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Worldwide Open Proficiency Test for X Ray Fluorescence Laboratories PTXRFIAEA/06: Determination of Minor and Trace Elements in Grass Mixture

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FOREWORD

The IAEA assists its Member States laboratories to maintain their readiness by producing reference materials, by developing standardized analytical methods, and by 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 in Seibersdorf, Austria organises tests.

This summary report presents the results of the worldwide proficiency test IAEA-PTXRF-06 on the determination of minor and trace elements in a grass mixture. Methodologies, data evaluation approach, summary evaluation of each element and individual evaluation reports for each laboratory are also described. The test was carried out under IAEA Project 1.4.3.4 (D.3.03), Nuclear Spectrometry for Analytical Applications, under the Nuclear Science Programme. The main objective of this project is to enhance the capability of interested Member States in effective utilization of nuclear spectrometries and analytical services in industry, human health, agriculture, and in monitoring and evaluation of environmental pollution.

This proficiency test was designed to identify analytical problems, to support IAEA Member States laboratories to improve the quality of their analytical results, to maintain their accreditation and to provide a regular forum for discussion and technology transfer in this area. The type of sample and the concentration levels of the analytes were designed in a way to enable identification of potential analytical problems. The next proficiency test exercise is expected to be organized in 2010.

The IAEA officer responsible for this publication was R. Padilla Alvarez, of the IAEA Nuclear Spectrometry and Applications Laboratory, Seibersdorf.

EDITORIAL NOTE

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1. INTRODUCTION

The PTXRFIAEA06 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 grass mixture sample.

Grass mixture test samples with established homogeneity and well characterized known target values of the mass fractions of analytes were distributed to participating laboratories. The laboratories were requested to analyze 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 results 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 April 2009. The deadline for submission of the results was July 31, 2009. The last results were received in September 2009. 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 3.3. The obtained results as well as the description of the data evaluation procedures are presented in this report. Each laboratory was assigned a code, therefore full anonymity of the presented results is guaranteed. The link between the laboratory code and the laboratory name is known only to the organizers of the proficiency test and to the laboratory itself.

2. DESCRIPTION OF THE TEST SAMPLE

The test sample was a grass mixture material prepared and tested by an external independent laboratory. The powdered, homogenized, and dried material was distributed to 42 laboratories in sealed plastic bags, each bag containing 20 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 should be submitted. Each result should 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, which were established by independent inter-laboratory surveys, were used as the assigned values of the analytes, X_A. The results for 31 analytes were submitted by participants of this proficiency test: As, Ba, Bi, Br, Ca, Cd, Ce, Cl, Cr, Cu, Fe, Ge, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Si, Sr, Ti, V, Y, Zn, and Zr. The *z*- and *u*-scores were calculated for all the submitted results of all analytes except Ge, Sc and Y, 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 [4]:

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

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 presented in Fig. 1.

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 immediately 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 reevaluate 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.

Description of symbols:

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

1. Coefficient of kurtosis [5], 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 [5], 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 [6, 7], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

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

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 [8], 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 [5], 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 [9], 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 [10], 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) takes 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 grass mixture test sample was distributed to 42 laboratories for chemical composition analysis. Out of the 42 laboratories, 19 participated in the test submitting 237 individual results for 31 chemical elements. The list of the participating laboratories is presented in Table 1. Four analytical techniques were used by the participants. The techniques' codes are listed in Table 2. 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 participants. In the case that insufficient information was available a generic type technique EDXRF was assumed.

TABLE 1. THE LABORATORIES PARTICIPATING IN THE PROFICIENCY TEST EXERCISE

Institution	Country
Institute of Nuclear Physics, Tirana	**Albania**
Centre de Recherche Nucléaire d'Alger, Alger-Gare	**Algeria**
Departamento de Física/CCE, Universidade Estadual de Londrina	**Brazil**
Institute for Nuclear Research and Nuclear Energy, Sofia	**Bulgaria**
Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN), La Habana	**Cuba**
Nuclear Physics Laboratory, Department of Physics, University of Ioannina	**Greece**
KFKI Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences, Budapest	**Hungary**
Institut National des Sciences et Techniques Nucléaires (INSTN), Antananarivo	**Madagascar**
Centre national de l'énergie, des sciences et des techniques nucléaires (CNESTEN), Agdal	**Morocco**
Comisión Nacional de Energía Atómica, San Lorenzo	**Paraguay**
LNEG - LAQ (former INETI - LAACQ), Lisboa	**Portugal**
Institute of Physics, Belgrade	**Serbia**
VINCA Institute for Nuclear Sciences, Chemical Dynamics Laboratory 060, Belgrade	**Serbia**
Jožef Stefan Institute, Ljubljana	**Slovenia**
Atomic Energy Authority, Orugodawatte	**Sri Lanka**
Department of Physics, University of Khartoum	**Sudan**
Tanzania Atomic Energy Commission, Arusha	**United Republic of Tanzania**
Laboratorio de Tecnogestión. Ministerio de Industria Energía y Minería, Montevideo	**Uruguay**
Departamento de Física, Universidad Simón Bolívar, Caracas	**Venezuela**

TABLE 2. THE CODING, DESCRIPTION AND THE ABBREVIATED NAMES OF THE ANALYTICAL TECHNIQUES USED BY PARTICIPANTS OF THE PROFICIENCY TEST EXERCISE.

Technique Code	Description	Abbreviation
1.0	Energy dispersive X ray fluorescence spectrometry	EDXRF
1.1	Energy dispersive X ray fluorescence, radioisotope source excitation	EDXRFISO
1.2	Energy dispersive X ray fluorescence, X ray tube excitation	EDXRFTUBE
1.3	Total reflection X ray fluorescence	TXRF

All submitted results have been evaluated. In Table 3 a summary of the assigned analyte values, the target values of standard deviation, the consensus values and their standard deviations are shown. The consensus values (Eqn. 19) and corresponding standard deviations (Eqn. 20) were calculated based on 205 reported analytical results after excluding 32 results classified as outliers. The correlation between the assigned and the consensus values is shown in Fig. 2. There were 4 elements (As, Bi, Cr and Na) for which a significant disagreement was observed between the assigned and the consensus values. These elements were reported by a relatively small number of the participating laboratories (1 to 4). All of these elements, except Cr, are usually considered "difficult" to determine by X ray fluorescence technique at trace levels of concentrations.

In Table 4 the values of the *z*- and *u*-scores for all submitted results are listed. The *z*- and *u*-scores were calculated for three different fit-for-purpose ranges, as defined by Eqn. (2).

In Figs. 3 and 4 the distributions of the proficiency test results are shown. The result of density distributions shown in Fig. 3 could only be used as indicators of the trends observed in the reported data due to the limited number of results. All the populations of results, after outlier rejection, have passed a normality test (Kolmogorov-Smirnov). In Fig. 4 the bar chart distributions of the *z*-scores are presented for the analytes with at least 3 submitted results. The results are sorted in ascending order versus laboratory/technique code. 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 Fig. 5. The plots presented in this figure relate all the *u*-scores and *z*-scores calculated for a given laboratory. 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. The better 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.

The partitioning of the results between different analytical techniques is presented in Fig.6. Most of the determinations were carried out without using sample digestion (~ 75 %), whereas about 25 % of the results were obtained by TXRF.

TABLE 3. THE ASSIGNED VALUES OF ANALYTES, THE TARGET VALUES OF THE STANDARD DEVIATIONS, OBTAINED BY USING MODIFIED HOROWITZ FUNCTION, EQN. (1), AND THE CONSENSUS VALUES. THE POPULATIONS WITH AT LEAST 5 REPORTED RESULTS WERE TESTED FOR NORMALITY BY USING KOLMOGOROV-SMIRNOV TEST, ALL EXAMINED POPULATIONS PASSED THE TEST. FOR THE ELEMENTS Cl, Cs, Eu, Hf, Pr, Sm, Sr, Ta, Tb, AND Yb THE ASSIGNED AND TARGET VALUES WERE NOT AVAILABLE. THE ASSIGNED VALUES OF ELEMENTS SHOWN IN *ITALICS* SHOULD BE CONSIDERED INDICATIVE.

Analyte symbol	Assigned value of the analyte, X_A	Target value of standard deviation, σ_A			Consensus value of the analyte, X_C	Consensus value of the standard deviation, σ_C	Number of results	Number of outliers
		$k = 0.5$	$k = 1.0$	$k = 1.5$				
		[mg/kg]						
As	0.298	0.028	0.057	0.086	4.34	0.72	1	0
Ba	19.10	0.98	1.96	2.94	20.39	3.39	6	0
Bi	*0.0344*	*0.0038*	*0.0076*	*0.0113*	2.30	0.40	1	0
Br	*12.40*	*0.68*	*1.36*	*2.04*	13.14	1.85	14	1
Ca	5411	119	237	356	4843	90	25	8
Cd	*2.93*	*0.20*	*0.40*	*0.60*	3.30	1.72	3	0
Ce	-	-	-	-	1.7	0.5	1	0
Cl	6240	134	268	402	5095	73	7	2
Cr	3.70	0.24	0.49	0.73	5.79	2.55	11	3
Cu	14.70	0.78	1.57	2.35	15.0	1.5	18	1
Fe	497	16	31	47	474	48	20	1
Ge	-	-	-	-	1.3	0.3	1	0
K	37769	618	1237	1855	40020	1659	23	5
Mg	1679	44	88	132	1123	57	1	0
Mn	81.5	3.4	6.7	10.1	80.4	10.8	20	1
Mo	5.68	0.35	0.70	1.05	4.13	0.94	4	0
Na	1297	35	70	105	240	38	1	0
Ni	6.71	0.40	0.80	1.20	8.26	1.31	13	1
P	4274	97	194	291	2561	731	3	0
Pb	6.50	0.39	0.78	1.18	5.92	0.84	14	1
Rb	*6.25*	*0.38*	*0.76*	*1.14*	6.88	0.85	18	2
S	3623	84	169	253	2666	416	5	0
Sb	0.124	0.014	0.027	0.041	0.165	0.032	1	0
Sc	-	-	-	-	3.23	0.65	1	0
Si	*10700*	*212*	*424*	*635*	7953	641	2	0
Sr	7.93	0.46	0.93	1.39	10.66	1.05	19	2
Ti	*13.0*	*0.7*	*1.4*	*2.1*	28.51	10.28	4	0
V	3.08	0.21	0.42	0.62	3.19	3.69	2	0
Y	-	-	-	-	1.02	0.36	1	0
Zn	82.1	3.4	6.8	10.1	78.7	7.1	22	2
Zr	-	-	-	-	3.62	0.48	7	2

TABLE 4. SUMMARY OF THE REPORTED RESULTS AND THE CALCULATED *z*- AND *u*-SCORES. THE RESULTS REJECTED BY THE OUTLIERS REJECTION PROCEDURES WERE MARKED WITH '*' IN THE "ANALYTE CONCENTRATION" COLUMN. IN BRACKETS NEXT TO THE ELEMENT SYMBOL THE ASSIGNED VALUES OF ELEMENT CONCENTRATION AND THE TARGET STANDARD DEVIATION FOR $k = 1$ ARE SHOWN.

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 (0.298 ± 0.057) [mg/kg]										
14	1	4.34	0.719	16.57	141	70.7	47.1	5.62	5.60	5.58
Ba (19.10 ± 1.96) [mg/kg]										
39	1.1	9.6	1.9	19.79	-9.69	-4.85	-3.23	4.44	3.48	2.71
6	1.1	12.95	2.15	16.6	-6.28	-3.14	-2.09	2.60	2.11	1.69
27	1.1	17	2	11.76	-2.14	-1.07	-0.71	0.943	0.750	0.591
22	1	26.5	1.3	4.91	7.55	3.78	2.52	4.55	3.15	2.30
19	1.3	27	5	18.52	8.06	4.03	2.69	1.55	1.47	1.36
31	1.1	29.31	1.19	4.06	10.4	5.21	3.47	6.62	4.45	3.22
Bi (0.0344 ± 0.0076) [mg/kg]										
22	1	2.3	0.4	17.39	599	299	200	5.66	5.66	5.66
Br (12.4 ± 1.36) [mg/kg]										
33	1.2	4.4	0.4	9.09	-11.8	-5.89	-3.93	10.2	5.65	3.85
2	1.3	4.44	1.67	37.61	-11.7	-5.86	-3.91	4.42	3.70	3.02
27	1.1	7	2	28.57	-7.95	-3.98	-2.65	2.56E	2.23	1.89
2	1.3	9.54	0.45	4.72	-4.21	-2.11	-1.40	3.51	2.00	1.37
31	1.1	12.39	0.95	7.67	-0.015	-0.007	-0.005	0.008	0.006	0.004
15	1.2	12.5	0.8	6.4	0.147	0.074	0.049	0.095	0.064	0.046
22	1	12.9	0.6	4.65	0.736	0.368	0.246	0.552	0.337	0.236
6	1.1	13.25	2.71	20.45	1.25	0.626	0.417	0.304	0.280	0.251
45	1.2	16	0.8	5	5.30	2.65	1.77	3.43	2.28	1.65
14	1	18.9	2.69	14.23	9.57	4.79	3.19	2.34	2.16	1.93
39	1.1	21.9	6.6	30.14	14.0	7.00	4.66	1.43	1.41	1.38
9	1.2	24.5	1.2	4.9	17.8	8.91	5.94	8.78	6.68	5.12
4	1.1	105*	0	0	136	68.2	45.5	136	68.2	45.5
Ca (5411 ± 237) [g/kg]										
3	1.3	314.7*	4.6	1.47	-42.9	-21.5	-14.3	42.9	21.5	14.3
5	1.2	1709*	49	2.87	-31.2	-15.6	-10.4	28.8	15.3	10.3
6	1.1	3913*	165	4.22	-12.6	-6.31	-4.21	7.37	5.18	3.82
31	1.1	4456	225	5.05	-8.05	-4.02	-2.68	3.75	2.92	2.27
2	1.3	4539	159	3.5	-7.35	-3.67	-2.45	4.39	3.05	2.24
33	1.2	4726	353	7.47	-5.77	-2.89	-1.92	1.84	1.61	1.37
27	1.1	4770	120	2.52	-5.40	-2.70	-1.80	3.79	2.41	1.71
2	1.3	4799	84	1.75	-5.16	-2.58	-1.72	4.21	2.43	1.67
22	1	4860	296	6.09	-4.64	-2.32	-1.55	1.73	1.45	1.19
15	1.2	4970	300	6.04	-3.72	-1.86	-1.24	1.37	1.15	0.947

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
37	1.2	5199	26	0.5	-1.79	-0.893	-0.595	1.74	0.888	0.594
24	1.2	5267	738	14.01	-1.21	-0.607	-0.404	0.193	0.186	0.176
45	1.2	6578*	210	3.19	9.83	4.92	3.28	4.84	3.68	2.82
14	1	7360*	1040	14.13	16.4	8.21	5.47	1.86	1.83	1.77
9	1.2	9642*	312	3.24	35.6	17.8	11.9	12.7	10.8	8.94
46	1.2	16814*	258	1.53	96.1	48.0	32.0	40.1	32.5	25.9
4	1.1	120000*	0	0	965	482	322	965	483	322
				Cd (2.93 ± 0.40) [mg/kg]						
39	1.1	0.102	0.028	27.4	-14.2	-7.09	-4.73	14.0	7.08	4.72
19	1.3	3.8	0.3	7.89	4.36	2.18	1.45	2.41	1.74	1.30
27	1.1	6	2	33.3	15.4	7.70	5.13	1.53	1.50	1.47
				Ce [mg/kg]						
22	1	1.7	0.5	29.4	0.000	0.000	0.000	0.000	0.000	0.000
				Cl (6240 ± 268) [mg/kg]						
2	1.3	384*	78	20.3	-43.7	-21.9	-14.6	37.8	20.9	14.3
2	1.3	1705*	169	9.92	-33.8	-16.9	-11.3	21.0	14.3	10.4
6	1.1	4966	555	11.18	-9.51	-4.76	-3.17	2.23	2.07	1.86
27	1.1	5100	150	2.94	-8.51	-4.26	-2.84	5.67	3.71	2.66
22	1	5220	393	7.53	-7.61	-3.81	-2.54	2.46	2.14	1.82
				Cr (3.70 ± 0.49) [mg/kg]						
3	1.3	0.33	0.05	15.15	-13.9	-6.93	-4.62	13.6	6.89	4.61
37	1.2	1.478	0.067	4.53	-9.14	-4.57	-3.04	8.81	4.53	3.03
2	1.3	4.93	1.02	20.69	5.06	2.53	1.68	1.17	1.09	0.981
6	1.1	7.6	0.7	9.21	16.0	8.02	5.34	5.26	4.57	3.86
22	1	14.6	2.8	19.18	44.8	22.4	14.95	3.88	3.83	3.77
46	1.2	30.14*	1.47	4.9	109	54.4	36.3	17.7	17.0	16.0
2	1.3	39.12*	13	33.23	146	72.9	48.6	2.72	2.72	2.72
4	1.1	2390*	0	0	9818	4909	3273	9818	4909	3273
				Cu (14.70 ± 1.57) [mg/kg]						
3	1.3	1.7	0.03	1.76	-16.570	-8.28	-5.52	16.6	8.28	5.52
33	1.2	7	1.4	20	-9.814	-4.91	-3.27	4.79	3.66	2.81
27	1.1	9	1	11.1	-7.265	-3.63	-2.42	4.48	3.06	2.23
6	1.1	10.2	1.5	14.7	-5.736	-2.87	-1.91	2.66	2.07	1.61
5	1.2	11.8	2.4	20.3	-3.696	-1.848	-1.23	1.11	1.01	0.863
19	1.3	13	1	7.69	-2.167	-1.083	-0.722	1.34	0.914	0.665
15	1.2	13.7	2.5	18.2	-1.275	-0.637	-0.425	0.382	0.339	0.291
45	1.2	16	1	6.25	1.657	0.829	0.552	1.02	0.699	0.508
2	1.3	16.13	2.08	12.9	1.823	0.911	0.608	0.643	0.549	0.455
14	1	16.2	2.44	15.1	1.912	0.956	0.637	0.585	0.517	0.442
22	1	18.6	1.1	5.91	4.971	2.48	1.657	2.89	2.03	1.50
24	1.2	19.2	1.4	7.29	5.736	2.87	1.91	2.80	2.14	1.64
37	1.2	21.49	0.42	1.95	8.654	4.33	2.88	7.63	4.18	2.84
2	1.3	21.64	14.25	66	8.846	4.42	2.95	0.486	0.484	0.481
46	1.2	22.11	0.59	2.67	9.446	4.72	3.15	7.54	4.42	3.05

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
9	1.2	22.3	1.7	7.62	9.687	4.84	3.23	4.06	3.28	2.62
4	1.1	2800*	0	0	3550	1775	1183	3550	1775	1183
Fe (497 ± 31) [mg/kg]										
3	1.3	66.1	0.37	0.56	-27.6	-13.8	-9.19	27.6	13.8	9.19
33	1.2	179.9	9.3	5.17	-20.3	-10.1	-6.77	17.4	9.73	6.64
6	1.1	263	46	17.5	-14.9	-7.49	-4.99	4.82	4.21	3.56
27	1.1	338	10	2.96	-10.2	-5.09	-3.39	8.575	4.85	3.32
5	1.2	351.1	6.3	1.79	-9.34	-4.67	-3.11	8.66	4.56	3.09
37	1.2	408.08	3.16	0.77	-5.69	-2.85	-1.89	5.58	2.83	1.89
24	1.2	433	31	7.16	-4.09	-2.05	-1.37	1.84	1.45	1.14
39	1.1	439	62	14.1	-3.71	-1.86	-1.24	0.907	0.836	0.746
19	1.3	440	69	15.7	-3.65	-1.82	-1.22	0.806	0.753	0.684
15	1.2	475	35	7.37	-1.41	-0.704	-0.470	0.574	0.469	0.376
31	1.1	500	18	3.6	0.192	0.096	0.064	0.126	0.083	0.060
2	1.3	534	92	17.3	2.39	1.19	0.798	0.399	0.383	0.361
45	1.2	539	28	5.19	2.69	1.34	0.897	1.31	1.001	0.770
22	1	541	25	4.62	2.82	1.41	0.939	1.49	1.100	0.829
2	1.3	590	76	12.9	5.94	2.97	1.98	1.19	1.12	1.03
9	1.2	723	54	7.41	14.5	7.25	4.83	4.05	3.65	3.18
14	1	814	116	14.2	20.3	10.1	6.77	2.71	2.64	2.53
11	1.1	890	210	23.6	25.2	12.6	8.39	1.87	1.85	1.83
4	1.1	9130*	0	0	553	276	184	553	276	184
Ge [mg/kg]										
22	1	1.3	0.3	23.08	0.000	0.000	0.000	0.000	0.000	0.000
K (37769 ± 1237) [mg/kg]										
3	1.3	1893.6*	8.12	0.43	-58.0	-29.0	-19.3	58	29.0	19.3
5	1.2	9263*	74	0.8	-46.1	-23.0	-15.4	46	23.0	15.3
2	1.3	20231*	1240	6.13	-28.4	-14.2	-9.45	12.7	10.0	7.86
39	1.1	28825	3170	11	-14.5	-7.23	-4.82	2.77	2.63	2.43
6	1.1	32750	3570	10.9	-8.12	-4.06	-2.70	1.38	1.33	1.25
31	1.1	35566	1786	5.02	-3.56	-1.78	-1.19	1.17	1.01	0.856
27	1.1	35600	400	1.12	-3.51	-1.75	-1.17	2.94	1.67	1.14
37	1.2	36483	292	0.8	-2.08	-1.04	-0.693	1.88	1.01	0.685
22	1	39100	2150	5.5	2.15	1.08	0.717	0.595	0.537	0.469
45	1.2	40771	1700	4.17	4.85	2.43	1.62	1.66	1.43	1.19
2	1.3	41129	3553	8.64	5.43	2.72	1.81	0.932	0.893	0.838
15	1.2	42500	2500	5.88	7.65	3.82	2.55	1.84	1.69	1.52
33	1.2	46250	3606	7.8	13.7	6.86	4.57	2.32	2.22	2.09
9	1.2	46483	3200	6.88	14.09	7.04	4.69	2.67	2.54	2.36
14	1	46700	6600	14.1	14.4	7.22	4.81	1.35	1.33	1.30
24	1.2	48104	3860	8.02	16.7	8.34	5.57	2.64	2.55	2.41
46	1.2	127202*	479	0.38	145	72	48.2	114	67.4	46.7
4	1.1	244000*	0	0	333	167	111	333	167	111
Mg (1679 ± 88) [mg/kg]										
37	1.2	1123	57	5.08	-12.67	-6.33	-4.22	7.73	5.31	3.87

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Mn (81.5 ± 6.7) [mg/kg]										
6	1.1	2.8	0.3	10.7	-23.4	-11.7	-7.80	23.3	11.7	7.80
3	1.3	8.61	0.14	1.63	-21.6	-10.8	-7.23	21.7	10.8	7.23
33	1.2	32.6	0.2	0.61	-14.5	-7.27	-4.85	14.5	7.27	4.85
5	1.2	46.3	0.4	0.86	-10.5	-5.24	-3.49	10.4	5.23	3.49
19	1.3	66	7	10.6	-4.61	-2.31	-1.54	1.99	1.59	1.26
37	1.2	70.9	1.4	1.97	-3.15	-1.58	-1.05	2.91	1.54	1.04
39	1.1	71	15	21.1	-3.12	-1.56	-1.04	0.683	0.639	0.581
2	1.3	72.85	1.01	1.39	-2.57	-1.29	-0.858	2.46	1.27	0.854
24	1.2	79.9	19.7	24.7	-0.476	-0.238	-0.159	0.080	0.077	0.072
27	1.1	82	6	7.32	0.149	0.074	0.050	0.073	0.055	0.043
45	1.2	83.5	3	3.59	0.595	0.298	0.198	0.444	0.272	0.190
31	1.1	83.8	13.5	16.1	0.684	0.342	0.228	0.165	0.153	0.137
22	1	85.1	5.4	6.35	1.07	0.536	0.357	0.566	0.418	0.315
2	1.3	88.4	13.7	15.5	2.04	1.02	0.681	0.487	0.450	0.404
15	1.2	91.5	9	9.84	2.97	1.49	0.992	1.04	0.890	0.740
9	1.2	142.2	8.7	6.12	18.1	9.03	6.02	6.50	5.52	4.56
14	1	154	22	14.3	21.6	10.8	7.19	3.24	3.14	2.98
46	1.2	185.9	5.8	3.16	31.1	15.5	10.3	15.4	11.7	8.94
4	1.1	1320*	0	0	368	184	123	368	184	123
Mo (5.68 ± 0.70) [mg/kg]										
6	1.1	2.54	0.35	13.8	-8.98	-4.48	-2.99	6.34	4.01	2.84
31	1.1	2.79	0.24	8.6	-8.26	-4.13	-2.75	6.81	3.90	2.68
22	1	4.6	0.2	4.3	-3.08	-1.54	-1.03	2.68	1.48	1.01
19	1.3	6.6	0.5	7.6	2.63	1.31	0.877	1.51	1.07	0.791
Na (1297 ± 70) [mg/kg]										
37	1.2	239.8	38.2	15.9	-29.9	-14.9	-9.99	20.3	13.2	9.39
Ni (6.71 ± 0.80) [mg/kg]										
3	1.3	0.75	0.04	5.33	-14.8	-7.39	-4.93	14.7	7.39	4.93
5	1.2	4.7	0.2	4.26	-4.98	-2.49	-1.66	4.47	2.42	1.64
37	1.2	5.487	0.233	4.25	-3.03	-1.52	-1.01	2.63	1.46	0.993
19	1.3	5.7	0.8	14.0	-2.51	-1.25	-0.835	1.13	0.889	0.697
22	1	6.4	1	15.6	-0.769	-0.385	-0.256	0.288	0.241	0.198
6	1.1	7.2	0.8	11.1	1.22	0.608	0.405	0.547	0.432	0.338
2	1.3	8.38	0.62	7.4	4.14	2.07	1.38	2.26	1.64	1.23
2	1.3	10.54	3.92	37.2	9.50	4.75	3.17	0.972	0.957	0.934
14	1	13	2.14	16.5	15.6	7.80	5.20	2.88	2.75	2.56
9	1.2	14.1	1.4	9.93	18.3	9.17	6.11	5.07	4.57	3.99
46	1.2	14.561	0.477	3.28	19.5	9.74	6.49	12.6	8.38	6.04
33	1.2	27.8*	1.6	5.76	52	26	17.4	12.8	11.8	10.5
P (4274 ± 194) [mg/kg]										
2	1.3	1198	176	14.7	-32	-15.8	-10.5	15.3	11.7	9.03
2	1.3	2786	734	26.4	-15.3	-7.6	-5.11	2.01	1.96	1.88
27	1.1	3700	330	8.92	-5.9	-2.95	-1.97	1.67	1.49	1.30

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
Pb (6.50 ± 0.78) [mg/kg]										
3	1.3	1	0.02	2	-14.0	-7.01	-4.67	14.0	7.01	4.67
6	1.1	1.84	0.33	17.9	-11.9	-5.94	-3.96	9.09	5.47	3.81
2	1.3	4.57	5.19	114	-4.92	-2.46	-1.64	0.371	0.368	0.363
14	1	4.74	0.89	18.7	-4.49	-2.24	-1.49	1.82	1.49	1.19
27	1.1	5	5	100	-3.82	-1.91	-1.27	0.299	0.296	0.292
39	1.1	5.4	1.1	20.4	-2.80	-1.40	-0.935	0.942	0.814	0.683
9	1.2	5.9	0.3	5.08	-1.53	-0.765	-0.510	1.21	0.714	0.494
19	1.3	6.5	0.8	12.3	0.000	0.000	0.000	0.000	0.000	0.000
33	1.2	6.7	0.3	4.48	0.510	0.255	0.170	0.405	0.238	0.165
22	1	8.4	0.5	5.95	4.84	2.42	1.61	2.99	2.04	1.49
2	1.3	10.4	2.7	25.9	10.0	5.02	3.34	1.44	1.40	1.34
15	1.2	10.5	2.5	23.8	10.2	5.09	3.39	1.58	1.53	1.45
4	1.1	473*	0	0	1189	595	396	1189	595	396
Rb (6.25 ± 0.76) [mg/kg]										
33	1.2	1.7	0.4	23.5	-11.9	-5.99	-3.99	8.25	5.30	3.77
39	1.1	2.75	0.8	29.1	-9.22	-4.61	-3.07	3.95	3.17	2.52
27	1.1	3	1	33.3	-8.57	-4.28	-2.85	3.04	2.59	2.14
2	1.3	5.83	0.51	8.75	-1.11	-0.554	-0.369	0.661	0.459	0.337
31	1.1	5.89	0.79	13.4	-0.949	-0.474	-0.316	0.411	0.329	0.260
45	1.2	6.3	0.5	7.94	0.132	0.066	0.044	0.080	0.055	0.040
22	1	6.5	0.3	4.62	0.659	0.330	0.220	0.517	0.306	0.212
2	1.3	7.12	1.23	17.3	2.29	1.15	0.764	0.676	0.602	0.519
19	1.3	7.2	0.8	11.1	2.50	1.25	0.835	1.07	0.862	0.683
6	1.1	7.74	0.86	11.1	3.93	1.96	1.31	1.58	1.29	1.04
15	1.2	8	0.5	6.25	4.61	2.31	1.54	2.78	1.93	1.41
3	1.3	9.9	0.16	1.62	9.62	4.81	3.21	8.86	4.71	3.18
9	1.2	11	0.7	6.36	12.5	6.26	4.17	5.96	4.60	3.55
14	1	13.4	1.92	14.3	18.8	9.42	6.28	3.65	3.46	3.20
46	1.2	17.862*	0.191	1.07	30.6	15.3	10.2	27.3	14.8	10.0
4	1.1	95.000*	0	0	234	117	78	234	117	78
S (3623 ± 169) [mg/kg]										
2	1.3	1326	142	10.7	-27	-13.6	-9.07	13.9	10.4	7.91
22	1	2170	347	15.9	-17	-8.61	-5.74	4.07	3.76	3.38
6	1.1	2978	263	8.8	-7.64	-3.82	-2.55	2.33	2.06	1.77
2	1.3	3135	807	25.7	-5.78	-2.89	-1.93	0.602	0.592	0.577
27	1.1	3720	150	4.03	1.15	0.575	0.383	0.564	0.430	0.330
Sb (0.124 ± 0.027) [mg/kg]										
39	1.1	0.165	0.032	19.4	3.02	1.51	1.01	1.18	0.977	0.792
Sc [mg/kg]										
3	1.3	3.23	0.65	20.1	0.000	0.000	0.000	0.000	0.000	0.000
Si (10700 ± 424) [mg/kg]										
27	1.1	7500	400	5.3	-15.1	-7.55	-5.04	7.07	5.49	4.26

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
6	1.1	8407	1556	18.5	-10.8	-5.41	-3.61	1.46	1.42	1.36
Sr (7.93 ± 0.93) [mg/kg]										
33	1.2	2.85	0.1	3.51	-10.9	-5.47	-3.65	10.7	5.44	3.64
27	1.1	5	2	40	-6.31	-3.15	-2.10	1.43	1.33	1.20
6	1.1	7.91	0.74	9.36	-0.043	-0.022	-0.014	0.023	0.017	0.013
45	1.2	9	0.5	5.56	2.30	1.15	0.768	1.57	1.01	0.723
22	1	9.2	0.43	4.67	2.73	1.37	0.912	2.01	1.24	0.871
37	1.2	9.61	0.12	1.25	3.62	1.81	1.21	3.50	1.79	1.20
19	1.3	10	1	10	4.45	2.23	1.49	1.88	1.52	1.21
31	1.1	10.54	1.36	12.9	5.62	2.81	1.87	1.82	1.58	1.34
2	1.3	10.71	3.4	31.7	5.99	2.99	1.99	0.810	0.789	0.757
2	1.3	10.93	0.72	6.59	6.46	3.23	2.15	3.50	2.55	1.91
15	1.2	12	0.6	5	8.76	4.38	2.92	5.36	3.68	2.68
14	1	12	1.73	14.4	8.76	4.38	2.92	2.27	2.07	1.83
9	1.2	14.1	1.1	7.8	13.3	6.64	4.43	5.17	4.29	3.48
39	1.1	17.9	4.4	24.6	21.5	10.7	7.16	2.25	2.22	2.16
3	1.3	18.23	0.28	1.54	22.2	11.1	7.39	18.9	10.6	7.25
46	1.2	26.074*	0.182	0.7	39.1	19.5	13.0	36.4	19.2	12.9
4	1.1	110*	0	0	220	110	73	220	110	73
Ti (13.0 ± 1.4) [mg/kg]										
3	1.3	6.2	0.2	3.24	-9.66	-4.83	-3.22	9.29	4.78	3.21
22	1	17.6	7.5	42.6	6.51	3.25	2.17	0.611	0.603	0.590
2	1.3	38	11	28.8	36	17.8	11.9	2.28	2.27	2.25
2	1.3	52.1	25.8	49.6	55	27.6	18.4	1.51	1.51	1.51
V (3.08 ± 0.42) [mg/kg]										
3	1.3	0.58	0.16	27.6	-12.0	-6.01	-4.01	9.53	5.61	3.88
2	1.3	5.8	2.8	48.6	13.1	6.54	4.36	0.962	0.954	0.942
Y [mg/kg]										
14	1	1.02	0.36	35.7	0.000	0.000	0.000	0.000	0.000	0.000
Zn (82.1 ± 3.4) [mg/kg]										
3	1.3	8.8	0.05	0.57	-21.7	-10.8	-7.22	21.7	10.8	7.22
33	1.2	22.7	0.6	2.64	-17.6	-8.78	-5.85	17.3	8.75	5.84
6	1.1	50.4	5.2	10.3	-9.37	-4.69	-3.12	5.11	3.72	2.78
31	1.1	66	6	9.09	-4.76	-2.38	-1.59	2.34	1.78	1.37
39	1.1	72	15	20.8	-2.98	-1.49	-0.995	0.657	0.614	0.558
5	1.2	74.1	1.4	1.89	-2.36	-1.18	-0.788	2.18	1.16	0.781
15	1.2	75.3	3.5	4.65	-2.01	-1.00	-0.670	1.39	0.893	0.634
37	1.2	76.7	0.68	0.89	-1.59	-0.798	-0.532	1.56	0.794	0.531
19	1.3	80	3	3.75	-0.621	-0.310	-0.207	0.465	0.284	0.199
24	1.2	81.7	3.7	4.53	-0.118	-0.059	-0.039	0.080	0.052	0.037
22	1	83.2	3.8	4.57	0.325	0.163	0.108	0.216	0.142	0.102
27	1.1	85	4	4.71	0.857	0.429	0.286	0.554	0.369	0.266
45	1.2	93.7	3.2	3.42	3.43	1.71	1.14	2.49	1.55	1.09
2	1.3	93.93	6.75	7.19	3.49	1.75	1.17	1.57	1.24	0.971

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
2	1.3	96.39	44.28	45.9	4.22	2.11	1.41	0.322	0.319	0.315
14	1	106	15	14.1	7.07	3.53	2.35	1.55	1.45	1.32
9	1.2	113.8	5.8	5.1	9.37	4.69	3.12	4.72	3.56	2.71
46	1.2	137.2	1.9	1.39	16.3	8.15	5.43	14.2	7.84	5.34
11	1.1	180*	50	27.8	28.9	14.5	9.65	1.95	1.94	1.92
4	1.1	853*	0	0	228	114	76	228	114	76
				Zr [mg/kg]						
22	1	2.8	0.2	7.14	0.000	0.000	0.000	0.000	0.000	0.000
2	1.3	3.6	2.38	66.1	0.000	0.000	0.000	0.000	0.000	0.000
31	1.1	4.45	0.44	9.89	0.000	0.000	0.000	0.000	0.000	0.000
6	1.1	7.27*	0.58	7.98	0.000	0.000	0.000	0.000	0.000	0.000
4	1.1	108*	0	0	0.000	0.000	0.000	0.000	0.000	0.000

TABLE 5. THE COMBINED *Z*-SCORES FOR THE PARTICIPATING LABORATORIES. THE ANALYTES WITHOUT ASSIGNED VALUES (Ce, Ge, Sc, Y and Zr) WERE NOT CONSIDERED

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
2	33	18.2	9.10	6.07	32380	8095	3598	50.72
3	13	-61.3	-30.6	-20.4	8615	2154	957	24.74
4	11	5305	2653	1768	112100000	28020000	12450000	21.92
5	7	-40.9	-20.4	-13.6	3339	834	371	16.01
6	17	-25.9	-12.9	-8.65	1922	480	213	30.19
9	11	48.8	24.4	16.26	3177	794	353	21.92
11	2	38.3	19.1	12.75	1471	368	163	7.38
14	12	78.3	39.2	26.1	22170	5543	2464	23.34
15	10	8.20	4.10	2.73	291	72.7	32.32	20.48
19	11	2.55	1.28	0.85	163	40.8	18.11	21.92
22	18	152	75.9	50.6	361000	90260	40120	31.53
24	6	6.75	3.38	2.25	331	82.7	36.7	14.45
27	16	-16.8	-8.39	-5.59	968	242	107.6	28.85
31	10	-2.75	-1.37	-0.91	310	77.5	34.43	20.48
33	11	-10.9	-5.45	-3.63	4391	1098	487.9	21.92
37	11	-17.1	-8.57	-5.71	1292	323	143.5	21.92
39	11	-6.55	-3.27	-2.18	1296	324	143.9	21.92
45	9	10.3	5.13	3.42	176	43.9	19.5	19.02
46	9	165	82.6	55.0	46140	11540	5127	19.02

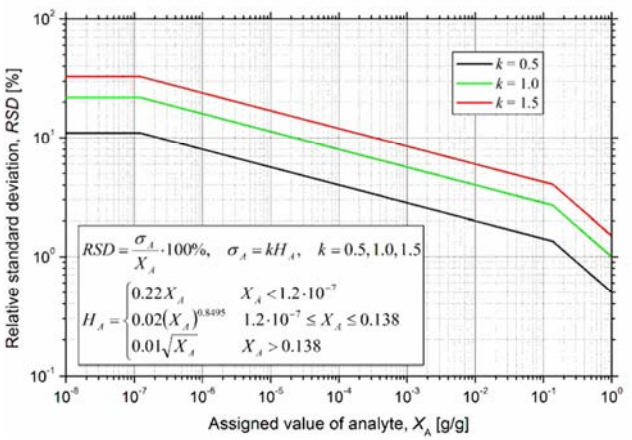


Fig. 1. Relative value of the target standard deviation, RSD, as a function of the assigned mass fraction of the analyte, X_A, calculated by using a modified Horowitz function, Eqn. (3). The target value, σ_A, is related to H_A by a factor k and it is recognized as fit-for-purpose in three levels of uncertainty: ***k = 0.5 - solid black line****, appropriate for high precision analysis;* ***k = 1.0 - solid green line****, appropriate for well established routine analysis;* ***k = 1.5 - solid red line****, satisfactory for common analytical tasks.*

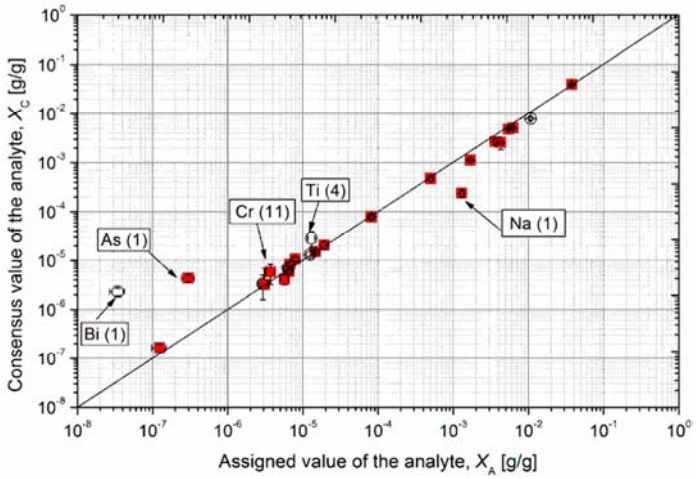
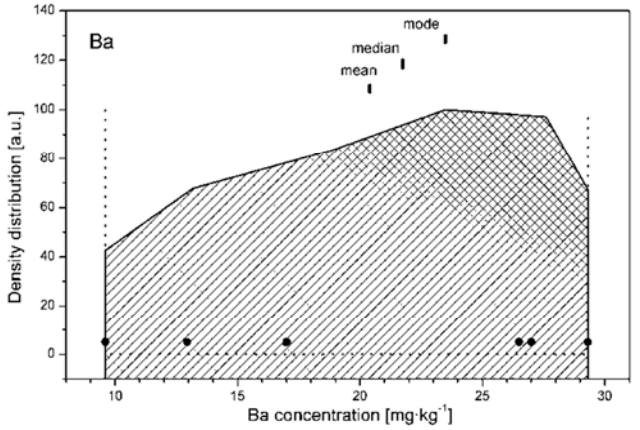
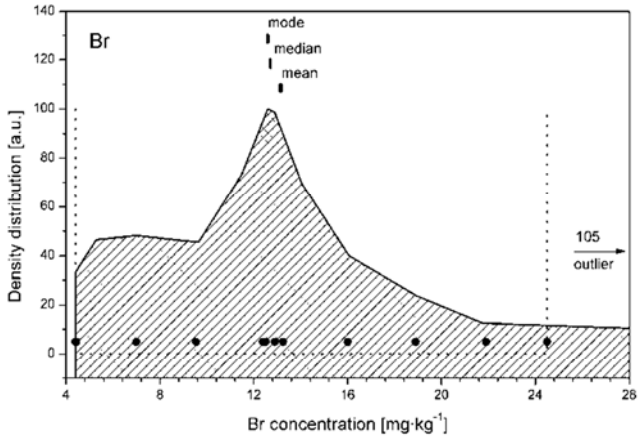
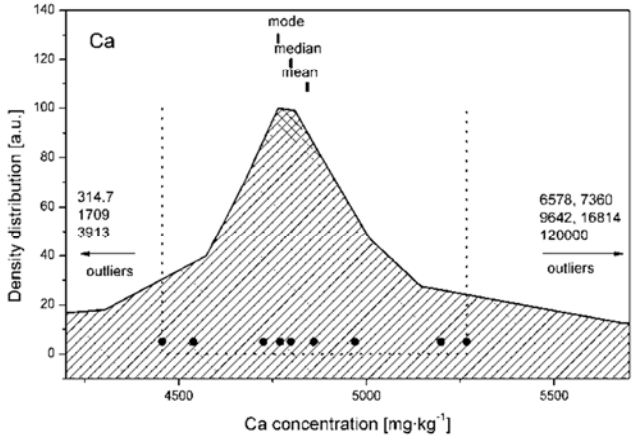
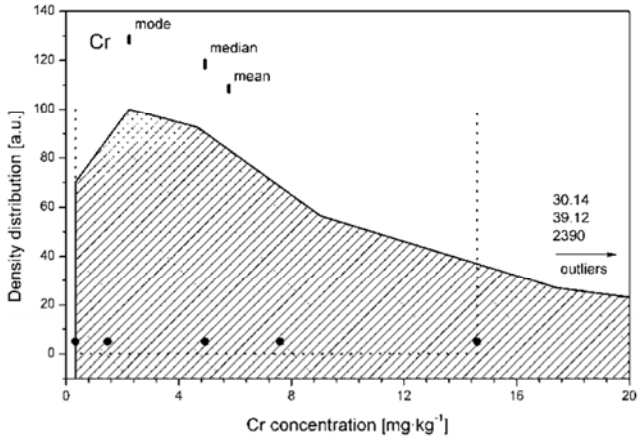


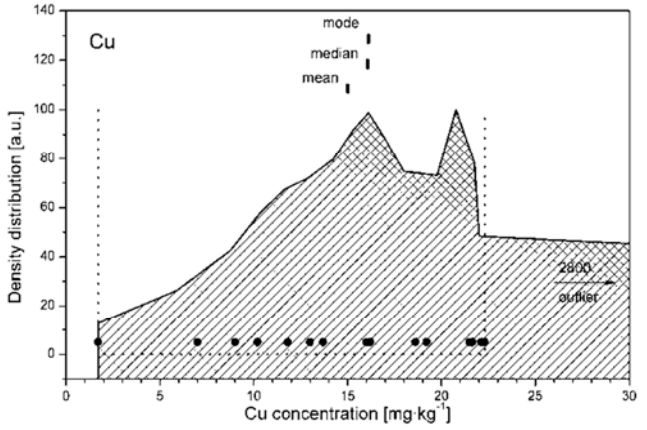
Fig. 2. Correlation between assigned, X_A, and consensus values of analytes, X_C. Solid red squares correspond to the elements the assigned values of which were known with high degree of accuracy. Hollow black circles correspond to the elements the assigned values of which can be considered as indicative/informative only. The analytes for which a significant disagreement was observed between the assigned and consensus values are indicated by arrows. In the brackets next to the element symbol the number of reported results is given. 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 single laboratory, in such a case the laboratory estimate of the uncertainty is shown in the plot.

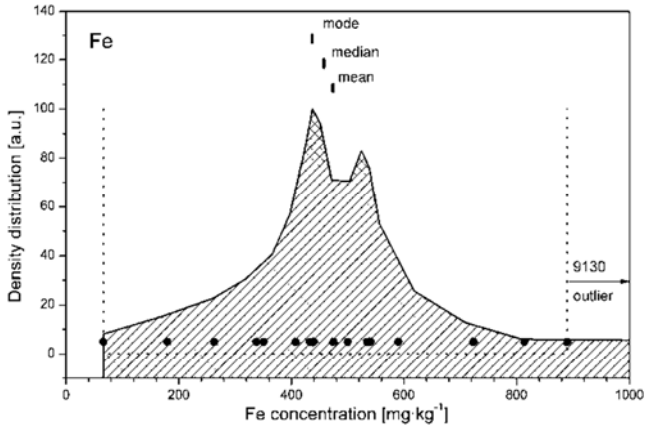

Ba
mode
median
mean
Density distribution [a.u.]
Ba concentration [mg·kg^{-1}]

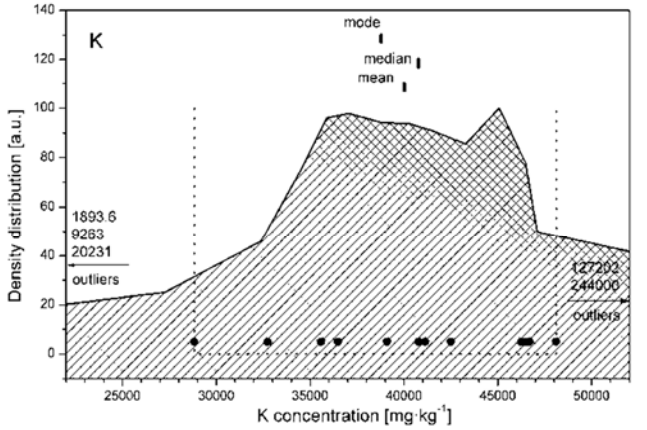

Br
mode
median
mean
105
outlier
Density distribution [a.u.]
Br concentration [mg·kg^{-1}]

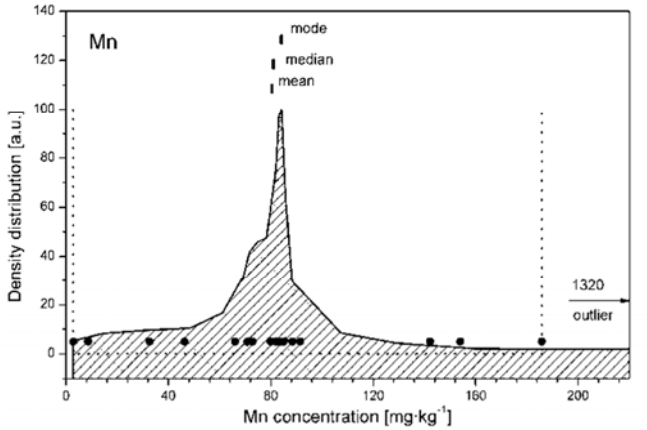

Ca
mode
median
mean
314.7
1709
3913
outliers
6578, 7360
9642, 16814
120000
outliers
Density distribution [a.u.]
Ca concentration [mg·kg^{-1}]

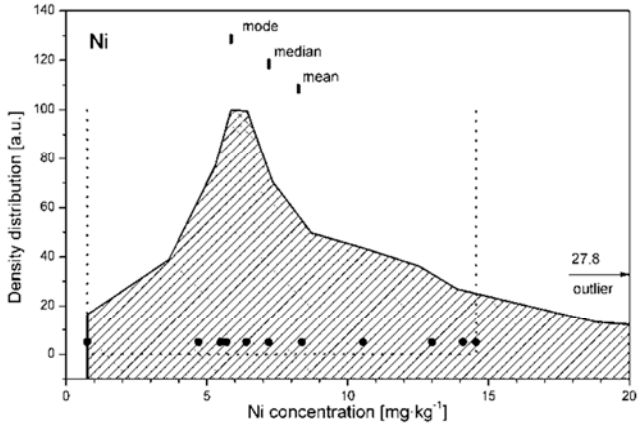

Cr
mode
median
mean
30.14
39.12
2390
outliers
Density distribution [a.u.]
Cr concentration [mg·kg^{-1}]

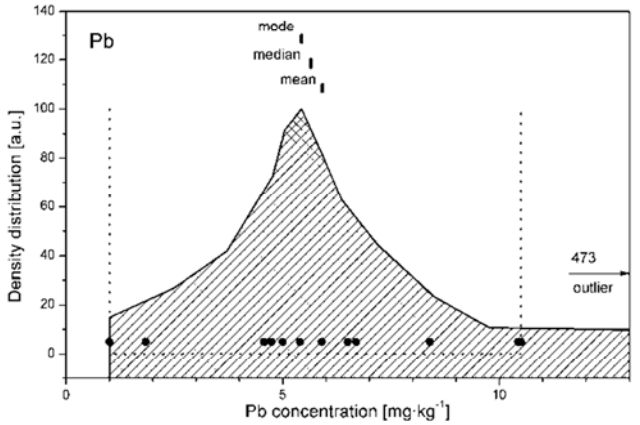

Cu
mode
median
mean
Density distribution [a.u.]
2800
outlier
Cu concentration [mg·kg^{-1}]

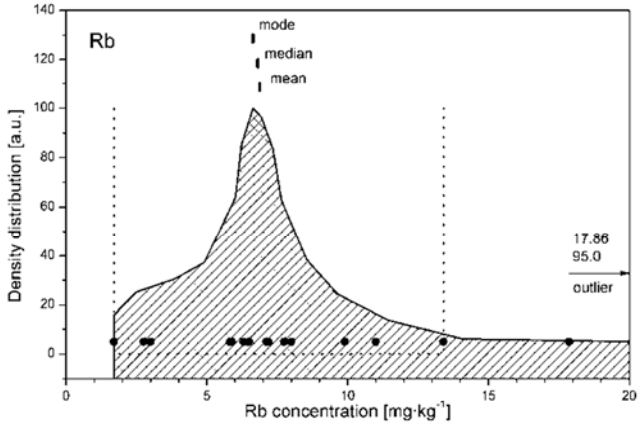

Fe
mode
median
mean
Density distribution [a.u.]
9130
outlier
Fe concentration [mg·kg^{-1}]

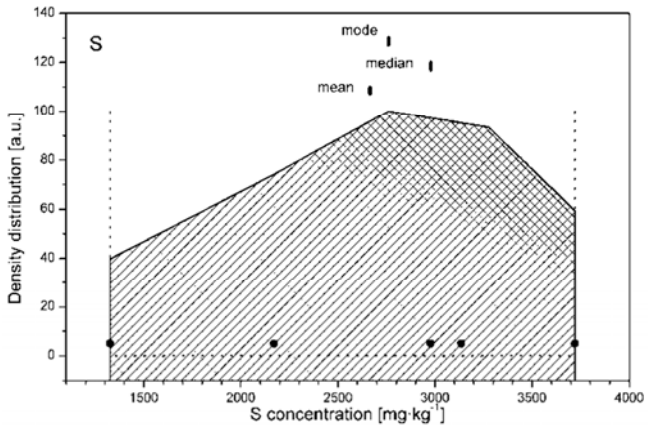

K
mode
median
mean
Density distribution [a.u.]
1893.6
9263
20231
outliers
127202
244000
outliers
K concentration [mg·kg^{-1}]


Mn
mode
median
mean
Density distribution [a.u.]
1320
outlier
Mn concentration [mg·kg^{-1}]


Ni
mode
median
mean
27.8
outlier
Density distribution [a.u.]
Ni concentration [mg·kg^{-1}]


Pb
mode
median
mean
473
outlier
Density distribution [a.u.]
Pb concentration [mg·kg^{-1}]


Rb
mode
median
mean
17.86
95.0
outlier
Density distribution [a.u.]
Rb concentration [mg·kg^{-1}]


S
mode
median
mean
Density distribution [a.u.]
S concentration [mg·kg^{-1}]

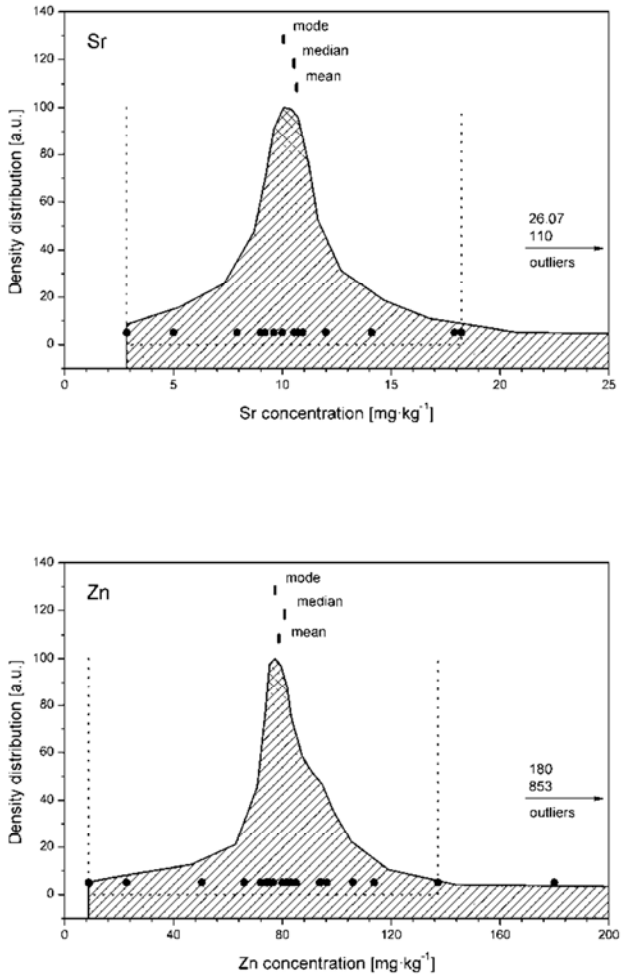
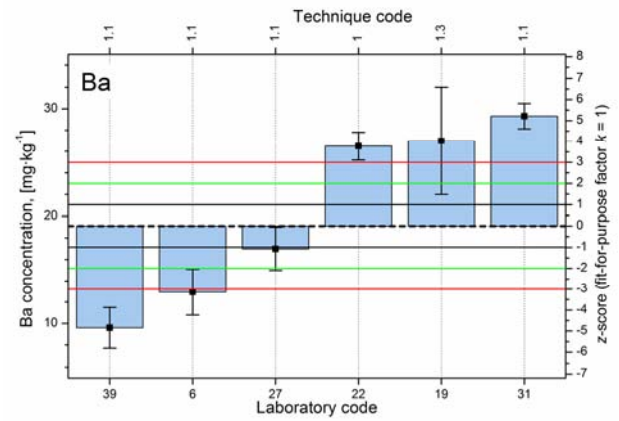
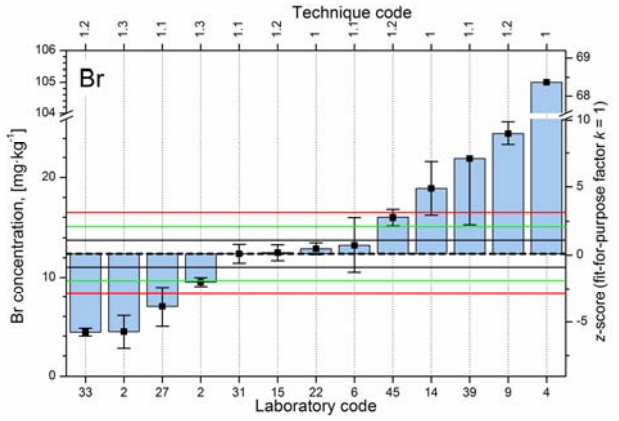
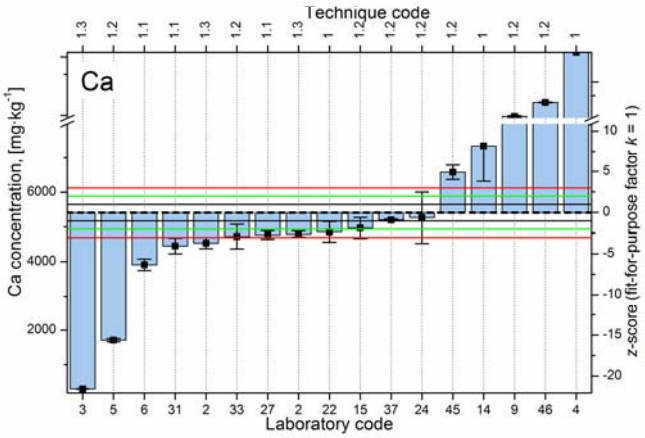
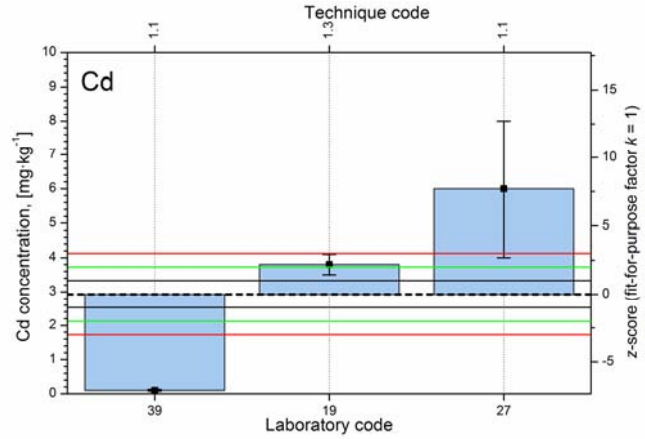


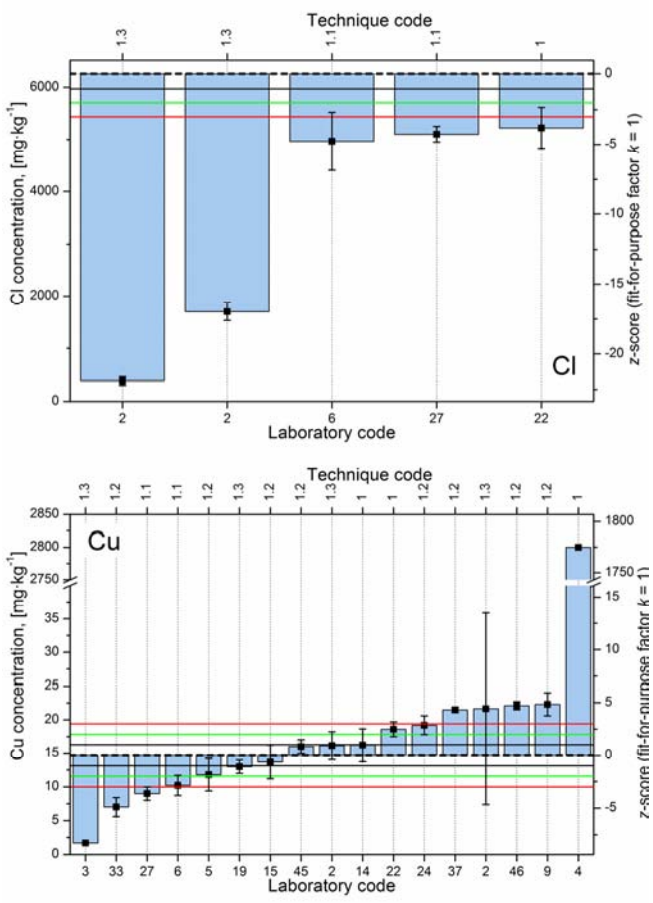
Fig. 3. The density distribution functions for the analytes for which at least 5 results passed the outlier rejection tests. The individual results are marked with filled circles. The dotted lines show the range of the accepted results – these results were used to calculate the consensus values. The outliers are marked with arrows. Also shown are the estimated parameters of the distribution (after outlier rejection): mode, median, and the mean value.

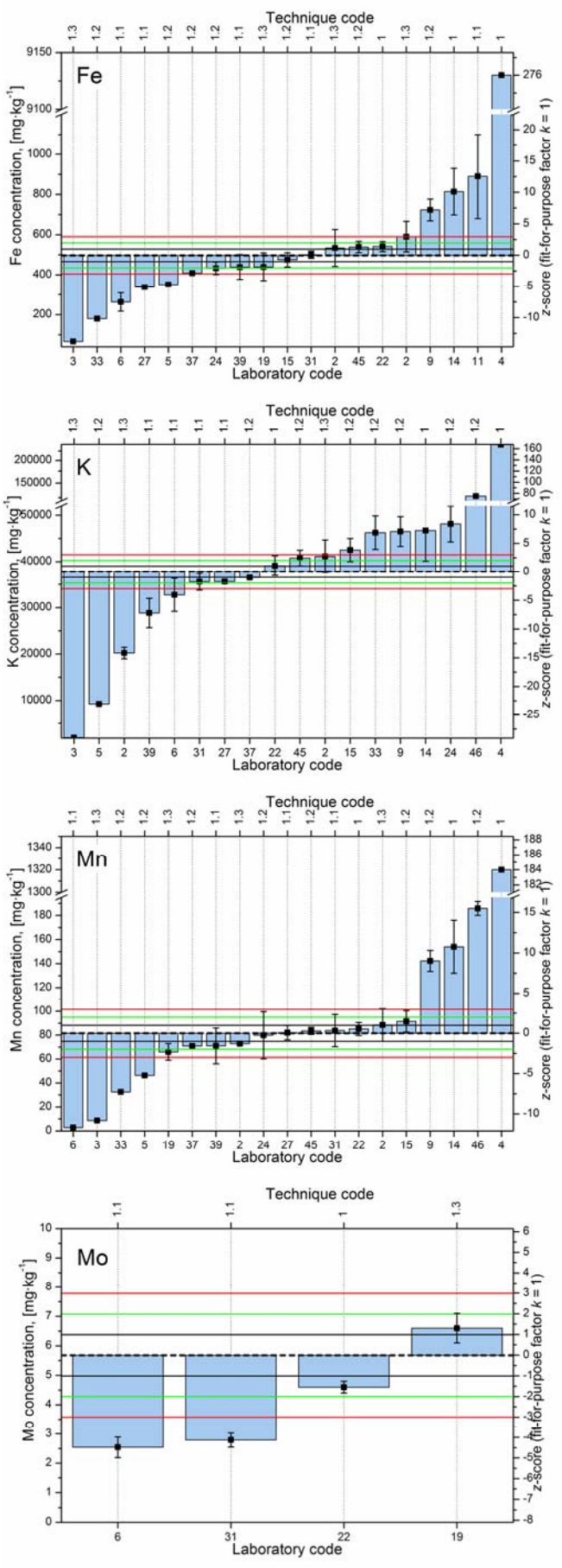

Technique code
Ba
Ba concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
39 6 27 22 19 31

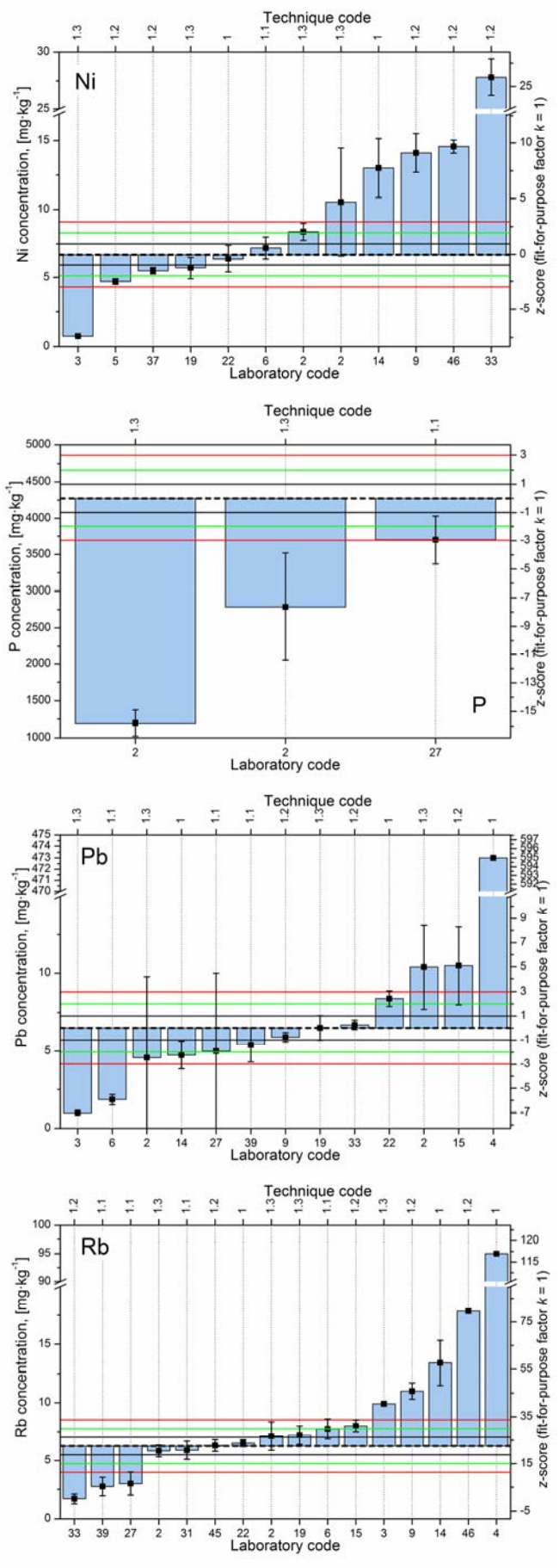

Technique code
Br
Br concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
33 2 27 2 31 15 22 6 45 14 39 9 4

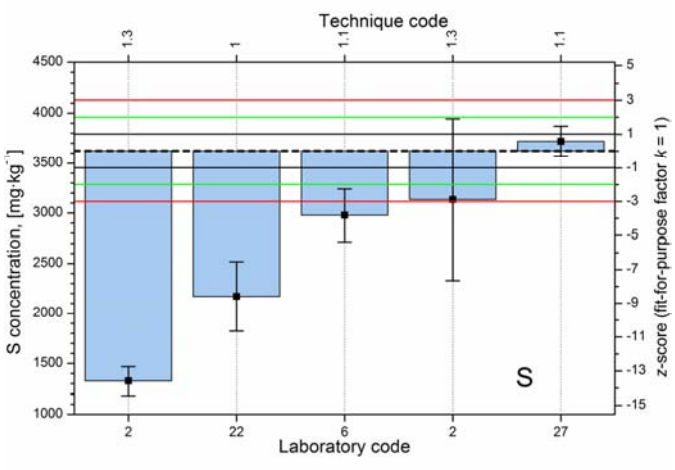

Technique code
Ca
Ca concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
3 5 6 31 2 33 27 2 22 15 37 24 45 14 9 46 4

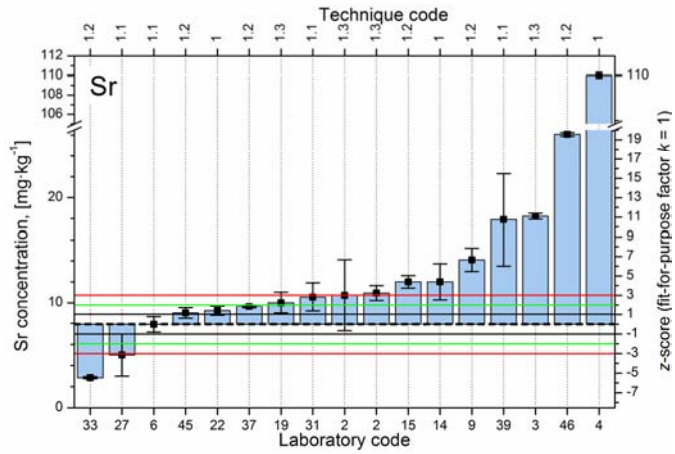

Technique code
Cd
Cd concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
39 19 27


Technique code
1.3
1.3
1.1
1.1
1
Cl concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Cl
Laboratory code
2
2
6
27
22
Technique code
Cu
Cu concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Laboratory code
3
33
27
6
5
19
15
45
2
14
22
24
37
2
46
9
4


Technique code
Fe
Fe concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Laboratory code
K
K concentration, [mg·kg⁻¹]
Mn
Mn concentration, [mg·kg⁻¹]
Mo
Mo concentration, [mg·kg⁻¹]


Technique code
Ni
Ni concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Laboratory code
P
P concentration, [mg·kg⁻¹]
Pb
Pb concentration, [mg·kg⁻¹]
Rb
Rb concentration, [mg·kg⁻¹]


Technique code
1.3
1
1.1
1.3
1.1
S concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
S
Laboratory code
2
22
6
2
27


Technique code
Sr
Sr concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Laboratory code
33
27
6
45
22
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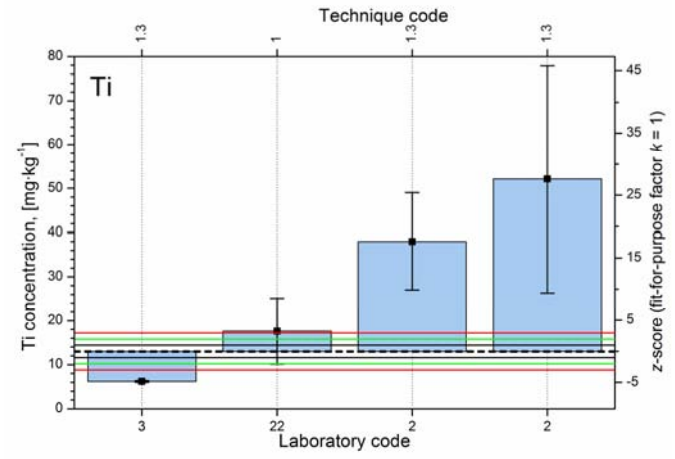
31
2
2
15
14
9
39
3
46
4


Technique code
Ti
Ti concentration, [mg·kg⁻¹]
z-score (fit-for-purpose factor k = 1)
Laboratory code
3
22
2
2

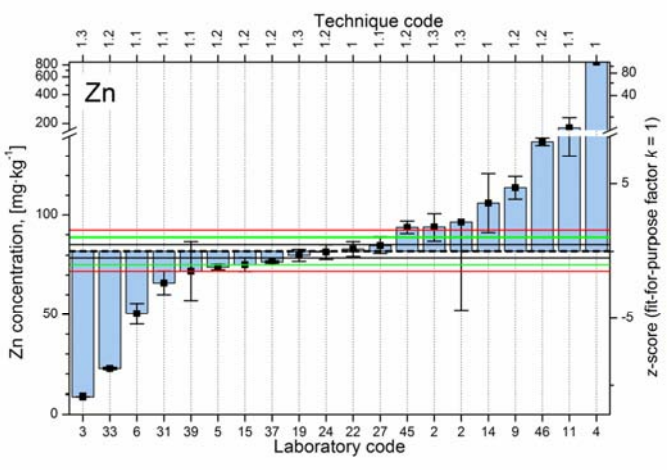
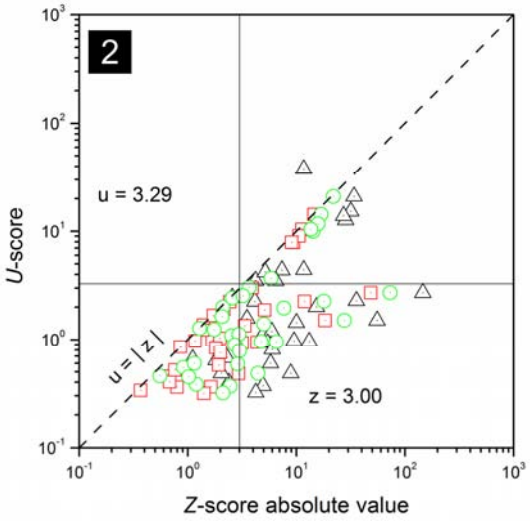
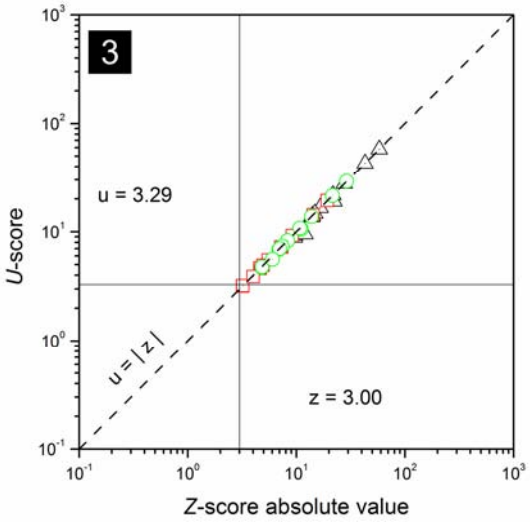
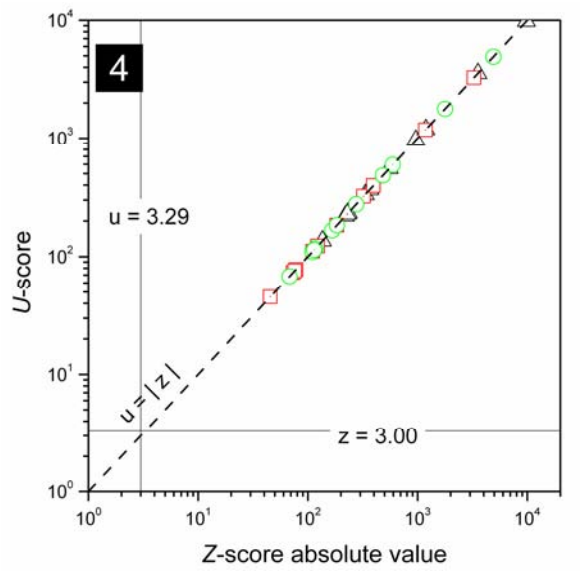


Fig. 4. Distributions of z-scores for analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties, as provided by the analysts, are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of z-score, $|z| < 2$, for three different fit-for-purpose 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****.*



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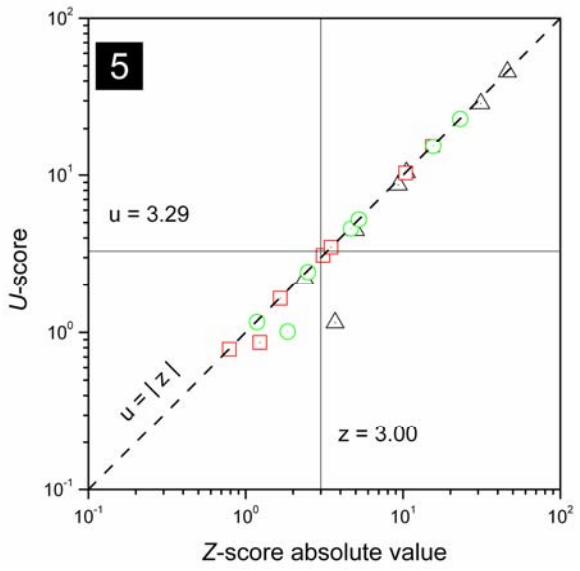
u = |z|
z = 3.00
U-score
Z-score absolute value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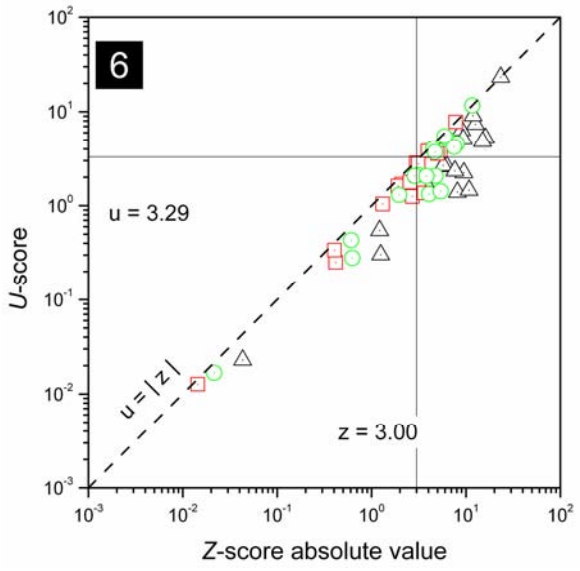
Z-score absolute value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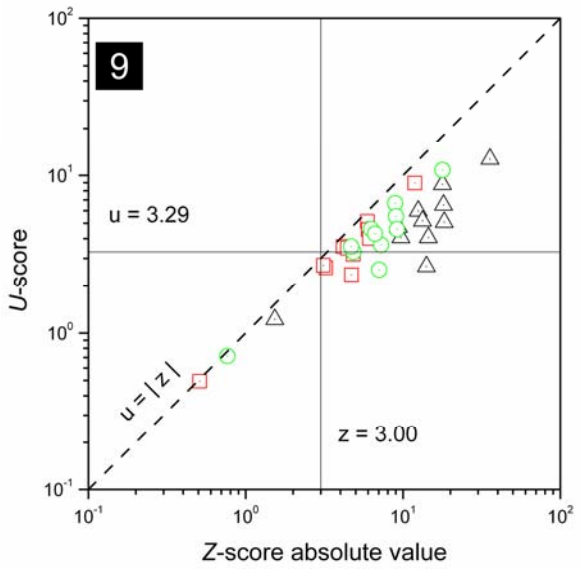
z = 3.00
U-score
Z-score absolute value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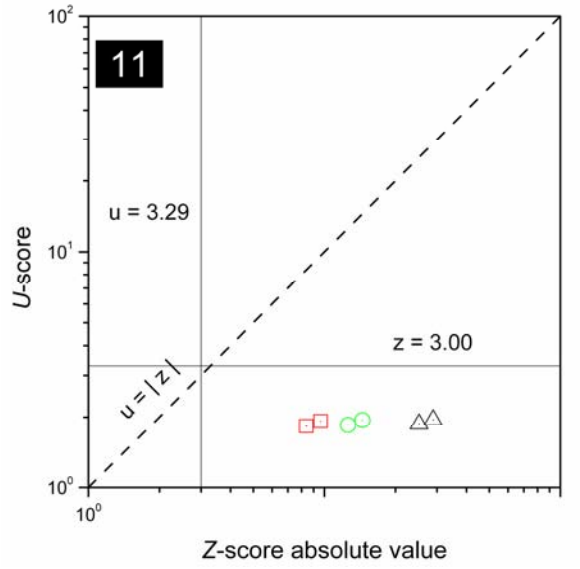
Z-score absolute value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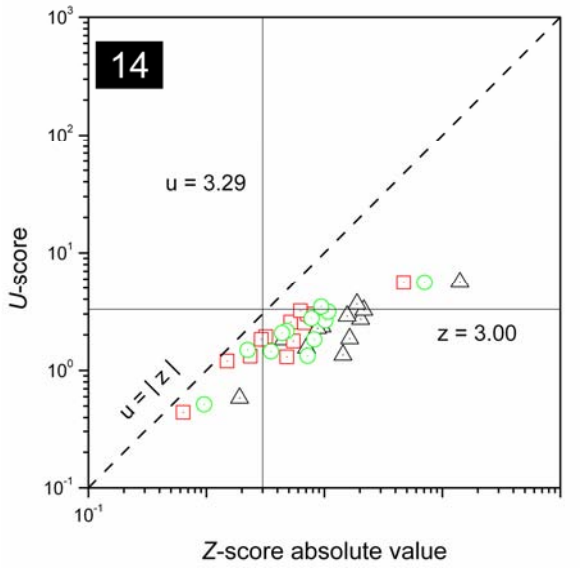
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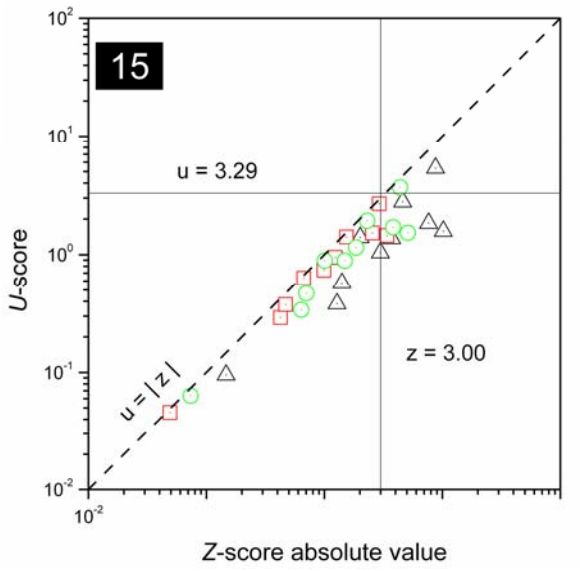
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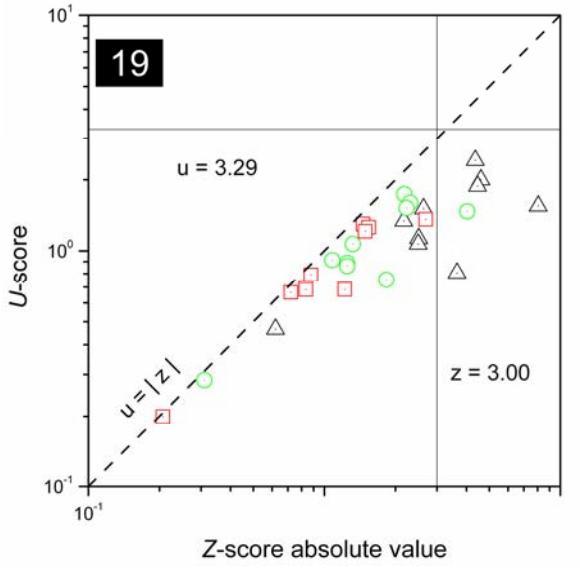
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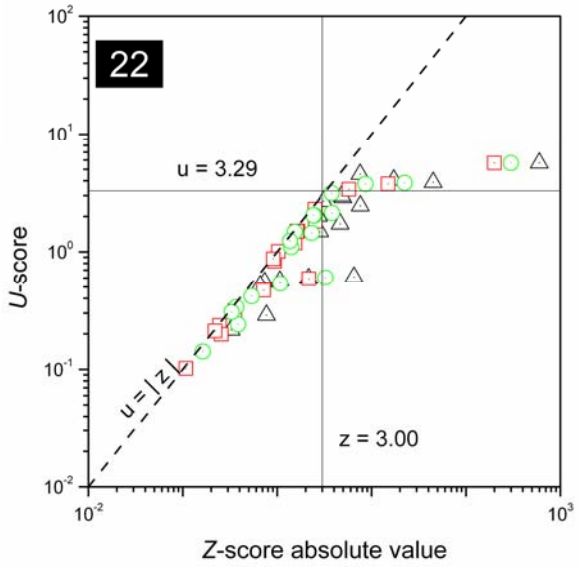
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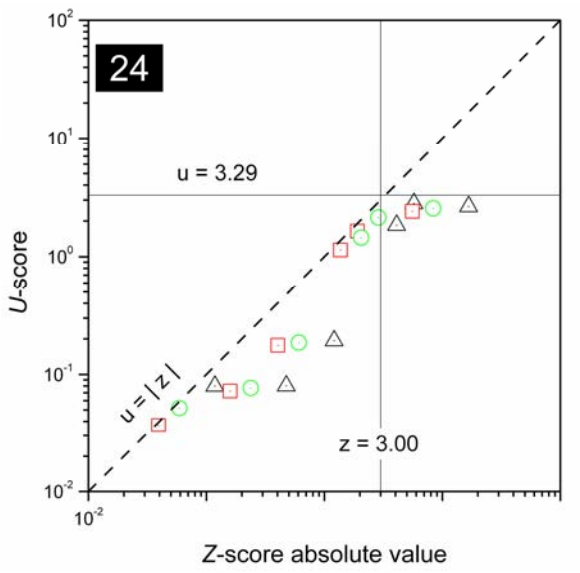
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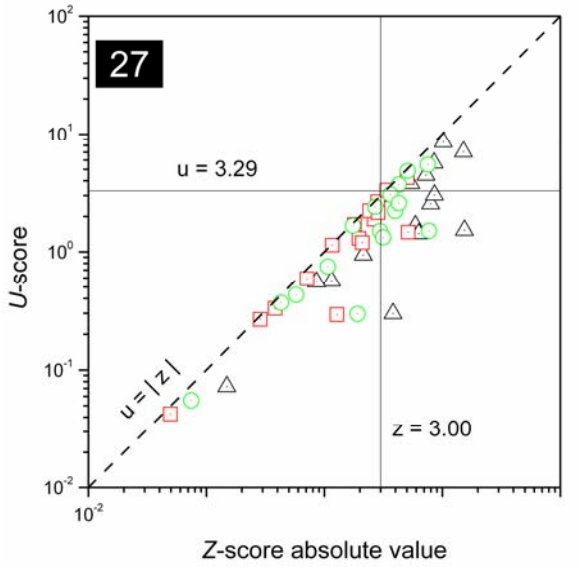
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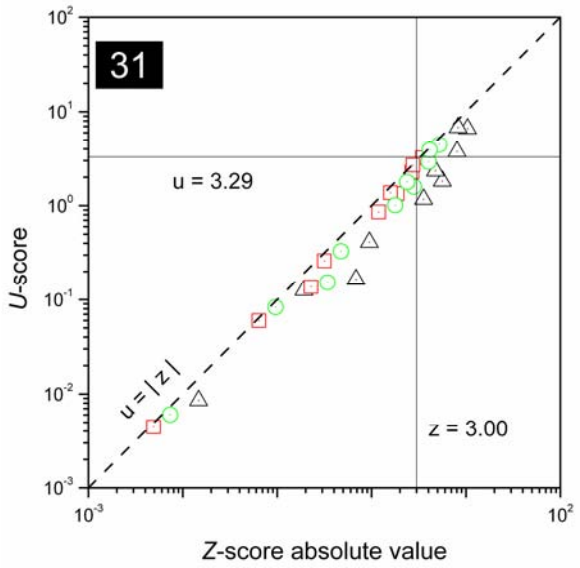
Z-score absolute value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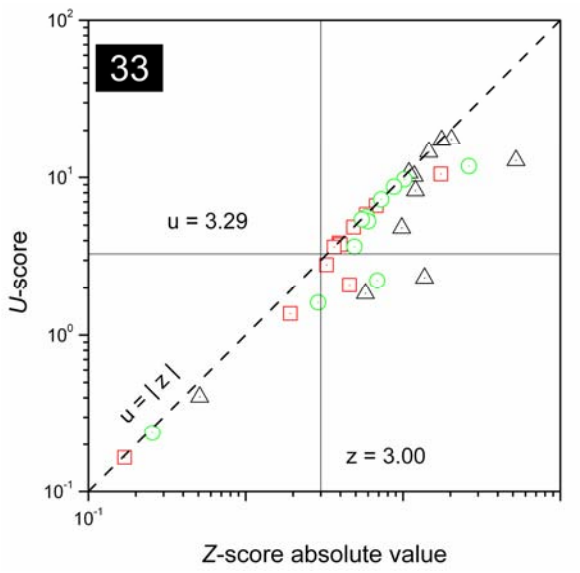
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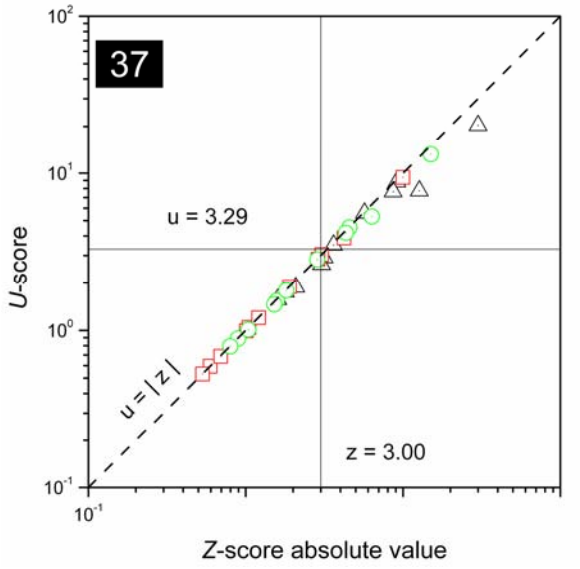
Z-score absolute value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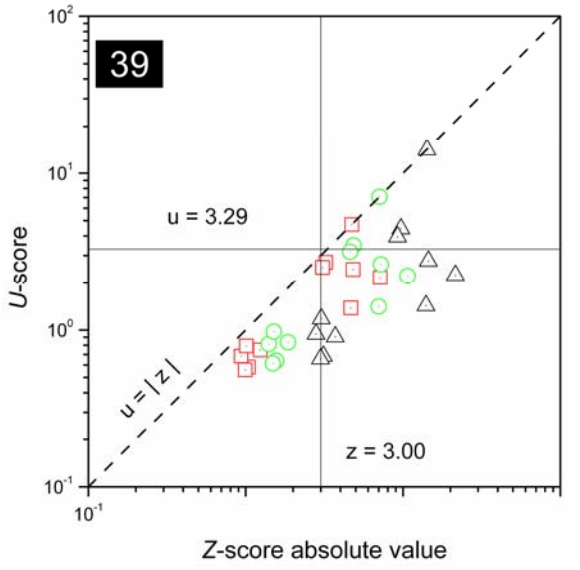
U-score
Z-score absolute value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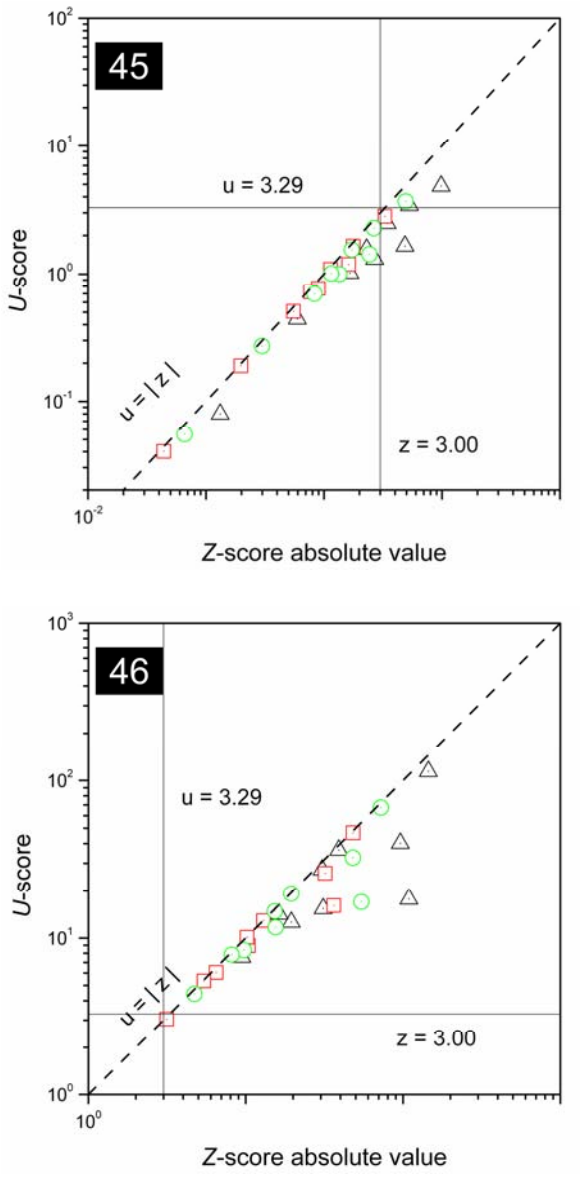

Fig. 5. Combined plots of z- and u-scores for participating laboratories. The laboratory code is shown in the left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2) with factor k, namely: ***k = 0.5 - black triangles****,* ***k = 1.0 - green circles****, and* ***k = 1.5 - red squares****. The solid lines mark the decision levels for z-score,* $|z| = 3$*, and u-score, u = 3.29. Points in the immediate proximity of the dashed diagonal line (u = |z|) have underestimated uncertainty values.*

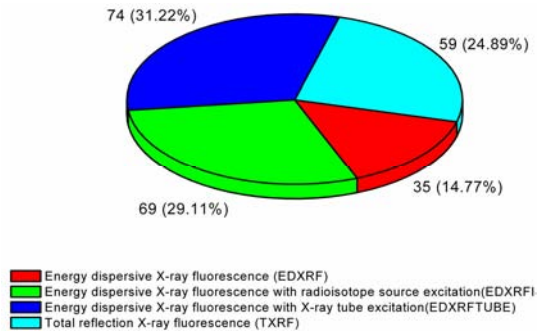

Fig. 6. Utilization of analytical techniques. For each analytical technique the number of submitted results is shown. The percent values relate to the total number of 237 submitted results.

ACKNOWLEDGEMENT

The IAEA is grateful to the participants of the proficiency test for providing information on their analytical procedures.

REFERENCES

[1] THOMPSON, M., WOOD, R., The international harmonised protocol for the proficiency testing of (chemical) analytical laboratories, J. Assoc. Off. Anal. Chem. Int. **76** (1993) 926.

[2] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Conformity assessment –General requirements for proficiency testing, ISO/IEC/DIS 17043:2008, ISO, Geneva, Switzerland (2008).

[3] HUND, E., MASSART, D.L., SMEYERS-VERBEKE, J., Inter-laboratory studies in analytical chemistry, Anal. Chim. Acta **423** (2000) 145.

[4] THOMPSON, M., Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing, Analyst **125** (2000) 385.

[5] GRUBBS, F.E., Procedures for detecting outlying observations in samples, Technometrics **11** (1969) 1.

[6] INTERNATIONAL ATOMIC ENERGY AGENCY, A Nonparametric Statistical Method for the Determination of a Confidence Interval for the Mean of a Set of Results Obtained in a Laboratory Intercomparison, IAEA/RL/84, IAEA, Vienna (1981).

[7] INTERNATIONAL ATOMIC ENERGY AGENCY, Report on the Intercomparison Run IAEA-Soil-7: Trace Elements in Soil, IAEA/RL/112, IAEA, Vienna (1984).

[8] NATRELLA, M.G., Experimental Statistic, Handbook 91, National Bureau of Standards, Unite States Department of Commerce (1963).

[9] ZIELINSKI R., Statistical Tables, PWN, Warsaw, Poland (1972).

[10] GRUBBS, F.E., Sample Criteria for Testing Outlying Observations, Ann. of Math. Stat. **21** (1950) 27.

DEFINITIONS

In this section 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 [1-3] 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.

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