IAEA/AQ/5

IAEA Analytical Quality in Nuclear Applications Series No. 5

Worldwide Proficiency Test for X Ray Fluorescence Laboratories PTXRFIAEA/5 Determination of Minor and Trace Elements in Marine Sediment

IAEA

International Atomic Energy Agency

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FOREWORD

The proficiency test (code PTXRFIAEA05) was the fifth worldwide exercise organized by the IAEA Seibersdorf Laboratories in order to assist X ray fluorescence laboratories in assessment and improvement of their analytical performance. The test was carried out within the IAEA Project 1.4.3.4 (D.3.03) on Nuclear Spectrometry for Analytical Applications, under the Nuclear Science Programme. The main objective of the project was to enhance 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.

Marine sediment 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 next proficiency test exercise will be executed in 2009.

The IAEA is grateful to the participants of the proficiency test for providing information on their analytical procedures. The evaluation of the data and preparation of the report was performed by the IAEA Scientific Secretary, D. Wegrzynek of the XRF Group, Instrumentation Unit, the IAEA Seibersdorf Laboratories. This IAEA officer responsible for this publication was D. Wegrzynek.

CONTENTS

1. INTRODUCTION

The PTXRFIAEA05 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 marine sediment sample. The samples, together with detailed instructions for analysts, were distributed to the participating laboratories in April 2008. The deadline for submission of the results was 31 July, 2008. The last results were received in October 2008. 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. DEFINITIONS AND TERMINOLOGY

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 Scheme: method of checking laboratory performance by means of interlaboratory tests, sometimes called 'round robin study'.

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.

3. DETAILS

3.1. Test Sample

The test sample was a marine sediment material prepared and tested by an external independent laboratory. The powdered, homogenized, and dried material was distributed to 49 laboratories in sealed plastic bottles, each bottle containing 100g 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.

3.2. Assigned Value and Target Standard Deviation

The consensus values established by independent interlaboratory surveys were used as the assigned values of the analytes, X_A. The results for 49 analytes were submitted by participants of this proficiency test: Ag, Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Ga, Hf, I, K, La, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, U, V, Y, Yb, Zn, and Zr. The *z*- and *u* scores were calculated for all the submitted results of all analytes except Cl, Cs, Eu, Hf, Pr, Sm, Sr, Ta, Tb and Yb, 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]:

$$H_A = \begin{cases} 0.22X_A & X_A < 1.2\cdot10^{-7} \\ 0.02(X_A)^{0.8495} & 1.2\cdot10^{-7} \le X_A \le 0.138 \\ 0.01\sqrt{X_A} & X_A > 0.138 \end{cases} \quad (1)$$

In Eq. (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.

3.3. *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 Eqs (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:

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

The advice to the laboratory is that falling for 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:

$$RSZ = \frac{\sum_{i=1}^{L} z_i}{\sqrt{L}} \quad (6)$$

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

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqs (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:

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

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:

$u \leq 1.64$ - reported result does not differ from the assigned value,
$1.64 < u \leq 1.95$ - reported result probably does not differ from the assigned value,
$1.95 < u \leq 2.58$ - it is not clear whether the reported and assigned values differ, (9)
$2.58 < u \leq 3.29$ - 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 Eq. (4) and Eq. (8) one can immediately notice that for corresponding values of u score and z score the following inequality is always fulfilled:

$$u \leq |z| \quad (10)$$

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.

3.4. 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: $5 \leq n \leq 100$, two-sided test, confidence level = 0.95:

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

- 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:

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

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 $h \le$ critical value.

4. Dixon's test [8], number of results: $3 \le n \le 25$, two-sided test, confidence level = 0.95:

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

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

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

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

- 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:

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

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 Eqs (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 marine sediment test sample was distributed to 49 laboratories for chemical composition analysis. Out of the 49 laboratories 33 participated in the test submitting 556 individual results for 49 different chemical elements. The list of the participating laboratories is presented in Table 1. Ten analytical techniques have been distinguished to be in use by the participants. The technique's 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 case of no sufficient information was available a generic type technique EDXRF was assumed. The techniques PIGE, NAA, FAAS and ICP-AES were not X ray emission related. All submitted results have been evaluated. In Table 3 a summary of the assigned analyte values, the target values of standard deviation, as well as the consensus values and their standard deviations are shown. The consensus values (Eq. 19) and corresponding standard deviations (Eq. 20) were calculated based on 452 reported analytical results after excluding 104 results classified as outliers. The correlation between the assigned and the consensus values is shown in Fig. 2. As can be noticed there wer 7 elements, Ag, Cd, Mo, Sc, Se, Sn, and U, for which there was significant disagreement observed between the assigned and the consensus values. These elements were reported by relatively small number of the participating laboratories, from 1 to 4. All of these elements, except Se, 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 Eq. (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 limited number of results. All the populations of the 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 analytes with at least 6 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. As can be noticed the majority of the determinations were carried out by energy dispersive XRF techniques (73.9 %): EDXRFISO + EDXRFTUBE + EDXRF, followed by WDXRF (8.6 %), TXRF (4.3 %). The rest of the submitted results was obtained by PIXE and PIXE-PIGE (5.8 %), NAA (3.4 %), ICP-AES (3.1 %), and FAAS (0.9 %).

Appendix I

TABLES 1-5

TABLE 1. THE LABORATORIES PARTICIPATING IN THE PROFICIENCY TEST EXERCISE

Institution	Country
Centre de Recherche Nucléaire d'Alger	**Algeria**
Técnicas Analíticas Nucleares – CAE (Comisión Nacional de Energía Atómica)	**Argentina**
Instituto de Pesquisas Energéticas e Nucleares (IPEN), Centro de Química e Meio Ambiente (CQMA), Laboratório de Fluorescência de Raios X (LFX)	**Brazil**
Institute for Nuclear Research and Nuclear Energy	**Bulgaria**
Centro de Investigación en Ciencias Atómicas Nucleares y Moleculares (CICANUM), Universidad de Costa Rica	**Costa Rica**
Laboratory for Ion Beam Interactions, Rudjer Boskovic Institute	**Croatia**
Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN)	**Cuba**
Department of Conservation of Antiquities & Works of Art, Technological Educational Institute (TEI) of Athens	**Greece**
Laboratory for Material Analysis, Institute of Nuclear Physics, National Center for Scientific Research "Demokritos",	**Greece**
13th Ephorate of Prehistorical and Classical Antiquities	**Greece**
Nuclear Physics Laboratory, Department of Physics, University of Ioannina	**Greece**
Laboratory of Archaeometry, Cultural and Educational Technology Institute, Research Center "Athena"	**Greece**
KFKI Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences	**Hungary**
Nuclear Science and Technology Research Institute, Nuclear Science Research School, Atomic Energy Organization	**Islamic Republic of Iran**
International Centre for Environmental and Nuclear Science	**Jamaica**

Materials Science and Development Section, Centre for Energy Research and Training, Ahmadu Bello University	**Nigeria**
Comisión Nacional de Energía Atómica	**Paraguay**
Instituto Peruano de Energía Nuclear	**Peru**
Analytical Measurements Research Group, Atomic Research Division, Philippine Nuclear Research Institute	**Philippines**
Faculty of Physics and Applied Computer Science, AGH University of Science and Technology	**Poland**
Faculty of Physics and Applied Computer Science, AGH University of Science and Technology	**Poland**
Laboratório de Análises Ambientais e Controlo de Qualidade (LAACQ), Instituto Nacional de Tecnologia Industrial (INETI)	**Portugal**
VINCA Institute for Nuclear Sciences	**Serbia**
Jožef Stefan Institute	**Slovenia**
Faculty of Mathematics and Physics, University of Ljubljana	**Slovenia**
Atomic Energy Authority	**Sri Lanka**
Department of Physics, University of Khartoum	**Sudan**
Department of Chemistry, Atomic Energy Commission of Syria	**Syrian Arab Republic**
Ministry of Environment and Physical Planning	**The Former Yugoslav Republic of Macedonia**
Centre National des Sciences et Technologies Nucléaires	**Tunisia**
Saraykoy Nuclear Research and Training Center	**Turkey**
Tanzania Atomic Energy Commission	**United Republic of Tanzania**
Center for Radiation Protection and Environment Monitoring, Institute for Nuclear Science and Technology (INST), Vietnam Atomic Energy Commission (VAEC)	**Vietnam**

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
2.0	Wavelength dispersive X ray fluorescence	WDXRF
4.0	Particle induced X ray emission	PIXE
4.5	Particle induced X ray emission + proton induced gamma emission	PIXE-PIGE
5.0	Neutron Activation Analysis	NAA
7.2	Flame Atomic Absorption Spectroscopy	FAAS
8.1	Inductively couples plasma atomic emission spectroscopy	ICP-AES

TABLE 3. THE ASSIGNED VALUES OF ANALYTES, THE TARGET VALUES OF THE STANDARD DEVIATIONS, OBTAINED BY USING MODIFIED HOROWITZ FUNCTION, EQ. (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				
				[g/kg]				
Al	49.4	0.77	1.55	2.32	52.0	1.67	13	2
Ca	46.4	0.73	1.47	2.20	49.8	2.11	30	4
Cl	-	-	-	-	11.97	0.925	10	2
Fe	33.5	0.56	1.12	1.7	33.89	0.74	34	5
K	16.6	0.31	0.62	0.93	16.94	0.62	27	4
Mg	10.5	0.21	0.42	0.63	12.9	1.08	7	1
Na	14.9	0.28	0.56	0.84	14.0	1.31	7	0
P	1.21	0.034	0.067	0.100	1.20	0.012	2	0
S	4.91	0.110	0.219	0.329	6.20	0.673	12	1
Si	269	2.60	5.19	7.79	259.3	9.4	18	2
Ti	3.25	0.077	0.154	0.231	3.33	0.084	27	7
				[mg/kg]				
Ag	*0.31*	*0.029*	*0.058*	*0.087*	*131*	*179*	*2*	*0*
As	18.1	0.94	1.88	2.81	19.18	0.578	13	3
Ba	316	10.7	21.3	31.9	332	14.9	14	5
Br	*102.0*	*4.07*	*8.14*	*12.2*	*98.6*	*5.75*	*20*	*2*
Cd	*0.390*	*0.036*	*0.0719*	*0.1079*	*1.21*	*0.545*	*3*	*0*
Ce	*53.0*	*2.34*	*4.67*	*7.00*	*52.91*	*0.124*	*9*	*6*
Co	10.5	0.59	1.18	1.77	11.16	0.138	8	5
Cr	99.9	4.00	8.00	11.99	100.5	6.55	17	4
Cs	-	-	-	-	7.64	0.658	4	0
Cu	16.9	0.89	1.77	2.65	20.1	1.10	23	7
Eu	-	-	-	-	0.845	0.0540	1	0
Ga	*12.0*	*0.66*	*1.32*	*1.99*	*11.9*	*0.91*	*7*	*1*
Hf	-	-	-	-	5.86	0.082	3	0
I	*44.2*	*2.00*	*4.00*	*6.00*	*53.1*	*1.36*	*5*	*2*
La	26.9	1.31	2.63	3.94	29.81	0.15	9	6
Mn	1050	29.5	59.0	88.5	1018	31.4	29	4
Mo	*3.41*	*0.227*	*0.454*	*0.681*	*27*	-	*1*	*0*
Nb	*10.4*	*0.59*	*1.17*	*1.76*	*11.067*	*0.0670*	*9*	*6*

Table 3 continued…

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
		$k = 0.5$	$k = 1.0$	$k = 1.5$				
Nd	*20.9*	*1.06*	*2.12*	*3.18*	*25.2*	*1.80*	*5*	*1*
Ni	27.8	1.35	2.70	4.05	28.1	1.72	16	3
Pb	49.7	2.21	4.42	6.63	46.55	3.29	23	3
Pr	-	-	-	-	4.4	1.20	1	0
Rb	90.7	3.69	7.37	11.05	88.2	3.05	25	5
Sb	*0.80*	*0.066*	*0.132*	*0.198*	*0.97*	*0.090*	*1*	*0*
Sc	*10.1*	*0.57*	*1.14*	*1.72*	*45*	*22.9*	*4*	*1*
Se	*0.475*	*0.0425*	*0.0850*	*0.128*	*8.5*	*0.40*	*1*	*0*
Sm	-	-	-	-	5.075	0.0360	1	0
Sn	*4.62*	*0.294*	*0.587*	*0.881*	*17.5*	*6.46*	*4*	*0*
Sr	-	-	-	-	201.2	5.21	28	5
Ta	-	-	-	-	49	67.8	2	0
Tb	-	-	-	-	0.84	0.286	1	0
Th	*7.90*	*0.463*	*0.926*	*1.389*	*8.33*	*0.784*	*4*	*0*
U	*1.80*	*0.132*	*0.264*	*0.396*	*3.9*	*2.37*	*2*	*0*
V	*95.8*	*3.86*	*7.72*	*11.6*	*99.8*	*4.66*	*7*	*1*
Y	22.0	1.11	2.21	3.32	20.0	1.51	16	2
Yb	-	-	-	-	1.87	0.250	1	0
Zn	145	5.49	11.0	16.5	146.1	7.31	31	2
Zr	222	7.88	15.8	23.7	200	12.3	19	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		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
				Al (49.4 ± 1.55) [g/kg]						
43	1.2	45.0	1.69	3.76	-5.66	-2.83	-1.89	2.37	1.92	1.53
22	1.0	45	10.1	22.28	-5.41	-2.70	-1.80	0.42	0.41	0.41
37	1.2	47.13	0.206	0.44	-2.92	-1.46	-0.97	2.82	1.45	0.97
21	2.0	49.39	0.900	1.82	-0.01	-0.01	0.00	0.01	0.01	0.00
18	2.0	49.50	0.506	1.02	0.13	0.07	0.04	0.11	0.06	0.04
34	1.2	51.2	2.75	5.38	2.35	1.17	0.78	0.64	0.58	0.51
7	8.1	52.98	-	-	4.61	2.30	1.54	4.61	2.30	1.54
17	1.0	54.00	0.184	0.34	5.92	2.96	1.97	5.76	2.94	1.97
25	1.2	57.2	7.07	12.35	10.07	5.03	3.36	1.10	1.08	1.05
27	1.1	58.0	9.00	15.52	11.07	5.54	3.69	0.95	0.94	0.93
6	1.1	62.17	0.243	0.39	16.43	8.22	5.48	15.68	8.12	5.45
1	4.5	76.9 *	7.00	9.10	35.40	17.70	11.80	3.91	3.84	3.73
41	1.0	113.3 *	-	-	82.26	41.13	27.42	82.26	41.13	27.42
				Ca (46.4 ± 1.47) [g/kg]						
33	1.2	27.3	1.13	4.14	-25.93	-12.97	-8.64	14.15	10.28	7.69
25	1.2	34.91	0.381	1.09	-15.60	-7.80	-5.20	13.86	7.55	5.13
32	1.3	36.7	2.80	7.63	-13.17	-6.59	-4.39	3.35	3.07	2.72
26	1.2	39.5	4.20	10.63	-9.37	-4.68	-3.12	1.62	1.55	1.45
4	1.0	40.2	-	-	-8.42	-4.21	-2.81	8.42	4.21	2.81
27	1.1	43.3	1.20	2.77	-4.21	-2.10	-1.40	2.20	1.63	1.23
21	2.0	44.1	1.60	3.62	-3.07	-1.53	-1.02	1.28	1.04	0.83
7	8.1	44.215	-	-	-2.97	-1.48	-0.99	2.97	1.48	0.99
14	1.0	44.6	1.54	3.45	-2.41	-1.21	-0.80	1.04	0.83	0.66
36	1.1	45.3	3.20	7.06	-1.49	-0.75	-0.50	0.34	0.31	0.28
18	2.0	45.84	0.368	0.80	-0.76	-0.38	-0.25	0.68	0.37	0.25
43	1.2	46.9	1.09	2.32	0.68	0.34	0.23	0.38	0.27	0.20
36	1.2	47.8	3.00	6.28	1.90	0.95	0.63	0.45	0.42	0.38
37	1.2	50.42	0.258	0.51	5.45	2.73	1.82	5.15	2.69	1.81
44	4.0	51.85	0.617	1.19	7.39	3.70	2.46	5.67	3.41	2.37
28	1.0	52.1	4.74	9.10	7.76	3.88	2.59	1.19	1.15	1.09
6	1.1	52.5	1.70	3.24	8.24	4.12	2.75	3.28	2.70	2.18
39	1.1	53.00	0.300	0.57	8.96	4.48	2.99	8.30	4.39	2.96
12	1.1	53.0	5.00	9.43	8.96	4.48	2.99	1.31	1.27	1.21
34	1.2	53.9	2.45	4.55	10.18	5.09	3.39	2.93	2.62	2.27
40	1.1	58.6	1.39	2.38	16.57	8.29	5.52	7.75	6.02	4.67
22	1.0	59.2	3.23	5.46	17.38	8.69	5.79	3.86	3.61	3.27
17	1.0	59.2	1.67	2.82	17.44	8.72	5.81	7.03	5.76	4.64
1	4.5	64.2	6.50	10.13	24.10	12.05	8.03	2.71	2.66	2.59
31	1.1	68.6	3.00	4.38	30.16	15.08	10.05	7.18	6.64	5.96

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z scores			u scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
19	1.3	77.0	8.02	10.42	41.56	20.78	13.85	3.80	3.75	3.68
29	1.2	116.1 *	5.61	4.83	94.66	47.33	31.55	12.32	12.02	11.56
41	1.0	118.6 *	-	-	98.02	49.01	32.67	98.02	49.01	32.67
42	1.0	130 *	-	-	113.50	56.75	37.83	113.50	56.75	37.83
16	1.1	662 *	117	17.67	835.80	417.90	278.60	5.26	5.26	5.26
					Cl [g/kg]					
37	1.2	8.110	0.0122	0.15	-	-	-	-	-	-
43	1.2	8.87	0.251	2.83	-	-	-	-	-	-
41	1.0	11.00	-	-	-	-	-	-	-	-
34	1.2	11.67	0.831	7.12	-	-	-	-	-	-
27	1.1	12.4	1.00	8.08	-	-	-	-	-	-
6	1.1	13.6	1.24	9.10	-	-	-	-	-	-
22	1.0	14.5	1.00	6.90	-	-	-	-	-	-
1	4.5	15.6	2.40	15.40	-	-	-	-	-	-
44	4.0	28 *	13.2	47.03	-	-	-	-	-	-
42	1.0	40 *	-	-	-	-	-	-	-	-
					Fe (33.5 ± 1.12) [g/kg]					
33	1.2	21.5 *	1.34	6.23	-21.49	-10.74	-7.16	8.27	6.88	5.60
26	1.2	23.3	2.20	9.44	-18.26	-9.13	-6.09	4.49	4.13	3.69
32	1.3	28.36	0.270	0.95	-9.20	-4.60	-3.07	8.29	4.47	3.03
35	1.0	28.4	1.54	5.41	-9.18	-4.59	-3.06	3.14	2.70	2.26
14	1.0	29.7	1.02	3.43	-6.75	-3.37	-2.25	3.24	2.49	1.92
36	1.1	30.8	1.00	3.25	-4.83	-2.42	-1.61	2.36	1.80	1.38
6	1.1	31.3	1.29	4.13	-4.00	-2.00	-1.33	1.59	1.31	1.06
25	1.2	31.70	0.678	2.14	-3.23	-1.62	-1.08	2.06	1.38	1.00
38	5.0	31.98	0.365	1.14	-2.72	-1.36	-0.91	2.28	1.29	0.89
28	1.0	32.2	2.90	9.01	-2.35	-1.18	-0.78	0.44	0.42	0.39
7	8.1	32.53	-	-	-1.74	-0.87	-0.58	1.74	0.87	0.58
19	1.3	32.6	1.14	3.49	-1.56	-0.78	-0.52	0.69	0.55	0.43
21	2.0	32.64	0.500	1.53	-1.54	-0.77	-0.51	1.15	0.70	0.49
36	1.2	32.90	0.700	2.13	-1.07	-0.54	-0.36	0.67	0.46	0.33
37	1.2	33.37	0.073	0.22	-0.22	-0.11	-0.07	0.22	0.11	0.07
39	1.1	33.60	0.500	1.49	0.18	0.09	0.06	0.13	0.08	0.06
4	1.0	33.80	-	-	0.54	0.27	0.18	0.54	0.27	0.18
17	1.0	34.79	0.697	2.00	2.30	1.15	0.77	1.44	0.98	0.71
44	4.0	35.18	0.623	1.77	3.01	1.50	1.00	2.01	1.31	0.94
24	1.2	35.6	2.32	6.52	3.77	1.89	1.26	0.88	0.82	0.74
22	1.0	35.7	1.56	4.37	3.94	1.97	1.31	1.33	1.15	0.96
40	1.1	35.74	0.538	1.51	4.01	2.01	1.34	2.89	1.81	1.27
1	4.5	36.0	1.80	5.00	4.43	2.22	1.48	1.31	1.17	1.01
12	1.1	36.0	9.00	25.00	4.48	2.24	1.49	0.28	0.28	0.27
18	2.0	36.19	0.411	1.14	4.82	2.41	1.61	3.88	2.26	1.56
24	7.2	36.92	1.11	3.00	6.13	3.06	2.04	2.76	2.18	1.70
43	1.2	38.0	4.47	11.76	8.06	4.03	2.69	1.00	0.98	0.94
34	1.2	38.5	2.34	6.09	8.86	4.43	2.95	2.06	1.91	1.72
27	1.1	41.82	0.400	0.96	14.90	7.45	4.97	12.11	7.01	4.83
31	1.1	43.2	1.19	2.75	17.36	8.68	5.79	7.39	5.95	4.72
41	1.0	88.20 *	-	-	97.94	48.97	32.65	97.94	48.97	32.65

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
29	1.2	99.6 *	5.63	5.65	118.40	59.19	39.46	11.69	11.52	11.26
42	1.0	166 *	-	-	237.20	118.60	79.08	237.20	118.60	79.08
16	1.1	539.00 *	0.700	0.13	905.10	452.50	301.70	564.50	383.50	278.40
K (16.6 ± 0.62) [g/kg]										
12	1.1	12.0	6.00	50.00	-14.95	-7.48	-4.99	0.77	0.76	0.76
32	1.3	12.4	2.80	22.58	-13.65	-6.83	-4.55	1.49	1.47	1.43
31	1.1	12.72	0.765	6.01	-12.60	-6.30	-4.20	4.70	3.95	3.23
14	1.0	13.24	0.485	3.66	-10.91	-5.46	-3.64	5.85	4.29	3.22
33	1.2	13.70	0.141	1.03	-9.43	-4.71	-3.14	8.57	4.59	3.11
43	1.2	14.40	0.393	2.73	-7.15	-3.58	-2.38	4.41	3.01	2.19
7	8.1	14.94	-	-	-5.40	-2.70	-1.80	5.40	2.70	1.80
4	1.0	15.50	-	-	-3.58	-1.79	-1.19	3.58	1.79	1.19
39	1.1	15.80	0.400	2.53	-2.60	-1.30	-0.87	1.59	1.09	0.80
36	1.2	15.90	0.600	3.77	-2.28	-1.14	-0.76	1.04	0.81	0.64
28	1.0	16.6	1.65	9.96	-0.09	-0.04	-0.03	0.02	0.02	0.01
21	2.0	16.69	0.400	2.40	0.29	0.15	0.10	0.18	0.12	0.09
37	1.2	18.26	0.053	0.29	5.40	2.70	1.80	5.32	2.69	1.80
34	1.2	18.7	1.15	6.16	6.75	3.37	2.25	1.74	1.59	1.41
44	4.0	18.71	0.726	3.88	6.87	3.44	2.29	2.68	2.22	1.80
6	1.1	18.78	0.395	2.10	7.09	3.54	2.36	4.35	2.98	2.17
1	4.5	19.1	1.90	9.95	8.13	4.06	2.71	1.30	1.25	1.18
18	2.0	19.14	0.150	0.78	8.25	4.13	2.75	7.42	4.01	2.72
22	1.0	19.8	1.12	5.66	10.40	5.20	3.47	2.76	2.50	2.21
27	1.1	19.90	0.500	2.51	10.73	5.36	3.58	5.62	4.16	3.14
19	1.3	20.4	3.31	16.26	12.19	6.10	4.06	1.13	1.11	1.09
25	1.2	21.21	0.308	1.45	14.97	7.49	4.99	10.58	6.70	4.74
40	1.1	21.8	1.16	5.30	16.96	8.48	5.65	4.36	3.98	3.53
17	1.0	27.37 *	0.398	1.45	35.02	17.51	11.67	21.42	14.70	10.72
26	1.2	28.5 *	3.30	11.58	38.69	19.34	12.90	3.59	3.55	3.47
29	1.2	34.2 *	1.28	3.74	57.35	28.67	19.12	13.40	12.42	11.18
41	1.0	35.2 *	-	-	60.47	30.23	20.16	60.47	30.23	20.16
Mg (10.5 ± 0.42) [g/kg]										
7	8.1	10.206	-	-	-1.41	-0.71	-0.47	1.41	0.71	0.47
21	2.0	10.42	0.400	3.84	-0.38	-0.19	-0.13	0.18	0.14	0.11
37	1.2	12.388	0.0562	0.45	9.06	4.53	3.02	8.74	4.49	3.01
18	2.0	12.64	0.198	1.57	10.28	5.14	3.43	7.45	4.64	3.27
1	4.5	15.0	1.50	10.00	21.59	10.79	7.20	2.97	2.89	2.77
25	1.2	17.08	0.906	5.31	31.55	15.77	10.52	7.07	6.59	5.97
41	1.0	22.9 *	-	-	59.49	29.74	19.83	59.49	29.74	19.83
Na (14.9 ± 0.56) [g/kg]										
37	1.2	8.29	0.214	2.58	-23.55	-11.78	-7.85	18.73	11.00	7.61
41	1.0	11.10	-	-	-13.54	-6.77	-4.51	13.54	6.77	4.51
18	2.0	14.38	0.390	2.71	-1.86	-0.93	-0.62	1.09	0.76	0.56
21	2.0	14.58	0.600	4.12	-1.14	-0.57	-0.38	0.48	0.39	0.31
38	5.0	15.05	0.560	3.72	0.54	0.27	0.18	0.24	0.19	0.15
7	8.1	15.212	-	-	1.11	0.56	0.37	1.11	0.56	0.37
1	4.5	19.3	2.00	10.39	15.50	7.75	5.17	2.15	2.09	2.01

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
				P (1.21 ± 0.067) [g/kg]						
37	1.2	1.193	0.0104	0.87	-0.52	-0.26	-0.17	0.50	0.26	0.17
18	2.0	1.199	0.0110	0.92	-0.33	-0.17	-0.11	0.31	0.16	0.11
				S (4.91 ± 0.219) [g/kg]						
17	1.0	1.54	0.100	6.51	-30.88	-15.44	-10.29	22.78	14.04	9.85
37	1.2	3.6966	0.00900	0.24	-11.10	-5.55	-3.70	11.07	5.55	3.70
22	1.0	4.97	0.818	16.46	0.55	0.27	0.18	0.07	0.07	0.07
27	1.1	5.1	1.00	19.61	1.74	0.87	0.58	0.19	0.19	0.18
44	4.0	6.64	0.714	10.76	15.79	7.89	5.26	2.39	2.31	2.20
6	1.1	6.735	0.0930	1.38	16.70	8.35	5.57	12.72	7.68	5.36
34	1.2	7.12	0.880	12.35	20.25	10.12	6.75	2.50	2.44	2.36
43	1.2	7.18	0.267	3.72	20.77	10.39	6.92	7.87	6.58	5.37
18	2.0	7.20	0.244	3.39	20.94	10.47	6.98	8.56	6.98	5.60
1	4.5	9.0	1.80	20.00	37.41	18.70	12.47	2.27	2.26	2.23
42	1.0	9	-	-	37.42	18.71	12.47	37.42	18.71	12.47
41	1.0	16.6 *	-	-	107.00	53.48	35.65	107.00	53.48	35.65
				Si (269.0 ± 5.19) [g/kg]						
44	4.0	196.4	9.84	5.01	-28.00	-14.00	-9.33	7.14	6.53	5.79
22	1.0	218	13.7	6.28	-19.67	-9.83	-6.56	3.66	3.48	3.24
43	1.2	222.0	5.27	2.37	-18.12	-9.06	-6.04	8.00	6.36	5.00
25	1.2	236.4	1.12	0.47	-12.56	-6.28	-4.19	11.54	6.14	4.15
17	1.0	237.2	1.14	0.48	-12.25	-6.13	-4.08	11.22	5.99	4.04
34	1.2	238.6	8.69	3.64	-11.74	-5.87	-3.91	3.36	3.01	2.61
37	1.2	242.55	0.413	0.17	-10.20	-5.10	-3.40	10.07	5.08	3.40
6	1.1	244.0	10.6	4.34	-9.64	-4.82	-3.22	2.29	2.12	1.90
18	2.0	255.6	1.09	0.43	-5.16	-2.58	-1.72	4.75	2.52	1.70
21	2.0	265.3	2.70	1.02	-1.43	-0.71	-0.48	0.99	0.63	0.45
27	1.1	272.0	5.00	1.84	1.16	0.58	0.39	0.53	0.42	0.32
1	4.5	278	14.0	5.05	3.28	1.64	1.09	0.60	0.57	0.53
39	1.1	293	18.0	6.14	9.26	4.63	3.09	1.32	1.28	1.22
12	1.1	300	60.0	20.00	11.95	5.98	3.99	0.52	0.51	0.51
29	1.2	320	15.8	4.94	19.67	9.83	6.56	3.18	3.07	2.89
26	1.2	330.0	8.50	2.58	23.52	11.76	7.84	6.86	6.13	5.29
41	1.0	550.7 *	-	-	108.60	54.31	36.21	108.60	54.31	36.21
42	1.0	587 *	-	-	122.60	61.31	40.88	122.60	61.31	40.88
				Ti (*3.25* ± *0.154*) [mg/kg]						
26	1.2	1.70 *	0.100	5.88	-20.14	-10.07	-6.71	12.28	8.44	6.16
33	1.2	1.86 *	0.114	6.12	-18.04	-9.02	-6.01	10.10	7.25	5.39
6	1.1	2.77	0.242	8.75	-6.30	-3.15	-2.10	1.91	1.69	1.45
28	1.0	2.87	0.286	9.98	-5.00	-2.50	-1.67	1.30	1.19	1.05
35	1.0	2.91	0.246	8.45	-4.39	-2.20	-1.46	1.31	1.17	1.00
14	1.0	2.91	0.106	3.64	-4.39	-2.20	-1.46	2.58	1.81	1.33
37	1.2	2.985	0.0118	0.39	-3.44	-1.72	-1.15	3.40	1.72	1.15
43	1.2	3.03	0.362	11.95	-2.86	-1.43	-0.95	0.59	0.56	0.51
36	1.2	3.040	0.0800	2.63	-2.73	-1.36	-0.91	1.89	1.21	0.86

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
17	1.0	3.118	0.0520	1.67	-1.72	-0.86	-0.57	1.42	0.81	0.56
21	2.0	3.21	0.100	3.12	-0.52	-0.26	-0.17	0.32	0.22	0.16
25	1.2	3.329	0.0921	2.77	1.02	0.51	0.34	0.66	0.44	0.32
18	2.0	3.35	0.103	3.07	1.30	0.65	0.43	0.78	0.54	0.40
36	1.1	3.40	0.330	9.71	1.95	0.97	0.65	0.44	0.41	0.37
39	1.1	3.510	0.0600	1.71	3.38	1.69	1.13	2.66	1.57	1.09
1	4.5	3.54	0.700	19.79	3.74	1.87	1.25	0.41	0.40	0.39
19	1.3	3.63	0.299	8.24	4.94	2.47	1.65	1.23	1.13	1.01
27	1.1	3.74	0.100	2.67	6.37	3.18	2.12	3.88	2.67	1.95
34	1.2	3.77	0.285	7.57	6.72	3.36	2.24	1.75	1.60	1.41
22	1.0	3.79	0.239	6.31	7.02	3.51	2.34	2.15	1.90	1.63
44	4.0	3.79	0.213	5.61	7.06	3.53	2.35	2.40	2.07	1.73
12	1.1	4.0	1.00	25.00	9.74	4.87	3.25	0.75	0.74	0.73
31	1.1	4.61 *	0.298	6.46	17.67	8.84	5.89	4.42	4.06	3.61
11	1.1	5.4 *	1.00	18.42	28.32	14.16	9.44	2.17	2.16	2.12
29	1.2	7.15 *	0.210	2.94	50.67	25.33	16.89	17.44	14.98	12.49
41	1.0	8 *	-	-	61.71	30.85	20.57	61.71	30.85	20.57
42	1.0	15 *	-	-	152.60	76.32	50.88	152.60	76.32	50.88
				Ag (*0.31 ± 0.058*) [mg/kg]						
39	1.1	4.42	0.550	12.44	141.10	70.54	47.03	7.47	7.44	7.39
41	1.0	257	-	-	8800.0	4400.0	2933.0	8800.0	4400.0	2933.0
				As (18.1 ± 1.88) [mg/kg]						
17	1.0	3.0	3.00	100.0	-16.13	-8.06	-5.38	4.81	4.27	3.67
22	1.0	16.1	8.70	54.04	-2.14	-1.07	-0.71	0.23	0.22	0.22
4	1.0	17.3	-	-	-0.85	-0.43	-0.28	0.85	0.43	0.28
14	1.0	17.5	1.00	5.71	-0.64	-0.32	-0.21	0.44	0.28	0.20
37	1.2	18.08	0.496	2.74	-0.02	-0.01	-0.01	0.02	0.01	0.01
35	1.0	19.9	2.80	14.07	1.92	0.96	0.64	0.61	0.53	0.45
21	2.0	20.0	1.20	6.00	2.03	1.02	0.68	1.25	0.85	0.62
19	1.3	20.0	3.00	15.00	2.03	1.02	0.68	0.60	0.54	0.46
38	5.0	20.4	2.03	9.97	2.43	1.21	0.81	1.02	0.82	0.66
7	8.1	20.5	-	-	2.56	1.28	0.85	2.56	1.28	0.85
34	1.2	22.0	5.00	22.73	4.17	2.08	1.39	0.77	0.73	0.68
31	1.1	32.6 *	6.13	18.83	15.43	7.72	5.15	2.33	2.25	2.14
41	1.0	52.0 *	-	-	36.21	18.10	12.07	36.21	18.10	12.07
				Ba (316 ± 21.3) [mg/kg]						
7	8.1	261	-	-	-5.18	-2.59	-1.73	5.18	2.59	1.73
21	2.0	282.0	8.00	2.84	-3.20	-1.60	-1.07	2.56	1.50	1.03
38	5.0	310	99.0	31.94	-0.56	-0.28	-0.19	0.06	0.06	0.06
27	1.1	323	14.0	4.33	0.66	0.33	0.22	0.40	0.28	0.20
39	1.1	324	41.0	12.65	0.75	0.38	0.25	0.19	0.17	0.15
24	1.2	352	33.0	9.38	3.39	1.69	1.13	1.04	0.92	0.78
31	1.1	361.8	3.28	0.91	4.31	2.16	1.44	4.12	2.13	1.43
22	1.0	368	15.0	4.08	4.89	2.45	1.63	2.83	2.00	1.48
37	1.2	403.1	9.30	2.31	8.19	4.10	2.73	6.17	3.75	2.62
41	1.0	645 *	0.00	0.00	30.95	15.48	10.32	30.95	15.48	10.32
6	1.1	710 *	32.0	4.51	37.07	18.53	12.36	11.68	10.26	8.72

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z scores			u scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
19	1.3	733 *	92.0	12.55	39.23	19.62	13.08	4.50	4.42	4.28
43	1.2	1260 *	174	13.81	88.82	44.41	29.61	5.42	5.39	5.34
4	1.0	4670 *	-	-	409.60	204.80	136.50	409.60	204.80	136.50
Br (*102.0* ± *8.14*) [mg/kg]										
4	1.0	51	-	-	-12.54	-6.27	-4.18	12.54	6.27	4.18
27	1.1	70.00	7.00	10.00	-7.87	-3.93	-2.62	3.95	2.98	2.28
6	1.1	74.00	7.00	9.46	-6.88	-3.44	-2.30	3.46	2.61	1.99
33	1.2	78	13.4	17.18	-5.96	-2.98	-1.99	1.74	1.55	1.34
35	1.0	80.9	8.00	9.89	-5.19	-2.59	-1.73	2.35	1.85	1.45
37	1.2	85.1	0.54	0.64	-4.15	-2.08	-1.39	4.12	2.07	1.38
14	1.0	86.9	3.00	3.45	-3.71	-1.86	-1.24	2.99	1.74	1.20
36	1.2	96.0	3.00	3.13	-1.48	-0.74	-0.49	1.19	0.69	0.48
36	1.1	96.0	9.00	9.38	-1.48	-0.74	-0.49	0.61	0.49	0.40
40	1.1	98.0	5.00	5.10	-0.98	-0.49	-0.33	0.62	0.42	0.30
1	4.5	99.1	8.00	8.07	-0.72	-0.36	-0.24	0.33	0.26	0.20
17	1.0	109	13.0	11.93	1.72	0.86	0.57	0.51	0.46	0.39
38	5.0	111.1	9.04	8.14	2.24	1.12	0.75	0.92	0.75	0.60
21	2.0	113.0	8.00	7.08	2.70	1.35	0.90	1.23	0.96	0.75
22	1.0	118.0	5.30	4.49	3.93	1.97	1.31	2.40	1.65	1.20
34	1.2	124	13.0	10.48	5.41	2.70	1.80	1.62	1.44	1.23
28	1.0	140	13.0	9.29	9.34	4.67	3.11	2.79	2.48	2.13
31	1.1	144.8	8.20	5.66	10.53	5.26	3.51	4.68	3.71	2.91
42	1.0	240 *	-	-	33.93	16.96	11.31	33.93	16.96	11.31
41	1.0	312 *	-	-	51.63	25.82	17.21	51.63	25.82	17.21
Cd (*0.390* ± *0.0719*) [mg/kg]										
7	8.1	0.58	-	-	5.29	2.64	1.76	5.29	2.64	1.76
25	1.2	0.76	0.562	73.64	10.39	5.19	3.46	0.66	0.66	0.65
22	1.0	2.3	1.80	78.26	53.14	26.57	17.71	1.06	1.06	1.06
Ce (*53.0* ± *4.67*) [mg/kg]										
21	2.0	51.0 *	3.20	6.27	-0.86	-0.43	-0.29	0.51	0.35	0.26
22	1.0	52.7	2.60	4.93	-0.13	-0.06	-0.04	0.09	0.06	0.04
39	1.1	52.9	1.80	3.40	-0.04	-0.02	-0.01	0.03	0.02	0.01
31	1.1	53.13	0.920	1.73	0.06	0.03	0.02	0.05	0.03	0.02
24	1.2	59.0 *	2.00	3.39	2.57	1.29	0.86	1.95	1.18	0.82
38	5.0	60.09 *	0.248	0.41	3.04	1.52	1.01	3.03	1.52	1.01
27	1.1	71.0 *	3.00	4.23	7.72	3.86	2.57	4.74	3.25	2.36
41	1.0	128 *	-	-	32.16	16.08	10.72	32.16	16.08	10.72
4	1.0	1250 *	-	-	513.20	256.60	171.10	513.20	256.60	171.10
Co (10.5 ± 1.18) [mg/kg]										
6	1.1	7.5 *	1.20	16.00	-5.09	-2.54	-1.70	2.24	1.78	1.40
37	1.2	10.1 *	1.47	14.63	-0.76	-0.38	-0.25	0.28	0.24	0.19
7	8.1	10.9	-	-	0.68	0.34	0.23	0.68	0.34	0.23
21	2.0	11.20	0.500	4.46	1.19	0.59	0.40	0.91	0.55	0.38
25	1.2	11.4	5.32	46.81	1.48	0.74	0.49	0.16	0.16	0.16
40	1.1	12.6 *	1.30	10.29	3.61	1.81	1.20	1.49	1.21	0.97

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
33	1.2	102.6 *	7.57	7.38	156.10	78.07	52.05	12.12	12.01	11.84
4	1.0	323 *	-	-	530.10	265.00	176.70	530.10	265.00	176.70
					Cr (99.9 ± 8.00) [mg/kg]					
37	1.2	67.3	1.43	2.13	-8.16	-4.08	-2.72	7.68	4.02	2.70
6	1.1	74.0	8.00	10.81	-6.48	-3.24	-2.16	2.90	2.29	1.80
31	1.1	84	40.0	47.71	-4.01	-2.00	-1.34	0.40	0.39	0.38
1	4.5	86	50.0	58.39	-3.57	-1.79	-1.19	0.28	0.28	0.28
19	1.3	86	10.0	11.63	-3.48	-1.74	-1.16	1.29	1.09	0.89
27	1.1	90	10.0	11.11	-2.48	-1.24	-0.83	0.92	0.77	0.63
39	1.1	94.4	7.00	7.42	-1.38	-0.69	-0.46	0.68	0.52	0.40
21	2.0	96.8	3.30	3.41	-0.78	-0.39	-0.26	0.60	0.36	0.25
35	1.0	109.0	1.00	0.92	2.28	1.14	0.76	2.21	1.13	0.76
38	5.0	112.3	3.54	3.15	3.09	1.55	1.03	2.32	1.41	0.99
18	2.0	127.0	8.00	6.30	6.78	3.39	2.26	3.03	2.40	1.88
25	1.2	140	17.5	12.53	9.97	4.99	3.32	2.22	2.07	1.88
29	1.2	140	14.0	10.00	10.03	5.02	3.35	2.75	2.49	2.18
22	1.0	207 *	26.3	12.71	26.80	13.40	8.93	4.03	3.90	3.71
17	1.0	251 *	28.0	11.16	37.81	18.91	12.60	5.34	5.19	4.96
32	1.3	258 *	10.0	3.88	39.56	19.78	13.19	14.68	12.35	10.13
41	1.0	948 *	-	-	212.20	106.10	70.74	212.20	106.10	70.74
					Cs [mg/kg]					
27	1.1	6.0	2.00	33.33	-	-	-	-	-	-
38	5.0	7.38	0.364	4.93	-	-	-	-	-	-
22	1.0	8.0	1.40	17.50	-	-	-	-	-	-
31	1.1	9.16	0.240	2.62	-	-	-	-	-	-
					Cu (16.9 ± 1.77) [mg/kg]					
27	1.1	11.0	2.00	18.18	-6.68	-3.34	-2.23	2.70	2.21	1.78
19	1.3	15.0	2.00	13.33	-2.15	-1.08	-0.72	0.87	0.71	0.57
33	1.2	15.9	1.48	9.34	-1.19	-0.59	-0.40	0.61	0.46	0.35
32	1.3	16.6	3.80	22.89	-0.34	-0.17	-0.11	0.08	0.07	0.06
7	8.1	16.8	-	-	-0.11	-0.06	-0.04	0.11	0.06	0.04
21	2.0	17.00	0.500	2.94	0.11	0.06	0.04	0.10	0.05	0.04
37	1.2	19.79	0.744	3.76	3.27	1.64	1.09	2.50	1.51	1.05
36	1.2	21.2	3.60	16.98	4.87	2.43	1.62	1.16	1.07	0.96
14	1.0	21.3	1.00	4.69	4.98	2.49	1.66	3.30	2.17	1.55
35	1.0	21.6	2.80	12.96	5.32	2.66	1.77	1.60	1.42	1.22
24	7.2	22.30	0.370	1.66	6.11	3.06	2.04	5.64	2.99	2.02
6	1.1	22.9	2.70	11.79	6.79	3.40	2.26	2.11	1.86	1.59
24	1.2	23.0	3.00	13.04	6.91	3.45	2.30	1.95	1.75	1.52
1	4.5	24.5	2.00	8.15	8.64	4.32	2.88	3.49	2.86	2.30
25	1.2	26.2	3.59	13.73	10.48	5.24	3.49	2.50	2.31	2.07
28	1.0	27.0	4.00	14.81	11.43	5.72	3.81	2.47	2.31	2.11
17	1.0	49.0 *	6.00	12.24	36.34	18.17	12.11	5.29	5.13	4.89
40	1.1	52.4 *	5.36	10.23	40.19	20.10	13.40	6.54	6.29	5.94
43	1.2	61.4 *	7.64	12.44	50.38	25.19	16.79	5.79	5.68	5.50
22	1.0	65.2 *	4.80	7.36	54.68	27.34	18.23	9.90	9.44	8.81
41	1.0	144 *	-	-	143.90	71.95	47.97	143.90	71.95	47.97

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
4	1.0	173 *	-	-	176.70	88.37	58.91	176.70	88.37	58.91
29	1.2	262 *	13.0	4.96	277.50	138.70	92.50	18.81	18.68	18.47
					Eu [mg/kg]					
38	5.0	0.845	0.0540	6.39	-	-	-	-	-	-
					Ga (12.0 ± 1.32)[mg/kg]					
22	1.0	8.6	2.00	23.26	-5.15	-2.57	-1.72	1.61	1.42	1.21
14	1.0	11.3	1.00	8.85	-1.06	-0.53	-0.35	0.58	0.42	0.32
21	2.0	11.30	0.300	2.65	-1.06	-0.53	-0.35	0.97	0.52	0.35
37	1.2	11.60	0.593	5.11	-0.60	-0.30	-0.20	0.45	0.28	0.19
1	4.5	14.2	2.00	14.06	3.37	1.69	1.12	1.06	0.93	0.79
6	1.1	14.6	1.90	13.01	3.94	1.97	1.31	1.29	1.12	0.95
41	1.0	55 *	-	-	65.12	32.56	21.71	65.12	32.56	21.71
					Hf [mg/kg]					
21	2.0	5.75	0.750	13.04	-	-	-	-	-	-
38	5.0	5.80	0.489	8.43	-	-	-	-	-	-
37	1.2	6.02	0.515	8.56	-	-	-	-	-	-
					I (44.2 ± 4.00) [mg/kg]					
27	1.1	38.0 *	3.00	7.89	-3.10	-1.55	-1.03	1.72	1.24	0.92
31	1.1	51.4	2.53	4.93	3.58	1.79	1.19	2.22	1.51	1.10
21	2.0	52.1	3.60	6.91	3.95	1.98	1.32	1.92	1.47	1.13
37	1.2	55.8	9.72	17.44	5.78	2.89	1.93	1.16	1.10	1.01
41	1.0	74 *	-	-	14.91	7.45	4.97	14.91	7.45	4.97
					La (26.9 ± 2.63) [mg/kg]					
39	1.1	13.70 *	0.800	5.84	-10.07	-5.04	-3.36	8.60	4.82	3.29
22	1.0	26.4 *	1.70	6.44	-0.38	-0.19	-0.13	0.23	0.16	0.12
31	1.1	26.62 *	0.510	1.92	-0.21	-0.11	-0.07	0.20	0.10	0.07
38	5.0	29.52	0.480	1.63	2.00	1.00	0.67	1.88	0.98	0.66
21	2.0	29.9	2.80	9.36	2.29	1.14	0.76	0.97	0.78	0.62
24	1.2	30.0	3.00	10.00	2.37	1.18	0.79	0.95	0.78	0.63
6	1.1	35.7 *	5.10	14.29	6.71	3.36	2.24	1.67	1.54	1.37
27	1.1	38.0 *	4.00	10.53	8.47	4.23	2.82	2.64	2.32	1.98
41	1.0	68 *	-	-	31.35	15.68	10.45	31.35	15.68	10.45
					Mn (1050 ± 59.0) [mg/kg]					
33	1.2	613	86.8	14.16	-14.81	-7.41	-4.94	4.76	4.16	3.52
35	1.0	822	130	15.82	-7.74	-3.87	-2.58	1.71	1.60	1.45
7	8.1	836	-	-	-7.26	-3.63	-2.42	7.26	3.63	2.42
4	1.0	884	-	-	-5.63	-2.82	-1.88	5.63	2.82	1.88
17	1.0	899	19.0	2.11	-5.12	-2.56	-1.71	4.31	2.44	1.67
14	1.0	917.2	3.00	0.33	-4.51	-2.25	-1.50	4.48	2.25	1.50
28	1.0	935	88.0	9.41	-3.90	-1.95	-1.30	1.24	1.09	0.92
37	1.2	938	15.5	1.66	-3.81	-1.91	-1.27	3.37	1.84	1.25
25	1.2	954	58.1	6.10	-3.26	-1.63	-1.09	1.47	1.16	0.91
6	1.1	956	125	13.08	-3.19	-1.59	-1.06	0.73	0.68	0.61

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
19	1.3	957	51.0	5.33	-3.16	-1.58	-1.05	1.58	1.19	0.91
32	1.3	981	16.0	1.63	-2.34	-1.17	-0.78	2.06	1.13	0.77
24	7.2	1012	32.0	3.16	-1.29	-0.64	-0.43	0.87	0.57	0.40
39	1.1	1040	40.0	3.85	-0.34	-0.17	-0.11	0.20	0.14	0.10
1	4.5	1050	100	9.52	0.00	0.00	0.00	0.00	0.00	0.00
36	1.1	1052	99.0	9.41	0.07	0.03	0.02	0.02	0.02	0.02
27	1.1	1077	47.0	4.36	0.92	0.46	0.31	0.49	0.36	0.27
36	1.2	1100	47.0	4.27	1.70	0.85	0.57	0.90	0.66	0.50
34	1.2	1122	180	16.04	2.44	1.22	0.81	0.39	0.38	0.36
21	2.0	1127	65.0	5.77	2.61	1.31	0.87	1.08	0.88	0.70
22	1.0	1140	53.4	4.68	3.05	1.53	1.02	1.48	1.13	0.87
44	4.0	1229	147	11.94	6.08	3.04	2.03	1.20	1.13	1.05
40	1.1	1245	65.0	5.22	6.62	3.31	2.21	2.73	2.22	1.78
18	2.0	1275	63.0	4.94	7.63	3.82	2.54	3.24	2.61	2.07
31	1.1	1290	49.8	3.86	8.16	4.08	2.72	4.16	3.12	2.37
26	1.2	2000 *	600	30.00	32.23	16.11	10.74	1.58	1.58	1.57
43	1.2	2100 *	248	11.81	35.62	17.81	11.87	4.20	4.12	3.99
41	1.0	2500 *	-	-	49.19	24.59	16.40	49.19	24.59	16.40
29	1.2	3230 *	100	3.10	73.95	36.98	24.65	20.91	18.78	16.33
Mo (3.41 ± 0.454) [mg/kg]										
41	1.0	27	-	-	104.00	52.01	34.68	104.00	52.01	34.68
Nb (10.4 ± 1.17) [mg/kg]										
4	1.0	3.8 *	-	-	-11.29	-5.64	-3.76	11.29	5.64	3.76
43	1.2	6.75 *	0.830	12.30	-6.24	-3.12	-2.08	3.60	2.55	1.88
6	1.1	9.6 *	1.30	13.54	-1.37	-0.68	-0.46	0.56	0.46	0.37
22	1.0	9.90 *	0.580	5.86	-0.86	-0.43	-0.29	0.61	0.38	0.27
36	1.1	11.0	1.00	9.09	1.03	0.51	0.34	0.52	0.39	0.30
36	1.2	11.0	1.00	9.09	1.03	0.51	0.34	0.52	0.39	0.30
21	2.0	11.20	0.300	2.68	1.37	0.68	0.46	1.22	0.66	0.45
31	1.1	16.2 *	1.68	10.38	9.89	4.94	3.30	3.25	2.82	2.38
41	1.0	31 *	-	-	35.23	17.61	11.74	35.23	17.61	11.74
Nd (20.9 ± 2.12) [mg/kg]										
22	1.0	20.70	1.70	8.21	-0.19	-0.09	-0.06	0.10	0.07	0.06
21	2.0	24.60	1.40	5.69	3.50	1.75	1.17	2.11	1.46	1.07
24	1.2	26.00	5.00	19.23	4.82	2.41	1.61	1.00	0.94	0.86
31	1.1	29.39	0.29	0.99	8.03	4.01	2.68	7.74	3.98	2.66
6	1.1	38.00 *	5.00	13.16	16.16	8.08	5.39	3.35	3.15	2.89
Ni (27.8 ± 2.70) [mg/kg]										
43	1.2	7.4 *	1.87	25.17	-15.11	-7.56	-5.04	8.84	6.21	4.57
7	8.1	18.7	-	-	-6.75	-3.38	-2.25	6.75	3.38	2.25
14	1.0	19.0	2.00	10.53	-6.53	-3.26	-2.18	3.65	2.62	1.95
22	1.0	22.4	5.00	22.32	-4.01	-2.00	-1.34	1.04	0.95	0.84
18	2.0	24.0	3.00	12.50	-2.82	-1.41	-0.94	1.16	0.94	0.75
19	1.3	25.0	4.00	16.00	-2.08	-1.04	-0.69	0.66	0.58	0.49
25	1.2	28.0	5.02	17.95	0.12	0.06	0.04	0.03	0.03	0.02

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	29.8	1.62	5.42	1.48	0.74	0.49	0.95	0.63	0.46
21	2.0	30.70	0.500	1.63	2.15	1.08	0.72	2.02	1.06	0.71
24	7.2	31.2	2.20	7.05	2.52	1.26	0.84	1.32	0.98	0.74
35	1.0	31.5	1.00	3.17	2.75	1.37	0.91	2.20	1.29	0.89
27	1.1	32.0	5.00	15.63	3.12	1.56	1.04	0.81	0.74	0.65
6	1.1	32.3	1.55	4.81	3.30	1.65	1.10	2.17	1.43	1.03
36	1.2	41.0	4.00	9.76	9.79	4.90	3.26	3.13	2.74	2.32
33	1.2	66.8 *	3.75	5.62	28.89	14.45	9.63	9.77	8.43	7.06
1	4.5	80 *	30.0	37.41	38.87	19.44	12.96	1.75	1.74	1.73
Pb (49.7 ± 4.42) [mg/kg]										
35	1.0	11.0	2.60	23.64	-17.52	-8.76	-5.84	11.34	7.55	5.44
4	1.0	24.6	-	-	-11.37	-5.68	-3.79	11.37	5.68	3.79
7	8.1	31.7	-	-	-8.15	-4.08	-2.72	8.15	4.08	2.72
36	1.2	33.0	7.00	21.21	-7.56	-3.78	-2.52	2.28	2.02	1.73
36	1.1	36.0	5.00	13.89	-6.20	-3.10	-2.07	2.51	2.05	1.65
34	1.2	37.7	8.00	21.22	-5.43	-2.72	-1.81	1.45	1.31	1.16
17	1.0	41.0	4.00	9.76	-3.94	-1.97	-1.31	1.90	1.46	1.12
31	1.1	44.4	7.08	15.96	-2.41	-1.21	-0.80	0.72	0.64	0.55
19	1.3	45.0	7.00	15.56	-2.13	-1.06	-0.71	0.64	0.57	0.49
37	1.2	46.5	0.608	1.31	-1.45	-0.72	-0.48	1.39	0.72	0.48
21	2.0	50.6	2.20	4.35	0.41	0.20	0.14	0.29	0.18	0.13
6	1.1	51.4	5.20	10.12	0.77	0.38	0.26	0.30	0.25	0.20
27	1.1	52.0	8.00	15.38	1.04	0.52	0.35	0.28	0.25	0.22
14	1.0	52.8	2.00	3.79	1.40	0.70	0.47	1.04	0.64	0.45
33	1.2	56.0	8.91	15.91	2.85	1.43	0.95	0.69	0.63	0.57
40	1.1	58.0	6.00	10.34	3.76	1.88	1.25	1.30	1.11	0.93
25	1.2	61	10.2	16.77	4.99	2.50	1.66	1.06	0.99	0.91
32	1.3	63	23.0	36.51	6.02	3.01	2.01	0.58	0.57	0.56
28	1.0	64	21.0	32.81	6.48	3.24	2.16	0.68	0.67	0.65
22	1.0	72	12.6	17.62	9.87	4.94	3.29	1.70	1.63	1.53
39	1.1	92.2 *	1.90	2.06	19.25	9.62	6.42	14.59	8.84	6.17
41	1.0	151 *	-	-	45.87	22.94	15.29	45.87	22.94	15.29
42	1.0	230 *	-	-	81.65	40.82	27.22	81.65	40.82	27.22
Pr [mg/kg]										
22	1.0	4.4	1.20	27	-	-	-	-	-	-
Rb (90.7 ± 7.37) [mg/kg]										
4	1.0	39.2 *	-	-	-13.99	-7.00	-4.66	13.99	7.00	4.66
43	1.2	65.6	7.77	11.84	-6.82	-3.41	-2.27	2.92	2.35	1.86
35	1.0	69.9	4.70	6.72	-5.65	-2.83	-1.88	3.48	2.38	1.73
27	1.1	70.0	7.00	10.00	-5.62	-2.81	-1.87	2.62	2.04	1.58
32	1.3	70.8	6.90	9.75	-5.41	-2.70	-1.80	2.55	1.97	1.53
14	1.0	76.7	3.00	3.91	-3.80	-1.90	-1.27	2.95	1.76	1.22
38	5.0	79.0	14.0	17.72	-3.18	-1.59	-1.06	0.81	0.74	0.66
33	1.2	79.5	12.4	15.57	-3.06	-1.53	-1.02	0.87	0.78	0.68
36	1.2	88.0	3.00	3.41	-0.73	-0.37	-0.24	0.57	0.34	0.24
36	1.1	88.0	4.00	4.55	-0.73	-0.37	-0.24	0.50	0.32	0.23
34	1.2	88.3	9.00	10.19	-0.65	-0.33	-0.22	0.25	0.21	0.17

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	88.5	6.50	7.34	-0.60	-0.30	-0.20	0.29	0.22	0.17
17	1.0	91.0	4.00	4.40	0.08	0.04	0.03	0.06	0.04	0.03
37	1.2	91.9	0.59	0.64	0.34	0.17	0.11	0.33	0.17	0.11
21	2.0	94.5	2.50	2.65	1.03	0.52	0.34	0.85	0.49	0.34
1	4.5	98	10.0	10.24	1.89	0.94	0.63	0.65	0.56	0.47
22	1.0	99.6	4.40	4.42	2.42	1.21	0.81	1.55	1.04	0.75
39	1.1	101.0	1.10	1.09	2.80	1.40	0.93	2.68	1.38	0.93
24	1.2	102.0	9.00	8.82	3.07	1.54	1.02	1.16	0.97	0.79
28	1.0	108	10.0	9.26	4.70	2.35	1.57	1.62	1.39	1.16
31	1.1	115.0	4.18	3.63	6.61	3.31	2.20	4.37	2.88	2.06
12	1.1	140 *	40.0	28.57	13.39	6.70	4.46	1.23	1.21	1.19
41	1.0	282 *	-	-	51.97	25.98	17.32	51.97	25.98	17.32
29	1.2	334 *	44.0	13.17	66.09	33.05	22.03	5.51	5.45	5.36
44	4.0	365 *	23.0	6.30	74.52	37.26	24.84	11.78	11.36	10.75
Sb (*0.80* ± *0.132*) [mg/kg]										
38	5.0	0.970	0.0900	9.28	2.66	1.33	0.89	1.57	1.10	0.81
Sc (*10.1* ± *1.14*) [mg/kg]										
21	2.0	13.20	0.700	5.30	5.44	2.72	1.81	3.43	2.32	1.68
6	1.1	32.3	9.60	29.72	38.92	19.46	12.97	2.31	2.30	2.28
38	5.0	89.237	0.0580	0.06	138.70	69.37	46.25	138.00	69.28	46.22
41	1.0	366 *	-	-	624.00	312.00	208.00	624.00	312.00	208.00
Se (*0.475* ± *0.0850*) [mg/kg]										
14	1.0	8.50	0.400	4.71	188.80	94.42	62.95	19.95	19.62	19.12
Sm [mg/kg]										
38	5.0	5.075	0.0360	0.71	-	-	-	-	-	-
Sn (*4.62* ± *0.587*) [mg/kg]										
21	2.0	5.38	0.600	11.15	2.59	1.30	0.86	1.14	0.91	0.71
27	1.1	8.0	2.00	25.00	11.52	5.76	3.84	1.67	1.62	1.55
37	1.2	24.7	2.06	8.32	68.48	34.24	22.83	9.67	9.40	8.98
41	1.0	32	-	-	93.29	46.64	31.10	93.29	46.64	31.10
Sr [mg/kg]										
4	1.0	86 *	-	-	-	-	-	-	-	-
7	8.1	155	-	-	-	-	-	-	-	-
35	1.0	161	12.4	7.72	-	-	-	-	-	-
14	1.0	172.6	6.00	3.48	-	-	-	-	-	-
32	1.3	173	22.0	12.72	-	-	-	-	-	-
16	1.1	174	24.0	13.79	-	-	-	-	-	-
43	1.2	178	21.0	11.80	-	-	-	-	-	-
6	1.1	188.0	6.00	3.19	-	-	-	-	-	-
33	1.2	194	26.7	13.74	-	-	-	-	-	-
12	1.1	196	36.0	18.37	-	-	-	-	-	-
27	1.1	200.0	7.00	3.50	-	-	-	-	-	-
36	1.1	206.0	8.00	3.88	-	-	-	-	-	-

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	z scores k = 0.5	z scores k = 1.0	z scores k = 1.5	u scores k = 0.5	u scores k = 1.0	u scores k = 1.5
39	1.1	206	12.0	5.83	-	-	-	-	-	-
1	4.5	208	30.0	14.44	-	-	-	-	-	-
37	1.2	209.45	0.537	0.26	-	-	-	-	-	-
24	1.2	211	10.0	4.74	-	-	-	-	-	-
34	1.2	211	17.0	8.06	-	-	-	-	-	-
21	2.0	212.0	4.00	1.89	-	-	-	-	-	-
36	1.1	214.0	7.00	3.27	-	-	-	-	-	-
40	1.1	221	15.0	6.79	-	-	-	-	-	-
28	1.0	223	20.0	8.97	-	-	-	-	-	-
22	1.0	224.0	9.80	4.38	-	-	-	-	-	-
44	4.0	226	30.8	13.65	-	-	-	-	-	-
31	1.1	265.9	7.29	2.74	-	-	-	-	-	-
42	1.0	410 *	-	-	-	-	-	-	-	-
17	1.0	541 *	10.0	1.85	-	-	-	-	-	-
29	1.2	643 *	50.0	7.78	-	-	-	-	-	-
41	1.0	667 *	-	-	-	-	-	-	-	-
				Ta [mg/kg]						
38	5.0	1.15	0.226	19.60	-	-	-	-	-	-
41	1.0	97	-	-	-	-	-	-	-	-
				Tb [mg/kg]						
38	5.0	0.84	0.286	34.17	-	-	-	-	-	-
				Th (*7.90* ± *0.926*) [mg/kg]						
22	1.0	6.30	0.900	14.29	-3.46	-1.73	-1.15	1.58	1.24	0.97
38	5.0	7.93	0.167	2.11	0.07	0.03	0.02	0.06	0.03	0.02
21	2.0	9.27	0.470	5.07	2.96	1.48	0.99	2.08	1.32	0.93
37	1.2	9.82	0.669	6.81	4.14	2.07	1.38	2.36	1.68	1.24
				U (*1.80* ± *0.264*) [mg/kg]						
21	2.0	2.30	0.220	9.57	3.79	1.90	1.27	1.95	1.46	1.11
37	1.2	5.59	0.675	12.08	28.76	14.38	9.59	5.51	5.23	4.85
				V (*95.8* ± *7.72*) [mg/kg]						
7	8.1	80.2	-	-	-4.05	-2.02	-1.35	4.05	2.02	1.35
6	1.1	96	14.0	14.58	0.05	0.03	0.02	0.01	0.01	0.01
27	1.1	97	10.0	10.31	0.31	0.16	0.10	0.11	0.10	0.08
37	1.2	105.5	4.60	4.36	2.53	1.26	0.84	1.62	1.08	0.78
21	2.0	109.0	3.00	2.75	3.42	1.71	1.14	2.70	1.60	1.10
17	1.0	111.0	9.00	8.11	3.94	1.97	1.31	1.55	1.28	1.04
43	1.2	315 *	43.1	13.68	56.84	28.42	18.95	5.07	5.01	4.91
				Y (22.0 ± 2.21) [mg/kg]						
4	1.0	8.3	-	-	-12.40	-6.20	-4.13	12.40	6.20	4.13
14	1.0	12.70	0.500	3.94	-8.42	-4.21	-2.81	7.67	4.10	2.77
28	1.0	17.0	2.00	11.76	-4.53	-2.26	-1.51	2.19	1.68	1.29
37	1.2	17.44	0.531	3.04	-4.13	-2.06	-1.38	3.72	2.01	1.36
34	1.2	17.5	4.00	22.86	-4.07	-2.04	-1.36	1.08	0.98	0.87

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
1	4.5	18	10.0	55.94	-3.73	-1.87	-1.24	0.41	0.40	0.39
36	1.1	20.0	2.00	10.00	-1.81	-0.90	-0.60	0.88	0.67	0.52
31	1.1	21.6	1.04	4.81	-0.35	-0.18	-0.12	0.26	0.16	0.11
6	1.1	21.8	2.50	11.47	-0.18	-0.09	-0.06	0.07	0.06	0.05
36	1.2	22.0	2.00	9.09	0.00	0.00	0.00	0.00	0.00	0.00
22	1.0	22.6	1.10	4.87	0.54	0.27	0.18	0.38	0.24	0.17
21	2.0	23.00	0.900	3.91	0.90	0.45	0.30	0.70	0.42	0.29
43	1.2	28.4	3.38	11.90	5.79	2.90	1.93	1.80	1.59	1.35
27	1.1	30.0	3.00	10.00	7.24	3.62	2.41	2.50	2.15	1.79
19	1.3	44.0 *	3.00	6.82	19.91	9.95	6.64	6.88	5.90	4.92
41	1.0	67 *	-	-	40.72	20.36	13.57	40.72	20.36	13.57
Yb [mg/kg]										
38	5.0	1.87	0.250	13.37	-	-	-	-	-	-
Zn (145 ± 11.0) [mg/kg]										
4	1.0	53.1	-	-	-16.76	-8.38	-5.59	16.76	8.38	5.59
35	1.0	73	10.0	13.70	-13.13	-6.57	-4.38	6.31	4.85	3.74
17	1.0	89.0	4.00	4.49	-10.21	-5.11	-3.40	8.25	4.80	3.31
33	1.2	98.1	8.98	9.16	-8.56	-4.28	-2.85	4.46	3.31	2.51
32	1.3	115.3	4.30	3.73	-5.42	-2.71	-1.81	4.26	2.52	1.75
14	1.0	124.1	4.00	3.22	-3.81	-1.91	-1.27	3.08	1.79	1.23
7	8.1	126	-	-	-3.47	-1.73	-1.16	3.47	1.73	1.16
18	2.0	129.0	8.00	6.20	-2.92	-1.46	-0.97	1.65	1.18	0.87
6	1.1	129.0	9.00	6.98	-2.92	-1.46	-0.97	1.52	1.13	0.85
11	1.1	140	10.0	7.14	-0.91	-0.46	-0.30	0.44	0.34	0.26
36	1.2	141.0	7.00	4.96	-0.73	-0.36	-0.24	0.45	0.31	0.22
37	1.2	144.2	1.09	0.75	-0.14	-0.07	-0.05	0.14	0.07	0.05
25	1.2	146	15.5	10.63	0.13	0.06	0.04	0.04	0.04	0.03
43	1.2	150	18.0	12.00	0.91	0.46	0.30	0.27	0.24	0.21
21	2.0	150.0	3.00	2.00	0.91	0.46	0.30	0.80	0.44	0.30
19	1.3	151.0	9.00	5.96	1.09	0.55	0.36	0.57	0.42	0.32
44	4.0	152	27.5	18.05	1.34	0.67	0.45	0.26	0.25	0.23
36	1.1	154	15.0	9.74	1.64	0.82	0.55	0.56	0.48	0.40
27	1.1	155.0	7.00	4.52	1.82	0.91	0.61	1.13	0.77	0.56
22	1.0	157.0	7.70	4.90	2.19	1.09	0.73	1.27	0.90	0.66
24	1.2	157	12.0	7.64	2.19	1.09	0.73	0.91	0.74	0.59
39	1.1	158.1	4.20	2.66	2.39	1.19	0.80	1.90	1.12	0.77
40	1.1	165.0	6.00	3.64	3.65	1.82	1.22	2.46	1.60	1.14
28	1.0	166	15.0	9.04	3.83	1.92	1.28	1.32	1.13	0.94
34	1.2	171	15.0	8.77	4.74	2.37	1.58	1.63	1.40	1.17
24	7.2	175	11.0	6.29	5.47	2.74	1.82	2.44	1.93	1.52
31	1.1	201	12.2	6.08	10.18	5.09	3.39	4.17	3.40	2.73
1	4.5	228	100	43.96	15.04	7.52	5.02	0.82	0.82	0.81
42	1.0	240	-	-	17.32	8.66	5.78	17.32	8.66	5.78
29	1.2	356 *	51.0	14.33	38.48	19.24	12.83	4.11	4.05	3.94
41	1.0	434 *	-	-	52.70	26.35	17.57	52.70	26.35	17.57

Zr (222 ± 15.8) [mg/kg]

28	1.0	14.0 *	2.00	14.29	-26.41	-13.21	-8.81	25.60	13.10	8.77
4	1.0	85	-	-	-17.40	-8.70	-5.80	17.40	8.70	5.80
19	1.3	129	10.0	7.75	-11.81	-5.91	-3.94	7.31	4.99	3.63
16	1.1	133	16.0	12.03	-11.30	-5.65	-3.77	4.99	3.96	3.12
43	1.2	157	18.5	11.78	-8.25	-4.13	-2.75	3.23	2.68	2.17
1	4.5	181	90.0	49.82	-5.25	-2.63	-1.75	0.46	0.45	0.44
34	1.2	193	18.0	9.33	-3.68	-1.84	-1.23	1.48	1.21	0.98
25	1.2	197.8	9.74	4.92	-3.08	-1.54	-1.03	1.93	1.31	0.95
39	1.1	205.0	9.20	4.49	-2.16	-1.08	-0.72	1.40	0.93	0.67
6	1.1	207	11.0	5.31	-1.91	-0.95	-0.64	1.11	0.78	0.58
36	1.1	214	16.0	7.48	-1.02	-0.51	-0.34	0.45	0.36	0.28
21	2.0	225.0	5.00	2.22	0.38	0.19	0.13	0.32	0.18	0.12
24	1.2	226	11.0	4.87	0.51	0.25	0.17	0.30	0.21	0.15
22	1.0	232	10.2	4.40	1.27	0.64	0.42	0.78	0.53	0.39
27	1.1	238.0	7.00	2.94	2.03	1.02	0.68	1.52	0.93	0.65
37	1.2	257.5	3.49	1.36	4.51	2.25	1.50	4.12	2.20	1.49
31	1.1	263.2	9.71	3.69	5.24	2.62	1.75	3.30	2.23	1.61
17	1.0	265.0	6.00	2.26	5.46	2.73	1.82	4.34	2.55	1.76
41	1.0	700 *	-	-	60.70	30.35	20.23	60.70	30.35	20.23

TABLE 5. THE COMBINED *Z* SCORES FOR THE PARTICIPATING LABORATORIES. THE ANALYTES WITHOUT ASSIGNED VALUES (Cl, Cs, Eu, Hf, Pr, Sm, Sr, Ta, Tb, AND Yb) 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
1	19	47.74	23.87	15.91	5931	1483	659	32.85
4	16	379.00	189.50	126.30	744900	186200	82770	28.85
6	25	22.72	11.36	7.57	4224	1056	469	40.65
7	16	-8.06	-4.03	-2.69	320	80	36	28.85
11	2	19.38	9.69	6.46	803	201	89	7.38
12	6	13.71	6.85	4.57	741	185	82	14.45
14	15	35.71	17.85	11.90	36060	9014	4006	27.49
16	3	998.60	499.30	332.90	1518000	379500	168700	9.35
17	17	15.95	7.98	5.32	5883	1471	654	30.19
18	14	12.37	6.19	4.12	789	197	88	26.12
19	14	25.28	12.64	8.43	4019	1005	447	26.12
21	32	5.31	2.66	1.77	162	40	18	49.48
22	26	31.52	15.76	10.51	7642	1911	849	41.92
24	14	12.97	6.49	4.32	236	59	26	26.12
25	16	14.36	7.18	4.79	2098	524	233	28.85
26	6	19.05	9.53	6.35	3915	979	435	14.45
27	23	12.69	6.34	4.23	1012	253	112	38.08
28	12	0.36	0.18	0.12	1121	280	125	23.34
29	10	255.10	127.60	85.04	117600	29410	13070	20.48
31	19	29.27	14.64	9.76	2488	622	276	32.85
32	9	-1.31	-0.66	-0.44	2110	528	235	19.02
33	12	22.93	11.46	7.64	27110	6778	3012	23.34
34	15	11.95	5.97	3.98	961	240	107	27.49
35	11	-15.23	-7.62	-5.08	746	187	83	21.92
36	24	-2.08	-1.04	-0.69	280	70	31	39.36
37	29	13.41	6.70	4.47	6736	1684	748	45.72
38	12	42.82	21.41	14.27	19310	4827	2145	23.34
39	15	44.27	22.13	14.76	20580	5145	2287	27.49
40	9	31.46	15.73	10.49	2279	570	253	19.02
41	29	2087.00	1043.00	695.60	78010000	19500000	8668000	45.72
42	8	281.50	140.80	93.85	117000	29260	13000	17.53
43	17	47.94	23.97	15.98	16260	4065	1807	30.19
44	9	31.35	15.68	10.45	6786	1697	754	19.02

Appendix II
FIGURES 1-6

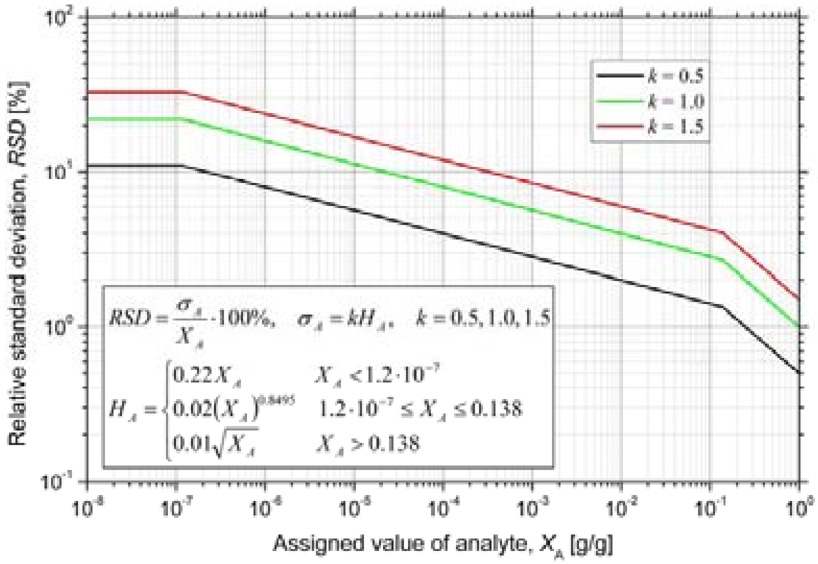


Fig. 1. Relative value of the target standard deviation, RSD, as a function of the assigned mass fraction of the analyte, X_A, calculated by using a modified Horowitz function, Eq. (3). The target value, σ_A, is related to H_A by a factor k and it is recognized as fit-for-purpose in three levels of uncertainty: ***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.*

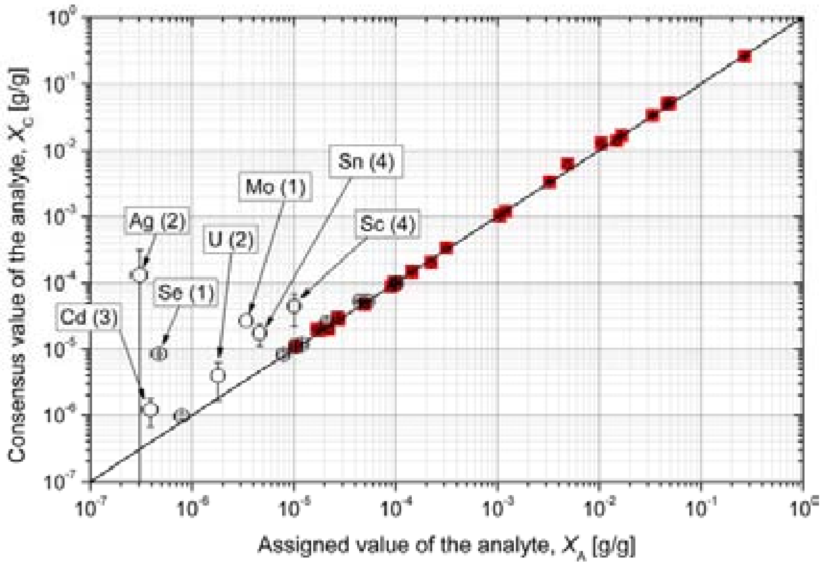


Fig. 2. Correlation between assigned, X_A, and consensus values of analytes, X_C. Solid red squares correspond to the elements the assigned values of which were known with high degree of accuracy. Hollow black circles correspond to the elements the assigned values of which can be considered as indicative/informative 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 Eq. (2) with k = 1. The uncertainties of the consensus values were calculated according to Eq.(20), except for the results reported by single laboratory, in such a case the laboratory estimate of the uncertainty is shown in the plot.

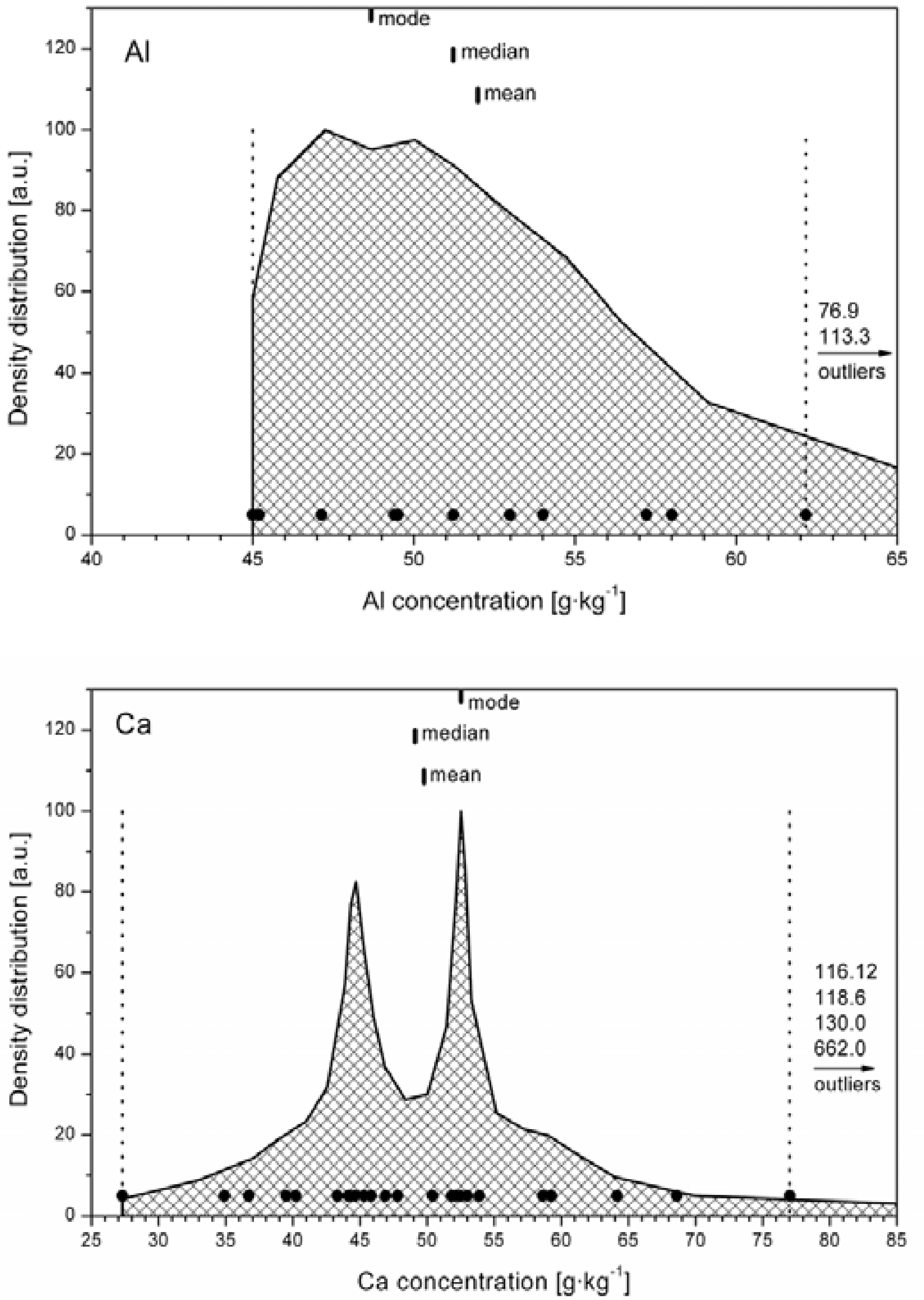
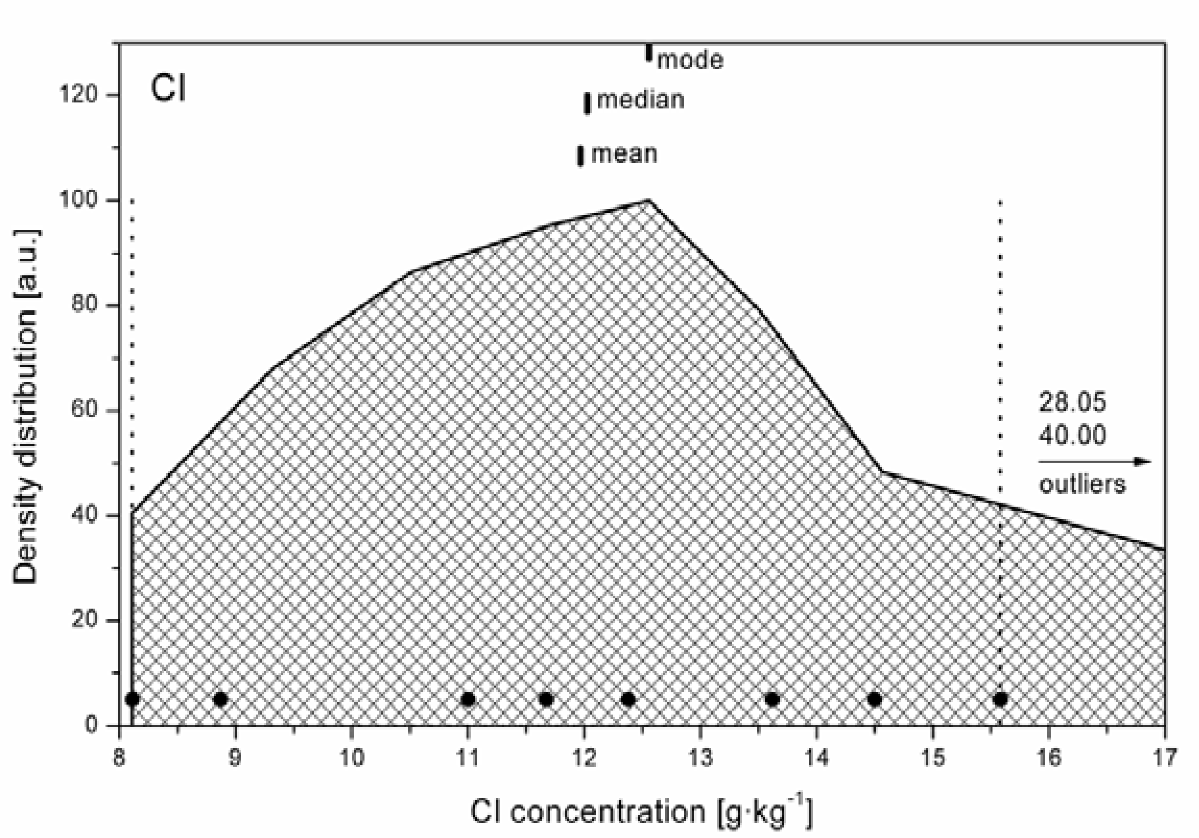
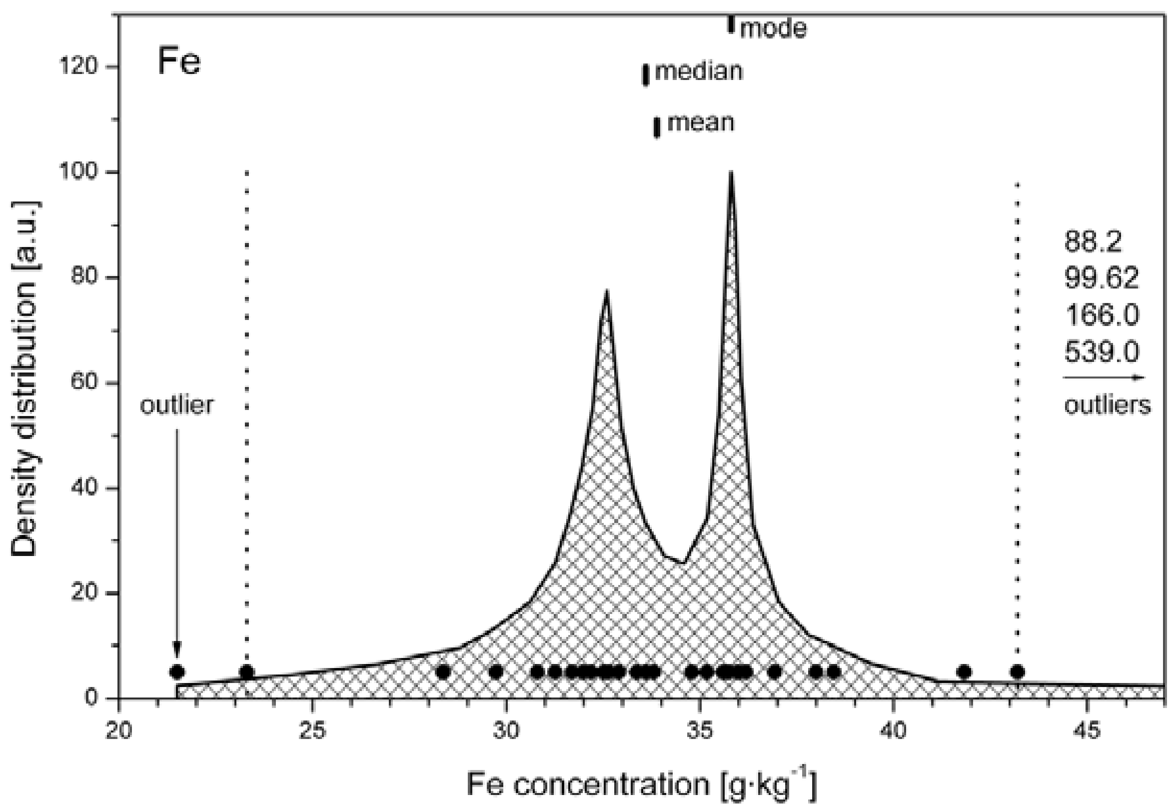


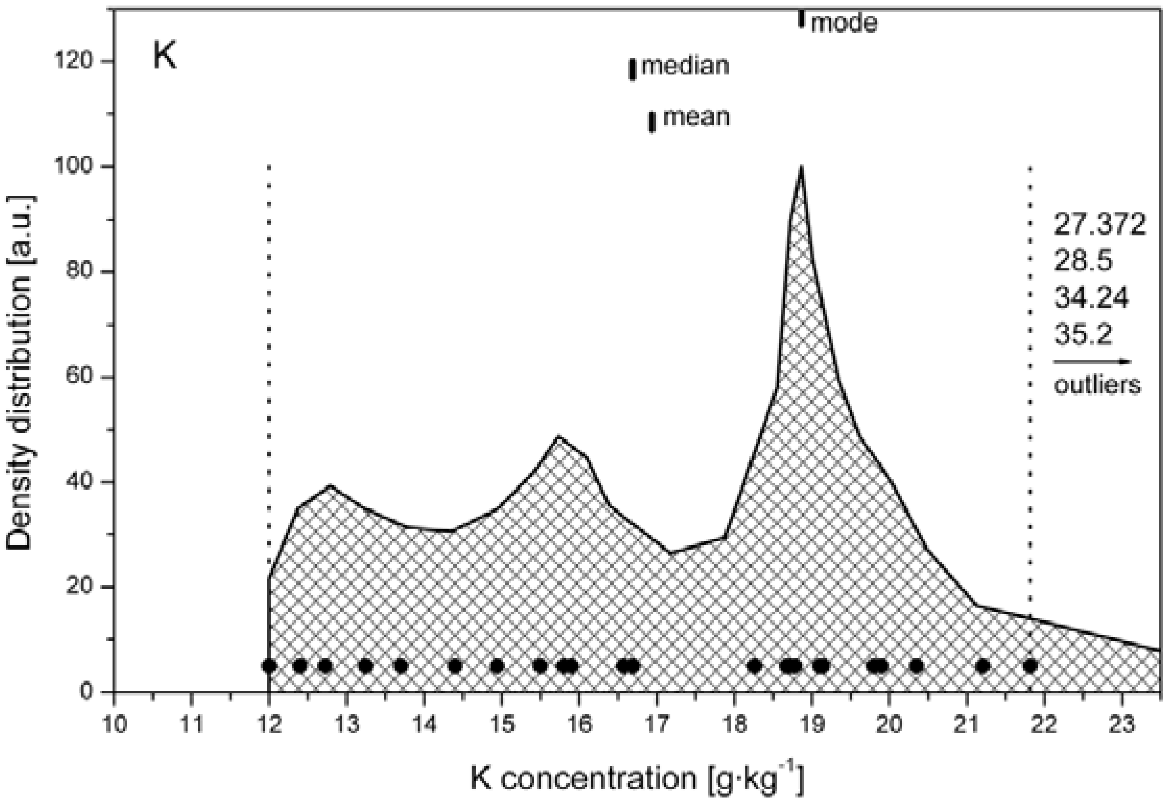
Fig. 3. The density distribution functions for the analytes for which at least 5 results passed the outlier rejection tests. The individual results are marked with filled circles. The dotted lines show the range of the accepted results – these results were used to calculate the consensus values. The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

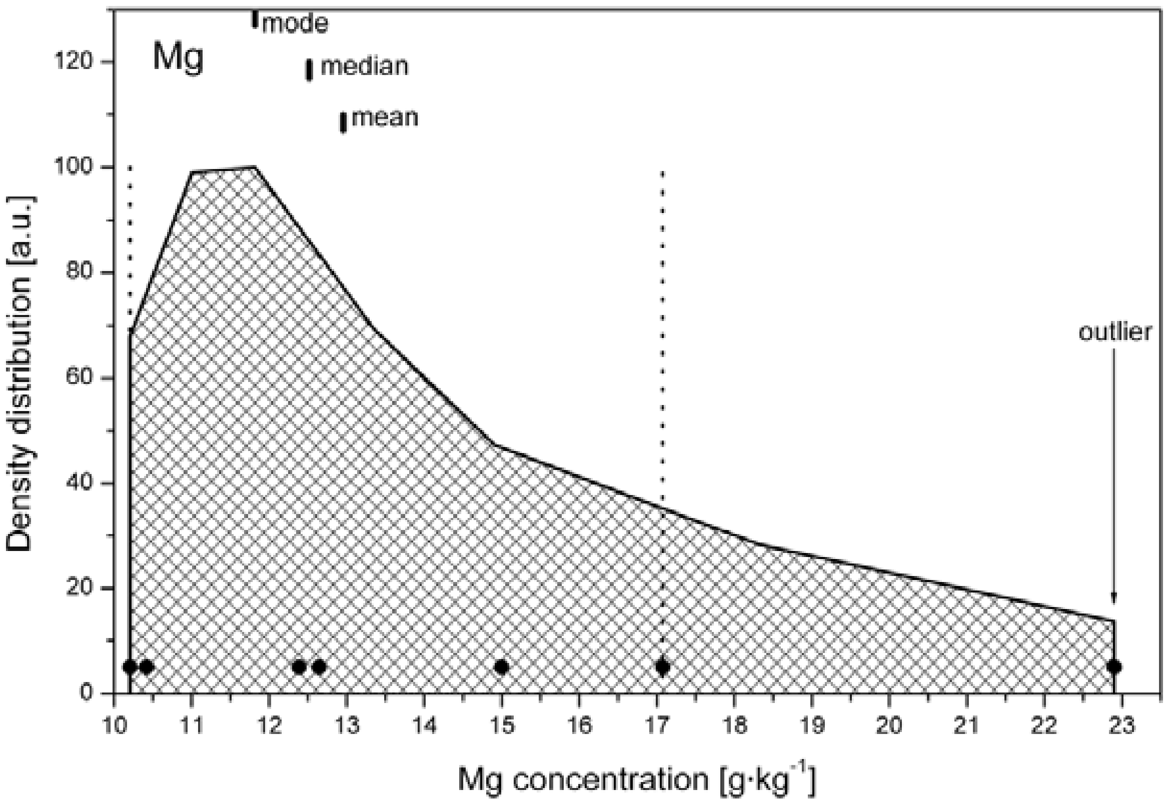


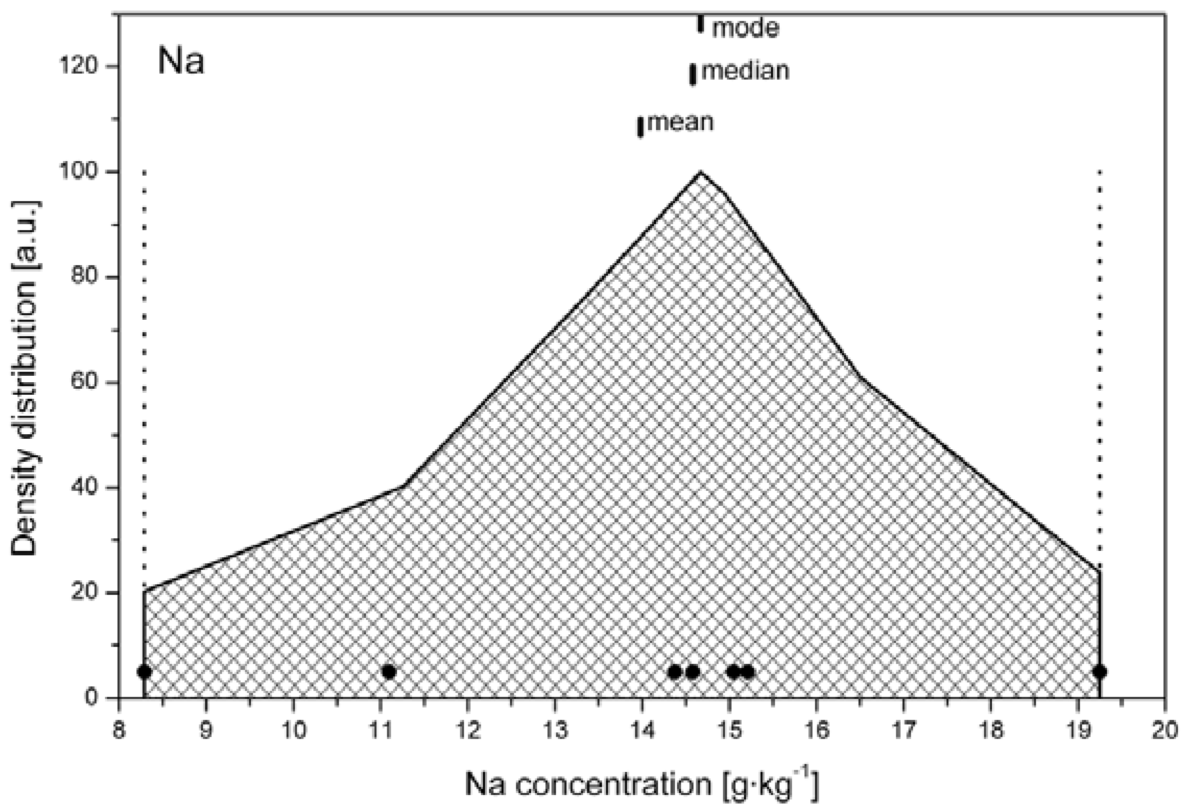
Cl
mode
median
mean
28.05
40.00
outliers
Density distribution [a.u.]
Cl concentration [g·kg-1]

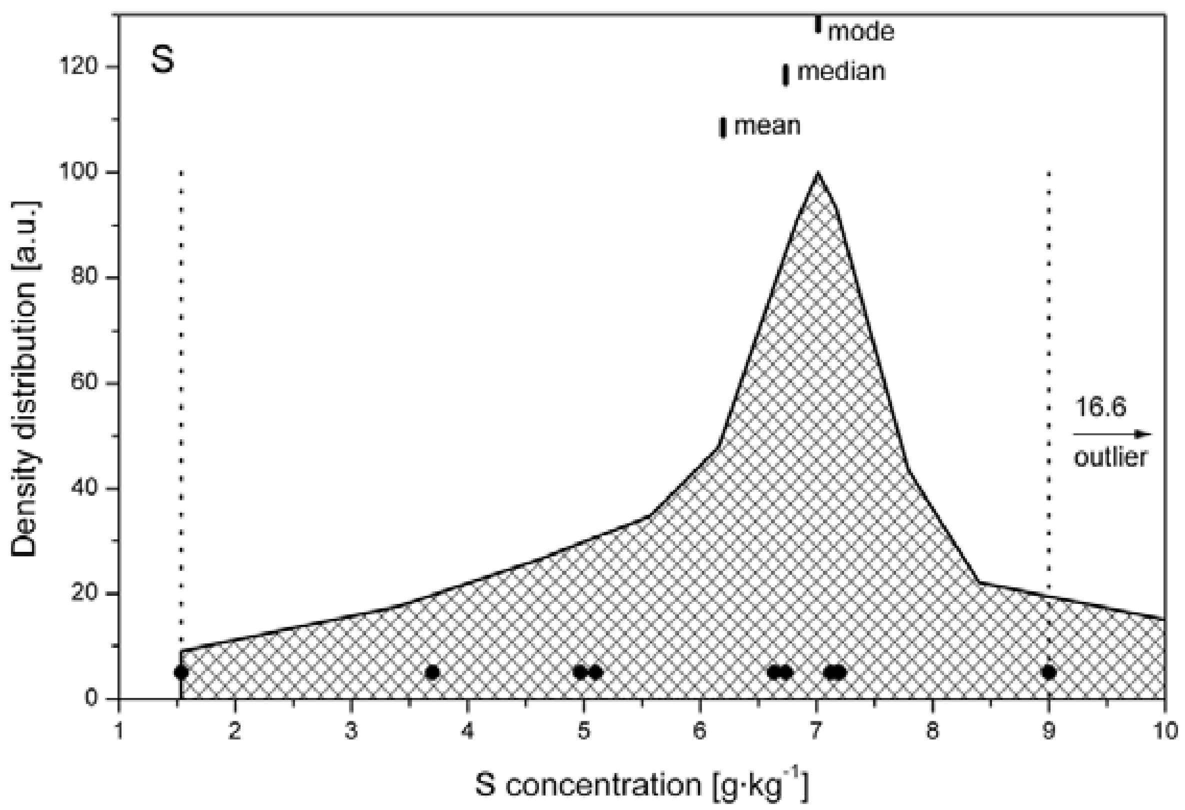


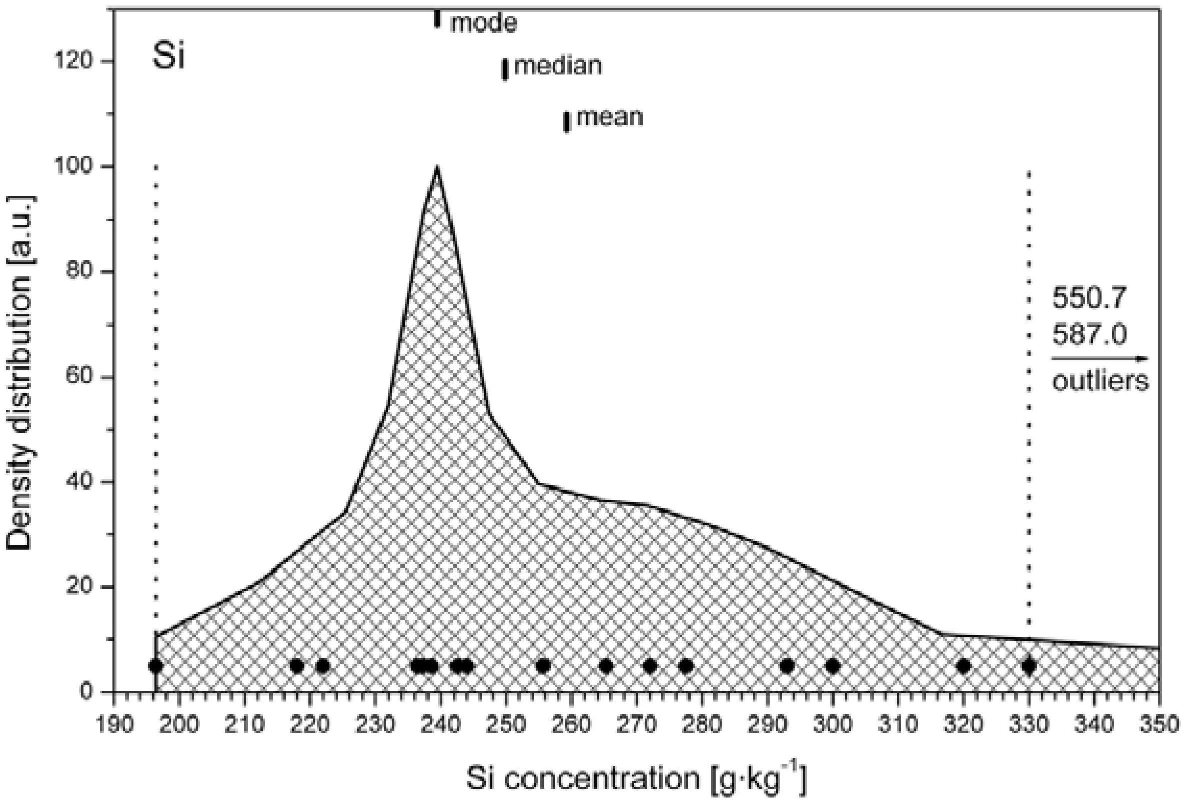
Fe
mode
median
mean
outlier
88.2
99.62
166.0
539.0
outliers
Density distribution [a.u.]
Fe concentration [g·kg-1]


K
mode
median
mean
27.372
28.5
34.24
35.2
outliers
Density distribution [a.u.]
K concentration [g·kg-1]

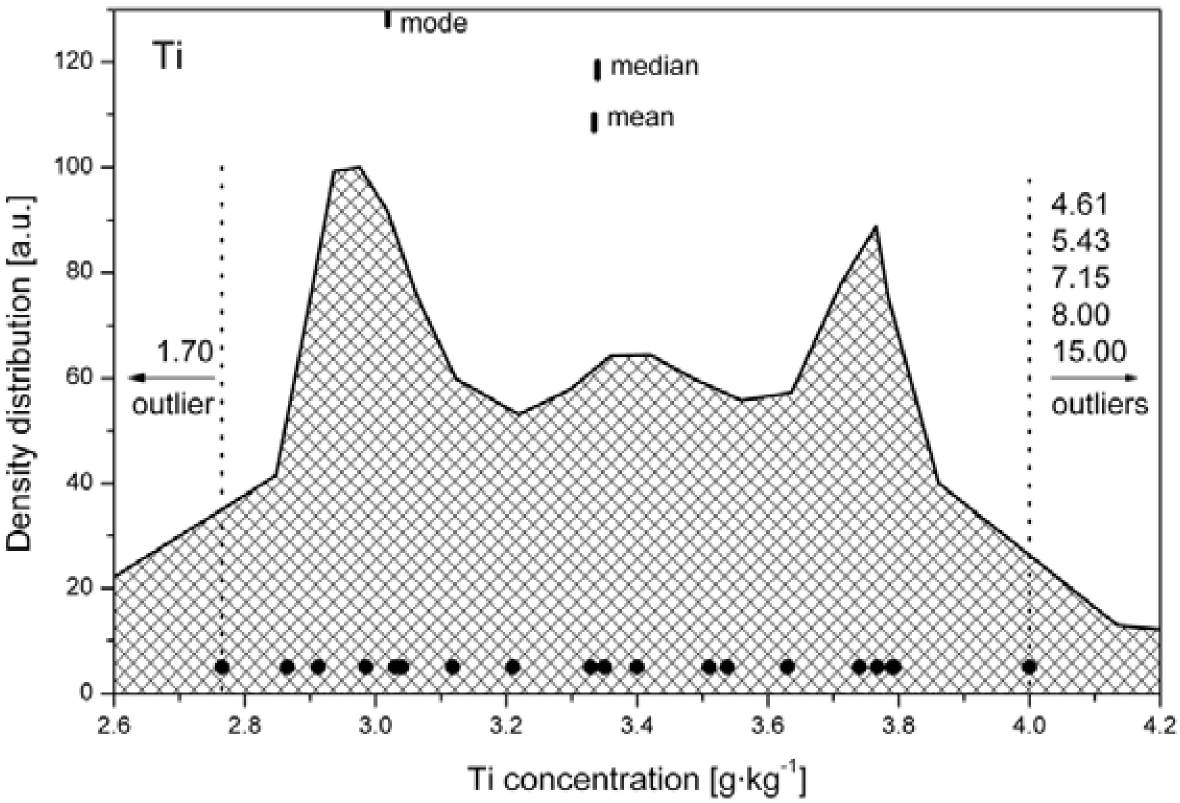

Mg
mode
median
mean
outlier
Density distribution [a.u.]
Mg concentration [g·kg-1]


Na
mode
median
mean
Density distribution [a.u.]
Na concentration [g·kg-1]
0
20
40
60
80
100
120
8
9
10
11
12
13
14
15
16
17
18
19
20

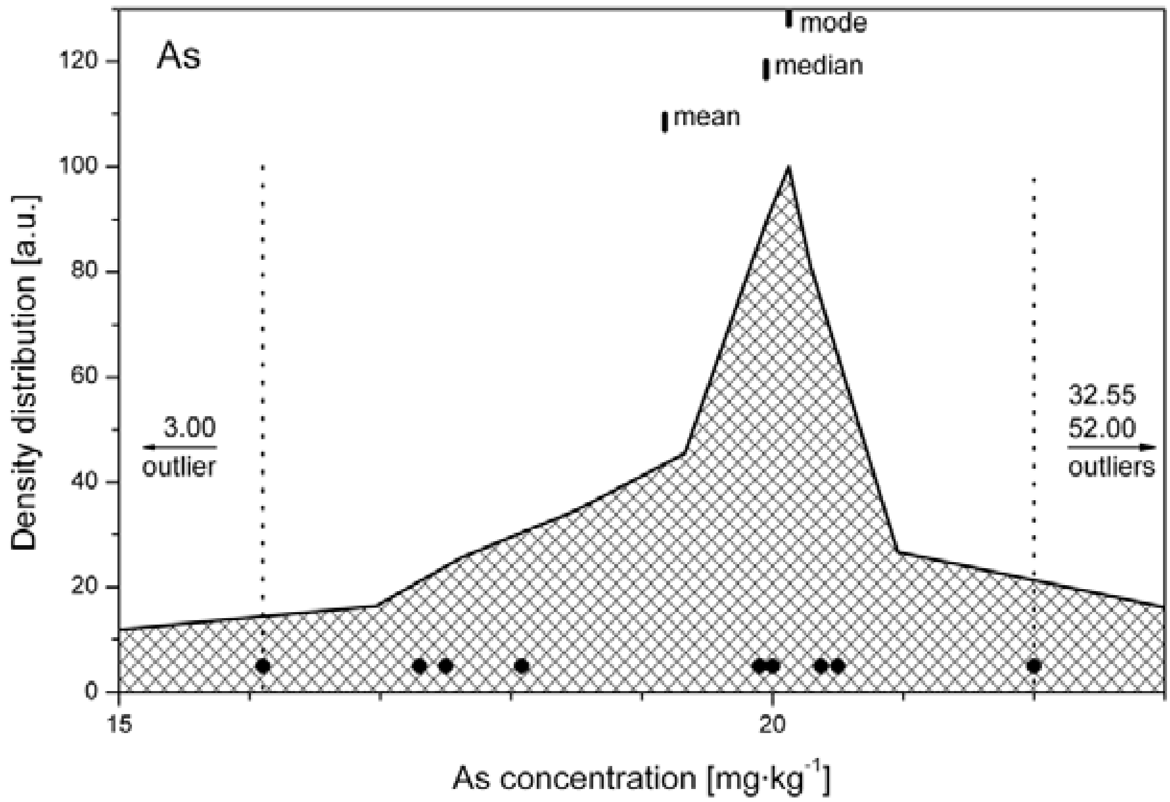

S
mode
median
mean
16.6
outlier
Density distribution [a.u.]
S concentration [g·kg-1]
0
20
40
60
80
100
120
1
2
3
4
5
6
7
8
9
10

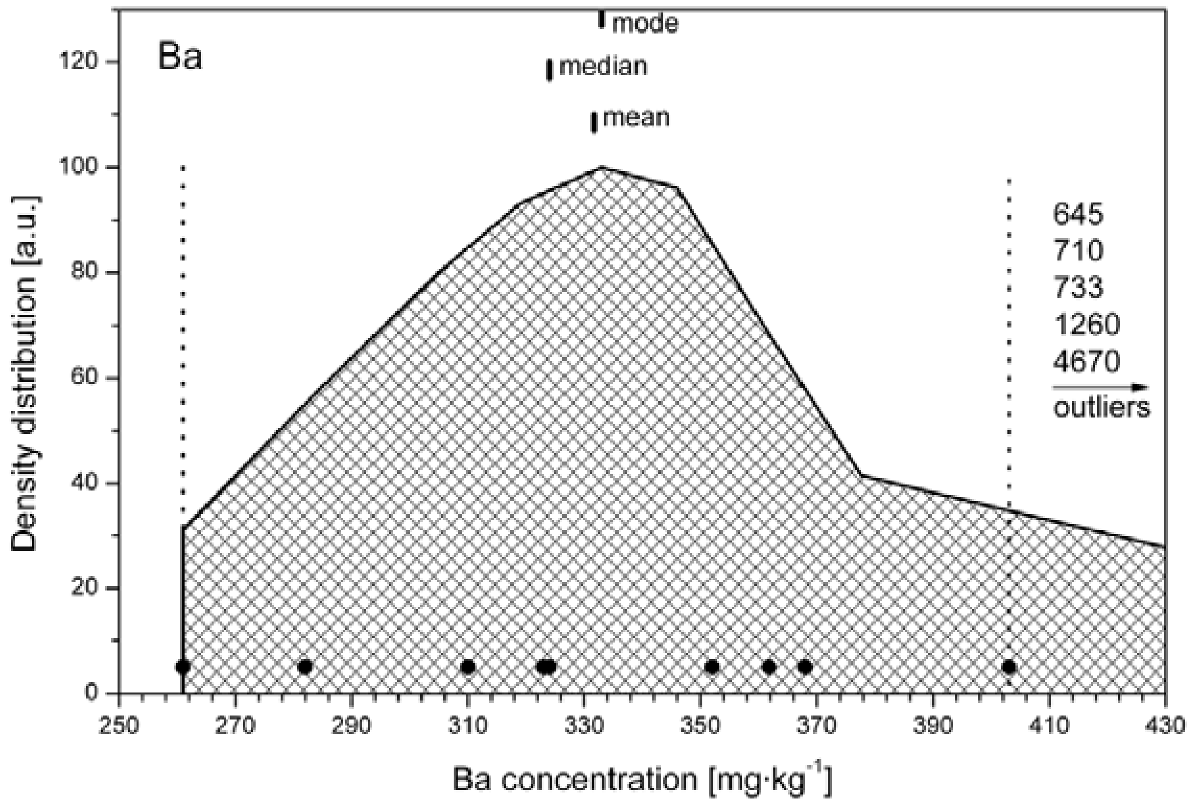


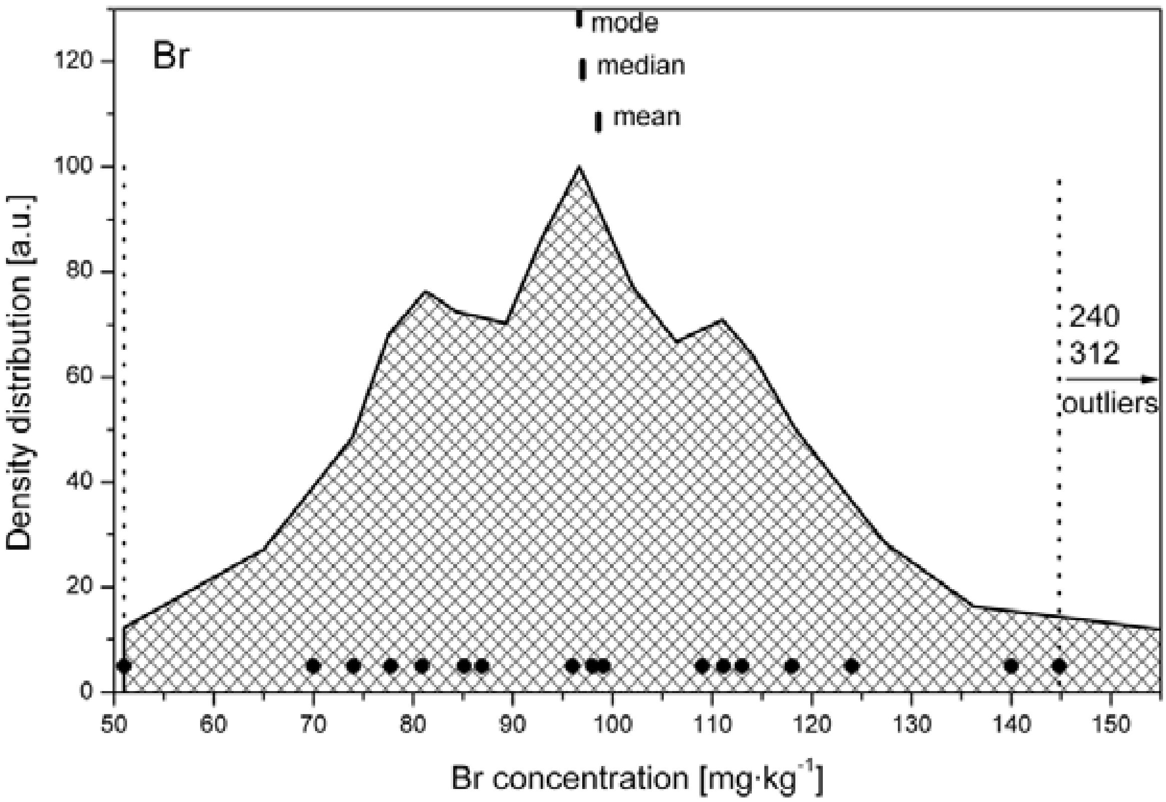
Si
mode
median
mean
550.7
587.0
outliers
Density distribution [a.u.]
Si concentration [g·kg⁻¹]

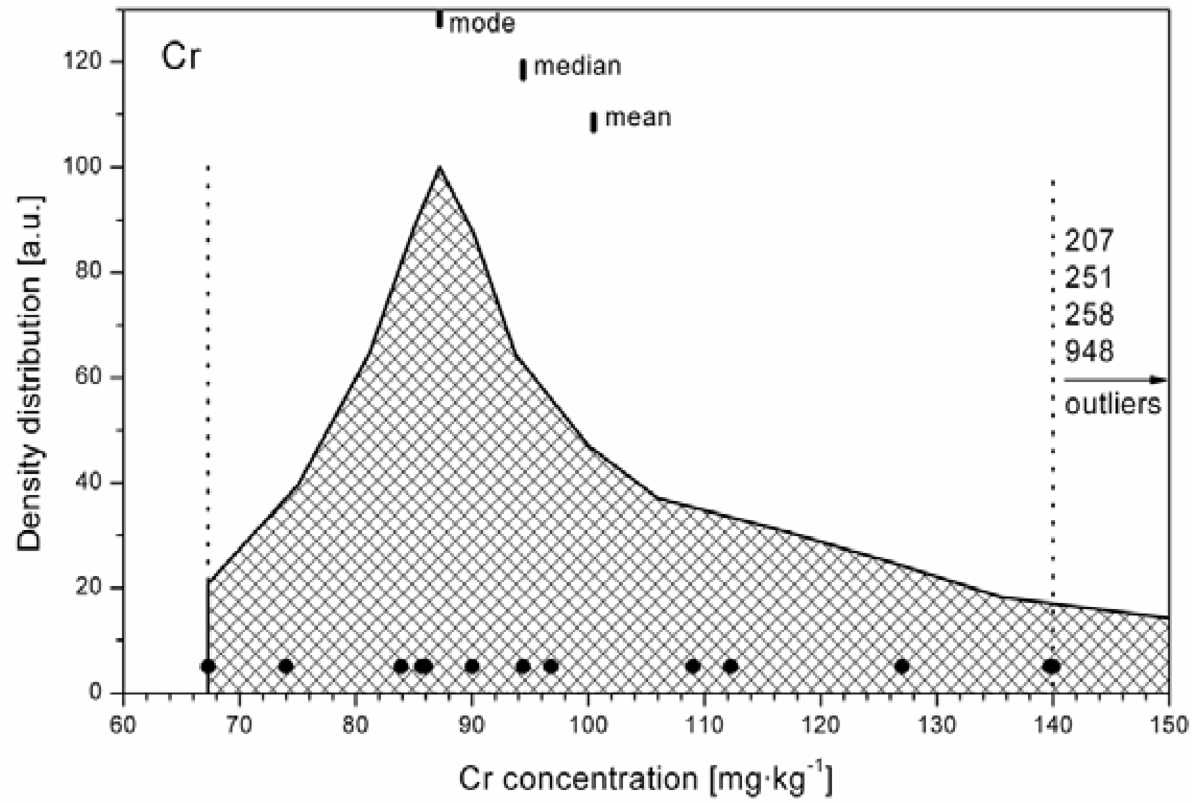


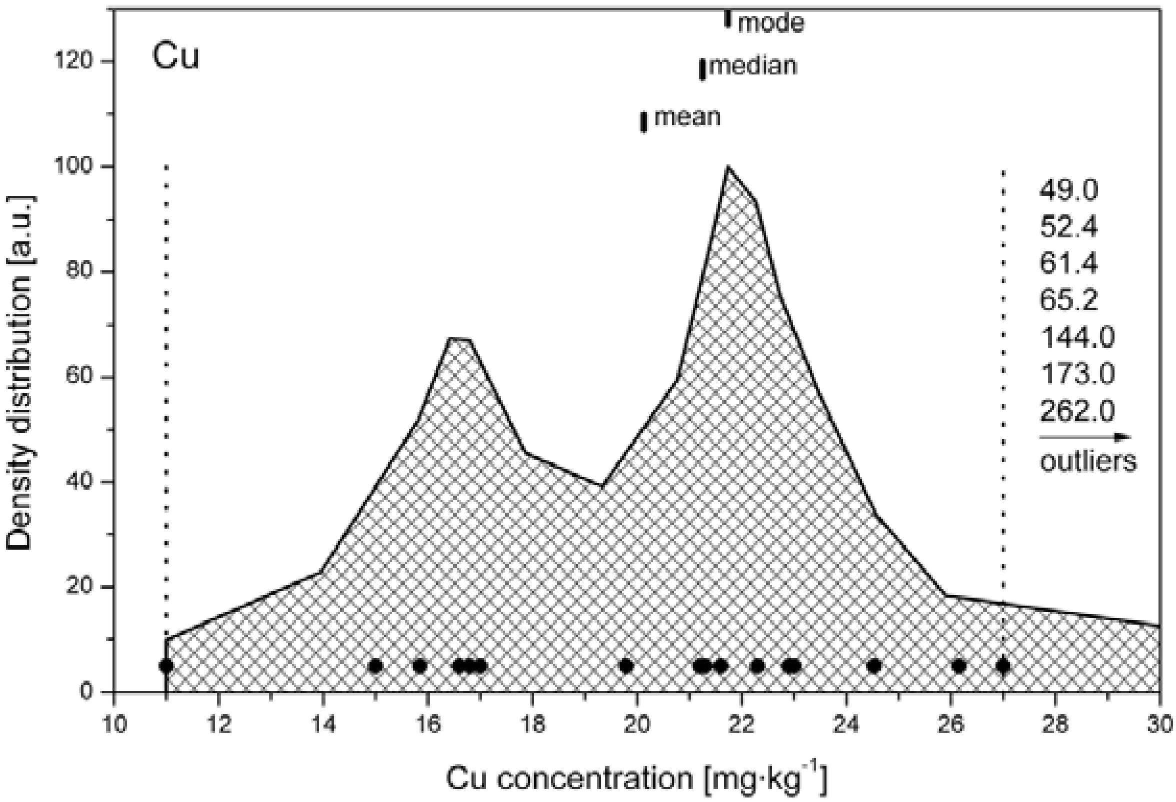
Ti
mode
median
mean
1.70
outlier
4.61
5.43
7.15
8.00
15.00
outliers
Density distribution [a.u.]
Ti concentration [g·kg⁻¹]

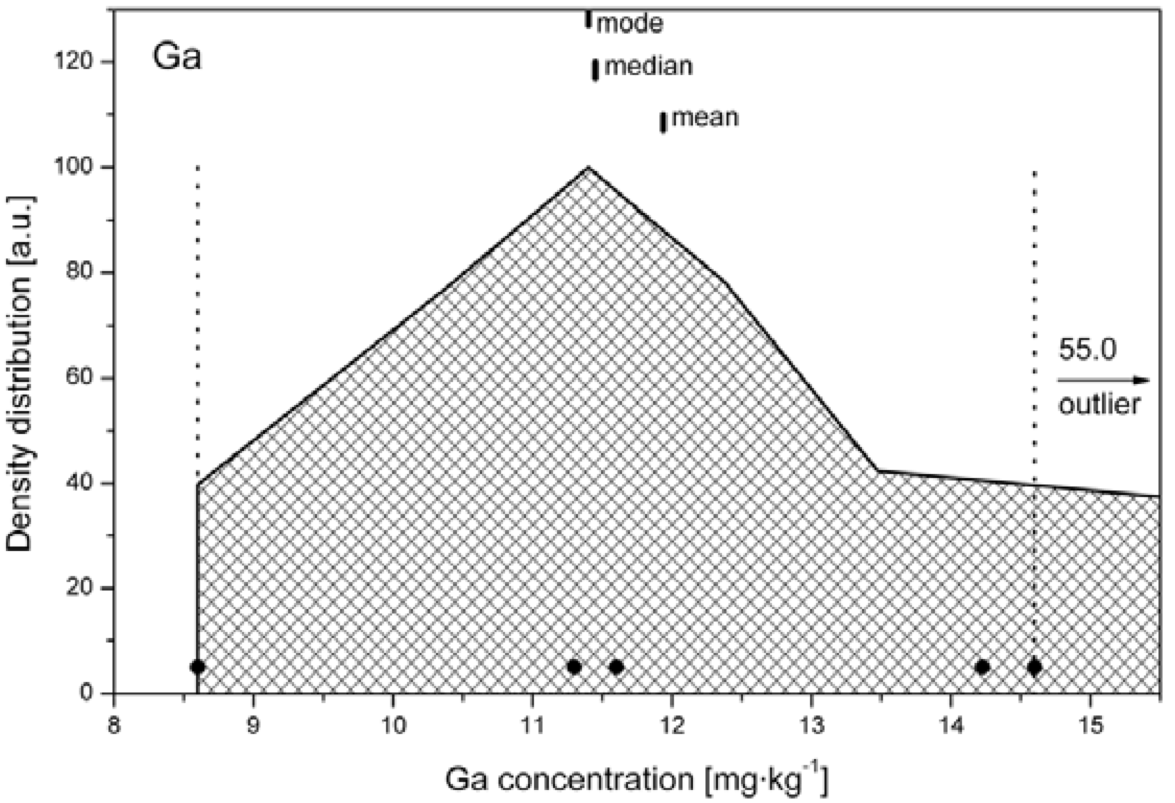

As
mode
median
mean
3.00
outlier
32.55
52.00
outliers
Density distribution [a.u.]
As concentration [mg·kg-1]
0
20
40
60
80
100
120
15
20

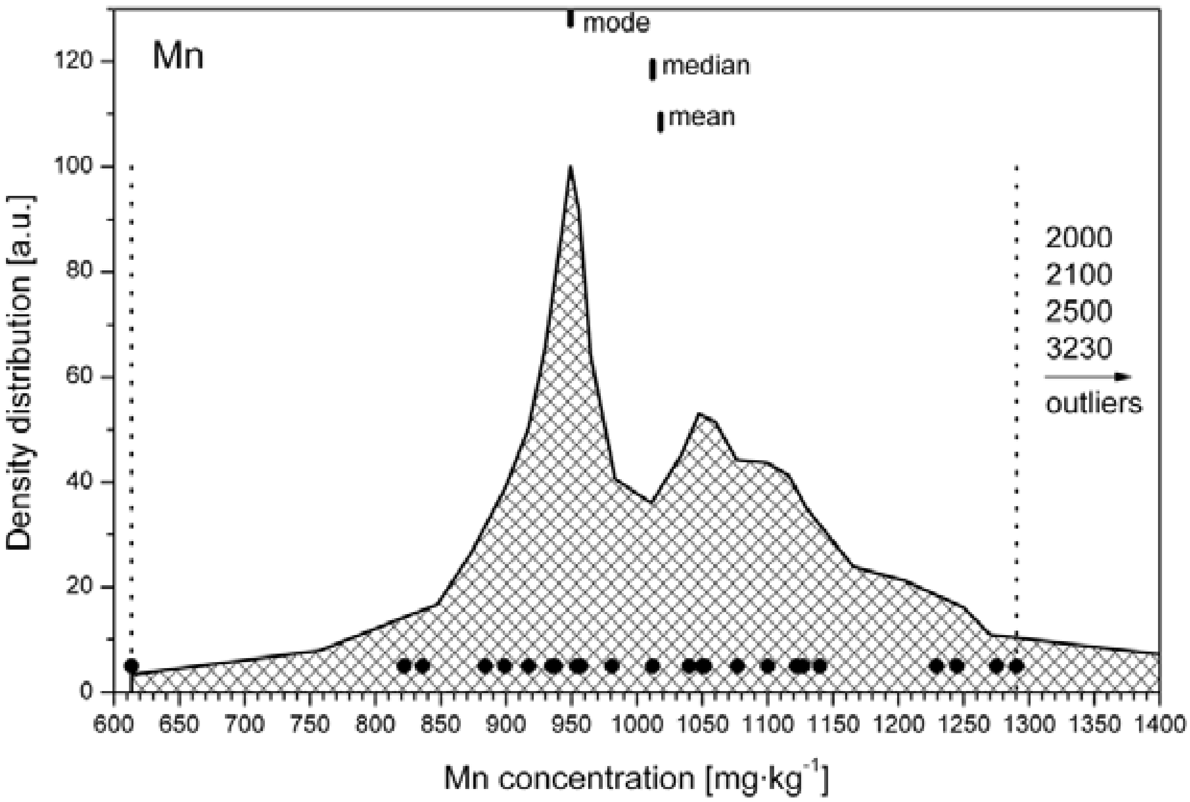

Ba
mode
median
mean
645
710
733
1260
4670
outliers
Density distribution [a.u.]
Ba concentration [mg·kg-1]
0
20
40
60
80
100
120
250
270
290
310
330
350
370
390
410
430

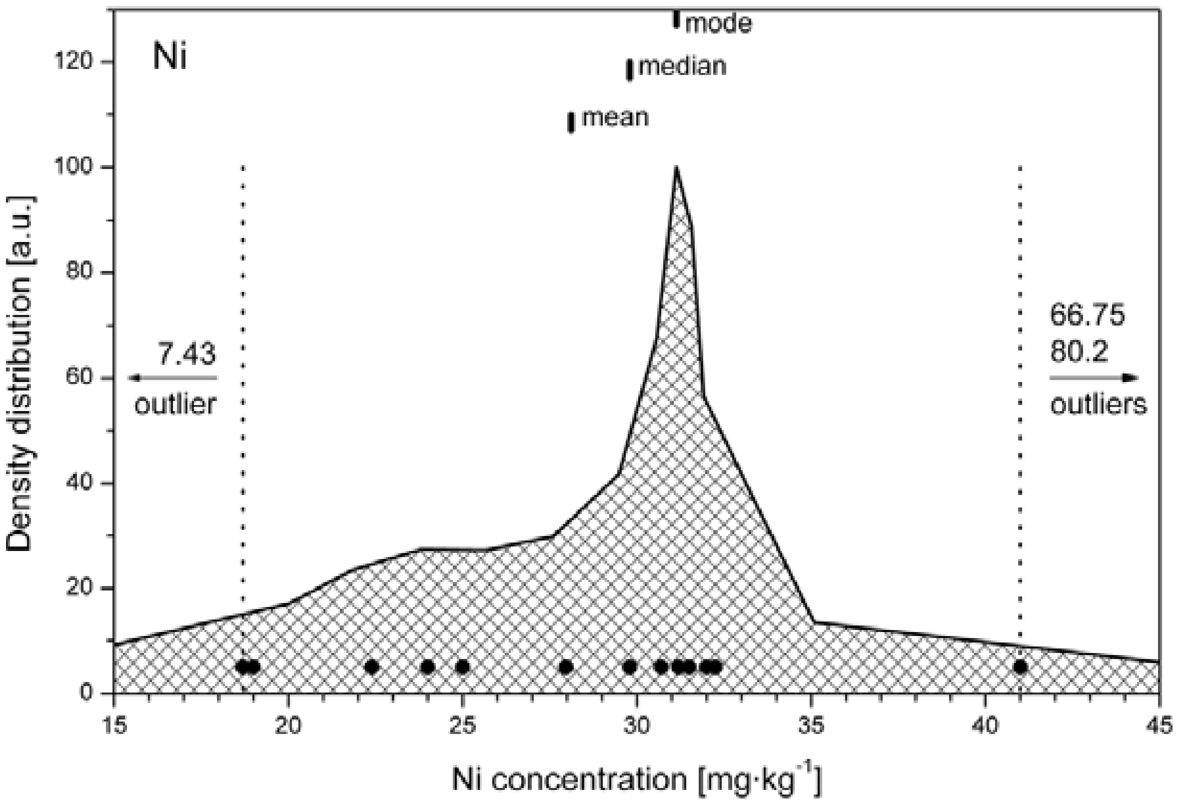

Br
mode
median
mean
240
312
outliers
Density distribution [a.u.]
Br concentration [mg·kg⁻¹]

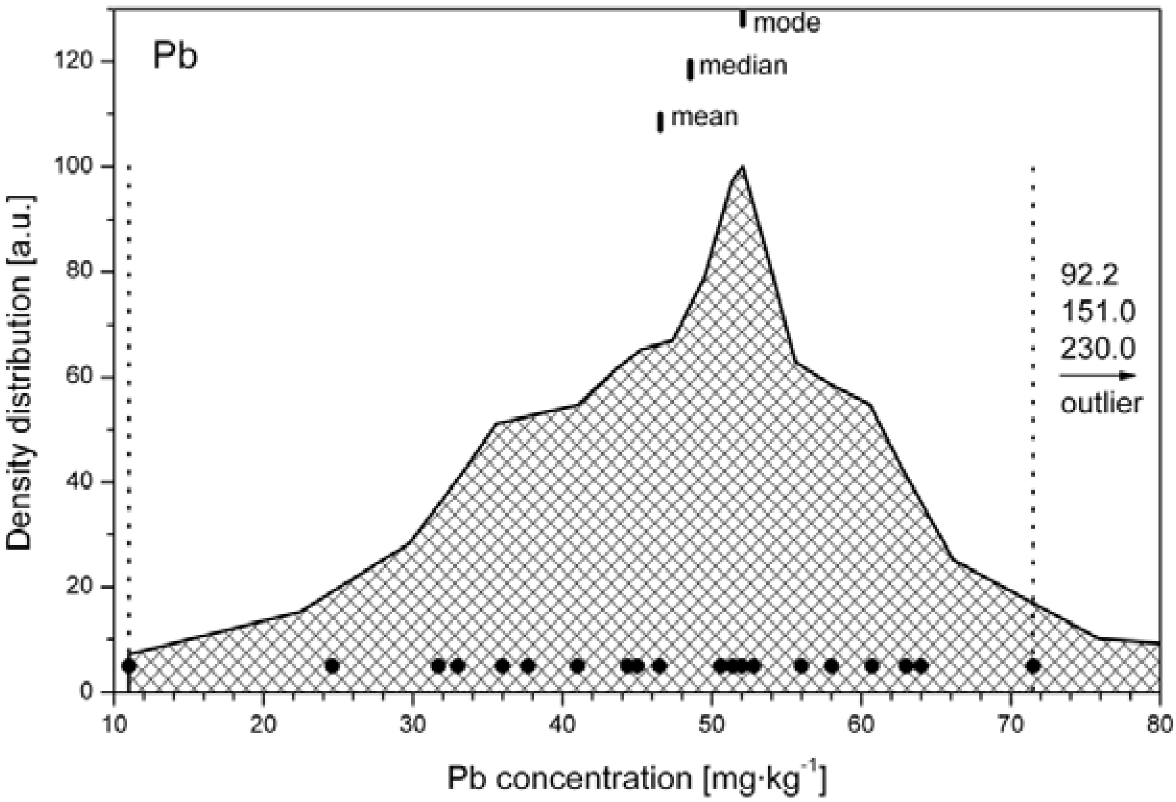

Cr
mode
median
mean
207
251
258
948
outliers
Density distribution [a.u.]
Cr concentration [mg·kg⁻¹]

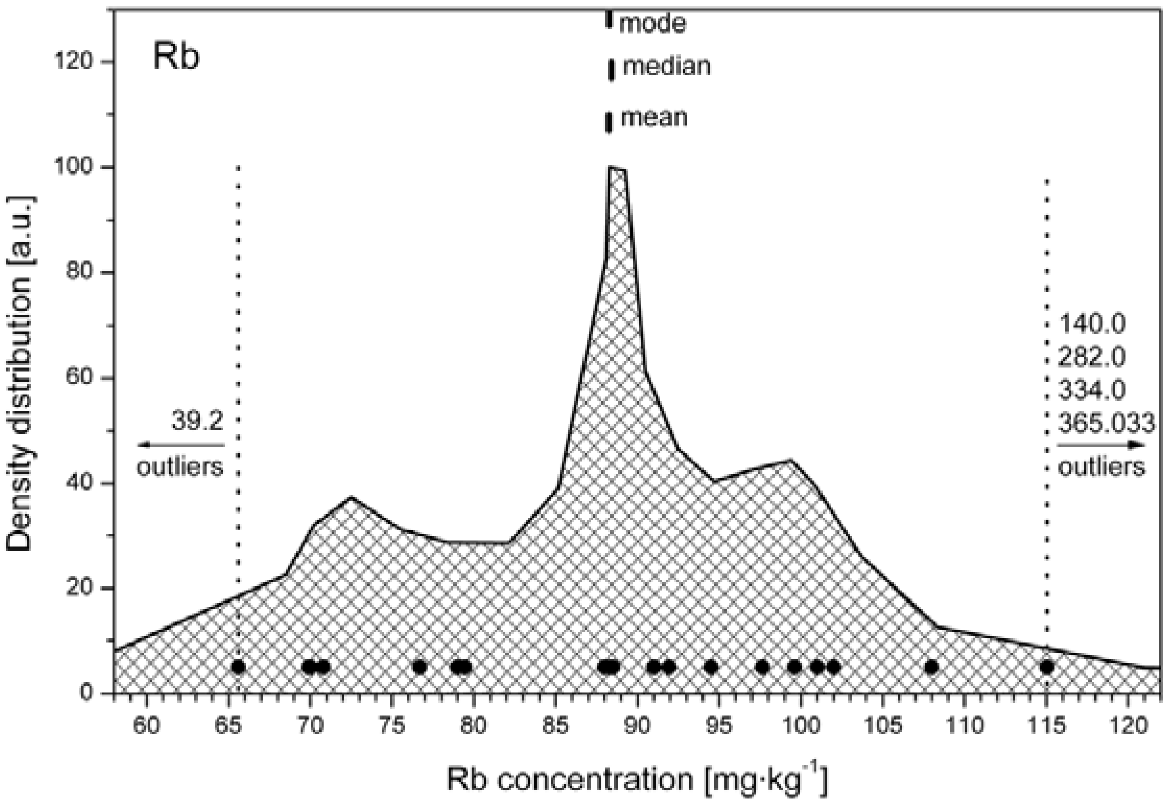

Cu
mode
median
mean
49.0
52.4
61.4
65.2
144.0
173.0
262.0
outliers
Density distribution [a.u.]
Cu concentration [mg·kg^{-1}]

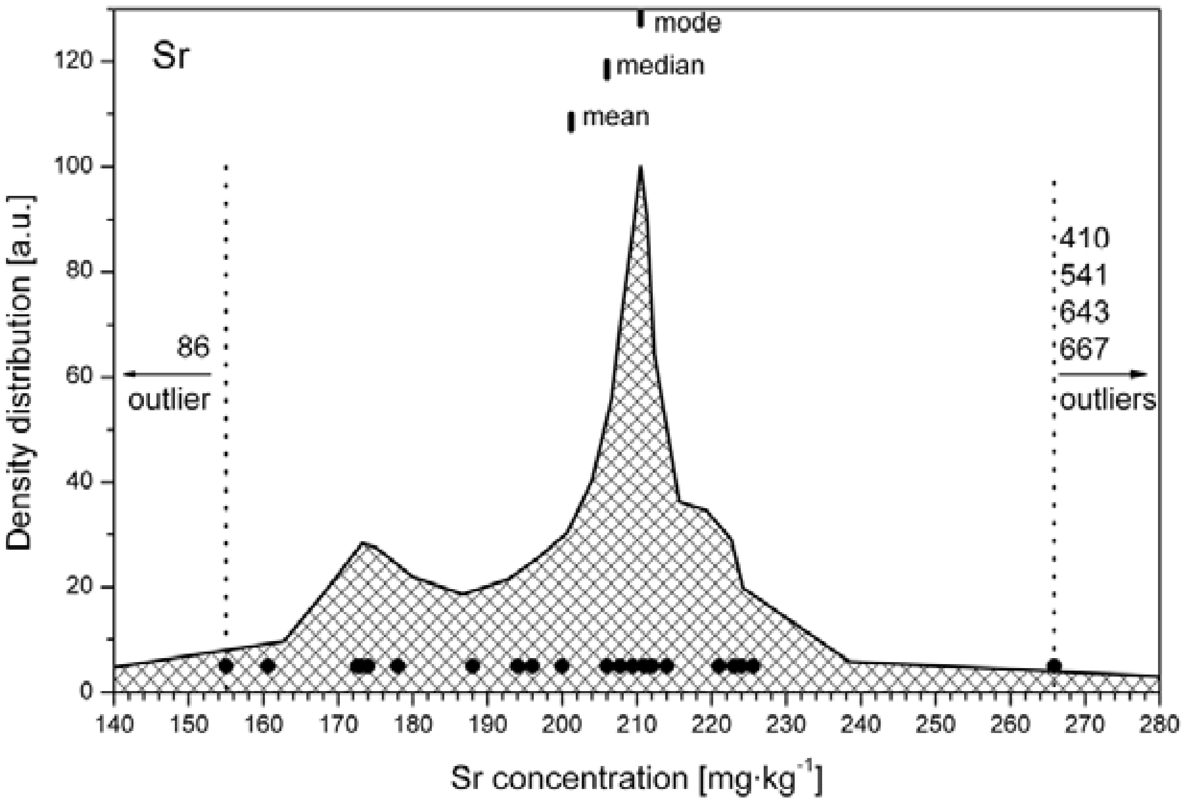

Ga
mode
median
mean
55.0
outlier
Density distribution [a.u.]
Ga concentration [mg·kg^{-1}]

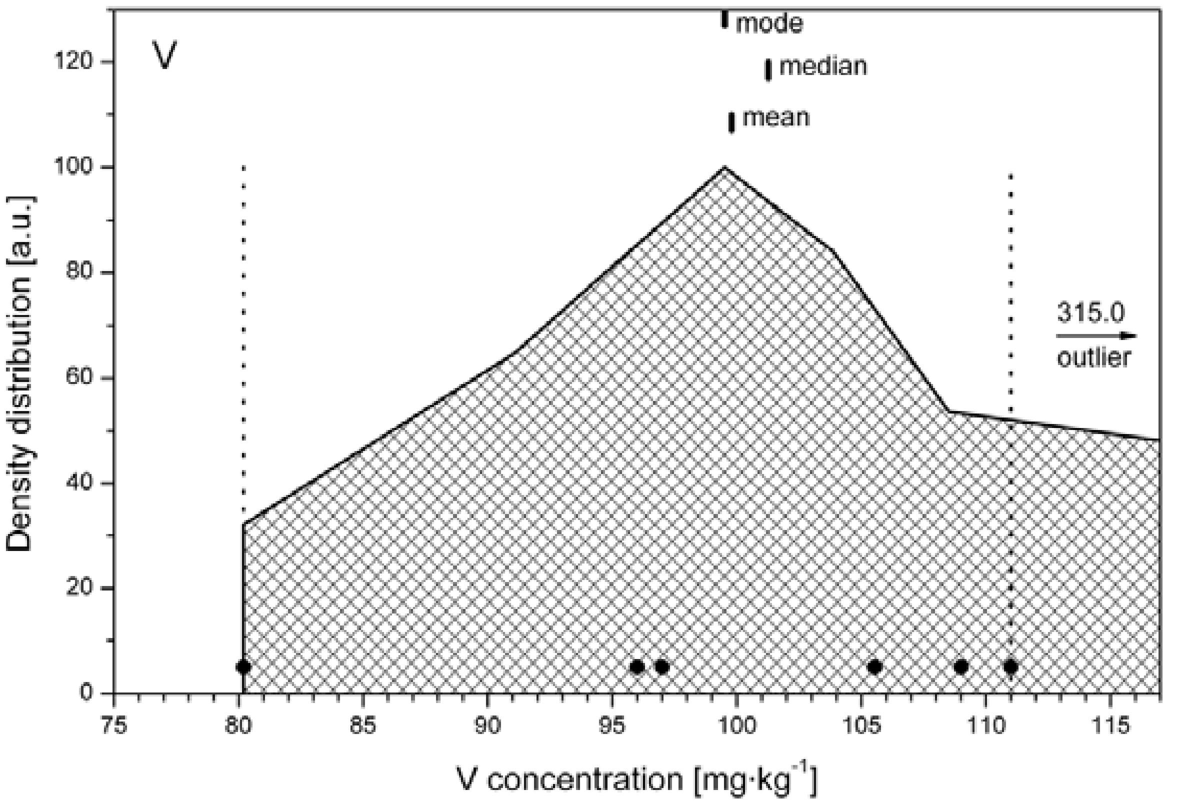

Mn
mode
median
mean
2000
2100
2500
3230
outliers
Density distribution [a.u.]
Mn concentration [mg·kg⁻¹]

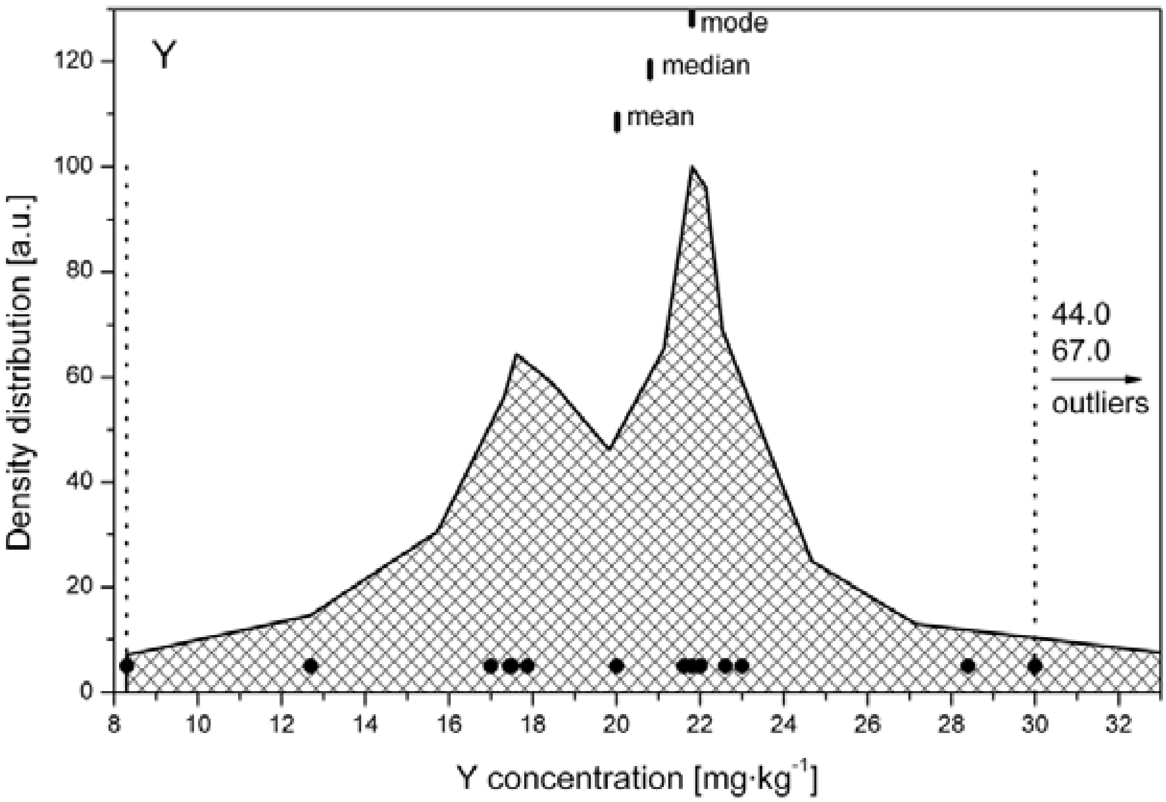

Ni
mode
median
mean
7.43
outlier
66.75
80.2
outliers
Density distribution [a.u.]
Ni concentration [mg·kg⁻¹]


Pb
mode
median
mean
92.2
151.0
230.0
outlier
Density distribution [a.u.]
Pb concentration [mg·kg-1]

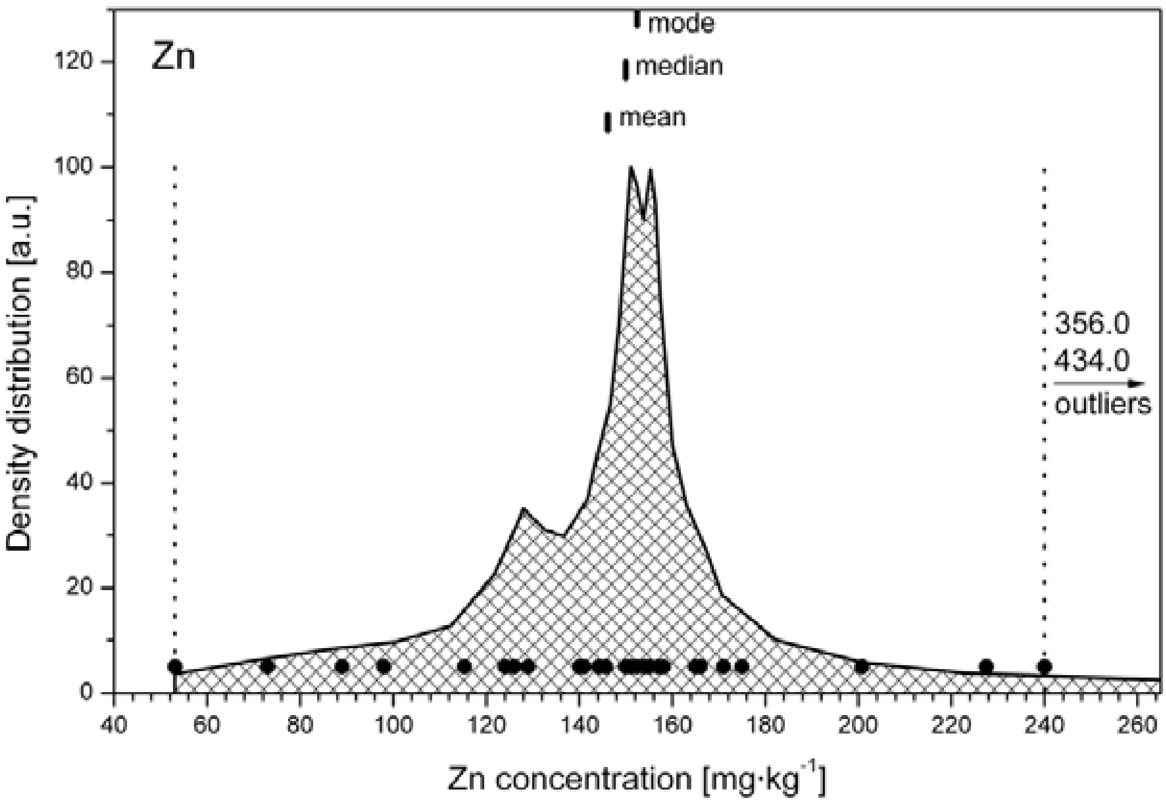

Rb
mode
median
mean
39.2
outliers
140.0
282.0
334.0
365.033
outliers
Density distribution [a.u.]
Rb concentration [mg·kg-1]


Sr
mode
median
mean
86
outlier
410
541
643
667
outliers
Density distribution [a.u.]
Sr concentration [mg·kg-1]

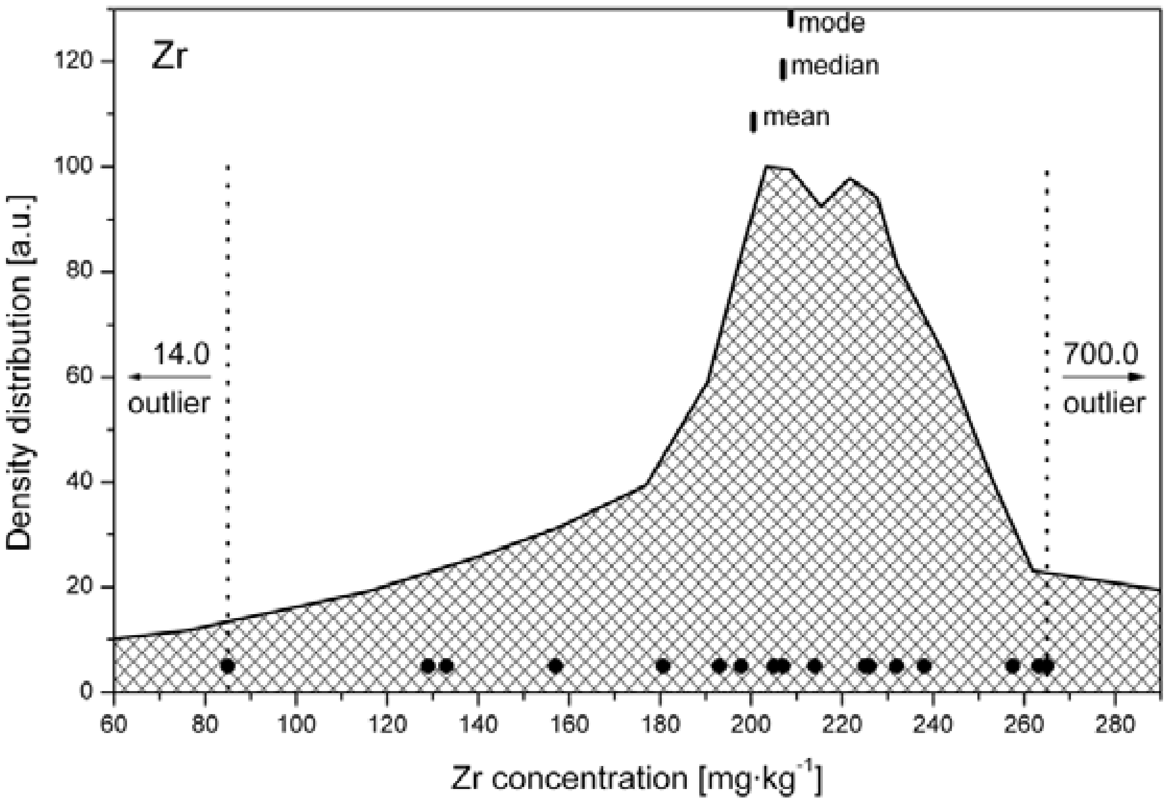

V
mode
median
mean
315.0
outlier
Density distribution [a.u.]
V concentration [mg·kg-1]



Y
mode
median
mean
44.0
67.0
outliers
Density distribution [a.u.]
Y concentration [mg·kg⁻¹]



Zn
mode
median
mean
356.0
434.0
outliers
Density distribution [a.u.]
Zn concentration [mg·kg⁻¹]



Zr
mode
median
mean
14.0
outlier
700.0
outlier
Density distribution [a.u.]
Zr concentration [mg·kg-1]
0
20
40
60
80
100
120
60
80
100
120
140
160
180
200
220
240
260
280

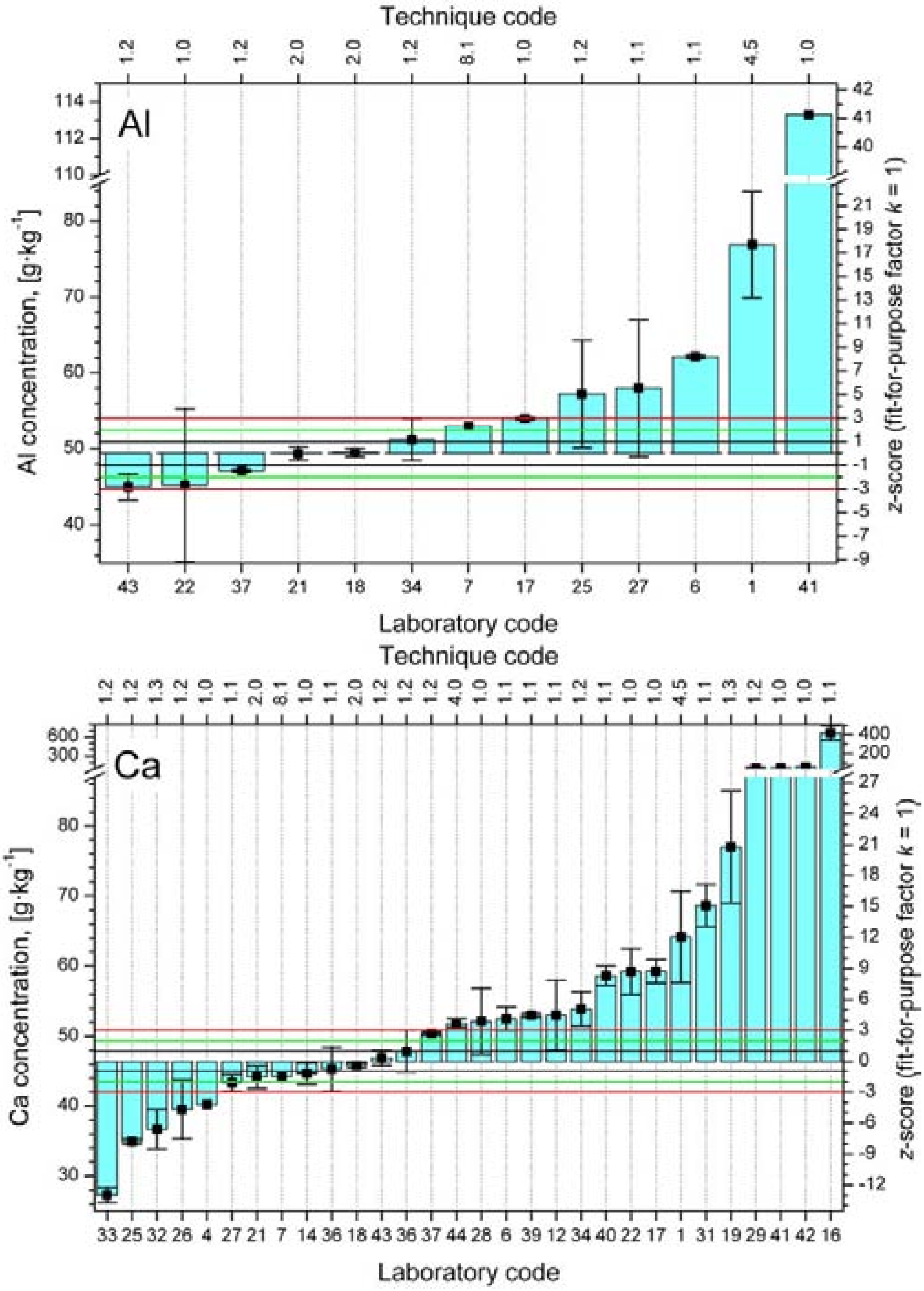
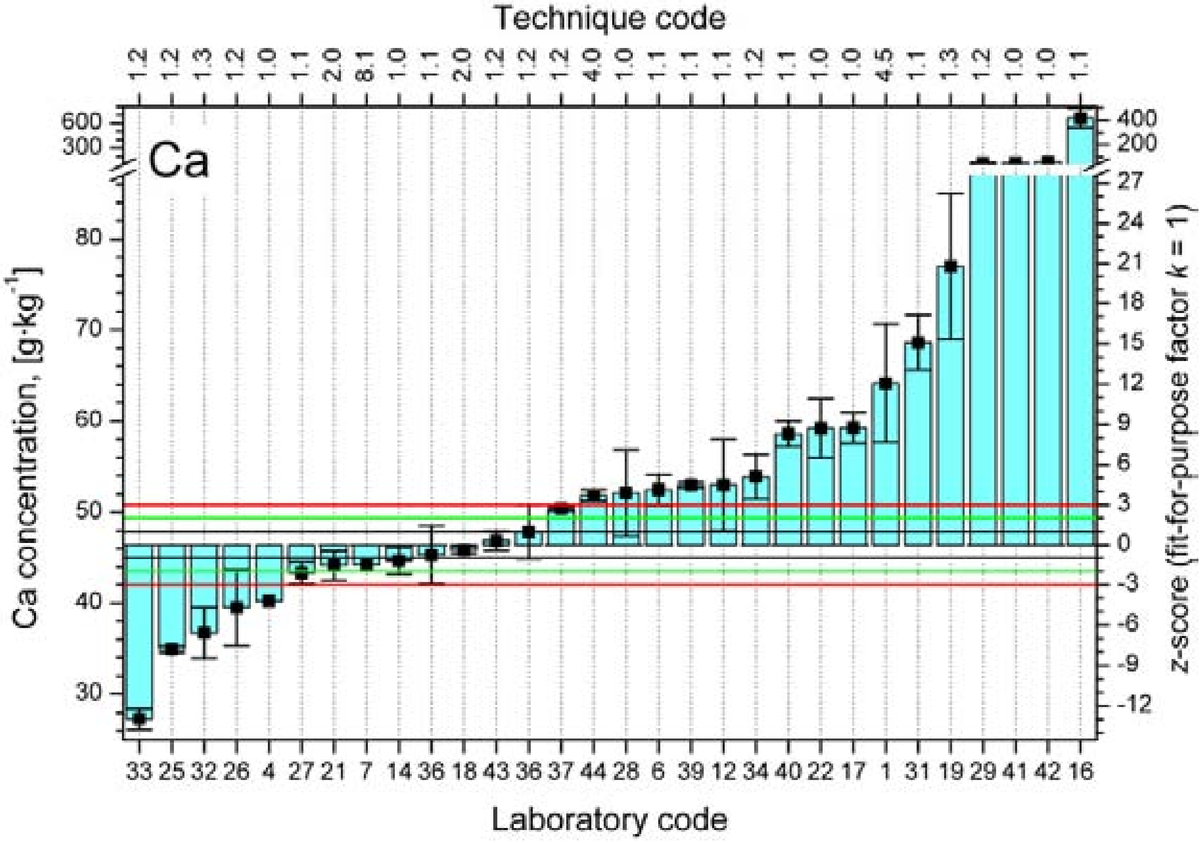
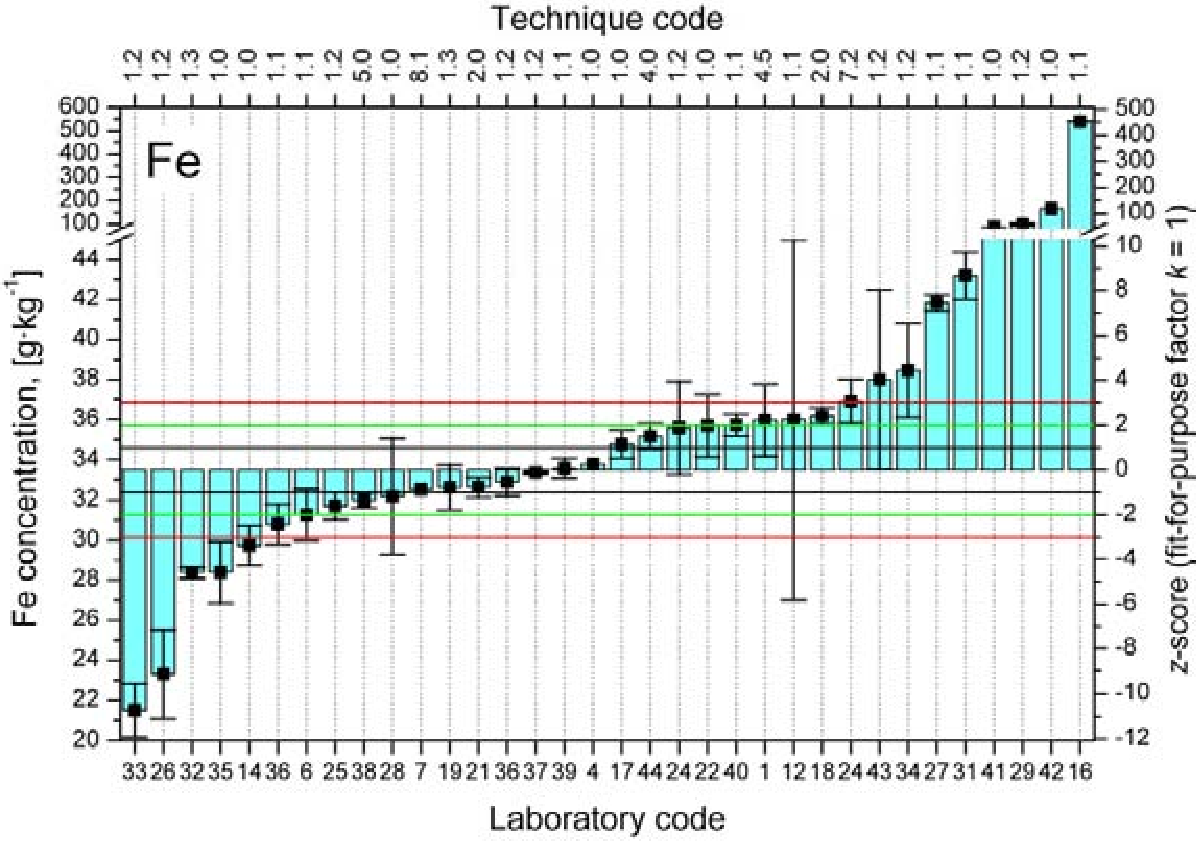
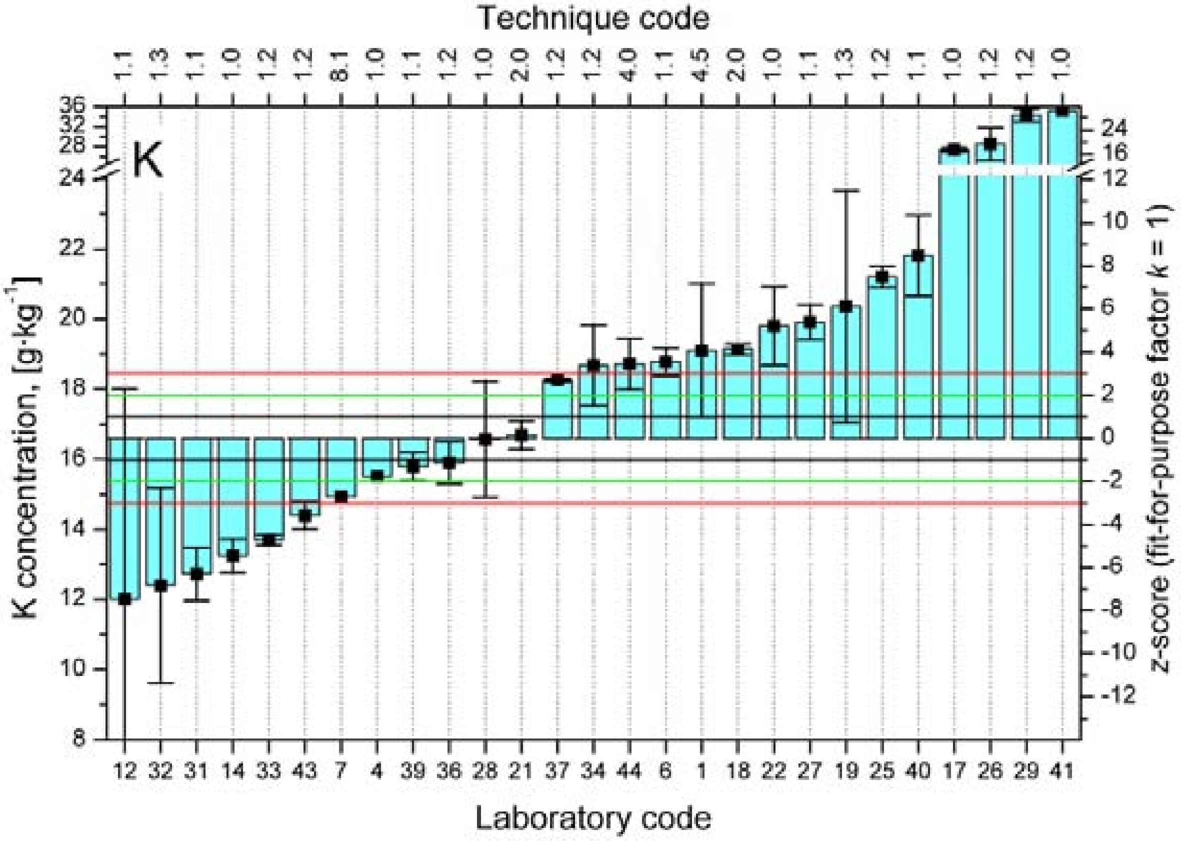
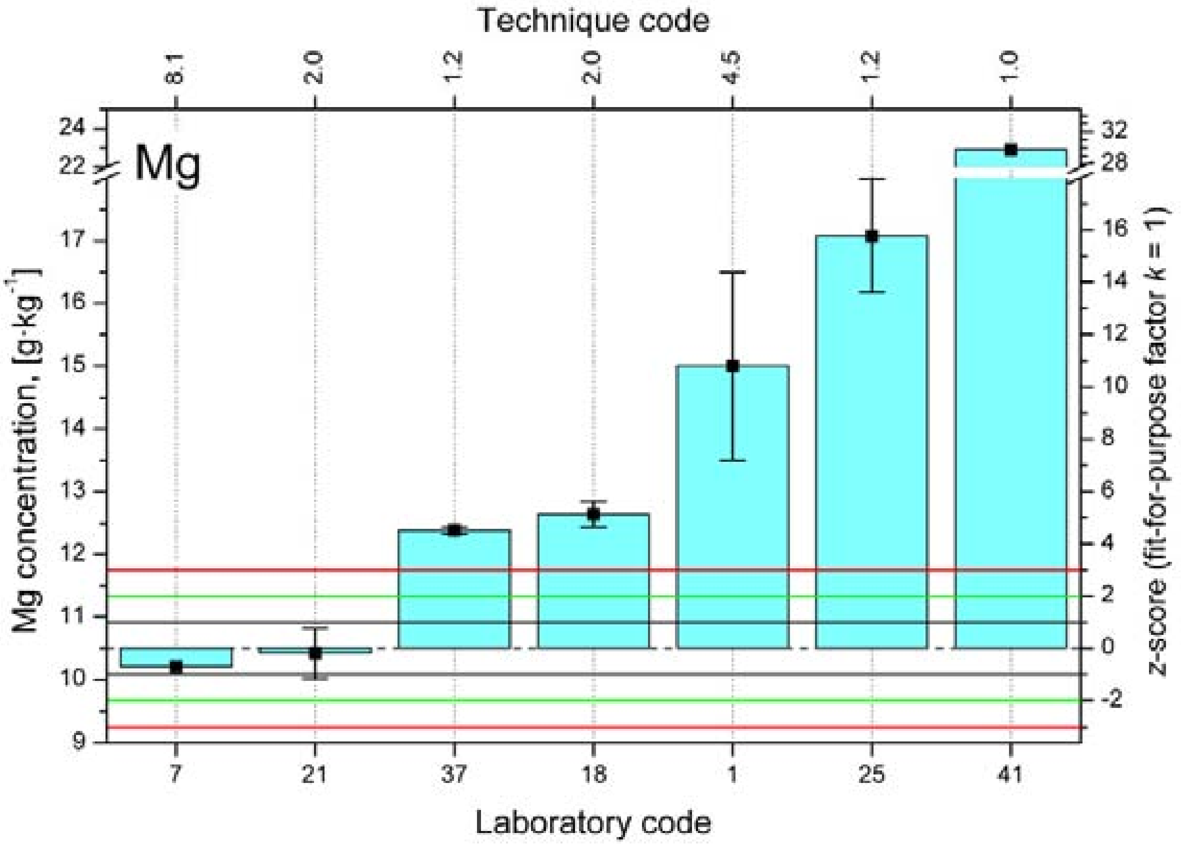


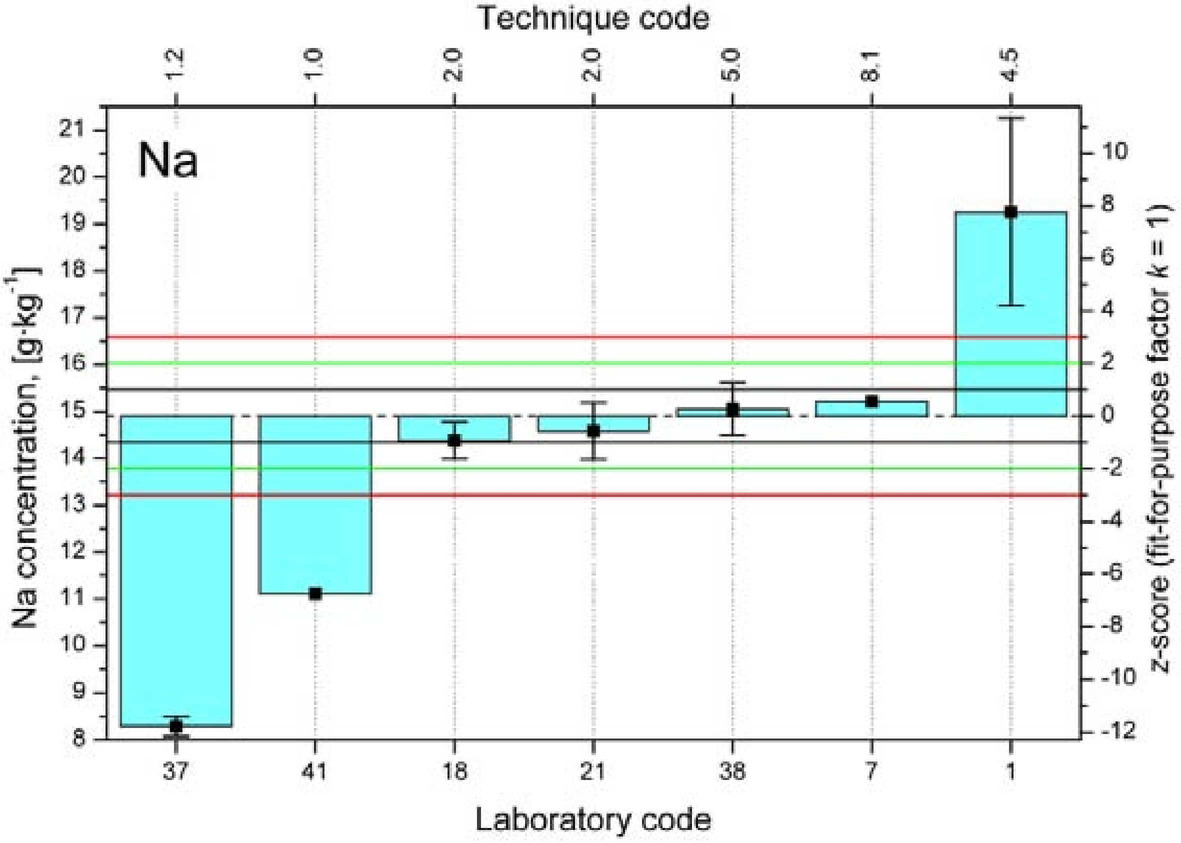
Fig. 4. Distributions of z scores for analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties, as provided by the analysts, are marked with filled squares accompanied by uncertainty 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 Eq. (2): ***k = 0.5 - solid black lines****,* ***k = 1.0 - solid green lines****, and* ***k = 1.5 - solid red lines****.*

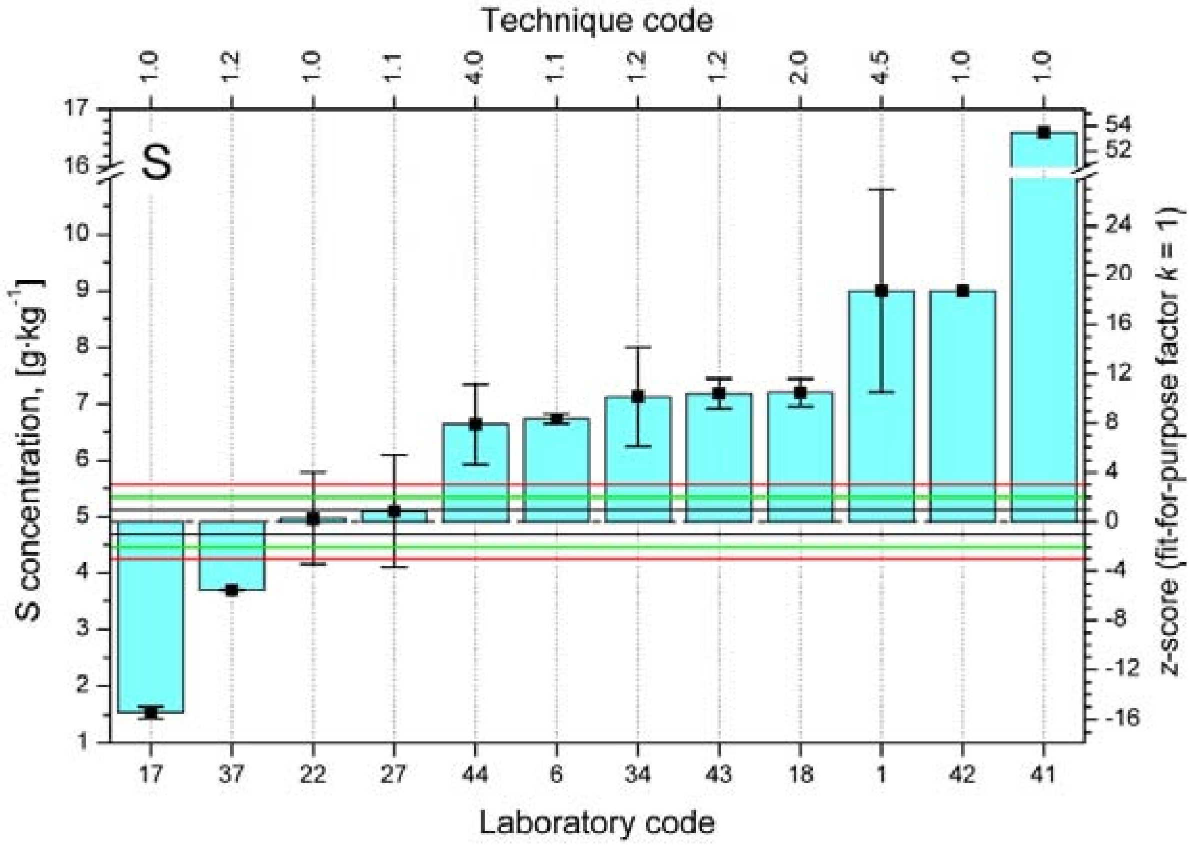

Technique code
1.2 1.2 1.3 1.2 1.0 1.1 2.0 8.1 1.0 1.1 2.0 1.2 1.2 1.2 4.0 1.0 1.1 1.1 1.1 1.2 1.1 1.0 1.0 4.5 1.1 1.3 1.2 1.0 1.0 1.1
Ca
Ca concentration, [g·kg-1]
600
300
80
70
60
50
40
30
z-score (fit-for-purpose factor k = 1)
400
200
27
24
21
18
15
12
9
6
3
0
-3
-6
-9
-12
33 25 32 26 4 27 21 7 14 36 18 43 36 37 44 28 6 39 12 34 40 22 17 1 31 19 29 41 42 16
Laboratory code

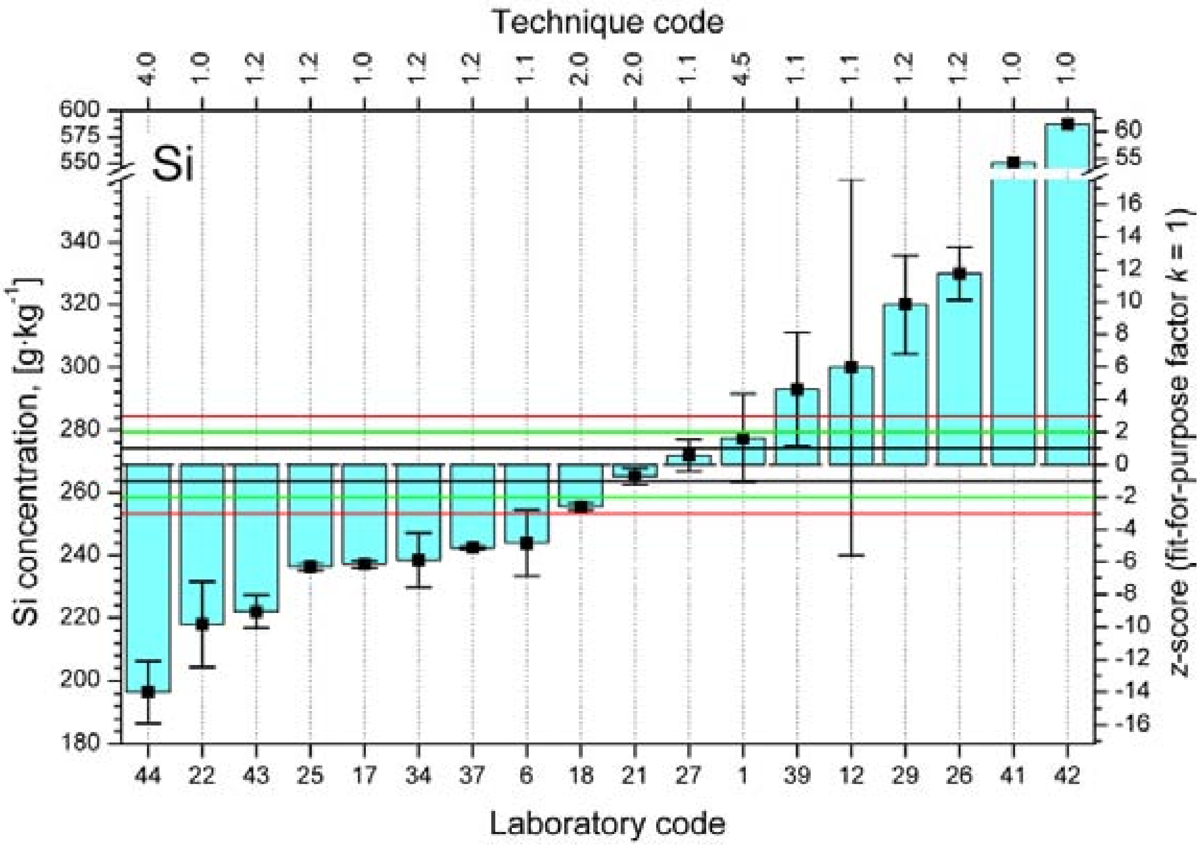

Technique code
1.2 1.2 1.3 1.0 1.0 1.1 1.1 1.2 5.0 1.0 8.1 1.3 2.0 1.2 1.2 1.1 1.0 1.0 4.0 1.2 1.0 1.1 4.5 1.1 2.0 7.2 1.2 1.2 1.1 1.1 1.0 1.2 1.0 1.1
Fe
Fe concentration, [g·kg-1]
600
500
400
300
200
100
44
42
40
38
36
34
32
30
28
26
24
22
20
z-score (fit-for-purpose factor k = 1)
500
400
300
200
100
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
33 26 32 35 14 36 6 25 38 28 7 19 21 36 37 39 4 17 44 24 22 40 1 12 18 24 43 34 27 31 41 29 42 16
Laboratory code


Technique code
1.1 1.3 1.1 1.0 1.2 1.2 8.1 1.0 1.1 1.2 1.0 2.0 1.2 1.2 4.0 1.1 4.5 2.0 1.0 1.1 1.3 1.2 1.1 1.0 1.2 1.2 1.0
K
K concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
12 32 31 14 33 43 7 4 39 36 28 21 37 34 44 6 1 18 22 27 19 25 40 17 26 29 41
Laboratory code

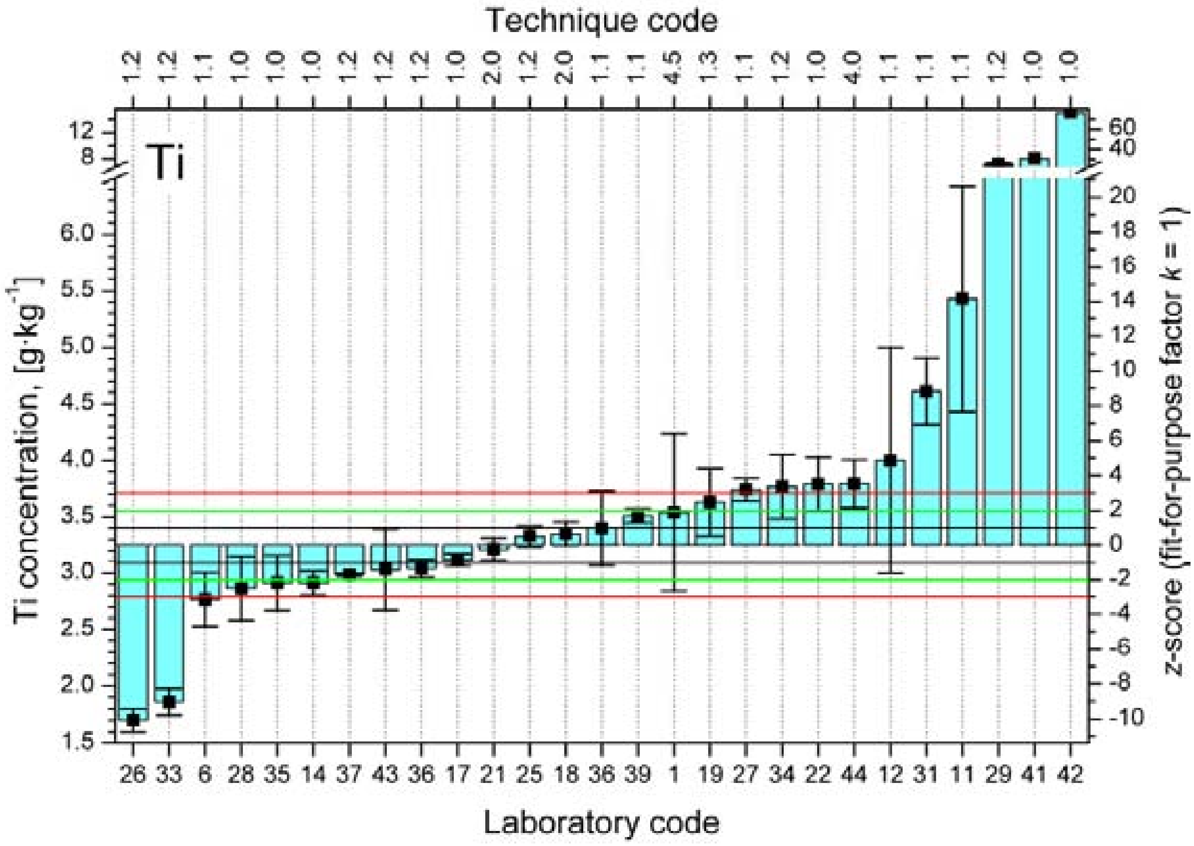

Technique code
8.1 2.0 1.2 2.0 4.5 1.2 1.0
Mg
Mg concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
7 21 37 18 1 25 41
Laboratory code


Technique code
1.2
1.0
2.0
2.0
5.0
8.1
4.5
Na
Na concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
37
41
18
21
38
7
1
Laboratory code

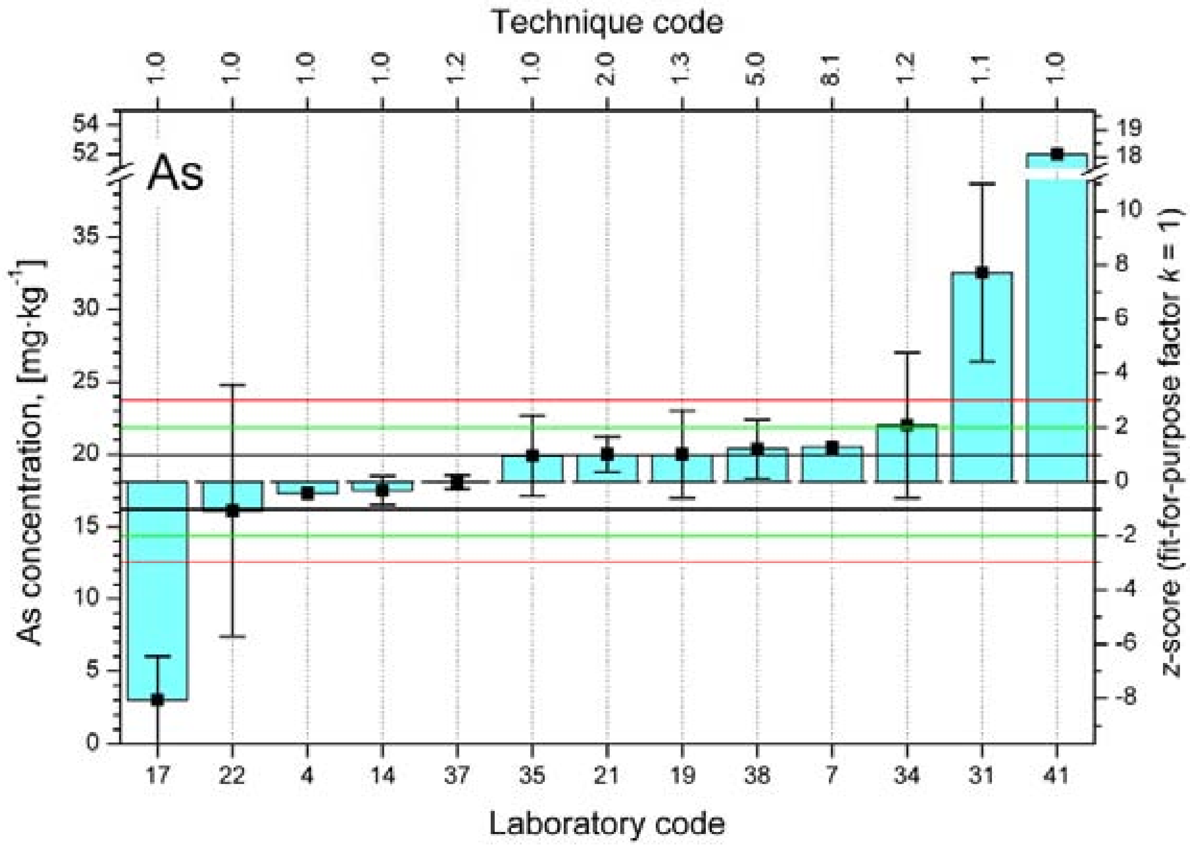

Technique code
1.0
1.2
1.0
1.1
4.0
1.1
1.2
1.2
2.0
4.5
1.0
1.0
S
S concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
17
37
22
27
44
6
34
43
18
1
42
41
Laboratory code

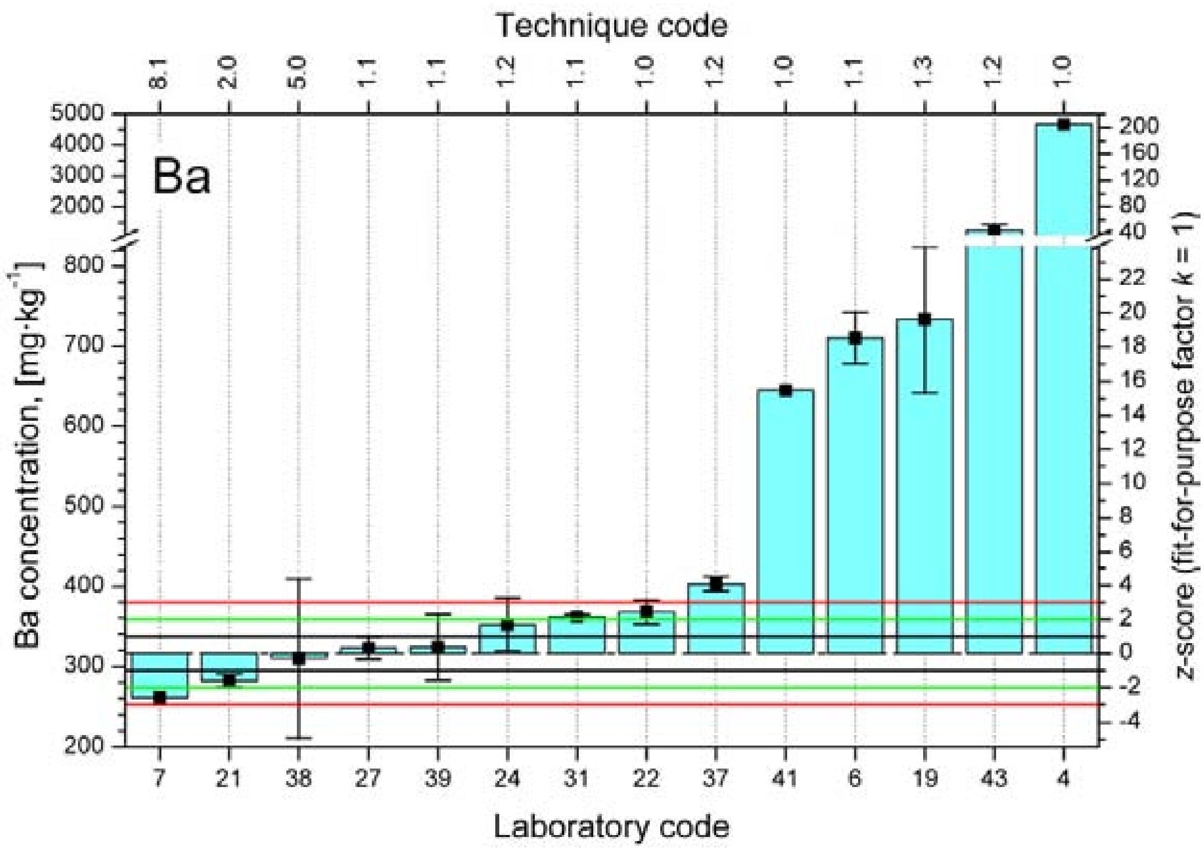


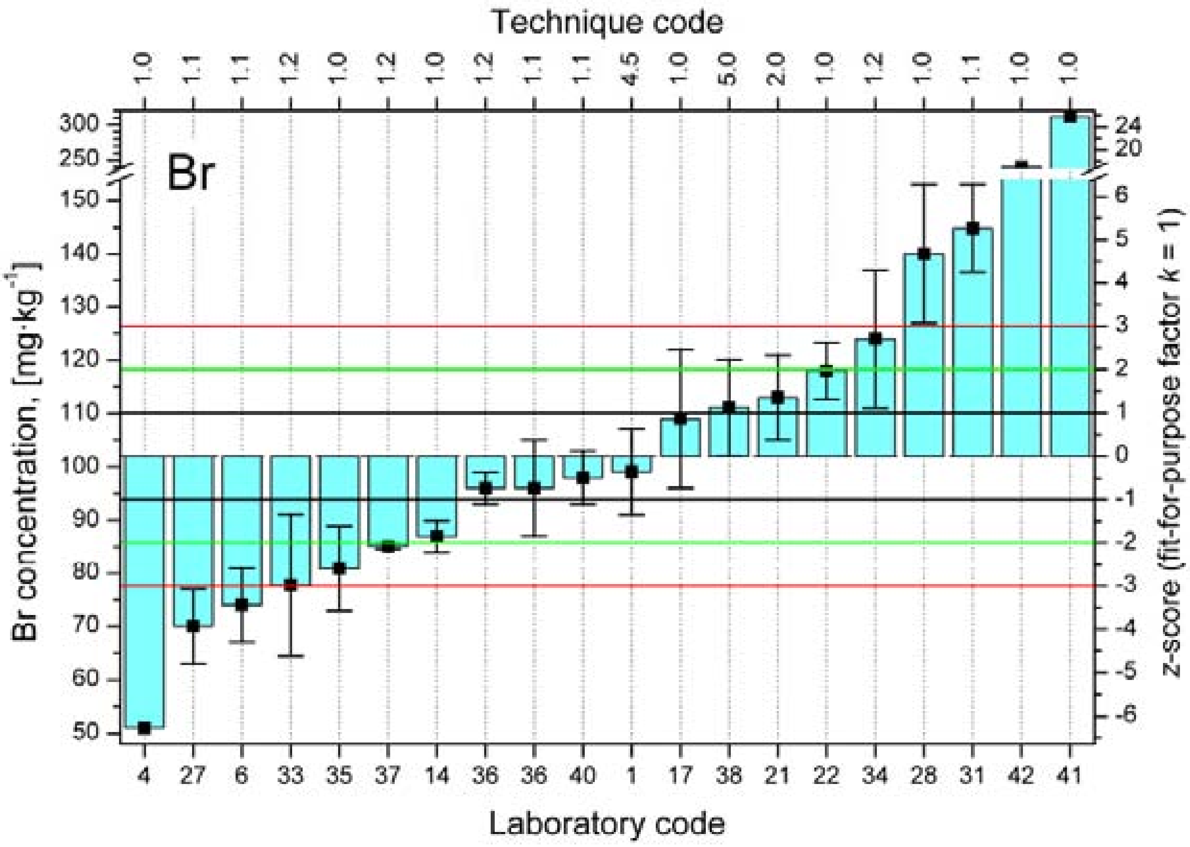
Technique code
4.0 1.0 1.2 1.2 1.0 1.2 1.2 1.1 2.0 2.0 1.1 4.5 1.1 1.1 1.2 1.2 1.0 1.0
Si
Si concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
44 22 43 25 17 34 37 6 18 21 27 1 39 12 29 26 41 42
Laboratory code

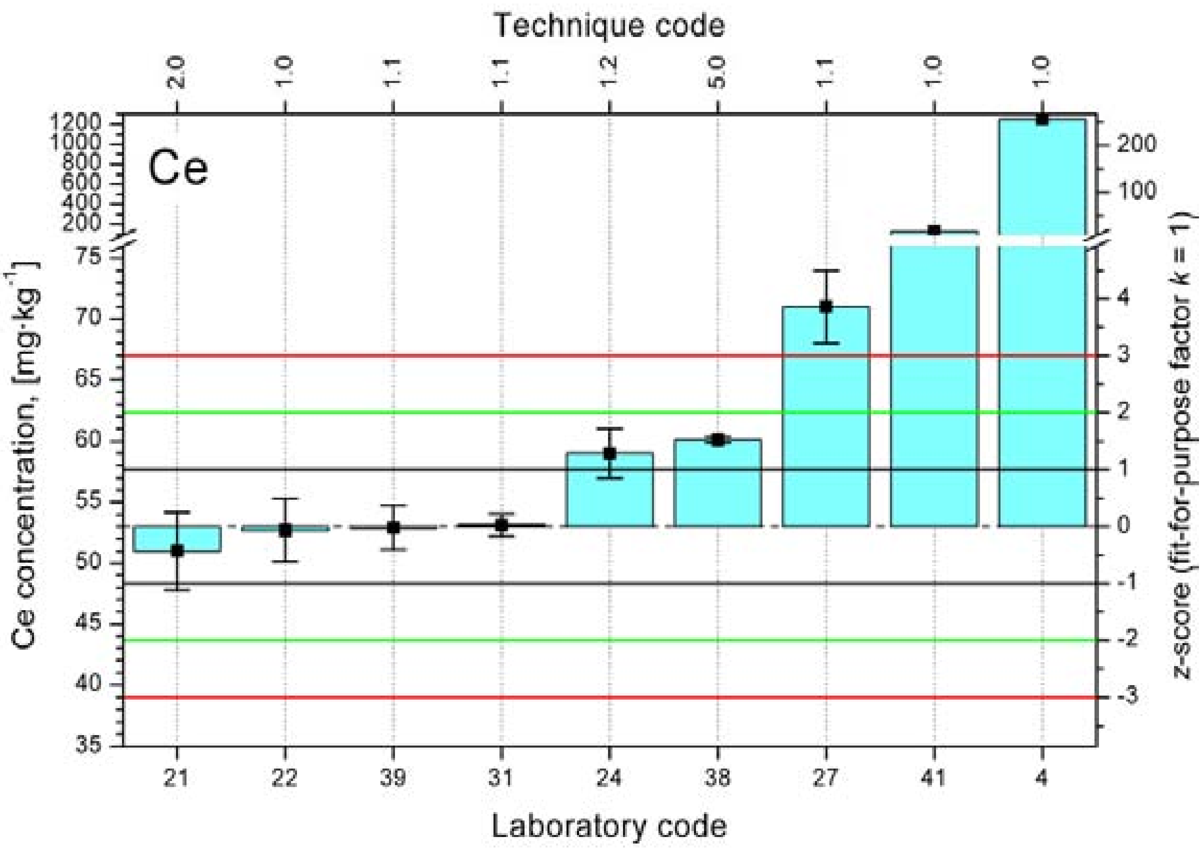


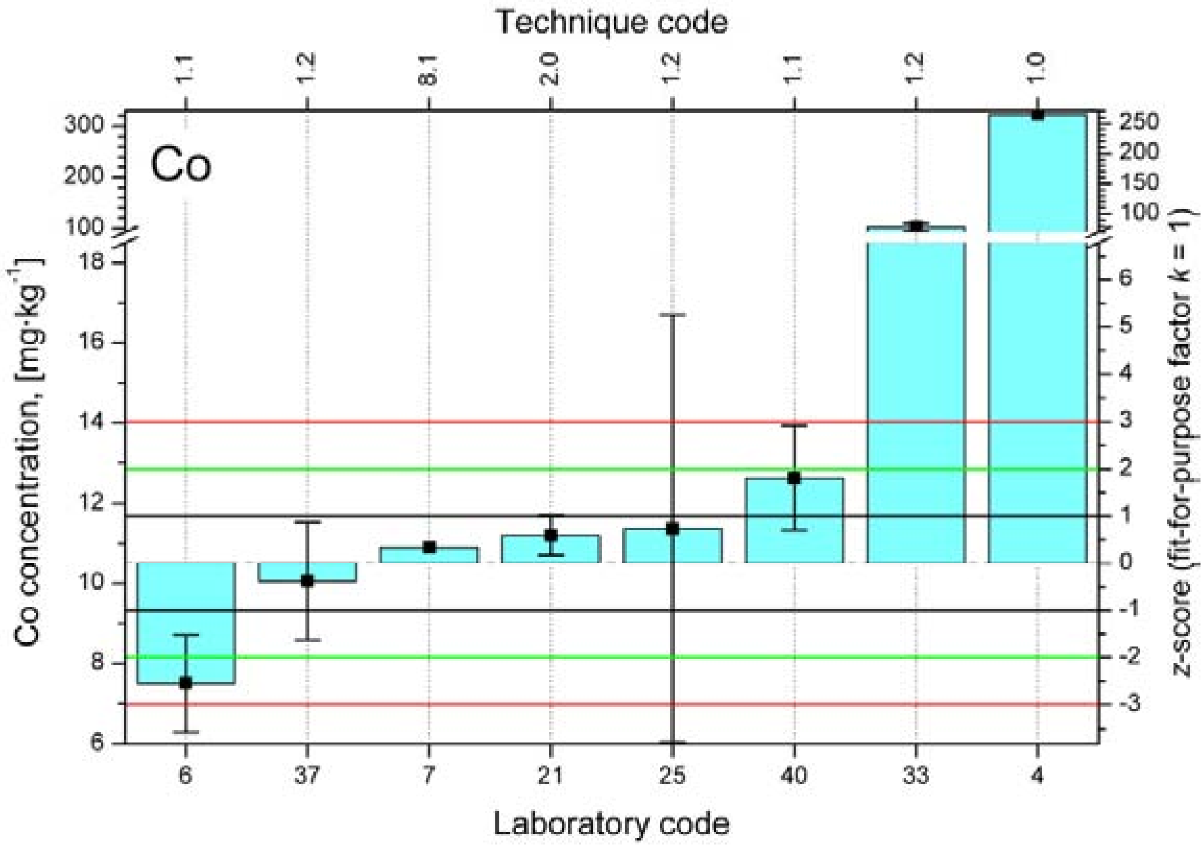
Technique code
1.2 1.2 1.1 1.0 1.0 1.0 1.2 1.2 1.2 1.0 2.0 1.2 2.0 1.1 1.1 4.5 1.3 1.1 1.2 1.0 4.0 1.1 1.1 1.1 1.2 1.0 1.0
Ti
Ti concentration, [g·kg-1]
z-score (fit-for-purpose factor k = 1)
26 33 6 28 35 14 37 43 36 17 21 25 18 36 39 1 19 27 34 22 44 12 31 11 29 41 42
Laboratory code

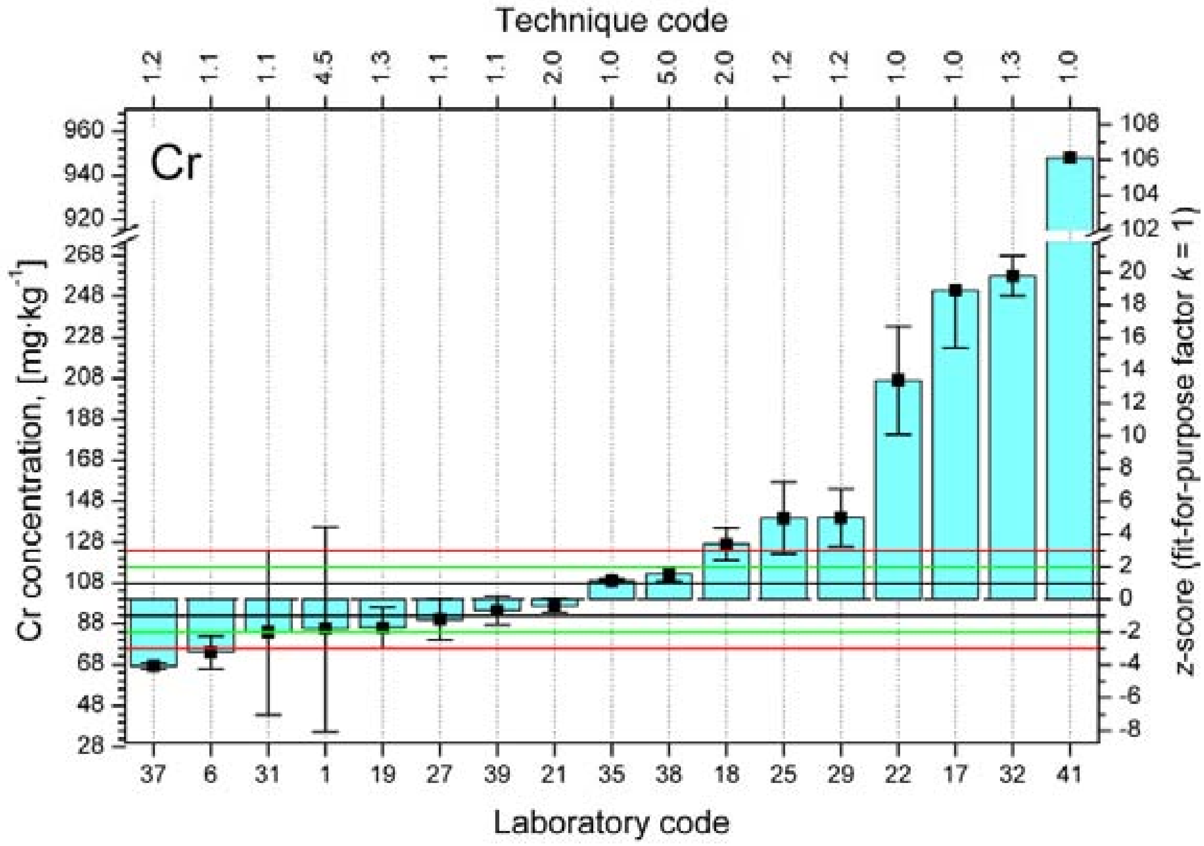

Technique code
1.0
1.0
1.0
1.0
1.2
1.0
2.0
1.3
5.0
8.1
1.2
1.1
1.0
As
As concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
17
22
4
14
37
35
21
19
38
7
34
31
41
Laboratory code

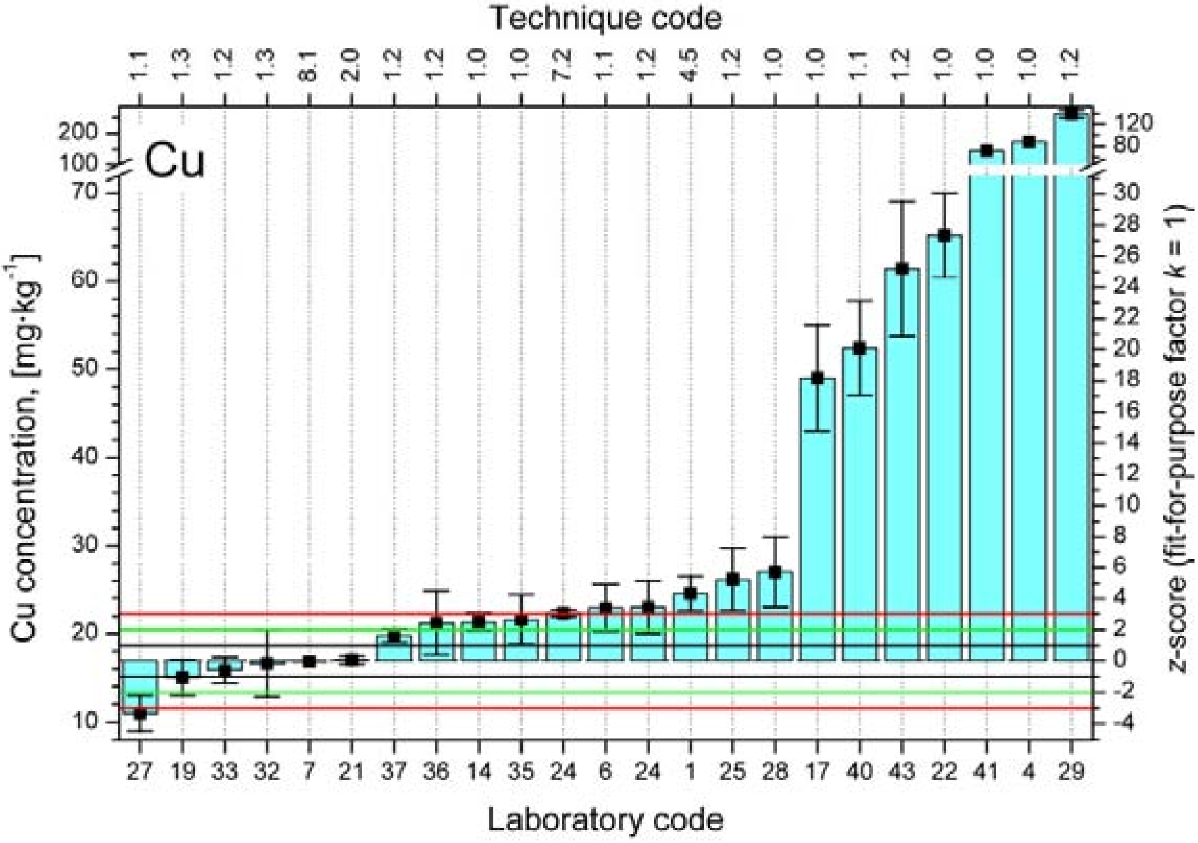

Technique code
8.1
2.0
5.0
1.1
1.1
1.2
1.1
1.0
1.2
1.0
1.1
1.3
1.2
1.0
Ba
Ba concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
7
21
38
27
39
24
31
22
37
41
6
19
43
4
Laboratory code


Technique code
1.0 1.1 1.1 1.2 1.0 1.2 1.0 1.2 1.1 1.1 4.5 1.0 5.0 2.0 1.0 1.2 1.0 1.1 1.0 1.0
Br
Br concentration, [mg·kg-1]
50 60 70 80 90 100 110 120 130 140 150 250 300
z-score (fit-for-purpose factor k = 1)
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 20 24
4 27 6 33 35 37 14 36 36 40 1 17 38 21 22 34 28 31 42 41
Laboratory code

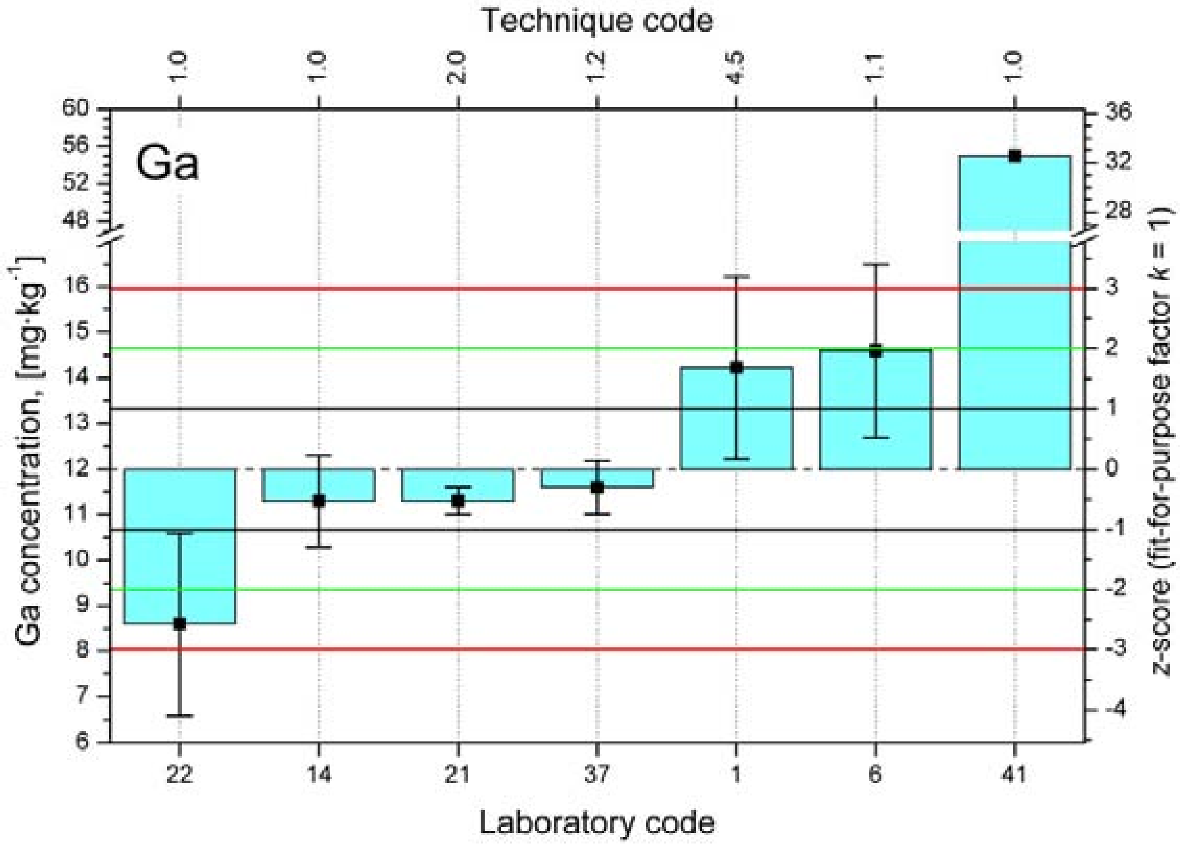

Technique code
2.0 1.0 1.1 1.1 1.2 5.0 1.1 1.0 1.0
Ce
Ce concentration, [mg·kg-1]
35 40 45 50 55 60 65 70 75 200 400 600 800 1000 1200
z-score (fit-for-purpose factor k = 1)
-3 -2 -1 0 1 2 3 4 100 200
21 22 39 31 24 38 27 41 4
Laboratory code


Technique code
1.1 1.2 8.1 2.0 1.2 1.1 1.2 1.0
Co
Co concentration, [mg·kg-1]
300 200 100 18 16 14 12 10 8 6
z-score (fit-for-purpose factor k = 1)
250 200 150 100 6 5 4 3 2 1 0 -1 -2 -3
6 37 7 21 25 40 33 4
Laboratory code

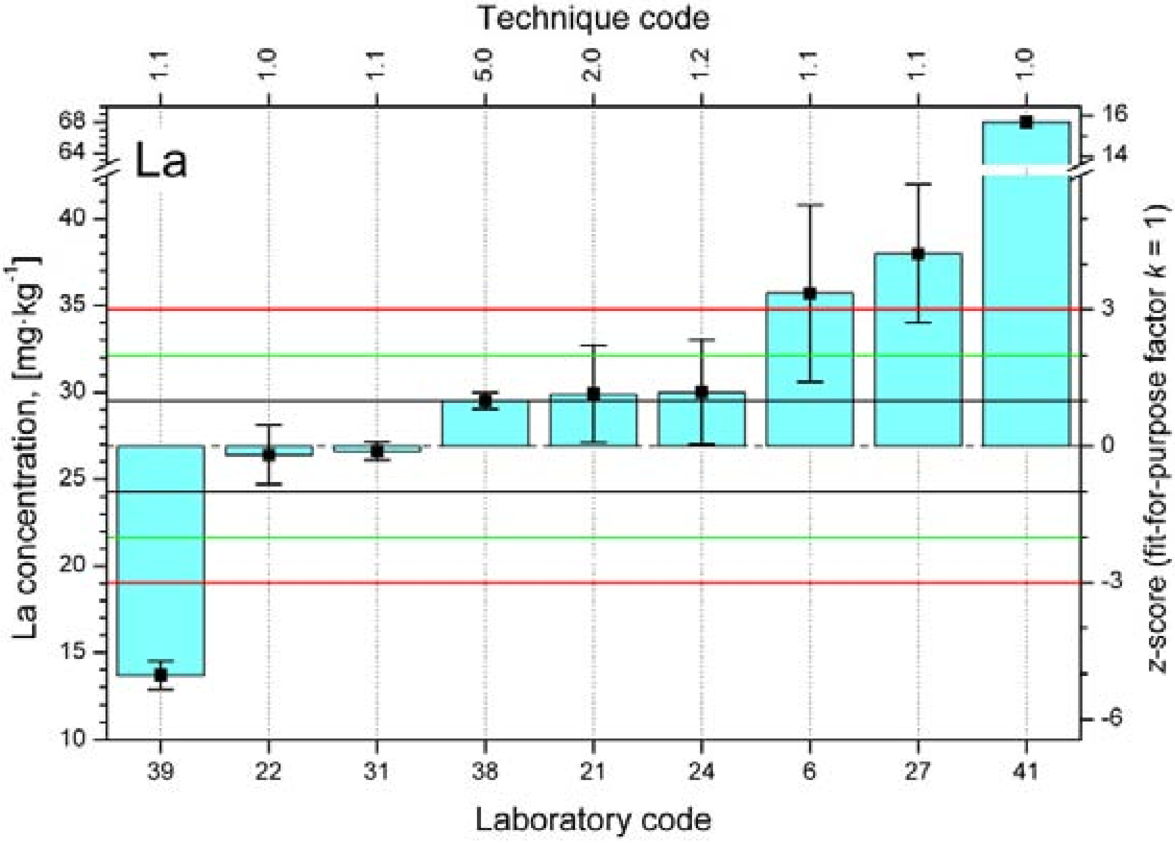

Technique code
1.2 1.1 1.1 4.5 1.3 1.1 1.1 2.0 1.0 5.0 2.0 1.2 1.2 1.0 1.0 1.3 1.0
Cr
Cr concentration, [mg·kg-1]
960 940 920 268 248 228 208 188 168 148 128 108 88 68 48 28
z-score (fit-for-purpose factor k = 1)
108 106 104 102 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8
37 6 31 1 19 27 39 21 35 38 18 25 29 22 17 32 41
Laboratory code

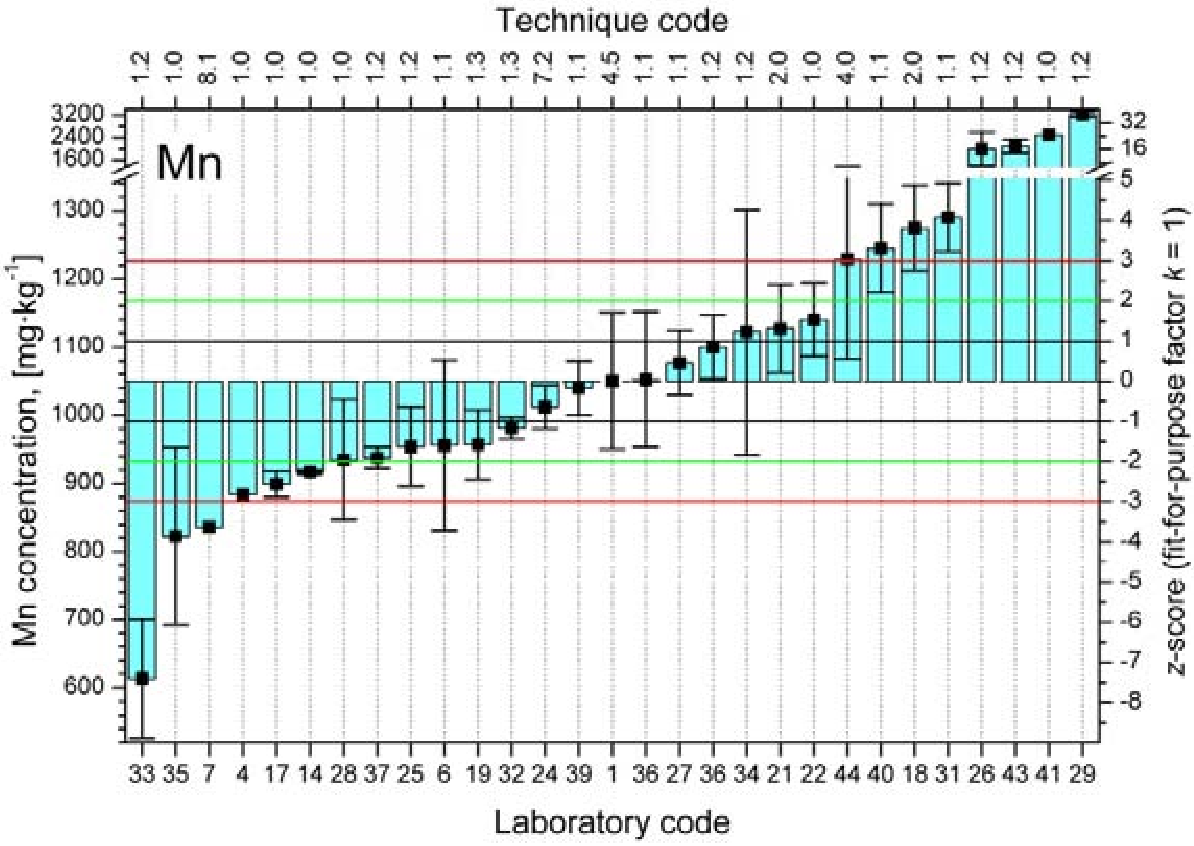


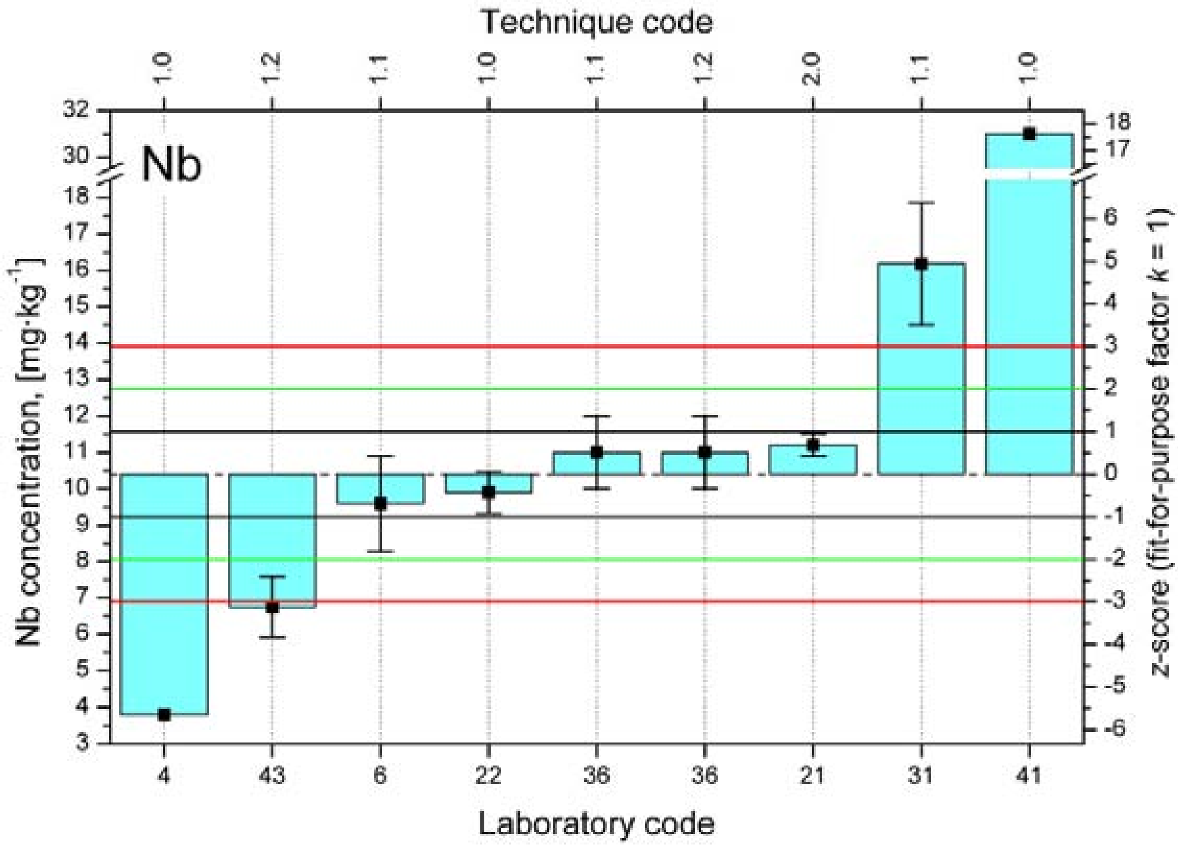
Technique code
1.1 1.3 1.2 1.3 8.1 2.0 1.2 1.2 1.0 1.0 7.2 1.1 1.2 4.5 1.2 1.0 1.0 1.1 1.2 1.0 1.0 1.0 1.2
Cu
Cu concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
27 19 33 32 7 21 37 36 14 35 24 6 24 1 25 28 17 40 43 22 41 4 29
Laboratory code

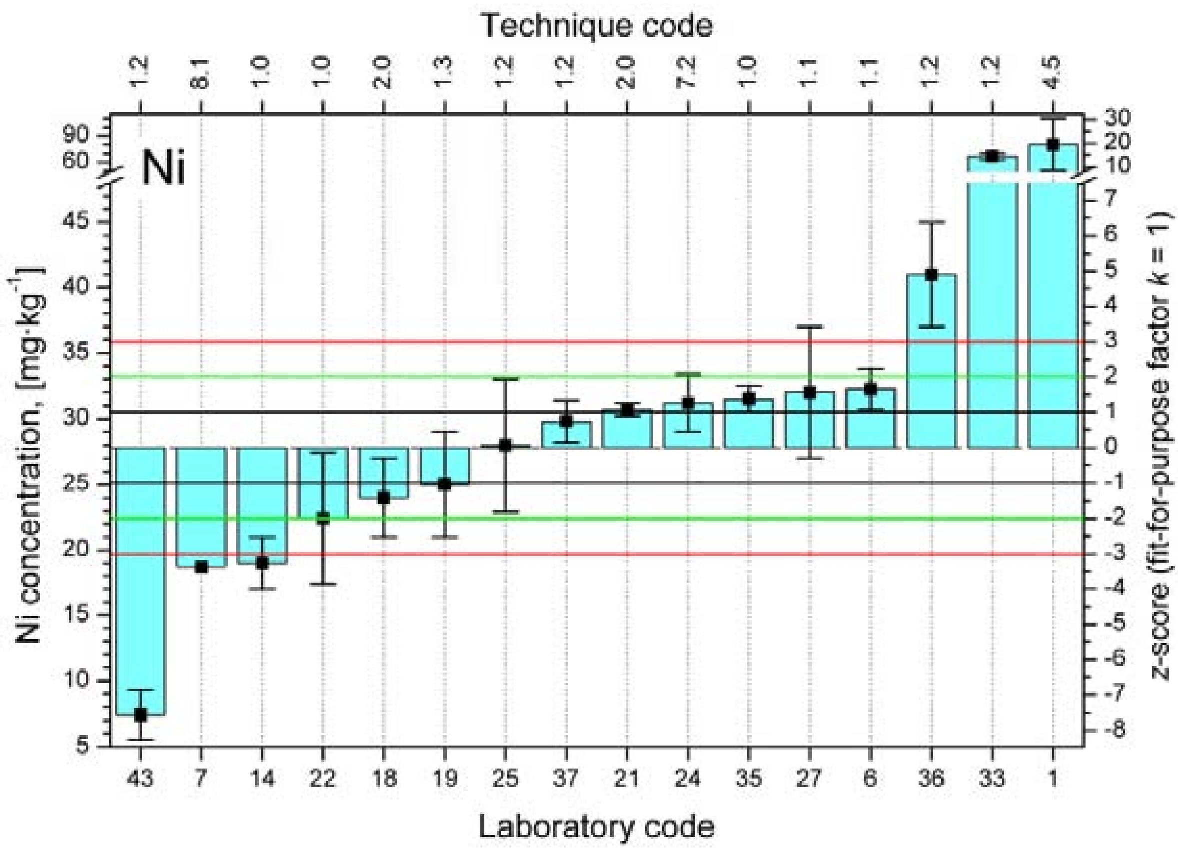


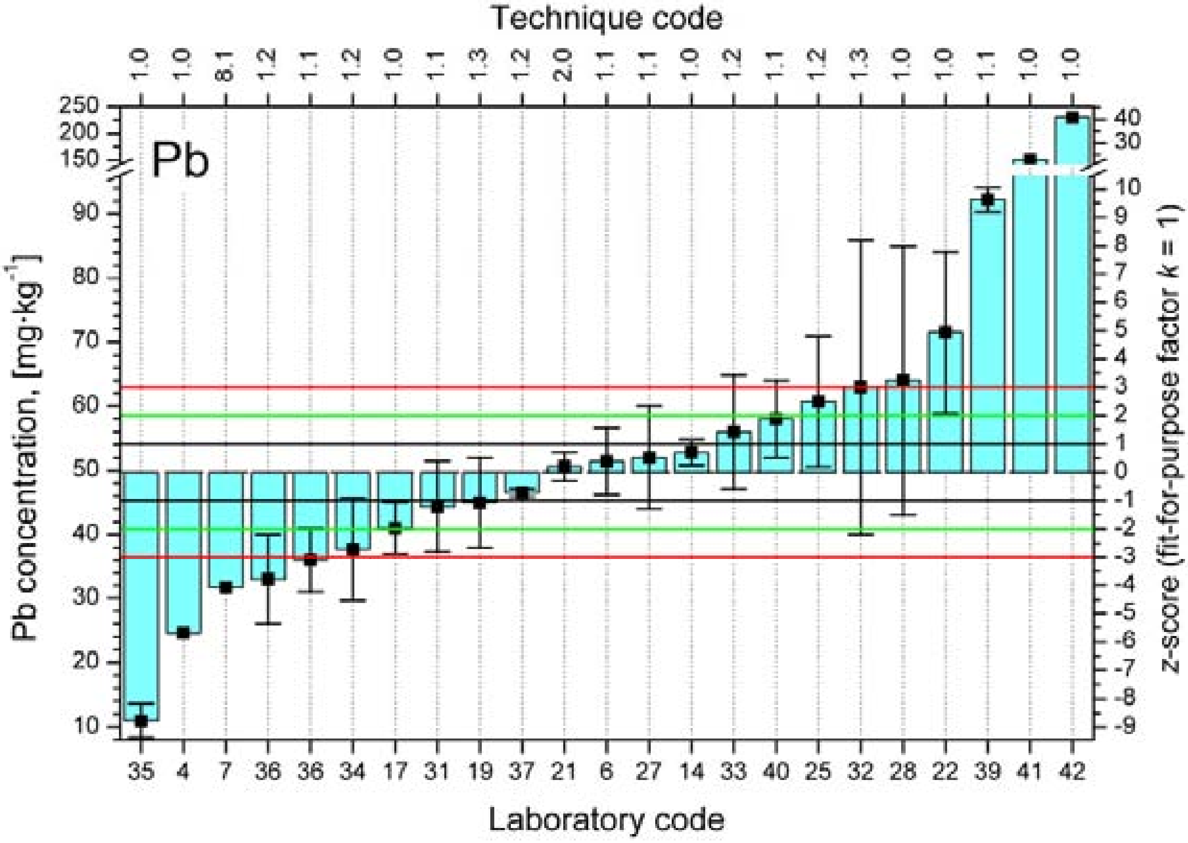
Technique code
1.0 1.0 2.0 1.2 4.5 1.1 1.0
Ga
Ga concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
22 14 21 37 1 6 41
Laboratory code

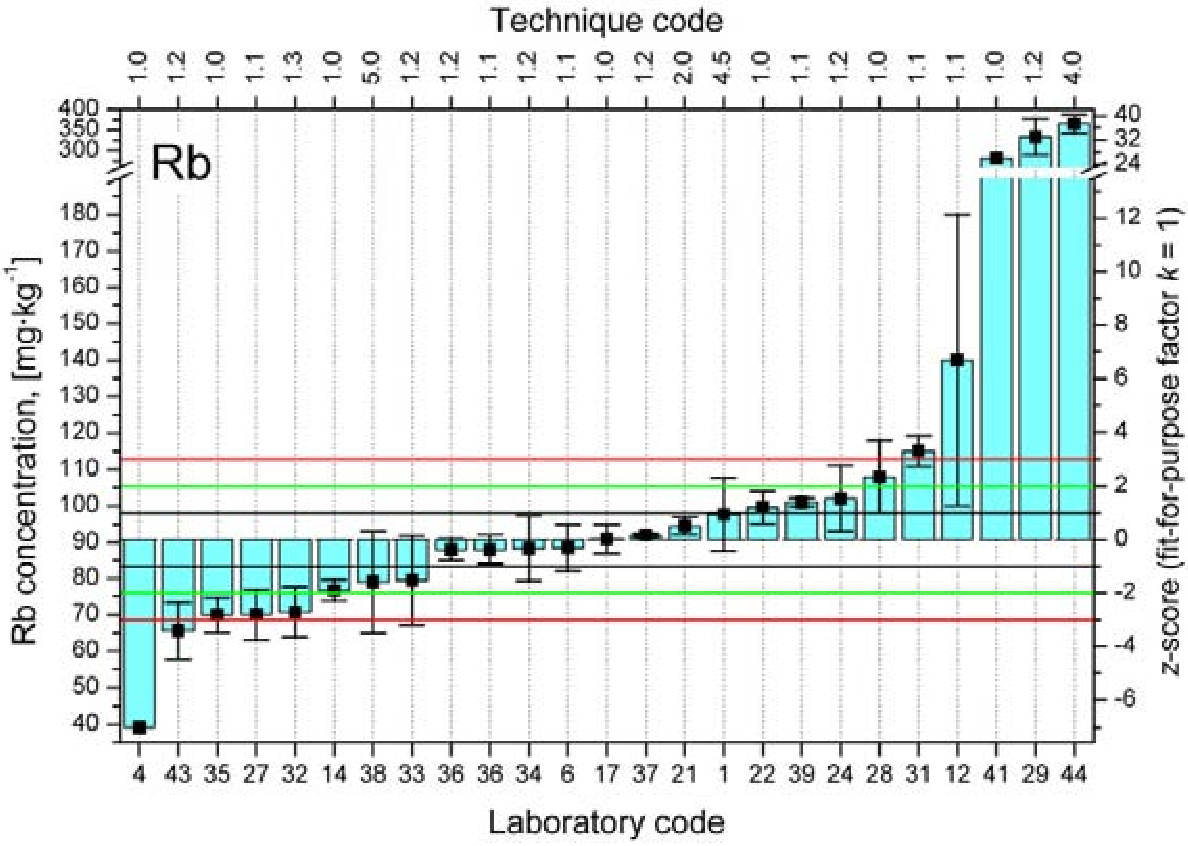

Technique code
1.1 1.0 1.1 5.0 2.0 1.2 1.1 1.1 1.0
La
La concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
39 22 31 38 21 24 6 27 41

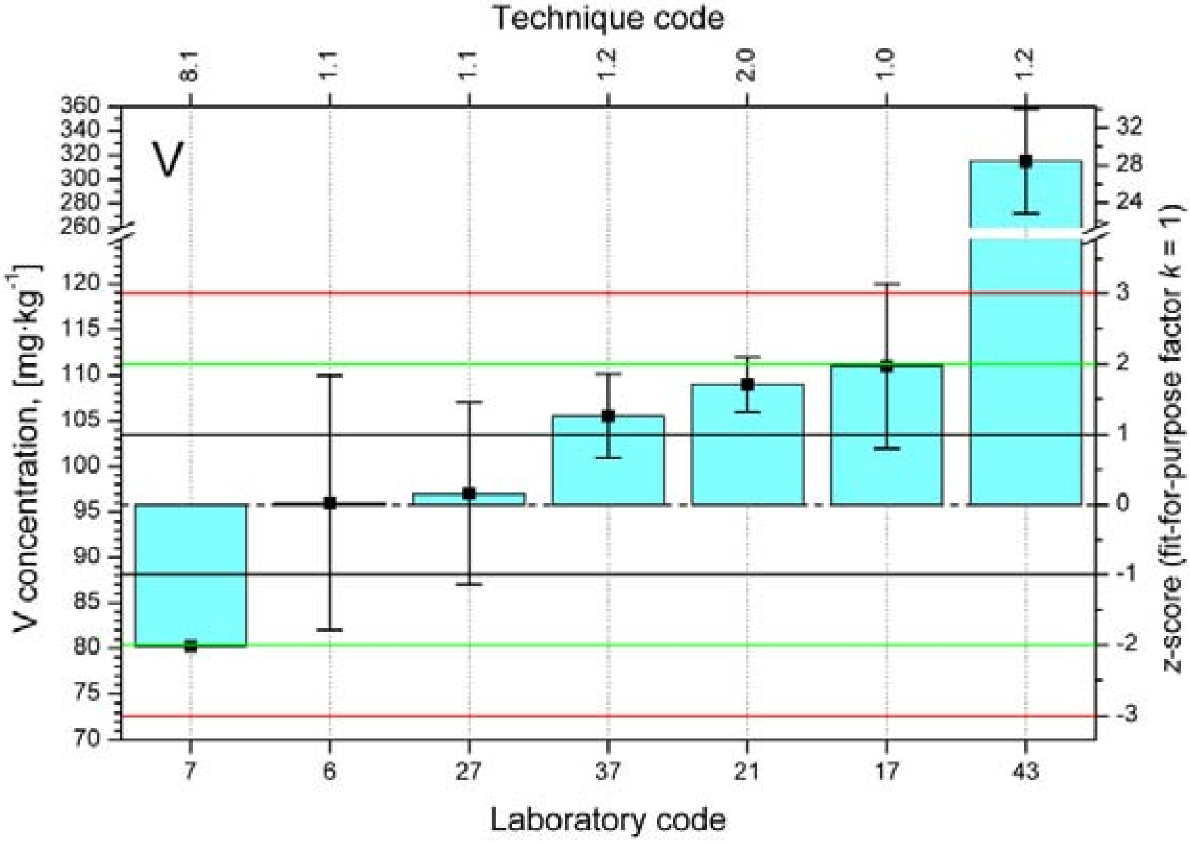

Technique code
1.2 1.0 8.1 1.0 1.0 1.0 1.0 1.2 1.2 1.1 1.3 1.3 7.2 1.1 4.5 1.1 1.1 1.2 1.2 2.0 1.0 4.0 1.1 2.0 1.1 1.2 1.2 1.0 1.2
Mn
Mn concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
Laboratory code
33 35 7 4 17 14 28 37 25 6 19 32 24 39 1 36 27 36 34 21 22 44 40 18 31 26 43 41 29

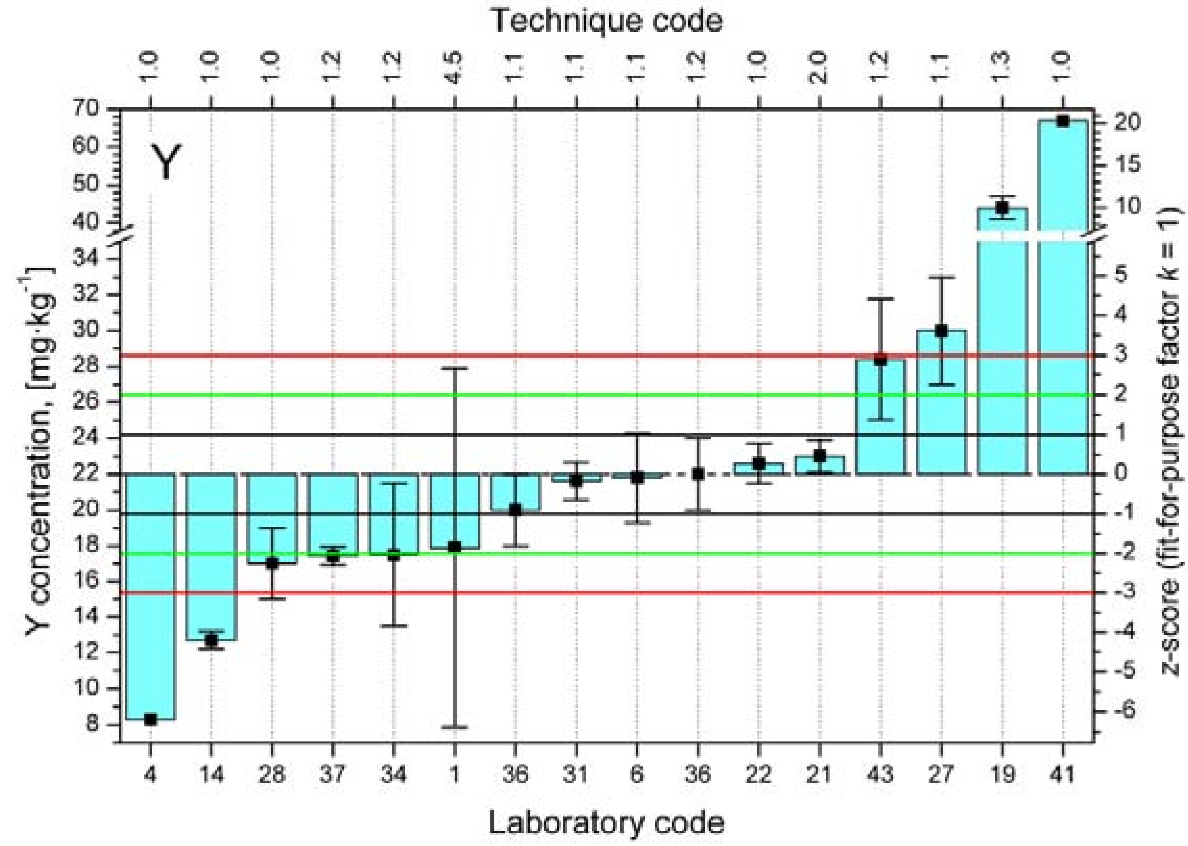

Technique code
1.0
1.2
1.1
1.0
1.1
1.2
2.0
1.1
1.0
Nb
Nb concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
4
43
6
22
36
36
21
31
41
Laboratory code

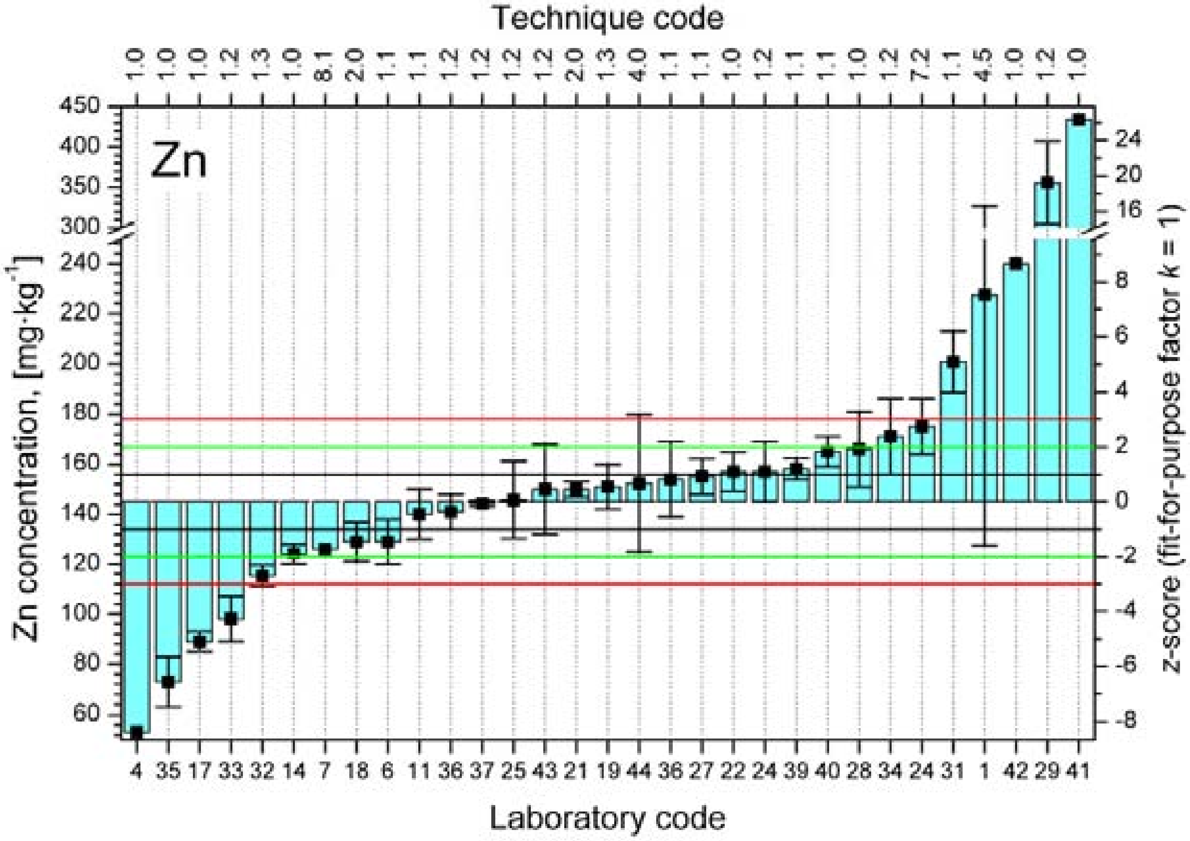

Technique code
1.2
8.1
1.0
1.0
2.0
1.3
1.2
1.2
2.0
7.2
1.0
1.1
1.1
1.2
1.2
4.5
Ni
Ni concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
43
7
14
22
18
19
25
37
21
24
35
27
6
36
33
1
Laboratory code

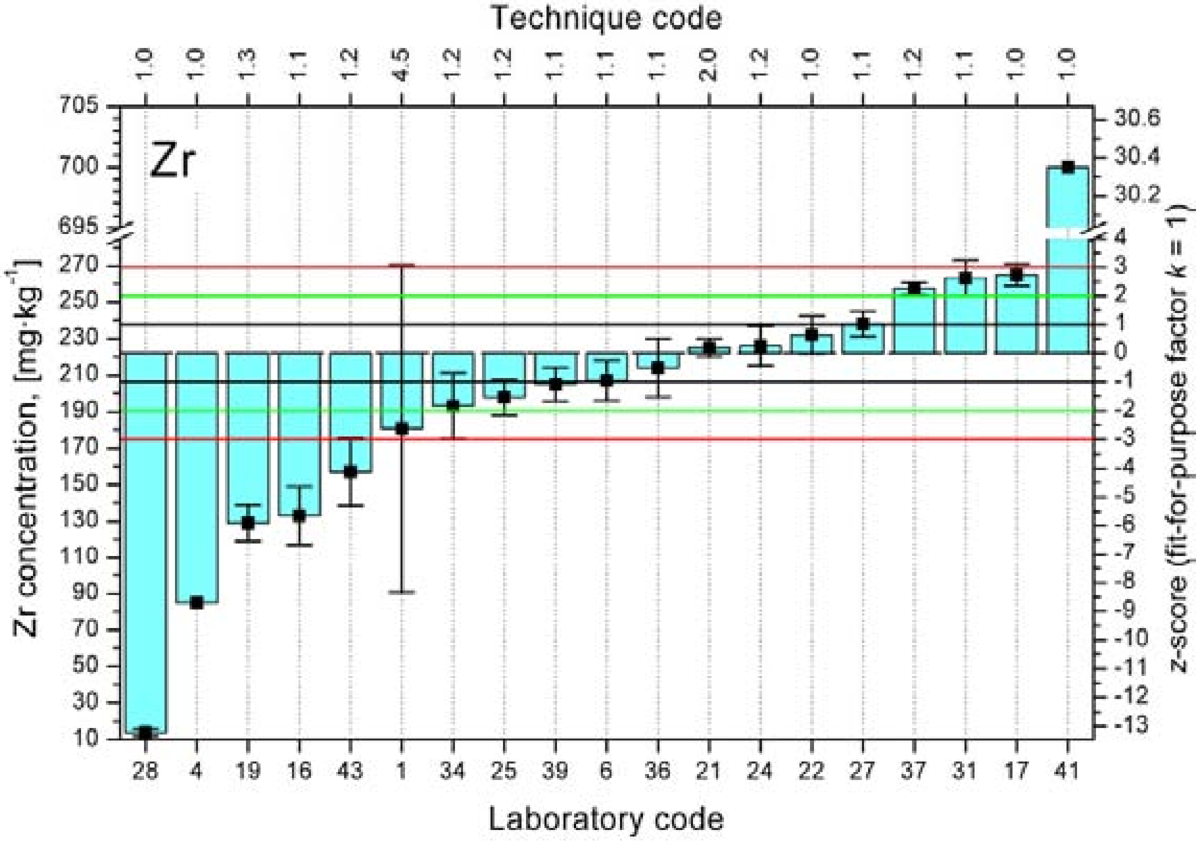

Technique code
1.0 1.0 8.1 1.2 1.1 1.2 1.0 1.1 1.3 1.2 2.0 1.1 1.1 1.0 1.2 1.1 1.2 1.3 1.0 1.0 1.1 1.0 1.0
Pb
Pb concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
35 4 7 36 36 34 17 31 19 37 21 6 27 14 33 40 25 32 28 22 39 41 42
Laboratory code


Technique code
1.0 1.2 1.0 1.1 1.3 1.0 5.0 1.2 1.2 1.1 1.2 1.1 1.0 1.2 2.0 4.5 1.0 1.1 1.2 1.0 1.1 1.1 1.0 1.2 4.0
Rb
Rb concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
4 43 35 27 32 14 38 33 36 36 34 6 17 37 21 1 22 39 24 28 31 12 41 29 44
Laboratory code


Technique code
8.1
1.1
1.1
1.2
2.0
1.0
1.2
V
V concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
7
6
27
37
21
17
43
Laboratory code


Technique code
1.0
1.0
1.0
1.2
1.2
4.5
1.1
1.1
1.1
1.2
1.0
2.0
1.2
1.1
1.3
1.0
Y
Y concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
4
14
28
37
34
1
36
31
6
36
22
21
43
27
19
41
Laboratory code


Technique code
1.0 1.0 1.0 1.2 1.3 1.0 8.1 2.0 1.1 1.1 1.2 1.2 1.2 1.2 2.0 1.3 4.0 1.1 1.1 1.0 1.2 1.1 1.1 1.0 1.2 7.2 1.1 4.5 1.0 1.2 1.0
Zn
Zn concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
4 35 17 33 32 14 7 18 6 11 36 37 25 43 21 19 44 36 27 22 24 39 40 28 34 24 31 1 42 29 41
Laboratory code


Technique code
1.0 1.0 1.3 1.1 1.2 4.5 1.2 1.2 1.1 1.1 1.1 2.0 1.2 1.0 1.1 1.2 1.1 1.0 1.0
Zr
Zr concentration, [mg·kg-1]
z-score (fit-for-purpose factor k = 1)
28 4 19 16 43 1 34 25 39 6 36 21 24 22 27 37 31 17 41
Laboratory code

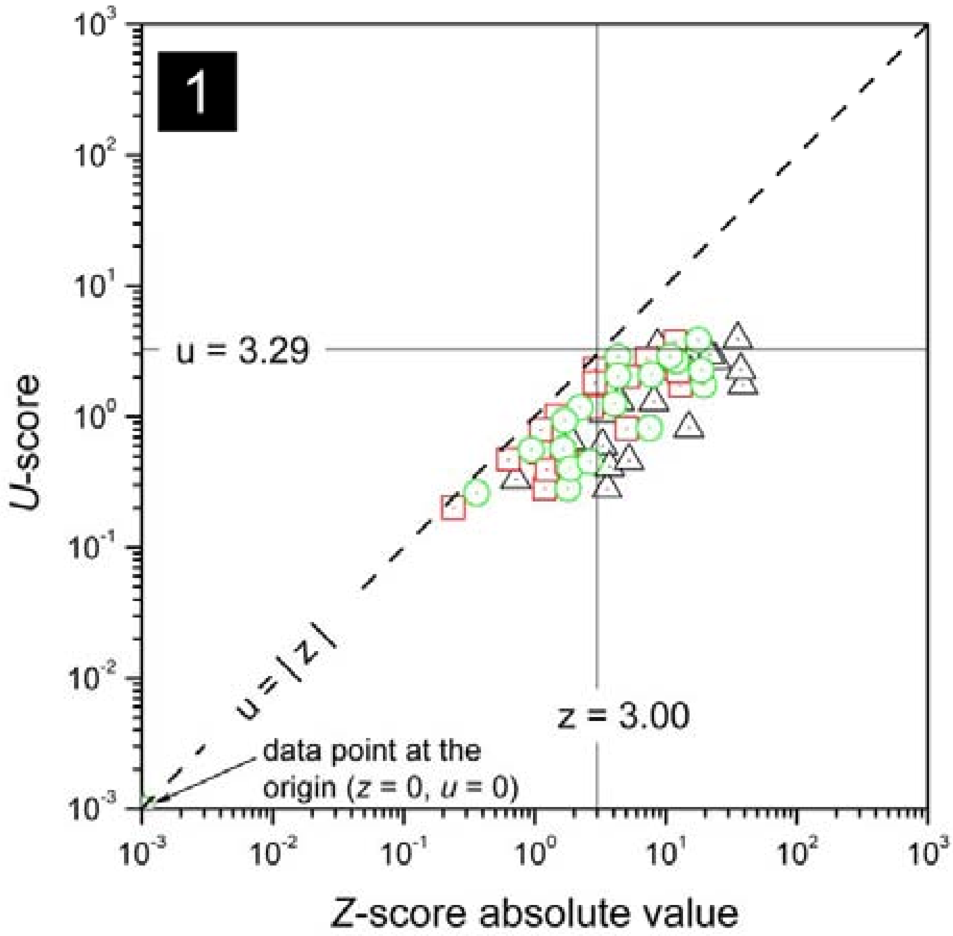
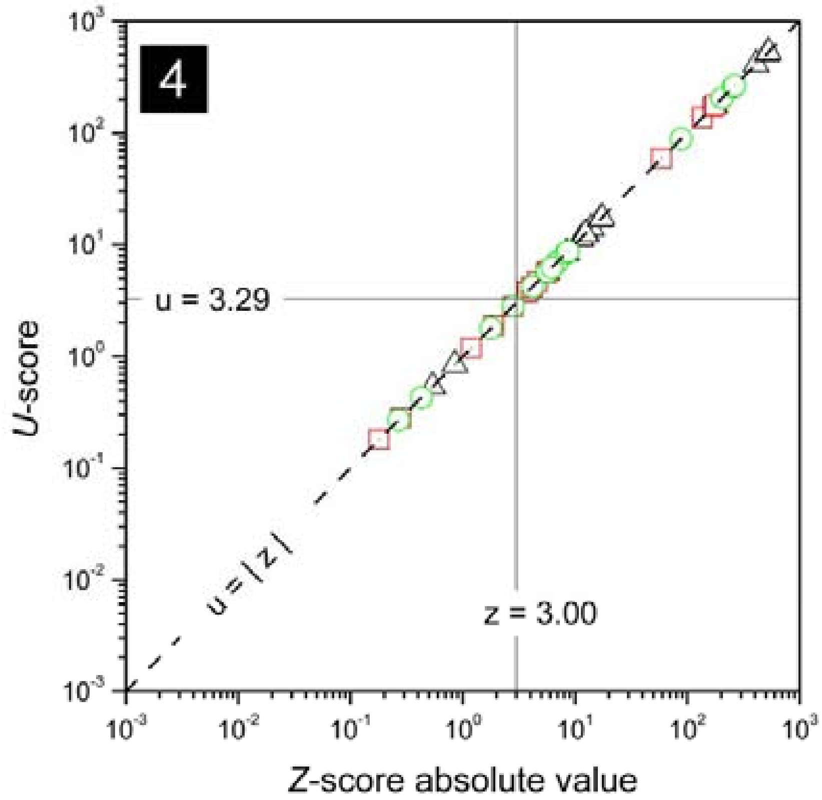
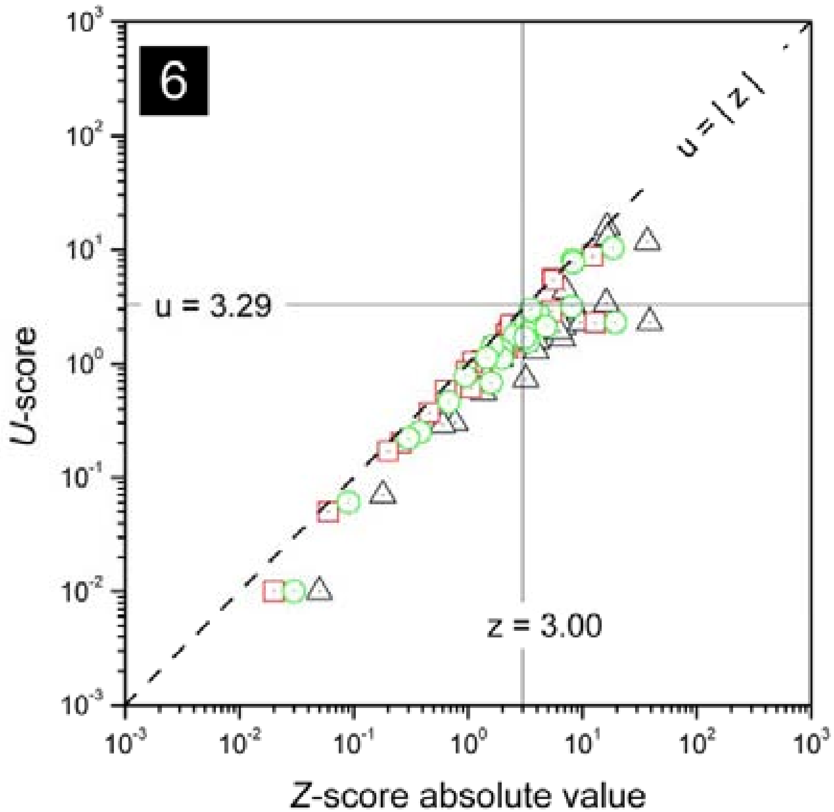
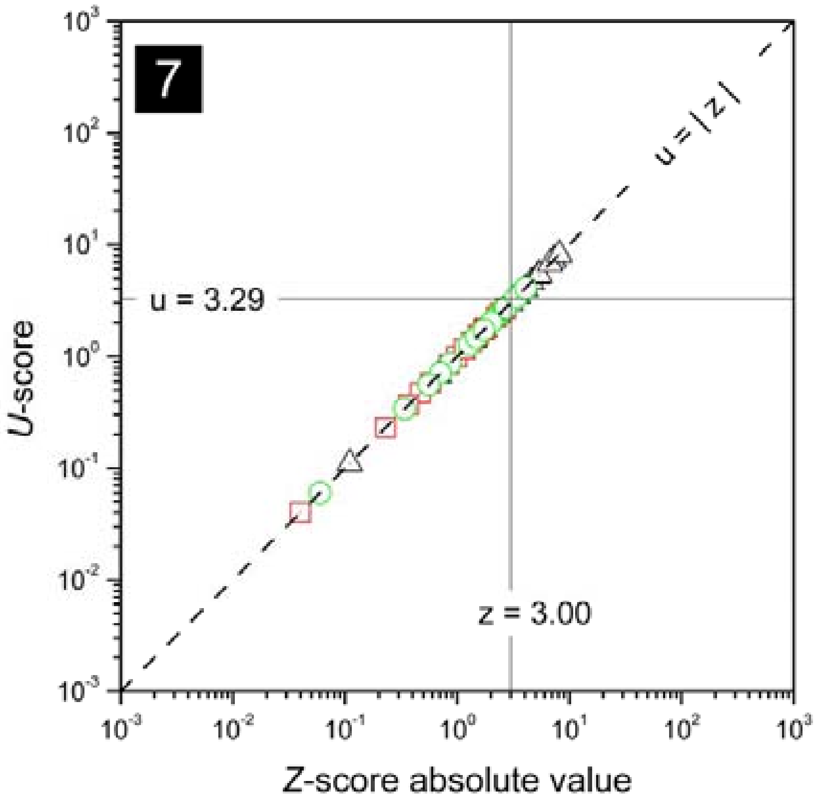
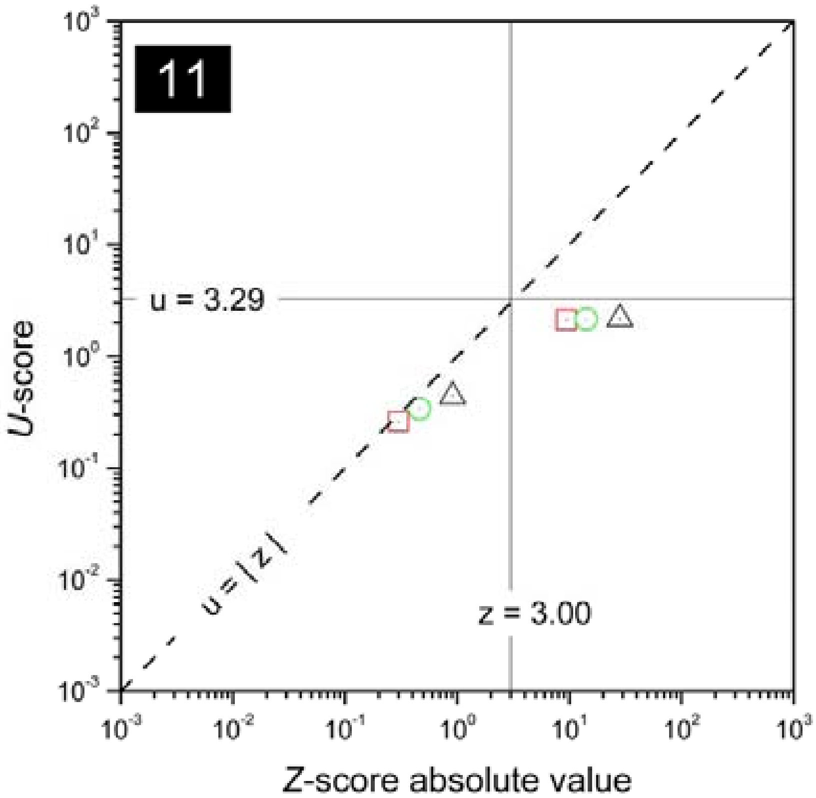


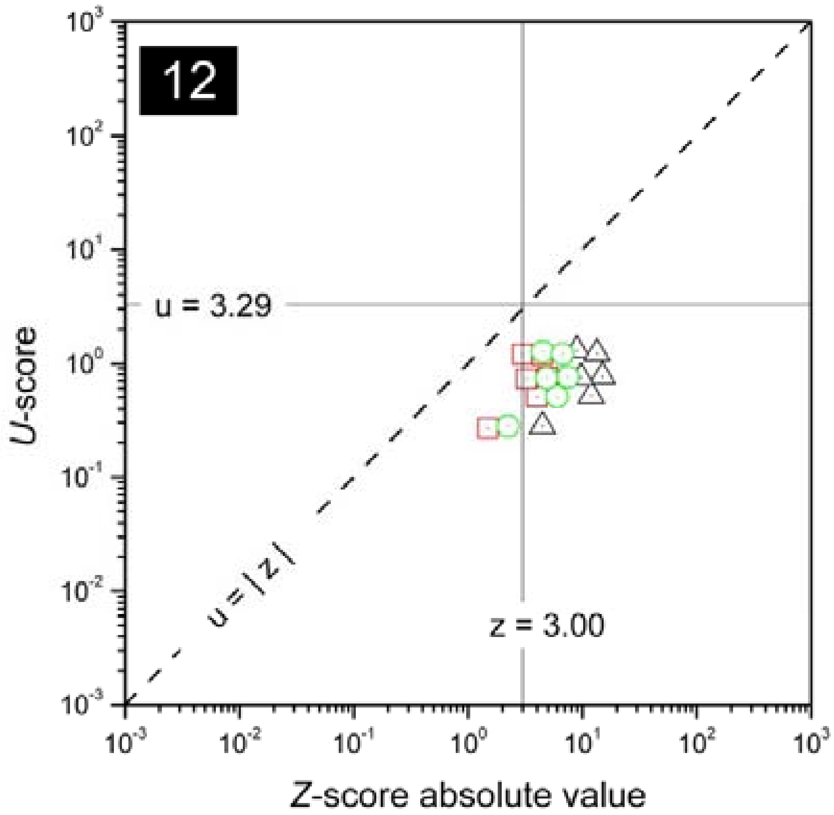
Fig. 5. Combined plots of z- and u scores for participating laboratories. The laboratory code is shown in the left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eq. (2) with factor k, namely: ***k = 0.5 - black triangles****,* ***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.*

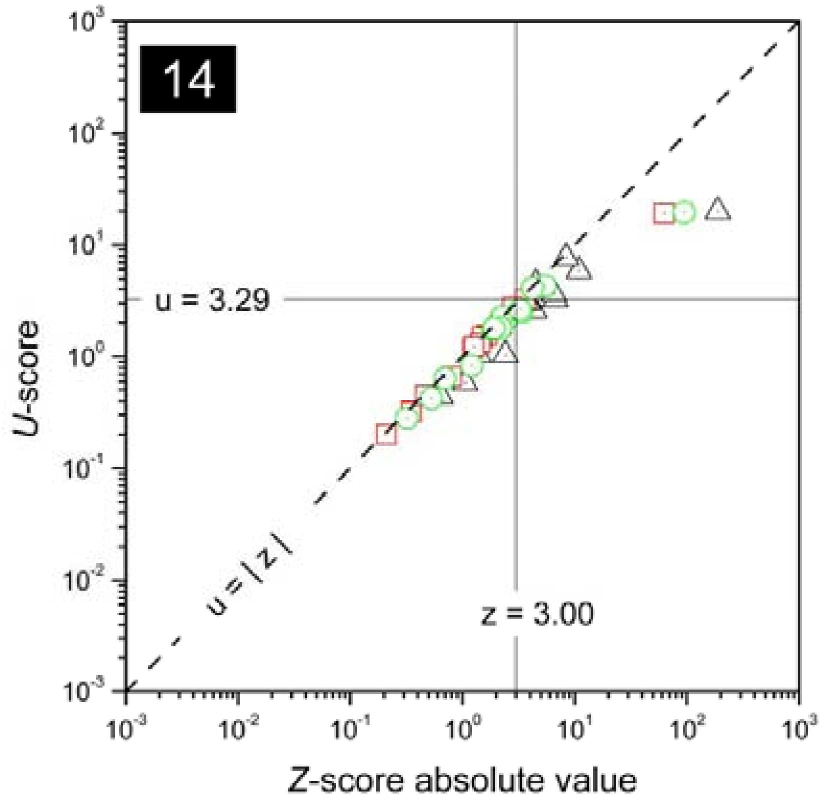

4
u = 3.29
u = | z |
z = 3.00
U-score
Z-score absolute value

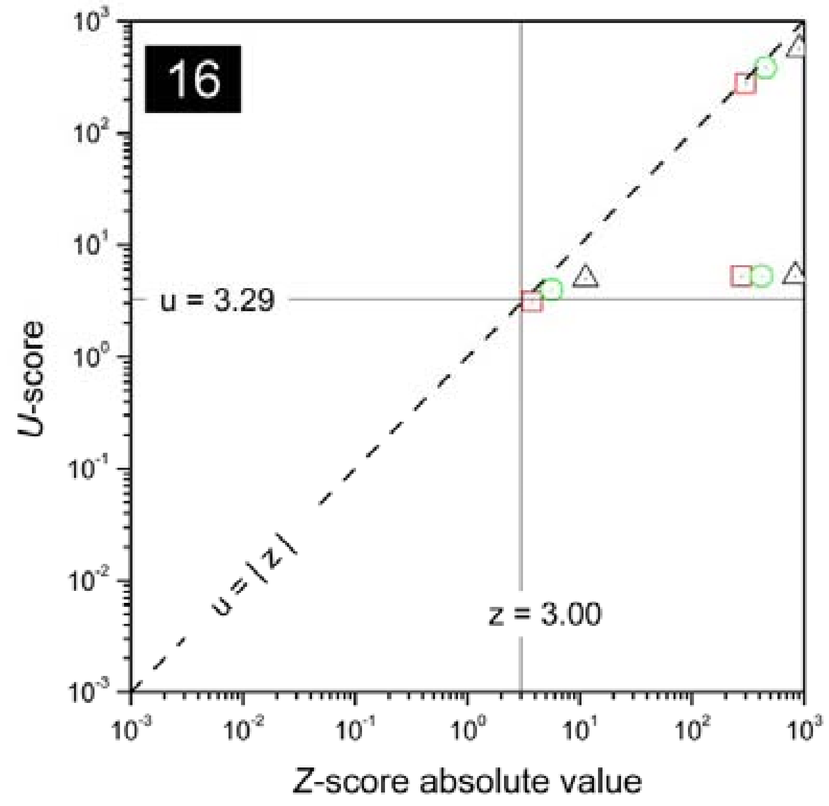

6
u = 3.29
u = | z |
z = 3.00
U-score
Z-score absolute value


7
u = |z|
u = 3.29
z = 3.00
U-score
Z-score absolute value


11
u = 3.29
u = |z|
z = 3.00
U-score
Z-score absolute value


12
u = 3.29
u = | z |
z = 3.00
U-score
Z-score absolute value


14
u = 3.29
u = | z |
z = 3.00
U-score
Z-score absolute value



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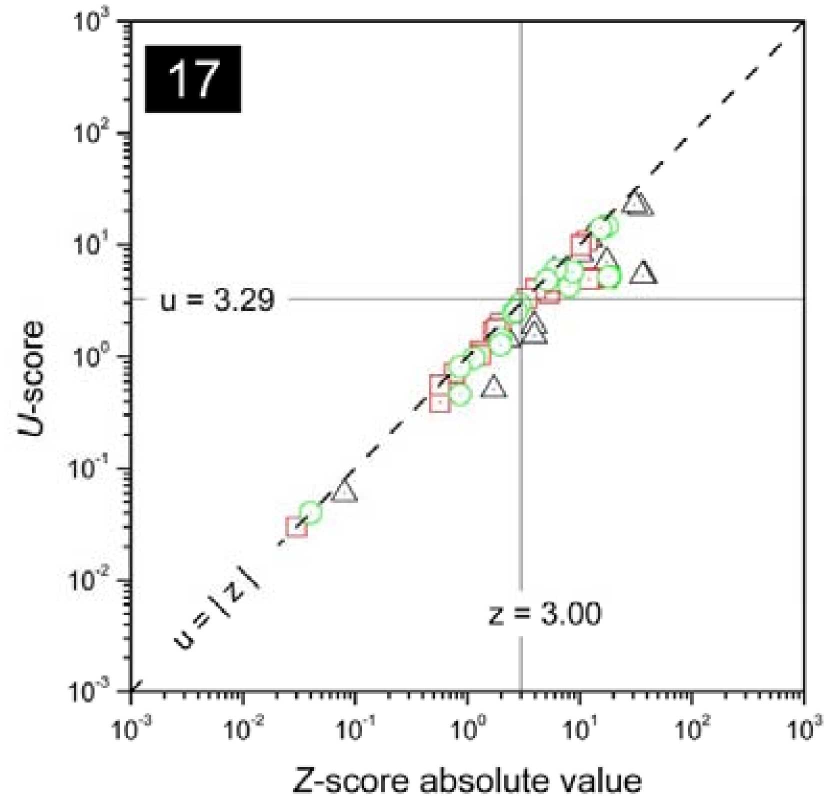

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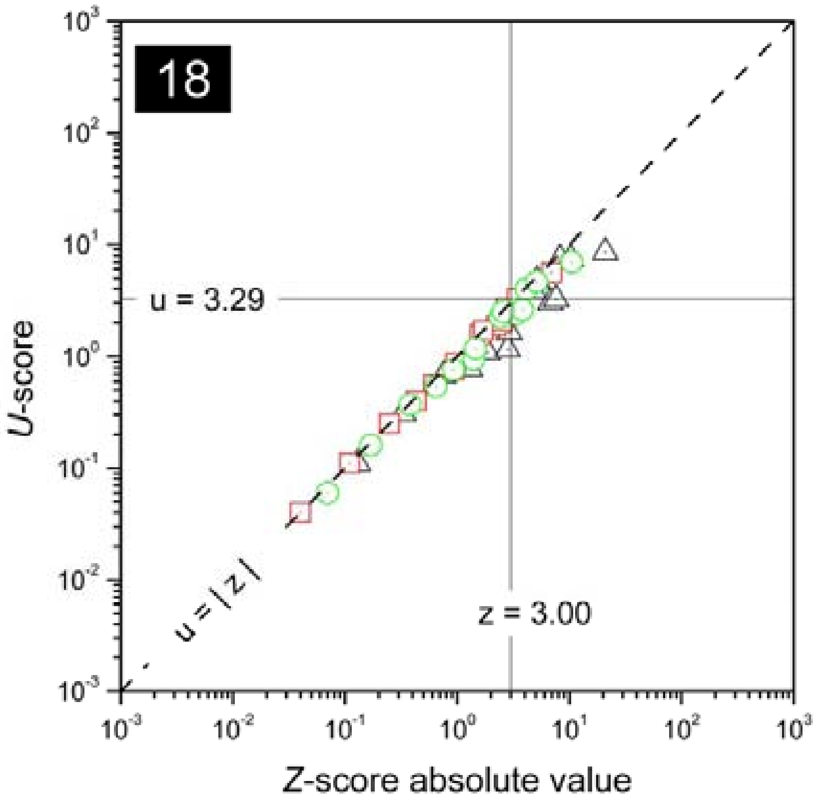
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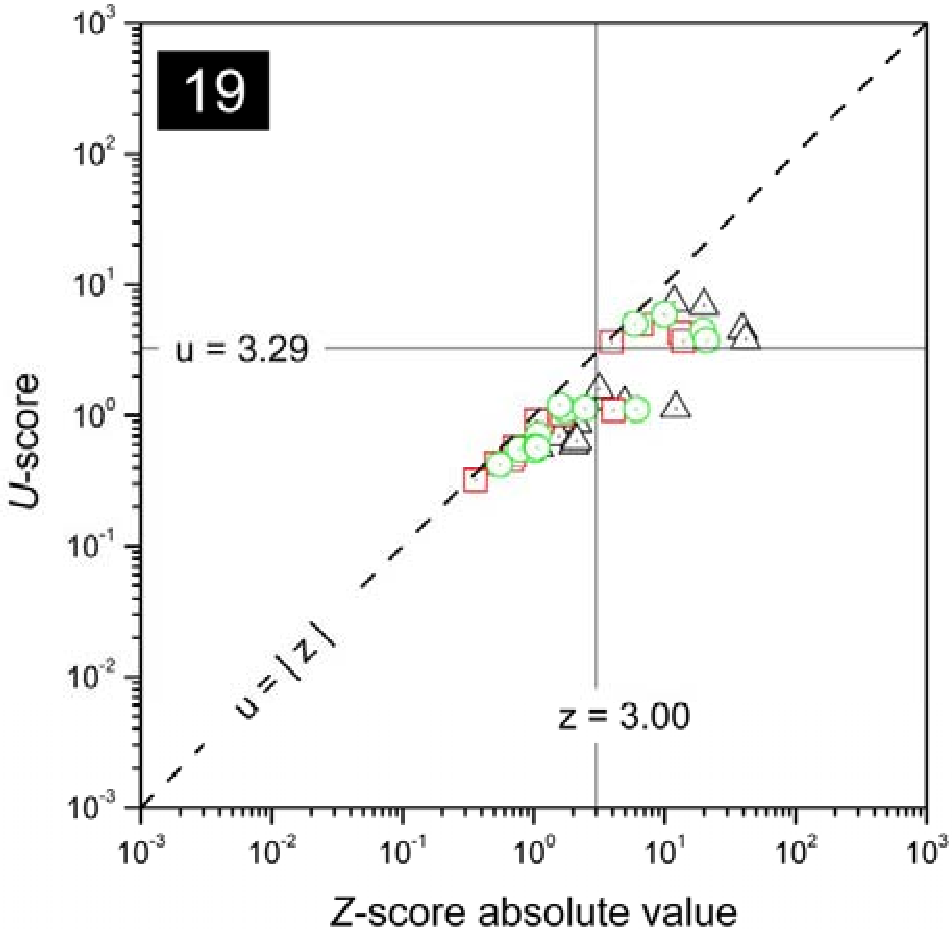
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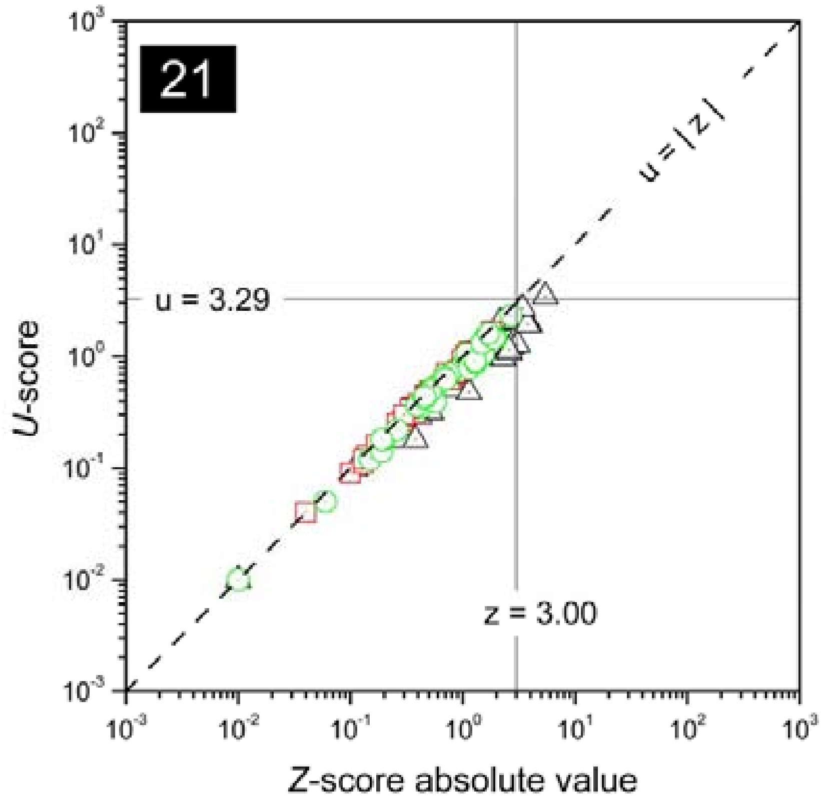
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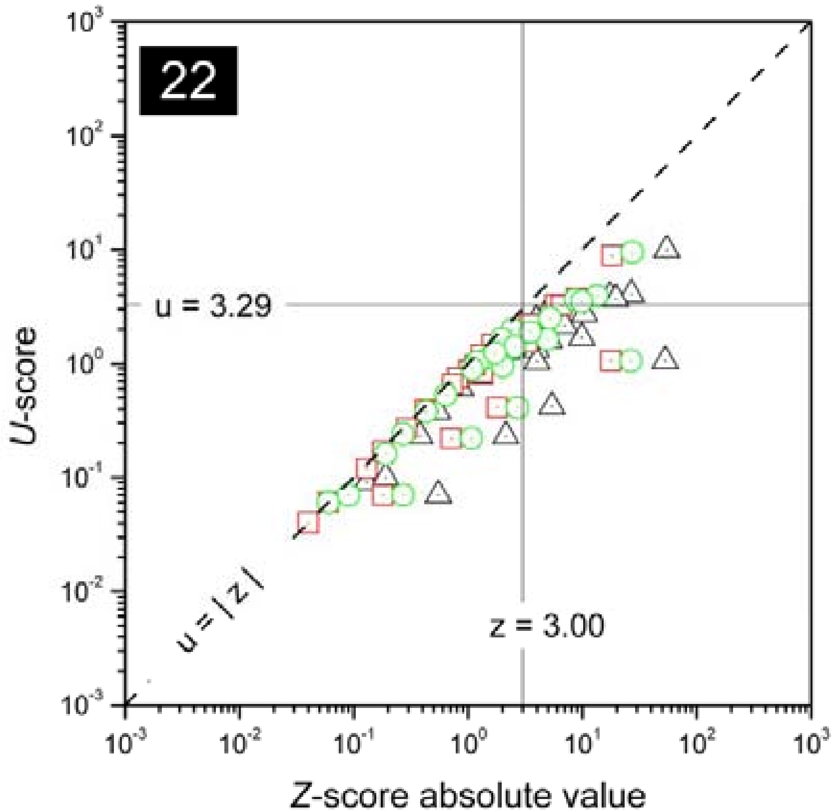
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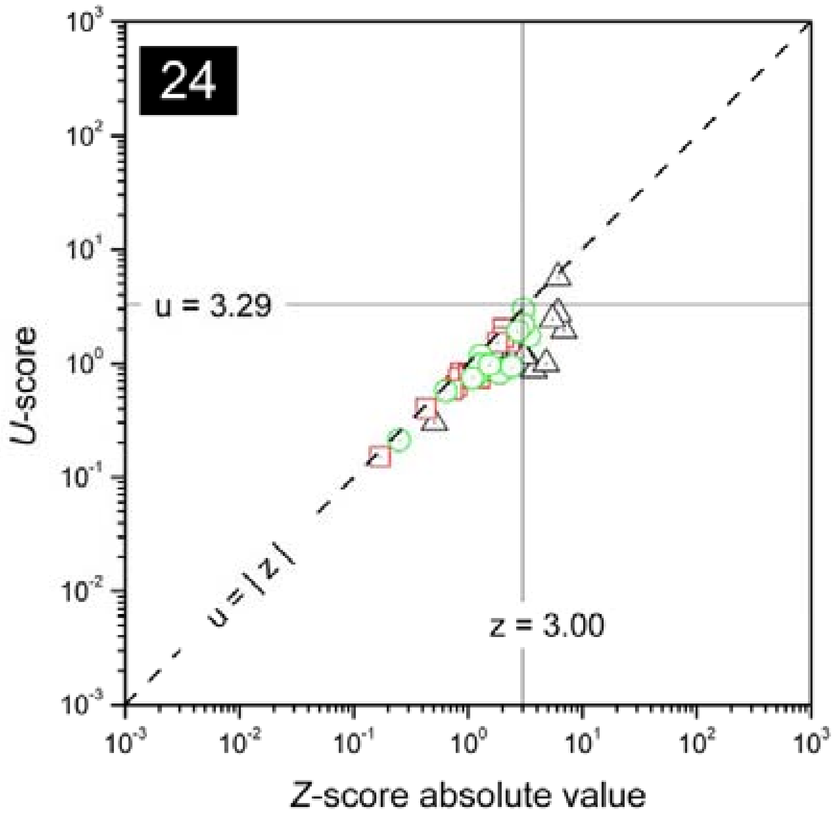
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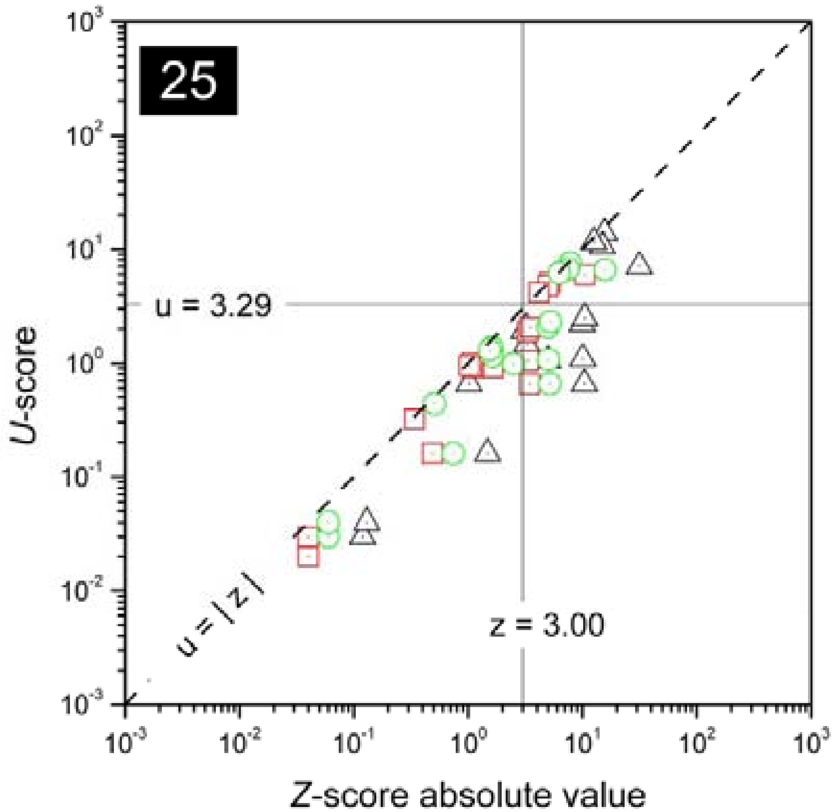
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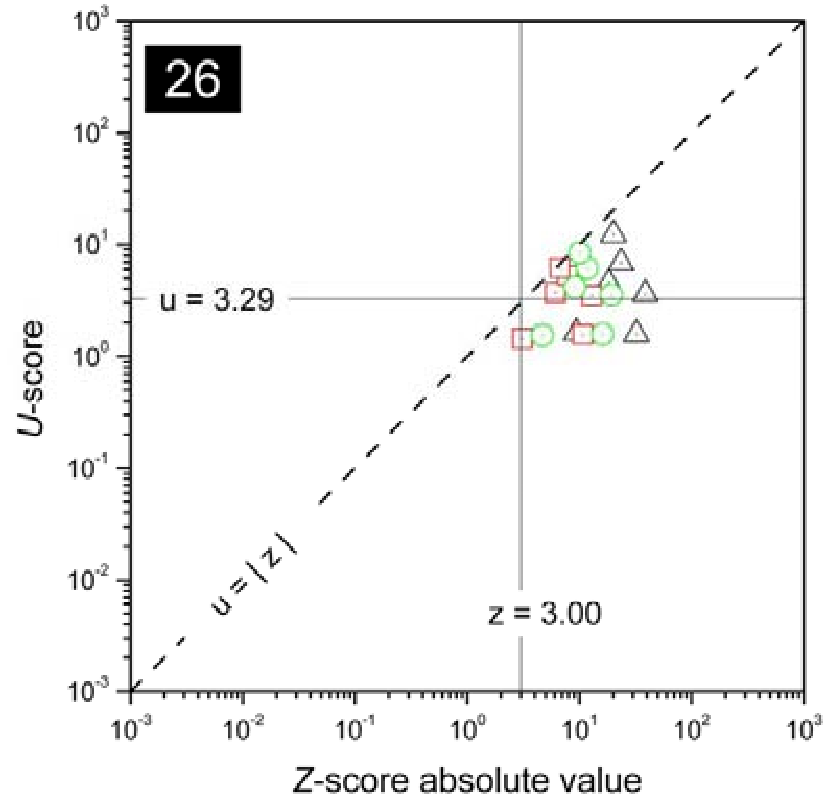
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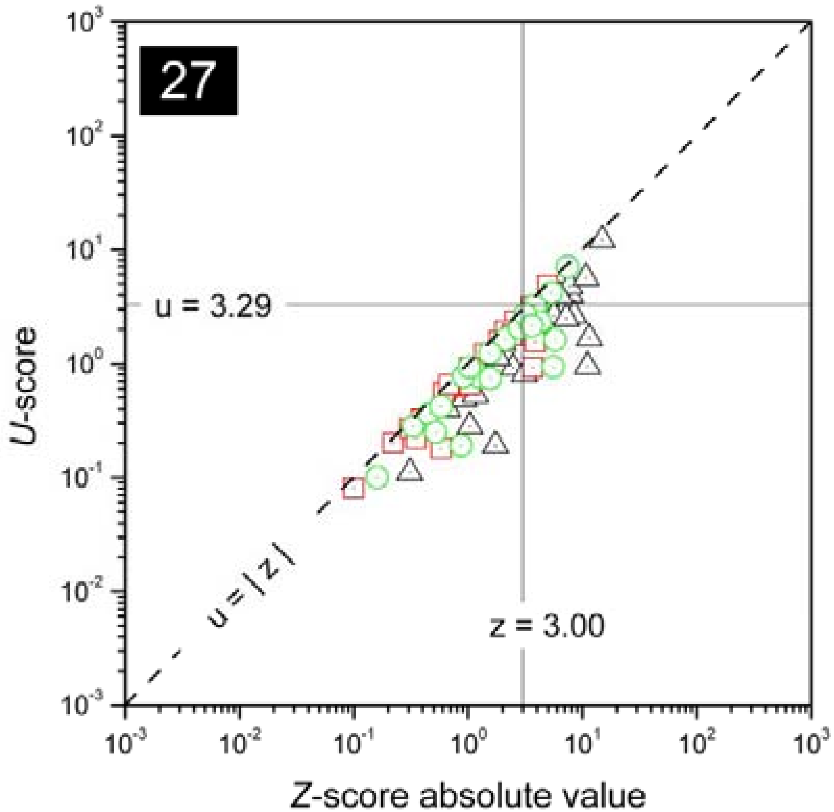
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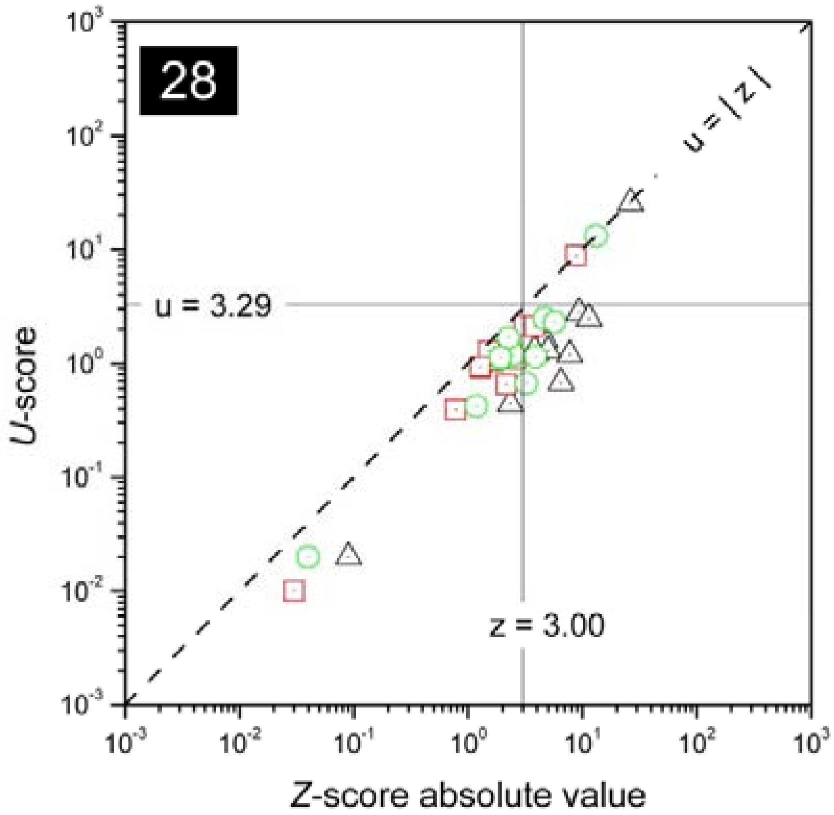

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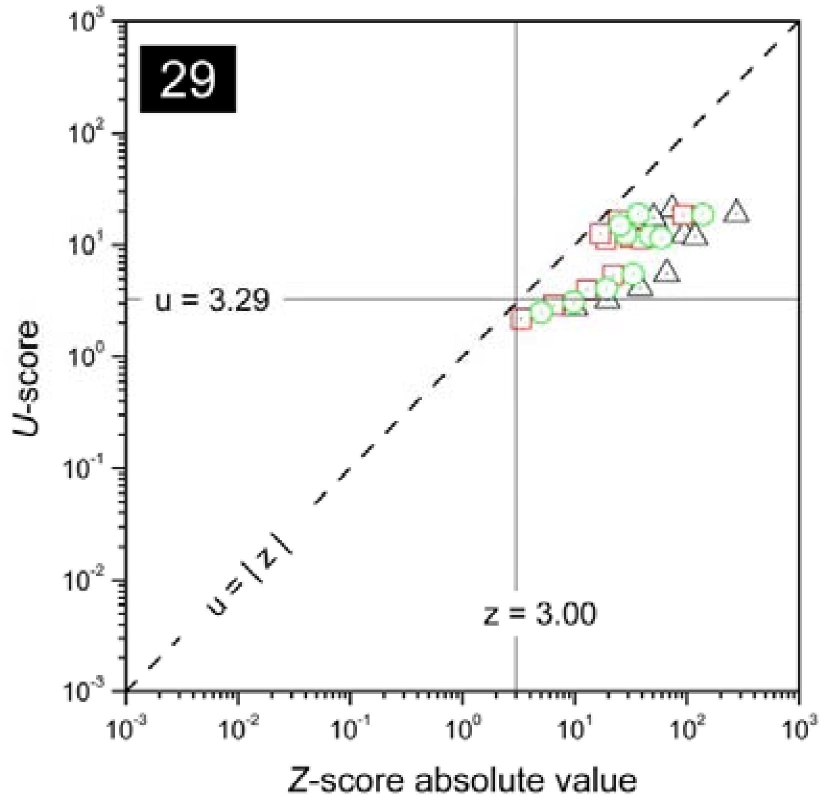

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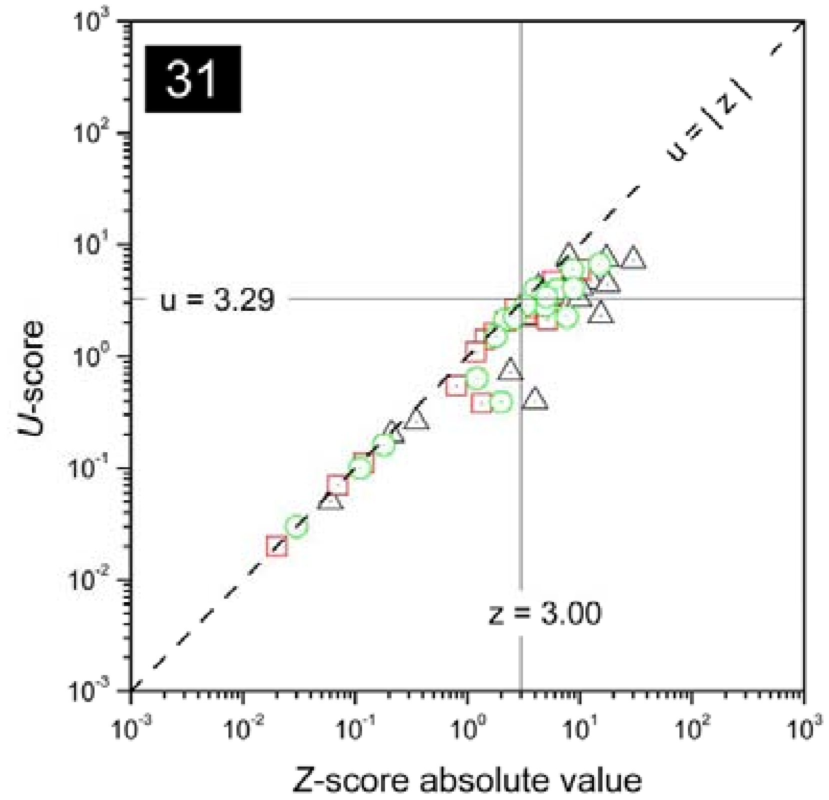
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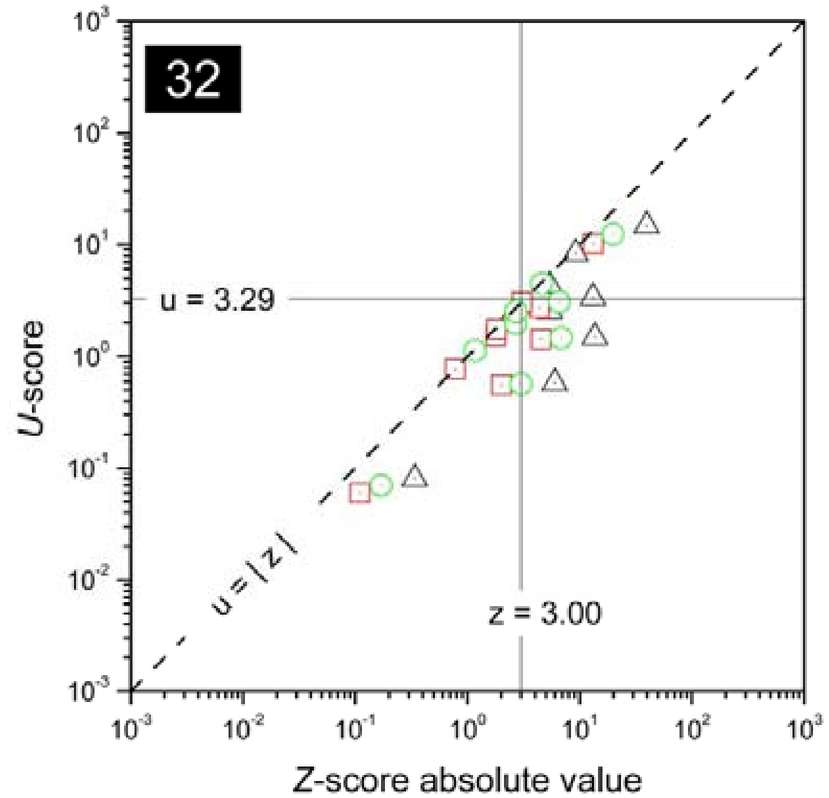
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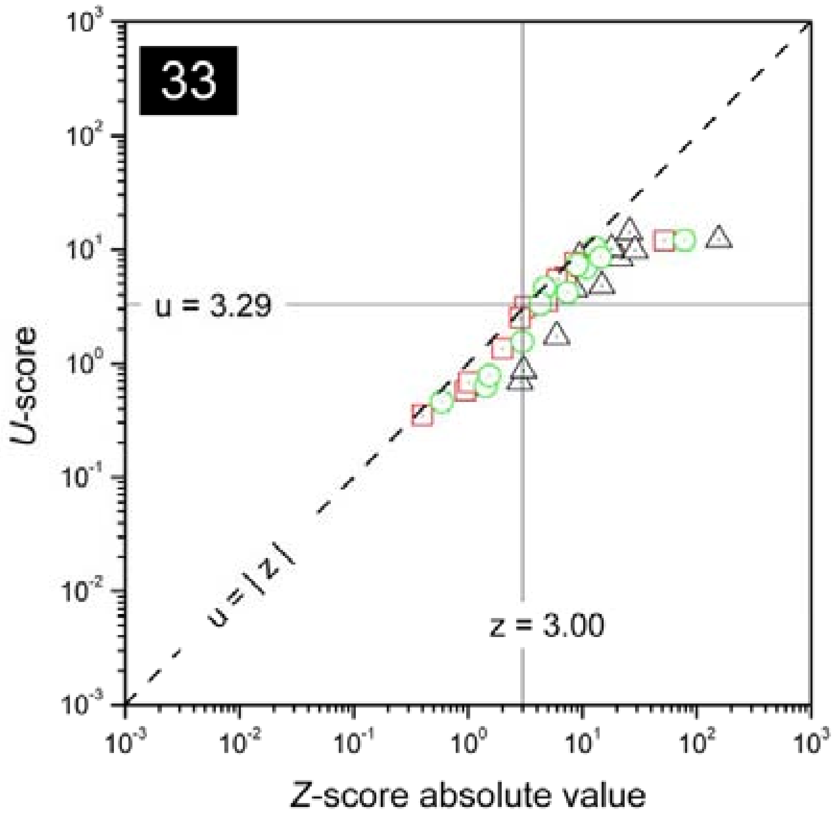
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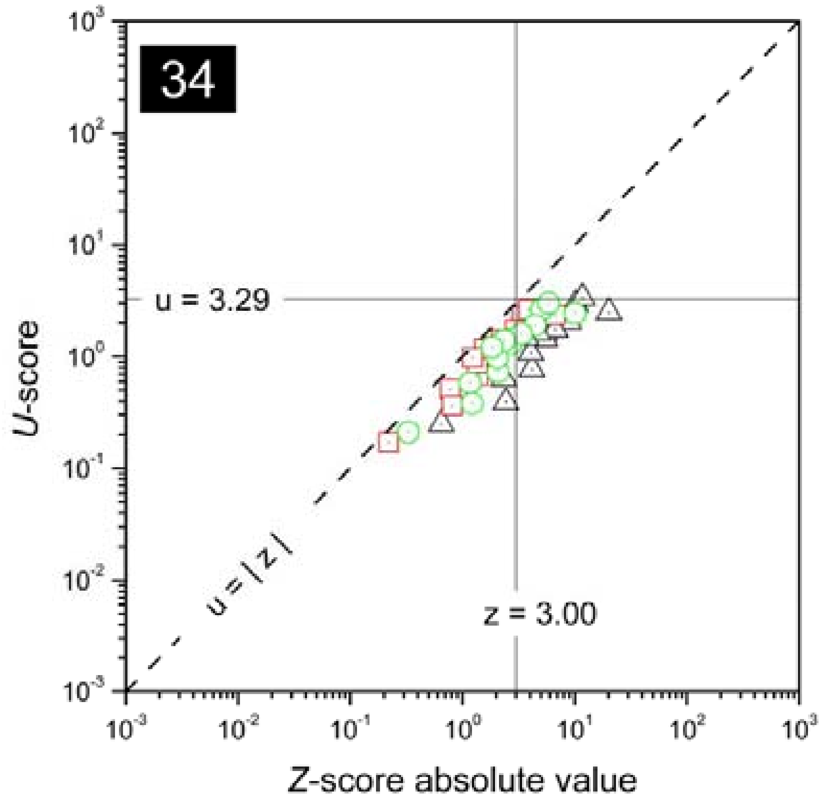
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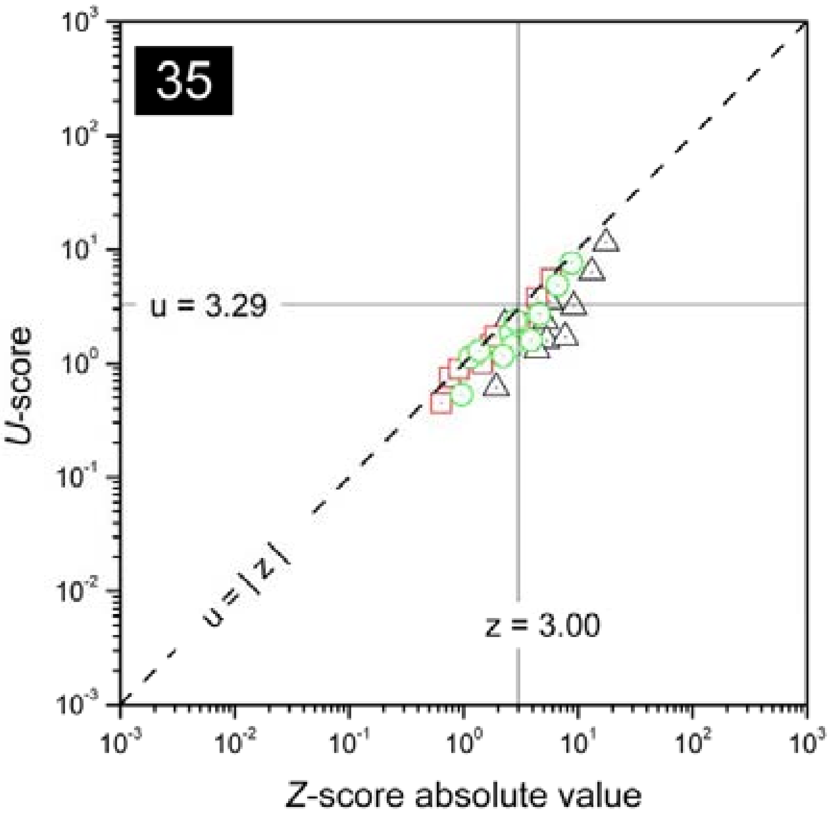
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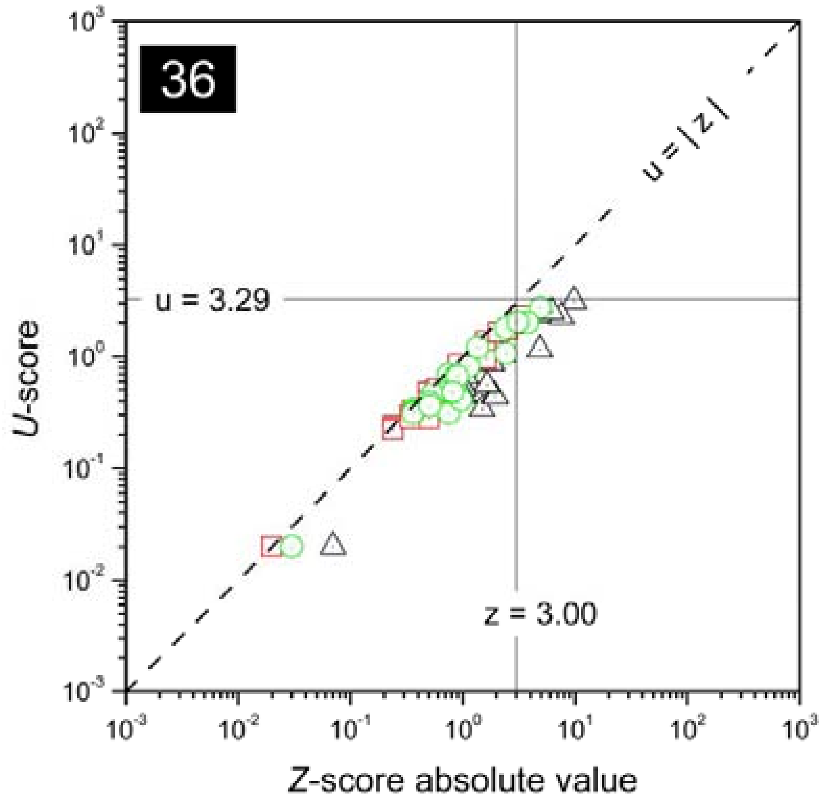
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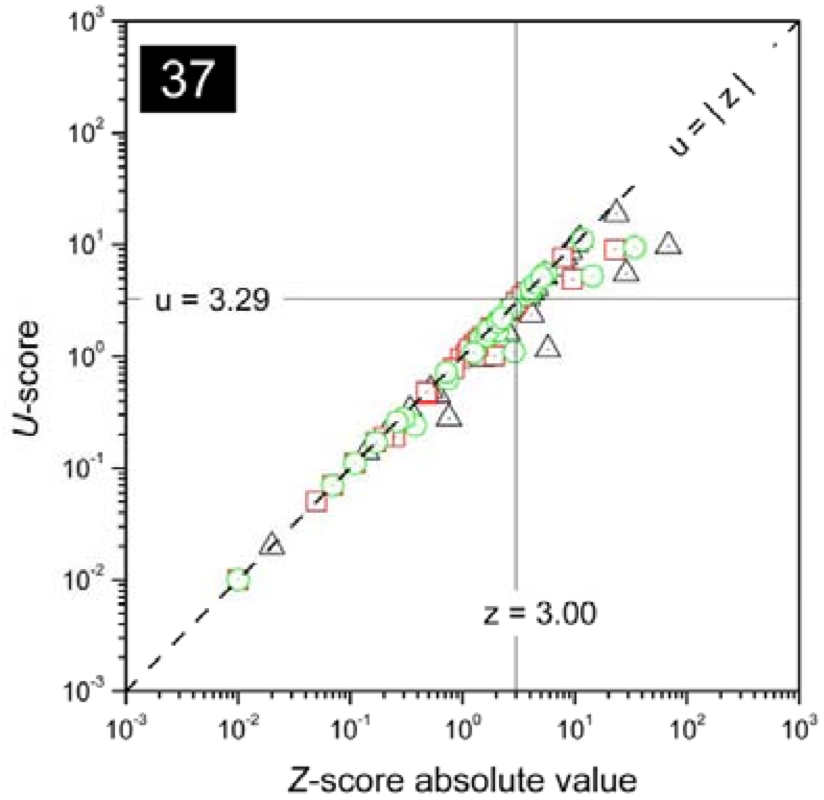
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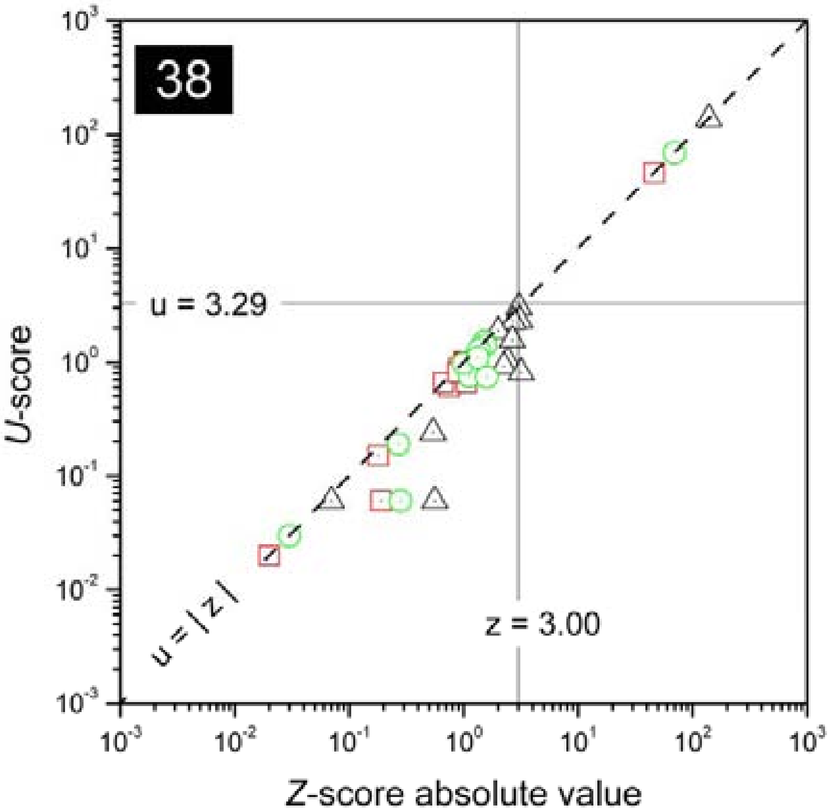
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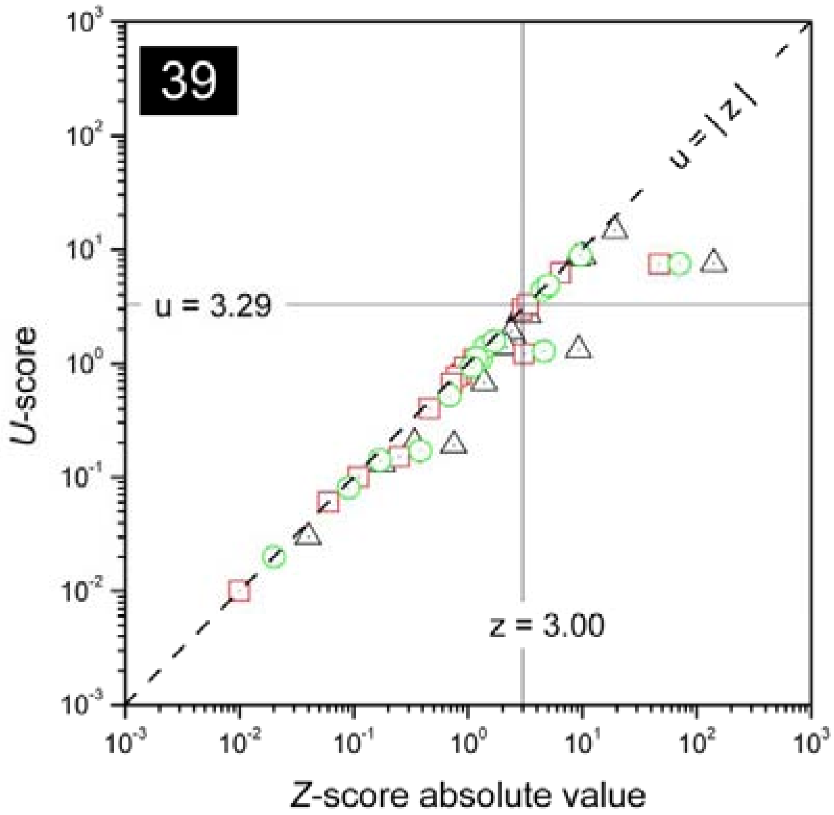
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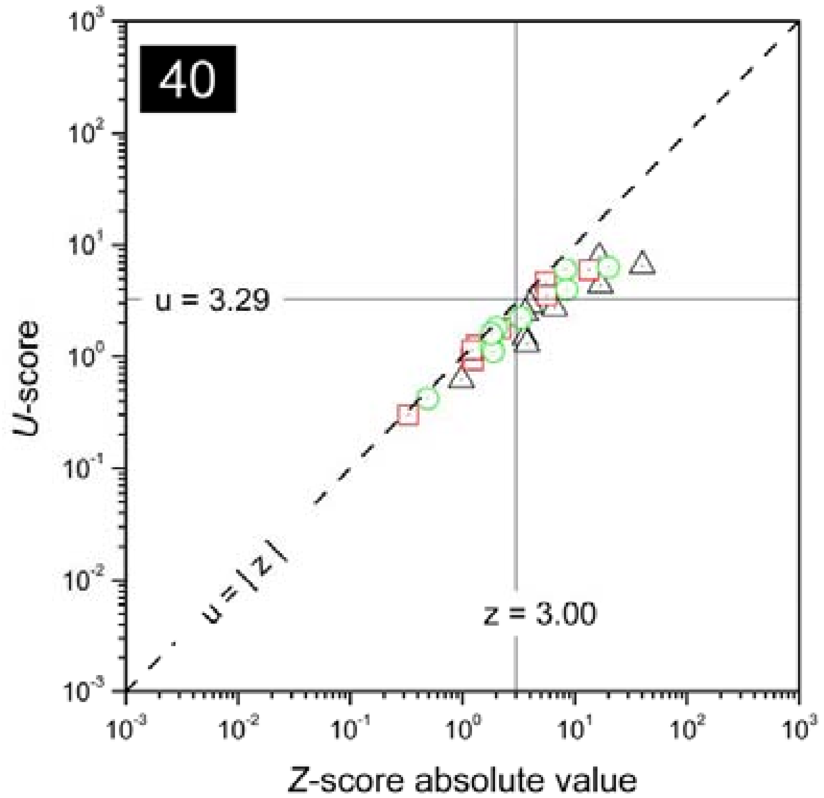
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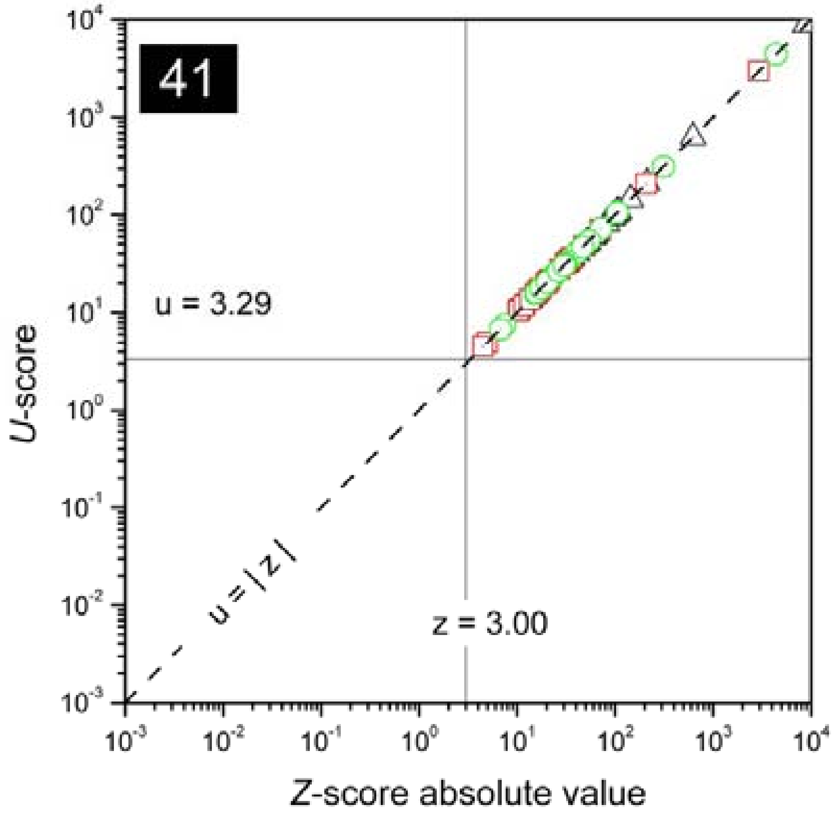
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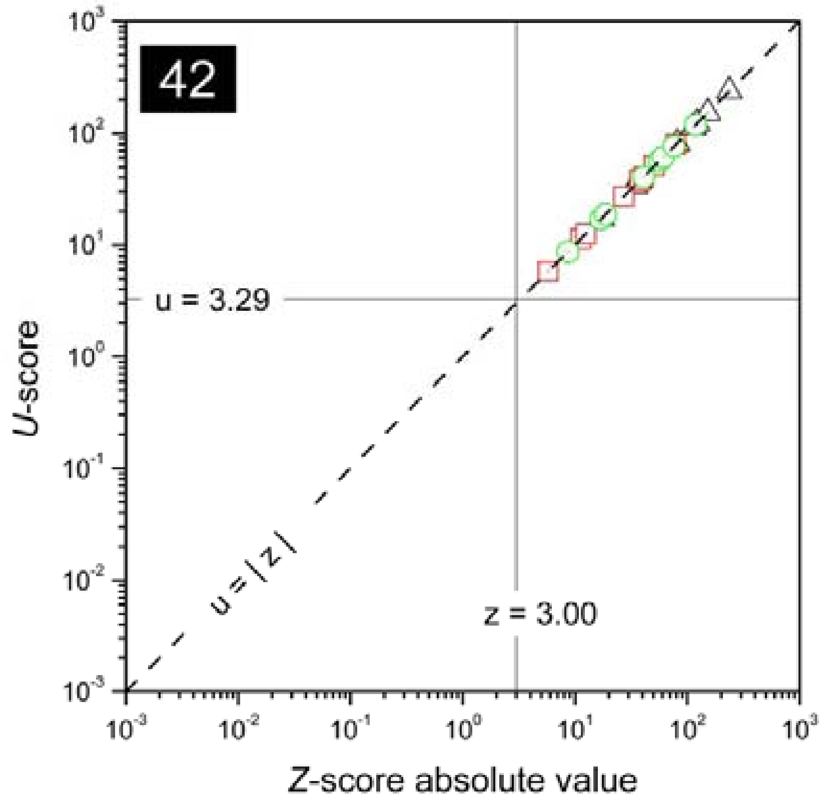
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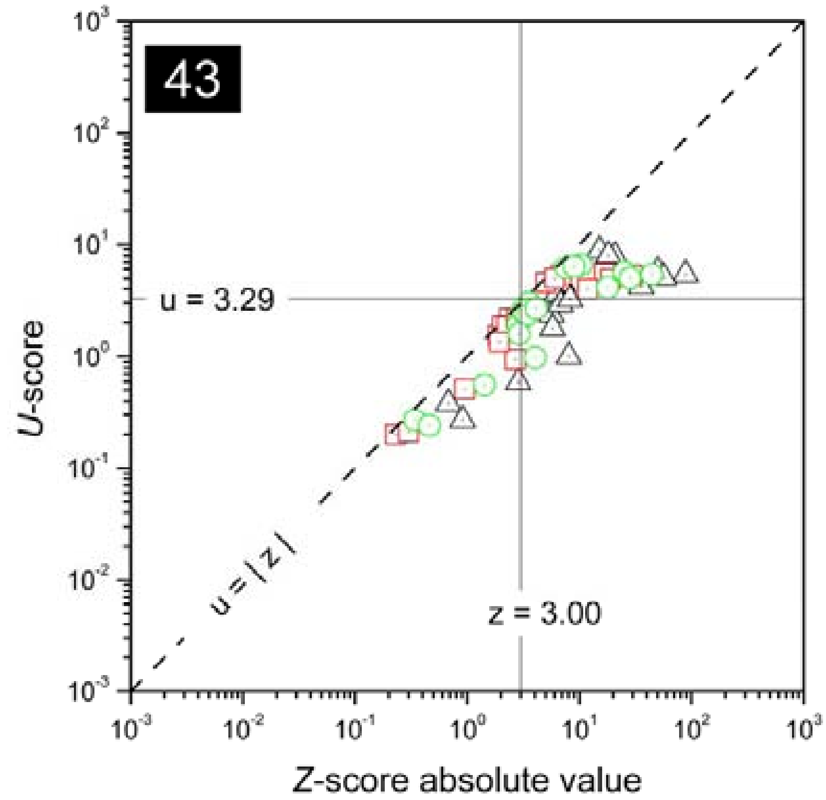
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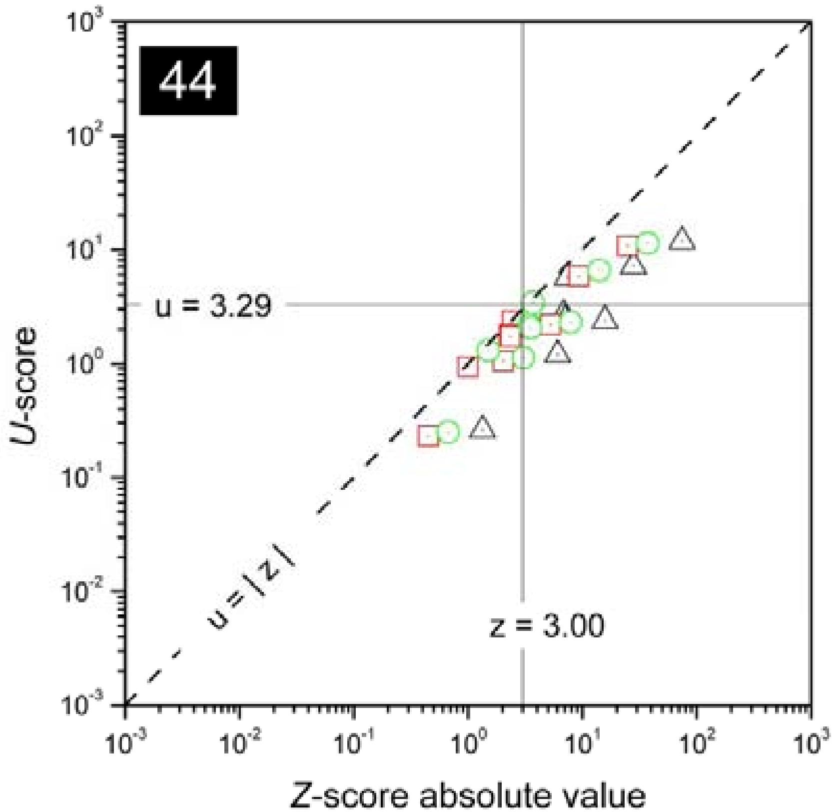
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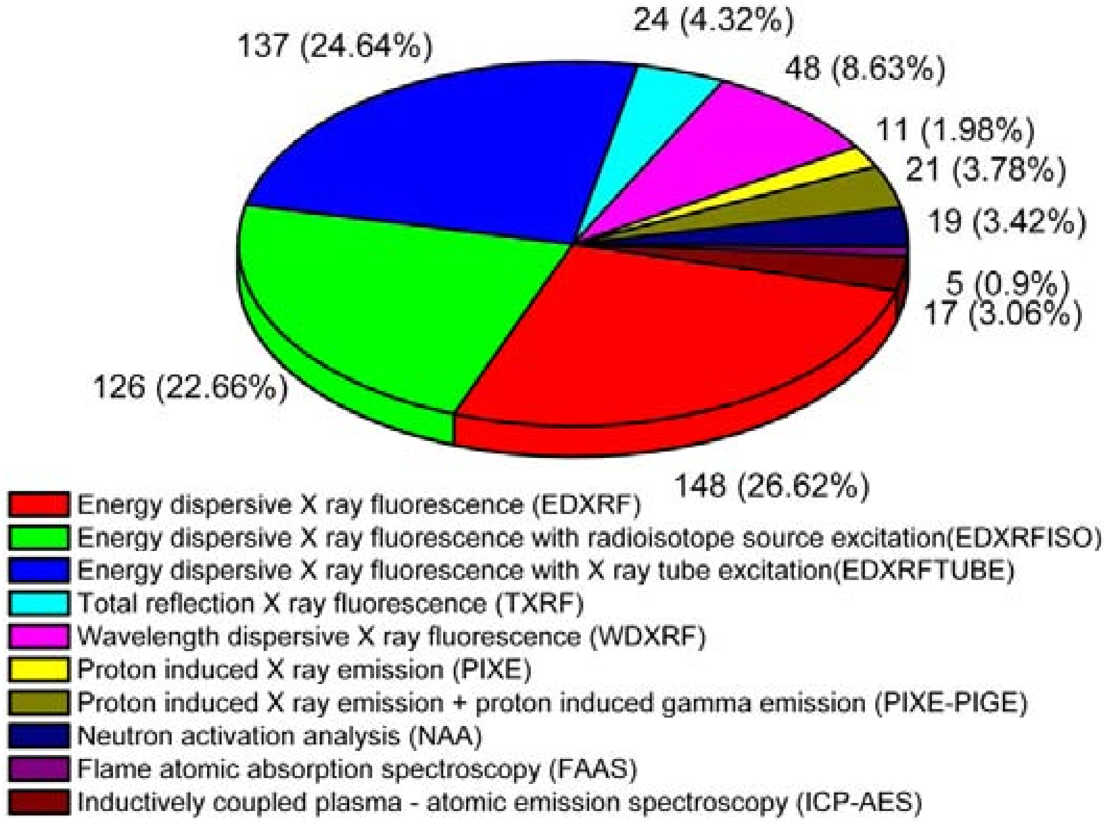

Fig. 6. Utilization of analytical techniques. For each analytical technique the number of submitted results is shown. The percent values relate to the total number of 556 submitted results.

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