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Worldwide Open Proficiency Test for X ray Fluorescence Laboratories PTXRFIAEA08: Determination of Minor and Trace Elements in Natural Soil

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WORLDWIDE OPEN PROFICIENCY TEST FOR X RAY FLUORESCENCE LABORATORIES PTXRFIAEA08: DETERMINATION OF MINOR AND TRACE ELEMENTS IN NATURAL SOIL

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For further information on this publication, please contact:

Physics Section
International Atomic Energy Agency
2444 Seibersdorf
Austria
Email: Official.Mail@iaea.org

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FOREWORD

The IAEA assists Member State laboratories to maintain their readiness by producing reference materials, developing standardized analytical methods, and conducting interlaboratory comparisons and proficiency tests as tools for quality control. To ensure a reliable, worldwide, rapid and consistent response, the IAEA Nuclear Spectrometry and Applications Laboratory organizes tests for Member State laboratories.

This publication presents the results of the worldwide proficiency test PTXRFIAEA08 on the determination of minor and trace elements in natural soil. Methodologies, a data evaluation approach, a summary evaluation of each element and individual evaluation reports for each laboratory are also described. The test was carried out within the IAEA project Nuclear Spectrometry for Analytical Applications, under the Nuclear Science Programme. The main objective of the project was to enhance the capability of interested Member States in effective utilization of nuclear spectrometries and analytical services in industry, human health and agriculture, and in monitoring and evaluating environmental pollution.

This proficiency test was designed to identify analytical problems and to support Member State laboratories in improving the quality of their analytical results, maintaining their accreditation and providing a regular forum for discussion and technology transfer in this area. The type of sample and the concentration levels of the analytes were designed to enable the identification of potential analytical problems.

The IAEA officer responsible for this publication was R. Padilla Alvarez of the Division of Physical and Chemical Sciences.

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CONTENTS

1. INTRODUCTION

The PTXRFIAEA08 proficiency test was aimed at analytical laboratories applying X-ray fluorescence (XRF) techniques in environmental monitoring. The participants were requested to use their established and proven analytical procedures for the determination of concentrations of chemical elements in a natural soil sample.

Natural soil test samples with established homogeneity and well characterised known target values of the mass fractions of analytes were distributed to participating laboratories. The laboratories were requested to analyse the sample using established techniques following their analytical procedures. Based on the results of the proficiency test presented in the report each participating laboratory should assess its analytical performance by using the specified criteria and, if appropriate, to identify discrepancies, and to correct relevant analytical procedures.

The samples, together with detailed instructions for analysts, were distributed to the participating laboratories in June 2011. The deadline for submission of the results was 1 September 2011. The last results were received on 7 October 2011. The submitted results were processed, grouped versus analytes/laboratories and compared with the analytes' assigned values. The values of *z*- and of *u*-scores were calculated for three fit-for-purpose levels. For the definitions of the *z*- and *u*-scores please see Section 3.2. The obtained results as well as the description of the data evaluation procedures have been presented in this report. Each laboratory was assigned a code, therefore full anonymity of the presented results was guaranteed. The link between the laboratory code and the laboratory name was known only to the organisers of the proficiency test and to the laboratory itself.

2. DESCRIPTION OF THE TEST SAMPLE

The test sample was a natural soil material prepared and tested by an external independent laboratory. The powdered, homogenized, and dried material was distributed to 27 laboratories in sealed plastic bottles, each bottle containing 100 g of the test sample. The participants were asked to conduct the determination of the mass fractions of chemical elements making up the sample according to their routine analytical procedures. They were also instructed to determine the moisture content of the material by using a separate sample and to report the results on a dry-weight basis. Only one result per element per analytical technique was to be submitted. Each result was to be accompanied by an estimate of its uncertainty expressed as one standard deviation. No restriction on the number of the reported elements was imposed.

3. DETAILS OF THE EXERCISE

3.1. ASSIGNED VALUE AND TARGET STANDARD DEVIATION

The reference values supplied by the provider of the material, established by independent inter-laboratory survey, were used as the assigned values of the analytes, X_A. The results for 34 analytes were submitted by participants of this proficiency test: Al, As, Ba, Bi, Br, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, I, K, La, Mn, Nb, Ni, Pb, Rb, S, Sc, Se, Si, Sr, Te, Th, Ti, U, V, Y, Zn, and Zr.

The *z*- and *u*-scores were calculated for all the submitted results of all analytes except Ba, Bi, Ca, Co, Rb, and Te, for which the assigned values were not available.

For each analyte a target value of the standard deviation has been assigned using a modified Horowitz function as proposed in the reference [1]:

$$H_A = \begin{cases} 0.22 X_A & X_A < 1.2 \cdot 10^{-7} \\ 0.02 (X_A)^{0.8495} & 1.2 \cdot 10^{-7} \le X_A \le 0.138 \\ 0.01 \sqrt{X_A} & X_A > 0.138 \end{cases} \quad (1)$$

In Eqn. (1) the assigned value of analyte, X_A, is expressed as a mass fraction. The target value of the standard deviation, σ_A is related to H_A by a factor k:

$$\sigma_A = kH_A, \quad k = 0.5, 1.0, 1.5 \quad (2)$$

Depending on the value of the factor k the target value of the standard deviation is recognized as fit-for-purpose at three levels of uncertainty: k = 0.5 - appropriate for high precision analysis; k = 1.0 - appropriate for well-established routine analysis; k = 1.5 - satisfactory for common analytical tasks. The relative value of the target standard deviation, *RSD*, expressed in per cent, is defined as follows:

$$RSD = \frac{\sigma_A}{X_A} \cdot 100\% \quad (3)$$

The relative value of the target standard deviation as a function of the assigned mass fraction of the analyte, X_A, is shown in Fig. 1 for the three different values of the k factor.

3.2. *z*-SCORES AND *u*-SCORES

The reported concentrations of analytes were compared with the assigned values by using the *z*-score analysis. For every result a *z*-score was calculated:

$$z = \frac{x - X_A}{\sigma_A} \quad (4)$$

The term '*x*' denotes the reported mass fraction of analyte. Defined by different fit-for-purpose ranges of the target standard deviation, three different values of *z*-scores were calculated by combining Eqns. (2) and (4). Assuming that appropriate values for X_A and σ_A have been used and that the underlying distribution of analytical errors is normal, apart from outliers, in a well-behaved analytical system *z*-scores would be expected to fall outside the range $-2 \le z \le 2$ in about 4.6% of instances, and outside the range $-3 < z < 3$ only in about 0.3%. Therefore, based on the z-scores the following decision limits were established:

$$\begin{aligned} |z| &\le 2 && \text{- a satisfactory result} \\ 2 < |z| &< 3 && \text{- the result is considered questionable} \\ |z| &\ge 3 && \text{- the result is considered unsatisfactory} \end{aligned} \quad (5)$$

The advice to the laboratory is that, independent of the fit-for-purpose range selected by the laboratory, any *z*-score for an element outside the range $-2 \le z \le 2$ should be examined by the

analyst and all steps of the analytical procedure verified to identify the source(s) of the analytical bias.

For every participant the rescaled sum of *z*-scores, *RSZ*, as well as the sum of squared *z*-scores, *SSZ*, were calculated as defined by the following equations:

$$RSZ = \frac{\sum_{i=1}^{L} z_i}{\sqrt{L}} \tag{6}$$

$$SSZ = \sum_{i=1}^{L} (z_i)^2 \tag{7}$$

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqns. (6) and (7) takes into account all *z*-scores for all analytes with known assigned values reported by participant. The *RSZ* can be interpreted as a standardized normally distributed variable, with expected value equal to zero and unit variance. It is sensitive in detecting a small consistent bias in an analytical system, however, it is not sensitive in cases where there are even big errors but having opposite signs. The *SSZ* takes no account of the signs because it depends on the squared *z*-scores. It has a chi-squared (χ^2) distribution with *L* degrees of freedom. The *SSZ* can be regarded as complementary to *RSZ*, which means that if *RSZ* is well within the range $-3 < RSZ < 3$ and if at the same time value of *SSZ* is above the $\chi^2_{critical}$ value the overall performance of the laboratory requires improvement.

The reported results were accompanied by the standard uncertainty estimate made by the participant. The values were used to calculate *u*-scores:

$$u = \frac{|x - X_A|}{\sqrt{(\sigma_A)^2 + (\sigma_x)^2}} \tag{8}$$

The symbol 'σ_x' denotes the standard uncertainty of the submitted result *x*. If the assumptions about X_A and σ_A and about the normality of the underlying distributions are correct, and the laboratory estimate of σ_x takes into account all the significant sources of uncertainty, the *u*-scores would have a truncated normal distribution with unit variance. In a well-behaved analytical system only 0.1% of *u*-scores would fall outside the range $u < 3.29$. Therefore, the following decision limits for the *u*-scores were established:

$u \le 1.64$ - reported result does not differ from the assigned value
$1.64 < u \le 1.95$ - reported result probably does not differ from the assigned value
$1.95 < u \le 2.58$ - it is not clear whether the reported and assigned values differ (9)
$2.58 < u \le 3.29$ - reported result is probably different from the assigned value
$3.29 < u$ - reported result differs from the assigned value

The *u*-scores are especially useful for deciding whether the laboratory fit-for-purpose criteria are fulfilled. By comparing Eqn. (4) and Eqn. (8) one can notice that for corresponding values of *u*-score and *z*-score the following inequality is always fulfilled:

$$u \le |z| \tag{10}$$

It implies that if the *u*-score is larger than 3.29 also the decision limit for the corresponding *z*-score is triggered and the laboratory has to check the analytical procedure as well as review the uncertainty budget estimation. If *u*-score stays below the value of 1.64 and at the same time the *z*-score decision limit is triggered ($|z| > 3$) the laboratory should re-evaluate its fit-for-purpose status for that particular analyte.

3.3. CONSENSUS VALUES

To examine the overall performance of the participating laboratories the submitted results have been statistically processed and the consensus values were calculated. The results were tested for the presence of outliers using a set of seven outlier rejection tests, shown below:

Description of symbols:

$x_1 < ... < x_n$ - set of analytical results,
$\bar{x}$ - mean value, (11)
s - standard deviation,

1. Coefficient of kurtosis [2], number of results: $5 \le n \le 100$, two-sided test, confidence level = 0.95:

$$b_2 = \frac{n\sum_{i=1}^{n}(\bar{x} - x_i)^4}{\left[\sum_{i=1}^{n}(\bar{x} - x_i)^2\right]^2} \tag{12}$$

- if b_2 > critical value then reject the result that is at the furthest distance from the mean, decrease *n*, repeat the procedure until $b_2 \le$ critical value.

2. Coefficient of skewness [2], number of results, $5 \le n \le 60$, one-sided test, confidence level = 0.95:

$$\sqrt{b_1} = \frac{\sqrt{n}\sum_{i=1}^{n}(x_i - \bar{x})^3}{\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]^{3/2}} \tag{13}$$

if $\left|\sqrt{b_1}\right|$ > critical value then: if $\sqrt{b_1}$ is positive then reject x_n, otherwise reject x_1, decrease *n*, repeat the procedure until $\left|\sqrt{b_1}\right| \le$ critical value.

3. Veglia's test [3, 4], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

$$h = \sqrt{\frac{n}{n-1}}\frac{|x_k - \bar{x}_{n-1}|}{s_{n-1}} \tag{14}$$

where:

x_k, examined value, the result at the furthest distance from the mean

$\bar{x}_{n-1}$, the mean value of the population of the results with the examined result excluded

s_{n-1}, the standard deviation of the population of the results with the examined result excluded

- if $h >$ critical value then reject x_k otherwise temporarily exclude the x_k from the population of results and proceed with testing the next outlier candidate, if the following value of $h >$ critical value then reject both results, decrease n respectively, repeat the procedure until $h \leq$ critical value.

4. Dixon's test [5], number of results: $3 \leq n \leq 25$, two-sided test, confidence level = 0.95:

- if x_1 is at the furthest distance from the mean value, then calculate:

$$r = \begin{cases} (x_2 - x_1)/(x_n - x_1), & 3 \leq n \leq 7 \\ (x_2 - x_1)/(x_{n-1} - x_1), & 8 \leq n \leq 10 \\ (x_3 - x_1)/(x_{n-1} - x_1), & 11 \leq n \leq 13 \\ (x_3 - x_1)/(x_{n-2} - x_1), & 14 \leq n \leq 25 \end{cases} \tag{15a}$$

- if x_n is at the furthest distance from the mean value then calculate:

$$r = \begin{cases} (x_n - x_{n-1})/(x_n - x_1), & 3 \leq n \leq 7 \\ (x_n - x_{n-1})/(x_n - x_2), & 8 \leq n \leq 10 \\ (x_n - x_{n-2})/(x_n - x_2), & 11 \leq n \leq 13 \\ (x_n - x_{n-2})/(x_n - x_3), & 14 \leq n \leq 25 \end{cases} \tag{15b}$$

- if $r >$ critical value then reject the tested result, decrease n, repeat the procedure until $r \leq$ critical value.

5. Outlier rejection test proposed in [2], number of results: $4 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$w/s = (x_n - x_1)/s \tag{16}$$

- if $w/s >$ critical value then: if $x_n - \bar{x} = \bar{x} - x_1$, reject both x_1 and x_n, otherwise reject x_k ($x_k = x_1$ *or* $x_k = x_n$), the result that is at the furthest distance from the mean, for the remaining population of results ($n` = n - 1$) calculate: $T_k = |\bar{x}' - x_k| / s'$, where: $\bar{x}'$ is the mean value and s' is the standard deviation of the population of the results excluding the rejected value x_k, if $T_k >$ critical value then reject also the second extreme result, decrease n respectively, repeat the procedure until w/s ≤ critical value.

6. Outlier rejection test proposed in [6], number of results: $3 \leq n < \infty$, two-sided test, confidence level = 0.95:

$$B_4 = |x_k - \bar{x}| / s \tag{17}$$

where:
x_k , examined value

- if B_4 > critical value then reject the tested result, repeat the procedure until $B_4 \leq$ critical value.

7. Outlier rejection test proposed in [7], number of results: $3 \leq n \leq 100$, two-sided test, confidence level = 0.95:

$$S_k^2 / S = \frac{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x}')^2}{\sum_{i=1, i \neq k}^{n} (x_i - \bar{x})^2}, \quad k = 1 \; or \; k = n \tag{18}$$

where:
x_k , examined value, the result at the furthest distance from the mean
$\bar{x}'$, the mean value of the population of the results with the examined result x_k excluded

- if $S_k^2 / S >$ critical value then reject x_k , decrease n, repeat the procedure until $S_k^2 / S \leq$ critical value.

The results which passed the outlier rejection procedures were used to calculate the consensus mean value of analyte, X_C, and corresponding consensus value of its standard deviation, σ_C:

$$X_C = \frac{\sum_{i=1}^{m} x_i}{m} \tag{19}$$

and

$$\sigma_C = \sqrt{\frac{\sum_{i=1}^{m} (x_i - X_C)^2}{m(m-1)}} \tag{20}$$

The term m denotes the number of reported values for a given analyte excluding the outliers rejected by at least one of the outlier rejections tests. The summing up in Eqn. (19) and (20) took into account only the results which passed all the outlier rejection tests. The obtained consensus values were compared with the assigned values of analytes.

4. RESULTS

The natural soil test sample was distributed to 27 laboratories for chemical composition analysis. Out of the 27 laboratories, 13 participated in the test submitting 172 individual results for 34 chemical elements. The list of the participating laboratories is presented at the end of this report.

The techniques used by the participants and their codes are listed in Table 1.

The techniques EDXRF, EDXRFISO, and EDXRFTUBE should be considered of similar type. The distinction between them (EDXRFISO or EDXRFTUBE) was based on information provided by the participants. In the case that insufficient information was available a generic type technique EDXRF was assumed. All submitted results have been evaluated.

In Table 2 a summary of the assigned analyte values, the target values of standard deviation (obtained by using modified Horowitz function), the consensus values and their standard deviations are shown. For the elements Ba, Bi, Ca, Cd, Co, Rb, and Te the assigned and target values were not available. The consensus values (Eqn. 19) and corresponding standard deviations (Eqn. 20) were calculated based on 143 reported analytical results after excluding 29 results classified as outliers. The correlation between the assigned and the consensus values is shown in Fig. 2.

TABLE 1. THE CODING, DESCRIPTION AND THE ABBREVIATED NAMES OF THE ANALYTICAL TECHNIQUES USED BY PARTICIPATING LABORATORIES IN THE PROFICIENCY TEST EXERCISE

Technique Code	Description	Abbreviation
1.0	Energy dispersive X-ray fluorescence	EDXRFS
1.1	EDXRF, radioisotope excitation	EDXRFISOTOP
1.2	EDXRF, X-ray tube excitation	EDXRFTUBE
1.3	EDXRF, excitation using X-ray tube and secondary targets	EDXRFTUBE-ST
1.4	Total reflection X-ray fluorescence	TXRF
2.0	Wavelength dispersive X-ray fluorescence	WDXRF
11	Not specified	Not specified

TABLE 2. THE ASSIGNED VALUES OF ANALYTES, THE TARGET VALUES OF THE STANDARD DEVIATIONS AND THE CONSENSUS VALUES[1]

Analyte symbol	Assigned value of the analyte, X_A	Target value of standard deviation, σA			Consensus value of the analyte, X_C	Consensus value of the standard deviation, σ_C	Number of results	Number of outliers
		$k = 0.5$	$k = 1.0$	$k = 1.5$				
				[g/kg]				
Al	152.0	1.95	3.90	5.85	137	23.4	7	0
Fe	90.2	1.30	2.59	3.89	92.3	2.95	11	2
Si	187.0	2.16	4.32	6.49	177.6	7.55	6	1
Ti	9.41	0.190	0.380	0.570	9.66	0.727	11	0
				[mg/kg]				
As	8.7	0.50	1.01	1.51	5.7	1.47	4	0
Ba	-	-	-	-	18.6	1.78	3	0
Bi	-	-	-	-	17.3	1.75	1	0
Br	15.4	0.82	1.63	2.45	12.3	1.47	8	1
Ca	-	-	-	-	105	41.8	3	0
Cd	-	-	-	-	2.40	0.300	1	0
Ce	11.2	0.62	1.25	1.87	8.09	0.440	3	1
Co	-	-	-	-	12.5	1.10	1	0
Cr	31.3	1.49	2.98	4.47	25.4	3.96	6	2
Cu	36.0	1.68	3.36	5.04	38.1	2.57	10	0
Ga	33.3	1.57	3.14	4.71	33.63	0.630	6	3
I	*25.1*	*1.24*	*2.47*	*3.71*	*32.0*	*5.69*	*2*	*0*
K	340	11.3	22.6	33.9	312	37.2	6	2
La	*6.11*	*0.372*	*0.744*	*1.120*	*6.4*	*1.85*	*2*	*0*
Mn	174	6.4	12.8	19.21	146.86	16.49	11	2
Nb	10.7	0.60	1.20	1.80	9.27	0.100	3	1
Ni	17.1	0.89	1.78	2.68	16.79	0.730	6	2
Pb	12.2	0.67	1.34	2.01	15.9	1.80	10	2
Rb	-	-	-	-	2.08	0.250	5	2
S	705	21.0	42.0	63.1	551	254	2	0
Sc	24.0	1.19	2.38	3.57	24.3	1.06	2	0
Se	*2.29*	*0.162*	*0.323*	*0.485*	*1.16*	*0.170*	*1*	*0*
Sr	*4.62*	*0.294*	*0.587*	*0.881*	*4.470*	*0.0900*	*6*	*3*
Te	-	-	-	-	29.3	5.38	1	0
Th	15.1	0.80	1.61	2.41	14.39	0.990	5	0
U	2.41	0.169	0.338	0.507	3.36	0.290	1	0
V	270	9.3	18.6	27.9	199	27.0	9	1
Y	*4.66*	*0.296*	*0.591*	*0.887*	*3.14*	*0.760*	*2*	*0*
Zn	68.7	2.91	5.81	8.72	61.1	4.97	11	1
Zr	266	9.2	18.4	27.6	264.0	5.20	6	3

[1] The assigned values of the elements shown in italics should be considered indicative.

Table 3 lists the values of the *z*- and *u*-scores for all submitted results. In brackets next to the element symbol the assigned values of element concentration and the target standard deviation for $k = 1$ are shown. The *z*- and *u*-scores were calculated for the three different fit-for-purpose ranges, as defined by Eqn. (2). The results rejected by the outliers rejection procedures were marked with "*" in the "Analyte concentration" column.

Table 4 shows the combined *z*-scores for the three different fit-for-purpose ranges, the RSZ and SSZ as defined in Eqns. (6) and (7), for the participating laboratories are shown. The analytes without assigned values (Ba, Bi, Ca, Cd, Co, Rb, and Te) were not considered.

Figures 3-13 and 14-29 present the distributions of the proficiency test results. In Figs 3-13 the individual results are marked with filled circles. The dotted lines show the range of the accepted results (these results were used to calculate the consensus values). The outliers are marked with arrows. Also shown are the estimated parameters of the distribution (after outlier rejection): mode, median, and the mean value. The result of density distributions shown in Figs. 3-13 could only be used as indicators of the trends observed in the reported data due to the limited number of results (only density distributions of analytes for which at least 5 results passed the outlier rejection tests are shown). All the populations of results, after outlier rejection, have passed a normality test (Kolmogorov-Smirnov). Figures 14-29 show the bar chart distributions of the *z*-scores for the analytes with at least 6 submitted results. The results are sorted in ascending order versus laboratory/technique code. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of z-score, $|z| < 2$, for three different ranges defined by factor k in Eqn. (2): $k = 0.5$ (solid black lines), $k = 1.0$ (solid green lines) and $k = 1.5$ (solid red lines). The decision levels of satisfactory results, $|z| < 2$, for different fit-for-purpose targets have also been marked.

For every participating laboratory its overall performance is presented in Figs. 30-42. The plots presented in this figure relate all the *u*-scores and *z*-scores calculated for a given laboratory. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2) with factor k, namely: $k = 0.5$ (black triangles), $k = 1.0$ (green circles), and $k = 1.5$ (red squares). The decision limits of unsatisfactory results were marked with black lines ($|z| > 3$, $u > 3.29$). They divide the plot area in four quadrants. Due to inequality (10) all the points accompanied by a laboratory estimate of the uncertainty fall always below the line $u = |z|$. The smaller the laboratory estimate of the uncertainty the closer the related point to the $u = |z|$ line. Points in the immediate proximity of the dashed diagonal line ($u = |z|$) have underestimated uncertainty values. The well performing laboratories would have more points located in the lower-left quadrant of the plot. If there are many points located in the upper-right quadrant it suggests that these results do not fall in the defined fit-for-purpose targets and that the laboratory provided too "narrow" uncertainty estimate.

Figure 43 shows the partitioning of the results between different analytical techniques. The largest fraction of analyses, about 77 %, was carried out with the energy dispersive spectrometry (EDXRF+TXRF), about 15 % with wavelength dispersive mode, and for about 8% of results the technique was not identified. Most of the determinations were carried out on samples prepared in the form of pellets (~ 69 %), about 22 % of the results were obtained after converting the sample to a liquid form by acid digestion or dissolution, and about 9 % of analyses were performed without any sample preparation.

TABLE 3. SUMMARY OF THE REPORTED RESULTS AND THE CALCULATED *z*- AND *u*-SCORES

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Al (152.0 ± 3.90) [g/kg]										
4	1.4	35.8	5.23	14.62	-59.61	-29.81	-19.87	20.8	17.8	14.81
13	1.4	88.0	7.00	7.95	-32.83	-16.42	-10.94	8.81	7.99	7.02
40	1.2	138.5	3.24	2.34	-6.91	-3.45	-2.3	3.57	2.66	2.02
15	1.3	149.6	21.00	14.04	-1.26	-0.63	-0.42	0.12	0.11	0.11
21	11	154.0	3.00	1.95	1.03	0.51	0.34	0.56	0.41	0.3
22	1.2	161.0	11.00	6.83	4.62	2.31	1.54	0.81	0.77	0.72
7	1.3	233.40	0.300	0.13	41.76	20.88	13.92	41.27	20.82	13.9
Fe (90.2 ± 2.59) [g/kg]										
4	1.4	58.5*	1.41	2.41	-24.47	-12.23	-8.16	16.56	10.75	7.67
7	1.3	83.140	0.0600	0.07	-5.45	-2.72	-1.82	5.44	2.72	1.82
40	1.2	84.28	0.381	0.45	-4.57	-2.28	-1.52	4.38	2.26	1.52
13	1.4	85.0	2.00	2.35	-4.01	-2.01	-1.34	2.18	1.59	1.19
22	1.2	87.0	4.73	5.44	-2.47	-1.24	-0.82	0.65	0.59	0.52
36	1.3	89	10.9	12.21	-0.69	-0.35	-0.23	0.08	0.08	0.08
21	11	92.8	1.90	2.05	2.01	1.00	0.67	1.13	0.81	0.60
52	11	99.3	2.47	2.49	7.02	3.51	2.34	3.26	2.54	1.98
15	1.3	101.0	6.50	6.44	8.34	4.17	2.78	1.63	1.54	1.43
14	1.0	108	17.8	16.44	14.10	7.05	4.70	1.02	1.01	1.00
9	1.2	124.6*	8.72	7.00	26.55	13.28	8.85	3.90	3.78	3.60
Si (187.0 ± 4.32) [g/kg]										
4	1.4	32.7*	4.69	14.36	-71.38	-35.69	-23.79	29.90	24.20	19.29
22	1.2	154	10.7	6.95	-15.26	-7.63	-5.09	3.02	2.86	2.64
15	1.3	172	16.5	9.62	-7.12	-3.56	-2.37	0.93	0.90	0.87
52	11	177.6	2.85	1.60	-4.34	-2.17	-1.45	2.63	1.81	1.33
21	11	185.0	2.00	1.08	-0.92	-0.46	-0.31	0.68	0.42	0.29
7	1.3	199.80	0.200	0.10	5.92	2.96	1.97	5.89	2.96	1.97
Ti (9.41 ± 0.380) [g/kg]										
4	1.4	5.20	0.125	2.41	-22.17	-11.09	-7.39	18.51	10.53	7.22
7	1.3	5.9890	$8.00 \cdot 10^{-3}$	0.13	-18.01	-9.01	-6.00	18.00	9.00	6.00
13	1.4	8.56	0.170	1.99	-4.48	-2.24	-1.49	3.33	2.04	1.43
36	1.3	9.3	1.13	12.19	-0.63	-0.32	-0.21	0.10	0.10	0.09
21	11	9.70	0.300	3.09	1.53	0.76	0.51	0.82	0.60	0.45
14	1.0	10.1	1.68	16.70	3.39	1.70	1.13	0.38	0.37	0.36
15	1.3	10.20	0.800	7.84	4.16	2.08	1.39	0.96	0.89	0.80
11	1.2	10.4	1.87	18.00	5.04	2.52	1.68	0.51	0.50	0.49
52	11	11.41	0.270	2.37	10.53	5.27	3.51	6.06	4.29	3.17
9	1.2	12.7	1.02	8.00	17.32	8.66	5.77	3.18	3.03	2.82
40	1.2	12.84	0.419	3.26	18.08	9.04	6.03	7.46	6.07	4.85

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
As (8.71 ± 1.01) [mg/kg]										
7	1.3	3.20	0.200	6.25	-10.95	-5.48	-3.65	10.18	5.37	3.62
40	1.2	3.43	0.200	5.82	-10.49	-5.24	-3.50	9.75	5.14	3.47
12	2.0	6.61	0.660	9.98	-4.18	-2.09	-1.39	2.53	1.75	1.28
21	2.0	9.39	0.550	5.86	1.35	0.68	0.45	0.91	0.59	0.42
Ba [mg/kg]										
22	1.2	16.0	1.40	8.75	-	-	-	-	-	-
4	1.4	17.9	2.63	14.73	-	-	-	-	-	-
12	2.0	22.0	1.42	6.45	-	-	-	-	-	-
Bi [mg/kg]										
4	1.4	17.3	1.75	10.11	-	-	-	-	-	-
Br (15.4 ± 1.63) [mg/kg]										
7	1.3	5.30	0.100	1.89	-12.37	-6.19	-4.12	12.28	6.18	4.12
4	1.4	10.18	0.310	3.04	-6.40	-3.20	-2.13	5.98	3.14	2.12
40	1.1	11.62	0.900	7.72	-4.63	-2.32	-1.54	3.12	2.03	1.45
9	1.2	11.70	0.900	7.69	-4.53	-2.27	-1.51	3.05	1.98	1.42
22	1.2	15.5	1.10	7.10	0.12	0.06	0.04	0.07	0.05	0.04
36	1.3	15.9	2.35	14.78	0.61	0.31	0.20	0.20	0.17	0.15
15	1.3	16.0	2.40	15.00	0.74	0.37	0.25	0.24	0.21	0.17
14	1.0	24.0*	5.17	21.55	10.52	5.26	3.51	1.64	1.58	1.50
Ca [mg/kg]										
4	1.4	44	10.7	24.39	-	-	-	-	-	-
22	1.2	87.0	7.50	8.62	-	-	-	-	-	-
15	1.3	185	55.0	29.73	-	-	-	-	-	-
Cd [mg/kg]										
22	1.2	2.4	0.30	12.50	-	-	-	-	-	-
Ce (11.2 ± 1.25) [mg/kg]										
12	2.0	7.8	1.83	23.52	-5.49	-2.75	-1.83	1.77	1.54	1.31
22	1.2	8.40	0.800	9.52	-4.50	-2.25	-1.50	2.76	1.89	1.38
4	1.4	30.8*	3.40	11.03	31.54	15.77	10.51	5.68	5.42	5.06
Co [mg/kg]										
9	1.2	12.5	1.10	8.80	-	-	-	-	-	-
Cr (31.3 ± 2.98) [mg/kg]										
7	1.3	14.80	0.400	2.70	-11.07	-5.53	-3.69	10.69	5.48	3.67
21	2.0	25.10	0.500	1.99	-4.16	-2.08	-1.39	3.94	2.05	1.38
12	2.0	28.1	2.30	8.18	-2.13	-1.07	-0.71	1.16	0.84	0.63
4	1.4	33.7	1.42	4.22	1.61	0.80	0.54	1.16	0.72	0.51
22	1.2	60*	13.0	21.67	19.25	9.62	6.42	2.19	2.15	2.09
9	1.2	93.8*	6.70	7.14	41.92	20.96	13.97	9.11	8.52	7.76

TABLE 3 (cont.)

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
				Cu (36.0 ± 3.36) [mg/kg]						
4	1.4	25.57	0.860	3.38	-6.21	-3.11	-2.07	5.52	3.01	2.04
15	1.3	30.0	7.00	23.33	-3.57	-1.79	-1.19	0.83	0.77	0.70
7	1.3	33.20	0.700	2.11	-1.67	-0.83	-0.56	1.54	0.82	0.55
13	1.4	34.0	2.00	5.88	-1.19	-0.60	-0.40	0.77	0.51	0.37
36	1.3	36.8	7.40	20.11	0.48	0.24	0.16	0.11	0.10	0.09
21	2.0	38.1	1.00	2.62	1.25	0.63	0.42	1.07	0.60	0.41
9	1.2	38.7	2.30	5.94	1.61	0.80	0.54	0.95	0.66	0.49
52	11	45.4	3.71	8.17	5.60	2.80	1.87	2.31	1.88	1.50
14	1.0	47	13.1	27.81	6.70	3.35	2.23	0.85	0.83	0.80
22	1.2	52.0	4.40	8.46	9.53	4.76	3.18	3.40	2.89	2.39
				Ga (33.3 ± 3.14) [mg/kg]						
4	1.4	20.20*	0.430	2.15	-8.34	-4.17	-2.78	8.04	4.13	2.77
13	1.4	29.0*	1.00	3.45	-2.74	-1.37	-0.91	2.31	1.30	0.89
15	1.3	33.0	6.50	19.70	-0.19	-0.10	-0.06	0.04	0.04	0.04
22	1.2	33.0	2.80	8.48	-0.19	-0.10	-0.06	0.09	0.07	0.05
12	2.0	34.9	2.40	6.88	1.02	0.51	0.34	0.56	0.40	0.30
14	1.0	43.0*	9.87	22.97	6.15	3.08	2.05	0.97	0.93	0.88
				I (*25.1 ± 2.47*) [mg/kg]						
22	1.2	28.0	2.20	7.86	2.35	1.17	0.78	1.15	0.88	0.67
4	1.4	36.0	8.47	23.49	8.85	4.43	2.95	1.28	1.24	1.18
				K (340 ± 22.6) [mg/kg]						
4	1.4	218	15.0	6.87	-10.80	-5.40	-3.60	6.51	4.50	3.29
22	1.2	300	22.0	7.33	-3.54	-1.77	-1.18	1.62	1.27	0.99
15	1.3	335	60.0	17.91	-0.44	-0.22	-0.15	0.08	0.08	0.07
7	1.3	396.3	6.40	1.61	4.98	2.49	1.66	4.33	2.39	1.63
21	11	870*	20.0	2.30	46.86	23.43	15.62	23.07	17.55	13.46
52	11	1410*	110	7.80	94.60	47.30	31.53	9.68	9.53	9.30
				La (*6.11 ± 0.744*) [mg/kg]						
22	1.2	5.10	0.500	9.80	-2.71	-1.36	-0.90	1.62	1.13	0.83
12	2.0	7.7	1.02	13.21	4.33	2.16	1.44	1.48	1.28	1.06
				Mn (174 ± 12.8) [mg/kg]						
7	1.3	60.80	0.400	0.66	-17.68	-8.84	-5.89	17.65	8.84	5.89
4	1.4	85.4	3.63	4.25	-13.84	-6.92	-4.61	12.04	6.66	4.53
13	1.4	118	18.0	15.25	-8.75	-4.37	-2.92	2.93	2.54	2.13
15	1.3	145	30.0	20.69	-4.53	-2.26	-1.51	0.95	0.89	0.81
12	2	167	12.0	7.19	-1.09	-0.55	-0.36	0.51	0.40	0.31
22	1.2	171	16.0	9.36	-0.47	-0.23	-0.16	0.17	0.15	0.12
36	1.3	176	33.0	18.75	0.31	0.16	0.10	0.06	0.06	0.05
40	1.2	188.5	3.74	1.99	2.27	1.14	0.76	1.96	1.09	0.74
21	11	210.0	5.00	2.38	5.62	2.81	1.87	4.43	2.62	1.81
14	1	325*	68.5	21.06	23.65	11.83	7.88	2.20	2.17	2.13
9	1.2	367*	28.9	7.87	30.16	15.08	10.05	6.52	6.11	5.56

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Nb (10.7 ± 1.20) [mg/kg]										
22	1.2	9.20	0.600	6.52	-2.50	-1.25	-0.83	1.77	1.12	0.79
40	1.1	9.34	0.770	8.27	-2.28	-1.14	-0.76	1.40	0.96	0.70
21	2.0	10.70*	0.200	1.87	0.00	0.00	0.00	0.00	0.00	0.00
Ni (17.1 ± 1.78) [mg/kg]										
40	1.2	7.31*	0.660	9.09	-10.97	-5.49	-3.66	8.80	5.14	3.55
4	1.4	9.25*	0.480	5.23	-8.80	-4.40	-2.93	7.73	4.25	2.89
7	1.3	14.90	0.400	2.68	-2.47	-1.23	-0.82	2.25	1.20	0.81
9	1.2	16.7	1.30	7.78	-0.45	-0.22	-0.15	0.25	0.18	0.13
12	2.0	17.2	1.70	9.90	0.08	0.04	0.03	0.04	0.03	0.02
21	2.0	18.40	0.300	1.63	1.46	0.73	0.49	1.38	0.72	0.48
Pb (12.2 ± 1.34) [mg/kg]										
22	1.2	9.0	3.00	33.33	-4.78	-2.39	-1.59	1.04	0.97	0.89
36	1.3	11.9	3.50	29.41	-0.45	-0.22	-0.15	0.08	0.08	0.07
21	2.0	12.60	0.400	3.17	0.60	0.30	0.20	0.51	0.29	0.20
9	1.2	14.30	0.700	4.90	3.14	1.57	1.05	2.17	1.39	0.99
40	1.1	16.6	1.48	8.95	6.51	3.25	2.17	2.68	2.18	1.75
15	1.3	18.0	4.00	22.22	8.66	4.33	2.89	1.43	1.37	1.30
12	2.0	19.2	1.85	9.62	10.51	5.26	3.50	3.58	3.08	2.58
52	11	25.3	7.80	30.83	19.56	9.78	6.52	1.67	1.66	1.63
14	1.0	42*	10.1	23.67	45.17	22.59	15.06	3.00	2.98	2.95
4	1.4	56.0*	5.05	9.02	65.34	32.67	21.78	8.59	8.38	8.05
Rb [mg/kg]										
12	2.0	1.63	0.220	13.50	-	-	-	-	-	-
21	2.0	2.120	0.0300	1.42	-	-	-	-	-	-
22	1.2	2.50	0.500	20.00	-	-	-	-	-	-
40	1.1	3.80*	0.470	12.31	-	-	-	-	-	-
4	1.4	8.7*	1.12	12.95	-	-	-	-	-	-
S (705 ± 42.0) [mg/kg]										
7	1.3	371.2	1.80	0.48	-15.88	-7.94	-5.29	15.83	7.93	5.29
22	1.2	730	77.0	10.55	1.19	0.59	0.40	0.31	0.28	0.25
Sc (24.0 ± 2.38) [mg/kg]										
21	2.0	23.50	0.900	3.83	-0.42	-0.21	-0.14	0.34	0.20	0.14
22	1.2	25.0	4.00	16.00	0.84	0.42	0.28	0.24	0.21	0.19
Se (*2.29 ± 0.323*) [mg/kg]										
4	1.4	1.16	0.170	14.67	-6.98	-3.49	-2.33	4.80	3.09	2.19

TABLE 3 (cont.)

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
				Sr (*4.62 ± 0.587*) [mg/kg]						
4	1.4	2.3*	1.04	45.41	-7.91	-3.96	-2.64	2.14	1.94	1.70
22	1.2	4.10*	0.400	9.76	-1.77	-0.89	-0.59	1.05	0.73	0.54
12	2.0	4.36	0.340	7.80	-0.89	-0.44	-0.30	0.58	0.38	0.28
40	1.1	4.40	0.480	10.99	-0.76	-0.38	-0.25	0.40	0.29	0.22
21	2.0	4.650	0.0500	1.08	0.10	0.05	0.03	0.10	0.05	0.03
14	1.0	6.1*	3.03	50.00	4.91	2.45	1.64	0.47	0.47	0.46
				Te [mg/kg]						
4	1.4	29.3	5.38	18.34	-	-	-	-	-	-
				Th (15.1 ± 1.61) [mg/kg]						
40	1.1	11.6	1.28	11.06	-4.38	-2.19	-1.46	2.33	1.71	1.29
22	1.2	13.5	1.20	8.89	-1.99	-1.00	-0.66	1.11	0.80	0.59
7	1.3	13.60	0.400	2.94	-1.87	-0.93	-0.62	1.67	0.91	0.61
21	2.0	16.40	0.700	4.27	1.62	0.81	0.54	1.22	0.74	0.52
12	2.0	16.9	1.70	10.08	2.21	1.10	0.74	0.94	0.76	0.60
				U (2.41 ± 0.338) [mg/kg]						
40	1.1	3.36	0.290	8.67	5.63	2.81	1.88	2.82	2.13	1.63
				V (270 ± 18.6) [mg/kg]						
22	1.2	86	18.0	20.93	-19.79	-9.89	-6.60	9.08	7.11	5.54
52	11	109	19.7	18.06	-17.30	-8.65	-5.77	7.39	5.94	4.71
7	1.3	161.5	2.90	1.80	-11.67	-5.83	-3.89	11.14	5.76	3.87
4	1.4	174	10.7	6.12	-10.27	-5.14	-3.42	6.75	4.45	3.20
12	2.0	251	19.0	7.57	-2.04	-1.02	-0.68	0.90	0.71	0.56
13	1.4	254.0	9.00	3.54	-1.72	-0.86	-0.57	1.24	0.77	0.55
21	2.0	265.0	4.00	1.51	-0.54	-0.27	-0.18	0.49	0.26	0.18
15	1.3	288	60.0	20.83	1.94	0.97	0.65	0.30	0.29	0.27
40	1.2	535*	29.7	5.55	28.47	14.24	9.49	8.51	7.56	6.50
				Y (*4.66 ± 0.591*) [mg/kg]						
22	1.2	2.60	0.400	15.38	-6.97	-3.48	-2.32	4.14	2.89	2.12
21	2.0	3.680	0.0500	1.36	-3.31	-1.66	-1.10	3.27	1.65	1.10
				Zn (68.7 ± 5.81) [mg/kg]						
13	1.4	29	1.00	3.45	-13.66	-6.83	-4.55	12.91	6.73	4.52
4	1.4	44.904	0.95	2.11	-8.18	-4.09	-2.73	7.78	4.04	2.71
40	1.1	52.559	2.54	4.83	-5.55	-2.78	-1.85	4.18	2.54	1.78
7	1.3	60.2	0.60	1.00	-2.92	-1.46	-0.97	2.86	1.45	0.97
22	1.2	65	0.50	0.77	-1.27	-0.64	-0.42	1.25	0.63	0.42
9	1.2	66.9	5.80	8.67	-0.62	-0.31	-0.21	0.28	0.22	0.17
21	2.0	67.9	1.30	1.91	-0.28	-0.14	-0.09	0.25	0.13	0.09
36	1.3	68.7	10.70	15.57	0.00	0.00	0.00	0.00	0.00	0.00
15	1.3	70	7.00	10.00	0.45	0.22	0.15	0.17	0.14	0.12
14	1.0	86.15	17.31	20.09	6.00	3.00	2.00	0.99	0.96	0.90
11	1.2	108*	20.00	18.52	13.52	6.76	4.51	1.94	1.89	1.80

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Zr (266 ± 18.4) [mg/kg]										
7	1.3	52.20*	0.400	0.77	-23.28	-11.64	-7.76	23.26	11.64	7.76
9	1.2	116*	12.0	10.36	-16.36	-8.18	-5.45	9.94	6.85	5.00
40	1.1	219.5*	9.63	4.38	-5.06	-2.53	-1.69	3.49	2.24	1.59
15	1.3	255	40.0	15.69	-1.20	-0.60	-0.40	0.27	0.25	0.23
21	2.0	264.0	4.00	1.52	-0.22	-0.11	-0.07	0.20	0.11	0.07
22	1.2	273	15.0	5.49	0.76	0.38	0.25	0.40	0.30	0.22

TABLE 4. THE COMBINED *z*-SCORES FOR THE PARTICIPATING LABORATORIES

Lab Code	Number of analytes	Rescaled sum of scores (RSZ)			Sum of squared scores (SSZ)			Critical value
		$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$	χ^2
4	18	-37.3	-18.6	-12.4	15903	3976	1767	31.5
7	16	-20.7	-10.3	-6.89	3817	954	424	28.9
9	10	31.2	15.6	10.4	3973	993	441	20.5
11	2	13.1	6.56	4.37	208	52.0	23.12	7.38
12	11	0.700	0.350	0.230	193	48.4	21.5	21.9
13	8	-24.5	-12.3	-8.18	1389	347	154	17.5
14	9	40.2	20.1	13.4	3064	766	340	19.0
15	13	1.65	0.830	0.550	254	63.4	28.2	24.7
21	19	12.3	6.14	4.10	2273	568	253	32.9
22	22	-6.30	-3.15	-2.10	1248	312	139	36.8
36	7	-0.140	-0.070	-0.050	1.78	0.450	0.20	16.0
40	15	1.38	0.690	0.460	1618	405	180	27.5
52	7	43.7	21.9	14.6	9842	2460	1094	16.0

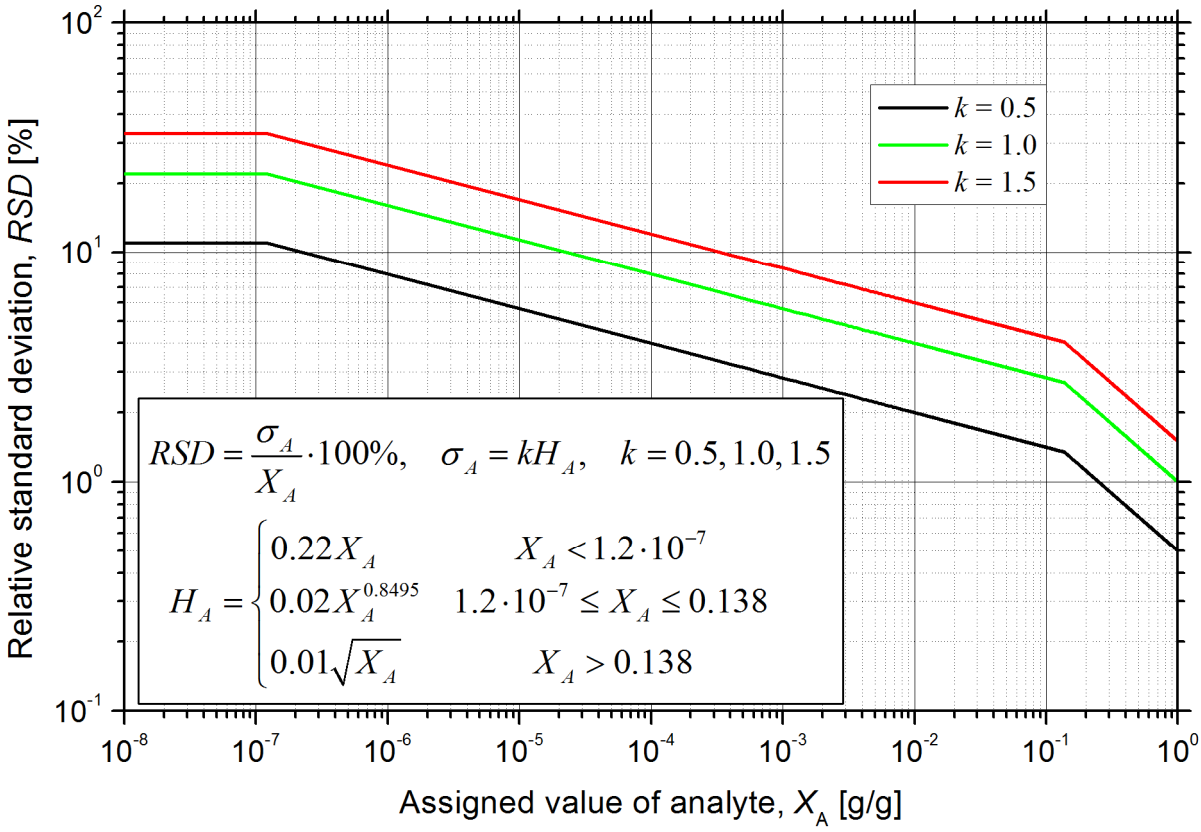

FIG. 1. Relative value of the target standard deviation, RSD, as a function of the assigned mass fraction of the analyte, X_A, calculated by using a modified Horowitz function, Eqn. (1).

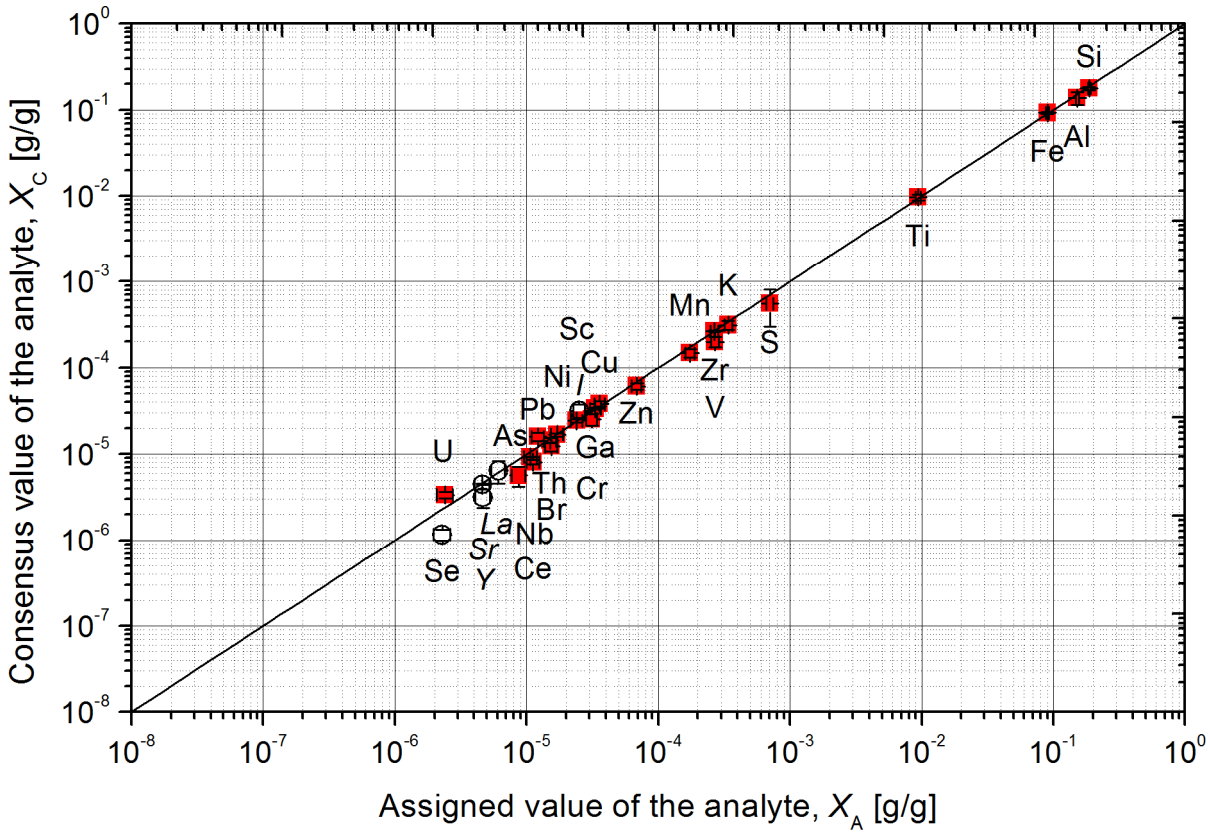

FIG. 2. Correlation between assigned, X_A, and consensus values of analytes, X_C[2].

[2] Solid red squares correspond to the elements of the assigned values, which were known with high degree of accuracy. Hollow black circles correspond to the elements of the assigned values, which can be considered as indicative/informative only. The uncertainties of the assigned values were calculated according to Eqn. (2) with $k = 1$. The uncertainties of the consensus values were calculated according to Eqn. (20), except for the results reported by a single laboratory, in such a case the laboratory estimate of the uncertainty was shown in the plot.

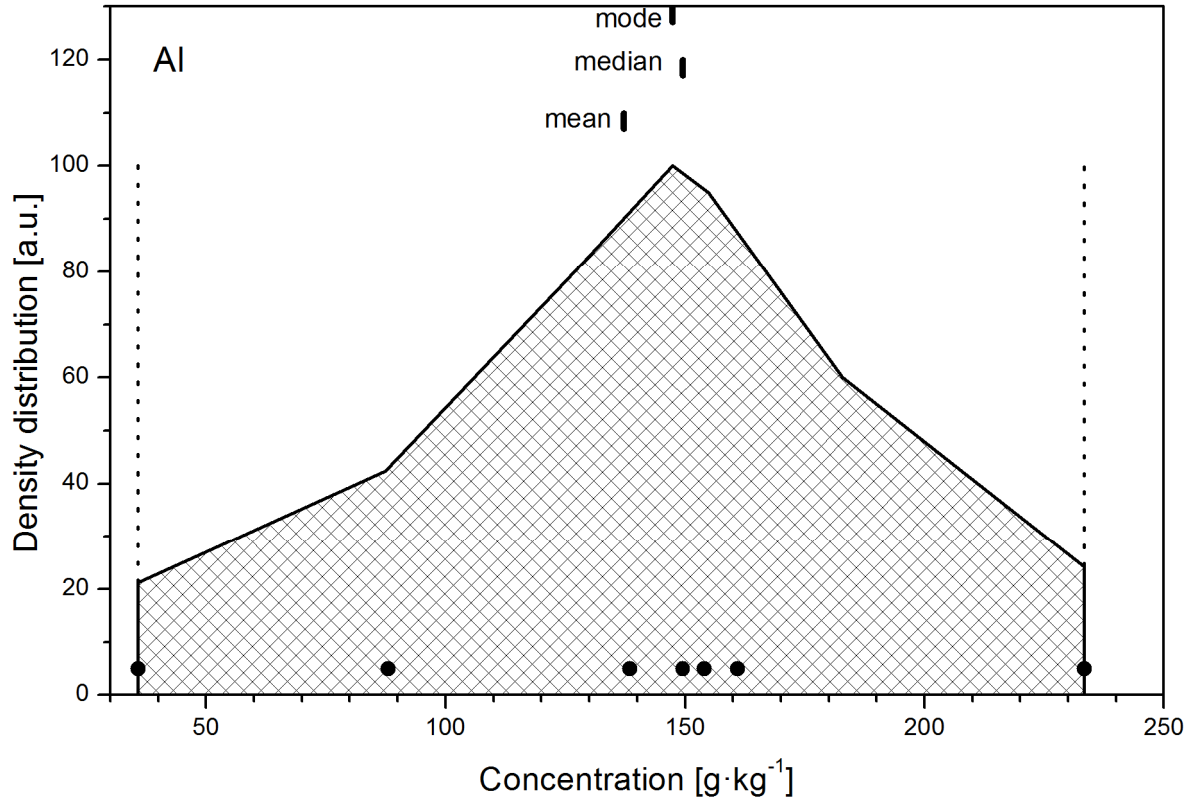

FIG. 3. The density distribution function for the analyte Al.

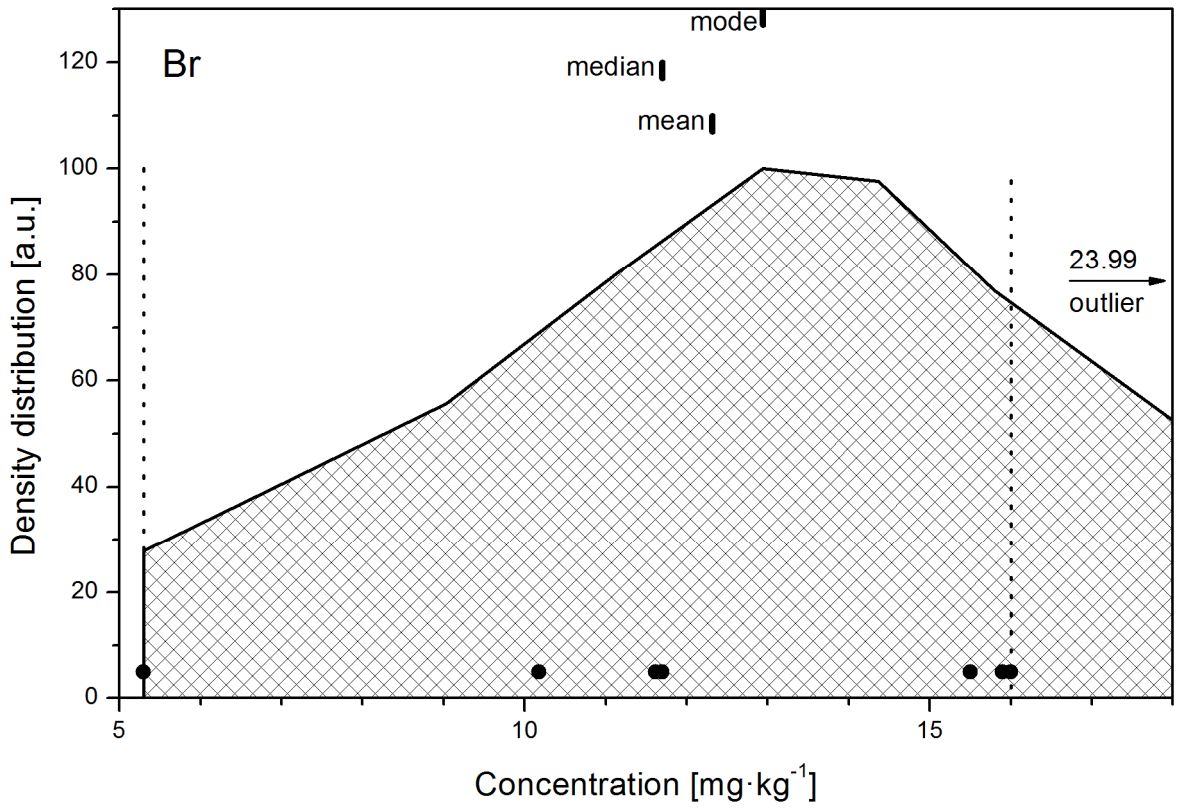

FIG. 4. The density distribution function for the analyte Br.

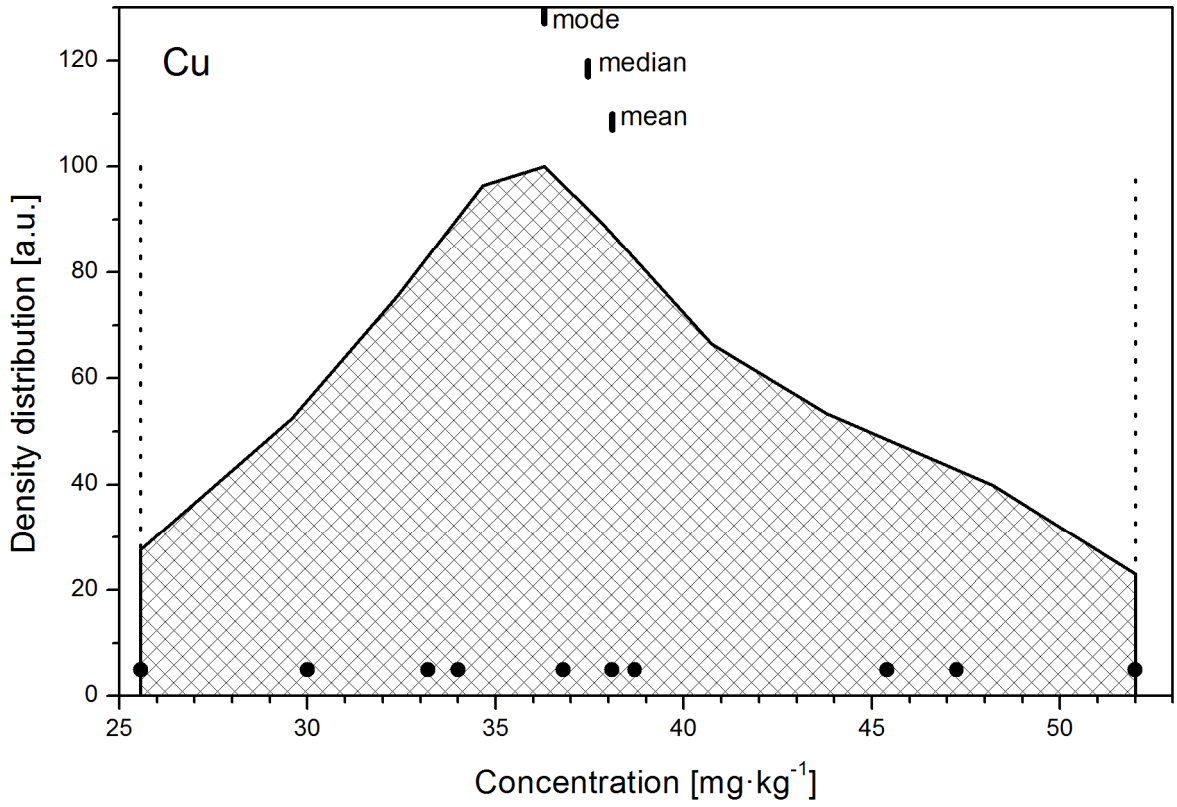

FIG. 5. The density distribution function for the analyte Cu.

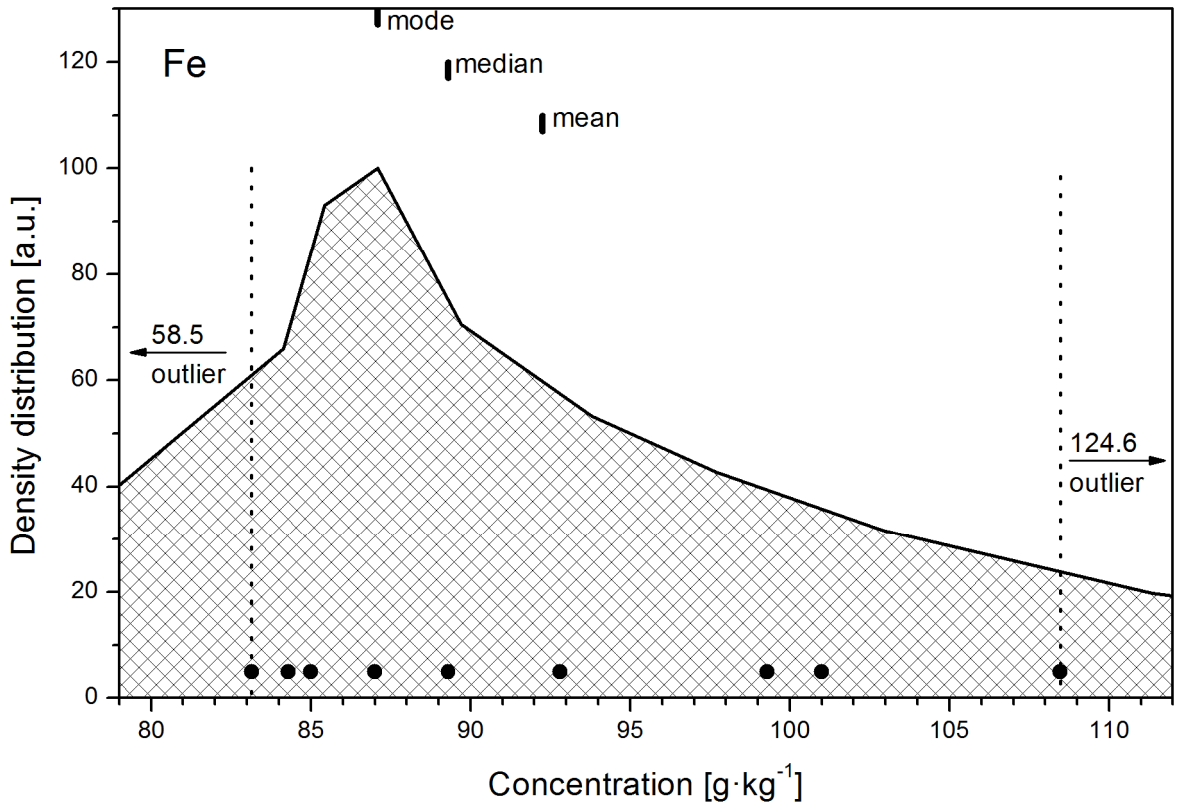

FIG. 6. The density distribution function for the analyte Fe.

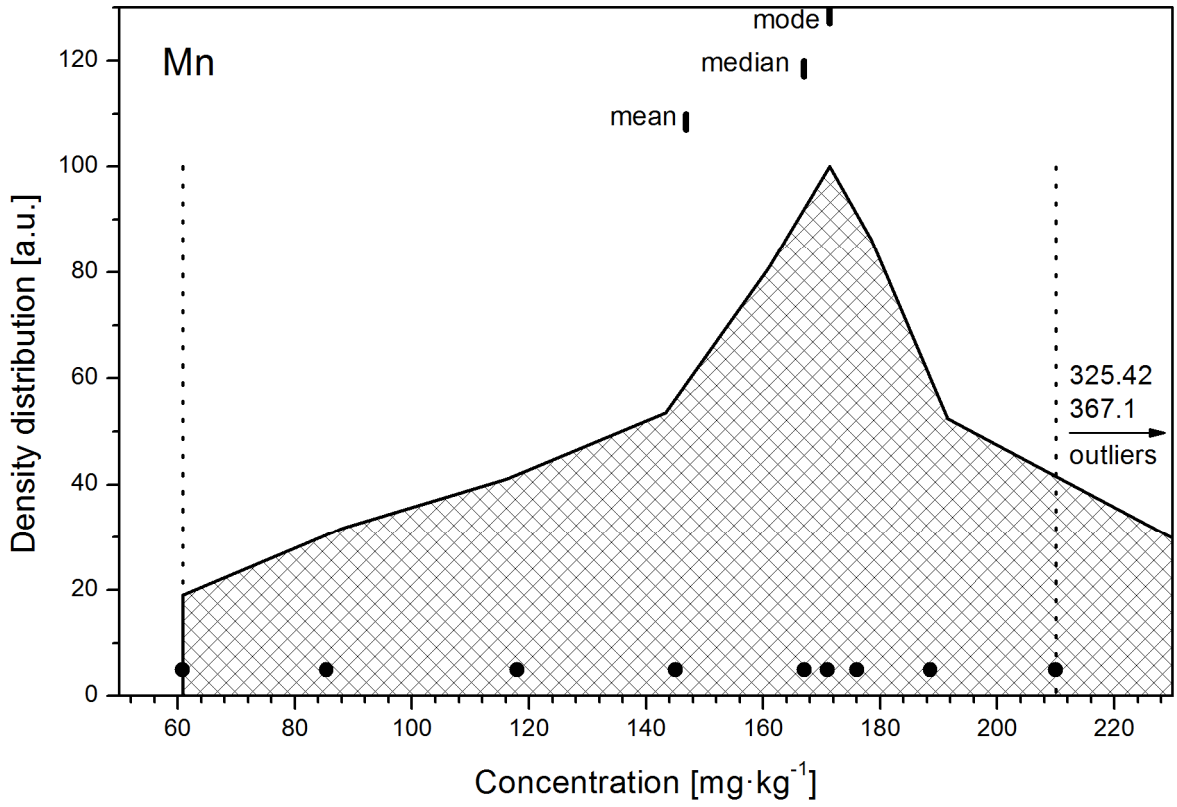

FIG. 7. The density distribution function for the analyte Mn.

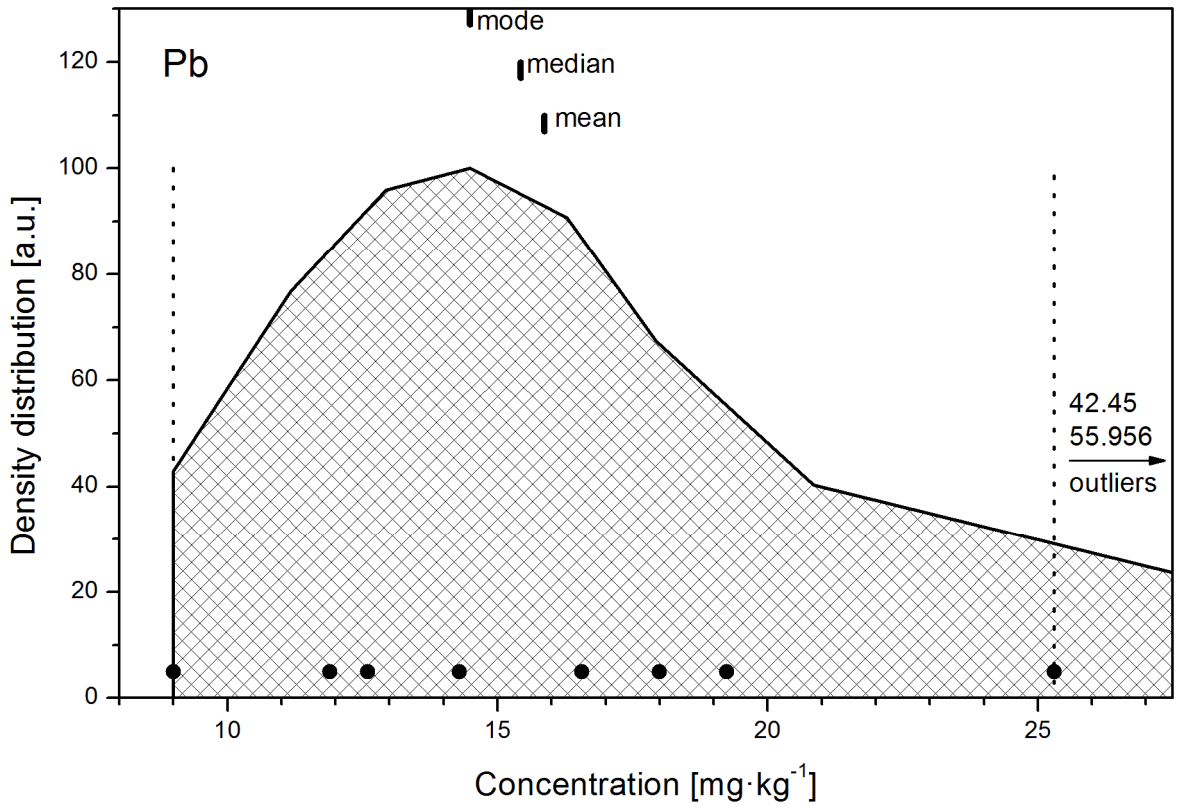

FIG. 8. The density distribution function for the analyte Pb.

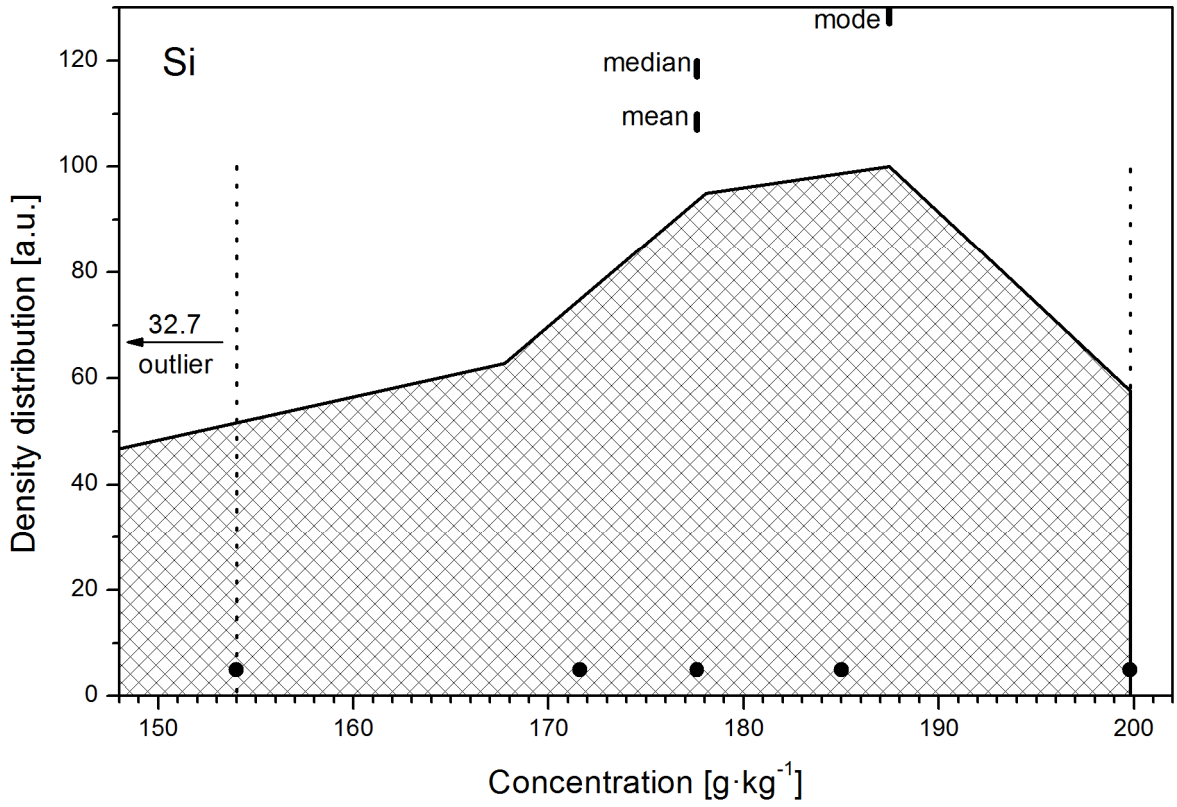

FIG. 9. The density distribution function for the analyte Si.

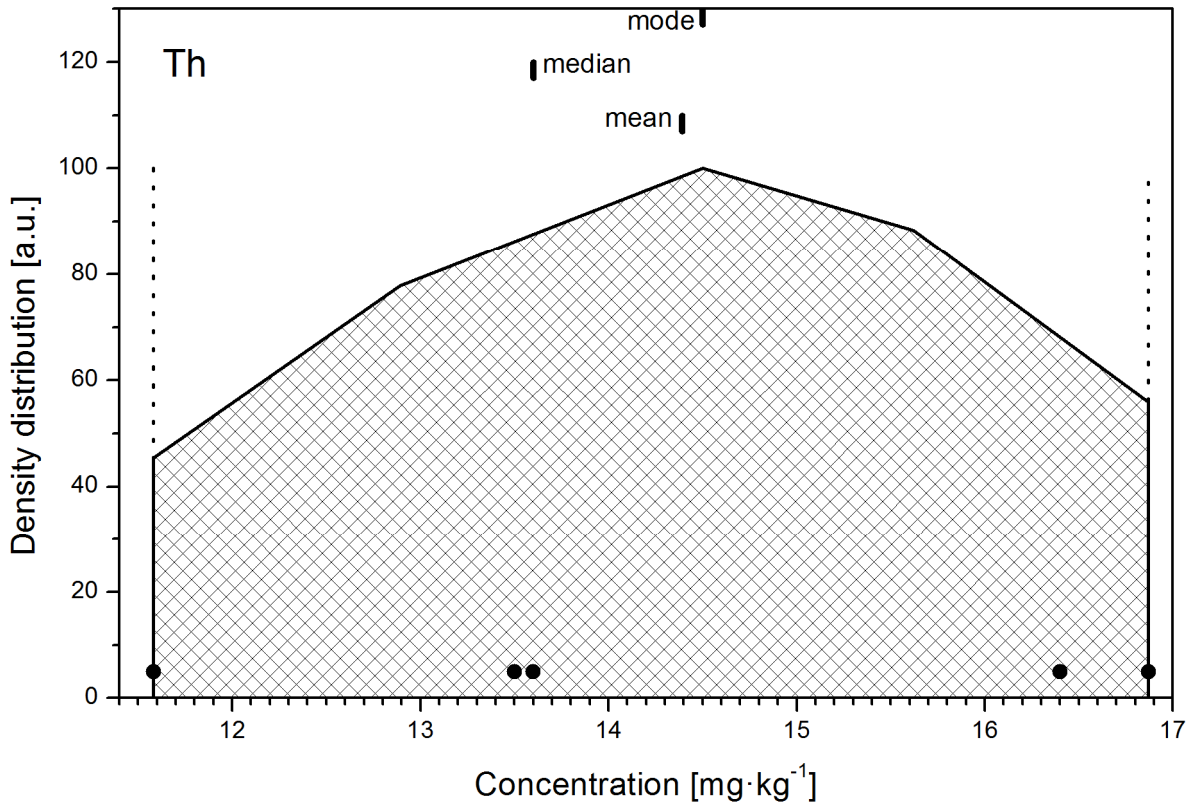

FIG. 10. The density distribution function for the analyte Th.

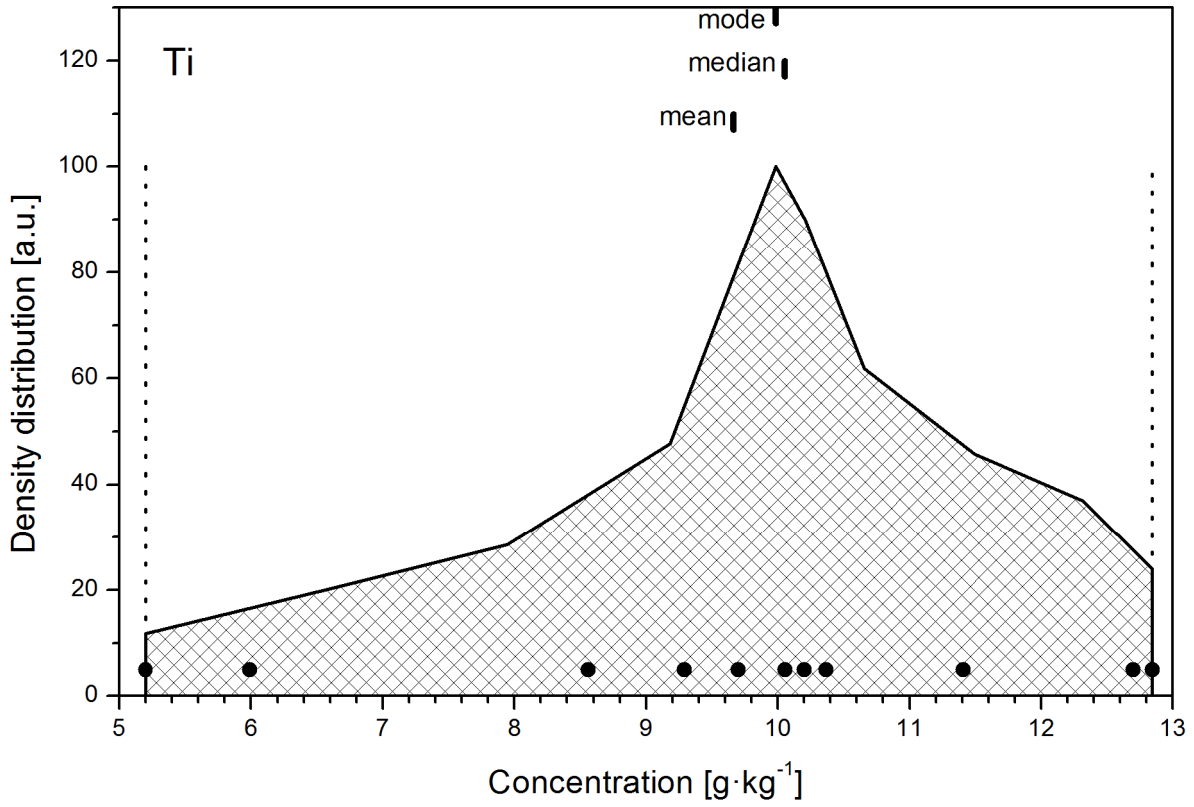

FIG. 11. The density distribution function for the analyte Ti.

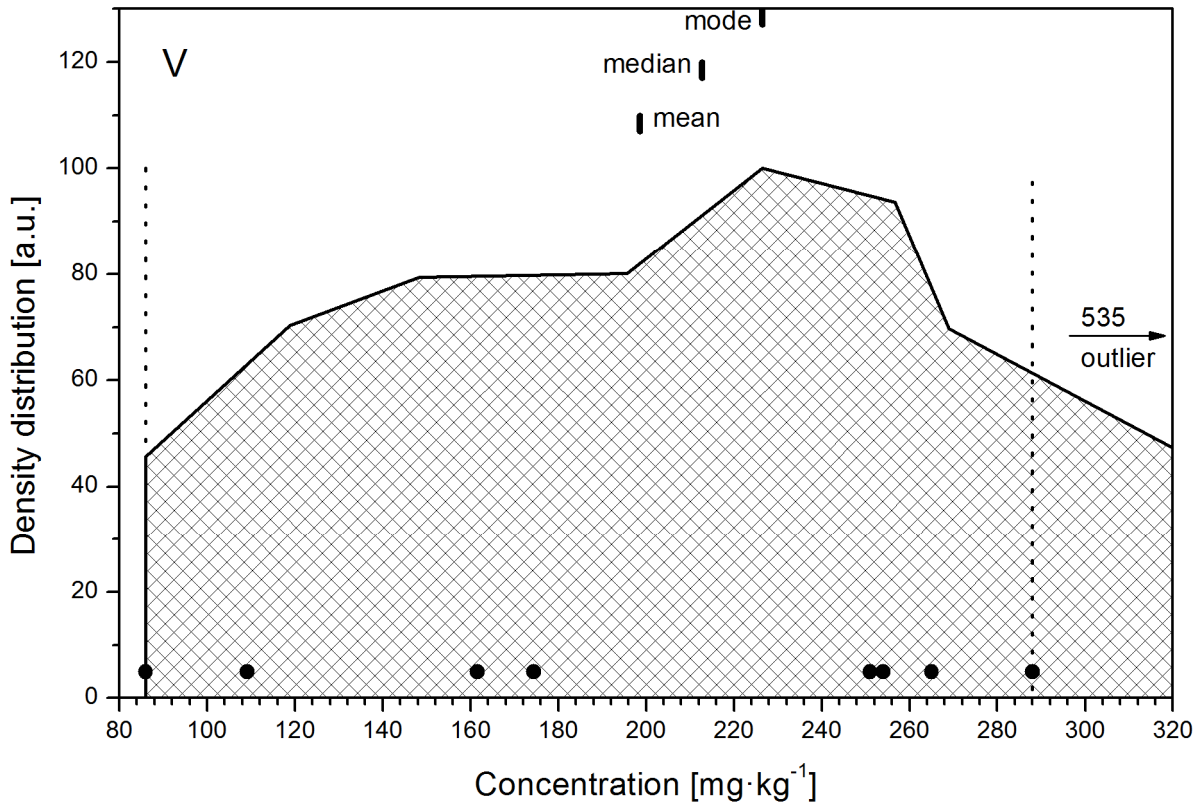

FIG. 12. The density distribution function for the analyte V.

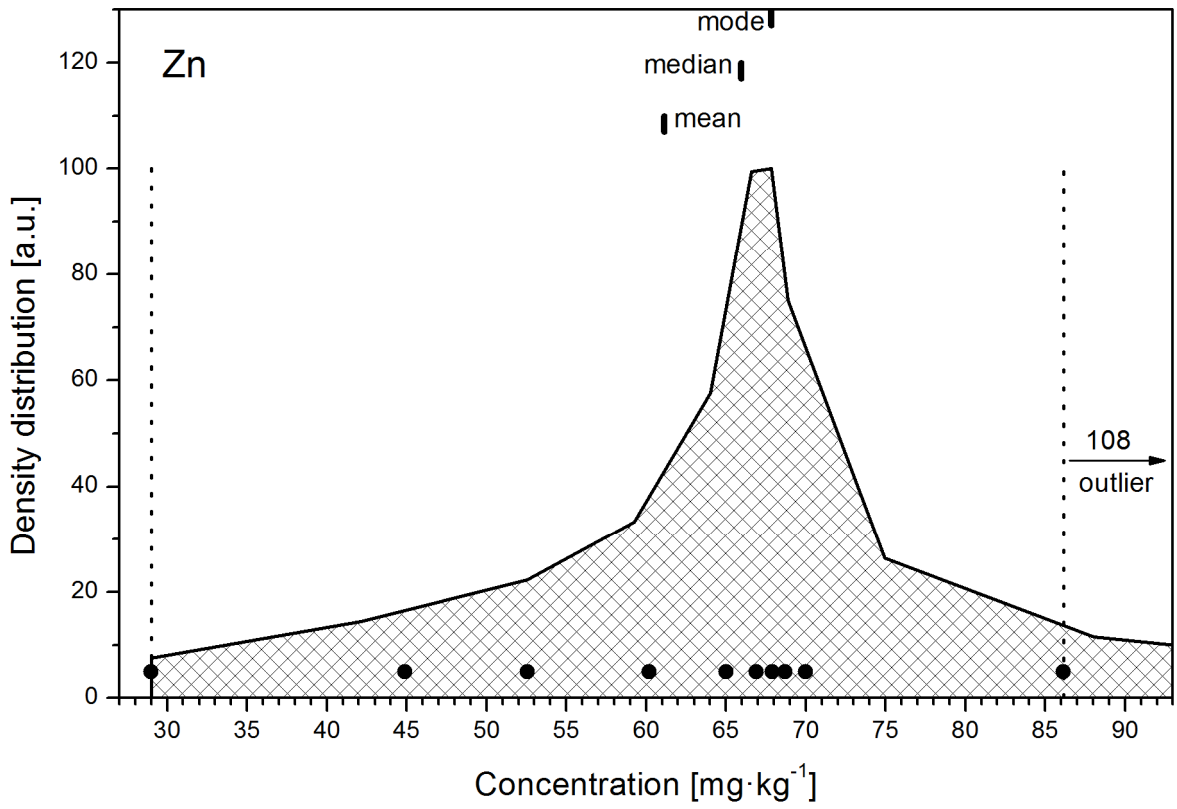

FIG. 13. The density distribution function for the analyte Zn.

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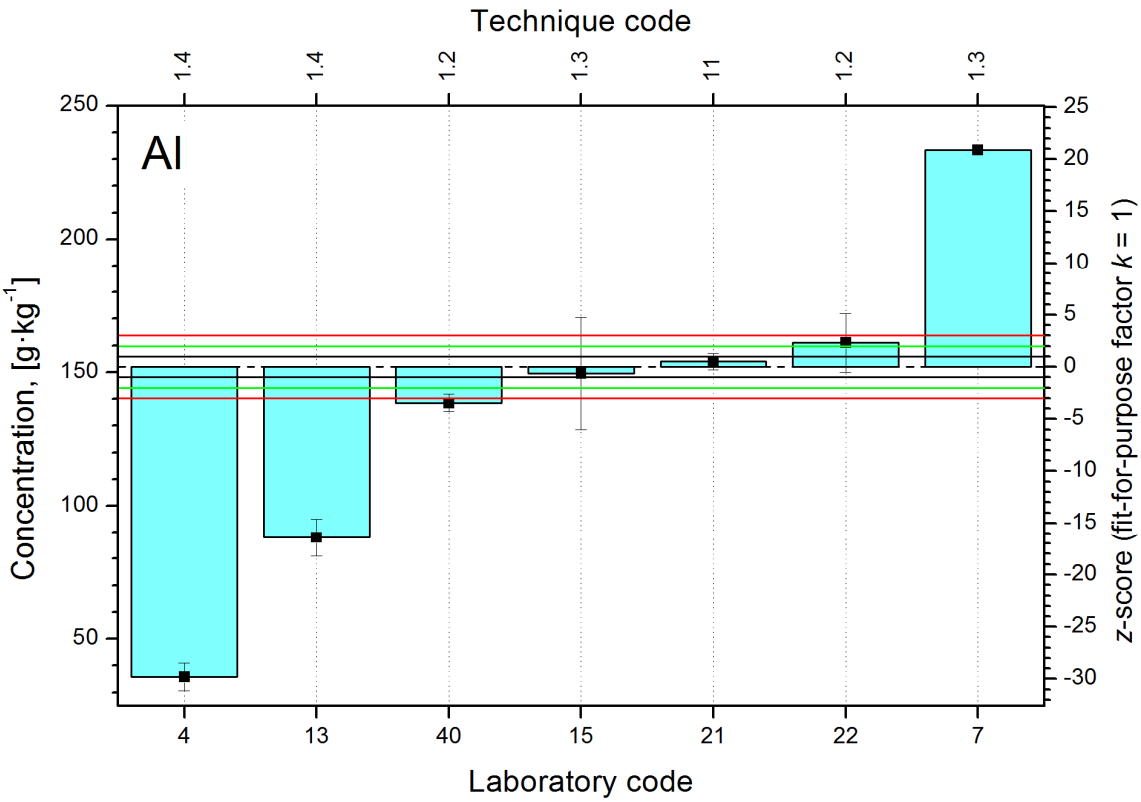

FIG. 14. Distributions of z-scores for analyte Al.

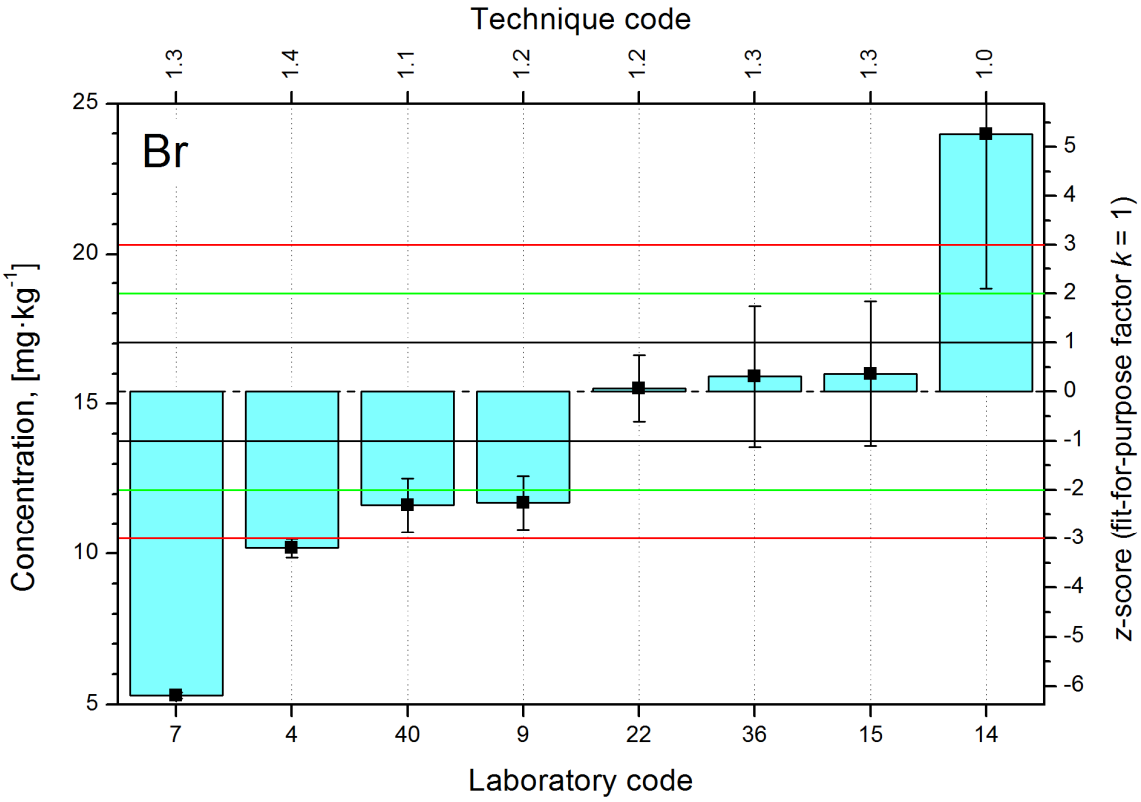

FIG. 15. Distributions of z-scores for analyte Br.

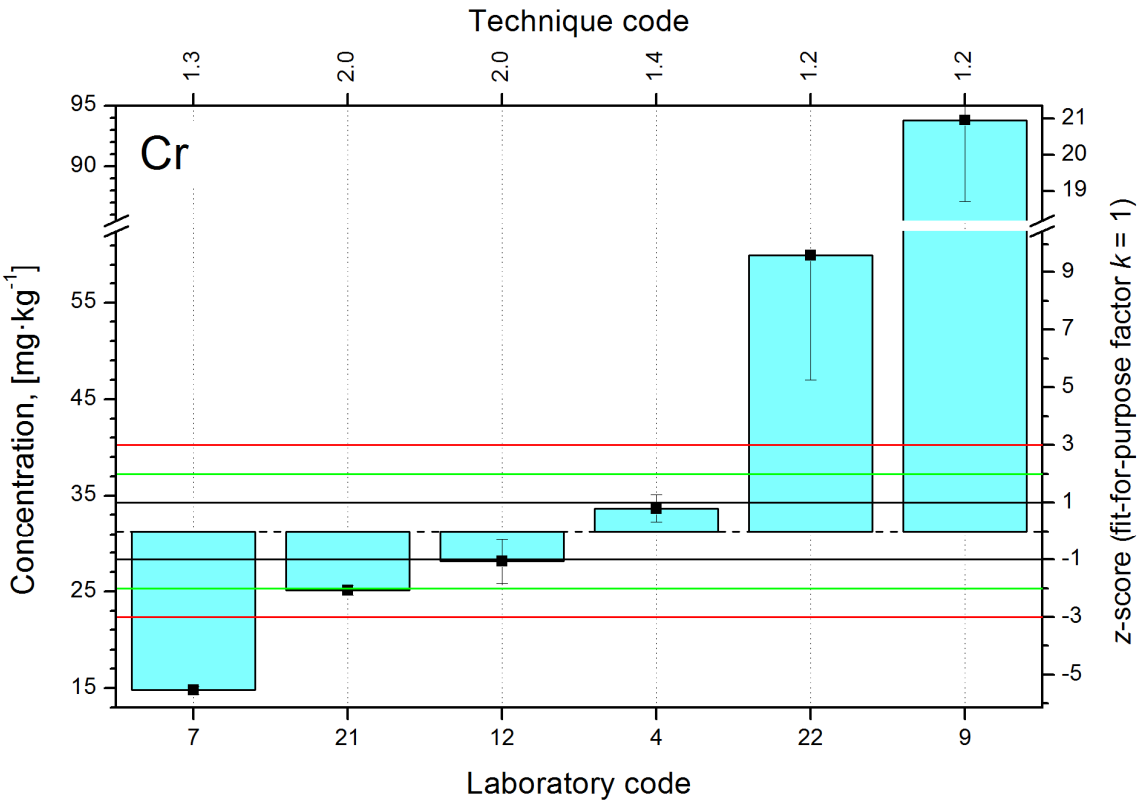

FIG. 16. Distributions of z-scores for analyte Cr.

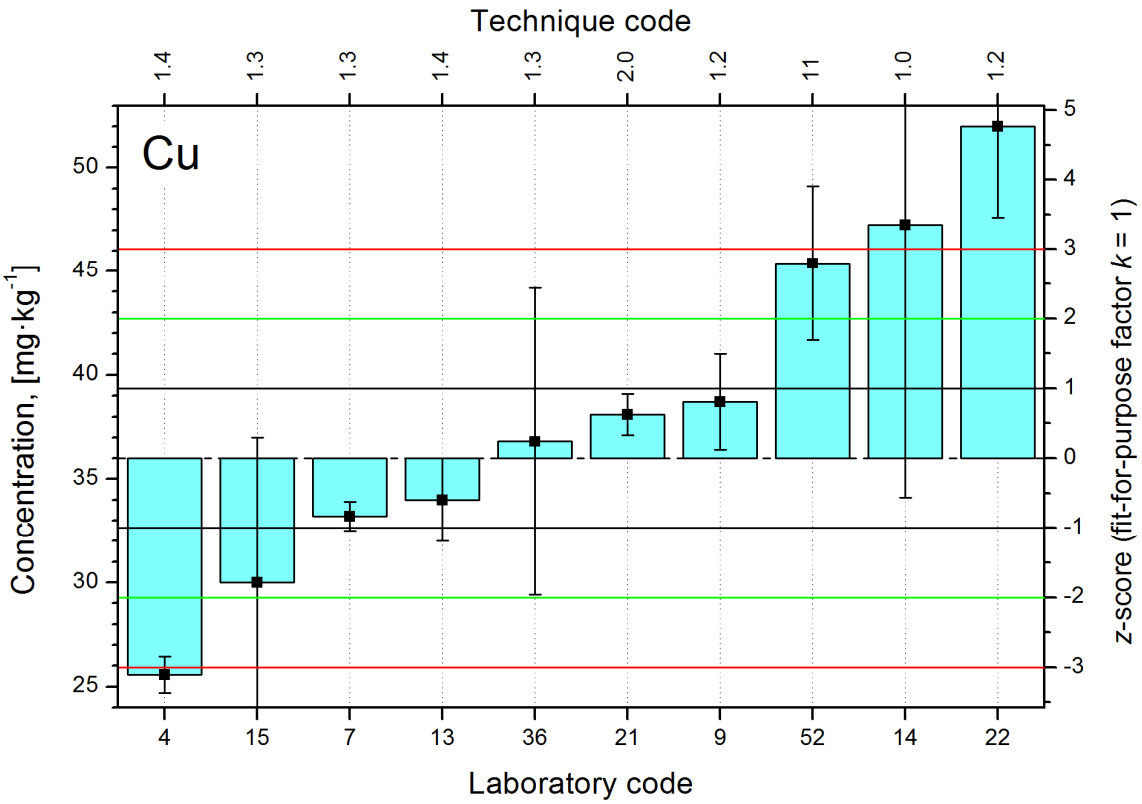

FIG. 17. Distributions of z-scores for analyte Cu.

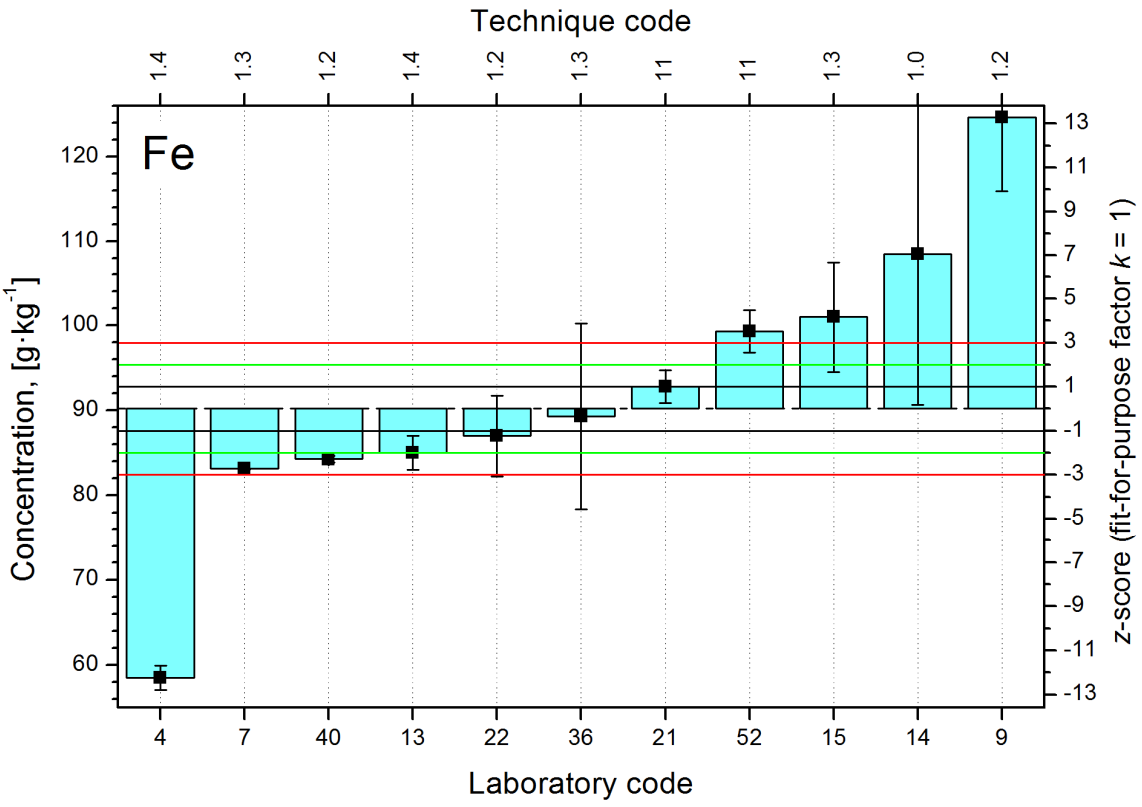

FIG. 18. Distributions of z-scores for analyte Fe.

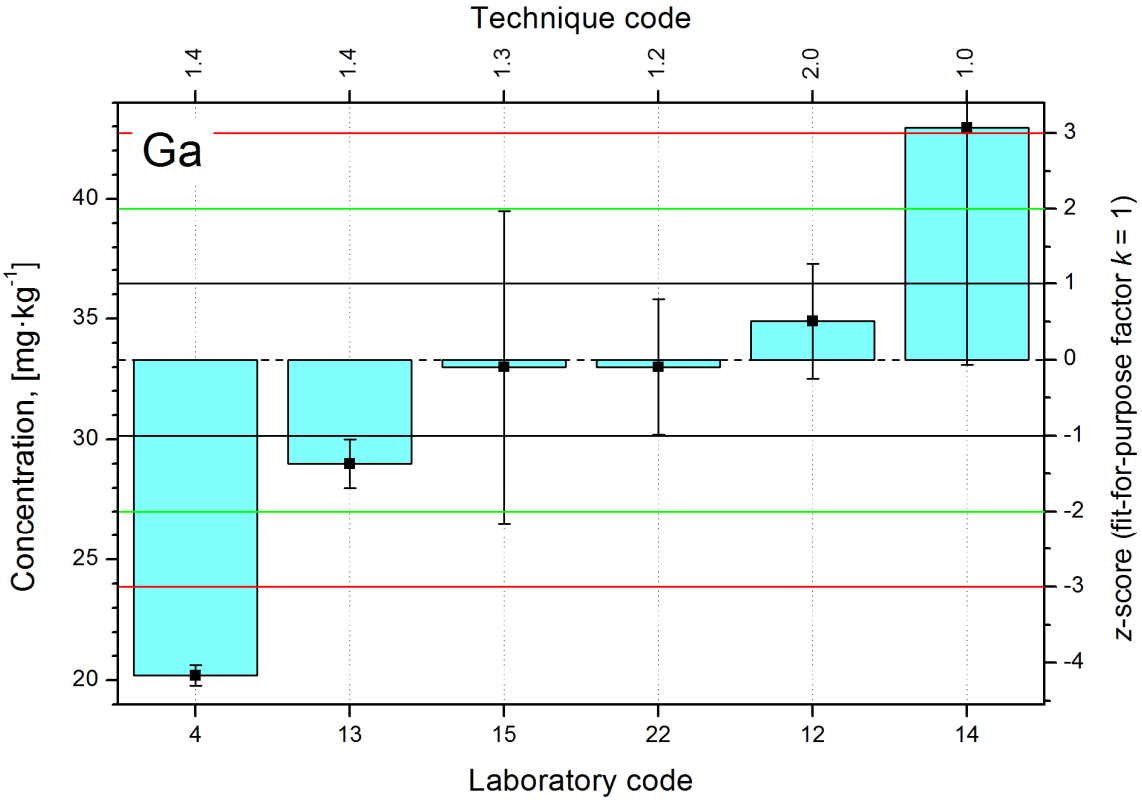

FIG. 19. Distributions of z-scores for analyte Ga.

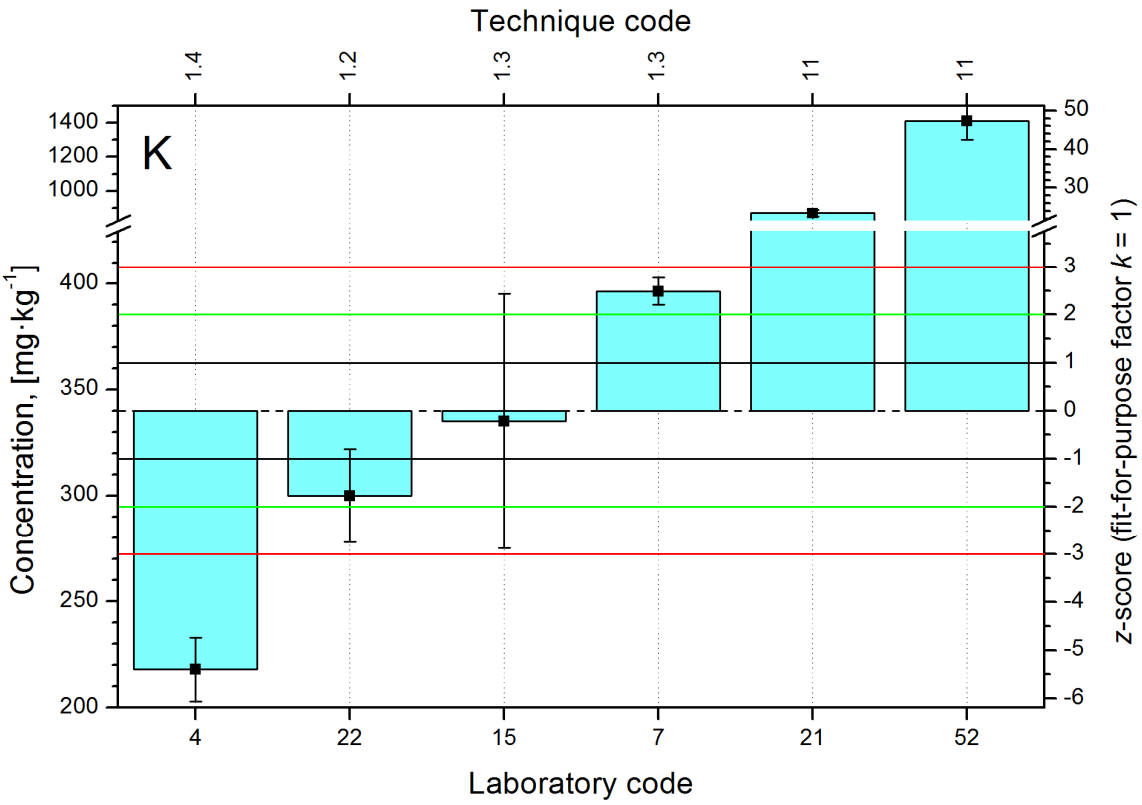

FIG. 20. Distributions of z-scores for analyte K.

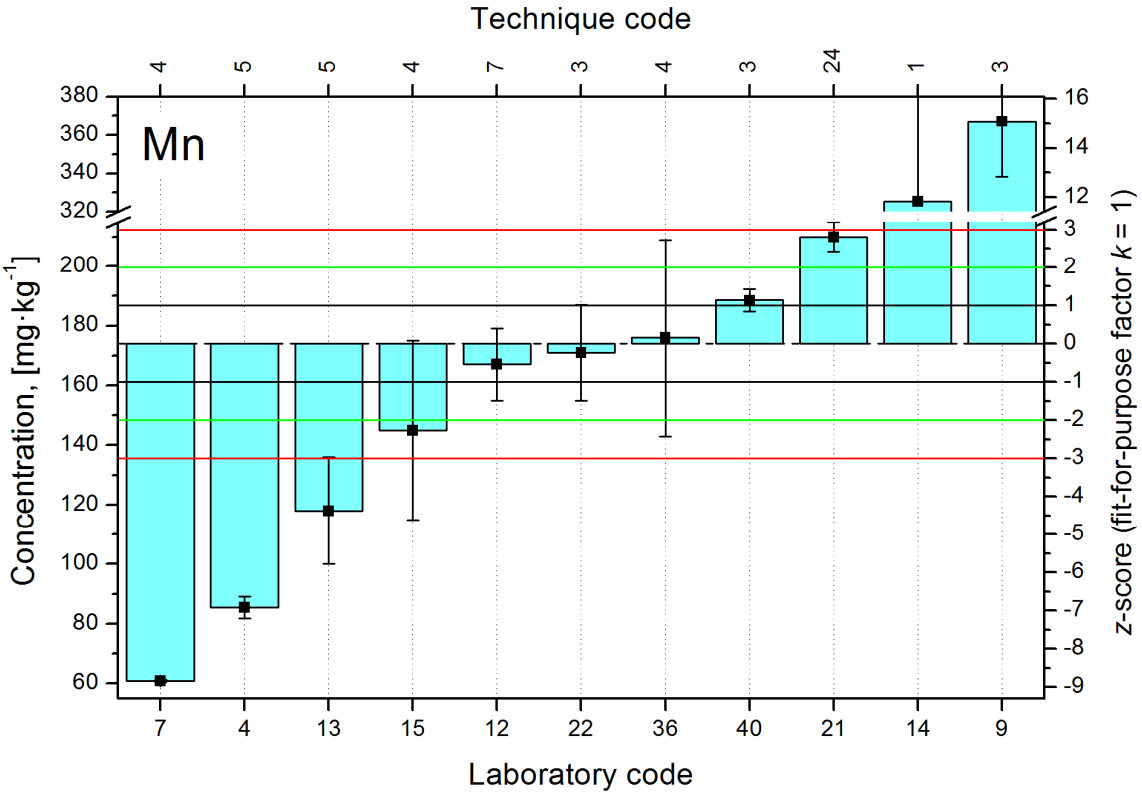

FIG. 21. Distributions of z-scores for analyte Mn.

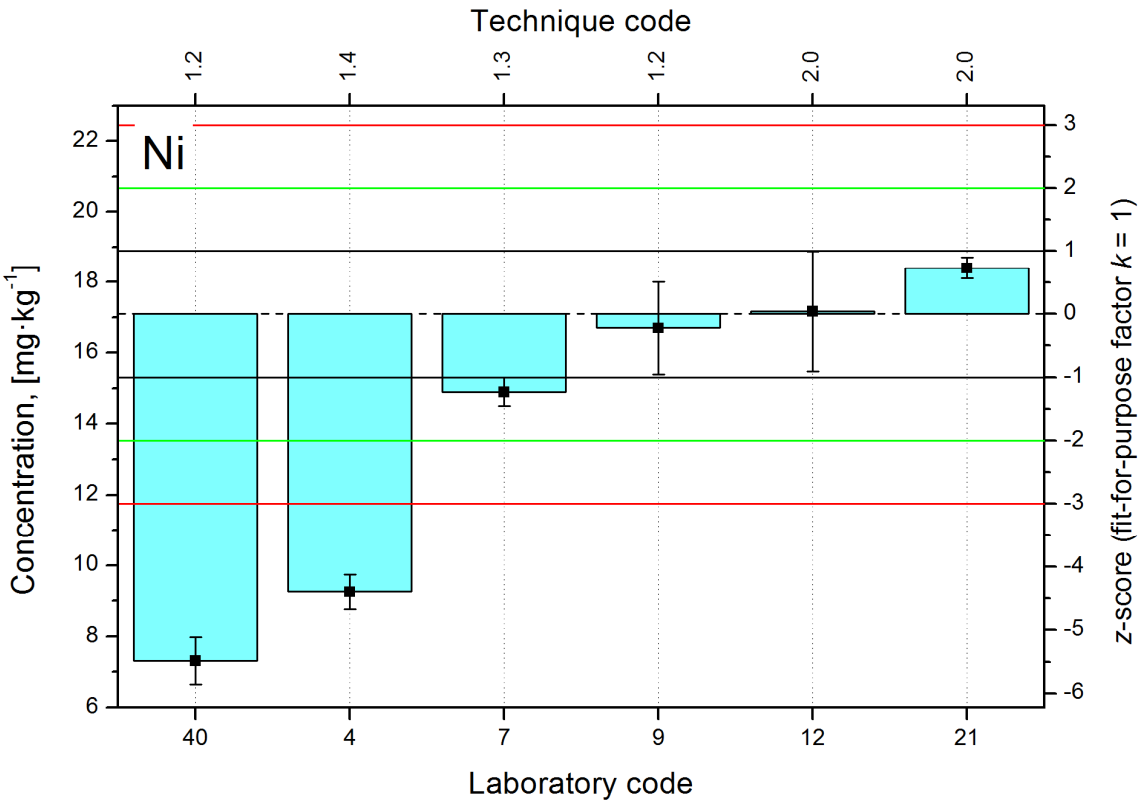

FIG. 22. Distributions of z-scores for analyte Ni.

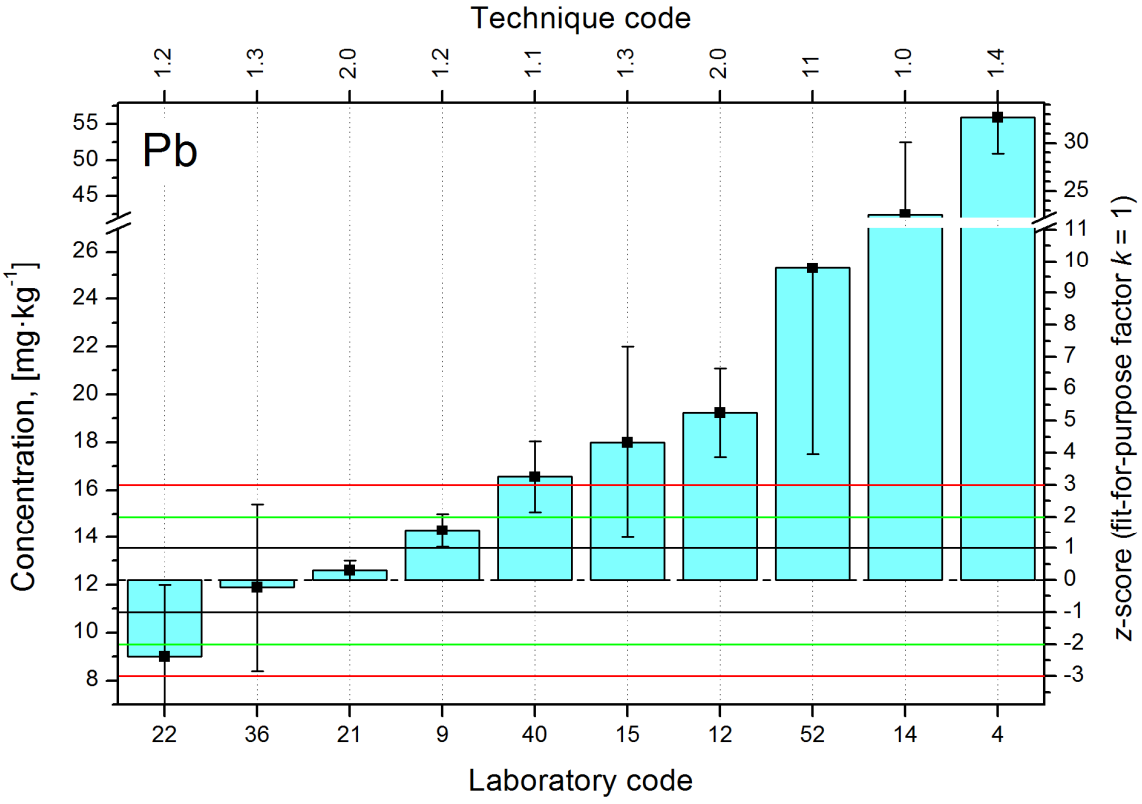

FIG. 23. Distributions of z-scores for analyte Pb.

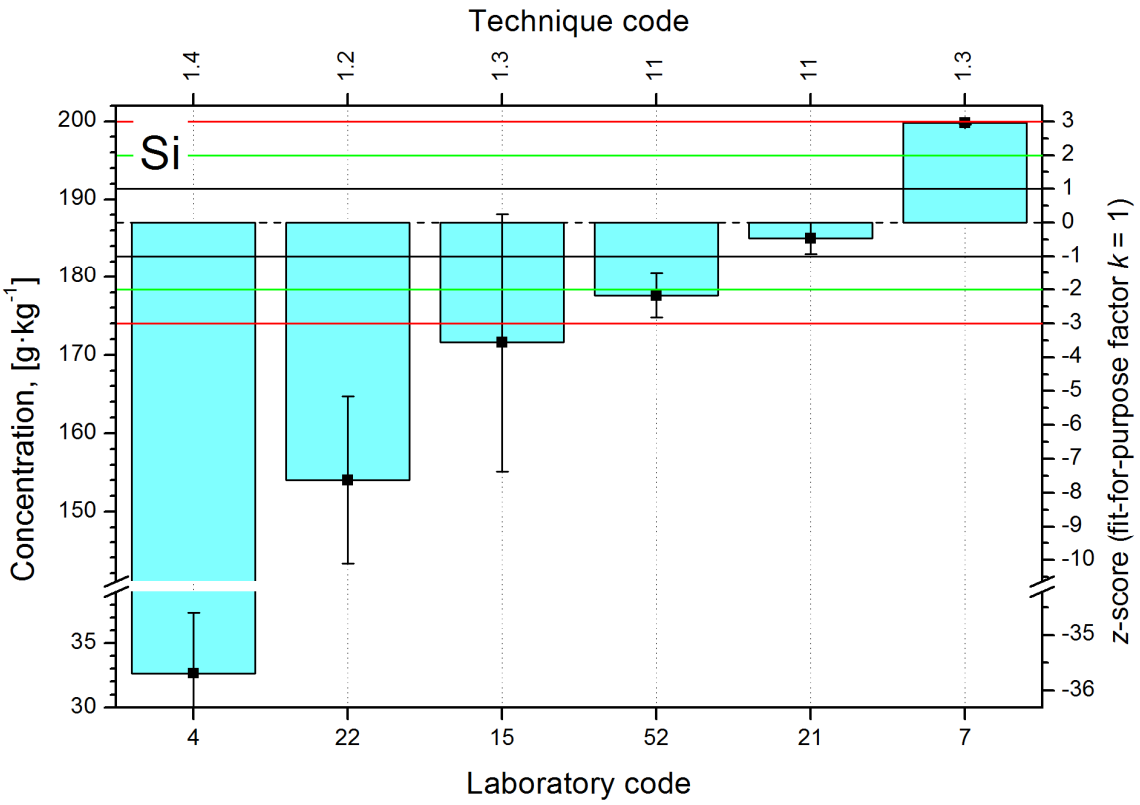

FIG. 24. Distributions of z-scores for analyte Si.

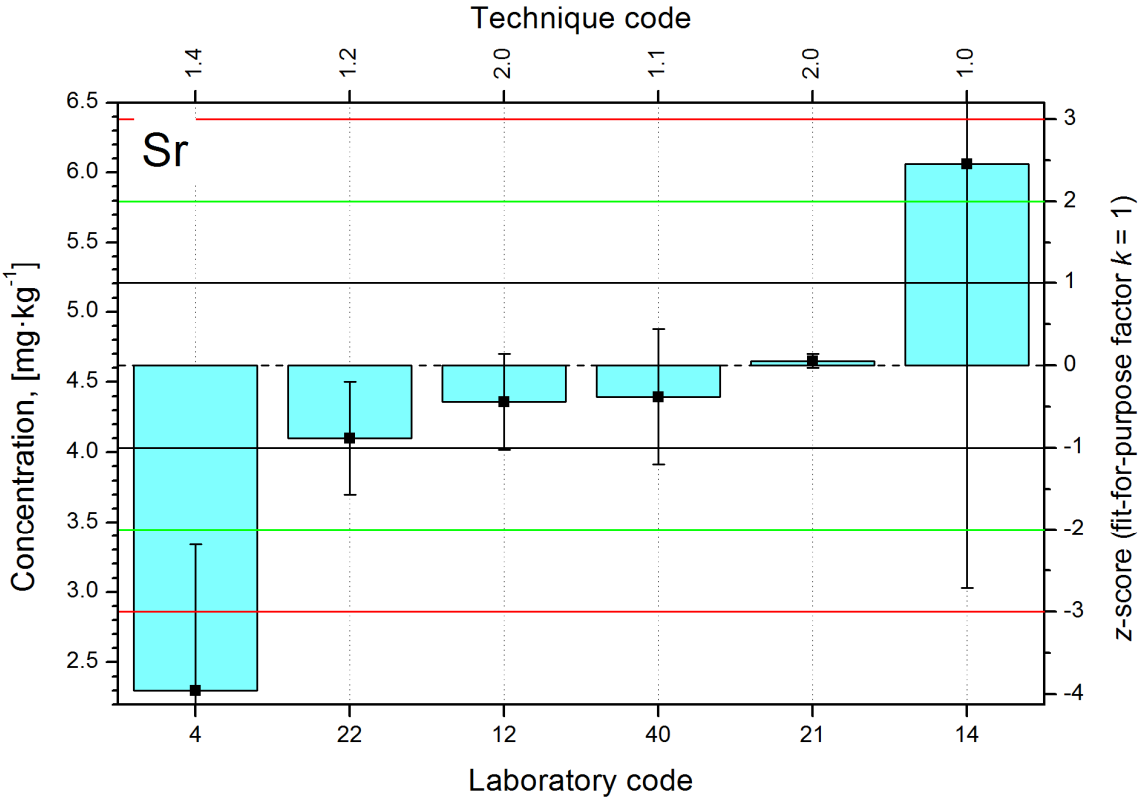

FIG. 25. Distributions of z-scores for analyte Sr.

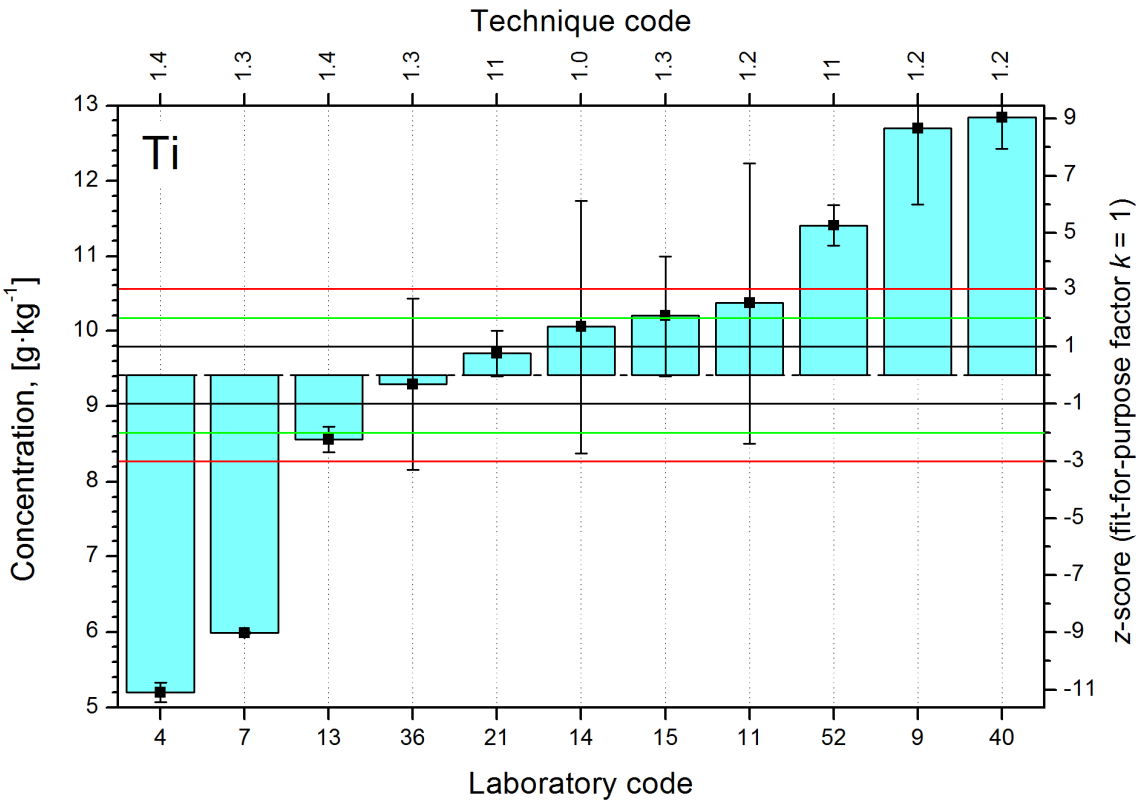

FIG. 26. Distributions of z-scores for analyte Ti.

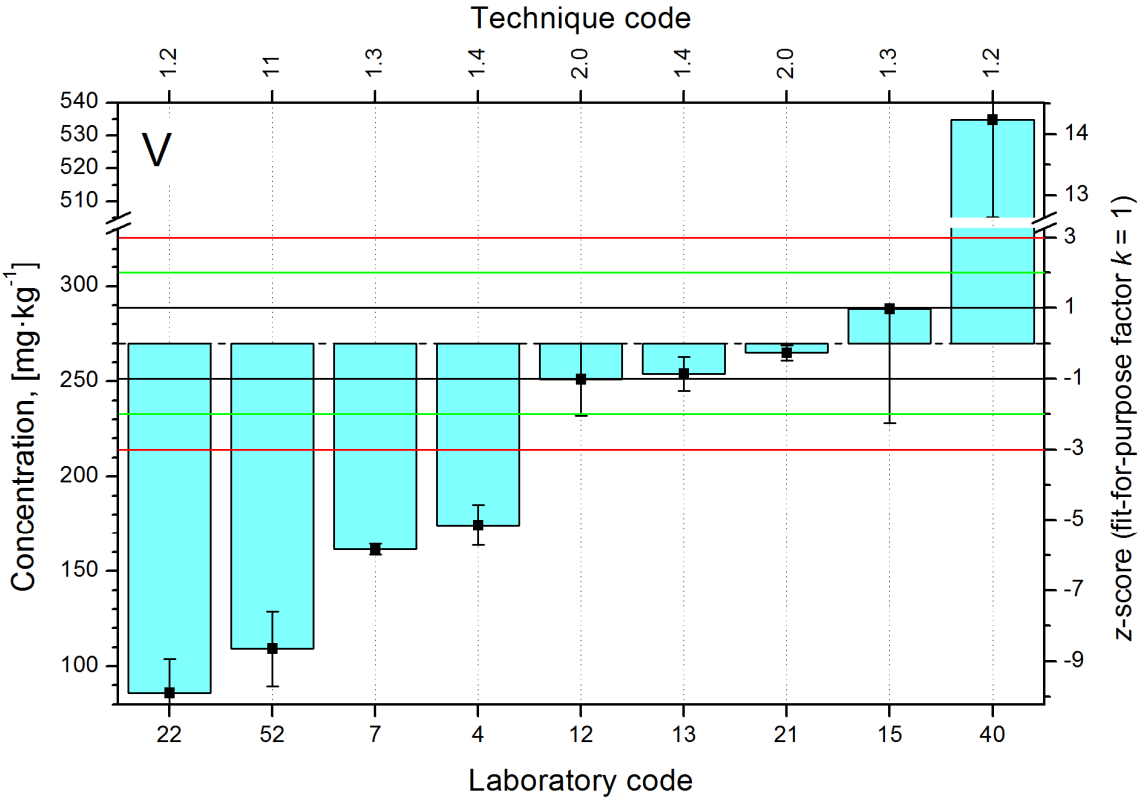

FIG. 27. Distributions of z-scores for analyte V.

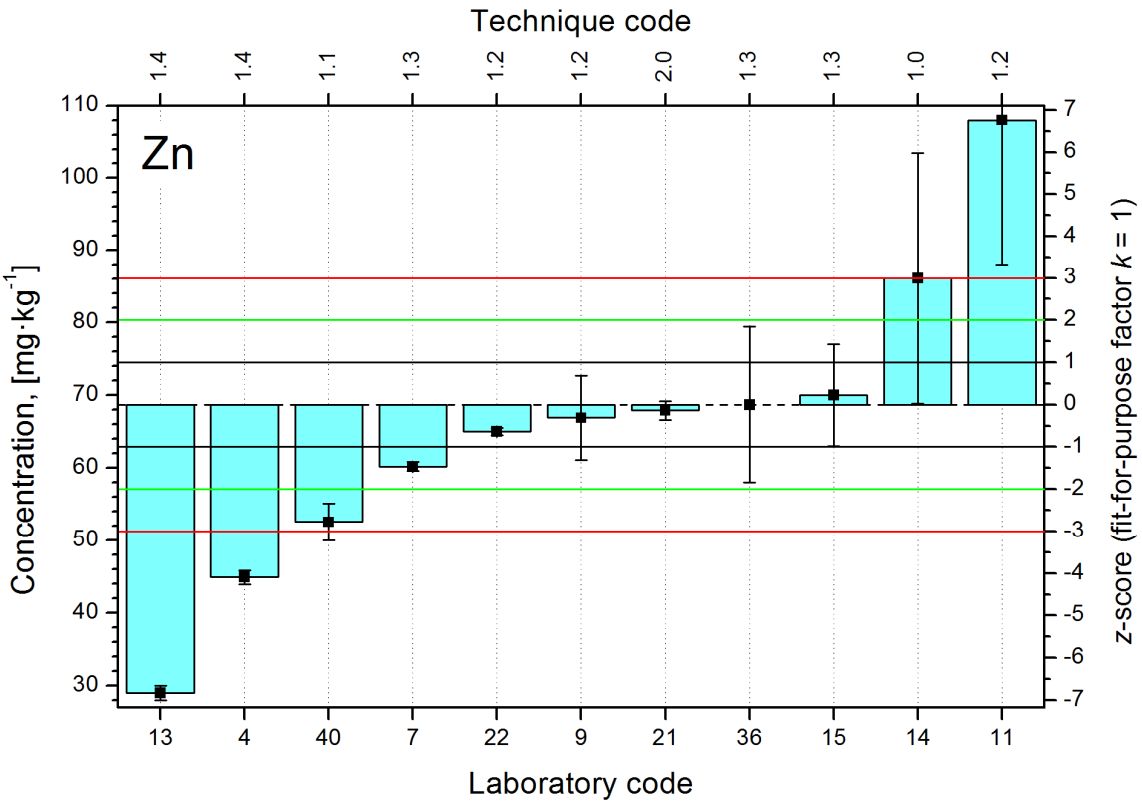

FIG. 28. Distributions of z-scores for analyte Zn.

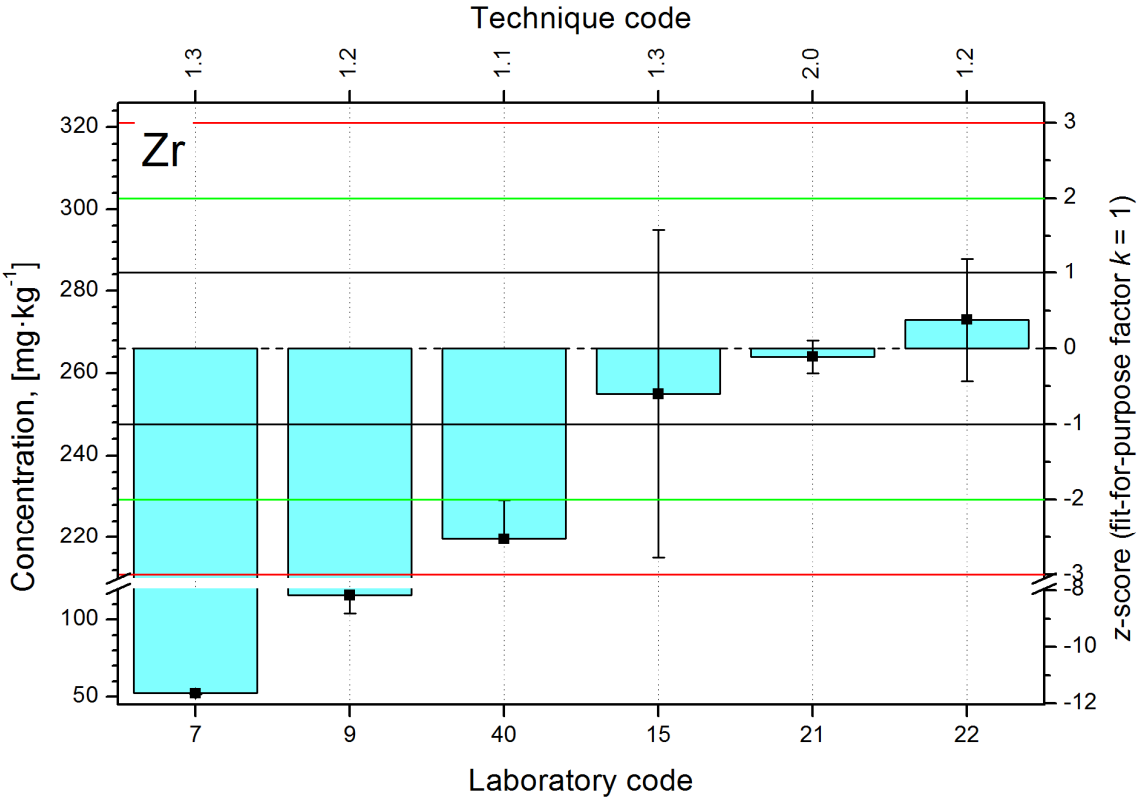

FIG. 29. Distributions of z-scores for analyte Zr.

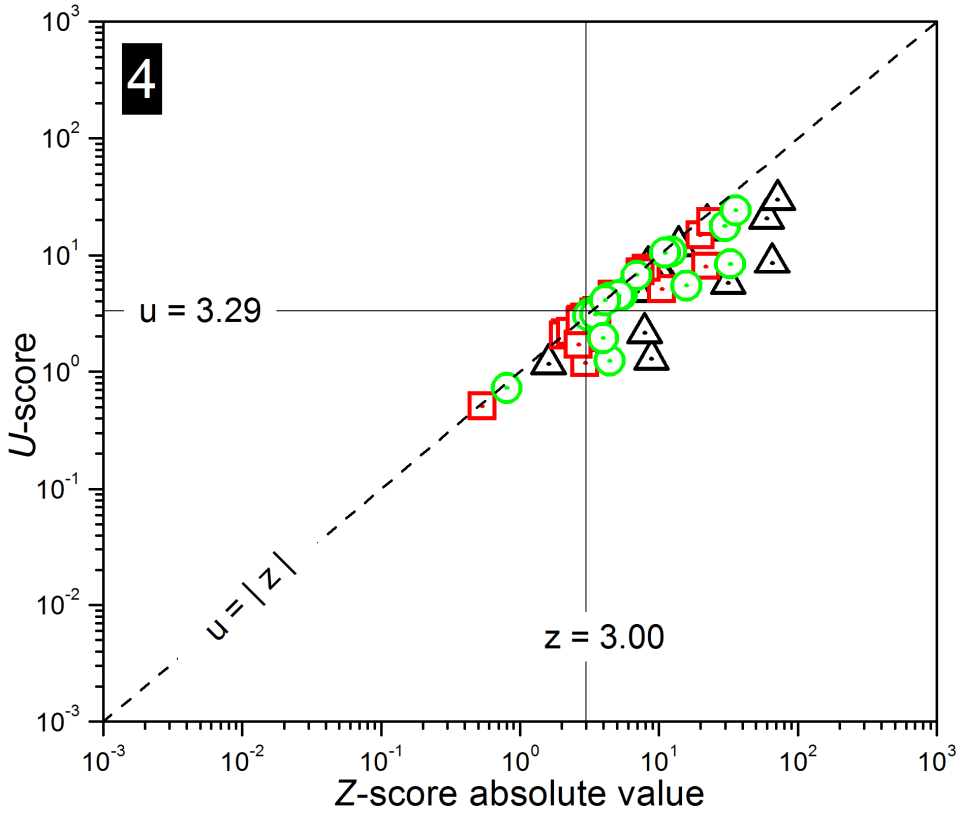

FIG. 30. Combined plots of z- and u-scores for the laboratory with code 4.

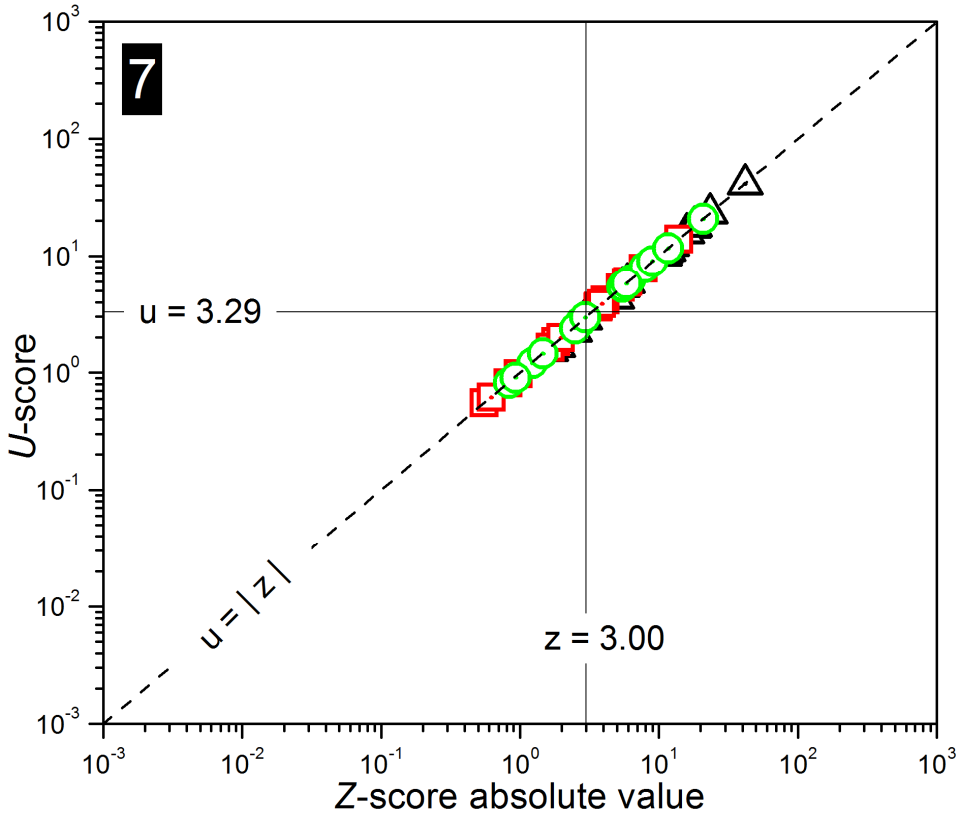

FIG. 31. Combined plots of z- and u-scores for the laboratory with code 7.

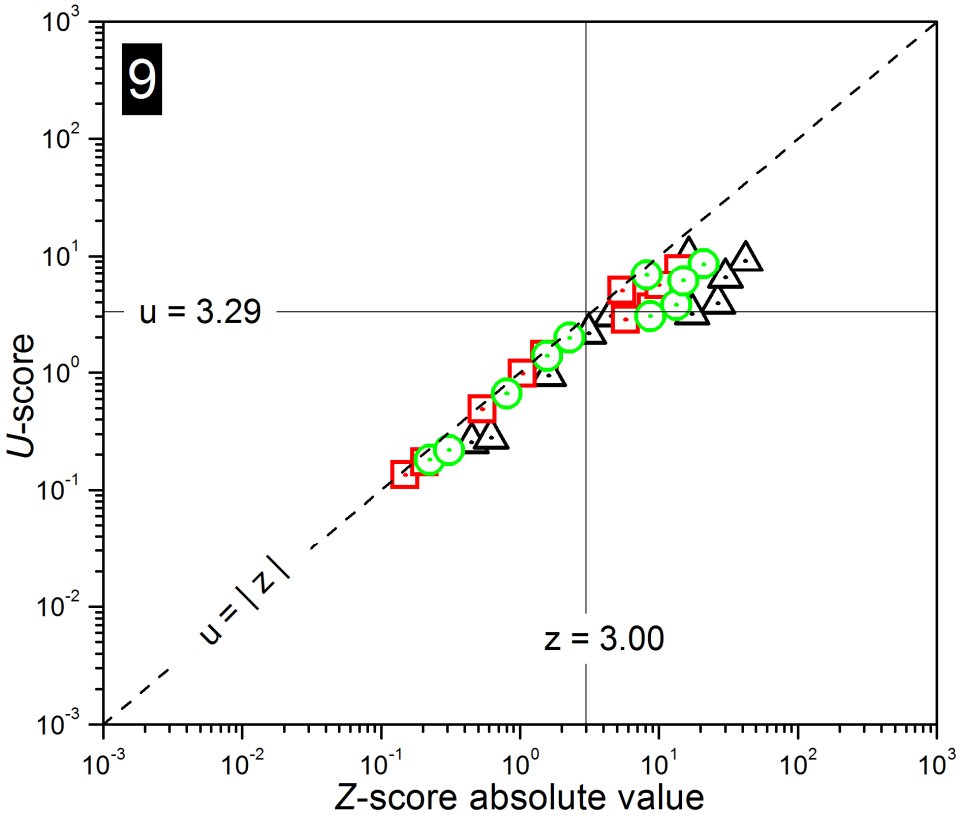

FIG. 32. Combined plots of z- and u-scores for the laboratory with code 9.

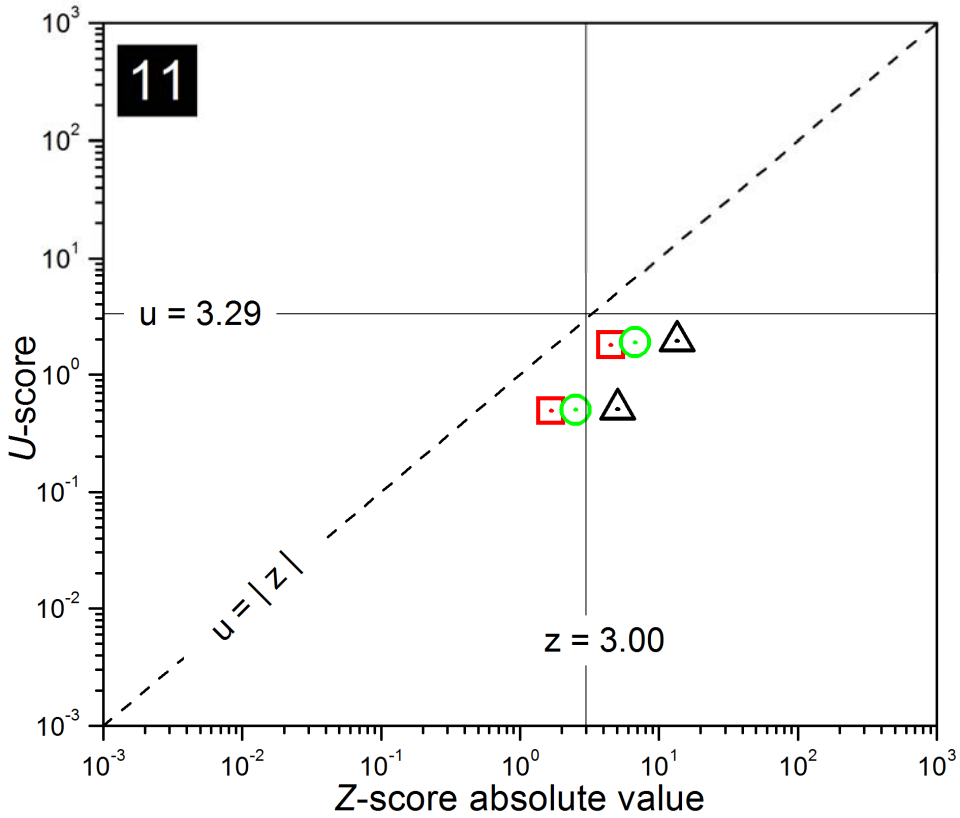

FIG. 33. Combined plots of z- and u-scores for the laboratory with code 11.

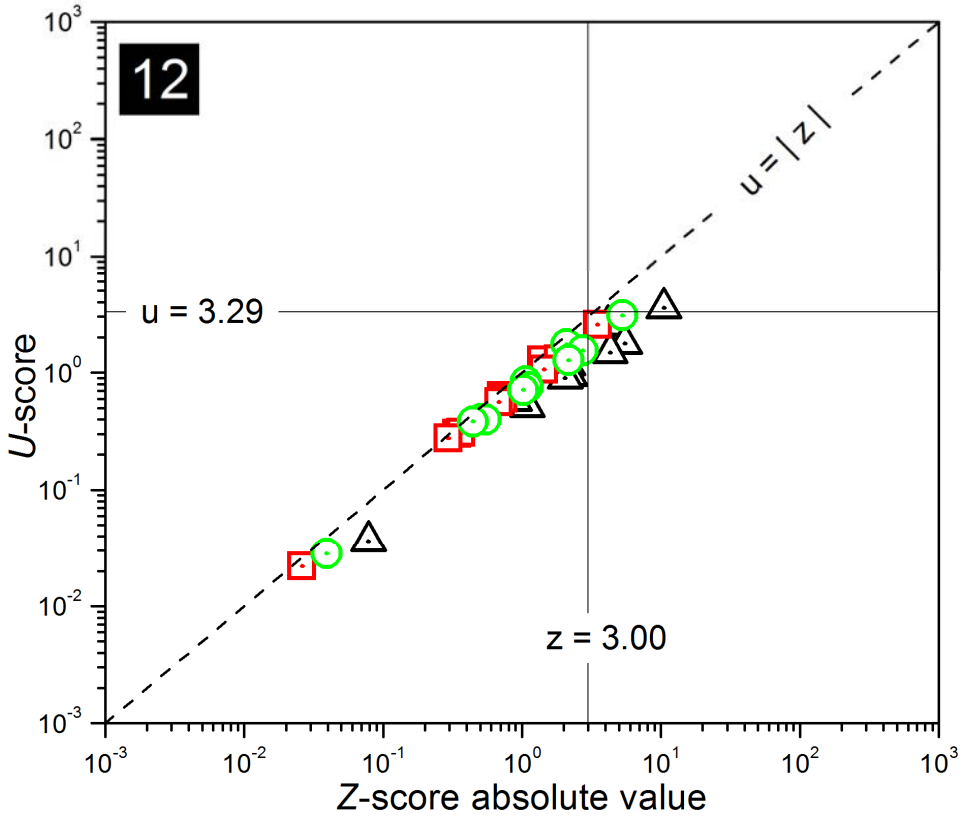

FIG. 34. Combined plots of z- and u-scores for the laboratory with code 12.

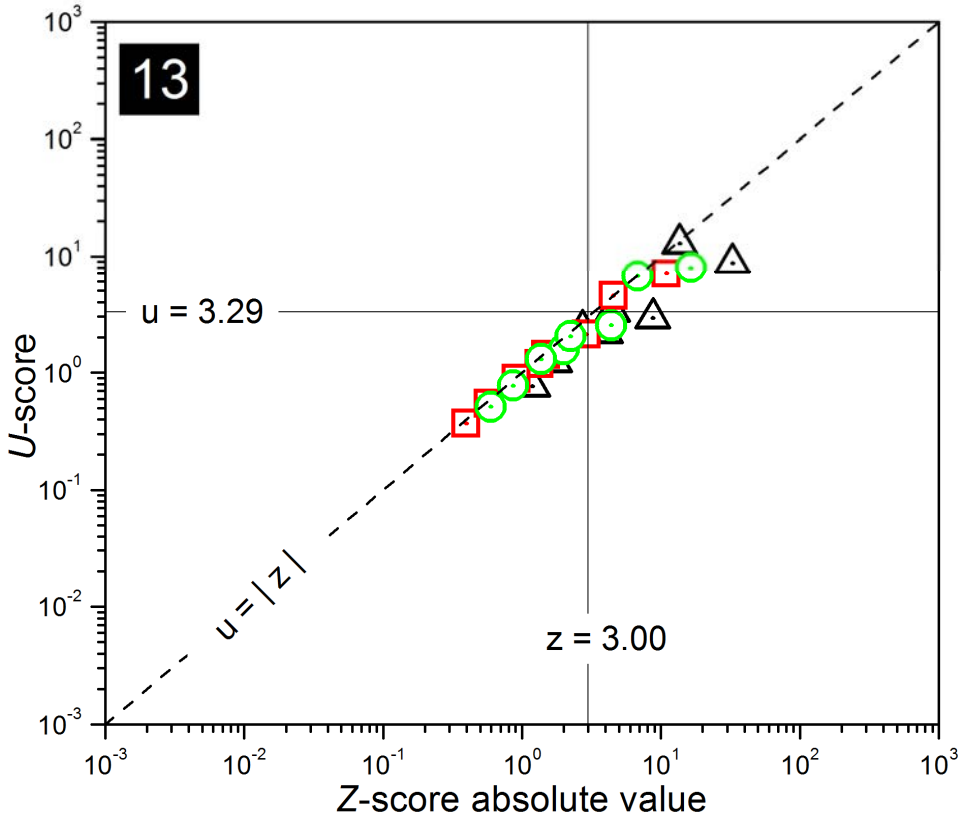

FIG. 35. Combined plots of z- and u-scores for the laboratory with code 13.

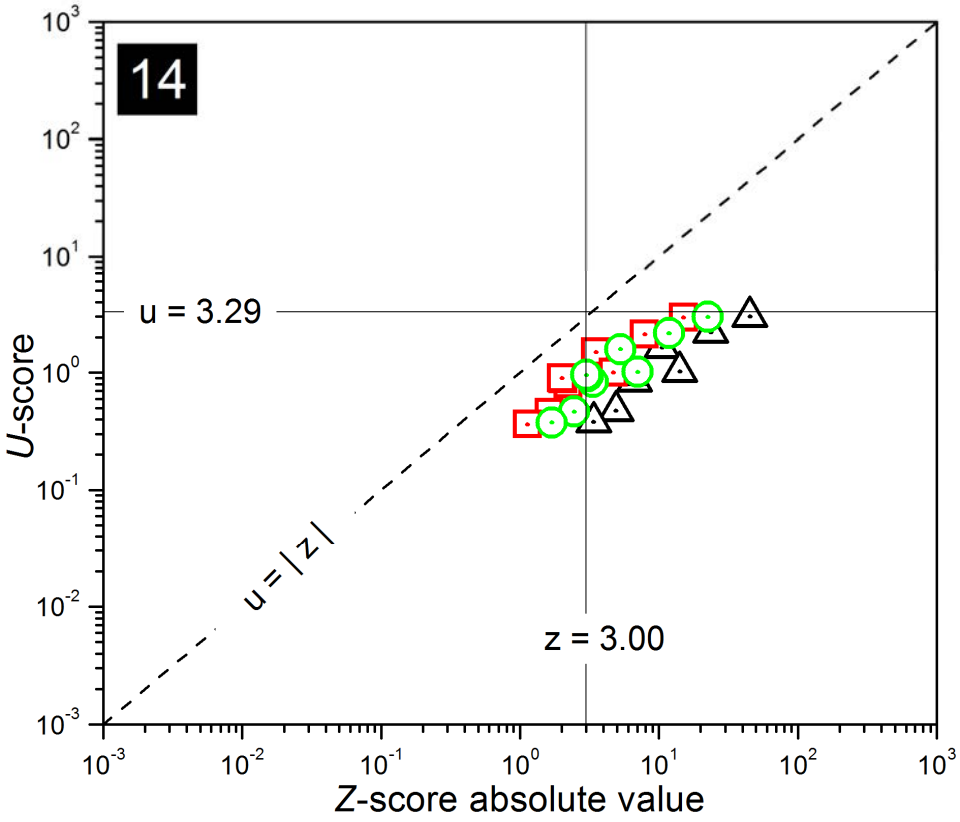

FIG. 36. Combined plots of z- and u-scores for the laboratory with code 14.

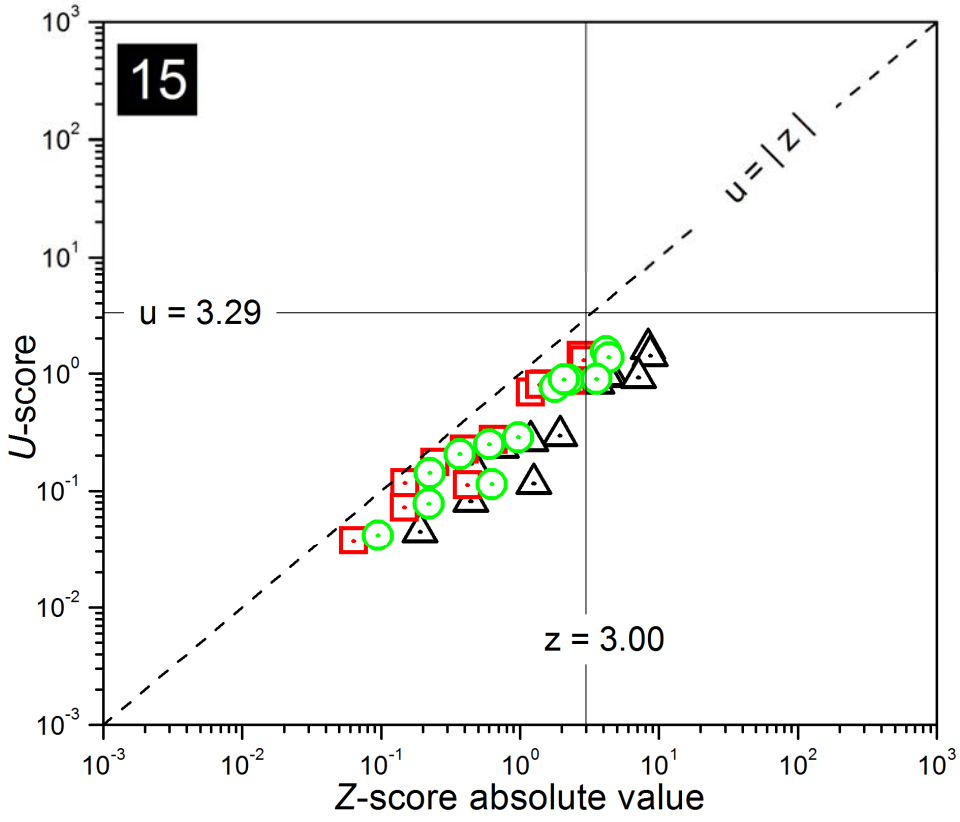

FIG. 37. Combined plots of z- and u-scores for the laboratory with code 15.

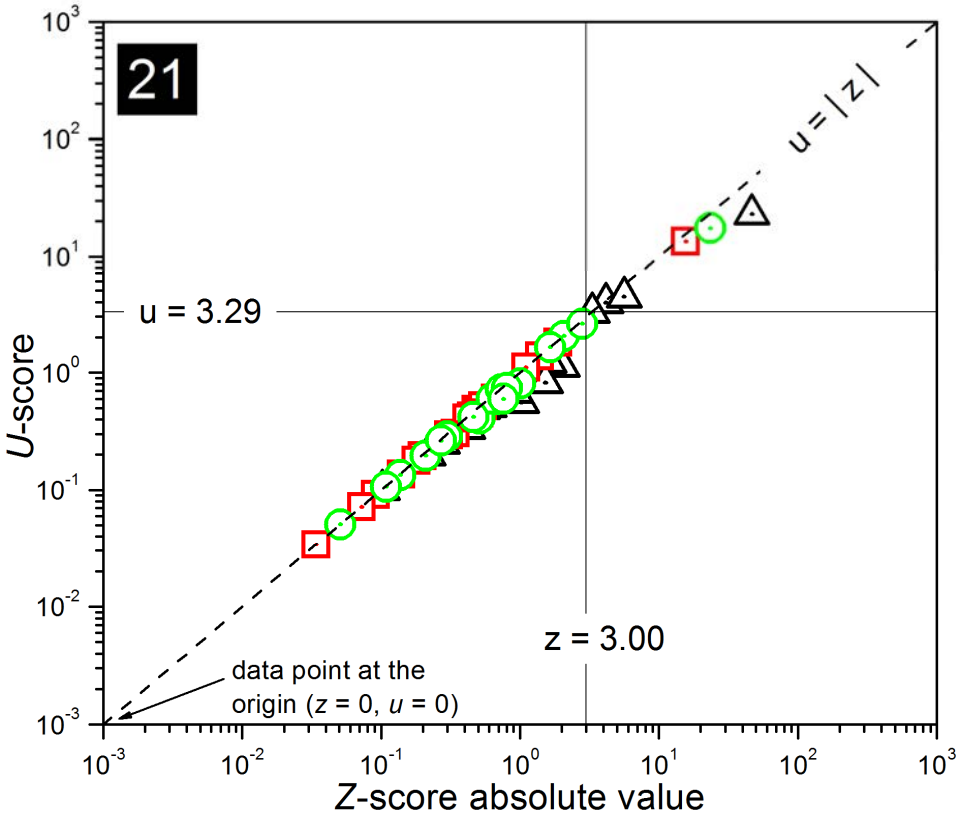

FIG. 38. Combined plots of z- and u-scores for the laboratory with code 21

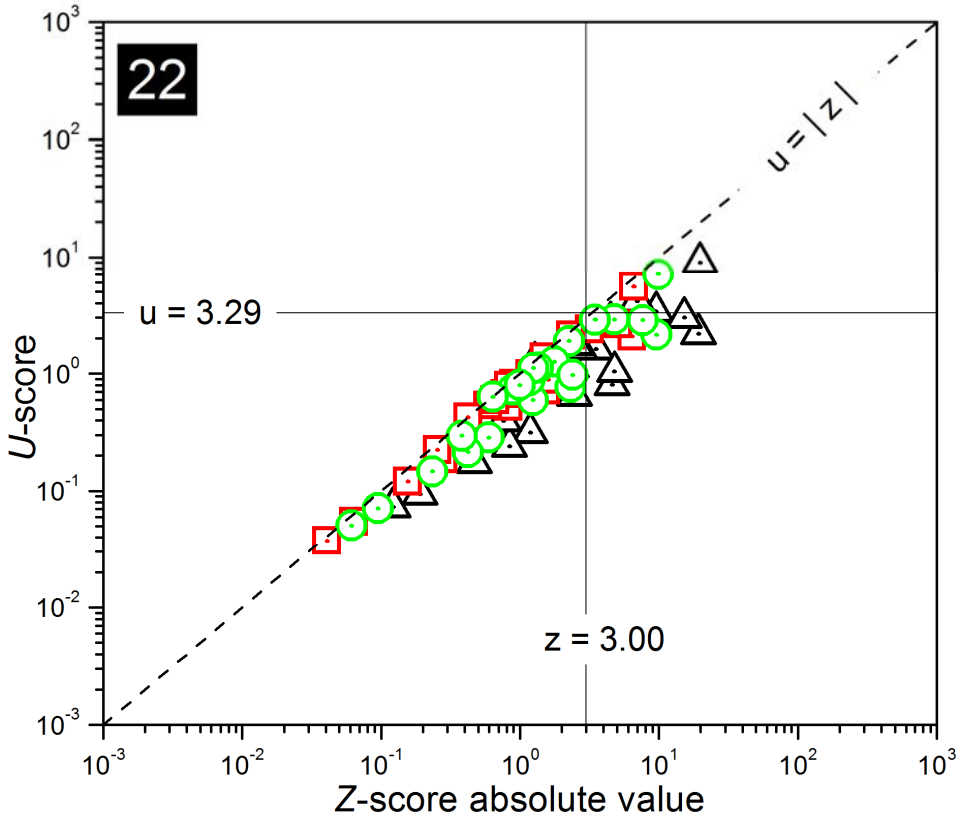

FIG. 39. Combined plots of z- and u-scores for the laboratory with code 22.

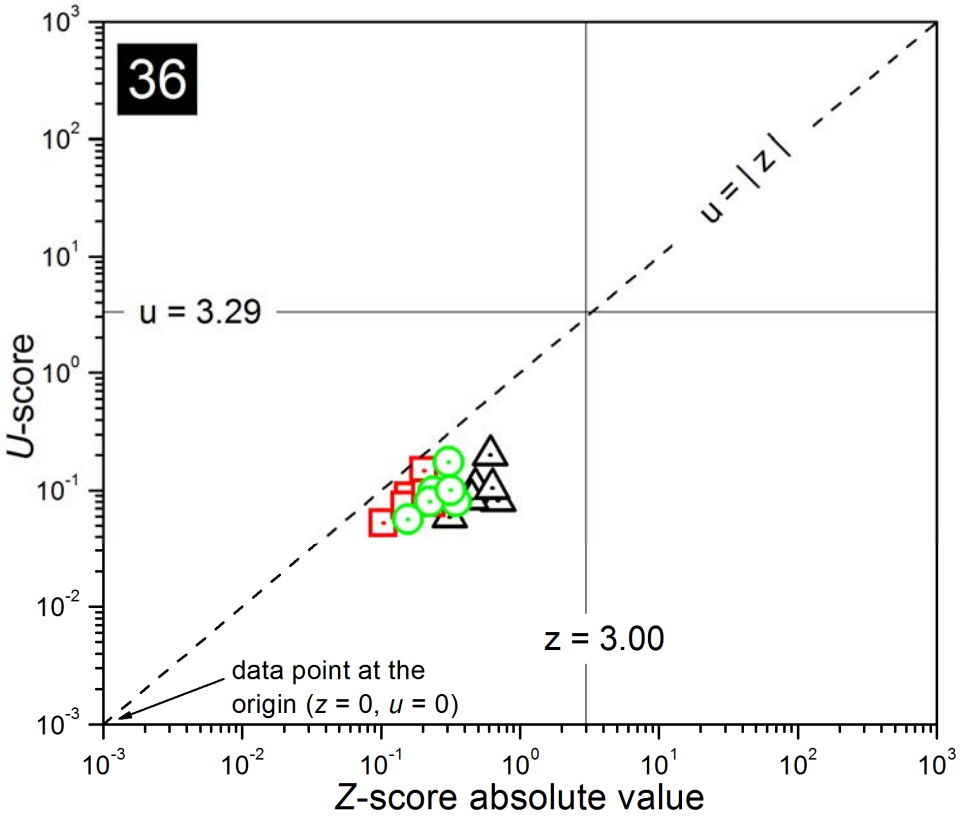

FIG. 40. Combined plots of z- and u-scores for the laboratory with code 36.

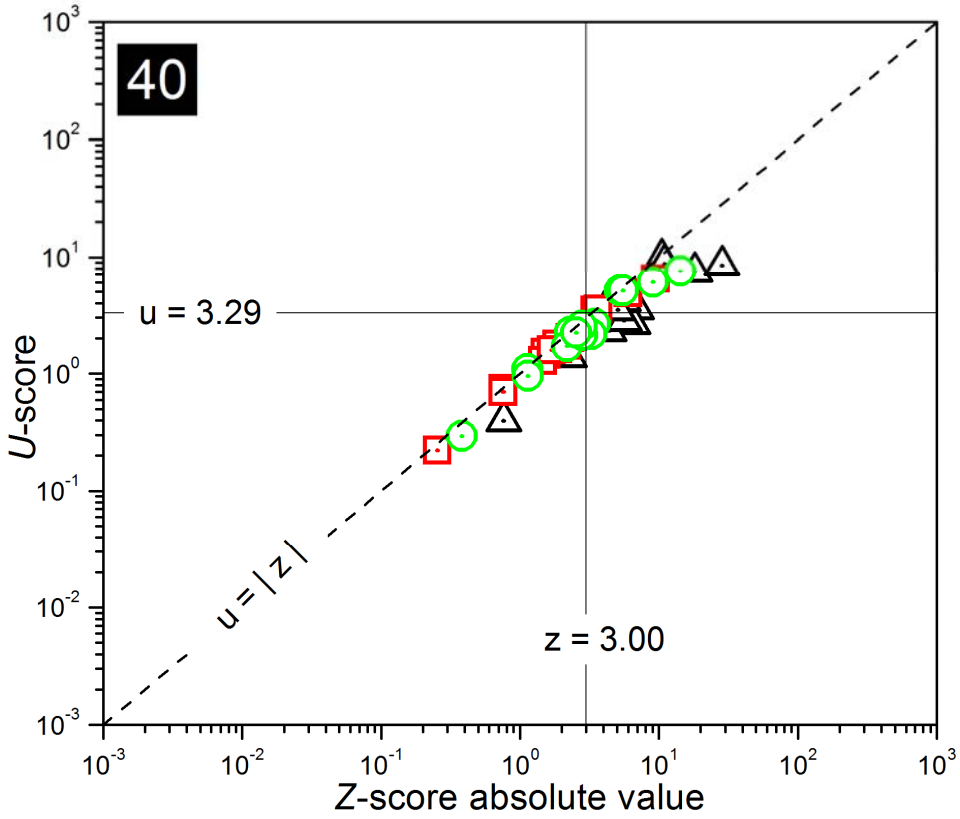

FIG. 41. Combined plots of z- and u-scores for the laboratory with code 40.

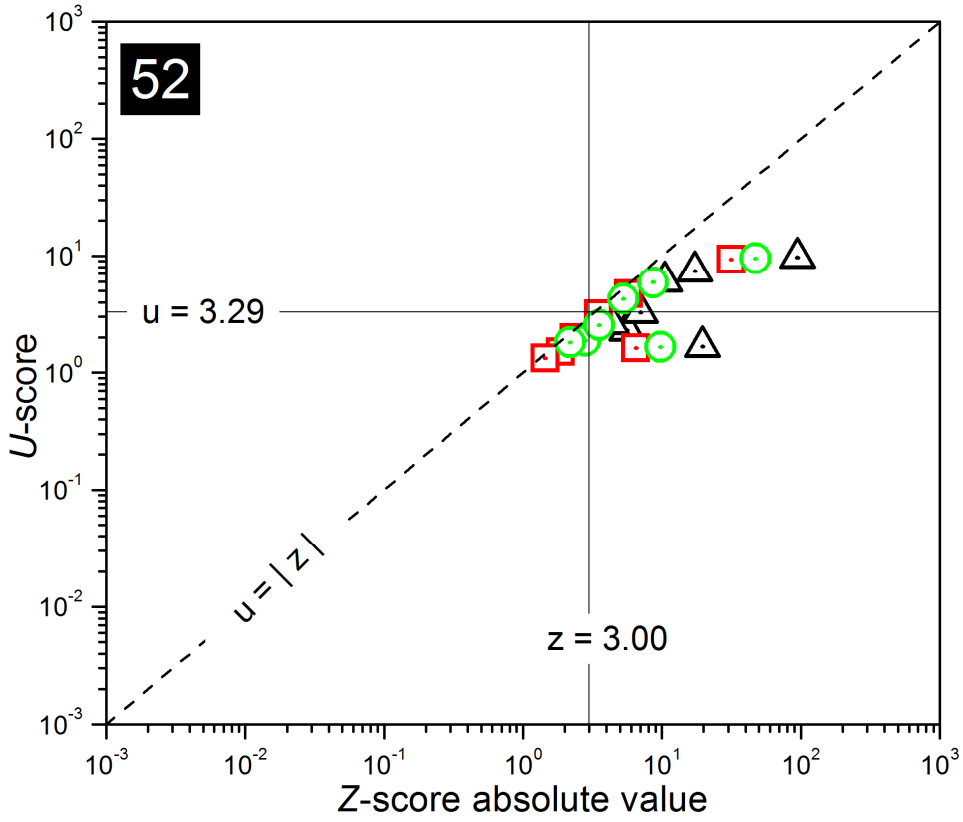

FIG. 42. Combined plots of z- and u-scores for the laboratory with code 52.

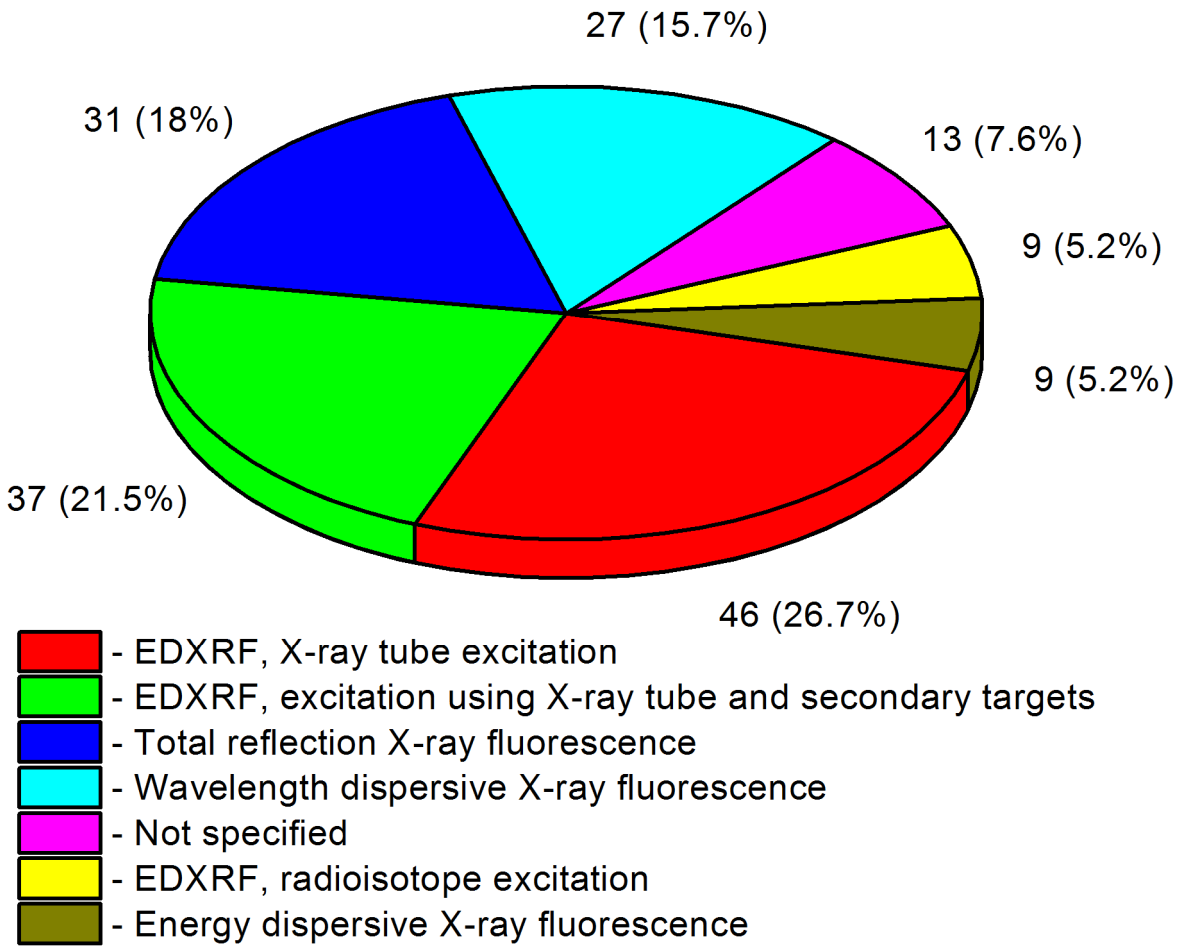

FIG. 43. Utilization of the analytical techniques. For each analytical technique the number of submitted results is shown. The percent values relate to the total number of 172 submitted results.

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GLOSSARY

The definitions of terms used in the proficiency testing schemes are provided. Although this terminology might be known to the participants or can be found elsewhere [8-10] the terms used in this report are clearly defined to avoid any ambiguity.

Proficiency testing: evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons

True value: the actual concentration of the analyte in the matrix.

Assigned value: the value of the concentration of the analyte in the matrix used as the true value by the proficiency testing coordinator in the statistical treatment of results (or the best available estimate).

Target value for standard deviation: a numerical value for the standard deviation of a measurement result, which has been designated as a target for measurement quality.

Consensus value: the mean value of the reported laboratory results after the removal of outliers.

Standard deviation of the consensus value: the standard deviation of the mean value of the reported laboratory results after the removal of outliers.

Certified Reference Material: A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

LIST OF PARTICIPATING LABORATORIES[3]

ALBANIA

Civici, N.

Institute of Nuclear Physics,
P.O.Box 85, Qesarake,
1001 Tirana,
Albania

GERMANY

Quass, U.

Institute for Energy
and Environmental Technology,
Bliersheimer Str. 60,
D-47229 Duisburg,
Germany

HUNGARY

Kocsonya, A.

Institute for Particle and Nuclear Physics,
Hungarian Academy of Sciences,
KFKI Atomic Energy Research Institute,
Konkoly-Thege Miklós út 29-33,
1121 Budapest,
Hungary

INDIA

Prasad, M.V.R.

Indira Gandhi Centre for Atomic Research,
Environment & Safety Division,
603102 Kalpakkam,
India

MADAGASCAR

Andriambololona, R.

Institut National des Sciences
et Tecniques Nucléaires,
Près Bloc Technique,
Enceinte de l'Université d'Antananarivo,
101 Antananarivo,
Madagascar

MONGOLIA

Lodoysamba, S.

Nuclear Research Center
of the National University of Mongolia,
Ikh Surguuliin 3,
P.O.Box 46/789,
210646 Ulaanbaatar,
Mongolia

[3] Only those laboratories who submitted their results were listed in the list of participating laboratories.

PERU

Olivera, P.
Instituto Peruano de Energia Nuclear,
Av.Canadá N° 1470,
Lima 41,
Peru

SLOVENIA

Kump, P.
Jozef Stefan Institute,
Jamova 39,
1000 Ljubljana,
Slovenia

SRI LANKA

Waduge, V.A.
Atomic Energy Authority,
No:60/460,
Baseline Road, Orugodawatte, Wellampitiya,
Colombo,
Sri Lanka

SYRIAN ARAB REPUBLIC

Khuder, A.
Atomic Energy Commission of Syria,
17 Nissan St. Kafer Sousah,
P.O. Box: 6091 Damascus,
Syrian Arab Republic

TURKEY

Zararsiz, A.
Saraykoy Nuclear Research
and Training Center,
Saray Mah., Atom Cad., No:27, Kazan,
6860 Ankara,
Turkey

Başsari, A.
Çekmece Nuclear Research
and Training Center,
Yarımburgaz Mah.,
Nükleer Araştırma Merkezi Yolu, No: 10,
Küçükçekmece,
34303 Istanbul,
Turkey

VENEZUELA

Greaves, E.D.
Universidad Simón Bolívar,
Laboratorio de Física Nuclear,
Valle de Sartenejas, Baruta, Edo. Miranda,
1080 Caracas,
Venezuela

LIST OF CONTRIBUTORS TO DRAFTING AND REVIEW

Karydas, A.G.	International Atomic Energy Agency
Migliori, A.	International Atomic Energy Agency
Padilla Alvarez, R.	International Atomic Energy Agency

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Suweco CZ, spol. S.r.o.
Klecakova 347, 180 21 Prague 9, CZECH REPUBLIC
Telephone: +420 242 459 202 • Fax: +420 242 459 203
Email: nakup@suweco.cz • Web site: http://www.suweco.cz

FINLAND
Akateeminen Kirjakauppa
PO Box 128 (Keskuskatu 1), 00101 Helsinki, FINLAND
Telephone: +358 9 121 41 • Fax: +358 9 121 4450
Email: akatilaus@akateeminen.com • Web site: http://www.akateeminen.com

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Telephone: +33 1 43 07 50 80 • Fax: +33 1 43 07 50 80
Email: livres@appeldulivre.fr • Web site: http://www.appeldulivre.fr

GERMANY
Goethe Buchhandlung Teubig GmbH
Schweitzer Fachinformationen
Willstätterstrasse 15, 40549 Düsseldorf, GERMANY
Telephone: +49 (0) 211 49 8740 • Fax: +49 (0) 211 49 87428
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