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Worldwide Proficiency Test on the Determination of Trace Elements and Uranium Isotopes in Drinking Water

IAEA-TEL-2015-01

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WORLDWIDE PROFICIENCY TEST ON THE DETERMINATION OF TRACE ELEMENTS AND URANIUM ISOTOPES IN DRINKING WATER

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IAEA-TEL-2015-01

INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The IAEA, through the Terrestrial Environment Laboratory of the IAEA Environment Laboratories, provides analytical quality control support to Member States in the areas of radionuclide, stable isotope and trace element measurements in environmental samples. This support includes the provision of reference materials, the organization of proficiency tests, and the development and publication of recommended procedures.

Reliable analytical results are crucial, as they are often the basis of decisions in the context of environmental or public health related issues, such as decisions concerning the safety of drinking water and required and suitable purification measures.

This publication presents the results of the worldwide proficiency test IAEA-TEL-2015-01 on the determination of selected trace elements and naturally occurring uranium isotopes in drinking water.

The IAEA thanks the National Food Chain Safety Office, Hungary, for providing the raw material for the proficiency test samples, and K. Sathrugnan (Singapore) for the design, preparation and practical realization of the proficiency test. The IAEA is grateful to the expert laboratories that participated in the characterization study and to all the participants in the proficiency test exercise who reported results and thus contributed to the present work. The IAEA officer responsible for this publication was M. Horsky of the IAEA Environment Laboratories.

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CONTENTS

1. INTRODUCTION

The International Atomic Energy Agency's Environment Laboratories provide assistance to Member States' laboratories by supporting them in quality control and quality assurance efforts related to their measurement data. This is accomplished through training activities, the production of and supply with (Certified) Reference Materials and the organization of Proficiency Tests. These activities are carried out in different areas, with a focus on measurement of radionuclides, stable isotopes, trace elements and methylmercury as well as organic contaminants in environmental samples. The Terrestrial Environment Laboratory of the IAEA Environment Laboratories sets an emphasis on samples from the terrestrial environment such as fresh water, vegetation or soil.

1.1. BACKGROUND

Access to safe drinking water is a human right. Clean Water and Sanitation was defined as one Sustainable Development Goal by the United Nations. The availability and quality of drinking water has a significant impact on public health. Therefore, the importance of high quality data in drinking water monitoring is evident, as these measurement results are used to assess the safety of drinking water for consumption based on defined thresholds. In addition, the level and type of contaminants encountered will have implications for the selection and viability of treatment measures. Suitable purification measures are one prerequisite for a sustainable supply of communities with potable water.

Typical sources of drinking water are groundwater, springs, surface water, collected precipitation and desalinated seawater. Contaminants that can affect the quality of water can be of microbial, chemical or radiological nature. Sources of chemical contaminants in water include natural presence (e.g., release from bedrock to groundwater) and anthropogenic sources such as pipe corrosion or leaching from industrial waste. The WHO lists key chemicals responsible for large-scale health effects through drinking water exposure, including the trace elements As, Pb and U. [1]

1.2. OBJECTIVES

Laboratories carrying out measurements for drinking water monitoring purposes are increasingly required to demonstrate competence, e.g. by participation in proficiency tests. In particular, this is a prerequisite for accreditation according to ISO 17025 [2]. Beyond formal requirements, participation in proficiency tests may help laboratories detect problems in their procedures or operation, to identify potential causes and consequently take measures to ensure that their analytical results are accurate and reliable.

The proficiency test (PT) IAEA-TEL-2015-01 was designed to provide laboratories with the possibility to assess their proficiency in analyses relevant to monitoring of drinking water quality.

1.3. SCOPE

Levels of trace elements were adjusted in a mineral water to be either around WHO guideline values (where applicable) or in typical concentration ranges to be expected in drinking water. The scope of the PT covered the following elements: arsenic, cadmium, copper, lead, uranium and zinc.

Arsenic is of significant health concern and can occur in natural waters at elevated levels due to release from certain bedrocks. The WHO has established a guideline value of 10 µg L^{-1}, which is provisional due to practical limitations in As removal by treatment and typical quantification limits in this low mass concentration range. The As mass fraction in the sample was adjusted to be about 25% lower than the provisional guideline value. [1]

Lead is a toxic heavy metal and its main source in drinking water is release from plumbing. The WHO guideline of 10 µg L^{-1} is provisional because no threshold for health effects could be found, but practical reasons related to treatment and analysis preclude a lower guideline value. The mass fraction of Pb in the PT sample is close to the guideline value. Similarly, the value for cadmium was chosen, for which the WHO determined a guideline value of 3 µg L^{-1} in drinking water. [1]

Concentrations of copper, which is both a nutrient and a contaminant, e.g. from pipe corrosion, vary widely in water. The guideline value is 2 mg L^{-1} and the mass concentration was adjusted in the lower range of typical concentrations in water at around 5 µg L^{-1} thus presenting an analytical challenge for some measurement techniques. [1]

The essential trace element zinc was added to obtain a mass concentration in the range typically found in ground waters. Levels in drinking water can be elevated due to corrosion of pipes. There is no WHO guideline value because Zn is not of health concern at levels found in drinking water. [1]

Uranium mass concentration was adjusted at around 10% of the provisional WHO guideline value of 30 µg L^{-1}, but about three times higher than the stated 'general' maximum level in drinking water. [1]

In addition to content of trace elements, the determination of individual mass fractions of the two major isotopes of uranium was requested from participants. The ratio of the two isotopes is characteristic of the type of uranium present in a sample: uranium of natural origin can be distinguished from enriched or depleted uranium from the nuclear fuel cycle. The combination of different requested measurands targeted users of different analytical techniques. Many analytical techniques used in trace element analyses are not capable of analysing individual isotopes. Exceptions are mass spectrometry-based techniques and radioanalytical techniques.

2. ORGANISATION

The proficiency test was announced on the web page of the IAEA Programme on Reference Products. Participants registered until 15 August 2015 and received their laboratory code and log–in information for the reporting platform. Samples were sent during August 2015. Reporting was possible via the on-line reporting platform accessible via the web page. Due to ambiguity in the labelling of the original reporting form and related questions received from participants, the reporting form was modified on 12 November 2015 and participants were informed about it by email. Further details can be found in Section 4.1. Participants were also informed that the reporting deadline (initially 31 October 2015) was extended to 27 November 2015. Individual evaluation reports were made available to participants at the on-line platform on 7 December 2015. One hundred twenty laboratories from 53 Member States registered for the proficiency test. The list of participants can be found in Appendix II. Only participants who reported results are listed there.

3. PROFICIENCY TEST MATERIAL

3.1. PREPARATION OF THE PROFICIENCY TEST MATERIAL

The proficiency test sample was prepared from Hungarian mineral water. Eighty litres of water were acidified in a plastic barrel to pH 2 using concentrated nitric acid (supra-pure quality) to stabilize the analytes in solution. Single-element standard solutions of As, Cd, Cu, Pb, U and Zn were added to obtain trace element mass concentrations in the desired range. The spiked water was circulated using a mixing pump for 1 hour to ensure complete mixing. High density polyethylene bottles with screw caps were cleaned by soaking in 10% nitric acid for at least 24 hours, rinsed with high purity water (18.2 MΩ·cm), dried and labelled. Aliquots of 500 mL were filled into bottles and packed individually in sealable plastic bags. In total, 160 units were prepared.

3.2. CHARACTERIZATION OF THE MATERIAL

The material was characterized by measurements at four expert laboratories. The analytical techniques applied in the characterization study were inductively coupled plasma-mass spectrometry with quadrupole (ICP–QMS) and sector-field (ICP–SFMS) mass analysers. The applied calibration strategies were isotope dilution, external calibration and standard addition.

The following four expert laboratories reported their results:

- Trace Elements Section, Government Laboratory, Hong Kong
- VIRIS Laboratory, Department of Chemistry, University of Natural Resources and Life Sciences, Austria
- Marine Environmental Studies Laboratory, NAEL, IAEA, Monaco
- Terrestrial Environment Laboratory, NAEL, IAEA, Austria

3.3. HOMOGENEITY AND STABILITY

The material was tested for stability and homogeneity using ICP–QMS. Eight units were randomly selected after bottling for the homogeneity study, three aliquots were taken from each bottle and mass fractions of As, Cd, Cu, Pb, U and Zn were analysed under repeatability conditions. Within-sample standard deviation and between-sample standard deviation were calculated according to ISO13528:2015, Annex B. Between bottle standard deviation was compared to the standard deviation for proficiency assessment (see Section 3.5) and found to be less than 0.3 times the standard deviation for proficiency assessment for all analytes, thus the samples could be considered sufficiently homogeneous for the purpose of this proficiency test.

Based on previous experience, the analytes of interest can be considered stable in aqueous nitric acid solution at pH 2 in the present mass fraction range. The only concern is a possible change in mass fraction value due to evaporation loss of water. The relative loss from a total mass of water of about 500 g was expected to be negligible at normal transport and storage conditions over the duration of the proficiency test of several weeks. Nonetheless, stability was confirmed by analysing aliquots from one bottle, which has been stored at room temperature (20–24 °C), for six months. Between two and six aliquots were taken and analysed in June, July, September and November 2015, respectively. No drifts were observed, indicating sufficient stability of the samples.

3.4. ASSIGNMENT OF PROPERTY VALUES AND ASSOCIATED UNCERTAINTIES

Four expert laboratory results were available for mass fractions of As, Cd and Pb each. The robust mean was calculated in accordance with ISO 13528 (Algorithm A) [3] and used as the assigned value. Only three expert laboratories provided values for Cu and Zn and the same procedure was applied. In case of uranium, four measurement results were available for total uranium, determined via external calibration inductively coupled plasma – mass spectrometry (ICP–MS). A fifth independent value was calculated from the results obtained for ^{235}U and ^{238}U by isotope dilution ICP–MS. These five values were used as a basis to calculate the robust mean. Only two measurement results were available for the mass fractions of ^{235}U and ^{238}U. Based on the known isotope ratio of natural uranium, three more values were calculated from the results for total uranium from three expert laboratories using isotope abundances published by the Commission on Isotopic Abundances and Atomic Weights [4].

Combined uncertainties were estimated taking into account characterisation uncertainty, i.e. standard uncertainty of the assigned value from individual uncertainties of measurement reported by the expert laboratories and between-laboratory robust standard deviation. Results from the homogeneity and stability studies were not included into uncertainty propagation.

The relative standard deviation for proficiency assessment $\hat{\sigma}_{rel}$ was assigned based on fitness for purpose as follows: 10% for mass fractions of As and Cd, 12.5% for mass fractions of Cu, U (total) and ^{238}U, and 15% for mass fractions of Pb, ^{235}U and Zn.

3.5. PROPERTY VALUES AND ASSOCIATED UNCERTAINTIES

All assigned property values, expanded uncertainties and relative standard deviations for proficiency assessment are summarized in Table 1.Table 1

TABLE 1. ASSIGNED VALUES FOR MASS FRACTIONS OF TARGET ANALYTES, ASSOCIATED UNCERTAINTIES AND RELATIVE STANDARD DEVIATION FOR PROFICIENCY ASSESSMENT

Analyte	Mass fraction / (ng/g)	Expanded uncertainty (k=2) / (ng/g)	Relative standard deviation for proficiency assessment
As	7.58	0.61	10%
Cd	1.99	0.14	10%
Cu	5.41	0.88	12.5%
Pb	9.7	1.8	15%
U (total)	3.08	0.28	12.5%
^{235}U	0.0222	0.0019	15%
^{238}U	3.06	0.28	12.5%
Zn	20.2	3.4	15%

4. DATA HANDLING AND EVALUATION

Participants reported their data using an online reporting form linked to a MySQL database. The open-source software R [5] was used for immediate data evaluation. An individual evaluation report based on data taken directly from the database was available online upon request by participants.

A database image was exported to Microsoft Excel after finalisation of the dataset and both spreadsheet software and in-house developed R scripts were used for data evaluation including

calculation of performance statistics and creation of plots. The data processing steps prior calculation of performance statistics are briefly described in the following. Appendix I contains summary tables and graphical representations created using R scripts and converted into pdf format.

4.1. UNCERTAINTY OF MEASUREMENT

The data reporting form included two fields for each result (each analyte) describing the precision or dispersion of data: a standard deviation of several replicate measurements/determinations (and the number of replicates used) and a combined standard uncertainty of measurement (per definition implying and explicitly stating a coverage factor k=1). An initial ambiguity in labelling, which was corrected during the reporting period, led to some confusion among participants and consequently inconsistencies in the dataset. Therefore, only performance statistics not considering uncertainties of measurement (i.e. z scores as a measure of trueness) were calculated in the first instance and reported back to participants in their individual evaluation reports.

The following approach was then used in the comprehensive evaluation to allow the calculation of further performance statistics and the careful interpretation of results also with respect to accuracy (including both trueness and precision). When a number was reported in the field 'Combined standard uncertainty (k=1)', this value was generally used as uncertainty in further evaluation and plotted as an error bar. An exception was made, when the recurrence of integer numbers (1, 2, 3…) in the field 'Combined standard uncertainty (k=1)' was found for all results of one laboratory; then the value in the field 'Standard deviation' was plotted instead. This was due to the fact, that the original label of the field was 'MU budget with k factor' which caused the misunderstanding that the applied k factor should be input. When the field 'Combined standard uncertainty (k=1)' was left blank, the value provided in the field 'Standard deviation' was used as reported uncertainty value.

The relative uncertainty of participants' results was calculated by dividing the reported uncertainty by the reported value. Results for analytes that indicated zero as the obtained mass fraction were excluded from this evaluation.

4.2. ANALYTICAL TECHNIQUES

The reporting form provided a free text field where participants were asked to input the applied analytical technique. In order to facilitate evaluation and interpretation, categories were defined and separate entries for each analyte were created manually based on the free text entries. When participants mentioned several techniques but did not specify which analytes had been determined by which method, 'unclear/several' was input for all analytes. Some laboratories indicated published standard methods (e.g., US EPA 6020A, APHA 3120B). When the stated method was specific to only one measurement technique, it was included into evaluation. When only sample preparation methods were indicated, the entry was categorized as 'unclear/several'. The applied analytical techniques were grouped into categories as defined in Table 2. The discussion in Section 6.1 includes the original information as provided by the laboratories.

TABLE 2. ANALYTICAL TECHNIQUE CATEGORIES, ACRONYMS AND EXPLANATIONS

category	*explanation*
AAS	atomic absorption spectrometry (including flame AAS, graphite furnace (GF) AAS, and hydride generation (HG) AAS)
ICP–OES or MP–OES	Inductively coupled plasma–optical emission spectrometry or microwave plasma–optical emission spectrometry
ICP–MS	inductively coupled plasma–mass spectrometry (with quadrupole mass analyser or not further specified)
ICP–SFMS	inductively coupled plasma–mass spectrometry with sector field (SF) mass analyser, equivalent to high resolution (HR) ICP–MS
polarography	polarography (special case of voltammetry)
alpha particle spectrometry	alpha particle spectrometry (equivalent to alpha spectrometry)
gamma ray spectrometry	gamma ray spectrometry (equivalent to gamma spectrometry)
fluorimetry or KPA	fluorimetry (not further specified) or kinetic phosphorescence analyser
unclear/several	statement of several techniques or other ambiguous information
not stated	participants did not input any information on applied analytical technique(s)

5. PERFORMANCE STATISTICS AND EVALUATION CRITERIA

Performance statistics were calculated in accordance with ISO/IEC 17043:2010 [6] and *The International Harmonized Protocol for the proficiency testing of analytical chemistry laboratories* [7] unless otherwise stated.

5.1. RELATIVE BIAS

The relative bias D_{rel} (or percent difference) of the reported value x from the assigned value X was calculated according to Equation (1).

$$D_{rel} = \frac{x-X}{X} \cdot 100\% \quad (1)$$

where

D_{rel} is the relative bias;
x is the reported mass fraction value; and
X is the assigned mass fraction value.

Thresholds can be set to define satisfactory performance based on a maximum acceptable relative bias. This approach is equivalent to the evaluation according to z scores.

If combined with an uncertainty of the bias, as obtained from propagating the uncertainties of the reported mass fraction value x and the assigned mass fraction value X (Equation (2)), a statement of accuracy of the reported measurement result can be derived. Typically, a coverage factor of two is employed, corresponding to approximately 95% confidence level (given normal distribution). As an example, a relative bias of 7.3% ± 8.5% (k=2) would indicate an in insignificant bias and hence an accurate result at the stated confidence level, whereas a relative bias of 5.1% ± 3.5% (k=2) – even though smaller – would be significant and indicate inaccuracy. The expanded uncertainty of the bias $U(D_{\mathrm{rel}})$ can be obtained by uncertainty propagation of both the combined uncertainty of the assigned value X and the combined uncertainty of the reported measurement result x and multiplication with an appropriate coverage factor k.

$$U(D_{rel}) = k \cdot u_c(D_{rel})$$

$$= k \cdot \sqrt{\left(\frac{\partial D_{rel}}{\partial x} \cdot u_c(x)\right)^2 + \left(\frac{\partial D_{rel}}{\partial X} \cdot u_c(X)\right)^2}$$

$$= k \cdot \sqrt{\left(\frac{1}{x} \cdot u_c(x)\right)^2 + \left(-\frac{x}{X^2} \cdot u_c(X)\right)^2} \qquad (2)$$

where

$U(D_{rel})$	is the expanded uncertainty of measurement of the relative bias;
k	is the coverage factor;
$u_c(D_{rel})$	is the combined uncertainty of measurement of the relative bias;
D_{rel}	is the relative bias (see Equation (1));
x	is the reported mass fraction value;
$u_c(x)$	is the combined uncertainty of measurement of the reported mass fraction value;
X	is the assigned mass fraction value; and
$u_c(X)$	is the combined uncertainty of measurement of the assigned mass fraction value.

A rating solely based on significance of the bias is not useful because it encourages the reporting of an overestimated uncertainty of measurement. It may help laboratories to recognize significant underestimation or reported uncertainty, though.

5.2. Z SCORE

The z score values are calculated according to Equation (3):

$$z = \frac{x - X}{\hat{\sigma}_{rel} \cdot X} \qquad (3)$$

where

z	is the z score;
$\hat{\sigma}_{rel}$	is the relative standard deviation for proficiency assessment (see Section 3.5);
x	is the reported mass fraction value; and
X	is the assigned mass fraction value.

Results were rated according to the following criteria for absolute values of the statistic *z*:

- $|z| \leq 2$ indicates satisfactory performance;
- $2 < |z| < 3$ indicates questionable performance;
- $|z| \geq 3$ indicates unsatisfactory performance.

This implies that a relative difference between the reported result and the assigned value of equal or less than two times the relative standard deviation for proficiency assessment was considered satisfactory. Assigned relative standard deviations for proficiency assessment are listed in Table 1 on page 4. Consequently, a relative difference of equal or less than 20% for mass fractions of As and Cd, 25% for mass fractions of Cu, U (total) and ^{238}U, and 30% for mass fractions of Pb, ^{235}U and Zn indicated satisfactory performance. Accordingly, performance was considered questionable at relative differences between the reported result and the assigned value of more than two times, but equal or less than three times the relative standard deviation for proficiency assessment. Relative differences of more than $3 \times \sigma_{rel}$ resulted in the rating 'unsatisfactory'.

5.3. ZETA SCORE

The ζ *(zeta)* score values allow a combined assessment of the reported value and the reported uncertainty of measurement, and thus of the accuracy of the reported result. *Zeta* scores are calculated according to Equation (4)

$$\zeta = \frac{x - X}{\sqrt{u_c^2(x) + u_c^2(X)}} \tag{4}$$

where

ζ is the zeta score
x is the reported mass fraction value;
X is the assigned mass fraction value;
$u_c(x)$ is the combined uncertainty of measurement of the reported value; and
$u_c(X)$ is the combined uncertainty of the assigned value.

Results are usually rated based on the following criteria for absolute values of the statistic ζ:

- $|\zeta| \leq 2$ indicates satisfactory performance;
- $2 < |\zeta| < 3$ indicates questionable performance;
- $|\zeta| \geq 3$ indicates unsatisfactory performance.

This rating was not applied in this exercise, but calculated zeta scores are listed for information in Appendix I.

6. RESULTS AND DISCUSSION

6.1. GENERAL PARTICIPANT STATISTICS AND APPLIED ANALYTICAL TECHNIQUES

One hundred and twenty laboratories from 53 Member States registered for participation in the proficiency test, of which 93 from 49 countries reported results (78%). Twenty-six laboratories submitted results for all requested analytes. This low proportion is due to the fact that only few methods are capable of analysing all requested analytes. Values for mass fractions of at least all five stable trace elements As, Cd, Cu, Pb and Zn were provided by 61 laboratories. Sixteen laboratories reported only values for the mass fraction of uranium, either for total uranium or for at least one of the isotopes. In total, 501 values were submitted.

Table 3 lists the number of values reported by all participating laboratories for each analyte and each analytical technique. The most commonly applied techniques are mass spectrometric techniques (ICP–QMS and ICP–SFMS) followed by the optical spectroscopic techniques ICP–OES and AAS. One laboratory applied MP–OES for Cu and Zn determination. Other optical spectroscopy techniques were rarely used; two laboratories mentioned fluorimetry and three laboratories applied kinetic phosphorescence analysis (KPA) for the measurement of total U mass fraction. Electroanalytical techniques (voltammetry and its special case polarography) were employed by four laboratories. Thirteen laboratories did not provide any information about the applied instrumentation or method.

One mass fraction value for Pb was reported to have been measured by gamma-ray spectrometry, probably either due to a reporting mistake or due to a misunderstanding of the fact that stable lead was the analyte of interest in this exercise and not a radioisotope of Pb.

TABLE 3. NUMBER OF VALUES REPORTED PER ANALYTE AND ANALYTICAL TECHNIQUE

Analytical technique	As	Cd	Cu	Pb	U_{total}	^{235}U	^{238}U	Zn	sum
AAS	11	12	12	13	0	0	0	10	58
ICP–OES or MP–OES	6	8	9	8	1	0	1	9	42
ICP–MS (including ICP–SFMS)	34	34	34	35	25	17	18	34	231
Polarography	1	2	2	2	0	0	0	2	9
Alpha-particle spectrometry	0	0	0	0	12	12	16	0	40
Gamma-ray spectrometry	0	0	0	0	3	2	2	0	7
Fluorimetry or KPA	0	0	0	0	3	0	0	0	3
Unclear/several	2	4	4	5	4	4	4	3	30
Not stated	10	12	13	12	9	4	9	12	81
Sum	64	72	74	75	57	39	50	70	501

6.2. STATISTICAL DESCRIPTION OF REPORTED MASS FRACTION VALUES

Histograms were created from all reported mass fraction values in the interval between zero and three times the assigned value. Distributions were found unimodal and roughly approximated by normal distributions for most of the measurands even though contaminated by outliers. In case of ^{235}U, the total number of results was low, and the dispersion was very wide. In addition, the high proportion of partly extreme outliers (likely blunder) biased the dataset for ^{235}U. Summary histograms are shown in Figures 4, 8, 12, 16, 20, 24, 28 and 32 in Appendix I.

6.3. REPORTED UNCERTAINTY OF MEASUREMENT

The information content and comparability of the compiled values for uncertainty of measurement as reported by all participants is limited. Two possible main reasons were identified: (a) the ambiguity in the reporting form as to what should be inserted there and consequent change of the labelling and (b) possible inconsistencies in the understanding of the concepts and terminology of uncertainty of measurement and the practical implementation between some participating laboratories. Both reasons may be related to a lack of instructions provided, what participants are expected to calculate and report (and how to calculate it).

For instance, the terms 'standard deviation' and 'uncertainty' are sometimes used ambiguously. In this report, the term 'combined standard uncertainty (of measurement)' or more briefly 'combined (measurement) uncertainty' u_c refers to a property of the measurement result describing its dispersion. It is obtained by combining the individual uncertainties of the values of the input quantities to the measurement model equation. It is usually calculated as part of the method validation or may be determined for every individual sample and expressed as a standard deviation. The expanded uncertainty (of measurement) U is obtained from the combined standard measurement uncertainty by multiplication with a coverage factor k. The expanded uncertainty U is a "quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand" [8]. It is typically reported with a coverage factor of 2 and relates to a confidence level of about 95% (given normal distribution).

Even though the combined standard uncertainty is expressed as a standard deviation, the term 'standard deviation' alone is typically used to express, that several replicate determinations of the sample of interest are performed (for practical reasons usually under repeatability conditions) and a standard deviation is calculated assuming normal distribution. Sometimes, the 'standard error of the mean' or 'standard deviation of the mean' is reported instead, which is obtained from the standard deviation by dividing it by the square root of the number of replicates.

The standard deviation obtained in this way describes the repeatability, intermediate precision or reproducibility of the measurement method, depending on which factors were varied between replicates. In most cases it will correspond to a repeatability precision. The combined uncertainty of measurement should include this 'source of uncertainty', but beyond that should it contain the uncertainties of all other input quantities to the measurement model that may influence the result. This may include, for example, the uncertainty of balances, volumetric devices or other equipment used during sample preparation and the uncertainty associated to the calibration, such as the uncertainty of the certified value of the reference material used for calibration. Therefore, the combined standard uncertainty of measurement must be larger than the simple standard deviation of a few replicate measurements of a sample. (If the dominant sources of uncertainty are varied between the replicate determinations, it can also be equal to the standard deviation within significant digits). For further information on theoretical background and practical advice on how to determine the combined standard uncertainty, we refer the reader to the Guide to the Expression of Uncertainty in Measurement (GUM, [8]) and the EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement [9].

Relative uncertainty values ranged from 0.02% to several values of more than 50% in the set of all reported data. A histogram with pre-selected bins of unequal width depicts the distribution of relative combined standard uncertainties colour–coded by analytical technique (FIG. 1). It shows approximately bimodal distribution with one maximum at $> 1\%$ and $\leq 3\%$ relative

combined uncertainty and another at >10% and ≤ 20%. There is no clear difference between different techniques or groups of techniques (e.g. radiometric vs. optical or mass-spectrometric).

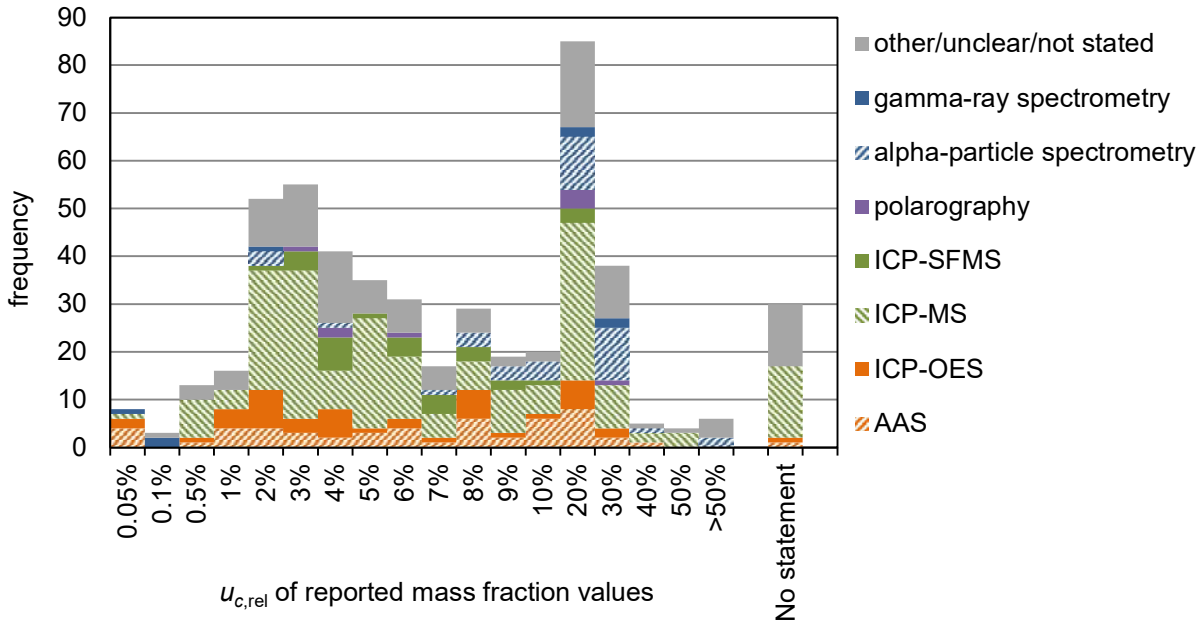

FIG. 1. Histogram of relative combined uncertainties of reported mass fraction values for different applied analytical techniques.

An evaluation by analyte (not shown) indicates similar reported relative uncertainties for all analytes with the exception of ^{235}U, where about two thirds of reported values were accompanied by relative uncertainties of more than 10%. This can reasonably be explained by the mass fraction value, which had to be determined, being two orders of magnitude lower. It must be noted, that for the reasons explained earlier, the informative value of the dataset related to uncertainty of measurement is limited and prevents meaningful conclusions on the actual uncertainties in relation to applied methods. Some additional observations are summarized in the following.

Out of 93 reporting laboratories, six laboratories (6.5%) left both the field for standard deviation and the field for combined uncertainty blank, either for all or some reported analyte mass fraction values. Two laboratories reported zero standard deviation and no combined uncertainty value for some analyte mass fractions. All these results cannot be considered complete, as a statement of uncertainty is an integral part of any measurement result. The lack of an uncertainty statement renders the interpretation of a value, e.g. for the purpose of conformity assessment, impossible. Even though the numeric result of a calculation can deliver zero, the combined uncertainty of measurement can never be zero.

Three laboratories reported the same numeric value for the combined standard uncertainty of all reported analyte mass fraction values. All these values may have been reported due to a confusion between absolute combined standard uncertainty, a quantity with the same unit as the result value, and the relative combined standard uncertainty, a dimensionless quantity, often expressed in percent.

36% of laboratories left one of the two dispersion related fields blank. 27% of reporting laboratories (n = 25) entered combined standard uncertainty values that are consistently higher

than the respective standard deviations, which is the reasonable expectation in accordance with the definitions stated above. Another six laboratories reported either higher or equal values. In two cases, the reported u_c value was found to be a multiple of the indicated standard deviation.

Twenty percent (n = 19) of the reporting laboratories reported at least one uncertainty value that was lower than the respective standard deviation of n replicate determinations of an analyte. This may be due to a lack of understanding of the concept of combined uncertainty, or due to unsuitable uncertainty propagation resulting in the underestimation of the combined uncertainty. In one case, the reported combined standard uncertainty was consistently half of the value in the field 'standard deviation' for each analyte. This may indicate, that 'standard deviation' was understood to denote an expanded uncertainty (k = 2). Another laboratory reported the standard error of the mean in the field 'combined standard uncertainty'.

The following observations were made related to the number of replicate determinations made by participants. It is most common to analyse three replicates (41% of the reported values), but replicate numbers ranging from 1 (7%) to 20 were reported. 6% of the reported values did not include a statement of the number of replicates. If the method has been validated and representative sampling of a homogeneous sample is ensured, it may be sufficient to measure one sample replicate (typically, each measurement will consist of the collection of several data points, though), and will not prevent the reporting of an accurate estimate of the combined standard uncertainty of measurement. It is strongly recommended, that laboratories apply the same procedures (including a typical number of replicate determinations) during participation in a proficiency test as they apply for routine samples, in order to get information on the quality of typical (routine) results of the laboratory.

6.4. PERFORMANCE STATISTICS

6.4.1. Relative bias

The relative bias was calculated for each reported measured value. Results are listed in Tables 6, 8, 10, 12, 14, 16 and 18 in Appendix I. The relative bias gives an indication of the trueness of a measured value. In addition, the expanded uncertainty of the relative bias was calculated and listed as well in above mentioned tables for information.

6.4.2. *z* Scores

The initial individual evaluation of performance of laboratories, as made available in individual evaluation reports on the reporting platform, was based solely on z scores. FIG. 2 gives a summary of the rating of all reported values based on z scores. Relative proportions in the pie chart refer to the total number of values reported for all analytes.

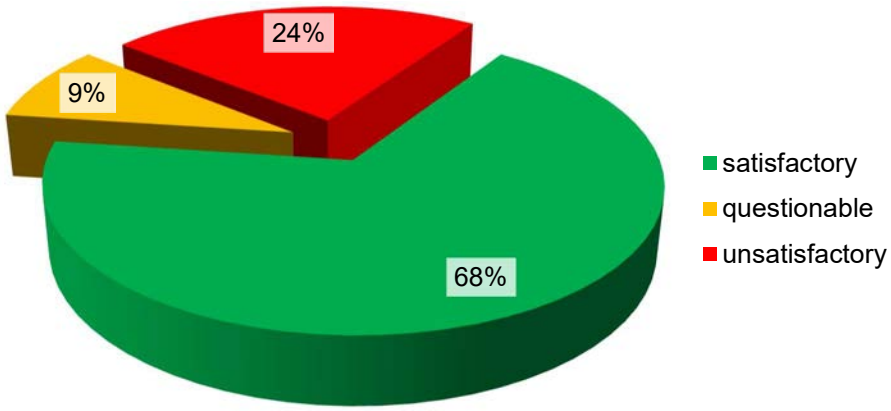

FIG. 2. Relative distribution of z scores for all reported values.

Tables 6, 8, 10, 12, 14, 16 and 18 listing individual laboratories' reported results for each analyte, calculated z scores and ratings can be found in Appendix I.

Table 4 lists *z* scores of all reported values in one row for each laboratory and one column for each analyte. Scores rated 'satisfactory' are shown with green background colour, while scores rated 'warning' are coded in light orange. Unsatisfactory ratings are indicated by dark orange background colour. Entries '*n.r.*' in the table indicate 'not reported'.

In total, 27 laboratories (29%) reported exclusively satisfactory results. On the other end of the scale, eleven laboratories reported only unsatisfactory results based on *z* scores. The relative proportion of satisfactory results per analyte was between 62% and 77% of all reported values for each analyte, except ^{235}U where only 44% of the values were acceptable. The relative proportion of satisfactory results increased for individual analytes in the following order: $^{235}U < Cu < U_{total} < ^{238}U < Zn < Cd < Pb < As$.

An evaluation by method code reveals that the highest proportion of satisfactory results was achieved by application of ICP–SFMS (97% of 30 reported values), followed by ICP–MS (85% of 201 reported values). The number of reported results obtained by some techniques (e.g. polarography and gamma-ray spectrometry) was very low, therefore meaningful conclusions are not possible. The relative proportion of satisfactory results was 55% of 42 values determined by ICP–OES or MP–OES and 40% of 58 values determined by AAS. In case of alpha particle spectrometry (only U), 38% of 40 reported values were rated satisfactory. The incompleteness of information available (111 values were accompanied by no or only unclear information about applied analytical techniques) and low number of reported values for individual techniques such as GF–AAS compromises further interpretation. The determination of the mass fraction of ^{235}U presented a particular challenge to participants, apparent by the wide distribution of results and low proportion of acceptable z scores.

TABLE 4. SUMMARY TABLE OF Z SCORES OF ALL REPORTED VALUES SORTED BY LABORATORY CODE AND ANALYTE

Lab code	As	Cd	Cu	Pb	Zn	U-total	U-238	U-235
1	-2.36	-1.06	-0.31	-0.25	-0.34	-1.35	*n.r.*	*n.r.*
2	9.38	3.32	0.26	0.82	-0.48	*n.r.*	*n.r.*	*n.r.*
3	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	1.90	1.73	22
4	0.71	-0.45	1.16	-0.09	-0.91	-0.47	-0.84	-0.06
5	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	39	37	234
6	1.96	0.07	-1.14	-0.88	1.55	152	153	*n.r.*
7	0.07	-3.32	-1.73	-3.63	-1.68	-2.47	-2.43	-0.54
8	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	2.13	1.78	46
9	4.25	-0.65	-2.01	0.15	-0.99	*n.r.*	*n.r.*	*n.r.*
10	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	0.10	0.16	-0.33
11	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	3.92	3.92	32
12	1.42	-0.90	-1.30	0.05	-1.58	0.95	0.94	0.84
13	1.91	1.11	0.67	0.34	0.23	-0.31	-0.31	-0.30
17	2.73	-1.06	-1.15	-0.27	-0.86	0.49	0.47	0.39
18	*n.r.*	-0.25	-4.23	-1.84	-2.21	*n.r.*	*n.r.*	*n.r.*
20	0.82	-0.95	0.43	-0.69	-0.56	1589	1571	3297
21	0.51	0.45	0.37	0.18	-0.86	*n.r.*	*n.r.*	*n.r.*
22	0.51	1.46	-0.53	0.12	0.46	1.32	1.32	1.14
23	-1.30	-0.91	-1.58	-0.55	-2.85	-0.12	*n.r.*	*n.r.*
25	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	2.47	*n.r.*	*n.r.*
26	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	2.64	*n.r.*
28	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	39	38	*n.r.*
29	0.12	-0.50	-0.16	0.03	0.40	*n.r.*	*n.r.*	*n.r.*
30	1.21	-0.95	1.46	-1.03	-1.39	-1.25	-1.20	*n.r.*
31	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	0.68	0.63	2.64
32	-0.80	-2.31	-0.86	-1.40	-1.94	-1.53	-1.54	-0.96
33	*n.r.*	*n.r.*	*n.r.*	165	*n.r.*	583	581	669
34	*n.r.*	*n.r.*	20	5.02	*n.r.*	*n.r.*	*n.r.*	*n.r.*
36	0.55	1.06	-0.61	0.21	-0.73	1.40	1.46	1.23
37	1.70	3.17	0.49	-0.30	-0.07	1.69	*n.r.*	*n.r.*
38	*n.r.*	-0.05	6.79	1.44	-0.79	337	*n.r.*	*n.r.*
40	-8.55	894	57	70	-6.04	*n.r.*	*n.r.*	*n.r.*
43	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	-2.43	*n.r.*
44	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	0.83	0.89	*n.r.*
45	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	-1.18	5.05
46	0.66	1.01	-0.84	0.41	-0.92	*n.r.*	0.65	*n.r.*
48	-1.49	13	0.81	2.60	-3.03	*n.r.*	*n.r.*	*n.r.*
50	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	0.10	0.06	3.84
51	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	-7.91	-6.07
53	19	8.94	94	14	*n.r.*	*n.r.*	4.29	1675
54	0.29	0.05	-1.20	-0.07	*n.r.*	*n.r.*	-0.68	*n.r.*
56	1.53	-1.31	-0.35	-1.84	0.65	-0.65	-0.60	861
58	-0.37	-1.86	-1.35	-2.28	-0.07	-2.26	-2.14	648
59	0.59	0.35	-1.46	0.57	-1.34	*n.r.*	*n.r.*	*n.r.*
63	0.53	-0.80	-0.68	-0.48	-1.34	-4.22	-4.26	405
64	-2.55	-1.56	3.39	-2.43	5.02	-0.44	-0.47	-0.36
65	0.07	-0.25	-0.72	0.41	-0.83	0.52	0.58	*n.r.*
67	-1.62	3.57	2.06	0.17	19	*n.r.*	*n.r.*	*n.r.*
68	-0.77	-1.68	-1.89	-1.78	-2.31	*n.r.*	*n.r.*	*n.r.*
69	*n.r.*	25	85	*n.r.*	-0.40	*n.r.*	*n.r.*	*n.r.*
70	-2.94	-1.26	-1.07	0.17	2.72	0.48	0.38	11
71	0.90	0.00	-0.72	-0.26	-0.34	-0.03	-0.03	-0.09
72	*n.r.*	*n.r.*	6.55	1.10	1.58	*n.r.*	*n.r.*	*n.r.*
73	2.43	0.45	60	11	12	5.56	5.65	*n.r.*
74	*n.r.*	15	19	11	7.19	*n.r.*	*n.r.*	*n.r.*
77	0.55	0.05	-0.61	-4.88	-1.72	-0.21	-0.16	5.05
78	0.57	0.75	-0.12	0.34	1.98	0.70	*n.r.*	*n.r.*
79	-2.10	91	22	7.08	6.24	*n.r.*	*n.r.*	*n.r.*
80	-1.84	91	22	14	3.16	*n.r.*	*n.r.*	*n.r.*
81	*n.r.*	-5.25	-6.64	3.21	-0.91	*n.r.*	*n.r.*	*n.r.*
82	*n.r.*	*n.r.*	35	*n.r.*	0.90	*n.r.*	*n.r.*	*n.r.*
83	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	3.07	2.92	19

TABLE 4. SUMMARY TABLE OF Z SCORES OF ALL REPORTED VALUES SORTED BY LABORATORY CODE AND ANALYTE (CONTD.)

Lab code	As	Cd	Cu	Pb	Zn	U-total	U-238	U-235
84	-1.38	-0.64	-0.62	0.15	1.28	1.77	*n.r.*	*n.r.*
85	-0.77	0.10	-1.05	-0.69	-0.36	0.03	0.00	0.21
86	1.08	0.20	-0.90	0.14	-0.64	0.57	*n.r.*	*n.r.*
87	0.82	0.05	-0.31	0.79	0.30	0.57	*n.r.*	*n.r.*
88	-10.00	-3.47	1.91	-4.67	3.56	3.48	2.72	89
89	0.16	0.55	-1.79	0.14	-0.89	*n.r.*	*n.r.*	*n.r.*
91	0.44	-0.80	-2.90	-0.38	1.36	-0.45	-0.56	16
92	1.32	0.20	-0.38	0.21	0.20	*n.r.*	*n.r.*	*n.r.*
95	*n.r.*	-3.47	6.79	-0.14	-3.20	2.73	*n.r.*	*n.r.*
97	1.87	1.41	-0.27	-3.89	-1.98	*n.r.*	*n.r.*	*n.r.*
99	-4.99	-1.21	-1.79	0.00	-1.95	*n.r.*	*n.r.*	*n.r.*
101	1.62	0.25	2.53	-1.09	0.03	*n.r.*	*n.r.*	*n.r.*
105	-3.01	-0.95	*n.r.*	-0.34	*n.r.*	*n.r.*	*n.r.*	*n.r.*
106	0.24	-3.52	*n.r.*	0.04	*n.r.*	*n.r.*	*n.r.*	*n.r.*
107	0.29	-0.70	-1.12	-0.84	-0.92	-0.60	-0.60	-0.36
108	*n.r.*	3.42	43	-1.04	-1.05	*n.r.*	*n.r.*	*n.r.*
109	0.95	-0.45	-1.05	-0.48	-0.50	1.35	1.41	*n.r.*
110	-1.50	-1.36	1.09	-0.94	-0.31	-1.22	*n.r.*	*n.r.*
111	-1.69	-2.24	-1.79	-1.17	-1.65	-0.99	-0.22	-2.91
112	0.29	0.85	8.27	0.89	-2.38	*n.r.*	*n.r.*	*n.r.*
113	1.74	-0.15	-1.15	-0.55	-0.69	0.13	0.13	0.06
115	-0.82	-2.06	2.20	-0.53	-0.50	-4.68	*n.r.*	*n.r.*
116	-8.50	-0.40	2.75	-2.53	-4.47	*n.r.*	*n.r.*	*n.r.*
117	0.08	-0.70	-0.84	-0.19	-0.23	-0.03	-0.04	-0.01
118	-0.58	-1.31	-1.15	-0.44	-2.18	-0.44	-0.44	0.24
119	*n.r.*	*n.r.*	*n.r.*	*n.r.*	*n.r.*	104	104	86
120	1.21	3.57	2.06	-0.82	2.21	2.13	1.93	21.26
121	*n.r.*	-0.30	3.49	0.96	*n.r.*	6.78	*n.r.*	*n.r.*
122	2.14	-1.01	-2.23	-3.57	-0.07	-1.19	-1.18	-0.96
123	1.74	0.05	-2.09	-0.48	-3.04	62	*n.r.*	*n.r.*
124	*n.r.*	*n.r.*	-8.00	-6.67	-6.67	*n.r.*	*n.r.*	*n.r.*

In general, the proportion of satisfactory values reflects to some extent the sensitivity of individual techniques and consequently fitness of purpose for the determination of the requested measurands at the present levels. However, high sensitivity instrumentation does not guarantee high quality results. On the other hand, reliable measurements at potentially challenging low levels are also possible using techniques typically applied at higher concentration ranges provided fit-for-purpose methods are developed and applied.

6.4.3. Zeta scores

Calculated zeta (ζ) scores are listed for individual laboratories' results for each analyte in Appendix I. The meaningfulness of ζ scores was limited in this exercise due to inconsistencies in reporting of uncertainties of measurement as explained before. Therefore, no rating was listed in the tables.

6.5. METHOD VALIDATION

Fifty-four laboratories (58%) reported that they had used validated methods. This information was requested per laboratory and not per analyte. Some labs inserted comments, that they had not validated all applied methods for the determination of reported analytes.

Among those laboratories with satisfactory *z* scores for all reported analyte mass fractions, 69% stated that they had used validated methods. In contrast, only 50% of laboratories with less than 50% satisfactory *z* scores (i.e. 50% or more reported values with warning or unsatisfactory

rating) used validated methods. It is apparent, though, that the use of validated methods (as stated) does not guarantee satisfactory results. The average percentage of results with satisfactory *z* scores is 65% for laboratories using validated methods and 56% for laboratories using non-validated methods. Unsatisfactory results may indicate that the method was not fit for the intended use. One possible deviation could be a discrepancy between the requested measurand and the scope of the validated method, e.g. that the method was validated for a different working range or a different matrix. Thus, the applied method may not have been fit for the intended use for this proficiency test sample. Particular attention should be paid to limits of detection and limits of quantification. Values below the latter can only be considered semi-quantitative and are accompanied by a higher uncertainty of measurement. It is important that this is reflected accordingly in the reported uncertainty.

No information was assessed regarding accreditation of laboratories. Several laboratories mentioned accreditation in a comment. Documented method validation is a prerequisite for accreditation according to ISO 17025 [2].

6.6. USE OF CERTIFIED REFERENCE MATERIALS

Out of 93 reporting laboratories, 55 provided information on the use of a (certified) reference material. Many used water matrix certified reference materials and a few used samples from other proficiency tests. In the majority of cases, the analytes present in the mentioned materials corresponded with the analytes reported by the laboratory. One laboratory reported the use of a solid certified reference material certified only for analytes not requested in this exercise. Around 20 laboratories mentioned single element or multielement standard solutions, but it was not clear, whether these were used for calibration and/or quality control purposes. Several laboratories working with alpha spectrometry mentioned the use of an isotope-enriched tracer. Four laboratories only stated ‘yes’, i.e. that they had used a reference material without giving further information, while two laboratories entered ‘no’ to the respective field in the questionnaire. Thirty-seven laboratories left the field blank.

The use of a matrix certified reference material which should match the composition of the sample and the concentration range of analytes as closely as possible is strongly recommended. It is mandatory, that values for all analytes of interest are known for the used material to make it fit for the intended use as validation or quality control material. In case of water analysis, it is possible to use single or multielement standard solutions to prepare an in-house quality control sample. It is important to account for purity of the used solutions in the uncertainty estimation and not to use the same stock solutions for both calibration and quality control solutions. Ideally, the matrix (total dissolved solids, anions present, etc.) of the water should be matched as closely as possible in such an in-house quality control sample.

6.7. TRACEABILITY

Traceability is defined as a ‘property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty’ [10]. The reference can be the definition of a measurement unit, such as an SI unit. The chain of calibrations may include the calibration of balances (using weights calibrated by a metrological institution which is using calibrated balances and weights itself for this purpose), the calibration of volumetric devices such as pipettes or volumetric flasks against a reliable reference (e.g. using a calibrated balance and a calibrated thermometer) or the calibration of a measuring instrument using certified reference materials, which were characterized by their producers using calibrated instrumentation. Reference material

producers, e.g. the National Institute of Standards (NIST), play a crucial role in the traceability of measurements in laboratories and therefore must ensure the traceability of the certified values stated in certificates of analysis accompanying the materials. Several participants stated 'traceability to NIST' or to a NIST material in the questionnaire. This is also a common statement on certificates of single element standard solutions prepared from solid NIST standards.

7. CONCLUSIONS

Ninety-three laboratories from 49 Member States participated in the proficiency test exercise IAEA-TEL-2015-01 and were consequently able to assess their proficiency in the analysis of trace elements and naturally occurring uranium isotopes ^{238}U and ^{235}U in drinking water. The low analyte levels in the water sample presented a challenge for many analytical techniques. Nonetheless, 68% of all submitted property values were rated satisfactory based on *z* scores. Several applied techniques are capable of reliable determination of trace elements in the low ng/g range in water. Knowledge of the figures of merit of the applied method is of key importance. In particular, the determination and consideration of the limits of detection and quantification, the working range and the uncertainty of measurement at the respective analyte mass fraction or concentration level in a sample are crucial parameters in method validation.

Results from statistical analysis of reported data reflect certain possible problems laboratories may have experienced in the measurement of related mass fractions. The dispersion of reported results for those trace elements that occur at higher abundance in the environment (Cu, Zn) is wider than that for As, Pb and Cd, indicating possible problems with high backgrounds or contamination introduced by the laboratory environment. The reliable quantification of mass fractions of these trace elements in the low ng/g range is challenging and requires countermeasures against metal contamination, such as cleanroom facilities with air filters and clean plastic labware.

The determination of the low mass fraction of uranium in the water sample, and in particular of the nuclide ^{235}U presented a challenge for many participants. It was particularly difficult for those laboratories applying traditional radiometric techniques due to the combination of low total mass of uranium provided (about 1.5 µg), and very long half-life of uranium resulting in very low activity (< 20 mBq total uranium, < 1 mBq ^{235}U) of the water sample.

One of the lessons learned from the organisation and evaluation of this proficiency test in the area of trace element analysis is that there is a need for providing better instructions in relation to what is expected to be reported as a result within the proficiency test. In particular, explanation of terms related to measures of dispersion, such as the uncertainty of measurement, should be provided to participants in future exercises. While related concepts are well-known in the radiometric community, many analytical chemists are not equally familiar with terms and calculation approaches. This observation may indicate that capacity building in relation to the calculation of appropriate combined uncertainties of measurement, which are a key component of any measurement result, would contribute to improved analytical results being available in Member States. These measurement results form the basis for the monitoring of heavy metals in drinking water, food or different environmental compartments. Statements of compliance to legal thresholds are only reliable when the uncertainty of measurement results is both appropriately estimated and fit for the purpose.

APPENDIX I. PERFORMANCE EVALUATION BY ANALYTE

I.1 ARSENIC

TABLE 5. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	7.58
Expanded uncertainty (k=2)/(ng/g)	0.61
Relative standard deviation for proficiency assessment/%	10

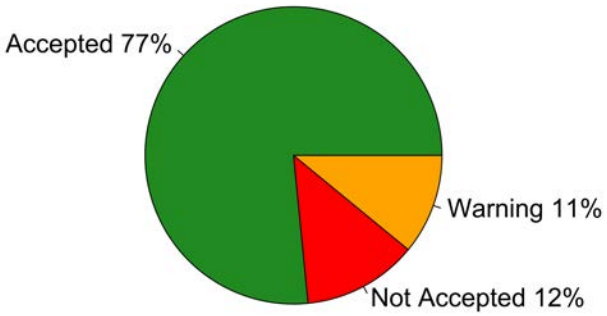

FIG. 3. Pie chart showing the percentage of results for As that were rated "accepted", "warning" and "not accepted".

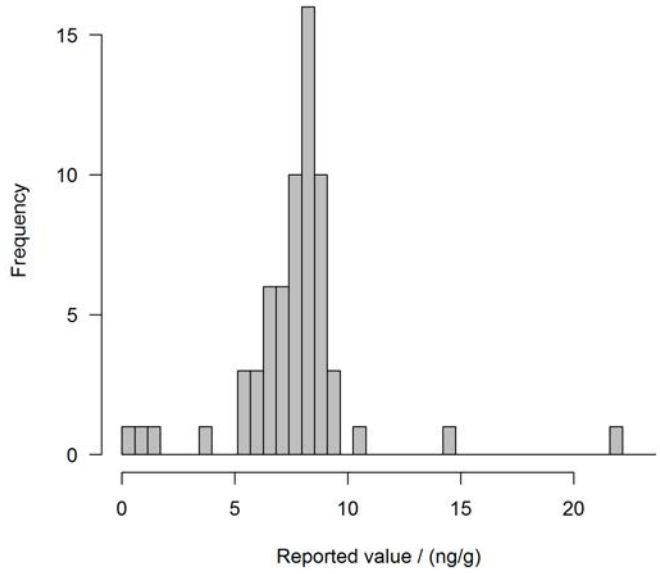

FIG. 4. Histogram showing frequency of reported values for As. Reported values exceeding 3× *the assigned value are not shown.*

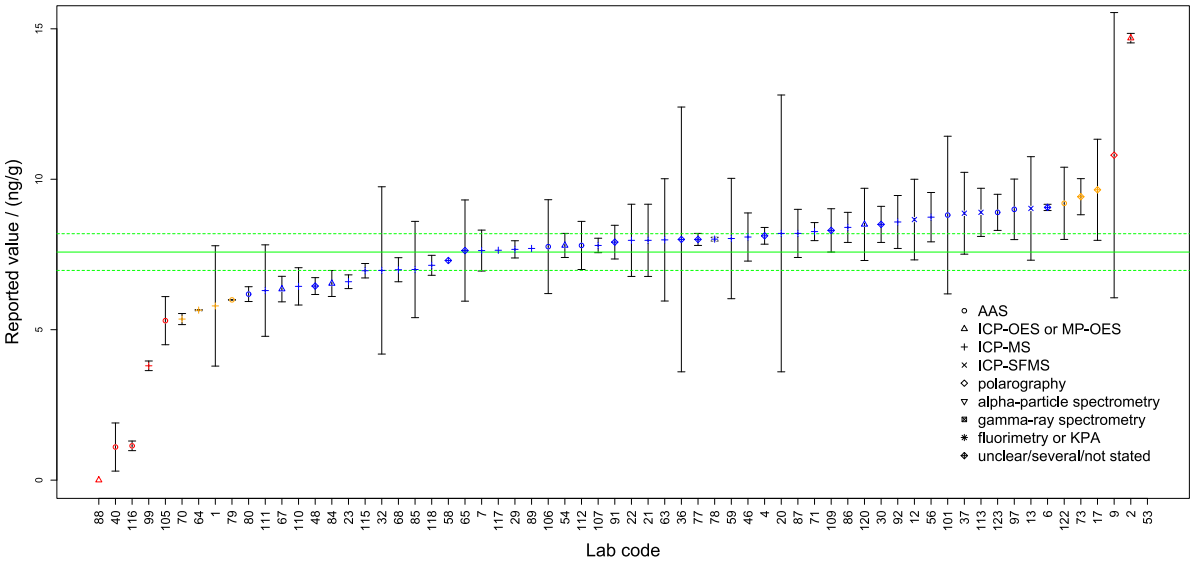

FIG. 5. Reported results for As, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

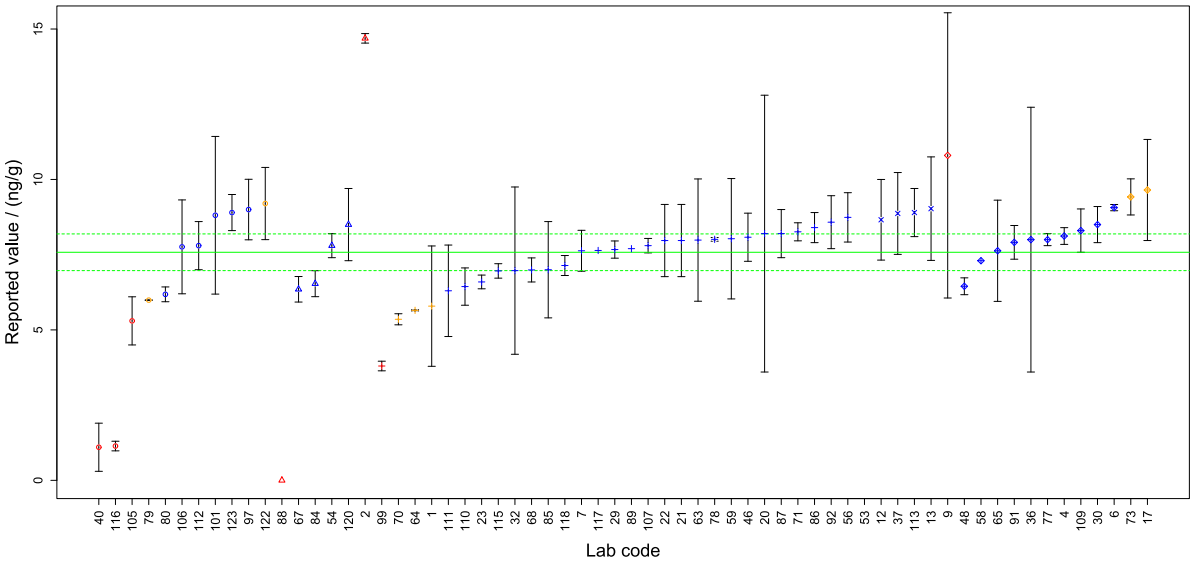

FIG. 6. Reported results for As, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 6. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
1	5.79	1	-23.6	35.1	-2.36	W	-1.71
2	14.69	0.079	93.8	15.6	9.38	N	22.57
4	8.12	0.139	7.1	9.3	0.71	A	1.61
6	9.064	0.052	19.6	9.7	1.96	A	4.80
7	7.63	0.34	0.7	12.0	0.07	A	0.11
9	10.8	2.37	42.5	45.4	4.25	N	1.35
12	8.66	0.67	14.2	18.0	1.42	A	1.47
13	9.03	0.86	19.1	21.3	1.91	A	1.59
17	9.65	0.84	27.3	20.2	2.73	W	2.32
20	8.2	2.3	8.2	56.8	0.82	A	0.27
21	7.97	0.6	5.1	17.3	0.51	A	0.58
22	7.97	0.6	5.1	17.3	0.51	A	0.58
23	6.594	0.114	-13.0	7.8	-1.30	A	-3.03
29	7.67	0.143	1.2	9.0	0.12	A	0.27
30	8.5	0.3	12.1	11.5	1.21	A	2.15
32	6.97	1.39	-8.0	40.6	-0.80	A	-0.43
36	8	2.2	5.5	55.7	0.55	A	0.19
37	8.87	0.68	17.0	18.0	1.70	A	1.73
40	1.1	0.4	-85.5	72.7	-8.55	N	-12.88
46	8.08	0.4	6.6	13.1	0.66	A	0.99
48	6.45	0.14	-14.9	8.1	-1.49	A	-3.37
53	21.7	1.3	186.3	26.0	18.63	N	10.57
54	7.8	0.2	2.9	9.7	0.29	A	0.60
56	8.74	0.41	15.3	13.2	1.53	A	2.27
58	7.3		-3.7		-0.37	A	
59	8.03	1	5.9	26.3	0.59	A	0.43
63	7.985	1.016	5.3	26.8	0.53	A	0.38
64	5.65	0.01	-25.5	6.0	-2.55	W	-6.32
65	7.63	0.841	0.7	23.5	0.07	A	0.06
67	6.35	0.2121	-16.2	9.5	-1.62	A	-3.31
68	6.993	0.2	-7.7	9.4	-0.77	A	-1.61
70	5.353	0.092	-29.4	6.6	-2.94	W	-6.99
71	8.26	0.15	9.0	9.5	0.90	A	2.00
73	9.42	0.3	24.3	11.9	2.43	W	4.30
77	8	0.1	5.5	8.9	0.55	A	1.31
78	8.01	0.030579	5.7	8.5	0.57	A	1.40
79	5.99	0.002	-21.0	6.4	-2.10	W	-5.21
80	6.182	0.123	-18.4	7.7	-1.84	A	-4.25
84	6.536	0.216	-13.8	9.6	-1.38	A	-2.79
85	7	0.8	-7.7	24.0	-0.77	A	-0.68
86	8.4	0.25	10.8	10.7	1.08	A	2.08
87	8.2	0.4	8.2	13.1	0.82	A	1.23
88	0		-100.0		-10.00	N	
89	7.7		1.6		0.16	A	
91	7.91	0.28	4.4	11.0	0.44	A	0.80
92	8.58	0.44	13.2	13.7	1.32	A	1.87
97	9	0.503	18.7	14.7	1.87	A	2.41
99	3.8	0.08	-49.9	5.8	-4.99	N	-11.99
101	8.81	1.31	16.2	31.2	1.62	A	0.91
105	5.3	0.4	-30.1	16.1	-3.01	N	-4.53
106	7.76	0.78	2.4	21.7	0.24	A	0.21
107	7.8	0.12	2.9	8.8	0.29	A	0.67
109	8.3	0.36	9.5	12.4	0.95	A	1.53
110	6.44	0.31	-15.0	11.8	-1.50	A	-2.62
111	6.3	0.76	-16.9	25.0	-1.69	A	-1.56
112	7.8	0.4	2.9	13.2	0.29	A	0.44

TABLE 6. EVALUATION RESULTS (CONTD.)

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
113	8.9	0.4	17.4	13.0	1.74	A	2.62
115	6.96	0.12	-8.2	8.2	-0.82	A	-1.89
116	1.14	0.08	-85.0	14.1	-8.50	N	-20.42
117	7.64		0.8		0.08	A	
118	7.14	0.166	-5.8	8.9	-0.58	A	-1.27
120	8.5	0.6	12.1	16.8	1.21	A	1.37
122	9.2	0.6	21.4	16.3	2.14	W	2.41
123	8.9	0.3	17.4	11.6	1.74	A	3.09

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TABLE 7. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	1.99
Expanded uncertainty (k=2)/(ng/g)	0.14
Relative standard deviation for proficiency assessment/%	10

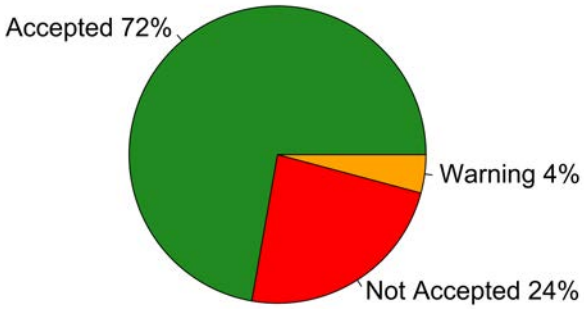

FIG. 7. Pie chart showing the percentage of results for Cd that were rated "accepted", "warning" and "not accepted".

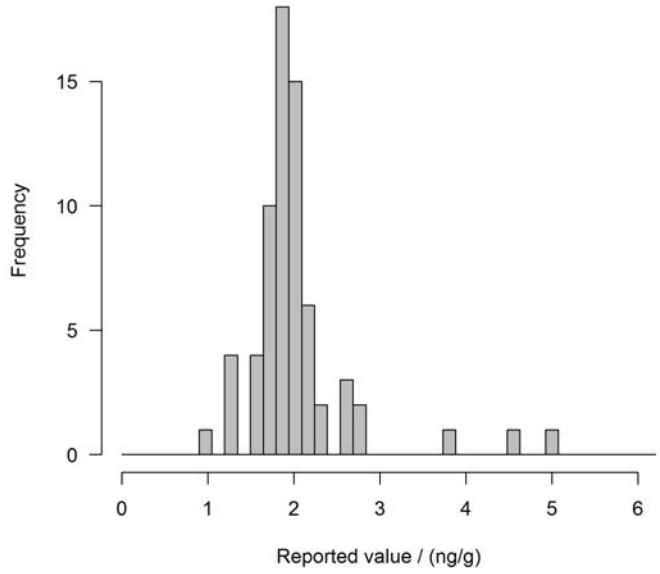

FIG. 8. Histogram showing frequency of reported values for Cd. Reported values exceeding 3× *the assigned value are not shown.*

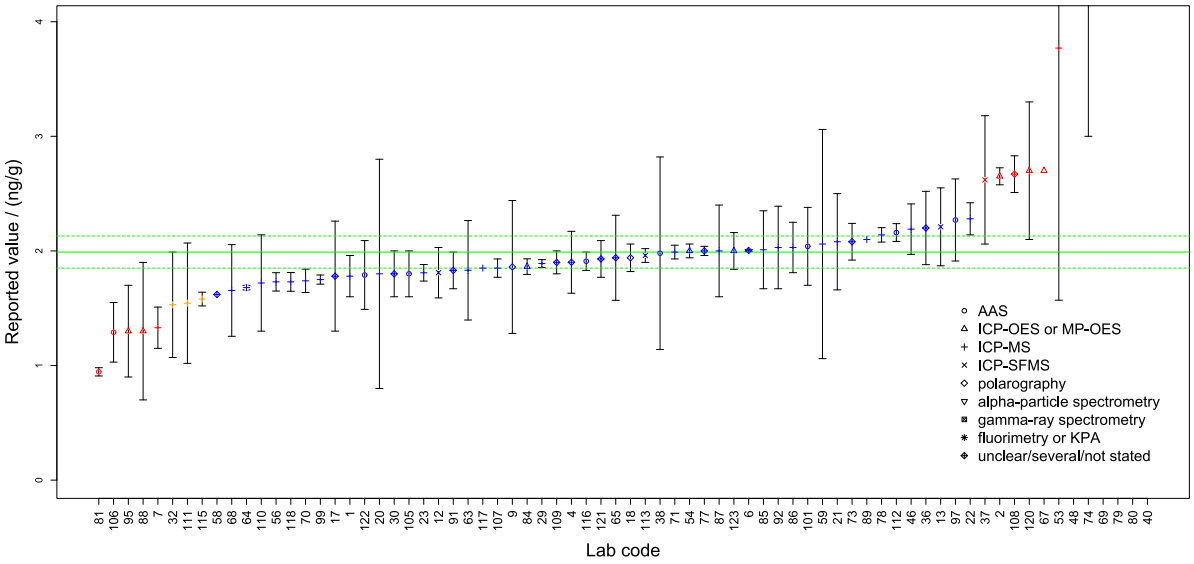

FIG. 9. Reported results for Cd, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

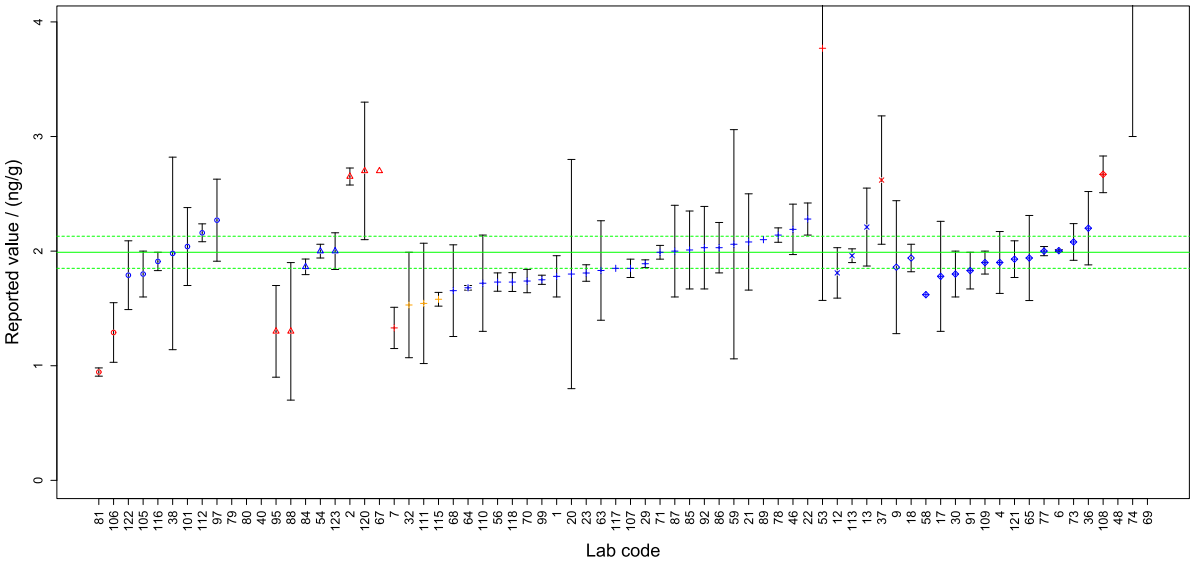

FIG. 10. Reported results for Cd, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 8. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
1	1.78	0.09	-10.6	11.9	-1.06	A	-1.84
2	2.651	0.0371	33.2	9.8	3.32	N	8.34
4	1.901	0.135	-4.5	15.7	-0.45	A	-0.59
6	2.0042	0.0041	0.7	7.1	0.07	A	0.20
7	1.33	0.09	-33.2	14.3	-3.32	N	-5.79
9	1.86	0.29	-6.5	31.9	-0.65	A	-0.44
12	1.81	0.11	-9.0	13.7	-0.90	A	-1.38
13	2.21	0.17	11.1	17.3	1.11	A	1.20
17	1.78	0.24	-10.6	27.7	-1.06	A	-0.84
18	1.94	0.06	-2.5	9.2	-0.25	A	-0.54
20	1.8	0.5	-9.5	55.9	-0.95	A	-0.38
21	2.08	0.21	4.5	21.5	0.45	A	0.41
22	2.28	0.07	14.6	10.1	1.46	A	2.93
23	1.809	0.036	-9.1	7.5	-0.91	A	-2.30
29	1.89	0.017	-5.0	6.9	-0.50	A	-1.39
30	1.8	0.1	-9.5	12.8	-0.95	A	-1.56
32	1.53	0.23	-23.1	30.5	-2.31	W	-1.91
36	2.2	0.16	10.6	16.5	1.06	A	1.20
37	2.62	0.28	31.7	23.3	3.17	N	2.18
38	1.98	0.42	-0.5	43.0	-0.05	A	-0.02
40	179.8	2.25	8935.2	635.6	893.52	N	78.99
46	2.19	0.11	10.1	12.7	1.01	A	1.53
48	4.48	0.16	125.1	17.4	12.51	N	14.26
53	3.77	1.1	89.4	59.9	8.94	N	1.61
54	2	0.03	0.5	7.7	0.05	A	0.13
56	1.73	0.04	-13.1	7.7	-1.31	A	-3.22
58	1.62		-18.6		-1.86	A	
59	2.06	0.5	3.5	49.1	0.35	A	0.14
63	1.831	0.217	-8.0	24.6	-0.80	A	-0.70
64	1.68	0.01	-15.6	6.1	-1.56	A	-4.38
65	1.94	0.1856	-2.5	20.3	-0.25	A	-0.25
67	2.7		35.7		3.57	N	
68	1.655	0.2	-16.8	24.9	-1.68	A	-1.58
69	7	0.4	251.8	27.3	25.18	N	12.34
70	1.739	0.051	-12.6	8.5	-1.26	A	-2.90
71	1.99	0.03	0.0	7.7	0.00	A	0.00
73	2.08	0.08	4.5	10.6	0.45	A	0.85
74	5	1	151.3	43.7	15.13	N	3.00
77	2	0.02	0.5	7.3	0.05	A	0.14
78	2.14	0.031419	7.5	8.1	0.75	A	1.95
79	20		905.0		90.50	N	
80	20	0.142	905.0	70.7	90.50	N	113.76
81	0.945	0.018	-52.5	5.1	-5.25	N	-14.46
84	1.863	0.034	-6.4	7.5	-0.64	A	-1.63
85	2.01	0.17	1.0	18.3	0.10	A	0.11
86	2.03	0.11	2.0	13.0	0.20	A	0.31
87	2	0.2	0.5	21.2	0.05	A	0.05
88	1.3	0.3	-34.7	46.4	-3.47	N	-2.24
89	2.1		5.5		0.55	A	
91	1.83	0.08	-8.0	10.9	-0.80	A	-1.51
92	2.03	0.18	2.0	19.1	0.20	A	0.21
95	1.3	0.2	-34.7	31.1	-3.47	N	-3.26
97	2.27	0.179	14.1	17.7	1.41	A	1.46
99	1.75	0.02	-12.1	6.6	-1.21	A	-3.30
101	2.04	0.17	2.5	18.2	0.25	A	0.27
105	1.8	0.1	-9.5	12.8	-0.95	A	-1.56

TABLE 8. EVALUATION RESULTS (CONTD.)

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
106	1.29	0.13	-35.2	20.7	-3.52	N	-4.74
107	1.85	0.04	-7.0	7.8	-0.70	A	-1.74
108	2.67	0.08	34.2	11.2	3.42	N	6.40
109	1.9	0.05	-4.5	8.5	-0.45	A	-1.05
110	1.72	0.21	-13.6	25.2	-1.36	A	-1.22
111	1.544	0.2625	-22.4	34.4	-2.24	W	-1.64
112	2.16	0.039	8.5	8.4	0.85	A	2.12
113	1.96	0.03	-1.5	7.6	-0.15	A	-0.39
115	1.58	0.03	-20.6	6.8	-2.06	W	-5.38
116	1.91	0.04	-4.0	7.9	-0.40	A	-0.99
117	1.85		-7.0		-0.70	A	
118	1.73	0.041	-13.1	7.7	-1.31	A	-3.20
120	2.7	0.3	35.7	24.2	3.57	N	2.30
121	1.93	0.08	-3.0	10.7	-0.30	A	-0.56
122	1.79	0.15	-10.1	17.9	-1.01	A	-1.21
123	2	0.08	0.5	10.7	0.05	A	0.09

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TABLE 9. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	5.41
Expanded uncertainty (k=2)/(ng/g)	0.88
Relative standard deviation for proficiency assessment/%	12.5

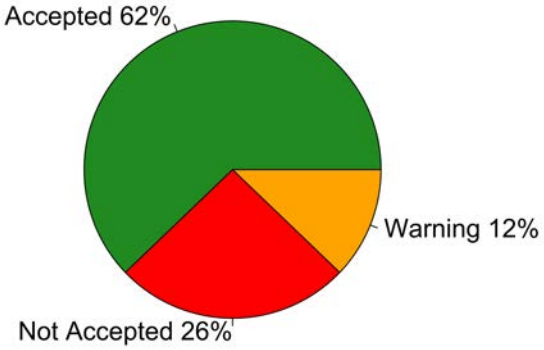

FIG. 11. Pie chart showing the percentage of results for Cu that were rated "accepted", "warning" and "not accepted".

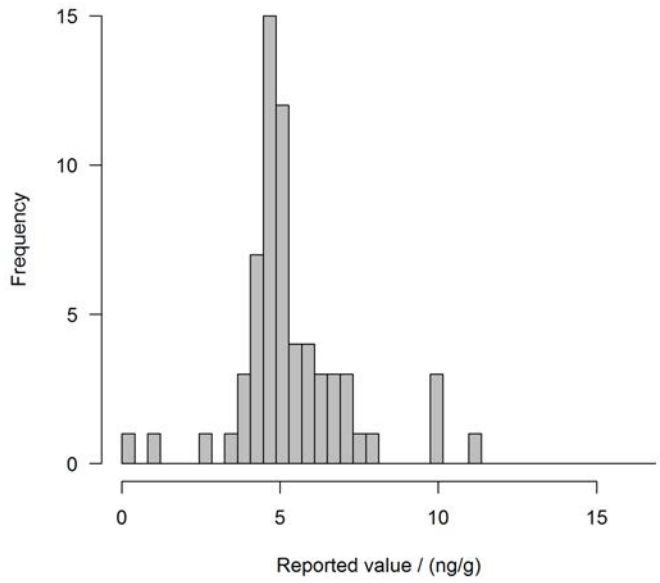

FIG. 12. Histogram showing frequency of reported values for Cu. Reported values exceeding 3× *the assigned value are not shown.*

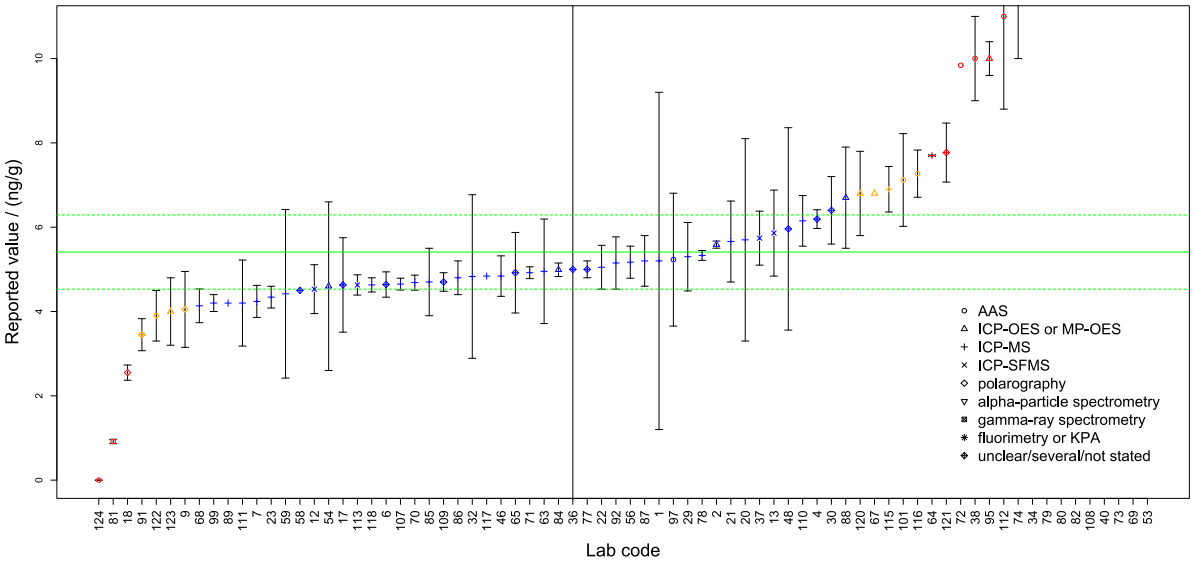

FIG. 13. Reported results for Cu, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

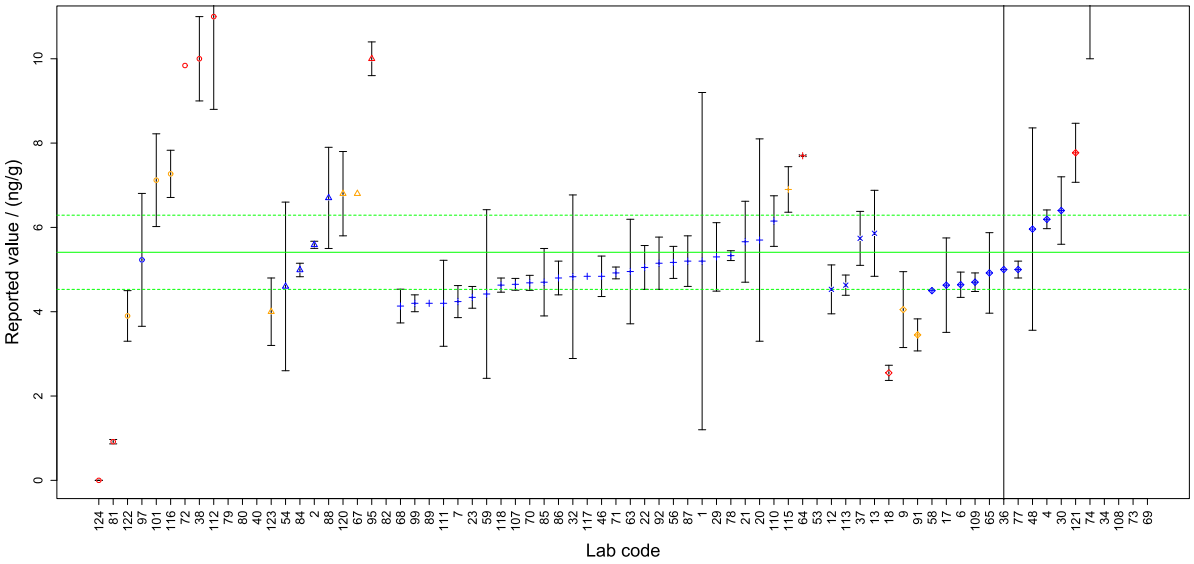

FIG. 14. Reported results for Cu, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 10. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
1	5.2	2	-3.9	78.5	-0.31	A	-0.10
2	5.587	0.0423	3.3	16.9	0.26	A	0.40
4	6.192	0.111	14.5	19.0	1.16	A	1.72
6	4.64	0.15	-14.2	15.4	-1.14	A	-1.66
7	4.24	0.19	-21.6	15.6	-1.73	A	-2.44
9	4.05	0.45	-25.1	25.3	-2.01	W	-2.16
12	4.53	0.29	-16.3	18.7	-1.30	A	-1.67
13	5.86	0.51	8.3	24.8	0.67	A	0.67
17	4.63	0.56	-14.4	27.9	-1.15	A	-1.10
18	2.55	0.09	-52.9	10.4	-4.23	N	-6.37
20	5.7	1.2	5.4	45.5	0.43	A	0.23
21	5.66	0.48	4.6	24.0	0.37	A	0.38
22	5.05	0.26	-6.7	18.3	-0.53	A	-0.70
23	4.341	0.129	-19.8	14.3	-1.58	A	-2.33
29	5.3	0.406	-2.0	22.1	-0.16	A	-0.18
30	6.4	0.4	18.3	22.9	1.46	A	1.66
32	4.83	0.97	-10.7	42.7	-0.86	A	-0.54
34	19	1	251.2	58.1	20.10	N	12.44
36	5	3.6	-7.6	144.8	-0.61	A	-0.11
37	5.74	0.32	6.1	20.5	0.49	A	0.61
38	10	0.5	84.8	31.7	6.79	N	6.89
40	44	4.3	713.3	133.7	57.06	N	8.93
46	4.84	0.24	-10.5	17.6	-0.84	A	-1.14
48	5.96	1.2	10.2	44.1	0.81	A	0.43
53	68.9	5.8	1173.6	207.8	93.89	N	10.92
54	4.6	1	-15.0	45.6	-1.20	A	-0.74
56	5.17	0.19	-4.4	17.2	-0.35	A	-0.50
58	4.5		-16.8		-1.35	A	
59	4.42	1	-18.3	47.2	-1.46	A	-0.91
63	4.953	0.62	-8.4	29.1	-0.68	A	-0.60
64	7.7	0.01	42.3	23.2	3.39	N	5.20
65	4.92	0.4775	-9.1	24.4	-0.72	A	-0.75
67	6.8		25.7		2.06	W	
68	4.134	0.2	-23.6	15.8	-1.89	A	-2.64
69	63	17.8	1064.5	197.7	85.16	N	3.23
70	4.685	0.089	-13.4	14.6	-1.07	A	-1.62
71	4.92	0.07	-9.1	15.1	-0.72	A	-1.10
72	9.84		81.9		6.55	N	
73	46.12	0.71	752.5	138.7	60.20	N	48.74
74	18	4	232.7	70.0	18.62	N	3.13
77	5	0.1	-7.6	15.6	-0.61	A	-0.91
78	5.33	0.05829	-1.5	16.2	-0.12	A	-0.18
79	20		269.7		21.57	N	
80	20	0.512	269.7	60.4	21.57	N	21.61
81	0.917	0.026	-83.0	6.3	-6.64	N	-10.19
82	29.39	1.68	443.3	89.1	35.46	N	13.81
84	4.99	0.08	-7.8	15.3	-0.62	A	-0.94
85	4.7	0.4	-13.1	22.1	-1.05	A	-1.19
86	4.8	0.2	-11.3	16.7	-0.90	A	-1.26
87	5.2	0.3	-3.9	19.4	-0.31	A	-0.39
88	6.7	0.6	23.8	27.0	1.91	A	1.73
89	4.2		-22.4		-1.79	A	
91	3.45	0.19	-36.2	15.1	-2.90	W	-4.09
92	5.15	0.31	-4.8	19.6	-0.38	A	-0.48
95	10	0.2	84.8	30.3	6.79	N	9.50
97	5.23	0.788	-3.3	34.0	-0.27	A	-0.20

TABLE 10. EVALUATION RESULTS (CONTD.)

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
99	4.2	0.1	-22.4	13.5	-1.79	A	-2.68
101	7.12	0.55	31.6	26.4	2.53	W	2.43
107	4.65	0.07	-14.0	14.3	-1.12	A	-1.71
108	34.41	0.03	536.0	103.5	42.88	N	65.76
109	4.7	0.11	-13.1	14.9	-1.05	A	-1.57
110	6.15	0.3	13.7	20.9	1.09	A	1.39
111	4.2	0.51	-22.4	27.4	-1.79	A	-1.80
112	11	1.1	103.3	38.7	8.27	N	4.72
113	4.63	0.12	-14.4	14.9	-1.15	A	-1.71
115	6.9	0.27	27.5	22.2	2.20	W	2.89
116	7.27	0.28	34.4	23.2	2.75	W	3.57
117	4.84		-10.5		-0.84	A	
118	4.631	0.084	-14.4	14.4	-1.15	A	-1.74
120	6.8	0.5	25.7	25.2	2.06	W	2.09
121	7.77	0.35	43.6	25.0	3.49	N	4.20
122	3.9	0.3	-27.9	19.3	-2.23	W	-2.84
123	4	0.4	-26.1	23.3	-2.09	W	-2.37
124	0	0.0014	-100.0	Inf	-8.00	N	-12.30

I.4 LEAD

TABLE 11. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	9.7
Expanded uncertainty (k=2)/(ng/g)	1.8
Relative standard deviation for proficiency assessment/%	15

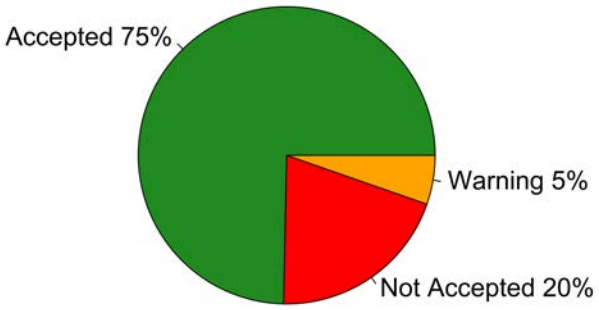

FIG. 15. Pie chart showing the percentage of results for Pb that were rated "accepted", "warning" and "not accepted".

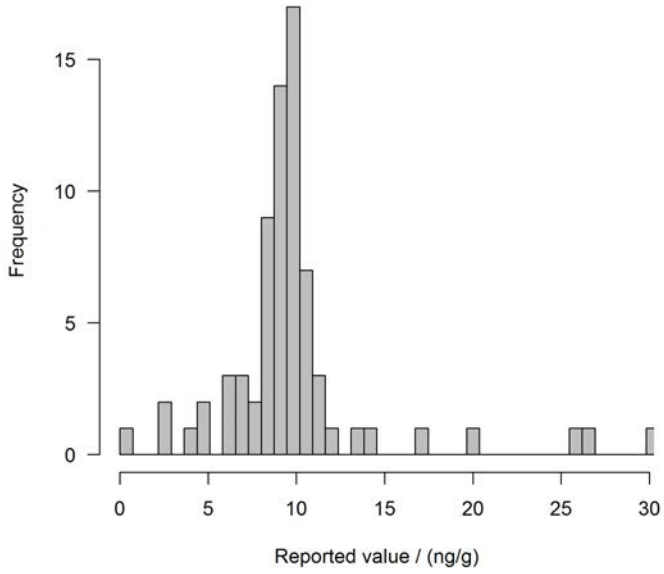

FIG. 16. Histogram showing frequency of reported values for Pb. Reported values exceeding 3× *the assigned value are not shown.*

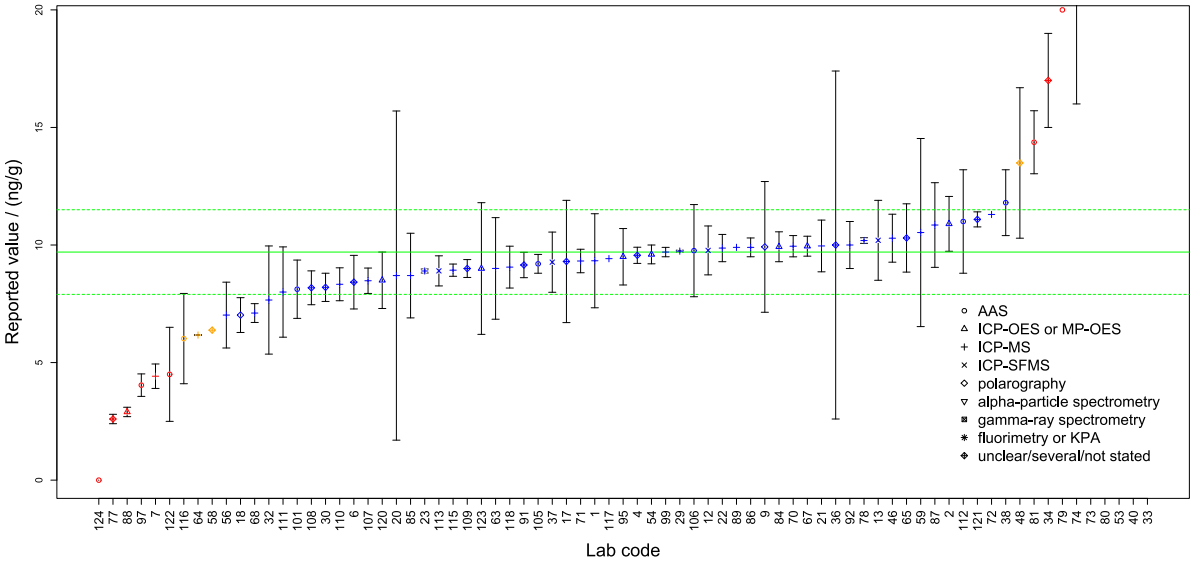

FIG. 17. Reported results for Pb, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

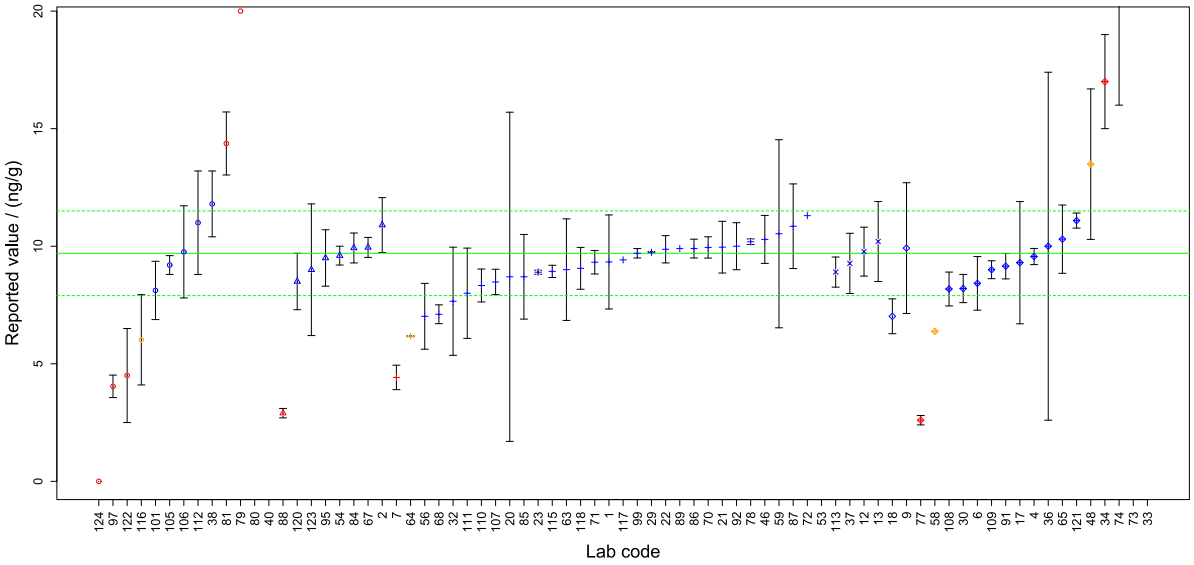

FIG. 18. Reported results for Pb, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 12. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
1	9.33	1	-3.8	27.9	-0.25	A	-0.28
2	10.9	0.583	12.4	23.4	0.82	A	1.12
4	9.562	0.172	-1.4	18.6	-0.09	A	-0.15
6	8.42	0.57	-13.2	21.0	-0.88	A	-1.20
7	4.42	0.26	-54.4	14.5	-3.63	N	-5.64
9	9.92	1.39	2.3	33.8	0.15	A	0.13
12	9.77	0.52	0.7	21.5	0.05	A	0.07
13	10.2	0.85	5.2	25.7	0.34	A	0.40
17	9.3	1.3	-4.1	33.1	-0.27	A	-0.25
18	7.02	0.37	-27.6	17.1	-1.84	A	-2.75
20	8.7	3.5	-10.3	82.2	-0.69	A	-0.28
21	9.96	0.55	2.7	22.0	0.18	A	0.25
22	9.87	0.29	1.8	19.8	0.12	A	0.18
23	8.895	0.042	-8.3	17.0	-0.55	A	-0.89
29	9.74	0.02	0.4	18.6	0.03	A	0.04
30	8.2	0.3	-15.5	17.3	-1.03	A	-1.58
32	7.66	1.15	-21.0	33.4	-1.40	A	-1.40
33	250	0.127	2477.3	478.3	165.15	N	264.38
34	17	1	75.3	34.6	5.02	N	5.43
36	10	3.7	3.1	76.4	0.21	A	0.08
37	9.27	0.64	-4.4	22.5	-0.30	A	-0.39
38	11.8	0.7	21.6	25.5	1.44	A	1.84
40	111.3	10.75	1047.4	213.8	69.83	N	9.42
46	10.29	0.51	6.1	22.0	0.41	A	0.57
48	13.49	1.6	39.1	35.1	2.60	W	2.06
53	30.7	1.8	216.5	59.9	14.43	N	10.43
54	9.6	0.2	-1.0	18.8	-0.07	A	-0.11
56	7.02	0.7	-27.6	24.0	-1.84	A	-2.35
58	6.38		-34.2		-2.28	W	
59	10.53	2	8.6	43.0	0.57	A	0.38
63	9.004	1.08	-7.2	29.5	-0.48	A	-0.50
64	6.17	0.01	-36.4	11.8	-2.43	W	-3.92
65	10.3	0.7261	6.2	24.2	0.41	A	0.52
67	9.95	0.2121	2.6	19.5	0.17	A	0.27
68	7.106	0.2	-26.7	14.7	-1.78	A	-2.81
70	9.949	0.226	2.6	19.6	0.17	A	0.27
71	9.32	0.25	-3.9	18.6	-0.26	A	-0.41
72	11.3		16.5		1.10	A	
73	26.25	0.95	170.6	50.7	11.37	N	12.65
74	26	5	168.0	62.9	11.20	N	3.21
77	2.6	0.1	-73.2	9.2	-4.88	N	-7.84
78	10.19	0.05922	5.1	19.5	0.34	A	0.54
79	20		106.2		7.08	N	
80	30	0.213	209.3	57.4	13.95	N	21.95
81	14.37	0.67	48.1	29.0	3.21	N	4.16
84	9.925	0.318	2.3	20.0	0.15	A	0.24
85	8.7	0.9	-10.3	26.6	-0.69	A	-0.79
86	9.9	0.2	2.1	19.4	0.14	A	0.22
87	10.85	0.9	11.9	26.6	0.79	A	0.90
88	2.9	0.1	-70.1	8.9	-4.67	N	-7.51
89	9.9		2.1		0.14	A	
91	9.15	0.27	-5.7	18.5	-0.38	A	-0.59
92	10	0.5	3.1	21.6	0.21	A	0.29
95	9.5	0.6	-2.1	22.1	-0.14	A	-0.18
97	4.04	0.239	-58.4	14.1	-3.89	N	-6.08
99	9.7	0.1	0.0	18.7	0.00	A	0.00

TABLE 12. EVALUATION RESULTS (CONTD.)

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
101	8.12	0.62	-16.3	21.8	-1.09	A	-1.45
105	9.2	0.2	-5.2	18.1	-0.34	A	-0.54
106	9.76	0.98	0.6	27.4	0.04	A	0.05
107	8.48	0.27	-12.6	17.4	-0.84	A	-1.30
108	8.18	0.36	-15.7	18.0	-1.04	A	-1.57
109	9	0.19	-7.2	17.7	-0.48	A	-0.76
110	8.33	0.35	-14.1	18.0	-0.94	A	-1.42
111	8	0.96	-17.5	28.5	-1.17	A	-1.29
112	11	1.1	13.4	29.0	0.89	A	0.91
113	8.9	0.32	-8.2	18.5	-0.55	A	-0.84
115	8.93	0.13	-7.9	17.3	-0.53	A	-0.85
116	6.02	0.96	-37.9	33.9	-2.53	W	-2.80
117	9.42		-2.9		-0.19	A	
118	9.06	0.445	-6.6	19.9	-0.44	A	-0.64
120	8.5	0.6	-12.4	21.5	-0.82	A	-1.11
121	11.09	0.16	14.3	21.4	0.96	A	1.52
122	4.5	1	-53.6	45.3	-3.57	N	-3.87
123	9	1.4	-7.2	35.6	-0.48	A	-0.42
124	0	0.0003	-100.0	Inf	-6.67	N	-10.78

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TABLE 13. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	0.0222
Expanded uncertainty (k=2)/(ng/g)	0.0019
Relative standard deviation for proficiency assessment/ %	15

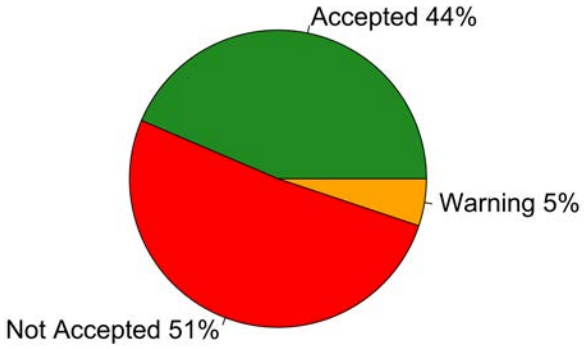

FIG. 19. Pie chart showing the percentage of results for U-235 that were rated "accepted", "warning" and "not accepted".

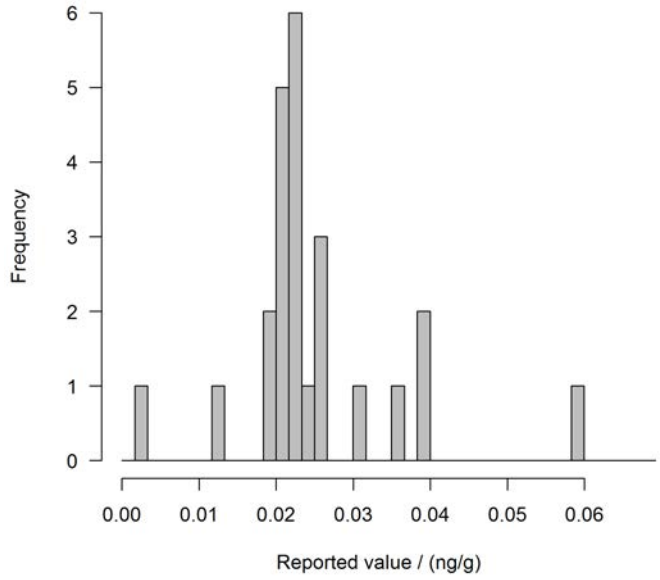

FIG. 20. Histogram showing frequency of reported values for U-235. Reported values exceeding 3× *the assigned value are not shown.*

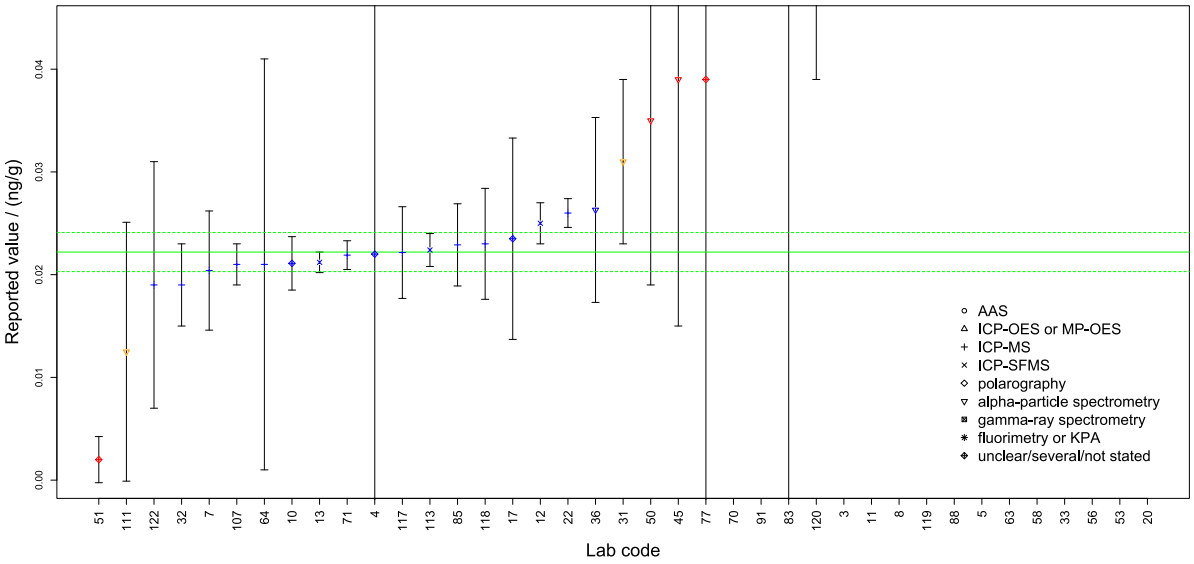

FIG. 21. Reported results for U-235, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

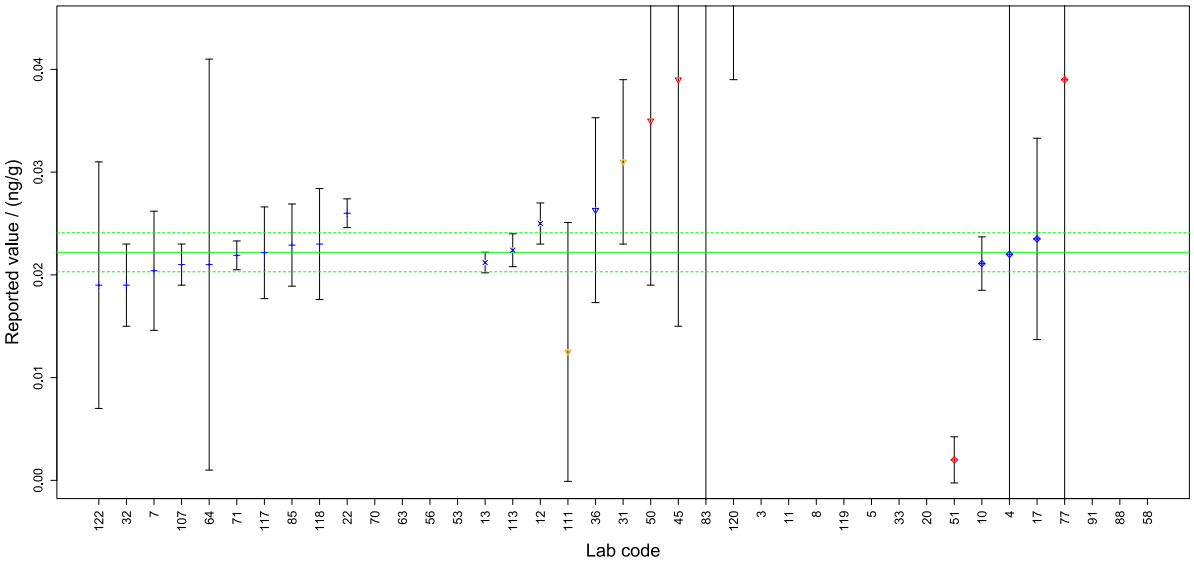

FIG. 22. Reported results for U-235, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 14. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
3	0.094	0.02	323.4	55.9	21.56	N	3.59
4	0.022	0.087	-0.9	791.0	-0.06	A	-0.00
5	0.8	0.12	3503.6	309.9	233.57	N	6.48
7	0.0204	0.0029	-8.1	29.5	-0.54	A	-0.59
8	0.176	0.042	692.8	83.0	46.19	N	3.66
10	0.0211	0.0013	-5.0	14.8	-0.33	A	-0.68
11	0.13	0.03	485.6	68.1	32.37	N	3.59
12	0.025	0.001	12.6	12.5	0.84	A	2.03
13	0.0212	0.0005	-4.5	9.4	-0.30	A	-0.93
17	0.0235	0.0049	5.9	42.7	0.39	A	0.26
20	11	1.8	49449.5	4240.9	3296.64	N	6.10
22	0.026	0.0007	17.1	11.4	1.14	A	3.22
31	0.031	0.004	39.6	28.4	2.64	W	2.14
32	0.019	0.002	-14.4	22.3	-0.96	A	-1.45
33	2.25121	0.0353	10040.6	867.9	669.37	N	63.12
36	0.0263	0.0045	18.5	35.7	1.23	A	0.89
45	0.039	0.012	75.7	63.3	5.05	N	1.40
50	0.035	0.008	57.7	47.7	3.84	N	1.59
51	0.001994	0.001123	-91.0	112.6	-6.07	N	-13.74
53	5.6	2.6	25125.2	2160.9	1675.02	N	2.15
56	2.89	0.06	12918.0	1114.2	861.20	N	47.79
58	2.18		9719.8		647.99	N	
63	1.37		6071.2		404.74	N	
64	0.021	0.01	-5.4	95.6	-0.36	A	-0.12
70	0.0586	0.0016	164.0	23.2	10.93	N	19.56
71	0.0219	0.0007	-1.4	10.6	-0.09	A	-0.25
77	0.039	0.025	75.7	129.1	5.05	N	0.67
83	0.084	1	278.4	2381.2	18.56	N	0.06
85	0.0229	0.002	3.2	19.6	0.21	A	0.32
88	0.32	0.05	1341.4	127.3	89.43	N	5.95
91	0.0739	0.0028	232.9	29.5	15.53	N	17.49
107	0.021	0.001	-5.4	12.5	-0.36	A	-0.87
111	0.0125	0.0063	-43.7	100.9	-2.91	W	-1.52
113	0.0224	0.0008	0.9	11.2	0.06	A	0.16
117	0.022151	0.002231138	-0.2	21.9	-0.01	A	-0.02
118	0.023	0.0027	3.6	25.1	0.24	A	0.28
119	0.31	0.05	1296.4	123.8	86.43	N	5.75
120	0.093	0.027	318.9	68.2	21.26	N	2.62
122	0.019	0.006	-14.4	63.6	-0.96	A	-0.53

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TABLE 15. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	3.06
Expanded uncertainty (k=2)/(ng/g)	0.28
Relative standard deviation for proficiency assessment/%	12.5

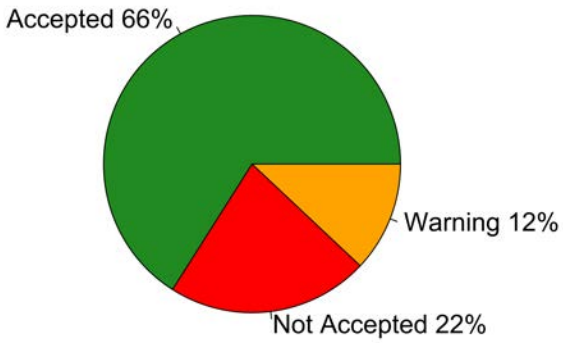

FIG. 23. Pie chart showing the percentage of results for U-238 that were rated "accepted", "warning" and "not accepted".

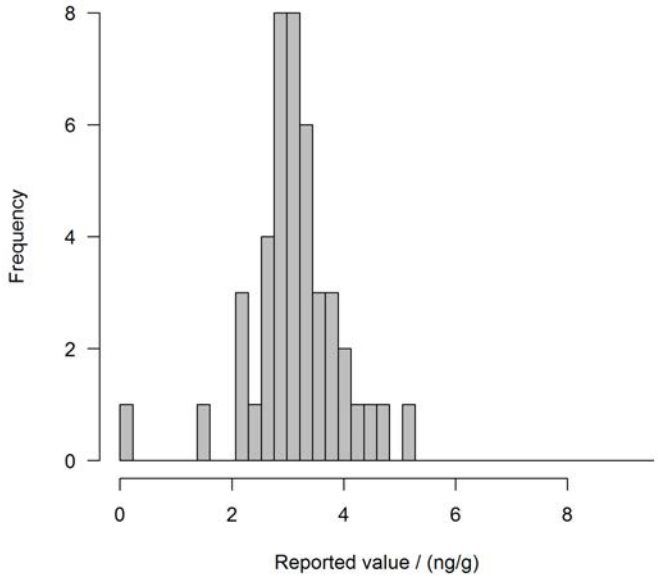

FIG. 24. Histogram showing frequency of reported values for U-238. Reported values exceeding 3× *the assigned value are not shown.*

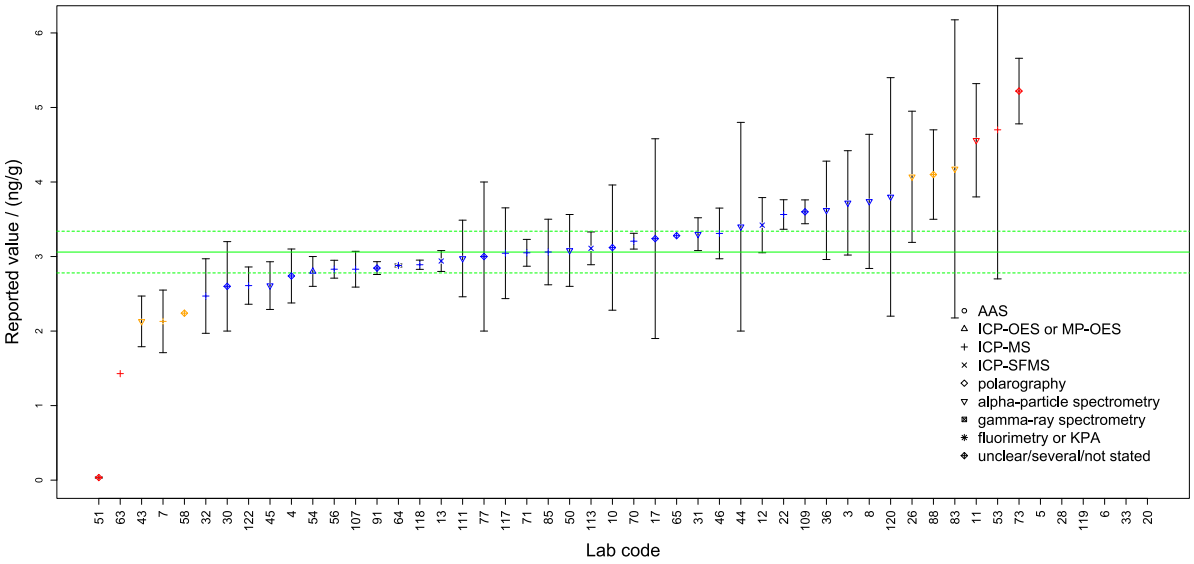

FIG. 25. Reported results for U-238, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

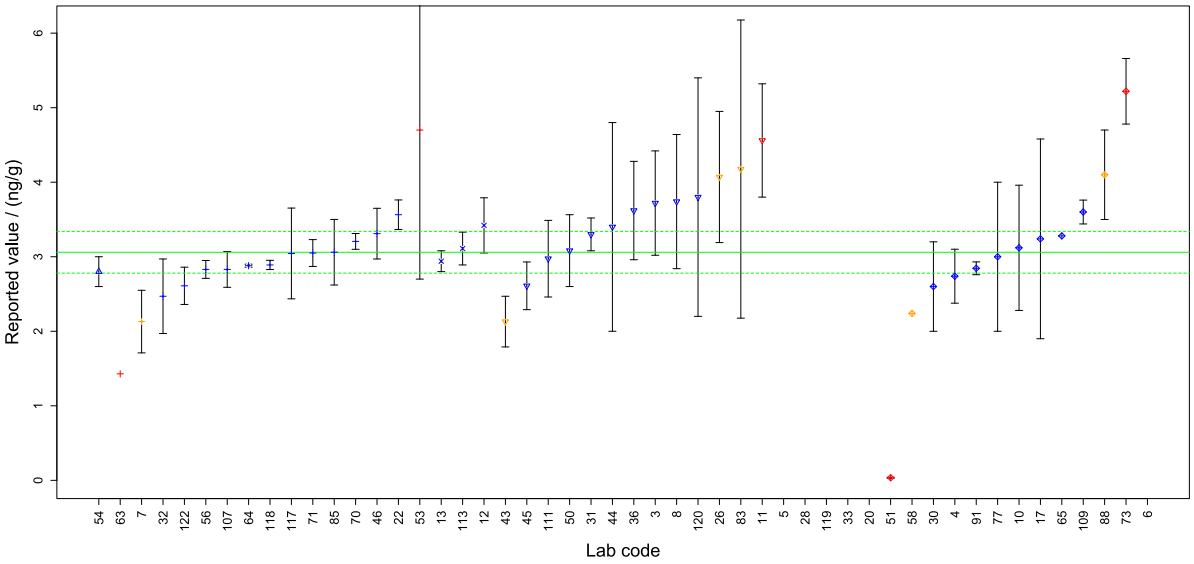

FIG. 26. Reported results for U-238, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 16. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
3	3.72	0.35	21.6	21.9	1.73	A	1.75
4	2.739	0.181	-10.5	15.5	-0.84	A	-1.40
5	17.3	2.8	465.4	61.0	37.23	N	5.08
6	61.45	14.55	1908.2	189.8	152.65	N	4.01
7	2.13	0.21	-30.4	20.7	-2.43	W	-3.68
8	3.74	0.45	22.2	26.5	1.78	A	1.44
10	3.12	0.42	2.0	28.5	0.16	A	0.14
11	4.56	0.38	49.0	21.5	3.92	N	3.70
12	3.421	0.185	11.8	14.9	0.94	A	1.56
13	2.94	0.07	-3.9	10.0	-0.31	A	-0.77
17	3.24	0.67	5.9	42.5	0.47	A	0.26
20	604	123	19638.6	1806.6	1571.08	N	4.89
22	3.564	0.099	16.5	12.0	1.32	A	2.94
26	4.07	0.44	33.0	24.8	2.64	W	2.19
28	17.6	0.23	475.2	52.7	38.01	N	54.00
30	2.6	0.3	-15.0	24.4	-1.20	A	-1.39
31	3.3	0.11	7.8	11.9	0.63	A	1.35
32	2.47	0.25	-19.3	21.5	-1.54	A	-2.06
33	225.2	0.141	7259.5	673.4	580.76	N	1117.98
36	3.62	0.33	18.3	21.2	1.46	A	1.56
43	2.13	0.17	-30.4	17.2	-2.43	W	-4.22
44	3.4	0.7	11.1	42.4	0.89	A	0.48
45	2.61	0.16	-14.7	14.5	-1.18	A	-2.12
46	3.31	0.17	8.2	14.3	0.65	A	1.14
50	3.082	0.241	0.7	18.2	0.06	A	0.08
51	0.03481	0.003709	-98.9	21.3	-7.91	N	-21.60
53	4.7	1	53.6	44.8	4.29	N	1.62
54	2.8	0.1	-8.5	11.0	-0.68	A	-1.51
56	2.83	0.06	-7.5	9.5	-0.60	A	-1.51
58	2.24		-26.8		-2.14	W	
63	1.429		-53.3		-4.26	N	
64	2.88	0.01	-5.9	8.6	-0.47	A	-1.28
65	3.28		7.2		0.58	A	
70	3.206	0.053	4.8	10.1	0.38	A	0.98
71	3.05	0.09	-0.3	10.9	-0.03	A	-0.06
73	5.22	0.22	70.6	17.7	5.65	N	8.28
77	3	0.5	-2.0	34.5	-0.16	A	-0.12
83	4.176	1	36.5	49.5	2.92	W	1.11
85	3.0608	0.22	0.0	17.0	0.00	A	0.00
88	4.1	0.3	34.0	19.1	2.72	W	3.14
91	2.845	0.043	-7.0	9.0	-0.56	A	-1.47
107	2.83	0.12	-7.5	12.0	-0.60	A	-1.25
109	3.6	0.08	17.6	11.6	1.41	A	3.35
111	2.974	0.257	-2.8	19.4	-0.22	A	-0.29
113	3.11	0.11	1.6	11.7	0.13	A	0.28
117	3.044229	0.304422907	-0.5	22.0	-0.04	A	-0.05
118	2.89	0.031	-5.6	8.9	-0.44	A	-1.19
119	42.7	6.4	1295.4	131.2	103.63	N	6.19
120	3.8	0.8	24.2	43.6	1.93	A	0.91
122	2.61	0.125	-14.7	12.4	-1.18	A	-2.40

I.7 URANIUM (TOTAL)

TABLE 17. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	3.08
Expanded uncertainty (k=2)/(ng/g)	0.28
Relative standard deviation for proficiency assessment/%	12.5

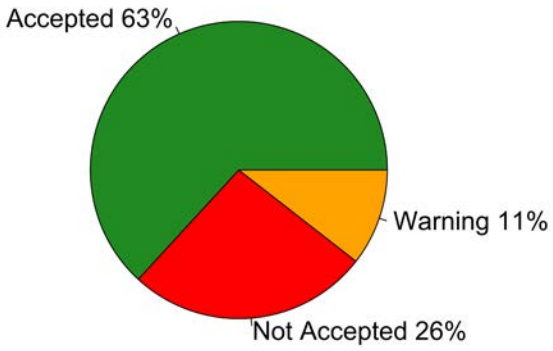

FIG. 27. Pie chart showing the percentage of results for U-total that were rated "accepted", "warning" and "not accepted".

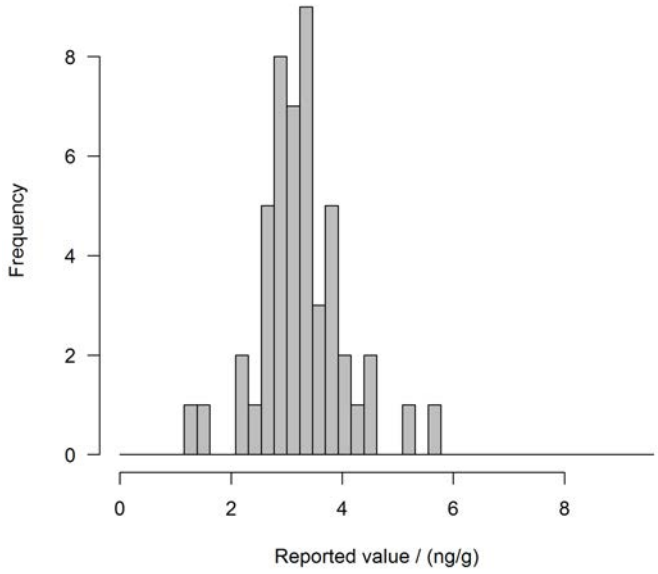

FIG. 28. Histogram showing frequency of reported values for U-total. Reported values exceeding 3× *the assigned value are not shown.*

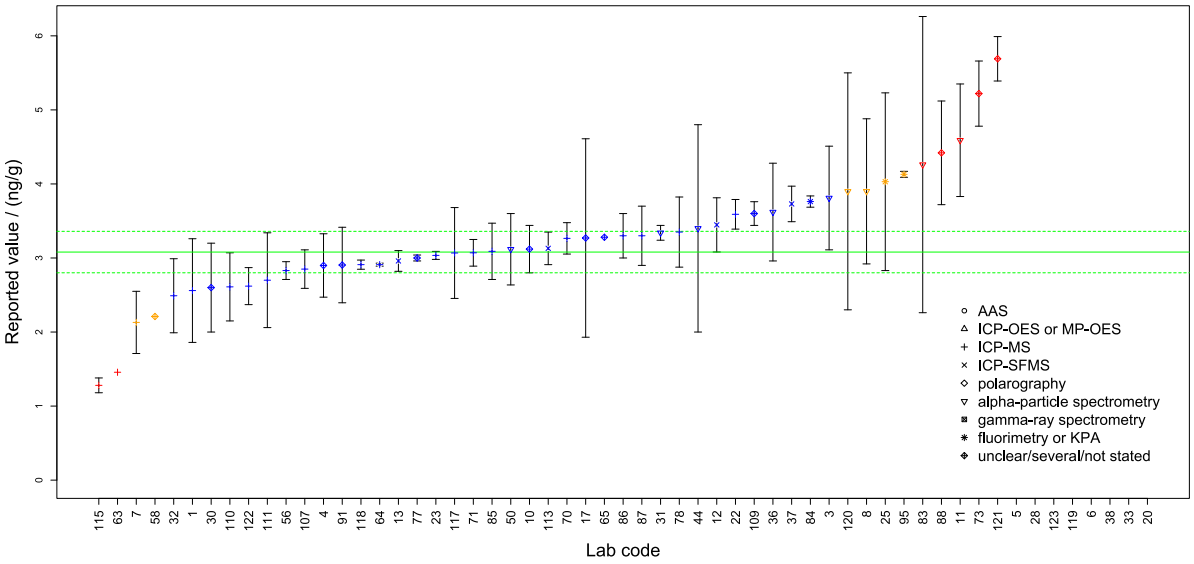

FIG. 29. Reported results for U-total, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

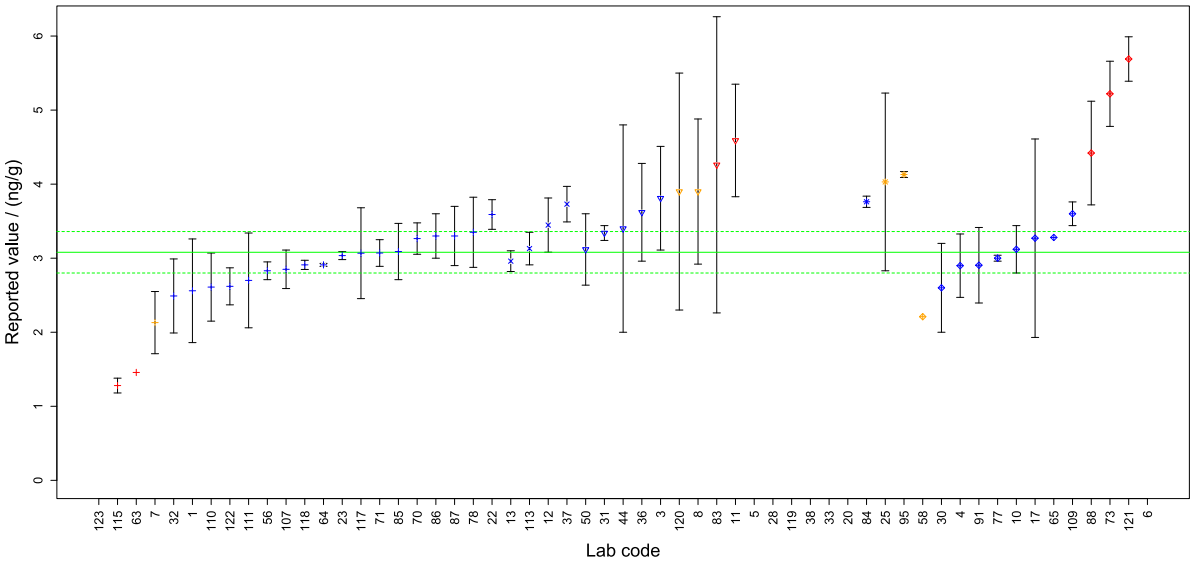

FIG. 30. Reported results for U-total, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 18. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
1	2.56	0.35	-16.9	28.4	-1.35	A	-1.38
3	3.81	0.35	23.7	21.5	1.90	A	1.94
4	2.899	0.214	-5.9	17.1	-0.47	A	-0.71
5	18.1	2.8	487.7	61.7	39.01	N	5.36
6	61.45	14.55	1895.1	187.5	151.61	N	4.01
7	2.13	0.21	-30.8	20.7	-2.47	W	-3.76
8	3.9	0.49	26.6	27.6	2.13	W	1.61
10	3.12	0.16	1.3	13.8	0.10	A	0.19
11	4.59	0.38	49.0	21.4	3.92	N	3.73
12	3.447	0.183	11.9	14.7	0.95	A	1.59
13	2.96	0.07	-3.9	9.9	-0.31	A	-0.77
17	3.27	0.67	6.2	42.1	0.49	A	0.28
20	615	144	19867.5	1815.8	1589.40	N	4.25
22	3.59	0.1	16.6	12.0	1.32	A	2.96
23	3.035	0.027	-1.5	9.1	-0.12	A	-0.32
25	4.03	0.6	30.8	32.1	2.47	W	1.54
28	18.2	0.24	490.9	53.8	39.27	N	54.42
30	2.6	0.3	-15.6	24.3	-1.25	A	-1.45
31	3.34	0.05	8.4	10.3	0.68	A	1.75
32	2.49	0.25	-19.2	21.4	-1.53	A	-2.06
33	227.45	0.0353	7284.7	671.3	582.78	N	1554.01
36	3.62	0.33	17.5	21.1	1.40	A	1.51
37	3.73	0.12	21.1	12.8	1.69	A	3.53
38	132.9	24.3	4214.9	394.0	337.19	N	5.34
44	3.4	0.7	10.4	42.4	0.83	A	0.45
50	3.118	0.241	1.2	18.0	0.10	A	0.14
56	2.83	0.06	-8.1	9.4	-0.65	A	-1.64
58	2.21		-28.2		-2.26	W	
63	1.457		-52.7		-4.22	N	
64	2.91	0.01	-5.5	8.6	-0.44	A	-1.21
65	3.28		6.5		0.52	A	
70	3.265	0.106	6.0	11.6	0.48	A	1.05
71	3.07	0.09	-0.3	10.8	-0.03	A	-0.06
73	5.22	0.22	69.5	17.6	5.56	N	8.21
77	3	0.02	-2.6	9.0	-0.21	A	-0.57
78	3.35	0.23679	8.8	17.3	0.70	A	0.98
83	4.261	1	38.3	48.6	3.07	N	1.17
84	3.762	0.038	22.1	11.3	1.77	A	4.70
85	3.09	0.19	0.3	15.3	0.03	A	0.04
86	3.3	0.15	7.1	13.3	0.57	A	1.07
87	3.3	0.2	7.1	15.5	0.57	A	0.90
88	4.42	0.35	43.5	20.5	3.48	N	3.55
91	2.905	0.255	-5.7	19.5	-0.45	A	-0.60
95	4.13	0.02	34.1	12.2	2.73	W	7.42
107	2.85	0.13	-7.5	12.4	-0.60	A	-1.20
109	3.6	0.08	16.9	11.5	1.35	A	3.22
110	2.61	0.23	-15.3	19.2	-1.22	A	-1.75
111	2.7	0.32	-12.3	25.0	-0.99	A	-1.09
113	3.13	0.11	1.6	11.6	0.13	A	0.28
115	1.28	0.05	-58.4	8.7	-4.68	N	-12.11
117	3.067452	0.306745175	-0.4	22.0	-0.03	A	-0.04
118	2.91	0.031	-5.5	8.8	-0.44	A	-1.19
119	43	6.5	1296.1	130.5	103.69	N	6.14
120	3.9	0.8	26.6	42.6	2.13	W	1.01
121	5.69	0.15	84.7	17.6	6.78	N	12.72
122	2.62	0.125	-14.9	12.3	-1.19	A	-2.45

TABLE 18. EVALUATION RESULTS (CONTD.)

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
123	27	2	776.6	81.1	62.13	N	11.93

I.8 ZINC

TABLE 19. ASSIGNED VALUES

Parameter	Value
Mass fraction/(ng/g)	20.2
Expanded uncertainty (k=2)/(ng/g)	3.4
Relative standard deviation for proficiency assessment/%	15

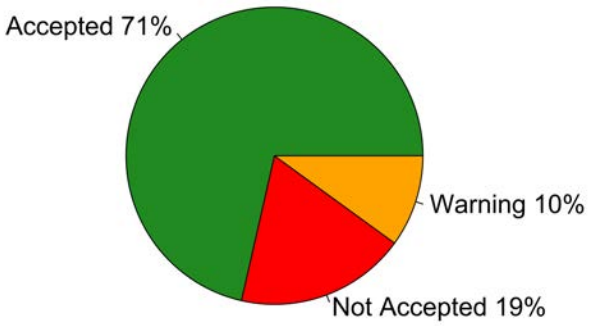

FIG. 31. Pie chart showing the percentage of results for Zn that were rated "accepted", "warning" and "not accepted".

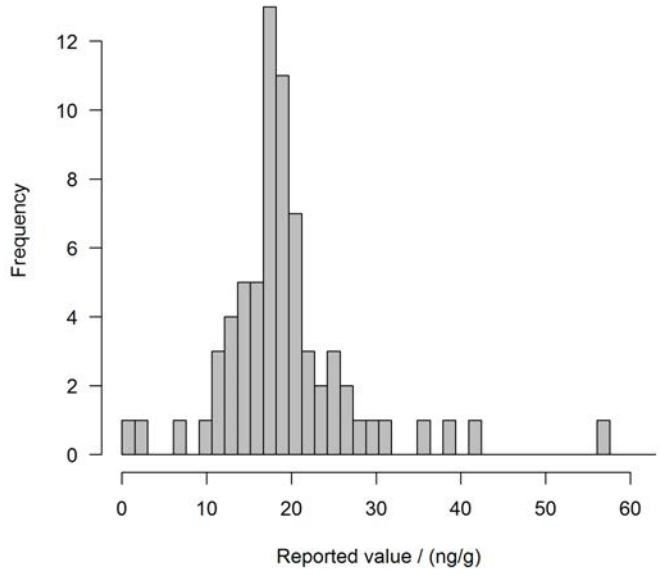

FIG. 32. Histogram showing frequency of reported values for Zn. Reported values exceeding 3× *the assigned value are not shown.*

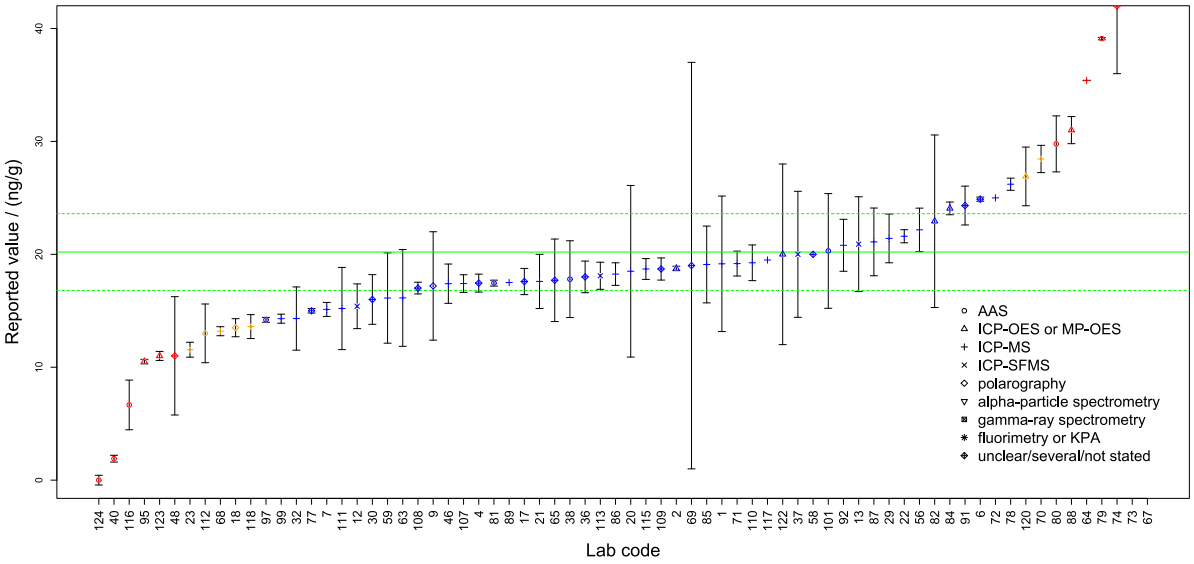

FIG. 33. Reported results for Zn, sorted by value. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

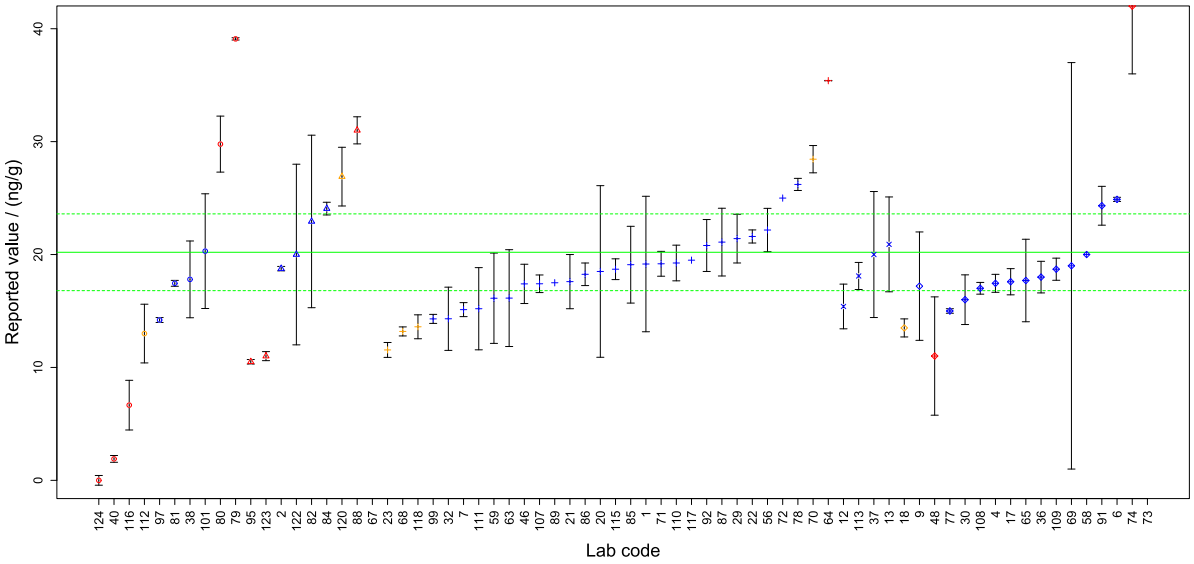

FIG. 34. Reported results for Zn, sorted by analytical technique. Blue data points show accepted results, yellow indicates warning and red not accepted result based on z score evaluation. Error bars represent expanded uncertainty of measurement (k=2) calculated from reported combined uncertainty. The green solid line indicates the assigned value, the dotted green lines indicate the assigned value ± expanded uncertainty (k=2) of the assigned value. Reported values exceeding 2× the assigned value are not shown.

TABLE 20. EVALUATION RESULTS

Lab code	Rep. value	Rep. unc.	Rel. bias/%	*U*(rel.bias)/%	*z* Score	*z* Eval.	zeta Score
1	19.16	3	-5.1	35.2	-0.34	A	-0.30
2	18.75	0.098	-7.2	15.7	-0.48	A	-0.85
4	17.45	0.398	-13.6	15.2	-0.91	A	-1.58
6	24.884	0.092	23.2	20.7	1.55	A	2.75
7	15.12	0.31	-25.1	13.2	-1.68	A	-2.94
9	17.2	2.4	-14.9	31.4	-0.99	A	-1.02
12	15.4	0.99	-23.8	18.2	-1.58	A	-2.44
13	20.9	2.1	3.5	26.6	0.23	A	0.26
17	17.59	0.58	-12.9	16.1	-0.86	A	-1.45
18	13.5	0.4	-33.2	12.7	-2.21	W	-3.84
20	18.5	3.8	-8.4	43.9	-0.56	A	-0.41
21	17.6	1.2	-12.9	20.0	-0.86	A	-1.25
22	21.6	0.29	6.9	18.2	0.46	A	0.81
23	11.55	0.33	-42.8	11.2	-2.85	W	-4.99
29	21.41	1.079	6.0	20.5	0.40	A	0.60
30	16	1.1	-20.8	19.2	-1.39	A	-2.07
32	14.31	1.4	-29.2	22.9	-1.94	A	-2.67
36	18	0.7	-10.9	16.9	-0.73	A	-1.20
37	20	2.79	-1.0	32.5	-0.07	A	-0.06
38	17.8	1.7	-11.9	24.2	-0.79	A	-1.00
40	1.9	0.15	-90.6	15.9	-6.04	N	-10.72
46	17.4	0.87	-13.9	17.6	-0.92	A	-1.47
48	11.01	2.62	-45.5	48.5	-3.03	N	-2.94
56	22.17	0.96	9.8	20.4	0.65	A	1.01
58	20		-1.0		-0.07	A	
59	16.13	2	-20.1	28.2	-1.34	A	-1.55
63	16.141	2.144	-20.1	29.8	-1.34	A	-1.48
64	35.4	0.01	75.2	29.5	5.02	N	8.94
65	17.7	1.8271	-12.4	25.4	-0.83	A	-1.00
67	78.5	0.3536	288.6	65.4	19.24	N	33.58
68	13.19	0.2	-34.7	11.4	-2.31	W	-4.10
69	19	9	-5.9	96.1	-0.40	A	-0.13
70	28.445	0.604	40.8	24.1	2.72	W	4.57
71	19.18	0.55	-5.0	17.0	-0.34	A	-0.57
72	25		23.8		1.58	A	
73	56.55	1.21	180.0	47.3	12.00	N	17.42
74	42	3	107.9	37.8	7.19	N	6.32
77	15	0.1	-25.7	12.6	-1.72	A	-3.05
78	26.21	0.26834	29.8	21.9	1.98	A	3.49
79	39.1	0.05	93.6	32.6	6.24	N	11.11
80	29.78	1.24	47.4	26.2	3.16	N	4.55
81	17.45	0.13	-13.6	14.6	-0.91	A	-1.61
82	22.93	3.82	13.5	38.4	0.90	A	0.65
84	24.068	0.281	19.1	20.2	1.28	A	2.24
85	19.1	1.7	-5.4	23.9	-0.36	A	-0.46
86	18.25	0.5	-9.7	16.2	-0.64	A	-1.10
87	21.1	1.5	4.5	22.6	0.30	A	0.40
88	31	0.6	53.5	26.1	3.56	N	5.99
89	17.5		-13.4		-0.89	A	
91	24.32	0.86	20.4	21.5	1.36	A	2.16
92	20.8	1.15	3.0	20.6	0.20	A	0.29
95	10.5	0.1	-48.0	9.0	-3.20	N	-5.70
97	14.2	0.109	-29.7	11.9	-1.98	A	-3.52
99	14.3	0.2	-29.2	12.2	-1.95	A	-3.45
101	20.3	2.54	0.5	30.2	0.03	A	0.03
107	17.41	0.39	-13.8	15.2	-0.92	A	-1.60

TABLE 20. EVALUATION RESULTS (CONTD.

Lab code	Rep. value	Rep. unc.	Rel. bias/%	U(rel.bias)/%	z Score	z Eval.	zeta Score
108	17.01	0.26	-15.8	14.5	-1.05	A	-1.85
109	18.7	0.49	-7.4	16.4	-0.50	A	-0.85
110	19.25	0.79	-4.7	18.0	-0.31	A	-0.51
111	15.2	1.82	-24.8	27.1	-1.65	A	-2.01
112	13	1.3	-35.6	22.7	-2.38	W	-3.36
113	18.1	0.6	-10.4	16.5	-0.69	A	-1.16
115	18.7	0.46	-7.4	16.3	-0.50	A	-0.85
116	6.66	1.1	-67.0	33.5	-4.47	N	-6.69
117	19.5		-3.5		-0.23	A	
118	13.6	0.53	-32.7	13.8	-2.18	W	-3.71
120	26.9	1.3	33.2	24.4	2.21	W	3.13
122	20	4	-1.0	43.3	-0.07	A	-0.05
123	11	0.2	-45.5	9.9	-3.04	N	-5.37
124	0	0.2155	-100.0	Inf	-6.67	N	-11.79

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