

Final Report

EMRP-SIB09: Euramet TC-MC 1377

“Comparison measurement for the validation of the developed
methods for Al and Mo”

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| | | | |
|---|-------|---|-------|
| 1 | PTB | 4 | INRIM |
| 2 | BRML | 5 | SMU |
| 3 | CENAM | | |

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1. Introduction

Mono-elemental solutions are required for calibration purposes in elemental analysis and are therefore a prerequisite for reliable measurement results. This EURAMET comparison in the framework of the *European Metrology Research Programme* (EMRP), within the Joint Research Project (JRP) called SIB09 *Primary standards for challenging elements*, addresses the particular importance of mono-elemental solutions. Aluminum and molybdenum were carefully selected as the analytes. The comparisons are part of the EMRP project SIB09, which comprises mainly of three work packages (WP): WP 1 *Development of methods for impurity analysis*, WP 2 *Elemental and isotopic characterization* and WP 3 *Standard solutions for challenging elements*. WP 3 included the preparation of mono-elemental solutions containing 1 g/kg of Rh and Mo, respectively, with an expanded uncertainty of $U \leq 0.001$ g/kg ($k = 2$). Additionally, methods have been developed to link liquid primary standards to liquid secondary standards with target uncertainties of $U_{\text{rel}} \leq 0.1$ %. The goal of this comparison was to validate the developed methods, e.g. Multi Collector Mass Spectrometry with an Inductively Coupled Plasma (MC-ICP-MS), Inductively Coupled Plasma with Optical Emission Spectrometry (ICP OES), titrimetry and/or Instrumental Neutron Activation Analysis (INAA), for linking liquid primary standards to liquid secondary standards.

2. The samples

Four mono-elemental solutions were prepared gravimetrically at PTB starting from the metal itself. After cleaning the solid starting materials, in case of Mo following the procedure described in [1] and in case of Al using HCl ($w(\text{HCl}) = 0.30$ g/g, suprapur, Merck KGaA, Germany), aliquots of approximately 2 g were dissolved using HNO₃ ($w = 0.30$ g/g, subboiled) in case of Mo [1] and excess amounts of HCl ($w = 0.20$ g/g, ultrapur) in case of Al. Afterwards, the Al solutions were evaporated to dryness and the residue was allowed to cool down to room temperature. Then, HNO₃ ($w = 0.20$ g/g, subboiled) was added to the residue and heated again on a hotplate to ensure complete dissolution. The Al solutions were adjusted with HNO₃ ($w = 0.025$ g/g) and water, respectively, to form stock solutions (500 g each) with an element mass fraction of $w(\text{Al}) \approx 4000$ µg/g. The Mo solutions were evaporated to dryness and their residues were allowed to cool down to room temperature. Then, ammonium hydroxide ($w(\text{NH}_3) = 0.25$ g/g, ultrapur, Merck KGaA, Germany) was added to the residues and heated again on the hotplate to ensure complete dissolution. The resulting clear solutions were evaporated to dryness and water was added to the residues to adjust molybdenum mass fractions of $w(\text{Mo}) \approx 4000$ µg/g. The final samples were gravimetrically prepared directly from the stock solutions by diluting each 500 g stock solution using HNO₃ ($w = 0.025$ g/g) in the case of Al and in the case of Mo using ultrapure water ($\sigma < 0.066$ µS/cm, Milli-Q Element A10, EMD Millipore Corporation, USA). Two different solutions of each element were prepared. For the calibration solutions a well-known element content along with its associated uncertainty have been provided in an excel file to each participant. The calibration solutions were intended to be used to calibrate the measurement(s) of the sample solutions. The calibration solutions were labelled “element symbol – cal – unique number” (e.g. “Al-cal-001”), while the sample solutions were indicated with “smp” instead of “cal” (e.g. “Al-smp-001”).

The solutions were filled in thoroughly cleaned, blank-checked, dried, labelled and weighed 125 mL-PFA bottles. Each bottle contained at least 100 g of the sample solution. Prior to sealing the bottles in film bags, each bottle was weighed again to keep track of losses during

shipment and be able to distinguish between unavoidable losses due to evaporation (and correct for them) and losses due to leaking bottles. The bottles were wrapped in tightly sealed film bags (12 µm polyester, 12 µm aluminum, 95 µm LDPE, type A 30 T, C. Waller, Eichstetten, Germany).

3. Participants

Five National Metrology Institutes (NMIs) and one industrial lab registered to participate in TC-MC 1377. For more details refer to table 1.

Table 1: Participants of TC-MC 1377 in alphabetical order of their acronyms, together with their selected analytes.

| Institute | Country | Contact | Aluminum | Molybdenum |
|---|----------|---------------------------------|----------|------------|
| BRML - National Institute of Metrology | Romania | Mirella Buzoianu | × | × |
| CENAM - Centro Nacional de Metrología | Mexico | Judith Velina Lara-Manzano | × | - |
| IL - Industry laboratory | — | Not to be disclosed | × | × |
| INRIM - Istituto Nazionale di Ricerca Metrologica | Italy | Luigi Bergamaschi | - | × |
| PTB - Physikalisch-Technische Bundesanstalt | Germany | Olaf Rienitz, Volker Görlitz | × | × |
| SMU - Slovak Institute of Metrology | Slovakia | Michal Máriássy | × | - |

4. Instructions to the participants

A technical protocol was sent to all participants of TC-MC 1377, together with the samples providing information about the properties of the samples, the sample handling and the recommended procedure to check for losses and correct for evaporation effects during storage. The sample bottles were accompanied by an individual table (Excel-file) compiling the masses of the empty bottles and of the respective solutions needed to carry out the loss checking/evaporation correction procedure.

The appendix shows the technical protocol of TC-MC 1377.

5. Reference materials, methods, and instrumentation

Participants were free to use methods, which were developed within the framework of EMRP-SIB09. All participants measured the samples as received. No digestion was necessary. A majority – though a small one – used ICP OES combined with different calibration strategies.

Table 2 gives an overview of the instrumentation and methods that have been used by the different participants.

Table 2: Instrumentation/method and calibration strategy used as reported by the participants (IS = internal standard).

| Instrumentation/method/calibration strategy | | |
|---|---|--------------------------|
| Institute | Aluminum | Molybdenum |
| BRML-1 | ICP-MS, bracketing + IS | ICP-MS, bracketing + IS |
| BRML-2 | EDTA back titrimetry | — |
| CENAM-1 | Gravimetric titration with potentiometric end-point detection | — |
| CENAM-2 | ICP OES, bracketing + IS | — |
| IL | ICP OES, IS | ICP OES, IS |
| INRIM | — | INAA |
| PTB | ICP OES, bracketing + IS | ICP OES, bracketing + IS |
| SMU-1 | Titration: Traceable to EDTA | — |
| SMU-2 | Titration: Traceable to the calibration solution sent by PTB | — |

6. Results

The participants' results as reported to the coordinating laboratory are shown in tables 3 and 4, as well as figures 1 and 2. Due to technical problems, INRIM did not report results. Also, the samples for the industry laboratory (IL) were bottled two months later than the other participants. Therefore, the evaporation of the stock solutions with time resulted in larger mass fractions compared to the other participants. This in turn was the reason why all reported values were normalized to their respective well-known gravimetric reference value prior to the evaluation in order to render all values comparable.

6.1 Aluminum

Table 3: Aluminum mass fractions $w_i(\text{Al})$ and their associated expanded and relative expanded uncertainties $U(w_i)$ and $U_{\text{rel}}(w_i)$, resp., for a coverage factor of $k = 2$ as reported by the participants in the order of increasing mass fraction values.

| Aluminum | | | |
|-------------|-------------------------------------|-----------------------------|----------------------------|
| Participant | $w_i(\text{Al})$ $\mu\text{g/g}$ | $U(w_i)$ $\mu\text{g/g}$ | $U_{\text{rel}}(w_i)$ % |
| BRML-1 | 999.3 | 1.0 | 0.10 |
| BRML-2 | 1000.2 | 2.0 | 0.20 |
| CENAM-1 | 1001.5 | 1.8 | 0.18 |
| SMU-1 | 1002.59 | 0.38 | 0.04 |
| CENAM-2 | 1002.7 | 1.1 | 0.11 |
| PTB | 1002.84 | 0.94 | 0.09 |
| SMU-2 | 1003.05 | 0.57 | 0.06 |
| IL | 1003.81 | 0.87 | 0.09 |

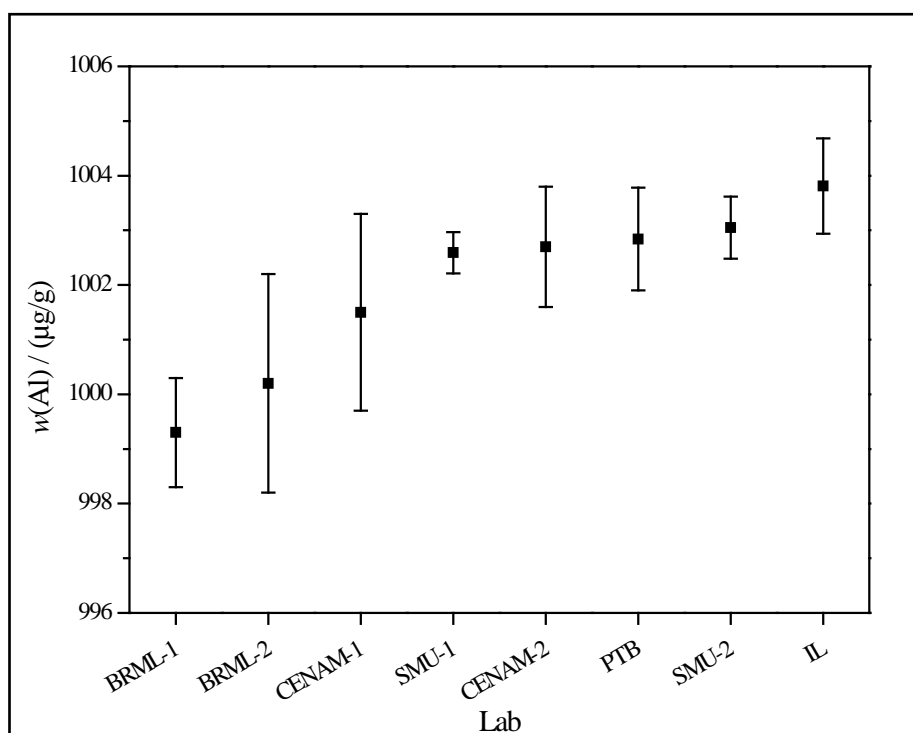


Figure 1: Aluminum mass fraction $w(\text{Al})$ as reported by the participants. Error bars denote the expanded uncertainty $U(w(\text{Al}))$ for a coverage factor of $k = 2$ as reported.

6.2 Molybdenum

Table 4: Molybdenum mass fractions $w_i(\text{Mo})$ and their associated expanded and relative expanded uncertainties $U(w_i)$ and $U_{\text{rel}}(w_i)$, resp., for a coverage factor of $k = 2$ as reported by the participants in the order of increasing mass fraction values.

| Molybdenum | | | |
|-------------|-------------------------------------|-----------------------------|----------------------------|
| Participant | $w_i(\text{Mo})$ $\mu\text{g/g}$ | $U(w_i)$ $\mu\text{g/g}$ | $U_{\text{rel}}(w_i)$ % |
| PTB | 993.99 | 0.66 | 0.07 |
| IL | 994.56 | 0.56 | 0.06 |
| BRML | 997.7 | 1.3 | 0.13 |

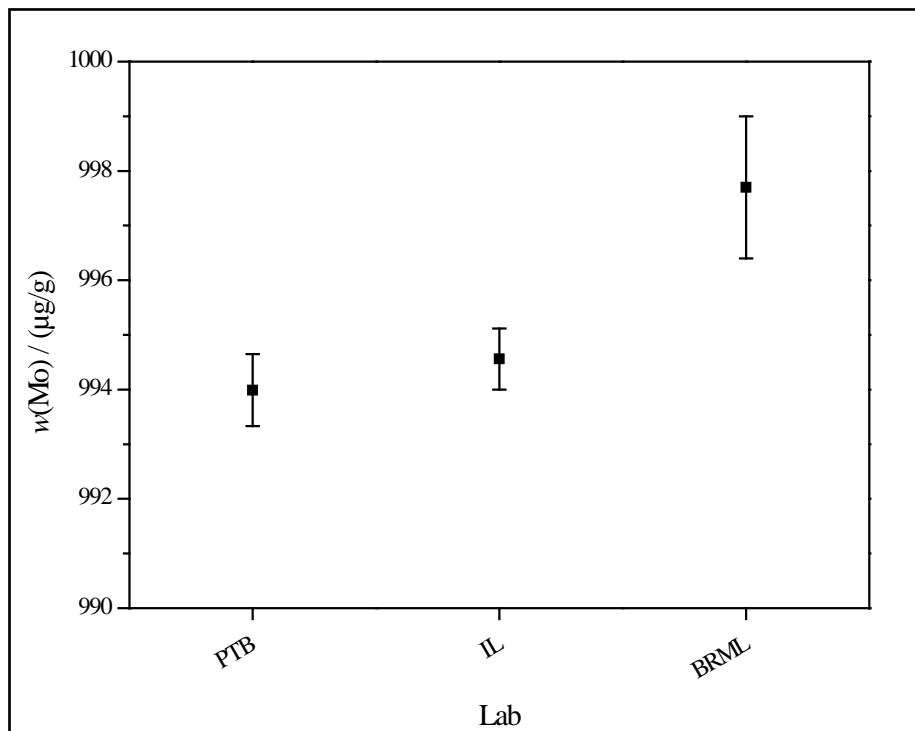


Figure 2: Molybdenum mass fraction $w(\text{Mo})$ as reported by the participants. Error bars denote the expanded uncertainty $U(w(\text{Mo}))$ for a coverage factor of $k = 2$ as reported.

6.3 Consensus values

As mentioned already above all results were normalized to their respective gravimetric reference value prior to the evaluation in order to render all values comparable.

6.3.1 Aluminum

Table 5: Ratio r_i of the aluminum mass fraction $w(\text{Al})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value, $w_{\text{ref},i}$, calculated from the preparation. The associated relative expanded uncertainties correspond to the relative expanded uncertainties ($k = 2$), which were provided by the participants.

| Aluminum | | | |
|-------------|--|---|----------------------------|
| Participant | $r_i = w_i(\text{Al})/w_{\text{ref},i}$ ($\mu\text{g/g}/(\mu\text{g/g})$) | $U(r_i)$ ($\mu\text{g/g}/(\mu\text{g/g})$) | $U_{\text{rel}}(r_i)$ % |
| BRML-1 | 0.99628 | 0.00100 | 0.10 |
| BRML-2 | 0.99718 | 0.00199 | 0.20 |
| CENAM-1 | 0.99847 | 0.00179 | 0.18 |
| SMU-1 | 0.99956 | 0.00038 | 0.04 |
| CENAM-2 | 0.99967 | 0.00110 | 0.11 |
| PTB | 0.99981 | 0.00094 | 0.09 |
| SMU-2 | 1.00002 | 0.00057 | 0.06 |
| IL | 1.00035 | 0.00087 | 0.09 |

6.3.2 Molybdenum

Table 6: Ratio r_i of the molybdenum mass fraction $w(\text{Mo})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value, $w_{\text{ref},i}$, calculated from the preparation. The associated relative expanded uncertainties correspond to the relative expanded uncertainties ($k = 2$), which were provided by the participants.

| Molybdenum | | | |
|-------------|--|---|----------------------------|
| Participant | $r_i = w_i(\text{Mo})/w_{\text{ref},i}$ ($\mu\text{g/g}/(\mu\text{g/g})$) | $U(r_i)$ ($\mu\text{g/g}/(\mu\text{g/g})$) | $U_{\text{rel}}(r_i)$ % |
| PTB | 1.00000 | 0.00066 | 0.07 |
| IL | 1.00012 | 0.00056 | 0.06 |
| BRML | 1.00374 | 0.00131 | 0.13 |

6.3.3 Calculation of consensus values

In case no independent reference values are available, usually location estimators based on the participants' results are considered to be used as the reference values. Three of the most common consensus values were calculated: Median (M), arithmetic mean (AM), and uncertainty weighted mean (UWM). Due to the small number of data sets no outliers were removed.

Subsequently, the data sets were checked for consistency using the chi-squared test proposed in [2]. The uncertainty weighted means \bar{r}_{UWM} were calculated according to eq. (1)

$$\bar{r}_{\text{UWM}} = \frac{\sum_{i=1}^N \frac{r_i}{u^2(r_i)}}{\sum_{i=1}^N \frac{1}{u^2(r_i)}} \quad (1)$$

yielding chi-squared χ_{obs}^2 according to eq. (2)

$$\chi_{\text{obs}}^2 = \sum_{i=1}^N \left(\frac{r_i - \bar{r}_{\text{UWM}}}{u(r_i)} \right)^2 \quad (2)$$

In case the 95 percentile of χ^2 with $N-1$ degrees of freedom $\chi_{0.05, N-1}^2$ (from [3]) is smaller than χ_{obs}^2 , the respective data set should be considered mutually inconsistent [2]. Both data sets did not pass the chi-squared test (table 7).

Table 7: Results of chi-squared test [2] applied to all data sets (E = element, N = number of values provided by participants). Values rounded to yield integer numbers.

| E | N | χ_{obs}^2 | $\chi_{0.05, N-1}^2$ | mutually consistent? |
|----|-----|-----------------------|----------------------|----------------------|
| Al | 8 | 56 | 14 | no |
| Mo | 3 | 28 | 6 | no |

Nevertheless, the uncertainty weighted mean \bar{r}_{UWM} (eq. (1)) as well as the arithmetic mean \bar{r}_{AM} (eq. (3)) and the median \bar{r}_{M} (eq. (4) and eq. (5), respectively) were calculated along with their associated uncertainties $u(\bar{r}_{\text{UWM}})$, $u(\bar{r}_{\text{AM}})$ and $u(\bar{r}_{\text{M}})$ (equations 6–8).

$$\bar{r}_{\text{AM}} = \frac{1}{N} \sum_{i=1}^N r_i \quad (3)$$

$$\bar{r}_{\text{M}} = \frac{1}{2} (r_{N/2} + r_{N/2+1}) \quad N \text{ even} \quad (4)$$

$$\bar{r}_{\text{M}} = \bar{r}_{(N+1)/2} \quad N \text{ odd} \quad (5)$$

$$u(\bar{r}_{\text{UWM}}) = \sqrt{\frac{\chi_{\text{obs}}^2}{N-1} \left(\sum_{i=1}^N \frac{1}{u^2(r_i)} \right)^{-1}} \quad (6)$$

$$u(\bar{r}_{\text{AM}}) = \sqrt{\frac{1}{N \cdot (N-1)} \sum_{i=1}^N (r_i - \bar{r}_{\text{AM}})^2} \quad (7)$$

$$u(\bar{r}_{\text{M}}) = \sqrt{\frac{\pi}{2N}} \cdot 1.483 \cdot \text{med}(|r_i - \bar{r}_{\text{M}}|) \quad (8)$$

Please note that when carrying out eq. (4) and (5), respectively, the participants' results (r_i) have to be arranged in the order of increasing values, while when carrying out equation (8) the

absolute deviations of the participants' results from the median $|r_i - \bar{r}_M|$ have to be arranged in the order of increasing values.

Table 8 summarizes all uncertainty weighted and arithmetic means as well as the medians according to equations (1)–(8). The consensus values for Al and Mo agree with each other within their associated uncertainties. In order to discuss the consensus estimators they were also plotted in figures 3–8. As usually the median seems to be least affected by “outliers”.

Table 8: Compilation of the three most common consensus values. The associated relative expanded uncertainties were calculated using a coverage factor of $k = 2$ from [4] according to $U_{\text{rel}}(w_i) = k_i \cdot u_c(w_i)/w_i$. Numbers were rounded following the recommendations in [4]. Degrees of equivalence (DoE) were calculated and figures drawn without rounding (UWM = uncertainty weighted mean, M = median, AM = arithmetic mean, E = element, i = type of estimator).

| E | i | $w_i(\text{E})/w_{\text{ref},i}$ ($\mu\text{g/g}$)/($\mu\text{g/g}$) | U ($\mu\text{g/g}$)/($\mu\text{g/g}$) | U_{rel} % |
|----|-----|---|--|-----------------------|
| Al | M | 0.99961 | 0.00075 | 0.075 |
| | AM | 0.9989 | 0.0010 | 0.10 |
| | UWM | 0.99947 | 0.00073 | 0.073 |
| Mo | M | 1.00012 | 0.00025 | 0.025 |
| | AM | 1.0013 | 0.0025 | 0.24 |
| | UWM | 1.0004 | 0.0015 | 0.15 |

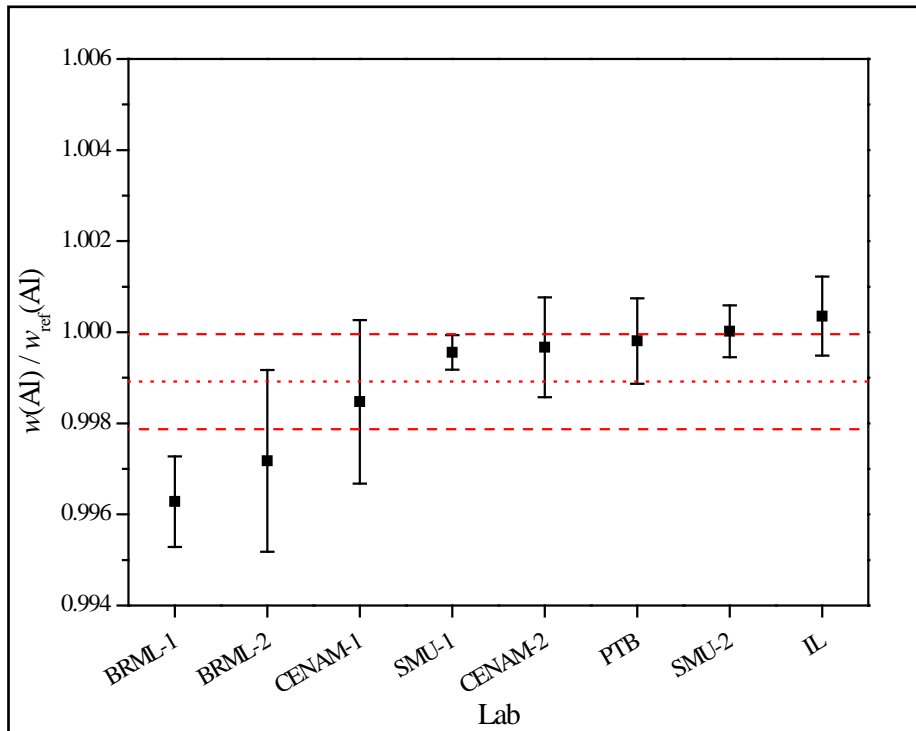


Figure 3: Ratio of the aluminum mass fraction $w(\text{Al})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Al}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the arithmetic mean: $\bar{r}_{\text{AM}}(\text{Al}) = 0.9989$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\text{AM}}(\text{Al}))$ associated with the AM.

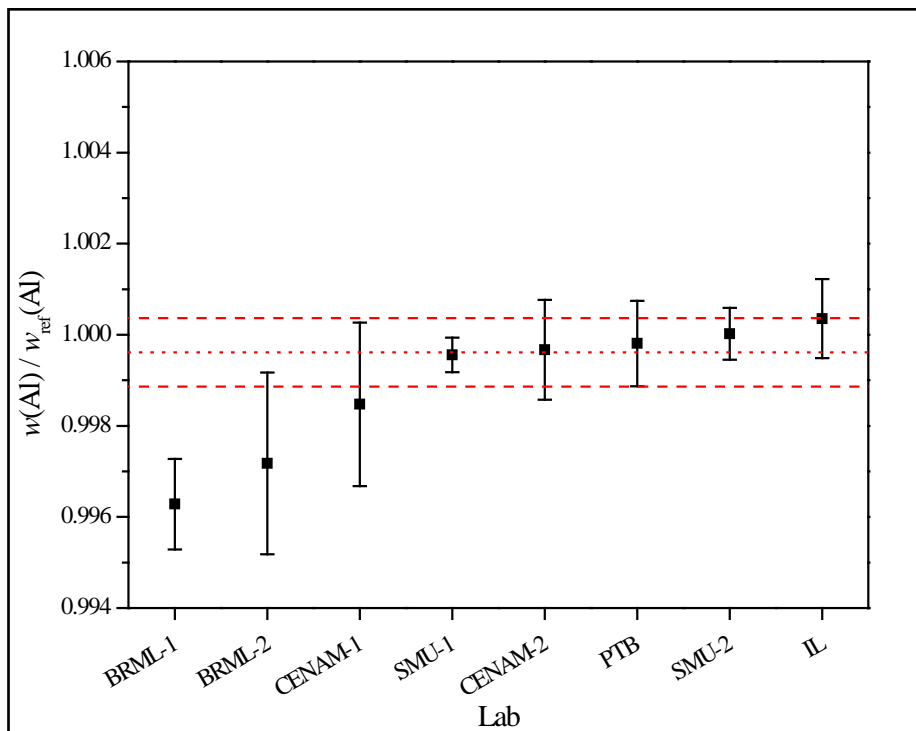


Figure 4: Ratio of the aluminum mass fraction $w(\text{Al})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Al}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the median: $\bar{r}_{\text{M}}(\text{Al}) = 0.99961$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\text{M}}(\text{Al}))$ associated with the M.

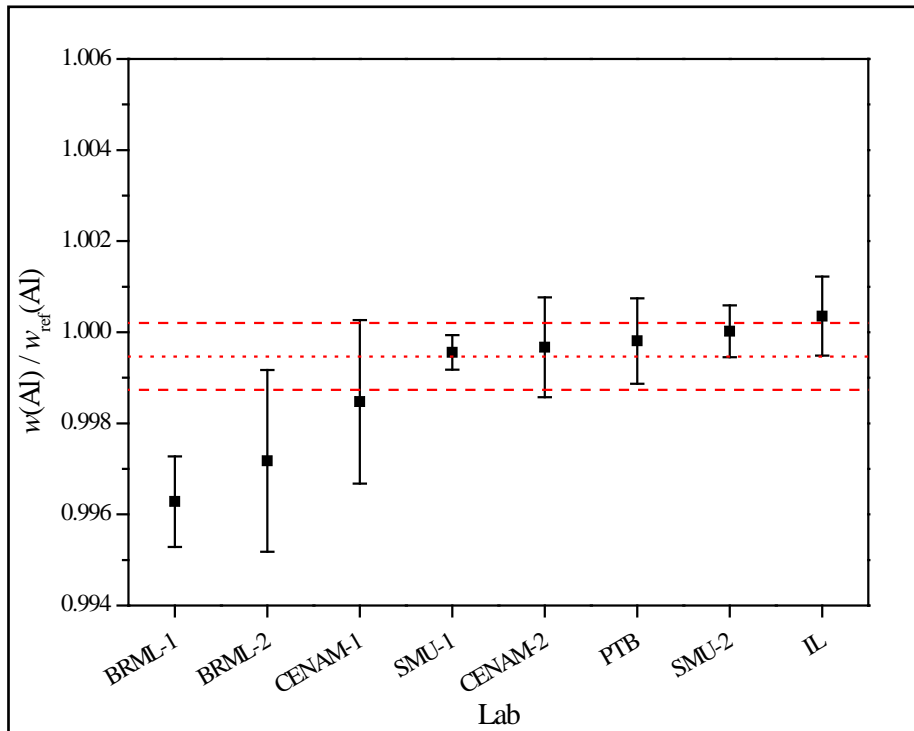


Figure 5: Ratio of the aluminum mass fraction $w(\text{Al})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Al}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the uncertainty weighted mean: $\bar{r}_{\text{UWM}}(\text{Al}) = 0.99947$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\text{UWM}}(\text{Al}))$ associated with the UWM.

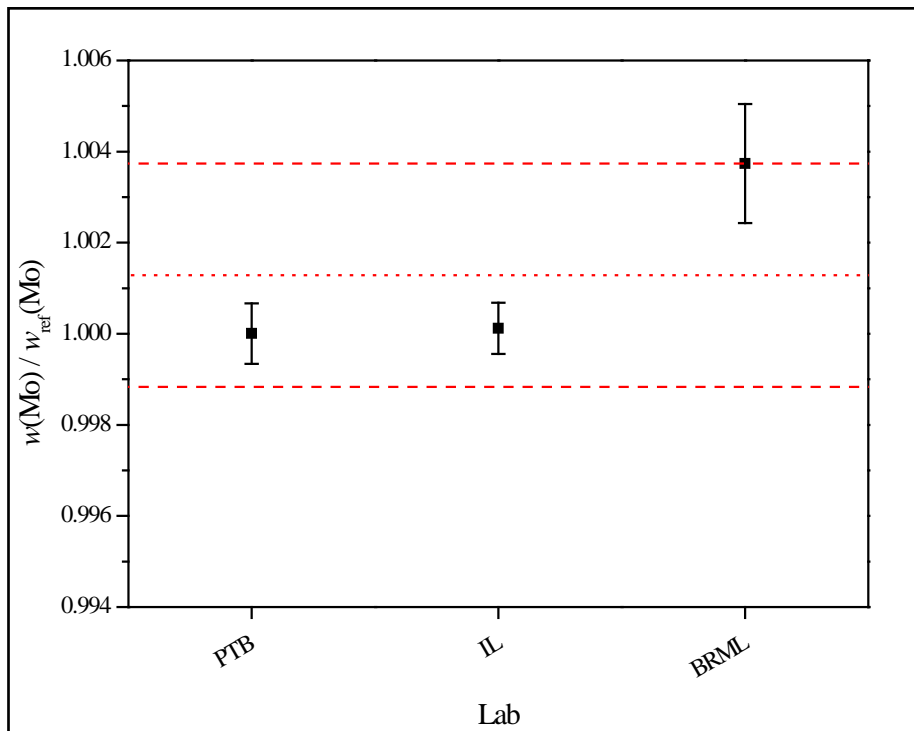


Figure 6: Ratio of the molybdenum mass fraction $w(\text{Mo})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Mo}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the arithmetic mean: $\bar{r}_{\text{AM}}(\text{Mo}) = 1.0013$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\text{AM}}(\text{Mo}))$ associated with the AM.

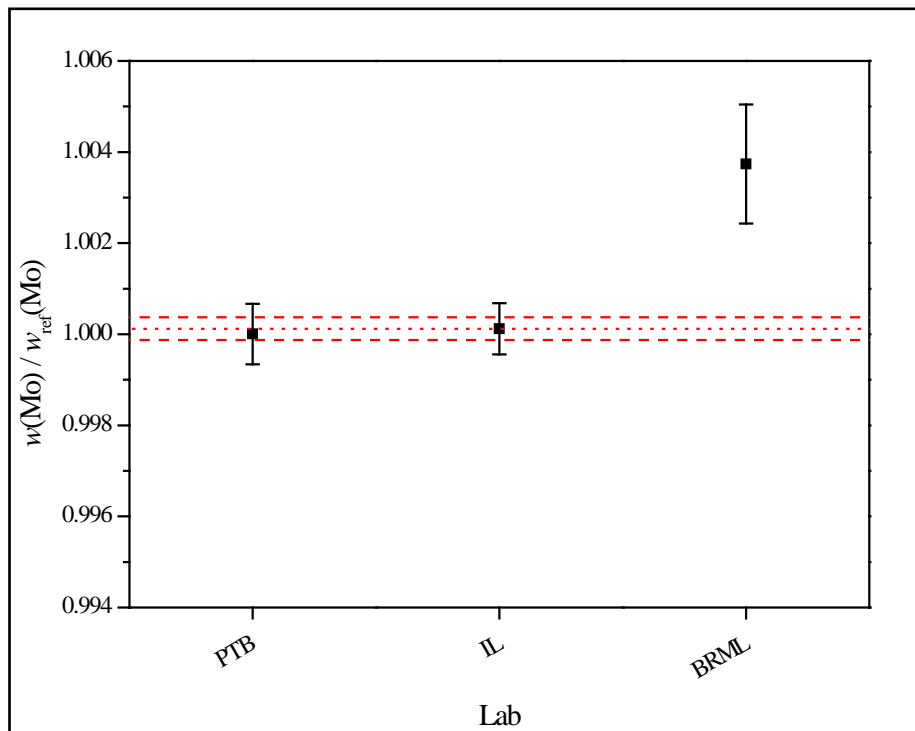


Figure 7: Ratio of the molybdenum mass fraction $w(\text{Mo})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Mo}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the median: $\bar{r}_M(\text{Mo}) = 1.00012$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_M(\text{Mo}))$ associated with the M.

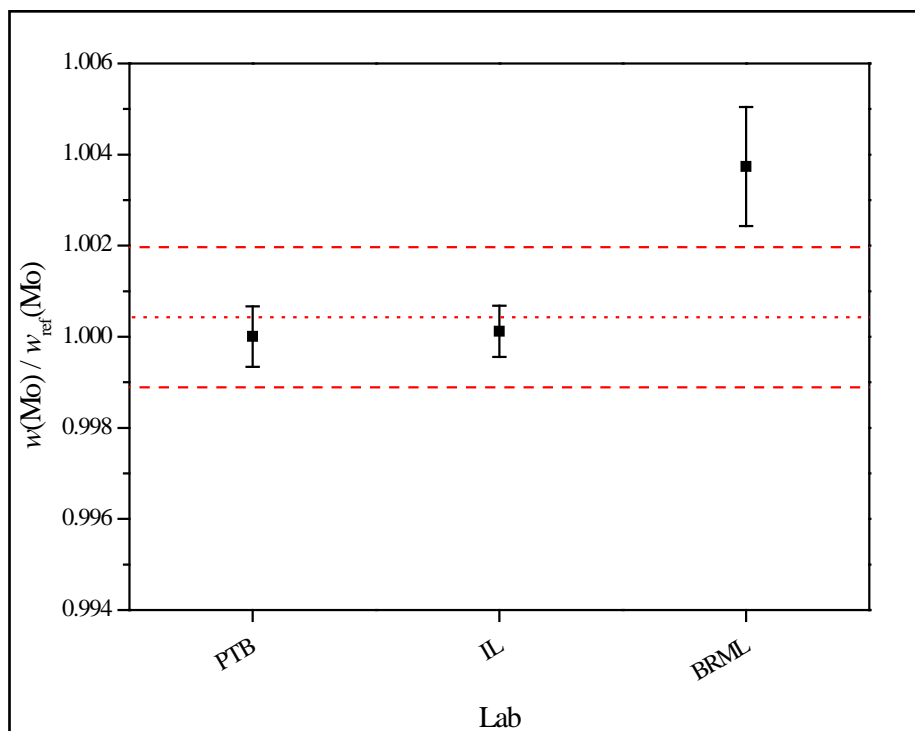


Figure 8: Ratio of the molybdenum mass fraction $w(\text{Mo})$ as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty $U(r(\text{Mo}))$ for a coverage factor of $k = 2$ as reported. The dotted red line shows the uncertainty weighted mean: $\bar{r}_{\text{UWM}}(\text{Mo}) = 1.0004$. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\text{UWM}}(\text{Mo}))$ associated with the UWM.

6.4 Degrees of equivalence d_i

Degrees of equivalence are not required in case of an EURAMET comparison. However, the degree of equivalence d_i (DoE) of an individual result w_i equals its deviation from the *key comparison reference value* w_{KCRV} or, in our case, the gravimetric reference value (w_{ref}). As the concept of DoEs is the most powerful tool to discuss the success of a comparison, the DoEs d_i as well as their associated uncertainties $u(d_i)$ were calculated following [2] and [5] according to equations (9) and (10).

$$d_i = w_i - w_{\text{ref}} \quad (9)$$

$$u(d_i) = \sqrt{u^2(w_i) + u^2(w_{\text{ref}})} \quad (10)$$

The uncertainty associated with d_i (equation 10) takes the uncertainty of the sample ($u(w_i)$) and the reference value ($u(w_{\text{ref}})$) into account. However, in some cases the uncertainty of the reference was already considered by the participant(s) when calculating the uncertainty of the sample. Therefore, this causes (at least to some degree) a correlation between the uncertainty of the sample and the reference. When this correlation is not properly taken into account this might lead to an overestimation of the uncertainty of d_i . But because, both the sample and the reference solution have changed during the transport from PTB to the according participant, the correlation coefficient is somewhere between one and zero. The uncertainty of the actual measurement is usually larger than the uncertainty calculated from the gravimetric preparation. Therefore, the uncertainty associated with d_i will not be affected no matter how often the uncertainty of the reference value is considered. As the actual correlation coefficient cannot be determined we decided to perform a conservative calculation that considers the uncertainty of the reference value (in some cases) twice in favor of the participant.

The results were summarized in tables 9–10 and plotted in figures 9–10 using the gravimetric value as the reference.

Table 9: Aluminum. Mass fractions $w_i(\text{Al})$ and their associated expanded and relative expanded uncertainties $U(w_i)$ and $U_{\text{rel}}(w_i)$, resp., as reported by the participants in the order of increasing mass fraction values. In case only expanded or relative combined uncertainties were reported, the values compiled were calculated accordingly. Degrees of equivalence d_i and their associated expanded uncertainty $U(d_i)$, resp., according to equation (9) and (10), are also compiled. A coverage factor of $k = 2$ was used to calculate $U(d_i) = k \cdot u(d_i)$. The gravimetric value for every participant, except for the industrial laboratory (IL), is $w_{\text{ref}}(\text{Al}) = (1003.03 \pm 0.51) \mu\text{g/g}$. The gravimetric value for the IL is $w_{\text{ref}}(\text{Al}) = (1003.45 \pm 0.51) \mu\text{g/g}$.

| Aluminum | | | | | |
|-------------|-------------------------------------|-----------------------------|----------------------------|--------------------------|-----------------------------|
| Participant | $w_i(\text{Al})$ $\mu\text{g/g}$ | $U(w_i)$ $\mu\text{g/g}$ | $U_{\text{rel}}(w_i)$ % | d_i $\mu\text{g/g}$ | $U(d_i)$ $\mu\text{g/g}$ |
| BRML-1 | 999.3 | 1.0 | 0.10 | -3.73 | 1.12 |
| BRML-2 | 1000.2 | 2.0 | 0.20 | -2.83 | 2.06 |
| CENAM-1 | 1001.5 | 1.8 | 0.18 | -1.53 | 1.87 |
| SMU-1 | 1002.59 | 0.38 | 0.04 | -0.44 | 0.64 |
| CENAM-2 | 1002.7 | 1.1 | 0.11 | -0.33 | 1.21 |
| PTB | 1002.84 | 0.94 | 0.09 | -0.19 | 1.07 |
| SMU-2 | 1003.05 | 0.57 | 0.06 | 0.02 | 0.76 |
| IL | 1003.81 | 0.87 | 0.09 | 0.36 | 1.01 |

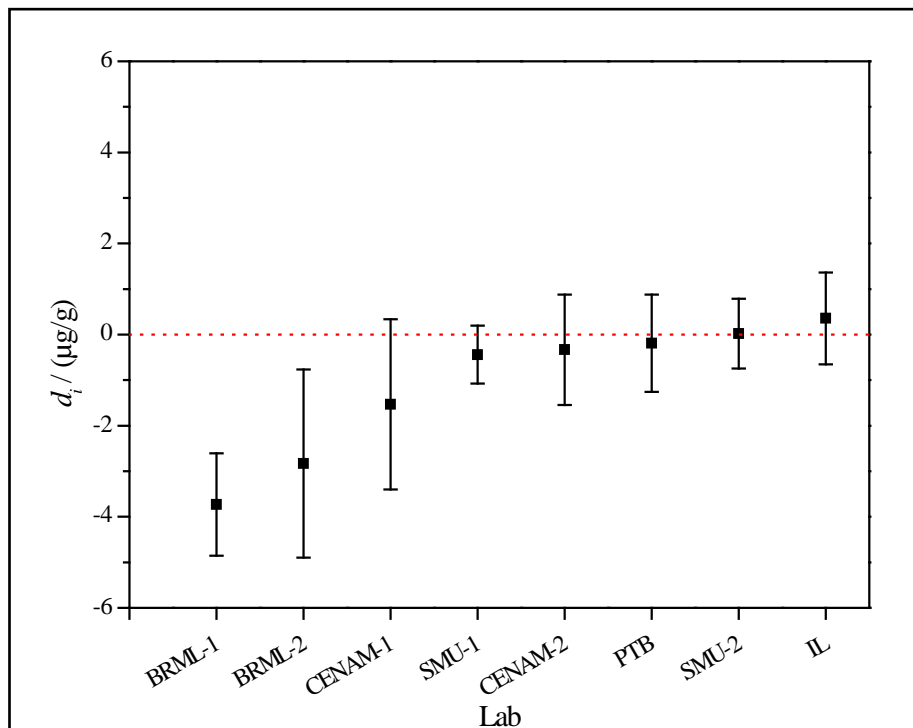


Figure 9: Aluminum. Graphical representation of the equivalence statements related to the gravimetric value – DoE-plot of the data reported by the TC-MC 1377 participants according to table 9. The black dots show the degree of equivalence d_i (DoE), while the error bars denote the expanded uncertainty associated with the degree of equivalence $U(d_i)$ according to eq. (10), calculated applying a coverage factor of $k = 2$, using $U(d_i) = k \cdot u(d_i)$. Results enclosing zero with their uncertainty interval are considered to be consistent with the gravimetric reference value.

Table 10: Molybdenum. Mass fractions $w_i(\text{Mo})$ and their associated expanded and relative expanded uncertainties $U(w_i)$ and $U_{\text{rel}}(w_i)$, resp., as reported by the participants in the order of increasing mass fraction values. In case only expanded or relative combined uncertainties were reported, the values compiled were calculated accordingly. Degrees of equivalence d_i and their associated expanded uncertainty $U(d_i)$, resp., according to equation (9) and (10), are also compiled. A coverage factor of $k = 2$ was used to calculate $U(d_i) = k \cdot u(d_i)$. The gravimetric value for BRML and PTB is $w_{\text{ref}}(\text{Mo}) = (993.99 \pm 0.11) \mu\text{g/g}$ and for the IL it is $w_{\text{ref}}(\text{Mo}) = (994.44 \pm 0.11) \mu\text{g/g}$.

| Molybdenum | | | | | |
|-------------|-------------------------------------|-----------------------------|----------------------------|--------------------------|-----------------------------|
| Participant | $w_i(\text{Mo})$ $\mu\text{g/g}$ | $U(w_i)$ $\mu\text{g/g}$ | $U_{\text{rel}}(w_i)$ % | d_i $\mu\text{g/g}$ | $U(d_i)$ $\mu\text{g/g}$ |
| PTB | 993.99 | 0.66 | 0.07 | 0.00 | 0.66 |
| IL | 994.56 | 0.56 | 0.06 | 0.12 | 0.56 |
| BRML | 997.7 | 1.3 | 0.13 | 3.71 | 1.30 |

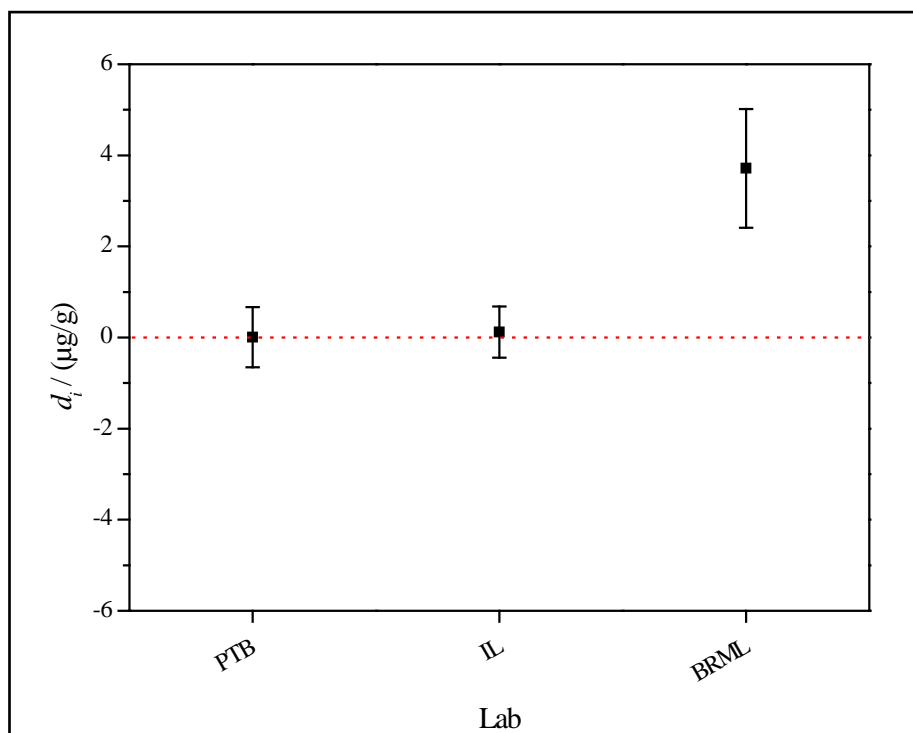


Figure 10: Molybdenum. Graphical representation of the equivalence statements related to the gravimetric value – DoE-plot of the data reported by the TC-MC 1377 participants according to table 10. The black dots show the degree of equivalence d_i (DoE), while the error bars denote the expanded uncertainty associated with the degree of equivalence $U(d_i)$ according to eq. (10), calculated applying a coverage factor of $k = 2$, using $U(d_i) = k \cdot u(d_i)$. Results enclosing zero with their uncertainty interval are considered to be consistent with the gravimetric reference value.

7. Discussion

DoEs were calculated using the gravimetric value as the representation of the “true” value. Using $|d_i|/U(d_i) \leq 1$ as the criterion of satisfactory or acceptable equivalence, 75 % of the aluminum results were at least satisfactory. In case of molybdenum approximately 67 % would meet the requirements. Especially figure 10 seem to suggest an underestimated uncertainty in one case. However, the goal of this comparison was to verify that methods has been established to link liquid primary standards to liquid secondary standards with a relative expanded uncertainty of up to 0.1 %. Therefore, if the expanded uncertainty of certain values would be enlarged to fit the criterion to match the “true” value, then those NMIs would have failed the original goal of this comparison. In general, the molybdenum measurements were clearly less successful than the aluminum measurements, which of course is also caused by the limited number of participants for this element compared to aluminum.

This EURAMET comparison was nevertheless successfully completed. Therefore, conducting another comparison within a wider scope will be the logical consequence, especially considering the importance of the capabilities demonstrated with these measurements. An according key comparison will therefore be suggested during the next EURAMET Sub-Committee for Inorganic Analysis (SCIA) meeting in 2016.

8. References

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EMRP-SIB09: Euramet comparison

“Comparison measurement for the validation of the developed methods for Al and Mo”

Technical Protocol

1. Introduction

Mono-elemental solutions are required for calibration purposes in elemental analysis and are therefore a prerequisite for reliable measurement results. This Euramet comparison within EMRP-SIB09 (WP 3) addresses the particular importance of mono-elemental solutions. Al and Mo were carefully selected as the analytes. The comparisons are part of the EMRP project SIB09 “Primary standards for challenging elements”: WP 1: Development of methods for impurity analysis, WP 2: Elemental and isotopic characterisation, WP 3: Standard solutions for challenging elements. WP 3 included the preparation of primary solutions containing 1 g/kg with an expanded uncertainty of $U \leq 0.001$ g/kg ($k = 2$) for Rh, Mo and Al. Additionally, methods have been developed to link liquid primary standards to liquid secondary standards with target uncertainties of $U_{\text{rel}} \leq 0.1$ %. The goal of this comparison is to validate the developed methods, e.g. MC-ICP-MS, ICP OES, titrimetry and INAA, for linking liquid primary standards to liquid secondary standards.

2. Samples

Four mono-elemental solutions were prepared gravimetrically at PTB starting from the metal itself. After cleaning the solid starting materials, in case of Mo following the procedure described in [1] and in case of Al using HCl ($w(\text{HCl}) = 0.30$ g/g, suprapur, Merck KGaA, Germany), aliquots of approximately 2 g were dissolved using HNO₃ ($w = 0.30$ g/g, subboiled) in case of Mo [1] and excess amounts of HCl ($w = 0.20$ g/g, ultrapur) in case of Al. Afterwards, the Al solutions were evaporated to dryness and the residue was allowed to cool down to room temperature. Then, HNO₃ ($w = 0.20$ g/g, subboiled) was added to the residue and heated again on the hotplate to ensure complete dissolution. The Al solutions were adjusted with HNO₃ ($w = 0.025$ g/g) and water, respectively, to form stock solutions (500 g each) with an element mass fraction of $w(\text{Al}) \approx 4000$ µg/g. The Mo solutions were evaporated to dryness and their residues were allowed to cool down to room temperature. Then,

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ammonium hydroxide ($w(\text{NH}_3) = 0.25 \text{ g/g}$, ultrapur, Merck KGaA, Germany) was added to the residues and heated again on the hotplate to ensure complete dissolution. The resulting clear solutions were evaporated to dryness and water was added to the residues to adjust molybdenum mass fractions of $w(\text{Mo}) \approx 4000 \text{ } \mu\text{g/g}$. The final samples were gravimetrically prepared directly from the stock solutions by diluting each 500 g stock solution using HNO_3 ($w = 0.025 \text{ g/g}$) in the case of Al and in the case of Mo using ultrapure water ($\sigma < 0.066 \text{ } \mu\text{S/cm}$, Milli-Q Element A10, EMD Millipore Corporation, USA) yielding approximately 1 kg of each of the four solutions.

| quantity | $w(\text{E})$ |
|------------|-----------------|
| Element E | $\mu\text{g/g}$ |
| Aluminum | 950...1050 |
| Molybdenum | 950...1050 |

The solutions were filled in thoroughly cleaned, blank-checked, dried, labelled and weighed 125 mL-PFA bottles. Each bottle contains at least 100 g of the sample solution. Prior to sealing the bottles in film bags, each bottle was weighed again to keep track of losses during shipment and be able to distinguish between unavoidable losses due to evaporation (and correct for them) and losses due to leaking bottles. The bottles were wrapped in tightly sealed film bags (12 μm polyester, 12 μm aluminium, 95 μm LDPE, type A 30 T, C. Waller, Eichstetten, Germany).

Please, weigh the bottles immediately after opening the film-bags using a balance with a resolution of at least 0.1 mg. Please, insert this weight in the provided excel file to calculate the recent weight of the bottles. The bottle with cap and label should be in the range of 140 g to 153 g. In case you are not equipped to measure the ambient conditions, please use reasonable estimations. Please, check whether the losses are in the usual range of evaporation or whether a bottle was leaking. Leaking bottles will be replaced. Refer to section 6 “Checking for losses” step 6 to calculate evaporation losses and correct for them.

Two different types of solutions were shipped: calibration solutions and sample solutions. For the calibration solutions a well-known element content along with its associated uncertainty will be provided in the according excel file. These calibration solutions are intended to be used to calibrate the measurement(s) of the sample solutions. The calibration solutions are labelled “element symbol – **cal** – unique number” (e.g. “Al-cal-001”), while the sample solutions are indicated with “smp” instead of “cal” (e.g. “Al-smp-001”).

3. Sample handling

Before opening the film-bag, please be prepared to weigh the bottles and to measure the ambient conditions (air pressure, air temperature, and relative humidity of the air). Please weigh the bottle immediately after opening the bag. Weigh them together with their screw-caps and label. Please, use a balance with a resolution of at least 0.1 mg and calculate possible losses according to section 6.

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4. Analysis

Please apply your most accurate methods of measurement (MC-ICP-MS, ICP OES, titrimetry as well as INAA), preferably primary methods. Note that the relative expanded measurement uncertainties U_{rel} associated with your results must not exceed 0.1 %. You are asked to determine the following quantities:

- Mass fractions w of the elements of interest (Mo and/or Al), in the sample solution (“smp”) expressed in $\mu\text{g/g}$ together with their associated uncertainties.
- Please, use the calibration solution(s) (“cal”) to calibrate your measurements after correcting the element content in the calibration solution(s) for evaporation losses. Use the uncertainty provided for the uncorrected element content since it was conservatively estimated and contains already the evaporation correction.

5. Reporting

The **deadline** for the submission of results is **26th of July 2015**. Please send your report via E-mail.

Please, report all your results in terms of a mass fraction w in $\mu\text{g/g}$. Please, calculate uncertainties for all the results reported according to the GUM [2,3]. Please, report a short description of the method(s) you used.

The results of this comparison cannot be used to support CMC claims.

If you need further assistance or encounter any kind of problem, please contact Janine Noordmann and/or Olaf Rienitz.

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6. Checking for losses / correcting evaporation effects

In addition to this “Technical Protocol” you should have received an excel file summarizing all bottles enclosed in your parcel together with the masses of the empty bottles m_{bottle} and the masses of the solutions in these bottles m_{solution} .

These masses were determined from the apparent masses (weighing values) of the empty bottle m_1 and the bottle containing the according solution m_2 determined at a time t_1 and t_2 , respectively. Since the ambient conditions (relative humidity of the air ϕ , air pressure p and air temperature ϑ) were different at these times (t_1 and t_2), according air buoyancy correction factors $K_{i,j}$ depending on the time j and the density of the weighed material i (PFA in case of the bottle, ρ_{bottle} , and the different solutions, ρ_{solution}) were calculated to convert the apparent masses m_1 and m_2 into the masses m_{bottle} and m_{solution} .

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$$m_{\text{bottle}} = K_{\text{bottle},1} \cdot m_1$$

$$K_{\text{bottle},1} = \frac{1 - \frac{\rho_{\text{air},1}}{\rho_{\text{cal}}}}{1 - \frac{\rho_{\text{air},1}}{\rho_{\text{bottle}}}}$$

$$\rho_{\text{air},1} = \frac{0.348444 \frac{\text{kg/m}^3}{\text{hPa}} \cdot p_1 - \varphi_1 \cdot \left(0.252 \frac{\text{kg/m}^3}{\text{°C}} \cdot \vartheta_1 - 2.0582 \frac{\text{kg}}{\text{m}^3} \right)}{273.15 + \frac{1}{\text{°C}} \cdot \vartheta_1}$$

$$m_{\text{solution}} = K_{\text{solution},2} \cdot \left(m_2 - \frac{m_{\text{bottle}}}{K_{\text{bottle},2}} \right)$$

$$K_{\text{bottle},2} = \frac{1 - \frac{\rho_{\text{air},2}}{\rho_{\text{cal}}}}{1 - \frac{\rho_{\text{air},2}}{\rho_{\text{bottle}}}} \quad \text{and} \quad K_{\text{solution},2} = \frac{1 - \frac{\rho_{\text{air},2}}{\rho_{\text{cal}}}}{1 - \frac{\rho_{\text{air},2}}{\rho_{\text{solution}}}}$$

$$\rho_{\text{air},2} = \frac{0.348444 \frac{\text{kg/m}^3}{\text{hPa}} \cdot p_2 - \varphi_2 \cdot \left(0.252 \frac{\text{kg/m}^3}{\text{°C}} \cdot \vartheta_2 - 2.0582 \frac{\text{kg}}{\text{m}^3} \right)}{273.15 + \frac{1}{\text{°C}} \cdot \vartheta_2}$$

The following parameters were used to perform the calculations above: $\rho_{\text{bottle}} = 2150 \text{ kg/m}^3$, $\rho_{\text{solution,Al}} = 1015.9 \text{ kg/m}^3$, and $\rho_{\text{solution,Mo}} = 998.8 \text{ kg/m}^3$ (determined according to [4,5]), respectively, as well as $\rho_{\text{cal}} = 7950 \text{ kg/m}^3$ (please be aware that most modern balances feature internal calibration masses of $\rho_{\text{cal}} = 8000 \text{ kg/m}^3$, therefore, refer to the manual of your balance).

Before sampling the first aliquot from a bottle, you are asked to weigh the bottle (including label and cap) at the time t_3 yielding its apparent mass m_3 , while also collecting the corresponding ambient conditions (relative humidity of the air φ_3 , air pressure p_3 and air temperature ϑ_3). This way you are able to observe even minor losses due to evaporation and are also able to correct for them. Please note: Directly before the weighing, you should unscrew the cap of the bottle and tighten it immediately afterwards to equilibrate the pressure inside and outside the bottle. To calculate the correction, please follow the step-by-step recipe:

Step 1: Calculate the air density $\rho_{\text{air},3}$

$$\rho_{\text{air},3} = \frac{0.348444 \frac{\text{kg/m}^3}{\text{hPa}} \cdot p_3 - \varphi_3 \cdot \left(0.252 \frac{\text{kg/m}^3}{\text{°C}} \cdot \vartheta_3 - 2.0582 \frac{\text{kg}}{\text{m}^3} \right)}{273.15 + \frac{1}{\text{°C}} \cdot \vartheta_3}$$

Step 2: Calculate the air buoyancy correction factor of the bottle $K_{\text{bottle},3}$

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$$K_{\text{bottle},3} = \frac{1 - \frac{\rho_{\text{air},3}}{\rho_{\text{cal},3}}}{1 - \frac{\rho_{\text{air},3}}{\rho_{\text{bottle}}}}$$

Step 3: Calculate the air buoyancy correction factor of the solution $K_{\text{solution},3}$

$$K_{\text{solution},3} = \frac{1 - \frac{\rho_{\text{air},3}}{\rho_{\text{cal},3}}}{1 - \frac{\rho_{\text{air},3}}{\rho_{\text{solution}}}}$$

Step 4: Calculate the mass $m_{\text{solution},3}$ of the solution at the time t_3 before sampling the first aliquot from the bottle

$$m_{\text{solution},3} = K_{\text{solution},3} \cdot \left(m_3 - \frac{m_{\text{bottle}}}{K_{\text{bottle},3}} \right)$$

Step 5: Calculate the loss Δm

$$\Delta m = m_{\text{solution},3} - m_{\text{solution}}$$

Step 6: In case it is reasonably small ($-10 \text{ mg} < \Delta m < 0 \text{ mg}$) this loss can be attributed to evaporation effects. In this case calculate an according evaporation losses correction factor $f_{\text{evap,cal}}$ (assuming the element content is still present completely in the bottle, causing a slightly elevated mass fraction of the element in question) and apply this to the mass fraction $w_{2,\text{cal}}$ you have been given for the calibration solution by PTB in order to retrieve the mass fraction $w_{3,\text{cal}}$ of the element at the time t_3 , which is the time you measure the sample solution.

$$w_{3,\text{cal}} = \frac{w_{2,\text{cal}}}{f_{\text{evap,cal}}} \quad \text{with} \quad f_{\text{evap,cal}} = \left(1 + \frac{\Delta m_{\text{cal}}}{m_{\text{solution,cal}}} \right)$$

Using the calculated mass fraction of the calibration solution ($w_{3,\text{cal}}$), you are now able to determine the mass fraction $w_{3,\text{smp}}$ in your sample solution with your method of choice. After you retrieved the mass fraction $w_{3,\text{smp}}$ in your sample solution, you need to apply the evaporation factor $f_{\text{evap,smp}}$ of the sample solution to the mass fraction $w_{3,\text{smp}}$ in order to retrieve the original mass fraction, $w_{2,\text{smp}}$, of the element at the time t_2 immediately after bottling the solution. Please report this corrected mass fraction $w_{2,\text{smp}}$ of the sample solution.

$$w_{2,\text{smp}} = f_{\text{evap,smp}} \cdot w_{3,\text{smp}} \quad \text{with} \quad f_{\text{evap,smp}} = \left(1 + \frac{\Delta m_{\text{smp}}}{m_{\text{solution,smp}}} \right)$$

When setting up an uncertainty budget please use the following standard uncertainties (type B, normal distribution, coverage factor $k = 1$) associated with the mass of the empty bottle

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m_{bottle} and with the mass of the solution m_{solution} , respectively: $u(m_{\text{bottle}}) = 0.0005$ g and $u(m_{\text{solution}}) = 0.0007$ g.

The following table summarizes all the symbols used throughout the equations above [6].

| Symbol | Unit | Quantity | Comment |
|-------------------------|------|---|---|
| m_{bottle} | g | Mass of the empty bottle (corrected for air buoyancy) | Individually listed for every bottle no. in the table sent to each participant |
| m_{solution} | g | Mass of the sample / calibration solution (corrected for air buoyancy) | Individually listed for every bottle no. in the table sent to each participant; determined immediately after bottling in the pilot laboratory (PTB) |
| $m_{\text{solution},3}$ | g | Mass of the sample / calibration solution (corrected for air buoyancy) | To be determined prior to sampling the first aliquot in the participant's laboratory |
| Δm | g | Mass difference (loss) of the sample / calibration solution (corrected for air buoyancy) | Difference between m_{solution} and $m_{\text{solution},3}$; determined prior to sampling in the participant's laboratory |
| m_1 | g | Apparent mass (reading of the balance) of the empty bottle | Determined in the pilot laboratory (PTB); used to calculate m_{bottle} |
| m_2 | g | Apparent mass (reading of the balance) of the sum of the empty bottle and the sample/calibration solution | Determined in the pilot laboratory (PTB) immediately after bottling; used to calculate m_{solution} |
| m_3 | g | Apparent mass (reading of the balance) of the sum of the empty bottle and the sample/calibration solution | Determined in the participant's laboratory prior to sampling; used to calculate $m_{\text{solution},3}$ |
| w_2 | g/kg | Mass fraction of the particular element | Value corrected for evaporation losses; calculated from w_3 |
| w_3 | g/kg | Mass fraction of the particular element | Value actually measured in the participant's laboratory |
| f_{evap} | 1 | Factor to correct the measured mass fraction for evaporation losses | To be calculated by the participant |
| $K_{\text{bottle},1}$ | g/g | Air buoyancy correction factor | Valid for the bottle material (PFA) at the time of the determination of m_1 |
| $K_{\text{bottle},2}$ | g/g | Air buoyancy correction factor | Valid for the bottle material (PFA) at the time of the determination of m_2 |
| $K_{\text{bottle},3}$ | g/g | Air buoyancy correction factor | Valid for the bottle material (PFA) at the time of the determination of m_3 |
| $K_{\text{solution},2}$ | g/g | Air buoyancy correction factor | Valid for the Al and Mo solutions at the time of the determination of m_2 |

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| | | | |
|--------------------------|-------------------|---|--|
| $K_{\text{solution},3}$ | g/g | Air buoyancy correction factor | Valid for the Al and Mo solutions at the time of the determination of m_3 |
| ρ_{cal} | kg/m ³ | Density of the calibration masses of the balance | Value for Mettler H315 balance used in the pilot laboratory (PTB) to determine m_1 and m_2 |
| $\rho_{\text{cal},3}$ | kg/m ³ | Density of the calibration masses of the balance | Value for the participant's balance used to determine m_3 ; usually 8000 kg/m ³ |
| $\rho_{\text{air},1}$ | kg/m ³ | Air density | At the time of the determination of m_1 in the pilot laboratory (PTB) |
| $\rho_{\text{air},2}$ | kg/m ³ | Air density | At the time of the determination of m_2 in the pilot laboratory (PTB) |
| $\rho_{\text{air},3}$ | kg/m ³ | Air density | At the time of the determination of m_3 in the participant's laboratory |
| ρ_{bottle} | kg/m ³ | Density of the bottle material (PFA) | Assumed to be sufficiently constant throughout the temperature range in question; $\rho_{\text{bottle}} = 2150 \text{ kg/m}^3$ |
| ρ_{solution} | kg/m ³ | Density of the particular sample/calibration solution | Determined in the pilot laboratory (PTB); listed in the text above; assumed to be sufficiently constant throughout the temperature range in question |
| p_1 | hPa | Air pressure | At the time of the determination of m_1 in the pilot laboratory (PTB) |
| p_2 | hPa | Air pressure | At the time of the determination of m_2 in the pilot laboratory (PTB) |
| p_3 | hPa | Air pressure | At the time of the determination of m_3 in the participant's laboratory |
| φ_1 | 1 | Relative air humidity | At the time of the determination of m_1 in the pilot laboratory (PTB) |
| φ_2 | 1 | Relative air humidity | At the time of the determination of m_2 in the pilot laboratory (PTB) |
| φ_3 | 1 | Relative air humidity | At the time of the determination of m_3 in the participant's laboratory; please use numerical values $0 \leq \varphi_3 \leq 1$ |
| ϑ_1 | °C | Air temperature | At the time of the determination of m_1 in the pilot laboratory (PTB) |
| ϑ_2 | °C | Air temperature | At the time of the determination of m_2 in the pilot laboratory (PTB) |
| ϑ_3 | °C | Air temperature | At the time of the determination of m_3 in the participant's laboratory |

Appendix

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7. References

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