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### **Establishing comparability and compatibility in the purity assessment of high purity zinc as demonstrated by the CCQM-P149 intercomparison**

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## Establishing comparability and compatibility in the purity assessment of high purity zinc as demonstrated by the CCQM-P149 intercomparison

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† Gregory C. Turk passed away on February 10, 2015. This publication is dedicated to Greg for his long-standing contributions to, and engagement in, Metrology in Chemistry.

## Abstract

For the first time, an international comparison was conducted on the determination of the purity of a high purity element. Participants were free to choose any analytical approach appropriate for their institute's applications and services. The material tested was a high purity zinc, which had earlier been assessed for homogeneity and previously used in CCQM-K72 for the determination of six defined metallic impurities. Either a direct metal assay of the Zn mass fraction was undertaken by EDTA titrimetry, or an indirect approach was used wherein all impurities, or at least the major ones, were determined and their sum subtracted from ideal purity of 100 %, or 1 kg/kg. Impurity assessment techniques included glow discharge mass spectrometry, inductively coupled plasma mass spectrometry and carrier gas hot extraction/combustion analysis. Up to 91 elemental impurities covering metals, non-metals and semi-metals/metalloids were quantified. Due to the lack of internal experience or experimental capabilities, some participants contracted external laboratories for specific analytical tasks, mainly for the analysis of non-metals. The reported purity, expressed as zinc mass fraction in the high purity zinc material, showed excellent agreement for all participants, with a relative standard deviation of 0.011 %. The calculated reference value,  $w(\text{Zn}) = 0.999\,873\text{ kg/kg}$ , was assigned an asymmetric combined uncertainty of  $+0.000025\text{ kg/kg}$  and  $-0.000028\text{ kg/kg}$ . Comparability amongst participating metrology institutes is thus demonstrated for the purity determination of high purity metals which have no particular difficulties with their decomposition / dissolution process when solution-based analytical methods are used, or which do not have specific difficulties when direct analysis approaches are used. Nevertheless, further development is required in terms of uncertainty assessment, quantification of non-metals and the determination of purity of less pure elements and/or for those elements suffering difficulties with the decomposition process.

## 1. Introduction

High purity materials in their elemental form can serve as a realization of *Le Système International d'Unités* (SI) unit *amount of substance* for specific elements. Solutions prepared from such materials using gravimetric techniques and the concept of molar mass are used as primary calibration solutions and are fundamental to many applications in analytical chemistry. Such prepared calibration solutions provide the traceability to the SI and are the metrological basis for elemental analysis.

The crucial point is the purity of such materials. Since ideal purity does not exist and cannot be realized, the purity of the material under use must be determined with a fit for purpose uncertainty. Relative uncertainties of approximately 0.01 % on the purity statement are required to achieve relative uncertainties of 0.05 % for primary calibration solutions, ultimately resulting in relative uncertainties of approximately 0.1 % for secondary calibration solutions. In almost all cases, a direct assay of the element itself is not possible because the available procedures are not sufficiently selective, and/or accurate or precise. Therefore, impurity assessments are often achieved only when all impurities are determined and the sum of their mass fractions is subtracted from the ideal purity value, which is 1 kg/kg.

Commonly, calibration solutions are homogeneous solutions of a high purity solvent and a metal (or salt). In most cases, the solvent is not the limiting factor, because the level of impurity with respect to the element of interest is usually negligible and rather easy to measure. The impurities associated with the metal are more critical, for three reasons. First, not a single element matters but rather the sum of impurities of all elements of the periodic table; second, metals are typically orders of magnitude less pure than solvents; third, some elemental impurities (e.g., O, H, C, and halogens) are not straightforward to quantify in metals. A very recent example of a complete characterization of a high purity Ag material is given in ref. [1]. More recently, a specific glow discharge mass spectrometric (GD-MS) procedure was debated as to whether it offers the capability of a primary method of measurement for the determination of purity of pure metallic elements [2].

1  
2 Many *National Metrology Institutes* (NMI) and *Designated Institutes* (DI) prepare elemental calibration  
3 solutions as calibrants for their measurement services, such as the certification of matrix *Reference*  
4 *Materials* or the provision of reference values for *Proficiency Testing* schemes. Other NMIs and/or DIs use  
5 their primary calibration solutions to calibrate secondary calibration solutions and provide both secondary  
6 and tertiary solutions to their customers. In both cases, the calibration solutions provide the source of  
7 traceability for the declared services, although at different levels of uncertainty. Hence, it is necessary for  
8 the NMI or DI to obtain data characterizing the purity of the pure metals or other materials used to prepare  
9 the primary solutions with measurement uncertainties meeting the needs of the above declared services.  
10 This is commonly undertaken as a “fit for purpose” assessment, appropriate for the uncertainty  
11 requirement of the service provided to customers.  
12

13  
14 As a consequence, total purity measurements remain a long-term strategy of the *Inorganic Analysis*  
15 *Working Group* (IAWG) within the *Consultative Committee for Amount of Substance: Metrology in*  
16 *Chemistry and Biology* (CCQM). As a first step, intercomparisons CCQM-P107 [3] and CCQM-K72 & P107.1  
17 [4] were conducted on the determination of the purity of zinc with respect to six defined metallic  
18 impurities. Zinc was chosen as the matrix because it is considered to be a comparatively easy matrix but of  
19 high relevance. These first steps were followed by this exercise, CCQM-P149, which is a comparison  
20 requiring complete purity characterization of zinc. Together with the key comparisons on the preparation  
21 of a copper calibration solution (CCQM-K143 & P181, currently running) and on the measurements  
22 necessary for linking calibration solutions to a primary solution (CCQM-K87 & P124 [5]), the complete  
23 procedure for the provision of SI-traceable calibration solutions to the field laboratory is covered.  
24  
25  
26  
27  
28

## 29 30 **2. Layout of the comparison**

31 In addition to achieving a comparison of measurement results, such as with other CCQM studies, CCQM-  
32 P149 is an attempt to obtain a snapshot of the actual procedures NMIs and DIs within the CCQM-IAWG  
33 apply to the purity characterization of their “fit for purpose” elemental standards. This means that the  
34 participants were fully free to use any approach they currently use to establish their purity assessments.  
35 The list of participants is reflected by the authors’ affiliation.  
36

37  
38 The mandatory measurand for all participants was the total purity of the distributed zinc material as  
39 required for its use as a primary zinc standard considering the participant’s uncertainty requirements,  
40 expressed as Zn mass fraction,  $w(\text{Zn})$ , in kg/kg. Whenever the impurity assessment is applied, the individual  
41 impurity contributions provided very valuable information and were regarded as mandatory interim results,  
42 when available. A rough guidance value for total purity ( $> 0.999$  kg/kg) was provided to all participants.  
43

44  
45 Analytical procedures with the highest metrological quality, such as isotope dilution mass spectrometry  
46 (IDMS), were in principle not excluded. It should be noted that, in contrast to conventional trace analysis,  
47 impurity analysis requires the quantification of *all* impurities. The entire range of elements, including  
48 mono-isotopic elements, is impracticable for IDMS alone. However, IDMS may be used to determine single  
49 impurities where lower uncertainties become necessary due to higher concentration levels.  
50

51  
52 Most suitable for this type of measurement seems to be procedures/methods, which are easily capable of  
53 multi-element analysis at trace levels, such as inductively coupled plasma mass spectrometry (ICP-MS) or  
54 glow discharge mass spectrometry (GD-MS). Important in this context is the ability to provide traceable  
55 measurement results. Procedures requiring matrix reference materials for calibration (e.g., solid sampling  
56 techniques) are not excluded, provided the matrix reference material used is stated, a proper uncertainty  
57 estimation is carried out and traceability is enabled. For non-metal determinations, carrier gas hot  
58 extraction, combustion analysis and other special techniques are currently the state-of-the-art. In contrast  
59 to the above described impurity assessment procedures, direct metal assay procedures capable of  
60 determining the analyte mass fraction, such as EDTA titration or coulometry, were also allowed.

All participants were free to apply whatever their current approach is to establish the purity assessment. A possible, however not complete, selection is given in the following:

- procedures which do not provide SI traceable measurement results in the shortest possible way;
- procedures which are not the ultimate reference procedure in the country;
- procedures which do not achieve the smallest possible uncertainty in the country;
- use of matrix CRMs for calibration;
- use of "standard" sensitivity factors for calibration (e.g. for GD-MS);
- expert judgments based on theoretical considerations, e.g. for noble gases;
- use of external contract laboratories for procedures that are not at the NMIs' or DIs' disposal;

Each participant was free to use any suitable procedure(s) for the measurement of the individual impurities. In case several procedures were used for one specific impurity, only one (composite) result could be reported.

No report template was provided for this comparison, because each participant used a different approach. However, every participant was asked to provide as many details as possible, including at least the following:

- a sufficiently detailed description of the quantification approach used (direct or indirect);
- description of the instrumental techniques applied;
- information on the calibration approach and the CRM used;
- traceability statement;
- use of any commercial laboratories for one or more measurement results;
- use of an expert judgement for one or more impurities;
- individual impurities and their measurement uncertainties;
- any other significant information.

The starting materials comprised five zinc ingots purchased from Alfa Aesar Johnson Matthey, Karlsruhe/DE having a nominal metal-based purity of 99.99 % (Lot No. F26S010). The same three ingots which had earlier been used for CCQM-K72 [4] were also used for CCQM-P149. The Zn ingots were cut into pieces of approximately 20 g. As the geometry of the ingots varied slightly, the resulting pieces showed a bar geometry with a diameter of 8 mm to 10 mm and a length between 35 mm and 45 mm. Each participant received one bottle containing one piece of about 20 g of the material. LGC received 6 additional pieces of pin geometry (about 3.5 mm x 3.5 mm x 20 mm) on request.

Investigations of the homogeneity of the material were already made for CCQM-K72 [4]. GD-MS measurements showed a spread of the results of < 20 % relative for Al, Ag, Cd, Cr, Ni and Tl, rendering the material suitable for CCQM-K72. Together with the reported results, the uncertainty contribution caused by inhomogeneity issues was estimated to be less than 10 % relative for the above-mentioned elements [3]. Thus, the material was well-suited for CCQM-P149.

### 3. Results

#### 3.1 Applied measurement techniques

The total of the reported measurement details provided a huge amount of information that would require several pages to list completely. Therefore, the amount of detail displayed here is restricted to the applied approach, the measurement and calibration technique, the sources of traceability and the elements measured and estimated (Table 1).

Two institutes, NMIJ and SMU, used direct metal assay and determined the purity by EDTA titration considering the main impurities influencing the Zn titration. All other institutes used the impurity

1  
2 assessment approach, wherein the impurities are measured, summed, and subtracted from the value of  
3 ideal purity, which is 1 kg/kg. For the quantification of the non-metals H, C, N, O and S, Carrier Gas Hot  
4 Extraction (CGHE), combustion analysis (CA) and GD-MS were mostly applied. Metals, metalloids and other  
5 non-metals were determined by GD-MS and/or ICP-MS techniques. Only BAM additionally used graphite  
6 furnace atomic absorption spectrometry (GF-AAS) for Fe and Pb and UNIIM applied spark source mass  
7 spectrometry (SSMS) for F and Cl. The applied calibration techniques were mainly external calibration (EC)  
8 and less frequently internal standardization (IS) or standard additions (SA) techniques. LGC and PTB used  
9 IDMS for major impurities. NRC used relative sensitivity factors to calibrate specific elements by GD-MS.  
10  
11

12 Six of thirteen institutes contracted external laboratories for the quantification of the major non-metals (H,  
13 C, N, O, and S), four institutes performed the measurements in-house and three institutes did not perform  
14 measurements of H, C, N, O and S, two of which applied the metal assay approach. It must be noted that  
15 for two of the latter three institutes, measurement of H, C, N, O and S is not necessary, as they applied  
16 direct metal assay using EDTA titration. From those institutes applying the impurity assessment, eight  
17 institutes measured 75 or more elements and three institutes reported between 18 and 26 impurities. Only  
18 three institutes, BAM, NIM and UNIIM, reported values for all natural occurring elements, whereby at least  
19 for noble gases and radioactive elements the values are based on estimates. The reported sources of  
20 traceability in most cases point to the NMI itself, NIST, BAM or commercial providers of high purity  
21 materials or calibration solutions. In some cases, such commercial providers claim traceability back to NIST,  
22 BAM, or another NMI.  
23  
24  
25  
26  
27

### 28 3.2 Purity of the Zn material as reported by the participants

29  
30 Using the analytical procedures summarized in Table 1, each participant obtained a result for the purity of  
31 the Zn material, expressed as Zn mass fraction,  $w(\text{Zn})$ , in kg/kg. The reported values with their (symmetric)  
32 measurement uncertainties are listed in ascending order in Table 2. Results and uncertainties were taken  
33 from the reports as provided. If only expanded uncertainties were reported, the standard uncertainty was  
34 calculated using the reported coverage factor, or vice versa. The arithmetic mean and the median were  
35 calculated for the complete data set ( $n = 13$ ) of the reported values.  
36  
37

38 Observation: All reported results in Table 2 confirm the nominal purity to be  $> 0.999$  kg/kg. Based on the  
39 reported values, no distinction between the direct metal assay and the impurity assessment procedure can  
40 be made. However, measurement uncertainties for the metal assay using EDTA titration are, in most cases,  
41 larger by a factor of 5 to 10. The results show a tight agreement for the purity statement of the P149 Zn  
42 sample. The spread of the results, reflected as the relative standard deviation, is 0.011 %, which is also  
43 demonstrated by the standard uncertainty of the calculated arithmetic mean and median.  
44  
45

46 Establishment of the reference value (RV): Given the very inhomogeneous uncertainty estimates from the  
47 different NMIs, a largest consistent subset approach executed on the original data is not applicable in this  
48 case. Physical limits such as the fact that purity values above 1 are not possible normally skew data  
49 distributions in one or the other direction. Using normal Gaussian statistics on such distributions is  
50 misleading, at least in the majority of cases. Therefore, the arithmetic mean as well as the median are  
51 unsuitable for providing a reference value. Suitable data transformation techniques help to transform data  
52 into a space where they may be considered normally distributed, allowing further processing using  
53 "classical" statistics.  
54  
55

56 The original data ( $n = 13$ ), together with three transforms, were processed, the latter being log-normal, the  
57 folded power transform [8], and the well-known  $z'$  transform used for the assessment of correlation  
58 coefficients (which are limited by -1 and 1). The folded power transform has the great advantage that it still  
59 covers the value of unity, which is not possible when using log-normal transforms. However, values above  
60 unity (which occur with assay procedures), are also not covered by this transform.

As already suspected by visual inspection, the original data display a significant skewness together with a significant kurtosis. The log-normal transform reduces skewness, but not to the needed extent. For the case given, only the power transform reduces skewness of the data set to insignificance, and kurtosis to around the critical value. Thus, this transform was used to further process the data based on (eqn. 1):

$$y = w^p - (1 - w)^p \quad \text{eqn. 1}$$

with  $p = 0.35$ . A reduction of skewness to zero might be achieved using a power of  $\approx 0.38$ , but kurtosis is set to approximately zero only at a power of  $\approx 0.42$ . Thus, the original proposal has been retained. Having found a result in the transformed space, re-transformation may be computation-intensive, but does not really require Monte Carlo simulations.

With the values from the power transform, the  $E_n$  number leads to consistency for most of the participating labs (see Table 2). The reference value was re-confirmed. Uncertainties in the original space are slightly asymmetric, but also a bit adjusted. For the calculation of the  $E_n$  number, direction was considered, i.e., values above the reference value were treated against the (asymmetric) uncertainty above, and vice versa.

Assessment of the results: The excellent agreement is also visualized in Fig. 1, where the “Degrees of Equivalence” (DoE, eqn. 2) for all reported results are displayed together. The corresponding reference value was obtained using the power transformation technique, because the distribution is slightly asymmetric or skewed. The mean (Table 2) in this case would unacceptably favour the low values and is therefore rejected. The median (Table 2) would provide a good estimate, but the associated uncertainty is underestimated and does not reflect the physical limits. What catches the eye in Fig. 1 is that not all DoEs encompass zero within their expanded uncertainty, which suggests a potential underestimation of the measurement uncertainty. However, it must be pointed out that the majority (77 %) of the reported results are compatible with the reference value and show perfect agreement for the purity characterization of a real-world sample.

$E_n$  number: According to VIM3 [9], measurement results are compatible when the difference,  $d_i$ , between them is smaller than a chosen multiple, here  $k = 2$ , of the standard uncertainty of this difference (eqn. 2). Eqn. 2 can be transformed into eqn. 3, expressing the so-called  $E_n$  number. For all results showing an  $E_n$  number equal to or below 1 ( $E_n \leq 1$ ) compatibility with the reference value is demonstrated to be established, which is consequently marked with the verdict “+” in the column marked “Compatibility” in Table 2, or with the verdict “-”, when compatibility is not demonstrated. This concept, of course, corresponds with the model of the “Degree of Equivalence” (DoE), which is applied for Key Comparisons.

$$|d_i| < k \cdot u_{d_i} \quad \text{eqn. 2}$$

for  $k = 2$  follows

$$E_n = \frac{|d_i|}{U(d_i)} = \frac{|(x_i - x_{\text{Ref}})|}{2 \cdot \sqrt{u^2(x_i) + u^2(x_{\text{Ref}}) - 2 \cdot \text{cov}(x_i, x_{\text{Ref}})}} \quad \text{eqn. 3}$$

Correlations between a single participant’s result and the reference value as well as correlations between the participants’ results were not considered, because the bases for quantitating such correlations were unclear. Therefore, the covariances in eqn. 3 were set to zero.

Expansion of uncertainties: The dataset presented in Table 1 and Fig. 1 clearly show that results from 10 of the 13 participants are compatible with the reference value, while 3 institutes are not compatible. Such problems arise, mainly as a consequence of either reporting estimates of uncertainty which are considered too small, or because of the existence of undetected components of systematic error (the concept of additional or so-called “dark” uncertainties [10], which are not contained in the cause-and-effect model of the “Guide to the expression of uncertainty in measurement” [6]). The latter have been introduced and applied to such data sets in recent years. However, further adding “dark” uncertainties obtained from a

1  
2 Bayesian Monte Carlo to the complete data set would penalize all participant's data which already are  
3 compatible with the reference value.  
4

5 Given the above, only three institutes need a slight increase in their stated uncertainties, namely NIST, LNE  
6 and LGC, mainly because of their low uncertainty estimates. When (quadratically) adding uncertainties of  
7 0.000 0131 kg/kg, 0.000 0262 kg/kg and 0.000 0057 kg/kg to the uncertainties reported by NIST, LNE and  
8 LGC, respectively, the full dataset becomes consistent and the participants results become equivalent in  
9 their measurement capabilities for the purity statement.  
10

11 Other participants also grossly underestimated their uncertainties and could be considered compliant with  
12 the reference value only due to its relatively large uncertainty: e.g., VNIIM stated an uncertainty of  
13 0.000 0017 kg/kg while the uncertainty of the reference value is more than 12 times larger and just covers  
14 the deviation of the measured value. A harmonisation of the uncertainty calculation approaches is thus  
15 desirable.  
16  
17

18 Note: The expansion of uncertainties is a tool to make the complete dataset consistent. This does not lead  
19 to new information on the comparison, but rather information on the minimum uncertainty required to  
20 make the individual results compatible with the reference value.  
21  
22

### 23 3.3 Individual impurities

24  
25 Although the measurand for this comparison is the total purity of Zn, the mass fractions of individual  
26 impurities, which are the basis of the indirect procedure or for providing corrections for the direct  
27 procedure, provide additional valuable information. The five major impurities in descending order are Fe >  
28 Pb > C > Cu > O, with mass fractions between 33 mg/kg and 6 mg/kg. This is in slight contrast to normal  
29 expectations for transition metals, which often presume oxygen or another non-metal to lead this list. The  
30 total of the reported impurities (> 600 values), however, is too large to display in the form of a table or  
31 figure within the manuscript itself. Therefore, five representative impurities have been selected for  
32 discussion: hydrogen as an example of a non-metallic impurity, and thallium as an example of a metallic  
33 impurity, both with mass fractions in the low mg/kg range; iron was selected as an example element of  
34 relatively high mass fraction (> 10 mg/kg); gallium and nitrogen were selected as impurities bearing some  
35 difficulties with the quantification.  
36  
37  
38  
39

40 In the following, the impurities are either graphically displayed or presented in tabular form, depending on  
41 the clarity of the overall result. In both cases, the results are listed in ascending order; results and  
42 associated uncertainties were taken from the data as reported. Uncertainties showing more than two digits  
43 were reduced to two digits. Upper limit values were truncated such that only one digit remained for the  
44 uncertainty. When only expanded uncertainties were reported, the standard uncertainty was calculated  
45 using the reported coverage factor.  
46  
47

48 Whenever compatibility between the majorities of the reported results was established, the mean value  
49 and the median for each measurand were added to the tables or figures. The displayed uncertainties are  
50 combined standard uncertainties as reported by the participants or as calculated for the mean and the  
51 median following footnote 1 in Table 2. The selected consensus values and the standard uncertainties are  
52 displayed in the figures as dotted lines.  
53  
54

55 Both the median and arithmetic mean have their advantages and disadvantages for establishing the  
56 consensus value. For ideal (or close to ideal) data sets, as in the case of H, there is hardly a difference. In  
57 the presence of asymmetric distributions, as in the data set for Tl, the median is more robust and the  
58 corresponding uncertainty is smaller than the uncertainty of the mean. Generally, the median is more  
59 robust towards inconsistent measurement results or asymmetric distributions than the arithmetic mean.  
60 Therefore, the median appears more appropriate for the evaluation of the interlaboratory comparison and

1  
2 is used as the consensus value for datasets having five or more reported values, while the mean is chosen  
3 as the consensus value for datasets having three or four reported values. Values being reported as “less  
4 than values” are not considered for calculating the consensus values.  
5

6 Each result reported by the participants for the individual impurities was additionally tested for its  
7 compatibility with the reference value. In the case of reported “less than values”, two cases are considered:  
8 1) if an uncertainty is reported, the “less than value” is treated as a normal value, however, only for the  
9 compatibility; 2) if no uncertainty is reported, the “less than value” is regarded as compatible when it is  
10 larger than the reference value minus the expanded uncertainty, otherwise it is regarded as incompatible.  
11 When the relative standard uncertainty of the reference value is less than 30 %, a relative standard  
12 uncertainty of 30 % was attributed to the reference value and was used for calculating the compatibility.  
13  
14

15 Hydrogen was selected as a representative non-metal impurity. The reported mass fractions of hydrogen  
16 (Fig. 2) show a standard deviation of 64 %, demonstrating very good agreement amongst all reported  
17 results, especially considering the low mass fraction. The median was selected as the consensus value for  
18 hydrogen (see above) and the compatibility between the median and the individual results was calculated  
19 using eqn. 3. Except for the result reported by CENAM, all reported results are compatible with the median.  
20 Considering the intrinsic difficulties with adsorbed water layers, the low level of hydrogen ( $\approx 3$  mg/kg), and  
21 the intended use for purity characterization, the overall result can be considered as very good. For the  
22 purpose of impurity analysis in zinc, compatibility of measurement results for hydrogen as an analyte at this  
23 concentration level is possible with a standard uncertainty of 35 %.  
24  
25  
26

27 Thallium was selected as a representative metallic impurity. The reported mass fractions of thallium (Fig. 3)  
28 show a standard deviation of 29 %, demonstrating an excellent agreement amongst all reported results.  
29 The median was selected as the consensus value for thallium (see above) and the compatibility between  
30 the median and the individual results was calculated using eqn. 3. Eleven out of twelve values are  
31 compatible with the median within a nominal uncertainty of 30 % ( $k=1$ ). The median also agrees with the  
32 reference value for thallium ( $KCRV = 0.861$  mg/kg,  $u_c = 0.044$  mg/kg) obtained in CCQM-K72 using the same  
33 batch of test material [3]. This reference value was determined by applying ID-MS as a primary method of  
34 measurement [3].  
35  
36

37 Except for the low level ( $\approx 0.8$  mg/kg) in a metal matrix, no specific difficulty could be observed for thallium.  
38 Nevertheless, the overall result can be considered as excellent. For the purpose of impurity analysis in zinc,  
39 compatibility of measurement results for thallium as an analyte is possible with a standard uncertainty of  $\leq$   
40 30 %.  
41  
42

43 Iron was selected as an example of a metallic impurity present at a relatively high mass fraction ( $> 10$   
44 mg/kg). For high level impurities, the relative measurement uncertainty must be significantly lower  
45 compared to low level impurities, otherwise the uncertainty of the total purity increases. In a  
46 Gedankenexperiment, let us consider the analysis of two metal samples which are identical in their  
47 impurity content except for their significant iron impurity: both samples show mass fractions of 1 mg/kg  
48 with a relative expanded ( $k=2$ ) uncertainty of 100% for 90 of the 91 naturally occurring elements; sample 1  
49 has an iron mass fraction of 10 mg/kg with a relative expanded ( $k=2$ ) uncertainty of 100% while sample 2  
50 offers an iron mass fraction of 100 mg/kg. In order to obtain the same expanded uncertainty for the purity  
51 as for sample 1 ( $\approx 14$  mg/kg), the absolute expanded uncertainty for the iron determination in sample 2  
52 must be  $\approx 10$  mg/kg. This results in a relative expanded uncertainty of 10 %, which is a factor of ten lower  
53 than for sample 1. Admittedly, most real-world examples are not so simple and clear, but the tendency is  
54 the same. Higher level impurities must therefore be analysed with significantly lower uncertainties to  
55 enable a constant or pre-set target uncertainty for purity.  
56  
57  
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59 In the case of iron, the reported mass fractions (Fig. 4) show a standard deviation of 51 %, demonstrating  
60 very good agreement amongst all reported results. Two groups of results occur, one at 25 mg/kg and one at  
5 mg/kg. As LGC applied ID-MS for quantitation, 25 mg/kg is likely the more reliable estimate. However,

1  
2 inhomogeneity issues cannot be completely excluded, especially for low level concentrations in a metal  
3 matrix. The median was thus selected as the consensus value for iron (see above) and the compatibility  
4 between the median and the individual results was calculated using eqn. 3. Ten out of thirteen values are  
5 compatible with the median within a nominal uncertainty of 30 % ( $k=1$ ). The three incompatible values are  
6 either significantly lower (INM) or significantly higher (CENAM, LNE). For the purpose of impurity analysis in  
7 zinc, compatibility of measurement results for iron as an analyte is possible with a standard uncertainty of  
8  $\leq 30$  %.

9  
10  
11 Gallium was selected as an example of a metal impurity having specific difficulties with quantification. The  
12 reported data (Table 3) fall into two groups: four of the reported mass fractions of gallium (LGC, NIM, LNE,  
13 PTB) show a standard deviation of 93 % with a hypothetical mean value of 1.47 mg/kg. The majority of the  
14 participants (NRC, NIST, BAM, NMIJ, UNIIM, VNIIM, CENAM) reported LOD values of  $< 1$  mg/kg, which are in  
15 good agreement with the mass fraction values reported by LGC and NIM; only LNE and PTB reported  
16 gallium mass fractions above 1 mg/kg. Inhomogeneity may play a role at this very low concentration level.  
17 However, it is more likely that matrix based interferences ( $^{68}\text{Zn}^{1}\text{H}$  on  $^{69}\text{Ga}$ ,  $^{70}\text{Zn}^{1}\text{H}$  on  $^{71}\text{Ga}$ ) biased the  
18 quantification of Ga by ICP-MS and led to elevated values. A reference value, therefore, could not be  
19 calculated.

20  
21  
22 Considering all results as equally valid, a mass fraction of  $< 1$  mg/kg seems to be more realistic than the  
23 mean of the four quantitative results. With a gallium mass fraction of  $< 1$  mg/kg, which can be described as  
24  $(0.5 \pm 0.5)$  mg/kg, all reported results agree within their expanded uncertainty. A better agreement could  
25 not be achieved for gallium.

26  
27  
28 Nitrogen was selected as a typical non-metallic impurity having specific difficulties with quantitation. The  
29 reported data (Table 4), which show a standard deviation of 136 %, fall into four groups: two low mass  
30 fractions (LGC, NRC) at around 0.05 mg/kg, two medium mass fractions (CENAM, PTB) at 0.5 mg/kg and 1.2  
31 mg/kg, two high mass fractions (NIST, LNE) between 8 mg/kg and 10 mg/kg and three mass fractions (BAM,  
32 NIM, UNIIM) with values below the specific detection limits. This disagreement cannot be resolved,  
33 especially as no technical reasons are known for discriminating against any of the applied analytical  
34 techniques. It may be assumed that the ambient nitrogen background and surface-adsorbed layers give rise  
35 to major problems in some analyses. Additionally, the relatively high detection limits of some analytical  
36 procedures (BAM, NIM, UNIIM) do not allow a more detailed assessment of the nitrogen mass fraction.

37  
38  
39 However, all reported results agree that the nitrogen mass fraction is less than 21 mg/kg. Compatibility of  
40 measurement results for nitrogen mass fractions below 21 mg/kg could not be achieved.

#### 44 45 **4. Conclusion**

46  
47 The analytical challenge was the quantification of the overall purity of a high purity (metallic) elemental  
48 material using the direct as well as the impurity assessment approaches and included quantification of non-  
49 metallic elements. The mass fractions of the impurities are summed and used to calculate a purity  
50 statement for the pure element. Up to 91 elemental impurities had to be assessed. Individual impurities  
51 present at the low mg/kg range or below hinder quantification due to the high matrix load, which may  
52 cause numerous interferences. For the purity determination of pure metallic zinc, the direct and impurity  
53 assessment approaches were applied with different variations. A perfect fit-for-purpose agreement  
54 between all reported results was achieved, clearly supported by the corresponding relative standard  
55 deviation of 0.011 %. Differences amongst the applied approaches cannot be elucidated on the basis of  
56 their reported results, excepting the fact that the uncertainties provided for the metal assay using EDTA  
57 titration are usually larger by a factor of approximately five to ten. Comparability and accuracy of the  
58 measurement results within the participating group of NMIs and designated laboratories is thus  
59 demonstrated to be established. Concerning the applicability, it must be noted that all approaches applied  
60

1  
2 in this study were well suited to assess the purity of pure elements to be used for calibration standards. For  
3 characterizing and certifying primary pure substances, however, realizing the SI amount of substance unit  
4 for the same element, it is indispensable to use only the impurity assessment approach.

5  
6 Limiting consideration to only the major impurities in this Zn sample, a surprisingly good result has been  
7 obtained. Admittedly, for some of the non-metallic impurities such as H and N, the spread of results is quite  
8 large and often exceeds a standard deviation of 100 %. However, the majority of the reported results show  
9 compatibility within a standard uncertainty of 35 % to 71%. For the rest of the major impurities the results  
10 are very good to excellent and compatibility of measurement results is achieved within a standard  
11 uncertainty of  $\leq 30\%$ , except for Ga (and Ge although not presented here) where the most probable value  
12 is below 1 mg/kg and where interferences impede an accurate quantification at this low mass fraction.  
13 However, it must be stressed that the measurand is the purity of zinc, expressed as mass fraction  $w(\text{Zn})$  and  
14 not the mass fractions of individual impurities. The major advantage of the impurity assessment is that for  
15 high purity elements ( $> 0.999$  kg/kg) the relative measurement uncertainties of individual impurities can be  
16 relatively large (30 % to 100 %), while the uncertainty of the purity remains relatively small ( $\approx 0.001$  kg/kg).  
17 The reason for this, of course, is that the individual impurities are summed and subtracted from ideal purity  
18 (1 kg/kg). Additionally, from a very simplistic viewpoint, the mass fraction of individual impurities in high  
19 purity elements is typically  $< 100$  mg/kg, and their associated uncertainties are also  $< 100$  mg/kg. Thus, the  
20 uncertainty on the purity is  $< 1000$  mg/kg or  $< 0.001$  kg/kg, when considering approximately 100 individual  
21 impurities.  
22  
23  
24  
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26 Based on the obtained results it can be stated that all listed approaches (Table 1) are capable of performing  
27 a purity determination of pure (metallic) elements which do not have intrinsic difficulties with their  
28 decomposition / dissolution process when analytical procedures that require solution samples are used.  
29 This also applies when direct analysis approaches are used, whereby the dissolution process has no impact;  
30 in this case, the applicability of this comparison is to all pure (metallic) elements, excepting those with  
31 specific difficulties in direct analysis approaches. The majority of participants in this pilot study determined  
32 individual impurities with relatively large uncertainties. Hence, the capability for performing purity  
33 determinations is proven only for cases where the overall purity of the metal is equal to or better than  
34  $0.999$  kg/kg and the expanded uncertainty of the sum of the (mass fractions of the) impurities is not greater  
35 than  $0.001$  kg/kg.  
36  
37  
38

39 In summary, it can be concluded that an excellent result has been obtained in CCQM-P149 for the purity  
40 characterization of a real-world sample.  
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43

## 44 5. Outlook

45 CCQM-P149 was the first worldwide comparison on assessment of purity of a real-world element. Although  
46 this comparison demonstrated excellent agreement amongst the thirteen participating NMIs/DIs  
47 concerning the purity determination of pure metallic elements, issues open for further development still  
48 remain.  
49  
50

51 Several participants provided combined uncertainties in the range of  $10^{-6}$  kg/kg, which are too optimistic. In  
52 the case of purity assessment, the smallest measurement uncertainties are often underestimated because  
53 the complete assessment includes several inputs, such as sufficient homogeneity and expert judgment for  
54 specific impurities which either cannot be measured or are assumed to be absent. Therefore, a realistic  
55 uncertainty budget requires profound expert knowledge and continuous verification of the applied  
56 uncertainty calculation strategy. A harmonization of the uncertainty calculation in the case of purity  
57 assessment would be advantageous.  
58  
59  
60

The agreement in the reported mass fractions of non-metals such as H, C, N and O was sufficient in that it  
did not compromise the overall result, the purity of Zn. However, for materials showing higher mass

1  
2 fractions of non-metals, such performance may become insufficient. Therefore, improvement in the  
3 measurement capabilities for non-metals is urgently needed.  
4

5 With CCQM-P149, the capability for purity determination of high purity elements not having particular  
6 difficulties with their decomposition process has been demonstrated; it has been as well demonstrated for  
7 all high purity elements not having specific difficulties with direct analysis approaches. Elements being  
8 available only with reduced purity (e.g., Mo), meaning higher mass fractions of specific impurities, require a  
9 more accurate quantification of those impurities, as the measurement uncertainty plays a bigger role the  
10 larger the mass fractions of the individual impurities are. As well, it should be intrinsically evident that the  
11 purity determination of a pure element showing difficulties with the dissolution process and/or the non-  
12 metal quantification will require further development to achieve sufficient international compatibility.  
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23 should not remain unacknowledged.  
24  
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26  
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## 28 **7. Disclaimer**

29  
30 Certain commercial entities, equipment or materials may be identified in this publication in order to  
31 describe an experimental procedure or concept adequately. Such identification is not intended to imply  
32 recommendation or endorsement by any of the study participants, nor is it intended to imply that the  
33 entities, materials or equipment are necessarily the best available for the purpose.  
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Table 1: Summary of the approach, applied analytical techniques, calibration strategies used, sources of traceability and determined and estimated impurities (abbreviations are explained above).

Institute	Approach	Technique(s)	Lab	Calibration	Traceability source	Elements		
						measured	estimated	total
BAM	indirect	CGHE, CA	in-house	EC	BAM <sup>1</sup>	H, C, N, O	halogens, noble gases, radioactive elements, 16	91
		GD-MS	in-house	EC	BAM <sup>1</sup>	Li, B, Mg, Si, P, K, Se, Sr, Os		
		ICP-SFMS, GF-AAS	in-house	EC	BAM <sup>1</sup>	63 elements; Fe, Pb by GF-AAS		
CENAM	indirect	CGHE, CA	in-house	EC	BAM	H, C, N, O, S	16	82
		ICP-SFMS	in-house	EC	NIST, CENAM, Commercial	61 elements		
INM	indirect	CGHE, CA	external	EC	BAS	H, C, O, S	-	18
		ICP-SFMS	in-house	SA + IS	NIST	14 elements		
LGC	indirect	GD-MS	external	EC			C, N, O, F, Cl, Br, I	26 <sup>3</sup>
		ICP-MS	in-house	SA	LGC	16 elements		
		ICP-MS	in-house	IDMS	NIST, LGC	Cr, Fe, Cu, Ni, Ag, Pb		
LNE	indirect	CGHE, CA	external	EC		H, C, N, O, S	-	22
		ICP-MS	in-house	SA	LNE	10 elements		
		ICP-MS	in-house	EC	Merck	7 elements		
NIM	indirect	CGHE, CA	in-house		Commercial	H, C, N, O, S	noble gases, radioactive elements	91
		GD-MS	in-house			60 elements		
		Multiple <sup>2</sup>	in-house		NIM	12 elements		
NIST	indirect	CGHE, CA	external	EC	NIST, Commercial	H, C, N, O, S	-	76
		GD-MS	external	EC	NMIs, Commercial	71 elements, incl. S		
NMIJ	direct	EDTA titration	in-house		NMIJ	Zn	-	17
		ICP-SFMS	in-house	EC + IS	NMIJ	16 elements		
NRC	indirect	GD-MS	in-house	EC/IS/RSF	BAM, IRMM, NIST	76 elements	-	76
PTB	indirect	CGHE, CA	external			H, C, N, O	-	77
		GD-MS	external			76 elements		
		ICP-SFMS	in-house	EC + IDMS	BAM, NIST, CENAM	65 elements, Pb by IDMS		
SMU	direct	EDTA titration	in-house	Coulometry	SMU	Zn	-	3
		Visual colorimetry	in-house	EC	SMU	Fe, Pb		
UNIIM	indirect	CGHE, CA	external	EC, SA	UNIIM	H, C, O, N, S	noble gases, radioactive elements, 14	91
		ICP-QMS, ICP-OES	in-house	EC, SA	NIST, UNIIM	70 elements		
		SS-MS	external	EC, SA		F, Cl		
VNIIM	indirect	ICP-QMS	in-house	EC	NIST, VNIIM	19 elements	-	19

<sup>1</sup> by means of commercial traceable standards, crosschecked in-house by BAM

<sup>2</sup> GD-MS, GF-AAS, ICP-OES, ICP-SFMS

<sup>3</sup> in total 75 elements were measured but 49 were found < LOD and were thus not reported

Table 2: Results for purity of zinc, expressed as mass fraction  $w(\text{Zn}) / (\text{kg}/\text{kg})$  with associated uncertainties obtained from the as reported data.

NMI/DI	Mass fraction $w(\text{Zn}) / (\text{kg}/\text{kg})$				$u_{c,\text{rel}} / \%$	Compatibility with RV	
	Value	$u_c^1$	$k$	$U^1$		$E_n$	Verdict
CENAM	0.999 55	0.000 23	2	0.000 45	0.023	0.713	+
NIST	0.999 772	0.000 040	1.967	0.000 078	0.0040	1.035	-
LNE	0.999 793	0.000 012	2	0.000 023	0.0012	1.320	-
SMU	0.999 84	0.000 30	2	0.000 59	0.030	0.056	+
UNIIM	0.999 855	0.000 009	2	0.000 017	0.000 85	0.310	+
INM	0.999 86	0.000 10	2	0.000 20	0.010	0.063	+
BAM	0.999 874	0.000 025	2	0.000 050	0.0025	0.012	+
VNIIM	0.999 8990	0.000 0017	2	0.000 0034	0.000 17	0.524	+
NRC	0.999 90	0.000 06	2	0.000 11	0.0055	0.223	+
NIM	0.999 911	0.000 006	2	0.000 011	0.000 55	0.751	+
PTB	0.999 911	0.000 014	2	0.000 028	0.0014	0.669	+
LGC	0.999 9235	0.000 0010	2	0.000 0020	0.000 10	1.023	-
NMIJ	0.999 99	0.000 20	2	0.000 39	0.020	0.297	+
Mean <sup>2</sup>	0.999 852	0.000 030	2	0.000 059	0.0030		
Median <sup>2</sup>	0.999 874	0.000 020	2	0.000 040	0.0020		
<b>RV</b>	<b>0.999 873</b>	<b>- 0.000 028</b>	<b>2</b>	<b>- 0.000 056</b>	<b>- 0.0028</b>	<b>Reference value</b>	
		<b>+ 0.000 025</b>	<b>2</b>	<b>+ 0.000 049</b>	<b>+ 0.0025</b>	<b>Reference value</b>	

<sup>1</sup> The combined standard uncertainties,  $u_c$ , of the participants' values have been calculated when only expanded uncertainties have been reported or vice versa. In case of the Mean, the Median and the Reference Value the expanded uncertainties have been calculated from the unrounded combined standard uncertainties. Therefore, a difference of 1 in the last digit may occur between the twofold standard uncertainty and the expanded uncertainty.

<sup>2</sup> standard uncertainties of the arithmetic mean and the median are calculated as follows:  $u_{\text{Mean}} = \frac{s}{\sqrt{n}}$  [6]

and  $u_{\text{Median}} = \sqrt{\frac{\pi}{2n}} \sqrt{\frac{n}{n-1}} \frac{MAD}{\alpha} \approx \frac{1.858}{\sqrt{n-1}} MAD$  [7], which applies for normal distribution only.

ACCEPTED

Table 3: Results for the mass fraction of gallium in pure zinc,  $w(\text{Ga})$  / mg/kg, with associated combined uncertainties.

NMI/DI	Mass fraction $w(\text{Ga})$ / (mg/kg)		$u_{c,rel}$ / %
	Value	$u_c$	
NRC	< 0.002	0.001	50
NIST	< 0.01	n.r.	n.a.
BAM	< 0.01	0.01	100
LGC	0.06	0.03	50
NMIJ	< 0.1	n.r.	n.a.
UNIIM	< 0.2	n.r.	n.a.
VNIIM	< 0.5	n.r.	n.a.
NIM	0.7	1.4	200
CENAM	< 0.84	0.24	29
LNE	2	1	50
PTB	3.1	1.6	52

n.r. not reported

n.a. not available

Table 4: Results for nitrogen mass fraction in pure zinc,  $w(\text{N})$  / mg/kg, with associated combined uncertainties.

NMI/DI	Mass fraction $w(\text{N})$ / (mg/kg)		$u_{c,rel}$ / %
	Value	$u_c$	
LGC	0.05 <sup>1</sup>	n.r.	n.a.
NRC	0.056	0.084	150
PTB	0.50	0.50	100
NIM	< 1.10	0.55	50
CENAM	1.2	0.37	31
UNIIM	< 5	n.r.	n.a.
LNE	8.3	3.1	37
NIST	10	3	30
BAM	< 21.0	10.5	50

<sup>1</sup> information value

n.r. not reported

n.a. not available

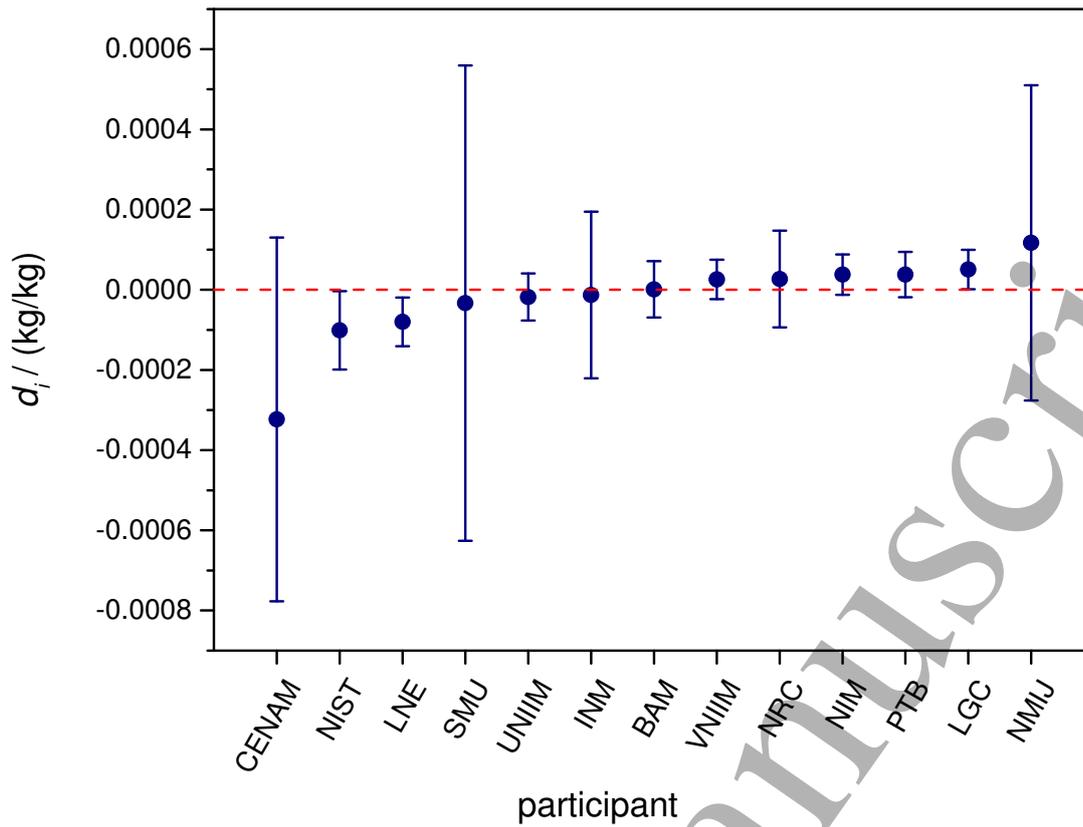


Fig. 1: Plot of the DoE data for the purity of zinc, expressed as mass fraction  $w(\text{Zn})$  in (kg/kg). The blue circles show the degree of equivalence (DoE),  $d_i$ , while the error bars denote the expanded uncertainty associated with the degree of equivalence  $U(d_i)$ . Results that encompass zero within their uncertainty interval are considered to be consistent with the reference value.

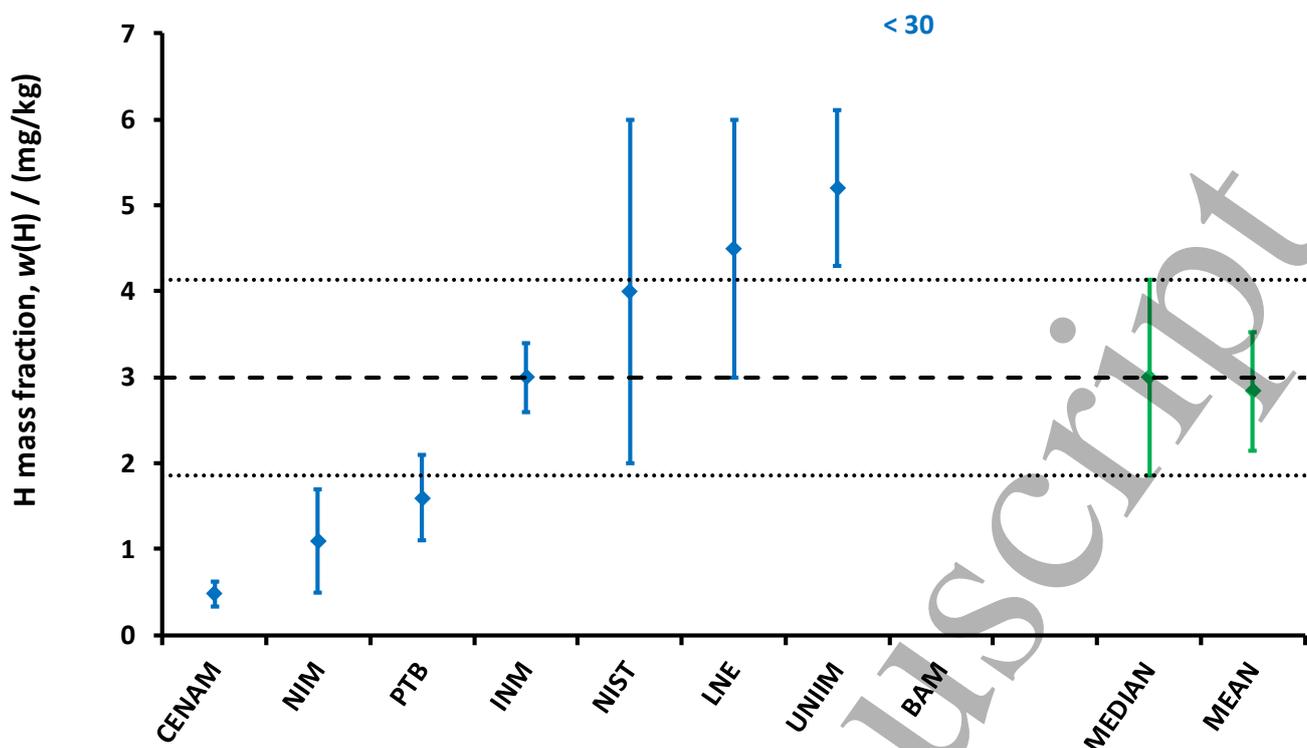


Fig. 2: Results for the hydrogen mass fraction in pure zinc with associated combined uncertainties ( $k=1$ ).

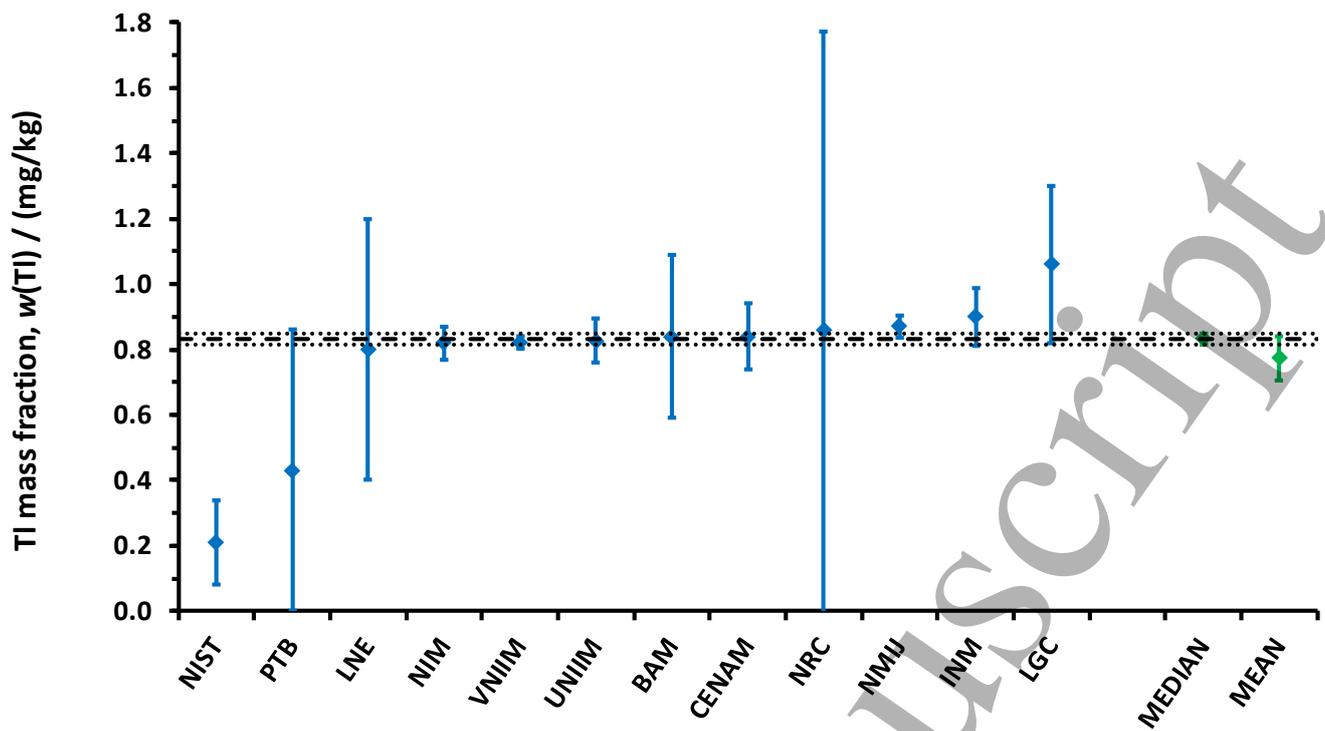


Fig. 3 Results for the thallium mass fraction in pure zinc with associated combined uncertainties ( $k=1$ ).

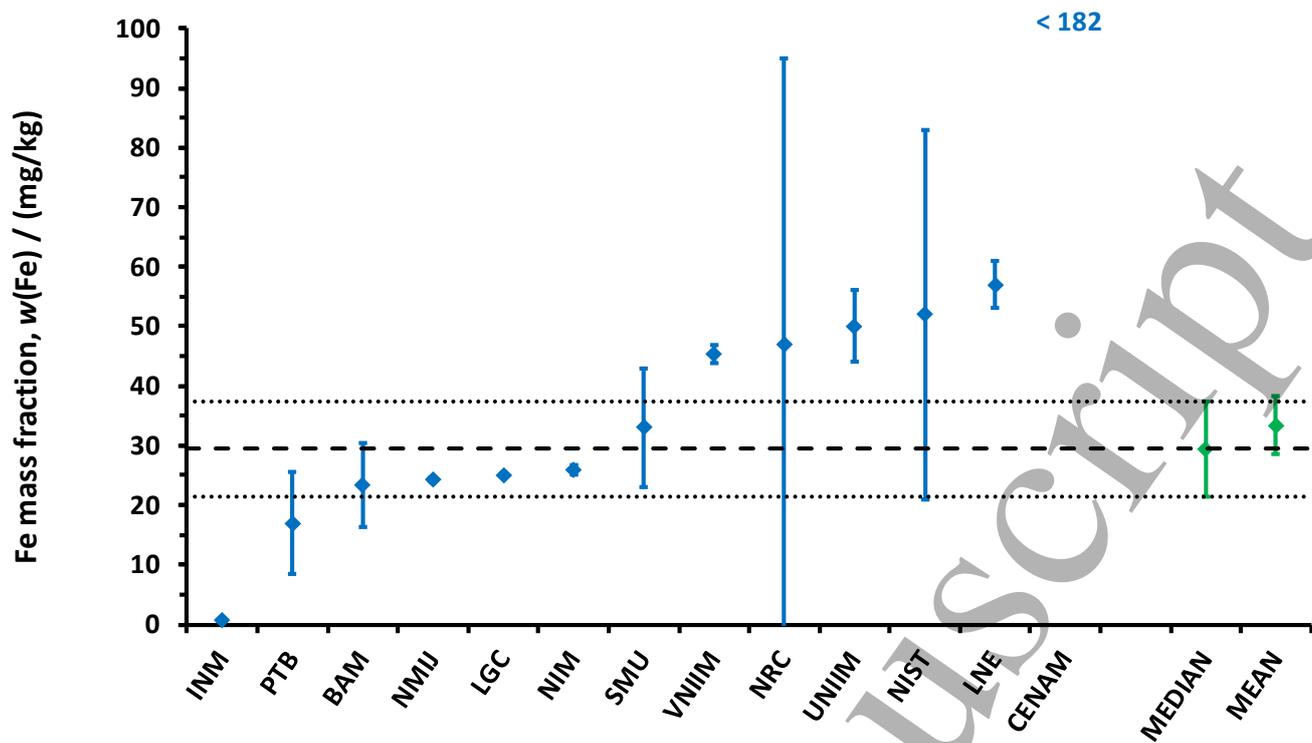


Fig. 4 Results for the iron mass fraction in pure zinc with the associated combined uncertainties ( $k=1$ ).

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