent the loss of As. Quality control materials of similar matrix (METRANAL 31 and 32) were used to verify recovery of As (NMIJ).<br>A digestion procedure with closed vessel microwave acid digestion was applied to avoid volatility problems for As a standard addition method was used to check the recovery (CENAM).<br>Quality controls were used to evaluate As loss (INMETRO).<br>Close vessel digestion. Cooling to room temperature (VNIIM).<br>Different digestion conditions selected for As (digestion in two consecutive days). Closed vessels (INM). |
| Pre-concentration<br>*Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | LNE(As, Fe, Mn)<br>GLHK<br>NIM<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Mn, As)<br>CENAM (As,Mn)<br>INTI<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | INMETRO (As) | Digested sample were evaporated to eliminate HF (INMETRO). |
| Vapor generation<br>*Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.* | GLHK<br>NIM<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Mn, As)<br>CENAM (As, Mn)<br>INMETRO (As)<br>INTI<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | | |
| Matrix separation<br>*Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s)* | LNE (As, Fe, Mn)<br>GLHK<br>TUBÍTAK UME<br>NMISA<br>NMIJ (Mn, As)<br>CENAM (As, Mn)<br>INMETRO (As)<br>INTI<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn) | NIM | Selection of isotopes; recommended correction for possible interferences caused by the matrix (NIM) |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | | | |
| Calibration of analyte concentration<br>*The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.* | | LNE (As, Fe, Mn)<br>GLHK<br>NIM<br>TUBÍTAK UME<br>NMISA (Mn, As)<br>NMIJ (Mn, As)<br>CENAM (As and Mn)<br>INMETRO (As)<br>INTI<br>VNIIM (Mn (55), Fe (56), As (75), Cd (111), Pb)<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | Accurate gravimetric preparation of high purity standard solutions for standard addition method or external calibration (LNE).<br>Gravimetric Standard Addition (GLHK).<br>Internal standard was used and compared with standard addition method (NIM).<br>Matrix matched standard addition method was used for the calibration. In order to monitor and minimize the drift on the signal, internal standard was used (TUBÍTAK UME).<br>External calibration for both As and Mn. Standard Addition for As (NMISA).<br>External calibration was performed. JCSS standard solutions were used to prepare calibration standards (NMIJ).<br>Internal standard with single point standard addition was used. Measurement was performed in high-resolution mode, the ratios measured were $^{75}$As/$^{71}$Ga and $^{55}$Mn/$^{72}$Ge. The analytical challenge was to find the best internal standard, as a result for As was used an internal standard present in the sample and it was confirmed using an external internal standards ($^{103}$Rh) (CENAM).<br>The matrix complexity was a challenging and does not allow to use internal standard (INMETRO).<br>Linear calibration (5 points) prepared from multielement standard solution by volumetric method. Tor measure Fe, sample was additional diluted 1:10 (VNIIM).<br>External calibration. The standards were prepared gravimetrically (JSI).<br>External calibration; bracketing; Preparation of calibration standard by weight. ERM CC141 used for validation (INM). |
| Signal detection<br>*The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low* | LNE (As, Fe, Mn)<br>TUBÍTAK UME<br>NMIJ (Mn, As)<br>INTI<br>VNIIM | GLHK<br>NIM<br>NMISA (As)<br>CENAM (As, Mn)<br>INMETRO (As) | As analysis performed in High Resolution mode, which required very good instrument sensitivity (NMISA). |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *concentrations, of low isotopic abundance, or that are poorly ionized.* | JSI (As, Cd, Fe, Pb, Mn) | INM | Instrument optimization; good detection limits; Reliable analytical signals ERM CC141 used for validation (INM). |
| Memory effect<br>*Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.* | NIM<br>NMISA(Mn)<br>NMIJ (Mn, As)<br>INMETRO (As) | LNE (Fe)<br>GLHK<br>TUBİTAK UME<br>NMISA (As)<br>CENAM (As, Mn)<br>INTI<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | Necessity of cleaning step between sample solutions analysis (LNE).<br>Tested by checking the blank signals between runs. No significant effect was observed (TUBİTAK UME).<br>Memory effect from As requiring long wash-out time between samples and careful blank correction (NMISA).<br>The cones were cleaned and it was applied a rinse between each measurement of samples with 2 % $HNO_3$ solution, however during the measuring process some still some significant memory effect was observed. The internal standard with single point standard addition method helped to correct a significant memory effect (CENAM).<br>Use washing solution between samples measuring (5% $HNO_3$) (VNIIM).<br>Washing procedures with 5 % and 1 % $HNO_3$, and MilliQ water were inserted between every sample measurement (JSI).<br>Washing procedures: before and after each measurement, 2 % $HNO_3$ (INM). |
| Correction or removal of isobaric/polyatomic interferences<br>*Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.* | INTI | LNE (As, Fe, Mn)<br>GLHK<br>NIM<br>TUBİTAK UME<br>NMISA (As, Mn)<br>NMIJ (Mn, As)<br>CENAM (As)<br>INMETRO (As)<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | Use of the collision cell with He (3 mL/min) to remove ArCl isobaric interferences on $^{75}$As, ArNH on $^{55}$Mn and ArO on $^{54,56,57}$ Fe (LNE).<br>Adopted different reaction/ collision gas and to reduce $^{40}$Ar$^{35}$Cl and other polyatomic interference to $^{75}$As (NIM).<br>As measurements were performed at high resolution mode of the HR-ICP-MS. The signals for the internal standard were corrected for isobaric interferences (TUBİTAK UME).<br>As analysis in High Resolution required, due to Ar-Cl interference on the $^{75}$As signal. Mn analyses were performed in Medium Resolution to avoid poly-atomic isobaric interferences (mostly related to Argon species) (NMISA).<br>Before analysis, the presence of potential interferences was cross-checked using high resolution ICP-MS and quadrupole ICP-MS with a |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | collision/reaction cell.<br>Collision/reaction cell technique was used for removal of interferences (NMIJ).<br>To avoid the polyatomic interferences on As and Mn high and medium resolution mode were used respectively. For non-contaminated soil, the low concentrations affected the sensitivity of the arsenic, due high contents of matrix components (high dissolved solids), which affected the degree of difficulty, and as a result some background was obtained, so it was needed some adjustments, which increased the measurement challenge in the instrument (CENAM).<br>Polyatomic interfering species were studied and after dilutions the effect from chloride was not significant (INMETRO).<br>Use He in ORS (Octopole Reaction System, Agilent 8800) (VNIIM).<br>Reaction-collision cell was used for the removal of interferences (JSI).<br>Instrument correction for isobaric/polyatomic interferences. To reduce the polyatomic interference of $^{40}Ar^{35}Cl$, high resolution mode was used (INM). |
| Correction or removal of matrix-induced signal suppression or enhancement<br>*Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement.* | LNE(As, Mn)<br>GLHK<br>INMETRO (As)<br>INTI<br>VNIIM | LNE(Fe)<br>NIM<br>TUBİTAK UME<br>NMISA (As, Mn)<br>NMIJ (Mn, As)<br>CENAM (As and Mn)<br>JSI (As, Cd, Fe, Pb, Mn)<br>INM | Tested but no effect in regards of the high level of dilution for Fe. For As and Mn, standard addition method overcomes matrix effect (LNE).<br>Adopted standard addition to correct possible bias of matrix effect (NIM).<br>Matrix matched standard additions method was applied during the measurements (TUBİTAK UME).<br>The use of an internal standard was critical due to the soil matrix and the acid combination ($HNO_3$, HCl, HF, $H_3BO_3$) required to achieve digestion of the sample (NMISA).<br>Internal standardization using Rh and In with no interferences with the analytes was performed for compensating matrix-induced effects (NMIJ).<br>Internal standard with single point standard addition was used as calibration method to compensate |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | for any matrix effects. In order to reduce the polyatomic interference of arsenic from $^{40}Ar^{35}Cl$, it was used high-resolution mode; this affected the sensitivity in the instrument for $^{75}As$ isotope and this increased the degree of difficulty in the measurement. For $^{55}Mn$ the measurement was made in medium resolution mode, to avoid the interferences from $Cd^{++}$ and $^{39}K^{16}O$ (CENAM).<br>Reaction-collision cell was used for the removal of interferences.<br>Internal standards (Y, Rh, Ir and In) were used (JSI).<br>Sufficient dilution (INM) |
| Detector deadtime correction<br>*Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.* | LNE (As, Fe, Mn)<br>NIM<br>TUBİTAK UME<br>INMETRO (As)<br>INTI<br>VNIIM<br>JSI (As, Cd, Fe, Pb, Mn) | GLHK<br>NMISA (As, Mn)<br>NMIJ (Mn, As)<br>INM<br>CENAM | Use of the calculated value by the producer of the ICP/MS (LNE).<br>Counting rate was controlled for minimizing the effect of detector deadtime, typically under 1000000 cps (NMIJ, CENAM).<br>Instrument optimization as recommended (INM). |
| Mass bias/fractionation control and correction<br>*Techniques used to determine, monitor, and correct for mass bias/fractionation.* | GLHK<br>NIM<br>TUBİTAK UME<br>NMIJ (Mn, As)<br>INMETRO (As)<br>JSI (As, Cd, Fe, Pb, Mn) | NMISA (As, Mn)<br>INTI<br>VNIIM<br>INM | For measuring Pb used correction equation:<br>$Pb = {}^{208}Pb + {}^{207}Pb + {}^{206}Pb + {}^{204}Pb$<br>SemiQuant analysis to ensure natural isotope abundance (VNIIM).<br>Instrument optimization; tuning solution (INM). |

## Inorganic Core Capabilities
## Summary Table

**CCQM Study: ✓ CCQM-K127 □ CCQM-P162**

**Institute(s): NRC-CNRC, GLHK, NIST, NIM, INMETRO, INTI, CSIR-NPLI, IRMM**

**Method: ICP-OES**

**Analyte(s): As (NRC-CNRC, INMETRO, CSIR-NPLI, IRMM), Cd (NRC-CNRC, INMETRO, CSIR-NPLI), Fe (NRC-CNRC, GLHK, NIST, NIM, INMETRO, INTI, CSIR-NPLI, IRMM), Mn (NRC-CNRC, GLHK, NIST, IRMM, NIM), Pb (NRC-CNRC, INMETRO, CSIR-NPLI)**

## Instructions:

*List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.*

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Contamination control and correction<br>*All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.* | | NRC-CNRC (Fe, As, Cd, Pb and Mn)<br>GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | Contamination is controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents (NRC-CNRC).<br>Microwave vessels were cleaned and rinsed thoroughly between digestions. Blanks were also run through the entire procedure to identify if contamination occurred (NIST).<br>Blank correction (NIM).<br>Adopted procedures to avoid contamination included: in-house distilled acid for purification and blank control (INMETRO).<br>Minimum of three Procedural blanks were taken to avoid all the possible contamination (CSIR-NPLI). |
| Digestion/dissolution of organic matrices<br>*All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.* | NIST (Fe, Mn)<br>NIM | GLHK<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | Dissolution of residue was a challenge (CSIR-NPLI). |
| Digestion/dissolution of inorganic matrices<br>*All techniques and procedures used to bring a sample that is primarily* | NIM | GLHK<br>NIST (Fe, Mn)<br>INMETRO (As, Cd, Pb, Fe)<br>INTI | After microwave digestion, Fe was observed to be lower than expected in the control soil samples SRMs 2709a and 2711a. Hydrochloric acid (4 mL) was added to the sample (prior to digestion) in |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *inorganic in nature into solution suitable for liquid sample introduction to the ICP.* | | CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | addition to the $HNO_3$ and HF used previously. The Fe was observed to be in control for this procedure (NIST).<br>HF acid was added in the microwave digestion procedure, but in the digested samples was observed a small amount of residue. This residue was not dissolved by adding more HF (INMETRO).<br>After digestion ($HNO_3$ + HF + HCl, microwave), dissolution of residues were a challenge. All the samples were filtered before introduction to ICP OES (CSIR-NPLI).<br>Colourless residue remained after sample digestion (IRMM). |
| Volatile element containment<br>*All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.* | GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (Cd, Pb, Fe)<br>IRMM | INMETRO (As)<br>INTI<br>CSIR-NPLI (As) | Quality controls were used to evaluate As loss (INMETRO).<br>After microwave digestion evaporation of HF and acid was done using waterbath (CSIR-NPLI). |
| Pre-concentration<br>*Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | GLHK<br>NIST (Fe, Mn)<br>NIM<br>INTI<br>CSIR-NPLI (Not required)<br>IRMM | INMETRO (As, Cd, Pb, Fe) | Digested sample were evaporated to eliminate HF (INMETRO). |
| Vapor generation<br>*Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.* | GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI<br>IRMM | | |
| Matrix separation<br>*Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange,* | GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (Not Tested)<br>IRMM | | |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *extraction, precipitation procedures, but not vapor generation procedures.* | | | |
| Calibration of analyte concentration<br>*The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.* | | NRC-CNRC<br>GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | Good linear calibration was obtained (NRC-CNRC).<br>Gravimetric Standard Addition (GLHK).<br>Single point standard addition was used as the calibration method to compensate for any matrix effects. The spike was typically 2x greater than the sample analyte mass fraction (NIST).<br>Used external calibration method, and QC solution was used during determination (NIM).<br>As all elements were in different ranges, the calibration standards of all ranges according to the expected concentration of analyte were prepared. Fe concentration was very high. Multipoint external calibration was used for As, Cd and Pb. Bracketing method was used for Fe (CSIR-NPLI). |
| Signal detection<br>*The detection and recording of the analyte signals. The degree of difficulty increases for analytes present at low concentrations, or that are have weak emission lines..* | INMETRO (Cd, Pb)<br>INTI | NRC-CNRC (Fe, As, Cd, Pb and Mn)<br>GLHK<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Pb)<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | With adequate signals but Cd in non-contaminated soil is low and thus it was measured using ICPMS (NRC-CNRC).<br>Blanks were typically < 100 cps and the samples were ≥ 8000 cps for both Fe and Mn lines with well-defined peaks (NIST).<br>As and Pb require more attention due weak emission lines. The conditions were optimized to have an optimal signal and work with the plasma under robust conditions (INMETRO).<br>Concentration in blanks was too low to be detected (CSIR-NPLI).<br>For all elements, external calibration was used. For As, a set of 5 standards was made with concentrations between 0.07 and 0.63 mg/kg and a linear calibration function was used. For Fe, 5 standards with concentrations between 0.88 and 9 mg/kg and linear calibration and for Mn, 5 standards with concentrations between 0.92 and 8.27 mg/kg and linear calibration (IRMM). |
| Memory effect<br>*Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.* | NIM | NRC-CNRC (Fe, As, Cd, Pb and Mn)<br>GLHK<br>NIST (Fe, Mn)<br>INMETRO (As, Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | Not significant, rinsed with 2 % $HNO_3$ solution (NRC-CNRC).<br>Rinse times were (50 – 60) s. There was no evidence of memory effect from the standards or samples (NIST).<br>Blank was run in-between consecutive measurements to avoid memory effects. It took time in case of Fe because of high concentration (CSIR-NPLI). |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Complex spectral backgrounds<br>*Any techniques used to remove, reduce, or mathematically correct for interferences caused by the overlap of analyte emission lines with atomic, ionic, or molecular emission from matrix components. The relative concentrations and sensitivities of the analyte and the interfering species will affect the degree of difficulty. Samples containing high concentration matrix components with large numbers of emission lines or molecular bands may increase the measurement challenge.* | GLHK<br>INTI<br>CSIR-NPLI | NRC-CNRC (Fe, As, Cd, Pb and Mn)<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (As, Cd, Pb, Fe)<br>IRMM | Choose wave lines without significant interference, inter element correction was applied (NRC-CNRC).<br>Single point standard addition was used as the calibration method to compensate for any matrix effects. The spectra were also examined to observe if interferences or background points needed adjustments (NIST).<br>As and Pb require special attention due spectral interferences. The spectral interference for As (189 nm) was avoid using an alternative wavelength and for Pb (220 nm) the signal was optimized and it allowed to minimize the spectral interference (INMETRO).<br>The spectral background was checked for each of the samples for each monitored line. For As, Fe and Mn, two spectral lines were monitored and the results compared to ensure that they matched. For As, a 20 % difference between the two spectral lines was observed. From the recovery of the control sample, it was determined that the measurement line was free of interference. The results were reported (IRMM). |
| Correction or removal of matrix-induced signal suppression or enhancement<br>*Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.* | GLHK | NRC-CNRC (Fe, As, Cd, Pb and Mn)<br>NIST (Fe, Mn)<br>NIM<br>INMETRO (Cd, Pb, Fe)<br>INTI<br>CSIR-NPLI (As, Cd, Fe, Pb)<br>IRMM | Standard additions calibration was applied (NRC-CNRC).<br>Single point standard addition was used as the calibration method to compensate for any matrix effects. Digested samples were diluted by at least a factor of 100 which could also aid in diminishing the impact of the matrix (NIST).<br>Evaluated matrix and acid effect to signal during determination (NIM).<br>Plasma was operated under robust conditions and samples were diluted to reduce matrix effect (INMETRO).<br>Acid concentration was a big challenge specially HF as it may destroy Torch of ICP and before making analyte solutions, the digested solutions were wet-dried at water bath to reduce the acid concentration. Specific spectral lines (characteristic wavelengths) were selected a metal determination such that at least determined metals are not interfere each other (CSIR-NPLI).<br>The acid content and composition of standards was matched to that of the samples by measuring the density of diluted extracts and matching the density of the nitric acid solution used to prepare the standards<br>Two CRMs of similar composition (ERM-CC141 and BCR-320R) were measured together with the samples (IRMM). |

## Inorganic Core Capabilities
## Summary Table

**CCQM Study: ✓ CCQM-K127**

**Institute(s): ANSTO, JSI**

**Method: INAA**

**Analyte(s): As, Cd, Fe, Mn (ANSTO, JSI)**

### Instructions:

*List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.*

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Sample preparation<br>*Procedures used to prepare samples for irradiation; determination of the mass basis (e.g., determination of dry mass basis); procedures to minimize sample loss during preparation; procedures to minimize contamination with the elements of interest (highest difficulty for determination of low levels of elements that are ubiquitous in the sample preparation environment).* | | ANSTO (As, Cd, Fe, Mn)<br>JSI | An aliquot varied from 0.20 to 0.25 g was sealed into a pure polyethylene ampoule (inside diameter 8 mm and 4 mm in height) (JSI). |
| Standards preparation<br>*Procedures used to prepare element standards or other comparators used for standardization. (e.g., low difficulty for use of pure elements or compounds; higher difficulty for procedures involving dissolution and dilution, or dilution with solid matrices.)* | ANSTO (As, Fe, Cd) | ANSTO (Mn)<br>JSI | $k_0$-NAA was used in all cases, using Au as the standard. For As, Fe and Cd, the Au standard was IRMM-530RC Al-0.1 % Au wire and in the case of Mn NIST SRM 3121 gold standard solution was used to prepare a standard (ANSTO).<br>IRMM-530R Al-0.1 % Au alloy in form of foil with thickness of 0.1 mm was used. Discs of about 7 mm diameter were prepared (JSI). |
| General applications<br>*Procedures associated with specific method of NAA and the evaluation of the associated uncertainties for comparator NAA, $k_0$ NAA, or other method specific parameters not described below.* | | ANSTO (As, Cd, Fe, Mn)<br>JSI | The measurements were undertaken in well-thermalized pneumatic facilities in the 20 MW OPAL research reactor. The method of $k_0$-NAA was used (ANSTO).<br>A sample and standard Al-0.1 % Au were stacked together, fixed in the polyethylene vial in sandwich |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| | | | form and irradiated in the 250 kW TRIGA Mark II reactor. Characterization of irradiation channel in the carousel facility (CF) of TRIGA reactor and absolute calibration of the HPGe detector are needed. Optimization and validation of the $k_0$-INAA with different matrix certified reference materials are necessary. Concentration levels in non-contaminated soil for As, Fe and Mn have to be suitable for INAA, but not for Cd. Concentration levels in contaminated soil for As, Cd and Fe have to be suitable for INAA (JSI). |
| Determination of peak areas (complex spectra/small peaks)<br>*Procedures used to determine peak areas. (e.g., high difficulty for small peak areas on complex backgrounds or determination of areas for multiple unresolved peaks.)* | ANSTO (As, Cd, Fe, Mn) | JSI | For peak area evaluation, the HyperLab 2002 program was used (JSI). |
| Correction for spectral interferences<br>*Procedures used to determine peak areas from interfering nuclides and subtraction of the appropriate number of counts from the peak of interest. Level of difficulty increases with the number of corrections needed and the magnitude of the corrections relative to the total peak area.* | ANSTO (As, Cd, Fe, Mn) | JSI | No difficulties in net peak areas determination were encountered for $^{76}$As at 559.1 keV, for Cd/$^{115m}$In at 336.2 keV, for $^{59}$Fe- at 1099.3 and 1291.6 keV and for $^{56}$Mn at 846.8 keV (JSI). |
| Correction of fast neutron and fission interferences<br>*Procedures used to determine the contributions from fast neutron reactions or fission of U to the peak area of interest. The level of difficulty is related to the magnitude of the corrections needed.* | ANSTO (As, Cd, Fe, Mn) | JSI | For studied radionuclides ($^{76}$As, Cd/$^{115m}$In, $^{59}$Fe and $^{56}$Mn) the threshold reactions are negligible (JSI). |
| Corrections for sample and standard geometry differences<br>*Procedures used to determine correction factors for differences in sample and standard irradiation and counting geometries. These may include, e.g., use of flux monitors to determine irradiation geometry correction factors, and calculated correction factors based on measured thicknesses and sample-to-detector distances. Level of difficulty increases with the magnitude of the correction.* | | ANSTO (As, Cd, Fe, Mn)<br>JSI | Corrections for geometry differences between sample and standard were calculated in proprietary Kayzero for Windows software (ANSTO).<br>Differences in sample/standard geometry are taken into account and they are calculated by Kayzero for Windows (KayWin®) software, which was used for effective solid angle calculations and elemental concentration calculations (JSI). |
| Corrections or uncertainty assessments for high count rates<br>*Procedures used to correct for losses in the analyzer due to high count rates;* | ANSTO (As, Cd, Fe, Mn) | JSI | Measurements were carried out at such distances that the dead time was kept below 10 % with negligible random coincidences. |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| *e.g., set up and validation of loss-free counting hardware, use of mathematical corrections for pulse pileup as a function of analyzer dead time, etc. Level of difficulty increases with the magnitude of the correction.* | | | Multichannel analyzer DSPECPLUSTM in ZDT mode and MULTIPORT II multichannel analyzer were used (JSI). |
| Corrections for neutron absorption or scattering differences between samples and standards<br>*Procedures used to correct for differences between neutron exposure of samples and standards associated with differences in the absorbing and scattering power; e.g., corrections derived from measurements of different amounts of materials or thicknesses of materials, or calculations based on cross-section values to correct for neutron attenuation. Level of difficulty increases with the magnitude of the correction.* | ANSTO (As, Cd, Fe, Mn) | JSI | Standard Al-0.1 % Au (nuclide $^{198}$Au ($T_{1/2}$=2.695 d) at gamma line of 411.8 keV) was used for axial flux gradient corrections in the sample. Radial flux gradient is negligible due to similar diameter of sample and standard. Thermal and epithermal self-shielding factors are equal to 1 (JSI). |
| Corrections for differences in neutron exposure of samples and standards<br>*For some NAA applications, samples and standards are irradiated individually and corrections are needed for any differences in neutron exposures. Corrections may be based on, e.g., results from flux monitors or estimates based on knowledge of the facility.* | ANSTO (As, Cd, Fe, Mn) | JSI | The samples and standards were irradiated together (see above) (JSI). |
| Corrections for gamma-ray attenuation<br>*Procedures used to correct for differences in gamma-ray attenuation between samples and standards; typically relevant only for high-z sample or standard matrices and where samples and standards differ. Level of difficulty increases with the magnitude of the correction.* | ANSTO (As, Cd, Fe, Mn) | JSI | Corrections for gamma-ray attenuations in sample/standard were calculated by Kayzero for Windows (KayWin®) software (JSI). |

# Inorganic Core Capabilities
# Summary Table

**CCQM Study: ✓ CCQM-K127 ☐ CCQM-P62**

**Institute(s): INACAL, JSI, INM**

**Method: ETA-AAS (or GF-AAS), FAAS**

**Analyte(s): ETA-AAS (or GF-AAS): As (INACAL), Cd (INACAL, JSI), Pb (INACAL)**
**FAAS: As (INM), Cd (INACAL, INM), Fe (INACAL, INM), Mn (INACAL, INM), Pb (INM)**

## Instructions:

*List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.*

| **Capabilities/Challenges** | **Not tested** | **Tested** | **Specific challenges encountered** |
|---|---|---|---|
| Contamination control and correction<br>*All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.* | | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | The blank values were under the limits of detection (JSI).<br>For each digestion, a separate blank sample was included. The blank samples containing all acids, without the sample itself, went through all analytical procedure stages and measured (INM). |
| Digestion/dissolution of organic matrices<br>*All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ETA-AAS.* | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | | |
| Digestion/dissolution of inorganic matrices<br>*All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ETA-AAS.* | JSI (Cd) | INACAL (As, Cd, Pb)<br>INM (As, Cd, Pb, Fe, Mn) | Optimization of acids combination for total digestion of the sample (INACAL). |
| Volatile element containment<br>*All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.* | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | | Different digestion conditions selected for As (digestion in two consecutive days). Closed vessels (INM). |
| Pre-concentration<br>*Techniques and procedures used to increase the concentration of the analyte* | JSI (Cd) | | |

| **Capabilities/Challenges** | **Not tested** | **Tested** | **Specific challenges encountered** |
|---|---|---|---|
| *introduced to the ETA-AAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | INM (As, Cd, Pb, Fe, Mn) | | |
| Matrix separation<br>*Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.* | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | | |
| Hydride preconcentration/matrix separation of volatile species.<br>*Coupling of a hydride system to the ETA-AAS and optimization of conditions.* | JSI (Cd) | INM (As, Cd, Pb, Fe, Mn) | |
| Calibration of analyte concentration<br>*The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures. Also use of matrix-matched standards to minimize effect of interferences.* | | INACAL (As, Cd, Pb)<br>JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | Use of standard addition calibration (INACAL).<br>External calibration (JSI).<br>Use of standard addition calibration (INACAL).<br>External calibration; bracketing method. ERM CC141 used for validation of Mn (INM). |
| Signal detection<br>*The detection and recording of the absorption signals of analytes. The degree of difficulty increases for analytes present at low concentrations, of low atomic absorption coefficient. Requires selection of operating conditions such as light source, absorption line, Zeeman background correction conditions. Includes selection of signal processing conditions (peak area or height).* | JSI (Cd) | INM (As, Cd, Pb, Fe, Mn) | Instrument parameters (spectrometer, flow, burner high etc.) optimization; Reliable analytical signals for Fe, Mn, Cd and Pb (contaminated soil)<br>ERM CC141 used for validation of Mn. High characteristic concentration for As (contaminated soil) (INM). |
| Memory effect<br>*Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.* | JSI (Cd) | INACAL (As, Cd, Pb)<br>INACAL (Cd, Fe, Mn)<br>INM (As, Cd, Pb, Fe, Mn) | Use of blank samples between standards and samples (INACAL).<br>Use of blank samples between standards and samples (INACAL).<br>Washing procedures: before and after each measurement, 2 % $HNO_3$ (INM). |
| Optimization of the furnace temperature program<br>*Optimization of temperature and duration of steps for sample drying, pyrolysis to remove (residual) organics, and atomization. Furnace temperature program to minimize analyte loss in the drying/pyrolysis steps, while maximizing analyte vaporization in the atomization step.* | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | INACAL (As, Cd, Pb) | Optimization of temperature and duration of steps in the furnace temperature program (INACAL). |

| Capabilities/Challenges | Not tested | Tested | Specific challenges encountered |
|---|---|---|---|
| Correction or removal of matrix effects or interferences<br>*Chemical or instrumental procedures used to avoid or correct for spectral and non-spectral interferences. Includes effects of differences in viscosity and chemical equilibrium states of analyte between the standard and sample. Selection of matrix modifier to adjust volatility of analyte and/or matrix to eliminate these effects is also included. Addition of reactive gases (eg oxygen) to the carrier gas to improve matrix separation. Also included is Zeeman or other background correction techniques to remove interference due to absorption and scattering from coexisting molecules/atoms in the sample.* | JSI (Cd)<br>INM (As, Cd, Pb, Fe, Mn) | INACAL (As, Cd, Pb) | Selection of matrix modifier to adjust volatility of analyte and matrix (INACAL). |

**Note:** red fonts belong to FAAS, black fonts belong to ETA-AAS (or GF-AAS)

CENAM
CENTRO NACIONAL DE METROLOGÍA

Jožef Stefan Institute

## Annex II:

# CALL FOR PARTICIPANTS

## Key Comparisons CCQM-K127 and Pilot Study CCQM-P162 Contaminant and other elements in soil

January, 2015

**From: The Co-ordinating Laboratories: CENAM and JSI**

**To: Members of the CCQM Inorganic Analysis Working Group (IAWG)**
**Other expert institutes**
(Answer is desired even if the institute or laboratory does not wish to participate)

**Dear IAWG Member,**

This letter is an invitation to participate in key comparison CCQM-K127 and/or in pilot study CCQM-P162, for the determination of mass fraction of total element contents in soil samples.

This is a follow-up comparison in the category 13; where three key comparisons have been carried out during the years 2000 (CCQM-K13), 2003 (CCQM-K28) and 2004 (CCQM-K44). Since it is important to update the capabilities of NMIs in this category, CENAM and JSI propose a key comparison in this category and run a pilot study in parallel. Currently 13 NMI has been claimed in Category 13: 29 CMCs soil and 96 CMCs of sediments.

The candidate soils samples to be used in both CCQM-K127 and CCQM-P162 represent a non-contaminated soil with low concentrations of elements, and a contaminated soil with much higher concentration of selected elements. This broadens the scope and a degree of complexity of earlier measurements in this field.

Organizations which are national metrological institutes (NMI), or appropriate designated institutes (DI) of the CIPM MRA system, are invited to participate in the key comparison or the pilot study.

The results of the key comparison will be presented in the form of a report to the CCQM, available to participants and to members of the IAWG. The report will identify the results with the names of the participating institutes. Preliminary (A) and final (B) drafts of the report will be circulated to participants for comments and corrections. The approved report will be submitted to the BIPM's Key Comparison Database (KCDB) and the results will be publicly available. A similar report will be prepared for the pilot study, for participants and members of the IAWG.

A short description of the study is given below. A detailed study protocol will be sent to registered participants later.

## Background

The main sources of elements as contaminants/pollutants in soils are mining and smelting activities, fossil fuel combustion, agricultural practices, industrial activities and waste disposal. Resulting contaminated/polluted sites are of great concern and represent serious environmental, health and economic problems. Characterization and identification of contaminated land is the first step in risk assessment and remediation activities. It is well known that soil is very complex matrix with huge variability locally and worldwide. Consequently, despite the available reference materials (RM) certified for trace and major elements in soils, there is a lack of concentration and matrix-matched soils RM at testing and calibration levels.

Non-contaminated soils contain trace and major elements at levels representing geochemical background of the region. In mining sites, toxic elements such As, Cd, Pb, Cr and Zn form many ore minerals, including traces of Au and Ag. During mining and ore processing these elements are emitted to environment causing anthropogenically elevated levels in soils. Once those are in the soil, the toxic elements present in ore mine fragments disperse mechanically by wind or water or leach from tailing dams and undergo oxidation and other weathering reactions leading to metal ion distribution within the soil system in more mobile forms and also potentially more bioavailable than the original ones.

Analytical laboratories should, therefore, demonstrate their measurement capabilities of trace and major elements in a wide concentration ranges, representing background/reference sites as well as highly contaminated soils by their available analytical method; so this facilitate to investigate the core capabilities of participants to measure the mass fraction of tested elements in soil and therefore to claim their Calibration and Measurement Capabilities.

## Sample materials

Non-contaminated soil sample was prepared by JSI. Soil was collected from a natural grassland and is characterized as eutric cambisol on gravel and sand. The sample was prepared according to ISO 11464: 2006, Soil quality - Pretreatment of samples for physic-chemical analysis. A fraction bellow 250 µm was finally homogenized for 60 h in ball drum. After homogeneity testing for 11 elements, the soils were bottled into 40 mL amber vials containing 20 g of soil each. Samples were sterilized by Co-60 irradiation at a dose between 18 – 24 kGy.

Contaminated soil sample was prepared by CENAM. The contaminated sandy soil of rhyolitic origin was characterized for total content of 5 metals proposed. The soil batch was homogenized using a homogenizer drum with three dimensions for 3 hours, and also in a sampler splitter of 10 positions, and then packaged with 20 g of soil with a particle size in the range between (75 - 90) µm, contained in a amber borosilicate glass bottle and packed in a vacuum double bag, the first was striated polyethylene bag and the second (outer) in a polyethylene terephthalate bag (Maylar ®). For stability purposes, the batch was irradiated with Co-60 at a dose between (17 - 22) kGy for microbiological control and bottled. The homogeneity of the candidate material it is fully investigated before it is distributed.

## Target measurands

**Four target elements** are selected in the contaminated soil sample and **five target elements** in non-contaminated soil sample for the key comparison and pilot study. These elements are Arsenic, Cadmium, Iron, Lead and Manganese for non-contaminated soil; Arsenic, Cadmium, Iron and Lead for contaminated soil. Optional choice is allowed only for the pilot study. This comparison would allow participants to better demonstrate and shine their capabilities on the measurement of various elements in category 13.

Mass fractions ranges of the total content of elements in soil samples

| Element | Non-contaminated | Contaminated |
|---|---|---|
| **As (mg/kg)** | 5 - 20 | 40 - 100 |
| **Cd (mg/kg)** | 0.1 - 1 | 100 - 600 |
| **Fe (g/kg)** | 20 - 50 | 10 - 30 |
| **Pb (mg/kg)** | 20 - 70 | 50 - 300 |
| **Mn (mg/kg)** | 500 - 1500 | - |

## Method of analysis

The participants are encouraged to use any method of their choice for the determination of total content of elements in soil samples. Results of analysis for the matrix sample should be dry mass corrected. The procedure for determination of moisture content will be provided. It is recommended that the preparation and dilution of solutions be carried out by weighing.
If participants are registered in the key comparison, it is necessary to provide all the necessary information about their methods in order to include it in the key comparison report; also, it must provide the core capability tables, which form part of the key comparison report.

## Time schedule

| | |
|---|---|
| Call for participation | February, 2015 |
| Deadline for registration of participation: | February 28, 2015 |
| Distribution of samples: | March, 2015 |
| Deadline for delivery of results: | August 31, 2015 |
| First discussion on results | October, 2015 |

## Registration

Please register using attached form. Please specify if you wish to participate in the key comparison K127 or pilot study P162. Please return the registration form by e-mail no later than February 28th, 2015 to:

**Contact Persons:**

María-Rocío Arvizu-Torres
E-Mail: marvizu@cenam.mx
Tel +52-442-2110500 Ext 3902
J. Velina Lara Manzano
vlara@cenam.mx
Tel +52-442-2110564
Centro Nacional de Metrología
El Marques, Querétaro.
México, 76246

We look forward to your participation in this comparison

Yours sincerely,

**María-del-Rocío Arvizu-Torres**
**CENAM**

**Prof. Dr. Milena Horvat**
**JSI**

CENAM
CENTRO NACIONAL DE METROLOGÍA

Jožef Stefan Institute

## Annex III:

# REGISTRATION FORM
# Key Comparisons CCQM-K127 and Pilot Study CCQM-P162
# Contaminant and other elements in soil

| | | |
|---|---|---|
| **Name of Institute:** | | |
| **NMI / DI:** | National Metrology Institute | Designated Institute |
| **Address:** | | |
| **Country:** | | |
| **Contact person:** | Title<br>Given name<br>Surname | |
| **E-mail:** | | |
| **Tel.:** | | |
| **Date :** | **Signature:** | |

| | | |
|---|---|---|
| I would like to register for **CCQM-K127** (delete as appropriate): | **Yes** | **No** |

I would like to register for **CCQM-P162** (indicate the sample and the elements for which you are interested to measure by inserting **Yes** or **No** under the heading of the appropriate sample).

| **Matrix / Measurand** | **Contaminated soil** | **Non-contaminated soil** | **Analytical method** |
|---|---|---|---|
| | **CCQM-P162 (Yes/No)** | **CCQM-P162 (Yes/No)** | |
| **Arsenic** | | | |
| **Cadmium** | | | |
| **Iron** | | | |
| **Lead** | | | |
| **Manganese** | ■ | | |

Please send completed registration form by e-mail no later than **February 28th, 2015** to:

**María-del-Rocío Arvizu-Torres**
Centro Nacional de Metrología
El Marques, Querétaro.
México, 76246
Tel +52-442-2110500 Ext 3902
E-Mail: marvizu@cenam.mx

**Annex IV:**

# Technical Protocol

March, 2015

## 1. Introduction

Non-contaminated soils contain trace and major elements at levels representing geochemical background of the region. The main sources of elements as contaminants/pollutants in soils are mining and smelting activities, fossil fuel combustion, agricultural practices, industrial activities and waste disposal. Resulting contaminated/polluted sites are of great concern and represent serious environmental, health and economic problems. Characterization and identification of contaminated land is the first step in risk assessment and remediation activities. It is well known that soil is very complex matrix with huge variability locally and worldwide. Consequently, despite the available reference materials (RM) certified for trace and major elements in soils, there is a lack of concentration and matrix-matched soils RM at testing and calibration levels.

According to the IAWG´s five year plan, it is recommended to have a key comparison under the measurement service category of soils and sediments for the year 2015. Currently 13 NMI has been claimed in Category 13: 29 CMCs soil and 96 CMCs of sediments. In this regards this is a follow-up comparison in the category 13; where three key comparisons have been carried out during the years 2000 (CCQM-K13), 2003 (CCQM-K28) and 2004 (CCQM-K44).

Since it is important to update the capabilities of NMIs in this category, at the CCQM-IAWG meeting held in April 2014, CENAM and JSI proposes a key comparison in this category and run a pilot study in parallel. The proposed study was agreed by IAWG members, where two soils samples will be used in both CCQM-K127 and CCQM-P162 and represent a non-contaminated soil with low concentrations of elements (Arsenic, Cadmium, Iron, Lead and Manganese), and a contaminated soil with much higher concentration of selected elements (Arsenic, Cadmium, Iron and Lead). This broadens the scope and a degree of complexity of earlier measurements in this field. National metrology institutes (NMIs)/designate institutes (DIs) should, therefore, demonstrate their measurement capabilities of trace and major elements in a wide concentration ranges, representing background/reference sites as well as highly contaminated soils by their available analytical method. This facilitate to investigate the core capabilities of participants to measure the mass fraction of tested elements in soil and therefore to claim their Calibration and Measurement Capabilities as listed in Appendix C of the Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA). Participants are requested to complete the Inorganic Core Capabilities Tables as a means of providing evidence for their CMC claims.

## 2. Sample materials

<u>Non-contaminated soil</u> sample was prepared by JSI. Soil was collected from a natural grassland and is characterized as eutric cambisol on gravel and sand. The sample was prepared according to ISO 11464: 2006, Soil quality - Pretreatment of samples for physic-chemical analysis. A fraction bellow 250 µm was finally homogenized for 60 h in ball drum. After homogeneity testing for 5 elements, the soils were bottled into 40 mL amber vials containing 20 g of soil each. Samples were sterilized by Co-60 irradiation at a dose between (18 – 24) kGy. The samples are stored at room temperature (20 ± 2) ºC before shipment. Homogeneity study (with sample size of 0.25 g) of the testing materials had been performed and the results were found to be satisfactory. Stability study of the prepared samples is conducted and will continue further to cover the entire exercise.

<u>Contaminated soil</u> sample was prepared by CENAM. The contaminated sandy soil of rhyolitic origin was characterized for total content of 5 metals proposed. The soil batch was homogenized using a homogenizer drum with three dimensions for 3 hours, and also in a sampler splitter of 10 positions, and then packaged with 60 g of soil with a particle size in the range between (75 - 90) µm, contained in a amber borosilicate glass bottle and packed in a vacuum double bag, the first was striated polyethylene bag and the second (outer) in a polyethylene terephthalate bag (Maylar ®). For stability purposes, the batch was irradiated with Co-60 at a dose between (17 - 22) kGy for microbiological control and bottled. The homogeneity of the candidate material it is fully investigated before it is distributed.
The samples are stored at room temperature (20 to 25) ºC before shipment. Homogeneity study (with sample size of 0.5 g) of the testing materials had been performed and the results were found to be satisfactory. Stability study of the prepared samples has been conducted and would be continued further to cover the entire exercise.

## 3. Target measurands

**Four target elements** are selected in the <u>contaminated soil sample</u> and **five target elements** in <u>non-contaminated soil sample</u> for the key comparison and pilot study. These elements are Arsenic, Cadmium, Iron, Lead and Manganese for non-contaminated soil; Arsenic, Cadmium, Iron and Lead for <u>contaminated soil</u>. Optional choice is allowed only for the pilot study. This comparison would allow participants to better demonstrate and shine their capabilities on the measurement of various elements in category 13.

Mass fractions ranges of the total content of elements in soil samples

| Element | Non-contaminated | Contaminated |
|---|---|---|
| **As (µg/g)** | 5 - 20 | 40 - 100 |
| **Cd (µg/g)** | 0.1 - 1 | 100 - 600 |
| **Fe (mg/g)** | 20 - 50 | 10 - 30 |
| **Pb (µg/g)** | 20 - 70 | 50 - 300 |
| **Mn (µg/g)** | 500 - 1500 | - |

## 4. Method of analysis

The participants are encouraged to use any method of their choice for the determination **of total content of elements in soil samples**.

The sample should be mixed thoroughly before processing and the analysis should be conducted with a recommended sample size of at least 0.5 g for contaminated soil and 0.25 g for non-contaminated soil. Participants are requested to perform independent measurements on at least five separate portions of the sample and to determine the total mass fractions of the analytes of interest. Measurement results of elements in the soil samples should be dry mass corrected. It is recommended that the preparation and dilution of solutions be carried out by weighing.

### Determination of moisture

A minimum of three separate portions (recommended size to be about 1 g each). The material should be dried in a ventilated oven at a temperature of (105 ± 2) °C. Dry the soil samples for minimum 2 hours. Then weight and repeat drying until constant mass is attained (as recommendation: successive weights should not different more that 1 mg). The loss of mass corresponds to the correction that should be applied (dry mass correction). It is advisable to perform this procedure at the same time when weighing the soil samples for the measurements of the measurands.

Note: valid for contaminated and non-contaminated soil.

## 5. Reporting

The registered participants must provide all the necessary information about their methods in order to include it in the key comparison report; for the participants in the key comparison, it is mandatory to provide the core capability tables, which form part of the key comparison report.

- All measured values for each subsample and the mean value of at least five independent separate portions of sample (subsamples) and its associated measurement uncertainty shall be reported on a dry mass basis. Any participant that chooses to use multiple methods can decide only one composite result (e.g., an average value from different methods) and also the individual results from different methods as the reporting value(s) for each measurand;

- Report the mass fractions of analytes in **µg/g** for each sample, except for Fe in **mg/g**;

- Participants shall provide (i) description of analytical methods (including sample digestion/dissolution methods, calibration methods and analytical instruments used) and (ii) details of the uncertainty estimation (including complete specification of the measurement equations and description of all uncertainty sources);

- Sources, purity and traceability of reference materials used for calibration purpose shall be provided; and

- Both the Report Form and the Inorganic Core Capabilities Tables should be submitted to the contact:

  Maria-Rocio Arvizu-Torres
  E-Mail: marvizu@cenam.mx
  Tel +52-442-2110500 Ext 3902

Please choose and download appropriate Inorganic Core Capabilities Tables from the IAWG webpage:

http://www.bipm.org/wg/CCQM/IAWG/Restricted/welcome.jsp
Username: IAWG
Password: INORG99
Select the link for Participant_Tables.

## 6. Programme schedule

| | |
|---|---|
| Call for participation | February, 2015 |
| Deadline for registration of participation | February 28, 2015 |
| Distribution of samples: | March, 2015 |
| Deadline for delivery of results: | August 31, 2015 |
| First discussion on results at the CCQM-IAWG Meeting | October, 2015 |

The results of the key comparison will be presented in the form of a report to the CCQM, available to participants and to members of the IAWG. The report will identify the results with the names of the participating institutes. Preliminary (A) and final (B) drafts of the report will be circulated to participants for comments and corrections. The approved report will be submitted to the BIPM's Key Comparison Database (KCDB) and the results will be publicly available. A similar report will be prepared for the pilot study, for participants and members of the IAWG.

## 7. Coordinating laboratories

The CCQM-K127 and CCQM-P162 are coordinated by CENAM (Maria-del-Rocio Arvizu-Torres and J. Velina Lara Manzano) and JSI (Milena Horvat).

## Annex V: Reporting Form

# Key Comparison CCQM-K127 Contaminant and other elements in soil

# Report Form

## A. Participating Laboratory Information

| | | | | |
|---|---|---|---|---|
| **Date :** | | | | |
| **Name of Institute** | | | | |
| **NMI / DI** | **National Metrology Institute** | | **Designated Institute** | |
| | | | | |
| **Technical Contact (name)** | **Title** | **Given name** | | **Surname** |
| **e-mail:** | | | | |
| **The number of unit used** | **Non-contaminated soil:** | | **Contaminated soil:** | |

**(Please email the completed report form to marvizu@cenam.mx on or before <u>31 August 2015</u>)**

**Analysts:**

| |
|---|
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## B. Comparison Data for Non-contaminated Soil

| Analyte | For each subsample mass fraction (on dry mass basis) | Mean mass fraction (on dry mass basis) | Combined standard uncertainty [$u(y)_c$] | Dry mass correction factor (g/g) |
|---|---|---|---|---|
| **Total Arsenic (µg/g)** | | | | |
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| | | | | |
| | | | | |
| **Total Cadmium (µg/g)** | | | | |
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| | | | | |
| **Total Iron (mg/g)** | | | | |
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| | | | | |
| **Total Lead (µg/g)** | | | | |
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| **Total Manganese (µg/g)** | | | | |
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## C. Comparison Data for Contaminated Soil

| Analyte | For each subsample mass fraction (on dry mass basis) | Mean mass fraction (on dry mass basis) | Combined standard uncertainty $[u(y)_c]$ | Dry mass correction factor (g/g) |
|---|---|---|---|---|
| **Total Arsenic (µg/g)** | | | | |
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| | | | | |
| | | | | |
| **Total Cadmium (µg/g)** | | | | |
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| | | | | |
| **Total Iron (mg/g)** | | | | |
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| | | | | |
| **Total Lead (µg/g)** | | | | |
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### D. Information on Analytical Method for Non-contaminated Soil

| Analyte | Sample preparation/Digestion procedure | Measurement technique | Calibration method | Reference materials used |
|---|---|---|---|---|
| **As** | | | | |
| **Cd** | | | | |
| **Fe** | | | | |
| **Pb** | | | | |
| **Mn** | | | | |

## E. Information on Analytical Method for Contaminated Soil

| Analyte | Sample preparation/Digestion procedure | Measurement technique | Calibration method | Reference materials used |
|---|---|---|---|---|
| **As** | | | | |
| **Cd** | | | | |
| **Fe** | | | | |
| **Pb** | | | | |

## F. Uncertainty Estimation

Please describe the approach for the uncertainty estimation and give the formula used for the calculation of the expanded uncertainty.

Please include the coverage factor used in each case for each analyte

**G) Please list the sources of uncertainties** included in the combined standard uncertainty estimation and indicate by putting “X” in the appropriate box, which uncertainty components were considered for each analyte.

**For Non-Contaminated Soil**

| Analyte<br>Uncertainty component | Arsenic | Cadmium | Iron | Lead | Manganese |
|---|---|---|---|---|---|
| | | | | | |
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**For Contaminated Soil**

| Analyte<br>Uncertainty component | Arsenic | Cadmium | Iron | Lead |
|---|---|---|---|---|
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