# REPORT
# ON
# THE PROFICIENCY TEST EXERCISE
# FOR
# X-RAY FLUORESCENCE LABORATORIES
# ORGANIZED BY
# INTERNATIONAL ATOMIC ENERGY AGENCY
# PTXRFIAEA/04
# "SAMPLE OF ENVIRONMENTAL ORIGIN"

IAEA

International Atomic Energy Agency

Atoms For Peace

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**FOREWORD**

The proficiency test (code PTXRFIAEA04) was the fourth worldwide exercise organized by the IAEA Laboratories at Seibersdorf in order to assist X-ray fluorescence laboratories in assessment and improvement of their analytical performance. This time, the test involved distribution to participating laboratories a sample of environmental origin (clay) with established homogeneity and known target values of the analytes. As usual, 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 be able to assess their analytical results by using the specified standard performance criteria and, if appropriate, to identify discrepancies, and to correct their analytical procedures. The next proficiency test exercise will be executed in 2008.

## INTRODUCTION

The PTXRFIAEA04 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 clay sample. The samples, together with detailed instructions for analysts, were distributed to the participating laboratories in March 2007. The deadline for submission of the results was June 30, 2007. The last results were received in October 2007. The submitted results were processed, grouped versus analytes/laboratories and compared with the analytes' assigned values. For the elements with known assigned values a set of *z*-scores and *u*-scores was calculated for each submitted result. The obtained results and description of the statistical 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.

## 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 inter-laboratory 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.

*Consensus value of the standard deviation*: 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.

## DETAILS

### Test Sample

The test sample was a clay material prepared and tested by an external independent laboratory. The powdered, homogenized, and dried material was distributed to 52 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. Their were also instructed to determine the moisture content of the material by using a separate sample and to report the results on a dry-weight basis. Only one result per element per analytical technique was to be submitted. Each result was to be accompanied by an estimate of its uncertainty expressed as one standard deviation. No restriction on the number of reported elements was imposed.

### 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 41 analytes were submitted by participants of this proficiency test: Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Ga, Hf, K, La, Mg, Mn, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Rb, S, Sc, Si, Sm, Sn, Sr, Th, Ti, U, V, Y, Zn, and Zr. The *z*- and *u*-scores were calculated for all the submitted results of all analytes except Cl, Cs, Hf, Pd, Pr, and Sm, for which the assigned values were not available. For each analyte a target value of the standard deviation has been assigned using a modified Horowitz function as proposed in the reference [4]:

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

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

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

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:

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

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.

### *Z*-Scores and *U*-Scores.

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

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

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

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

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:

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

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

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqns. (6) and (7) takes into account all *z*-scores for all analytes 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 ($\chi^2$) 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:

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

The symbol '$\sigma_x$' denotes the standard uncertainty of the submitted result *x*. If the assumptions about $X_A$ and $\sigma_A$ and about the normality of the underlying distributions are correct, and the laboratory estimate of $\sigma_x$ 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:

$1.64 \geq u$ - 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 Eqn. (4) and Eqn. (8) one can immediately notice that for corresponding values of *u*-score and *z*-score the following inequality is always fulfilled:

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

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

**Consensus Values**

To examine the overall performance of the participating laboratories the submitted results have been also 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:

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

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

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

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

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

3. Veglia's test [6, 7], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

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

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:

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

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

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

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

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

$$w/s = (x_n - x_1)/s \qquad (16)$$

- 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: $3 \le n < \infty$, two-sided test, confidence level = 0.95:

$$B_4 = |x_k - \bar{x}| / s \qquad (17)$$

where:
$x_k$, examined value

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

7. Outlier rejection test proposed in [10], number of results: $3 \le n \le 100$, two-sided test, confidence level = 0.95:

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

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 $S_k^2 / S \le$ 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, $\sigma_C$:

$$X_C = \frac{\sum_{i=1}^{m} x_i}{m} \quad (19)$$

and

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

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

## RESULTS

The clay test sample was distributed to 52 laboratories for chemical composition analysis. Out of the 52 laboratories 24 participated in the test. The list of the participating laboratories is presented in Table 1. Seven analytical techniques have been distinguished to be in use by the participants. The techniques and technique codes are listed in Table 2. The techniques types 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 no sufficient information available a generic type EDXRF was assigned. The technique ICP-AE (code: 8.0) was not X-ray emission related. The participants submitted 362 individual results for 41 analytes. 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 are shown. The consensus values were calculated by using Eqns.(19) and (20) based on 317 reported analytical results after excluding 45 results classified as outliers. The correlation between the assigned and the consensus values is shown in Fig. 2. As can be noticed there are only a few elements for which there is significant disagreement between these values. These elements include Pb, S, Sn, and U. In Table 4 the values of the *z*- and *u*-scores for all the submitted results are listed. The *z*- and *u*-scores were calculated for the three different fit-for-purpose ranges, as defined in Eqn. (2). In Figs. 3 and 4 the distributions of the proficiency test results are shown. In Fig. 3 the distributions of results for the analytes for which at least 5 results passed the outlier rejection tests are shown. Due to rather low number of results, these graphs could only be used as indicators of the trends observed in the reported data. 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 code and they are accompanied by technique codes marked on a linked upper *X*-axis. 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 marked with black lines ($|z| < 3$, $u < 3.29$) divide the plot area in four quadrants. Due to inequality (10) all the points accompanied by a laboratory estimate of the uncertainty lay always below the line $u = |z|$. The smaller the laboratory estimated uncertainty is the closer the related point lays 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 "optimistic" uncertainty estimate. The participants are advised to examine in detail their results presented in Table 4, Figs. 4 and 5 in order to better define their fit-for-purpose status as well to identify the analytes requiring improvement in the analytical procedures.

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 (51.11%): EDXRFISO + EDXRFTUBE + EDXRF, followed by WDXRF (29.83%), TXRF (8.29%). The rest of the submitted results was obtained by PIXE-PIGE (6.08%), and ICP-AE (4.7%).

We would like to encourage the analysts to take part in the forthcoming proficiency tests as the real benefits arise from a regular participation in the scheme.

**ACKNOWLEDGMENT**

The organizers of the proficiency test are grateful to the participants for taking part in the proficiency test and for providing the additional information on their analytical procedures.

**LITERATURE**

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## APPENDIX I

## Tables 1-5

Table 1. The laboratories participating in the proficiency test exercise.

| Analyst Name | Institution | Country |
|---|---|---|
| **Nikolla Civici** | Institute of Nuclear Physics | **Albania** |
| **Idir Toumert** | Centre de Recherche Nucléaire d'Alger | **Algeria** |
| **Ivone Mulako Sato** | Instituto de Pesquisas Energéticas e Nucleares (IPEN), Centro de Química e Meio Ambiente (CQMA), Laboratório de Fluorescência de Raios X (LFX) | **Brazil** |
| **Carlos Roberto Appoloni** | Departamento de Física/CCE, Universidade Estadual de Londrina | **Brazil** |
| **Wu Jizong** | Chemical Analysis and Test Center, China Institute of Atomic Energy | **China** |
| **Nancy Alberro Macias** | Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN) | **Cuba** |
| **Zoltán Szőkefalvi-Nagy** | KFKI Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences | **Hungary** |
| **Raoelina Andriambololona** | Institut National des Sciences et Techniques Nucléaires (INSTN) | **Madagascar** |
| **Moussa Bounakhla** | Centre National de l'Énergie, des Sciences et des Techniques Nucléaires (CNESTEN) | **Marocco** |
| **Idris Isa Funtua** | Materials Science and Development Section, Centre for Energy Research and Training, Ahmadu Bello University | **Nigeria** |
| **M. Alexandra Barreiros** | Laboratório de Análises Ambientais e Controlo de Qualidade (LAACQ), Instituto Nacional de Tecnologia Industrial (INETI) | **Portugal** |
| **Peter Kump** | Jožef Stefan Institute | **Slovenia** |

Table 1 continued

| Analyst Name | Institution | Country |
|---|---|---|
| **Ziga Smit** | Faculty of Mathematics and Physics, University of Ljubljana | **Slovenia** |
| **Zoran Milič** | Narodni Muzej Slovenije | **Slovenia** |
| **Shirani Seneviratne** | Atomic Energy Authority | **Sri Lanka** |
| **Farouk Idris Habbani** | Department of Physics, University of Khartoum | **Sudan** |
| **Sarinrat Wonglee** | Thailand Institute of Nuclear Technology | **Thailand** |
| **Chavalek Chayavadhanangkur** | Rare Earth Research Center | **Thailand** |
| **Aleksandra Nestorovska-Krsteska** | Ministry of Environment and Physical Planning | **The Former Yugoslav Republic of Macedonia** |
| **Haifa Ben Abdelwahed** | Centre National des Sciences et Technologies Nucléaires | **Tunisia** |
| **Abdullah Zararsiz** | Saraykoy Nuclear Research and Training Center | **Turkey** |
| **John S. Watson** | The Open University, Department of Earth Sciences | **United Kingdom** |
| **Eduardo D. Greaves** | Departamento de Física, Universidad Simón Bolívar | **Venezuela** |
| **Vuong Thu Bac** | 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 |
| 4.5 | Proton induced X-ray emission + proton induced gamma emission | PIXE-PIGE |
| 8.0 | Inductively couples plasma atomic emission | ICP-AES |

Table 3. The assigned values of analytes, the target values of the standard deviations, obtained by using modified Horowitz function, Eqn. (1), and the consensus values. The populations with at least 5 reported results were tested for normality by using Kolmogorov-Smirnov test, all examined populations passed the test. For the elements Cl, Cs, Hf, Pd, Pr, and Sm, 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, $\sigma_A$ | | | Consensus value of the analyte, $X_C$ | Consensus value of the standard deviation, $\sigma_C$ | Number of results | Number of outliers |
|---|---|---|---|---|---|---|---|---|
| | | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 | | | | |
| | | | | [g/kg] | | | | |
| Al | 111.0 | 1.55 | 3.09 | 4.64 | 110.9 | 6.03 | 11 | 2 |
| Ca | 2.07 | 0.053 | 0.105 | 0.158 | 2.18 | 0.157 | 17 | 0 |
| Cl | - | - | - | - | 1.31 | 0.131 | 1 | 0 |
| Fe | 47.9 | 0.76 | 1.52 | 2.28 | 49.9 | 1.64 | 22 | 2 |
| K | 19.60 | 0.355 | 0.709 | 1.064 | 19.6 | 0.726 | 17 | 1 |
| Mg | 8.24 | 0.170 | 0.340 | 0.510 | 8.592 | 0.0149 | 6 | 3 |
| Na | 4.21 | 0.096 | 0.192 | 0.288 | 4.73 | 0.687 | 6 | 0 |
| Si | 253.0 | 2.52 | 5.03 | 7.55 | 253.0 | 5.03 | 12 | 1 |
| Ti | 5.57 | 0.122 | 0.244 | 0.366 | 5.95 | 0.195 | 20 | 3 |
| | | | | [mg/kg] | | | | |
| As | 16.4 | 0.86 | 1.72 | 2.58 | 19.3 | 2.47 | 8 | 0 |
| Ba | 414 | 13.35 | 26.7 | 40.1 | 420 | 15.3 | 10 | 1 |
| *Br* | *8.52* | *0.494* | *0.988* | *1.48* | *9.14* | *0.078* | *6* | *3* |
| *Cd* | *0.081* | *0.00895* | *0.0179* | *0.0269* | *2.20* | *0.708* | *2* | *0* |
| *Ce* | *95.0* | *3.83* | *7.66* | *11.5* | *99.6* | *6.04* | *6* | *1* |
| Co | 10.0 | 0.57 | 1.14 | 1.71 | 12.3 | 1.30 | 7 | 1 |
| Cr | 90.7 | 3.685 | 7.37 | 11.06 | 79.8 | 6.58 | 13 | 4 |
| Cs | - | - | - | - | 10.0 | 1.34 | 1 | 0 |
| Cu | 21.7 | 1.095 | 2.19 | 3.29 | 21.9 | 2.05 | 16 | 4 |
| Ga | 26.2 | 1.285 | 2.57 | 3.86 | 25.23 | 0.447 | 10 | 3 |
| Hf | - | - | - | - | 21 | 18.1 | 2 | 0 |
| *La* | *45.1* | *2.04* | *4.07* | *6.11* | *54.0* | *2.31* | *6* | *0* |
| Mn | 193 | 7 | 14.0 | 21.0 | 230 | 12.6 | 18 | 2 |
| *Nb* | *19.3* | *0.990* | *1.98* | *2.97* | *20.4* | *1.21* | *9* | *0* |
| *Nd* | *43.1* | *1.96* | *3.91* | *5.87* | *41.70* | *0.135* | *3* | *1* |
| Ni | 27.2 | 1.325 | 2.65 | 3.98 | 28.2 | 1.34 | 10 | 2 |
| P | 448 | 14.3 | 28.6 | 42.9 | 359 | 26.4 | 1 | 0 |
| Pb | 29.6 | 1.425 | 2.85 | 4.28 | 42.2 | 3.69 | 15 | 1 |
| Pd | - | - | - | - | 16.9 | 2.20 | 1 | 0 |
| Pr | - | - | - | - | 7.90 | 0.800 | 1 | 0 |
| Rb | 137 | 5.25 | 10.5 | 15.8 | 138.7 | 5.89 | 17 | 0 |
| S | 613 | 18.7 | 37.4 | 56.1 | 1504 | 330 | 4 | 0 |
| *Sc* | *15.8* | *0.835* | *1.67* | *2.51* | *16.75* | *0.396* | *4* | *1* |
| Sm | - | - | - | - | 7 | - | 1 | 0 |
| Sn | 4.09 | 0.265 | 0.530 | 0.795 | 6.2 | 1.34 | 1 | 0 |

Table 3 continued…

| Analyte symbol | Assigned value of the analyte, $X_A$ | Target value of standard deviation, $\sigma_A$ | | | Consensus value of the analyte, $X_C$ | Consensus value of the standard deviation, $\sigma_C$ | Number of results | Number of outliers |
|---|---|---|---|---|---|---|---|---|
| | | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 | | | | |
| Sr | 109.0 | 4.305 | 8.61 | 12.92 | 102.6 | 4.74 | 18 | 2 |
| *Th* | *15.7* | *0.83* | *1.66* | *2.49* | *18.7* | *2.18* | *4* | *0* |
| *U* | *2.86* | *0.196* | *0.391* | *0.587* | *4.25* | *0.631* | *2* | *0* |
| V | 140 | 5.35 | 10.7 | 16.1 | 167 | 29.8 | 9 | 0 |
| Y | 27.9 | 1.355 | 2.71 | 4.07 | 27.1 | 1.32 | 11 | 2 |
| Zn | 161 | 6 | 12.0 | 18.0 | 166.2 | 5.65 | 20 | 4 |
| Zr | 177 | 6.5 | 13.0 | 19.5 | 176.7 | 9.04 | 14 | 1 |

Table 4. Summary of the reported results and the calculated *z*-scores and *u*-scores. The results rejected by the outliers rejection procedures were marked with '*' in the "Analyte concentration" column. In brackets, following the element symbol, the assigned values of element concentration and 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 (111.0 ± 3.09) [g/kg] | | | | | | | | | | |
| 8 | 2.0 | 7.510* | 0.0900 | 1.20 | -66.97 | -33.49 | -22.32 | 66.86 | 33.47 | 22.32 |
| 21 | 2.0 | 11.1* | 1.03 | 9.26 | -64.64 | -32.32 | -21.55 | 53.80 | 30.66 | 21.03 |
| 17 | 1.2 | 83.33 | 0.328 | 0.39 | -17.91 | -8.95 | -5.97 | 17.52 | 8.90 | 5.95 |
| 22 | 1.1 | 99 | 14.0 | 14.21 | -8.09 | -4.05 | -2.70 | 0.89 | 0.87 | 0.85 |
| 15 | 1.2 | 101.6 | 9.60 | 9.45 | -6.10 | -3.05 | -2.03 | 0.97 | 0.94 | 0.88 |
| 3 | 2.0 | 102.92 | 0.510 | 0.50 | -5.23 | -2.61 | -1.74 | 4.96 | 2.58 | 1.73 |
| 13 | 2.0 | 109.17 | 0.945 | 0.87 | -1.19 | -0.59 | -0.40 | 1.01 | 0.57 | 0.39 |
| 10 | 1.2 | 112.2 | 2.01 | 1.79 | 0.76 | 0.38 | 0.25 | 0.47 | 0.32 | 0.23 |
| 20 | 2.0 | 114.699 | - | - | 2.39 | 1.20 | 0.80 | 2.39 | 1.20 | 0.80 |
| 7 | 8.0 | 131.848 | - | - | 13.49 | 6.75 | 4.50 | 13.49 | 6.75 | 4.50 |
| 1 | 4.5 | 144.0 | 7.20 | 5.00 | 21.36 | 10.68 | 7.12 | 4.48 | 4.21 | 3.85 |
| Ca (2.07 ± 0.105) [g/kg] | | | | | | | | | | |
| 17 | 1.2 | 0.898 | 0.0200 | 2.23 | -22.34 | -11.17 | -7.45 | 20.87 | 10.97 | 7.39 |
| 14 | 1.2 | 1.21 | 0.188 | 15.55 | -16.46 | -8.23 | -5.49 | 4.43 | 4.02 | 3.53 |
| 4 | 1.0 | 1.3 | - | - | -14.67 | -7.34 | -4.89 | 14.67 | 7.34 | 4.89 |
| 12 | 1.1 | 1.8200 | 0.00800 | 0.44 | -4.77 | -2.38 | -1.59 | 4.71 | 2.38 | 1.59 |
| 10 | 1.2 | 1.90 | 0.131 | 6.88 | -3.16 | -1.58 | -1.06 | 1.18 | 0.99 | 0.81 |
| 6 | 1.1 | 1.96 | 0.520 | 26.48 | -2.02 | -1.01 | -0.67 | 0.20 | 0.20 | 0.20 |
| 20 | 2.0 | 2.087 | - | - | 0.32 | 0.16 | 0.11 | 0.32 | 0.16 | 0.11 |
| 3 | 2.0 | 2.249 | 0.0209 | 0.93 | 3.41 | 1.70 | 1.14 | 3.17 | 1.67 | 1.13 |
| 21 | 2.0 | 2.26 | 0.103 | 4.55 | 3.71 | 1.85 | 1.24 | 1.68 | 1.32 | 1.03 |
| 7 | 8.0 | 2.309 | - | - | 4.56 | 2.28 | 1.52 | 4.56 | 2.28 | 1.52 |
| 22 | 1.1 | 2.40 | 0.216 | 9.00 | 6.29 | 3.15 | 2.10 | 1.49 | 1.37 | 1.24 |
| 15 | 1.2 | 2.46 | 0.210 | 8.54 | 7.43 | 3.72 | 2.48 | 1.80 | 1.66 | 1.49 |
| 13 | 2.0 | 2.50 | 0.347 | 13.86 | 8.25 | 4.13 | 2.75 | 1.23 | 1.19 | 1.14 |
| 1 | 4.5 | 2.59 | 0.130 | 5.02 | 9.91 | 4.96 | 3.30 | 3.71 | 3.11 | 2.55 |
| 9 | 1.2 | 2.68 | 0.398 | 14.87 | 11.55 | 5.78 | 3.85 | 1.51 | 1.47 | 1.42 |
| 18 | 2.0 | 2.91 | 0.226 | 7.76 | 16.03 | 8.01 | 5.34 | 3.63 | 3.38 | 3.05 |
| 2 | 1.3 | 3.53 | 0.330 | 9.36 | 27.77 | 13.88 | 9.26 | 4.36 | 4.21 | 3.99 |
| Cl [g/kg] | | | | | | | | | | |
| 1 | 1 | 4.5 | 1.31 | 0.131 | 10.00 | - | - | - | - | - |

Table 4 continued…

| 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 $k = 1.5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Fe (47.9 ± 0.76) [g/kg] | | | | | | |
| 12 | 1.2 | 5.60* | 0.300 | 5.36 | -55.90 | -27.95 | -18.63 | 51.96 | 27.42 | 18.47 |
| 13 | 2.0 | 43.02 | 0.970 | 2.25 | -6.45 | -3.23 | -2.15 | 3.97 | 2.72 | 1.98 |
| 2 | 1.3 | 43.03 | 0.253 | 0.59 | -6.44 | -3.22 | -2.15 | 6.11 | 3.18 | 2.13 |
| 14 | 1.2 | 44.3 | 4.04 | 9.10 | -4.70 | -2.35 | -1.57 | 0.87 | 0.83 | 0.77 |
| 21 | 2.0 | 44.47 | 0.618 | 1.39 | -4.54 | -2.27 | -1.51 | 3.52 | 2.10 | 1.46 |
| 1 | 4.5 | 44.6 | 2.30 | 5.16 | -4.36 | -2.18 | -1.45 | 1.36 | 1.20 | 1.02 |
| 23 | 1.1 | 44.7 | 1.39 | 3.11 | -4.28 | -2.14 | -1.43 | 2.05 | 1.58 | 1.22 |
| 16 | 1.1 | 44.75 | 0.770 | 1.72 | -4.16 | -2.08 | -1.39 | 2.92 | 1.86 | 1.31 |
| 3 | 2.0 | 45.40 | 0.272 | 0.60 | -3.30 | -1.65 | -1.10 | 3.11 | 1.62 | 1.09 |
| 19 | 1.3 | 45.7 | 1.20 | 2.62 | -2.88 | -1.44 | -0.96 | 1.54 | 1.13 | 0.85 |
| 24 | 1.2 | 46.38 | 0.506 | 1.09 | -2.02 | -1.01 | -0.67 | 1.68 | 0.96 | 0.66 |
| 22 | 1.1 | 47.3 | 3.35 | 7.08 | -0.79 | -0.40 | -0.26 | 0.17 | 0.16 | 0.15 |
| 10 | 1.2 | 48.71 | 0.210 | 0.43 | 1.07 | 0.54 | 0.36 | 1.03 | 0.53 | 0.36 |
| 5 | 1.2 | 49.0 | 1.13 | 2.30 | 1.39 | 0.70 | 0.46 | 0.78 | 0.56 | 0.42 |
| 15 | 1.2 | 49.5 | 2.92 | 5.90 | 2.11 | 1.06 | 0.70 | 0.53 | 0.49 | 0.43 |
| 7 | 8.0 | 49.95 | - | - | 2.71 | 1.35 | 0.90 | 2.71 | 1.35 | 0.90 |
| 17 | 1.2 | 56.88 | 0.100 | 0.18 | 11.86 | 5.93 | 3.95 | 11.76 | 5.92 | 3.95 |
| 20 | 2.0 | 59.06 | 0.000 | 0.00 | 14.75 | 7.37 | 4.92 | 14.75 | 7.37 | 4.92 |
| 9 | 1.2 | 60.1 | 8.94 | 14.87 | 16.17 | 8.08 | 5.39 | 1.36 | 1.35 | 1.33 |
| 6 | 1.1 | 62.8 | 7.07 | 11.26 | 19.65 | 9.82 | 6.55 | 2.09 | 2.06 | 2.00 |
| 4 | 1.0 | 67.8 | - | - | 26.30 | 13.15 | 8.77 | 26.30 | 13.15 | 8.77 |
| 3 | 1.3 | 403.57* | 0.502 | 0.12 | 470.00 | 235.00 | 156.70 | 391.60 | 223.00 | 153.00 |
| | | | | K (19.60 ± 0.709) [g/kg] | | | | | | |
| 12 | 1.2 | 1.810* | 0.0500 | 2.76 | -50.22 | -25.11 | -16.74 | 49.73 | 25.05 | 16.72 |
| 17 | 1.2 | 13.75 | 0.100 | 0.73 | -16.52 | -8.26 | -5.51 | 15.90 | 8.18 | 5.48 |
| 14 | 1.2 | 14.3 | 1.36 | 9.50 | -14.88 | -7.44 | -4.96 | 3.75 | 3.44 | 3.05 |
| 4 | 1.0 | 15.70 | - | - | -11.01 | -5.51 | -3.67 | 11.01 | 5.51 | 3.67 |
| 5 | 1.2 | 18.8 | 4.46 | 23.78 | -2.37 | -1.18 | -0.79 | 0.19 | 0.19 | 0.18 |
| 7 | 8.0 | 19.41 | - | - | -0.53 | -0.27 | -0.18 | 0.53 | 0.27 | 0.18 |
| 6 | 1.1 | 19.54 | 0.380 | 1.94 | -0.17 | -0.08 | -0.06 | 0.12 | 0.07 | 0.05 |
| 3 | 2.0 | 19.753 | 0.0256 | 0.13 | 0.43 | 0.22 | 0.14 | 0.43 | 0.22 | 0.14 |
| 20 | 2.0 | 19.85 | - | - | 0.70 | 0.35 | 0.23 | 0.70 | 0.35 | 0.23 |
| 13 | 2.0 | 19.867 | 0.0130 | 0.07 | 0.75 | 0.38 | 0.25 | 0.75 | 0.38 | 0.25 |
| 10 | 1.2 | 20.58 | 0.310 | 1.51 | 2.75 | 1.38 | 0.92 | 2.07 | 1.26 | 0.88 |
| 21 | 2.0 | 20.59 | 0.515 | 2.50 | 2.78 | 1.39 | 0.93 | 1.58 | 1.13 | 0.84 |
| 1 | 4.5 | 20.6 | 1.10 | 5.34 | 2.82 | 1.41 | 0.94 | 0.87 | 0.76 | 0.65 |
| 15 | 1.2 | 21.4 | 1.39 | 6.50 | 5.00 | 2.50 | 1.67 | 1.23 | 1.14 | 1.01 |
| 22 | 1.1 | 23.2 | 1.42 | 6.12 | 10.16 | 5.08 | 3.39 | 2.46 | 2.27 | 2.03 |
| 9 | 1.2 | 23.3 | 2.33 | 10.02 | 10.35 | 5.18 | 3.45 | 1.56 | 1.51 | 1.43 |
| 2 | 1.3 | 23.6 | 1.03 | 4.37 | 11.18 | 5.59 | 3.73 | 3.64 | 3.17 | 2.68 |

Table 4 continued…

| 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 $k = 1.5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Mg (8.24 ± 0.340) [g/kg] | | | | | | | | | | |
| 13 | 2.0 | 7.803* | 0.0100 | 0.13 | -2.58 | -1.29 | -0.86 | 2.57 | 1.29 | 0.86 |
| 21 | 2.0 | 8.44* | 0.412 | 4.88 | 1.18 | 0.59 | 0.39 | 0.45 | 0.38 | 0.31 |
| 20 | 2.0 | 8.563 | - | - | 1.90 | 0.95 | 0.63 | 1.90 | 0.95 | 0.63 |
| 7 | 8.0 | 8.601 | - | - | 2.13 | 1.06 | 0.71 | 2.13 | 1.06 | 0.71 |
| 3 | 2.0 | 8.612 | 0.0276 | 0.32 | 2.19 | 1.10 | 0.73 | 2.16 | 1.09 | 0.73 |
| 1 | 4.5 | 27.9* | 1.40 | 5.02 | 115.90 | 57.94 | 38.63 | 13.94 | 13.65 | 13.20 |
| Na (4.21 ± 0.192) [g/kg] | | | | | | | | | | |
| 3 | 2.0 | 2.17 | 0.214 | 9.87 | -21.29 | -10.65 | -7.10 | 8.71 | 7.11 | 5.70 |
| 21 | 2.0 | 3.71 | 0.309 | 8.33 | -5.26 | -2.63 | -1.75 | 1.56 | 1.39 | 1.20 |
| 20 | 2.0 | 4.778 | 0.00 | 0.00 | 5.92 | 2.96 | 1.97 | 5.92 | 2.96 | 1.97 |
| 13 | 2.0 | 4.8970 | 0.00300 | 0.06 | 7.16 | 3.58 | 2.39 | 7.16 | 3.58 | 2.39 |
| 1 | 4.5 | 5.77 | 0.290 | 5.03 | 16.27 | 8.13 | 5.42 | 5.11 | 4.49 | 3.82 |
| 18 | 2.0 | 7.06 | 0.566 | 8.02 | 29.67 | 14.83 | 9.89 | 4.96 | 4.76 | 4.48 |
| Si (253.0 ± 5.03) [g/kg] | | | | | | | | | | |
| 21 | 2.0 | 24.8* | 3.09 | 12.45 | -90.74 | -45.37 | -30.25 | 57.30 | 38.66 | 27.99 |
| 3 | 2.0 | 227.73 | 0.381 | 0.17 | -10.05 | -5.02 | -3.35 | 9.94 | 5.01 | 3.35 |
| 6 | 1.1 | 238 | 29.8 | 12.52 | -5.85 | -2.93 | -1.95 | 0.49 | 0.49 | 0.48 |
| 15 | 1.2 | 240 | 21.1 | 8.80 | -5.22 | -2.61 | -1.74 | 0.62 | 0.61 | 0.59 |
| 22 | 1.1 | 242 | 16.6 | 6.86 | -4.37 | -2.19 | -1.46 | 0.66 | 0.63 | 0.60 |
| 13 | 2.0 | 248.17 | 0.335 | 0.13 | -1.92 | -0.96 | -0.64 | 1.91 | 0.96 | 0.64 |
| 12 | 1.2 | 250 | 30.0 | 12.00 | -1.19 | -0.60 | -0.40 | 0.10 | 0.10 | 0.10 |
| 20 | 2.0 | 257.13 | - | - | 1.64 | 0.82 | 0.55 | 1.64 | 0.82 | 0.55 |
| 17 | 1.2 | 258.96 | 0.497 | 0.19 | 2.37 | 1.19 | 0.79 | 2.33 | 1.18 | 0.79 |
| 1 | 4.5 | 262 | 13.1 | 5.00 | 3.58 | 1.79 | 1.19 | 0.67 | 0.64 | 0.60 |
| 10 | 1.2 | 274.10 | 0.747 | 0.27 | 8.39 | 4.20 | 2.80 | 8.04 | 4.15 | 2.78 |
| 8 | 2.0 | 285.0 | 3.00 | 1.05 | 12.72 | 6.36 | 4.24 | 8.17 | 5.46 | 3.94 |

Table 4 continued…

| 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 |
| | | | | Ti (5.57 ± 0.244) [g/kg] | | | | | | |
| 11 | 1.1 | 0.886* | 0.0840 | 9.48 | -38.50 | -19.25 | -12.83 | 31.68 | 18.20 | 12.51 |
| 1 | 4.5 | 4.90 | 0.245 | 5.00 | -5.51 | -2.75 | -1.84 | 2.45 | 1.94 | 1.52 |
| 13 | 2.0 | 4.980 | 0.0140 | 0.28 | -4.85 | -2.43 | -1.62 | 4.82 | 2.42 | 1.62 |
| 2 | 1.3 | 5.09 | 0.217 | 4.26 | -3.91 | -1.96 | -1.30 | 1.91 | 1.46 | 1.12 |
| 14 | 1.2 | 5.12 | 0.474 | 9.26 | -3.67 | -1.83 | -1.22 | 0.91 | 0.84 | 0.75 |
| 3 | 2.0 | 5.171 | 0.0134 | 0.26 | -3.28 | -1.64 | -1.09 | 3.26 | 1.64 | 1.09 |
| 3 | 1.3 | 5.24 | 0.081 | 1.54 | -2.73 | -1.37 | -0.91 | 2.27 | 1.30 | 0.89 |
| 21 | 2.0 | 5.66 | 0.206 | 3.64 | 0.75 | 0.37 | 0.25 | 0.38 | 0.29 | 0.22 |
| 19 | 1.3 | 5.72 | 0.531 | 9.28 | 1.23 | 0.62 | 0.41 | 0.28 | 0.26 | 0.23 |
| 10 | 1.2 | 5.80 | 0.119 | 2.05 | 1.91 | 0.95 | 0.64 | 1.36 | 0.86 | 0.60 |
| 22 | 1.1 | 6.09 | 0.385 | 6.32 | 4.28 | 2.14 | 1.43 | 1.29 | 1.14 | 0.98 |
| 15 | 1.2 | 6.22 | 0.440 | 7.08 | 5.30 | 2.65 | 1.77 | 1.41 | 1.28 | 1.13 |
| 17 | 1.2 | 6.38 | 0.050 | 0.78 | 6.63 | 3.32 | 2.21 | 6.14 | 3.25 | 2.19 |
| 9 | 1.2 | 6.69 | 0.567 | 8.47 | 9.22 | 4.61 | 3.07 | 1.94 | 1.82 | 1.66 |
| 6 | 1.1 | 6.744 | 0.0980 | 1.45 | 9.65 | 4.83 | 3.22 | 7.52 | 4.48 | 3.11 |
| 12 | 1.2 | 7.00 | 0.100 | 1.43 | 11.76 | 5.88 | 3.92 | 9.08 | 5.44 | 3.78 |
| 5 | 1.2 | 7.1 | 1.50 | 21.29 | 12.25 | 6.12 | 4.08 | 0.99 | 0.98 | 0.96 |
| 4 | 1.0 | 7.30 | - | - | 14.22 | 7.11 | 4.74 | 14.22 | 7.11 | 4.74 |
| 16 | 1.1 | 44.75* | 0.770 | 1.72 | 322.10 | 161.00 | 107.40 | 50.26 | 48.52 | 45.98 |
| 8 | 2.0 | 77.30* | 0.900 | 1.16 | 589.70 | 294.80 | 196.60 | 78.98 | 76.94 | 73.86 |
| | | | | As (16.4 ± 1.72) [mg/kg] | | | | | | |
| 19 | 1.3 | 11.0 | 4.00 | 36.36 | -6.27 | -3.14 | -2.09 | 1.32 | 1.24 | 1.13 |
| 20 | 2.0 | 12.2 | - | - | -4.88 | -2.44 | -1.63 | 4.88 | 2.44 | 1.63 |
| 7 | 8.0 | 15.9 | - | - | -0.58 | -0.29 | -0.19 | 0.58 | 0.29 | 0.19 |
| 22 | 1.1 | 17.6 | 3.30 | 18.75 | 1.39 | 0.70 | 0.46 | 0.35 | 0.32 | 0.29 |
| 21 | 2.0 | 17.7 | 1.44 | 8.14 | 1.51 | 0.76 | 0.50 | 0.78 | 0.58 | 0.44 |
| 14 | 1.2 | 23.5 | 2.60 | 11.06 | 8.25 | 4.12 | 2.75 | 2.59 | 2.28 | 1.94 |
| 4 | 1.0 | 24.7 | - | - | 9.64 | 4.82 | 3.21 | 9.64 | 4.82 | 3.21 |
| 1 | 4.5 | 31.8 | 6.40 | 20.13 | 17.89 | 8.94 | 5.96 | 2.39 | 2.32 | 2.23 |
| | | | | Ba (414 ± 26.7) [mg/kg] | | | | | | |
| 7 | 8.0 | 340 | - | - | -5.54 | -2.77 | -1.85 | 5.54 | 2.77 | 1.85 |
| 3 | 2.0 | 382 | 67.2 | 17.60 | -2.42 | -1.21 | -0.81 | 0.47 | 0.45 | 0.41 |
| 6 | 1.1 | 403 | 33.3 | 8.27 | -0.86 | -0.43 | -0.29 | 0.32 | 0.27 | 0.22 |
| 24 | 1.2 | 403.4 | 3.23 | 0.80 | -0.80 | -0.40 | -0.27 | 0.77 | 0.40 | 0.26 |
| 21 | 2.0 | 408.6 | 9.26 | 2.27 | -0.40 | -0.20 | -0.13 | 0.33 | 0.19 | 0.13 |
| 15 | 1.1 | 434 | 10.0 | 2.30 | 1.50 | 0.75 | 0.50 | 1.20 | 0.70 | 0.48 |
| 19 | 1.3 | 462 | 69.0 | 14.94 | 3.59 | 1.80 | 1.20 | 0.68 | 0.65 | 0.60 |
| 22 | 1.1 | 468 | 28.0 | 5.98 | 4.04 | 2.02 | 1.35 | 1.74 | 1.40 | 1.10 |
| 20 | 2.0 | 483.6 | - | - | 5.21 | 2.60 | 1.74 | 5.21 | 2.60 | 1.74 |
| 1 | 4.5 | 1100* | 110 | 10.00 | 51.31 | 25.65 | 17.10 | 6.19 | 6.06 | 5.86 |

Table 4 continued…

| 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 |
| | | | | *Br* (*8.52* ± *0.988*) [mg/kg] | | | | | | |
| 14 | 1.2 | 3.10* | 0.800 | 25.81 | -10.98 | -5.49 | -3.66 | 5.77 | 4.27 | 3.22 |
| 22 | 1.1 | 7.00* | 0.600 | 8.57 | -3.08 | -1.54 | -1.03 | 1.96 | 1.32 | 0.95 |
| 6 | 1.1 | 8.4* | 3.15 | 37.32 | -0.16 | -0.08 | -0.05 | 0.03 | 0.02 | 0.02 |
| 17 | 1.2 | 9.0 | 3.00 | 33.33 | 0.97 | 0.49 | 0.32 | 0.16 | 0.15 | 0.14 |
| 21 | 2.0 | 9.16 | 0.412 | 4.49 | 1.30 | 0.65 | 0.43 | 1.00 | 0.60 | 0.42 |
| 24 | 1.2 | 9.3 | 1.02 | 11.02 | 1.51 | 0.76 | 0.50 | 0.66 | 0.53 | 0.42 |
| | | | | *Cd* (*0.081* ± *0.0179*) [mg/kg] | | | | | | |
| 7 | 8.0 | 1.7 | - | - | 181.00 | 90.50 | 60.33 | 181.00 | 90.50 | 60.33 |
| 22 | 1.1 | 2.70 | 0.400 | 14.81 | 292.80 | 146.40 | 97.61 | 6.55 | 6.54 | 6.53 |
| | | | | *Ce* (*95.0* ± *7.66*) [mg/kg] | | | | | | |
| 6 | 1.1 | 45* | 16.0 | 35.92 | -13.15 | -6.57 | -4.38 | 3.05 | 2.83 | 2.55 |
| 3 | 2.0 | 83.8 | 6.77 | 8.08 | -2.94 | -1.47 | -0.98 | 1.45 | 1.10 | 0.84 |
| 15 | 1.1 | 92 | 11.0 | 11.96 | -0.78 | -0.39 | -0.26 | 0.26 | 0.22 | 0.19 |
| 21 | 2.0 | 98.2 | 8.03 | 8.18 | 0.83 | 0.42 | 0.28 | 0.36 | 0.29 | 0.23 |
| 22 | 1.1 | 105.0 | 7.00 | 6.67 | 2.61 | 1.31 | 0.87 | 1.25 | 0.96 | 0.74 |
| 24 | 1.2 | 119.3 | 2.09 | 1.75 | 6.35 | 3.17 | 2.12 | 5.57 | 3.06 | 2.08 |
| | | | | Co (10.0 ± 1.14) [mg/kg] | | | | | | |
| 3 | 2.0 | 8.9 | 1.23 | 13.86 | -1.94 | -0.97 | -0.65 | 0.81 | 0.66 | 0.52 |
| 20 | 2.0 | 9.7 | 0.00 | 0.00 | -0.53 | -0.27 | -0.18 | 0.53 | 0.27 | 0.18 |
| 21 | 2.0 | 10.9 | 0.62 | 5.66 | 1.61 | 0.81 | 0.54 | 1.09 | 0.71 | 0.50 |
| 4 | 1.0 | 12.9 | - | - | 5.13 | 2.56 | 1.71 | 5.13 | 2.56 | 1.71 |
| 7 | 8.0 | 13.7 | - | - | 6.54 | 3.27 | 2.18 | 6.54 | 3.27 | 2.18 |
| 6 | 1.1 | 17.6 | 6.84 | 38.97 | 13.35 | 6.67 | 4.45 | 1.10 | 1.09 | 1.07 |
| 9 | 1.2 | 144* | 15.0 | 10.42 | 236.90 | 118.50 | 78.97 | 8.93 | 8.91 | 8.88 |
| | | | | Cr (90.7 ± 7.37) [mg/kg] | | | | | | |
| 6 | 1.1 | 51 | 15.3 | 29.69 | -10.68 | -5.34 | -3.56 | 2.51 | 2.32 | 2.09 |
| 17 | 1.2 | 61.0 | 5.00 | 8.20 | -8.07 | -4.03 | -2.69 | 4.78 | 3.34 | 2.45 |
| 4 | 1.0 | 73.3 | - | - | -4.73 | -2.36 | -1.58 | 4.73 | 2.36 | 1.58 |
| 7 | 8.0 | 75.9 | - | - | -4.02 | -2.01 | -1.34 | 4.02 | 2.01 | 1.34 |
| 3 | 2.0 | 76.7 | 1.36 | 1.78 | -3.81 | -1.91 | -1.27 | 3.57 | 1.87 | 1.26 |
| 3 | 1.3 | 79 | 11.2 | 14.25 | -3.25 | -1.62 | -1.08 | 1.01 | 0.89 | 0.76 |
| 21 | 2.0 | 86.2 | 1.54 | 1.79 | -1.24 | -0.62 | -0.41 | 1.14 | 0.60 | 0.41 |
| 20 | 2.0 | 95 | - | - | 1.17 | 0.58 | 0.39 | 1.17 | 0.58 | 0.39 |
| 19 | 1.3 | 120 | 40.0 | 33.33 | 7.96 | 3.98 | 2.65 | 0.73 | 0.72 | 0.71 |
| 22 | 1.1 | 174* | 18.0 | 10.34 | 22.63 | 11.31 | 7.54 | 4.53 | 4.28 | 3.95 |
| 1 | 4.5 | 224* | 45.0 | 20.09 | 36.21 | 18.11 | 12.07 | 2.95 | 2.92 | 2.88 |
| 2 | 1.3 | 249* | 51.6 | 20.72 | 43.00 | 21.50 | 14.33 | 3.06 | 3.04 | 3.00 |
| 14 | 1.2 | 273* | 29.7 | 10.87 | 49.58 | 24.79 | 16.53 | 6.10 | 5.96 | 5.76 |
| | | | | Cs [mg/kg] | | | | | | |
| 21 | 2.0 | 10.0 | 1.34 | 13.40 | - | - | - | - | - | - |

Table 4 continued…

| Laboratory code | Technique code | Analyte concentration | Standard dev. | Relative std. dev., [%] | z-scores | | | u-scores | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 |
| Cu (21.7 ± 2.19) [mg/kg] | | | | | | | | | | |
| 14 | 1.2 | 9.2 | 2.30 | 25.00 | -11.44 | -5.72 | -3.82 | 4.91 | 3.94 | 3.12 |
| 4 | 1.0 | 12.9 | - | 0.00 | -8.06 | -4.03 | -2.69 | 8.06 | 4.03 | 2.69 |
| 19 | 1.3 | 13.0 | 5.00 | 38.46 | -7.97 | -3.98 | -2.66 | 1.70 | 1.59 | 1.46 |
| 20 | 2.0 | 20.1 | - | - | -1.47 | -0.73 | -0.49 | 1.47 | 0.73 | 0.49 |
| 21 | 2.0 | 20.28 | 0.618 | 3.05 | -1.30 | -0.65 | -0.43 | 1.13 | 0.63 | 0.43 |
| 15 | 1.2 | 22 | 11.0 | 50.00 | 0.27 | 0.14 | 0.09 | 0.03 | 0.03 | 0.03 |
| 3 | 2.0 | 22.99 | 0.890 | 3.87 | 1.18 | 0.59 | 0.39 | 0.92 | 0.55 | 0.38 |
| 7 | 8.0 | 26.9 | - | - | 4.76 | 2.38 | 1.59 | 4.76 | 2.38 | 1.59 |
| 24 | 1.2 | 27.9 | 8.33 | 29.82 | 5.70 | 2.85 | 1.90 | 0.74 | 0.72 | 0.70 |
| 2 | 1.3 | 28.9 | 4.82 | 16.67 | 6.60 | 3.30 | 2.20 | 1.46 | 1.36 | 1.24 |
| 1 | 4.5 | 29.3 | 5.90 | 20.14 | 6.96 | 3.48 | 2.32 | 1.27 | 1.21 | 1.13 |
| 3 | 1.3 | 29.5 | 9.84 | 33.32 | 7.17 | 3.58 | 2.39 | 0.79 | 0.78 | 0.76 |
| 22 | 1.1 | 62.0* | 5.00 | 8.06 | 36.90 | 18.45 | 12.30 | 7.87 | 7.39 | 6.74 |
| 6 | 1.1 | 72* | 23.1 | 31.97 | 46.28 | 23.14 | 15.43 | 2.19 | 2.18 | 2.17 |
| 17 | 1.2 | 133* | 10.0 | 7.52 | 101.90 | 50.95 | 33.97 | 11.06 | 10.87 | 10.58 |
| 13 | 2.0 | 245.0* | 5.00 | 2.04 | 204.40 | 102.20 | 68.15 | 43.63 | 40.92 | 37.35 |
| Ga (26.2 ± 2.57)[mg/kg] | | | | | | | | | | |
| 6 | 1.1 | 16.0* | 6.00 | 37.50 | -7.96 | -3.98 | -2.65 | 1.66 | 1.56 | 1.43 |
| 1 | 4.5 | 21.2* | 4.30 | 20.28 | -3.90 | -1.95 | -1.30 | 1.11 | 1.00 | 0.87 |
| 14 | 1.2 | 23.3 | 2.60 | 11.16 | -2.26 | -1.13 | -0.75 | 1.00 | 0.79 | 0.62 |
| 22 | 1.1 | 24.2 | 2.10 | 8.68 | -1.56 | -0.78 | -0.52 | 0.81 | 0.60 | 0.46 |
| 21 | 2.0 | 25.01 | 0.412 | 1.65 | -0.93 | -0.46 | -0.31 | 0.88 | 0.46 | 0.31 |
| 20 | 2.0 | 25.2 | - | - | -0.78 | -0.39 | -0.26 | 0.78 | 0.39 | 0.26 |
| 15 | 1.2 | 26 | 10.5 | 40.38 | -0.16 | -0.08 | -0.05 | 0.02 | 0.02 | 0.02 |
| 3 | 1.3 | 26.2 | 2.01 | 7.66 | 0.03 | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 |
| 3 | 2.0 | 26.62 | 0.494 | 1.86 | 0.33 | 0.16 | 0.11 | 0.31 | 0.16 | 0.11 |
| 9 | 1.2 | 41.0* | 8.00 | 19.51 | 11.55 | 5.77 | 3.85 | 1.83 | 1.76 | 1.67 |
| Hf [mg/kg] | | | | | | | | | | |
| 3 | 2.0 | 8.2 | 1.46 | 17.88 | - | - | - | - | - | - |
| 4 | 1.0 | 33.7 | - | - | - | - | - | - | - | - |
| *La* (*45.1* ± *4.07*) [mg/kg] | | | | | | | | | | |
| 3 | 2.0 | 46.4 | 6.43 | 13.84 | 0.65 | 0.32 | 0.22 | 0.19 | 0.17 | 0.15 |
| 22 | 1.1 | 49.0 | 3.00 | 6.12 | 1.92 | 0.96 | 0.64 | 1.08 | 0.77 | 0.57 |
| 21 | 2.0 | 54.6 | 4.12 | 7.55 | 4.65 | 2.32 | 1.55 | 2.06 | 1.63 | 1.28 |
| 4 | 1.0 | 56 | 0.00 | 0.00 | 5.36 | 2.68 | 1.79 | 5.36 | 2.68 | 1.79 |
| 15 | 1.1 | 56.0 | 6.00 | 10.71 | 5.36 | 2.68 | 1.79 | 1.72 | 1.50 | 1.27 |
| 24 | 1.2 | 62.3 | 2.24 | 3.59 | 8.47 | 4.23 | 2.82 | 5.70 | 3.71 | 2.65 |

Table 4 continued…

| Laboratory code | Technique code | Analyte concentration | Standard dev. | Relative std. dev., [%] | z-scores | | | u-scores | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 | $k$ = 0.5 | $k$ = 1.0 | $k$ = 1.5 |
| | | | | Mn (193 ± 14.0) [mg/kg] | | | | | | |
| 9 | 1.2 | 152 | 19.0 | 12.50 | -5.86 | -2.93 | -1.96 | 2.03 | 1.74 | 1.45 |
| 7 | 8.0 | 158 | - | - | -5.01 | -2.50 | -1.67 | 5.01 | 2.50 | 1.67 |
| 21 | 2.0 | 169.8 | 9.26 | 5.45 | -3.31 | -1.66 | -1.10 | 2.00 | 1.38 | 1.01 |
| 3 | 2.0 | 203.64 | 0.858 | 0.42 | 1.52 | 0.76 | 0.51 | 1.51 | 0.76 | 0.51 |
| 2 | 1.3 | 205 | 52.0 | 25.39 | 1.69 | 0.84 | 0.56 | 0.22 | 0.22 | 0.21 |
| 20 | 2.0 | 209 | - | - | 2.29 | 1.14 | 0.76 | 2.29 | 1.14 | 0.76 |
| 15 | 1.2 | 210 | 19.0 | 9.05 | 2.43 | 1.22 | 0.81 | 0.84 | 0.72 | 0.60 |
| 3 | 1.3 | 227 | 62.4 | 27.51 | 4.84 | 2.42 | 1.61 | 0.54 | 0.53 | 0.51 |
| 19 | 1.3 | 234 | 12.0 | 5.13 | 5.86 | 2.93 | 1.96 | 2.95 | 2.23 | 1.70 |
| 10 | 1.2 | 243 | 47.0 | 19.34 | 7.15 | 3.58 | 2.38 | 1.05 | 1.02 | 0.97 |
| 22 | 1.1 | 245 | 20.0 | 8.16 | 7.44 | 3.72 | 2.48 | 2.45 | 2.13 | 1.79 |
| 1 | 4.5 | 253 | 25.0 | 9.88 | 8.58 | 4.29 | 2.86 | 2.31 | 2.10 | 1.84 |
| 18 | 2.0 | 263 | 78.0 | 29.66 | 10.01 | 5.01 | 3.34 | 0.89 | 0.88 | 0.87 |
| 13 | 2.0 | 271.0 | 8.00 | 2.95 | 11.16 | 5.58 | 3.72 | 7.34 | 4.84 | 3.48 |
| 14 | 1.2 | 318 | 31.8 | 10.02 | 17.81 | 8.90 | 5.94 | 3.82 | 3.58 | 3.27 |
| 4 | 1.0 | 326.8 | - | - | 19.14 | 9.57 | 6.38 | 19.14 | 9.57 | 6.38 |
| 17 | 1.2 | 432* | 10.0 | 2.31 | 34.18 | 17.09 | 11.39 | 19.59 | 13.90 | 10.29 |
| 6 | 1.1 | 1381* | 226 | 16.36 | 169.90 | 84.96 | 56.64 | 5.25 | 5.25 | 5.23 |
| | | | | *Nb* (*19.3* ± *1.98*) [mg/kg] | | | | | | |
| 22 | 1.1 | 15.0 | 1.10 | 7.33 | -4.35 | -2.17 | -1.45 | 2.91 | 1.90 | 1.36 |
| 23 | 1.1 | 16.0 | 3.00 | 18.75 | -3.34 | -1.67 | -1.11 | 1.05 | 0.92 | 0.78 |
| 21 | 2.0 | 19.04 | 0.309 | 1.62 | -0.26 | -0.13 | -0.09 | 0.25 | 0.13 | 0.09 |
| 20 | 2.0 | 19.5 | - | - | 0.20 | 0.10 | 0.07 | 0.20 | 0.10 | 0.07 |
| 15 | 1.2 | 21.0 | 4.50 | 21.43 | 1.72 | 0.86 | 0.57 | 0.37 | 0.35 | 0.32 |
| 6 | 1.1 | 21.1 | 5.45 | 25.88 | 1.78 | 0.89 | 0.59 | 0.32 | 0.30 | 0.28 |
| 24 | 1.2 | 21.3 | 1.74 | 8.19 | 2.02 | 1.01 | 0.67 | 1.00 | 0.76 | 0.58 |
| 1 | 4.5 | 25.0 | 7.00 | 28.00 | 5.77 | 2.88 | 1.92 | 0.81 | 0.78 | 0.75 |
| 16 | 1.1 | 26 | 10.0 | 38.46 | 6.78 | 3.39 | 2.26 | 0.67 | 0.66 | 0.64 |
| | | | | *Nd* (*43.1* ± *3.91*) [mg/kg] | | | | | | |
| 22 | 1.1 | 41.6 | 2.60 | 6.25 | -0.77 | -0.38 | -0.26 | 0.46 | 0.32 | 0.23 |
| 21 | 2.0 | 41.8 | 2.16 | 5.17 | -0.67 | -0.33 | -0.22 | 0.45 | 0.29 | 0.21 |
| 24 | 1.2 | 44.54* | 0.379 | 0.85 | 0.73 | 0.37 | 0.24 | 0.72 | 0.37 | 0.24 |
| | | | | Ni (27.2 ± 2.65) [mg/kg] | | | | | | |
| 19 | 1.3 | 22.0 | 5.00 | 22.73 | -3.93 | -1.97 | -1.31 | 1.01 | 0.92 | 0.81 |
| 7 | 8.0 | 24.4 | - | - | -2.12 | -1.06 | -0.71 | 2.12 | 1.06 | 0.71 |
| 3 | 1.3 | 27.0 | 4.47 | 16.54 | -0.14 | -0.07 | -0.05 | 0.04 | 0.03 | 0.03 |
| 3 | 2.0 | 27.66 | 0.906 | 3.28 | 0.35 | 0.17 | 0.12 | 0.29 | 0.16 | 0.11 |
| 24 | 1.2 | 28.7 | 7.59 | 26.44 | 1.15 | 0.57 | 0.38 | 0.20 | 0.19 | 0.18 |
| 20 | 2.0 | 30.3 | - | - | 2.34 | 1.17 | 0.78 | 2.34 | 1.17 | 0.78 |
| 21 | 2.0 | 31.39 | 0.823 | 2.62 | 3.17 | 1.59 | 1.06 | 2.69 | 1.51 | 1.03 |
| 22 | 1.1 | 33.8 | 3.70 | 10.95 | 4.99 | 2.49 | 1.66 | 1.68 | 1.45 | 1.22 |
| 1 | 4.5 | 74* | 15.0 | 20.27 | 35.37 | 17.68 | 11.79 | 3.11 | 3.07 | 3.02 |
| 6 | 1.1 | 136* | 29.0 | 21.32 | 82.22 | 41.11 | 27.41 | 3.75 | 3.74 | 3.72 |

Table 4 continued…

| 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 (448 ± 28.6) [mg/kg] | | | | | | |
| 3 | 2.0 | 359 | 26.4 | 7.35 | -6.23 | -3.12 | -2.08 | 2.97 | 2.29 | 1.77 |
| | | | | Pb (29.6 ± 2.85) [mg/kg] | | | | | | |
| 7 | 8.0 | 20.2 | - | - | -6.61 | -3.31 | -2.20 | 6.61 | 3.31 | 2.20 |
| 20 | 2.0 | 29.7 | - | - | 0.07 | 0.04 | 0.02 | 0.07 | 0.04 | 0.02 |
| 24 | 1.2 | 30.2 | 2.14 | 7.09 | 0.44 | 0.22 | 0.15 | 0.24 | 0.18 | 0.13 |
| 21 | 2.0 | 31.8 | 1.13 | 3.56 | 1.55 | 0.78 | 0.52 | 1.21 | 0.72 | 0.50 |
| 22 | 1.1 | 33.0 | 7.00 | 21.21 | 2.39 | 1.20 | 0.80 | 0.48 | 0.45 | 0.41 |
| 2 | 1.3 | 34.7 | 8.38 | 24.16 | 3.58 | 1.79 | 1.19 | 0.60 | 0.58 | 0.54 |
| 6 | 1.1 | 35.4 | 9.80 | 27.68 | 4.08 | 2.04 | 1.36 | 0.59 | 0.57 | 0.54 |
| 19 | 1.3 | 45.0 | 9.00 | 20.00 | 10.83 | 5.42 | 3.61 | 1.69 | 1.63 | 1.55 |
| 3 | 2.0 | 46.0 | 1.60 | 3.47 | 11.53 | 5.77 | 3.85 | 7.67 | 5.03 | 3.60 |
| 9 | 1.2 | 47.0 | 9.00 | 19.15 | 12.24 | 6.12 | 4.08 | 1.91 | 1.84 | 1.75 |
| 4 | 1.0 | 50.1 | - | - | 14.42 | 7.21 | 4.81 | 14.42 | 7.21 | 4.81 |
| 17 | 1.2 | 58.0 | 6.00 | 10.34 | 19.97 | 9.99 | 6.66 | 4.61 | 4.28 | 3.86 |
| 15 | 1.2 | 60 | 14.2 | 23.67 | 21.38 | 10.69 | 7.13 | 2.13 | 2.10 | 2.05 |
| 12 | 1.2 | 69.0 | 2.00 | 2.90 | 27.71 | 13.85 | 9.24 | 16.06 | 11.33 | 8.36 |
| 11 | 1.1 | 141.0* | 9.00 | 6.38 | 78.35 | 39.17 | 26.12 | 12.23 | 11.80 | 11.19 |
| | | | | Pd [mg/kg] | | | | | | |
| 14 | 1.2 | 16.9 | 2.20 | 13.02 | - | - | - | - | - | - |
| | | | | Pr [mg/kg] | | | | | | |
| 22 | 1.1 | 7.90 | 0.800 | 10.13 | - | - | - | - | - | - |
| | | | | Rb (137 ± 10.5) [mg/kg] | | | | | | |
| 23 | 1.1 | 98.0 | 6.00 | 6.12 | -7.46 | -3.73 | -2.49 | 4.90 | 3.24 | 2.32 |
| 12 | 1.2 | 106 | 54.0 | 50.94 | -5.93 | -2.97 | -1.98 | 0.57 | 0.56 | 0.55 |
| 14 | 1.2 | 118 | 10.8 | 9.19 | -3.73 | -1.87 | -1.24 | 1.63 | 1.30 | 1.02 |
| 16 | 1.1 | 123 | 19.0 | 15.45 | -2.68 | -1.34 | -0.89 | 0.71 | 0.65 | 0.57 |
| 17 | 1.2 | 128.0 | 4.00 | 3.13 | -1.72 | -0.86 | -0.57 | 1.37 | 0.80 | 0.56 |
| 22 | 1.1 | 130 | 10.0 | 7.69 | -1.34 | -0.67 | -0.45 | 0.62 | 0.48 | 0.38 |
| 3 | 2.0 | 130.4 | 2.89 | 2.22 | -1.26 | -0.63 | -0.42 | 1.10 | 0.61 | 0.41 |
| 2 | 1.3 | 135.6 | 7.58 | 5.59 | -0.27 | -0.14 | -0.09 | 0.16 | 0.11 | 0.08 |
| 20 | 2.0 | 136.1 | - | - | -0.17 | -0.09 | -0.06 | 0.17 | 0.09 | 0.06 |
| 15 | 1.2 | 137.0 | 8.70 | 6.35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 13 | 2.0 | 141 | 15.0 | 10.64 | 0.77 | 0.38 | 0.26 | 0.25 | 0.22 | 0.18 |
| 21 | 2.0 | 142.0 | 1.54 | 1.09 | 0.97 | 0.48 | 0.32 | 0.93 | 0.48 | 0.32 |
| 24 | 1.2 | 144.5 | 1.04 | 0.72 | 1.44 | 0.72 | 0.48 | 1.41 | 0.71 | 0.48 |
| 1 | 4.5 | 147.0 | 15.0 | 10.20 | 1.91 | 0.96 | 0.64 | 0.63 | 0.55 | 0.46 |
| 6 | 1.1 | 172 | 44.9 | 26.17 | 6.63 | 3.31 | 2.21 | 0.77 | 0.75 | 0.73 |
| 4 | 1.0 | 175.3 | - | - | 7.33 | 3.67 | 2.44 | 7.33 | 3.67 | 2.44 |
| 9 | 1.2 | 195 | 19.0 | 9.74 | 11.10 | 5.55 | 3.70 | 2.94 | 2.68 | 2.36 |

Table 4 continued…

| 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 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | S (613 ± 37.4) [mg/kg] | | | | | | |
| 13 | 2.0 | 925.0 | 3.00 | 0.32 | 16.72 | 8.36 | 5.57 | 16.51 | 8.33 | 5.57 |
| 18 | 2.0 | 979 | 327 | 33.40 | 19.61 | 9.81 | 6.54 | 1.12 | 1.11 | 1.10 |
| 17 | 1.2 | 1853 | 41.0 | 2.21 | 66.45 | 33.22 | 22.15 | 27.53 | 22.36 | 17.87 |
| 1 | 4.5 | 2260 | 230 | 10.18 | 88.26 | 44.13 | 29.42 | 7.14 | 7.07 | 6.96 |
| | | | | *Sc* (*15.8* ± *1.67*) [mg/kg] | | | | | | |
| 6 | 1.1 | 13.0* | 4.38 | 33.82 | -3.42 | -1.71 | -1.14 | 0.64 | 0.61 | 0.57 |
| 3 | 2.0 | 16.0 | 1.78 | 11.15 | 0.19 | 0.10 | 0.06 | 0.08 | 0.07 | 0.05 |
| 20 | 2.0 | 17.1 | 0.00 | 0.00 | 1.56 | 0.78 | 0.52 | 1.56 | 0.78 | 0.52 |
| 21 | 2.0 | 17.2 | 1.13 | 6.59 | 1.67 | 0.83 | 0.56 | 0.99 | 0.69 | 0.51 |
| | | | | Sm [mg/kg] | | | | | | |
| 4 | 1.0 | 7 | - | - | - | - | - | - | - | - |
| | | | | Sn (4.09 ± 0.530) [mg/kg] | | | | | | |
| 21 | 2.0 | 6.2 | 1.34 | 21.63 | 7.92 | 3.96 | 2.64 | 1.54 | 1.46 | 1.35 |
| | | | | Sr (109.0± 8.61) [mg/kg] | | | | | | |
| 23 | 1.1 | 59.0 | 4.00 | 6.78 | -11.62 | -5.81 | -3.87 | 8.51 | 5.27 | 3.70 |
| 7 | 8.0 | 75 | - | - | -7.90 | -3.95 | -2.63 | 7.90 | 3.95 | 2.63 |
| 1 | 4.5 | 90.4 | 9.00 | 9.96 | -4.32 | -2.16 | -1.44 | 1.87 | 1.49 | 1.18 |
| 16 | 1.1 | 93 | 17.0 | 18.28 | -3.72 | -1.86 | -1.24 | 0.91 | 0.84 | 0.75 |
| 14 | 1.2 | 96.2 | 8.80 | 9.15 | -2.98 | -1.49 | -0.99 | 1.31 | 1.04 | 0.82 |
| 12 | 1.2 | 100 | 25.0 | 25.00 | -2.09 | -1.05 | -0.70 | 0.35 | 0.34 | 0.32 |
| 2 | 1.3 | 100.2 | 6.08 | 6.07 | -2.05 | -1.03 | -0.68 | 1.19 | 0.84 | 0.62 |
| 15 | 1.2 | 106.0 | 7.20 | 6.79 | -0.70 | -0.35 | -0.23 | 0.36 | 0.27 | 0.20 |
| 17 | 1.2 | 106.0 | 3.00 | 2.83 | -0.70 | -0.35 | -0.23 | 0.57 | 0.33 | 0.23 |
| 3 | 2.0 | 106.54 | 0.912 | 0.86 | -0.57 | -0.29 | -0.19 | 0.56 | 0.28 | 0.19 |
| 22 | 1.1 | 108.0 | 8.00 | 7.41 | -0.23 | -0.12 | -0.08 | 0.11 | 0.09 | 0.07 |
| 20 | 2.0 | 108.6 | - | - | -0.09 | -0.05 | -0.03 | 0.09 | 0.05 | 0.03 |
| 24 | 1.2 | 110.6 | 2.96 | 2.67 | 0.38 | 0.19 | 0.13 | 0.31 | 0.18 | 0.12 |
| 21 | 2.0 | 111.2 | 1.03 | 0.93 | 0.50 | 0.25 | 0.17 | 0.49 | 0.25 | 0.17 |
| 9 | 1.2 | 135 | 17.0 | 12.59 | 6.04 | 3.02 | 2.01 | 1.48 | 1.37 | 1.22 |
| 4 | 1.0 | 136.5 | - | - | 6.39 | 3.20 | 2.13 | 6.39 | 3.20 | 2.13 |
| 18 | 2.0 | 166.0* | 4.00 | 2.41 | 13.25 | 6.62 | 4.42 | 9.70 | 6.01 | 4.22 |
| 6 | 1.1 | 198* | 39.0 | 19.70 | 20.68 | 10.34 | 6.89 | 2.27 | 2.23 | 2.17 |
| | | | | *Th* (*15.7* ± *1.66*) [mg/kg] | | | | | | |
| 22 | 1.1 | 14.0 | 2.00 | 14.29 | -2.05 | -1.02 | -0.68 | 0.79 | 0.65 | 0.53 |
| 20 | 2.0 | 17.5 | - | - | 2.17 | 1.09 | 0.72 | 2.17 | 1.09 | 0.72 |
| 21 | 2.0 | 18.73 | 0.618 | 3.30 | 3.66 | 1.83 | 1.22 | 2.93 | 1.71 | 1.18 |
| 6 | 1.1 | 24.5 | 9.50 | 38.78 | 10.61 | 5.30 | 3.54 | 0.92 | 0.91 | 0.90 |

Table 4 continued…

| 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 |
| | | | | | *U (2.86 ± 0.391)* [mg/kg] | | | | | |
| 21 | 2.0 | 3.81 | 0.309 | 8.11 | 4.86 | 2.43 | 1.62 | 2.60 | 1.91 | 1.43 |
| 20 | 2.0 | 4.7 | - | - | 9.42 | 4.71 | 3.14 | 9.42 | 4.71 | 3.14 |
| | | | | | V (140 ± 10.7) [mg/kg] | | | | | |
| 4 | 1.0 | 39.6 | - | - | -18.86 | -9.43 | -6.29 | 18.86 | 9.43 | 6.29 |
| 3 | 2.0 | 104.3 | 2.45 | 2.35 | -6.71 | -3.35 | -2.24 | 6.09 | 3.27 | 2.21 |
| 7 | 8.0 | 120 | 0 | 0.00 | -3.76 | -1.88 | -1.25 | 3.76 | 1.88 | 1.25 |
| 3 | 1.3 | 148 | 51.9 | 35.05 | 1.49 | 0.75 | 0.50 | 0.15 | 0.15 | 0.15 |
| 20 | 2.0 | 150.2 | - | - | 1.92 | 0.96 | 0.64 | 1.92 | 0.96 | 0.64 |
| 21 | 2.0 | 150.3 | 2.06 | 1.37 | 1.93 | 0.97 | 0.64 | 1.80 | 0.95 | 0.64 |
| 6 | 1.1 | 187 | 21.0 | 11.23 | 8.83 | 4.42 | 2.94 | 2.17 | 2.00 | 1.78 |
| 22 | 1.1 | 267 | 29.0 | 10.86 | 23.86 | 11.93 | 7.95 | 4.31 | 4.11 | 3.84 |
| 17 | 1.2 | 341 | 10.0 | 2.93 | 37.76 | 18.88 | 12.59 | 17.74 | 13.76 | 10.67 |
| | | | | | Y (27.9 ± 2.71) [mg/kg] | | | | | |
| 24 | 1.2 | 21.9 | 2.70 | 12.33 | -4.44 | -2.22 | -1.48 | 1.99 | 1.57 | 1.23 |
| 23 | 1.1 | 22.0 | 4.00 | 18.18 | -4.36 | -2.18 | -1.45 | 1.40 | 1.22 | 1.04 |
| 15 | 1.2 | 24.0 | 2.40 | 10.00 | -2.88 | -1.44 | -0.96 | 1.42 | 1.08 | 0.83 |
| 22 | 1.1 | 26.0 | 2.00 | 7.69 | -1.41 | -0.70 | -0.47 | 0.79 | 0.56 | 0.42 |
| 21 | 2.0 | 28.41 | 0.309 | 1.09 | 0.38 | 0.19 | 0.13 | 0.37 | 0.19 | 0.13 |
| 20 | 2.0 | 28.6 | - | - | 0.52 | 0.26 | 0.17 | 0.52 | 0.26 | 0.17 |
| 4 | 1.0 | 29.3 | - | - | 1.04 | 0.52 | 0.35 | 1.04 | 0.52 | 0.35 |
| 9 | 1.2 | 30.2 | 4.90 | 16.23 | 1.70 | 0.85 | 0.57 | 0.45 | 0.41 | 0.36 |
| 3 | 2.0 | 33.62 | 0.384 | 1.14 | 4.23 | 2.12 | 1.41 | 4.07 | 2.09 | 1.40 |
| 14 | 1.2 | 42.4* | 4.00 | 9.43 | 10.72 | 5.36 | 3.57 | 3.43 | 3.00 | 2.55 |
| 6 | 1.1 | 81* | 24.5 | 30.14 | 39.57 | 19.78 | 13.19 | 2.18 | 2.17 | 2.15 |

Table 4 continued…

| 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 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Zn (161 ± 12.0) [mg/kg] | | | | | | |
| 14 | 1.2 | 130 | 12.3 | 9.47 | -5.19 | -2.59 | -1.73 | 2.27 | 1.81 | 1.43 |
| 6 | 1.1 | 147 | 41.0 | 27.89 | -2.34 | -1.17 | -0.78 | 0.34 | 0.33 | 0.31 |
| 1 | 4.5 | 148 | 15.0 | 10.14 | -2.17 | -1.08 | -0.72 | 0.80 | 0.68 | 0.56 |
| 3 | 2.0 | 153.9 | 1.08 | 0.70 | -1.19 | -0.59 | -0.40 | 1.17 | 0.59 | 0.40 |
| 21 | 2.0 | 154.4 | 3.09 | 2.00 | -1.10 | -0.55 | -0.37 | 0.98 | 0.53 | 0.36 |
| 20 | 2.0 | 154.9 | - | - | -1.02 | -0.51 | -0.34 | 1.02 | 0.51 | 0.34 |
| 7 | 8.0 | 157 | - | - | -0.67 | -0.33 | -0.22 | 0.67 | 0.33 | 0.22 |
| 22 | 1.1 | 159 | 12.0 | 7.55 | -0.33 | -0.17 | -0.11 | 0.15 | 0.12 | 0.09 |
| 19 | 1.3 | 159 | 14.0 | 8.81 | -0.33 | -0.17 | -0.11 | 0.13 | 0.11 | 0.09 |
| 24 | 1.2 | 160 | 13.1 | 8.17 | -0.17 | -0.08 | -0.06 | 0.07 | 0.06 | 0.04 |
| 3 | 1.3 | 168.9 | 4.32 | 2.56 | 1.32 | 0.66 | 0.44 | 1.07 | 0.62 | 0.43 |
| 11 | 1.1 | 174 | 10.0 | 5.75 | 2.17 | 1.08 | 0.72 | 1.12 | 0.83 | 0.63 |
| 15 | 1.2 | 177 | 18.3 | 10.34 | 2.67 | 1.34 | 0.89 | 0.83 | 0.73 | 0.62 |
| 17 | 1.2 | 196.0 | 6.00 | 3.06 | 5.84 | 2.92 | 1.95 | 4.13 | 2.61 | 1.85 |
| 16 | 1.1 | 204 | 72.0 | 35.29 | 7.17 | 3.59 | 2.39 | 0.60 | 0.59 | 0.58 |
| 13 | 2.0 | 216 | 25.0 | 11.57 | 9.18 | 4.59 | 3.06 | 2.14 | 1.98 | 1.79 |
| 4 | 1.0 | 226.7* | - | - | 10.96 | 5.48 | 3.65 | 10.96 | 5.48 | 3.65 |
| 18 | 2.0 | 237* | 30.0 | 12.66 | 12.68 | 6.34 | 4.23 | 2.48 | 2.35 | 2.17 |
| 2 | 1.3 | 287* | 16.2 | 5.64 | 21.07 | 10.54 | 7.02 | 7.31 | 6.27 | 5.22 |
| 9 | 1.2 | 299* | 32.0 | 10.70 | 23.02 | 11.51 | 7.68 | 4.24 | 4.04 | 3.76 |
| | | | | Zr (177 ± 13.0) [mg/kg] | | | | | | |
| 1 | 4.5 | 121 | 24.0 | 19.83 | -8.62 | -4.31 | -2.87 | 2.25 | 2.05 | 1.81 |
| 16 | 1.1 | 132 | 13.0 | 9.85 | -6.93 | -3.46 | -2.31 | 3.10 | 2.45 | 1.92 |
| 23 | 1.1 | 151.0 | 6.00 | 3.97 | -4.00 | -2.00 | -1.33 | 2.94 | 1.82 | 1.28 |
| 22 | 1.1 | 159 | 11.0 | 6.92 | -2.77 | -1.39 | -0.92 | 1.41 | 1.06 | 0.80 |
| 24 | 1.2 | 161.2 | 5.85 | 3.63 | -2.44 | -1.22 | -0.81 | 1.81 | 1.11 | 0.78 |
| 15 | 1.2 | 170 | 10.8 | 6.35 | -1.08 | -0.54 | -0.36 | 0.56 | 0.41 | 0.31 |
| 20 | 2.0 | 175.1 | - | - | -0.29 | -0.15 | -0.10 | 0.29 | 0.15 | 0.10 |
| 21 | 2.0 | 182.2 | 2.06 | 1.13 | 0.80 | 0.40 | 0.27 | 0.76 | 0.39 | 0.26 |
| 17 | 1.2 | 183.0 | 4.00 | 2.19 | 0.92 | 0.46 | 0.31 | 0.79 | 0.44 | 0.30 |
| 12 | 1.2 | 206 | 65.0 | 31.55 | 4.46 | 2.23 | 1.49 | 0.44 | 0.44 | 0.43 |
| 4 | 1.0 | 215.9 | - | - | 5.99 | 2.99 | 2.00 | 5.99 | 2.99 | 2.00 |
| 9 | 1.2 | 217 | 25.0 | 11.52 | 6.16 | 3.08 | 2.05 | 1.55 | 1.42 | 1.26 |
| 3 | 2.0 | 224.4 | 1.48 | 0.66 | 7.30 | 3.65 | 2.43 | 7.11 | 3.62 | 2.43 |
| 6 | 1.1 | 302* | 47.0 | 15.56 | 19.24 | 9.62 | 6.41 | 2.64 | 2.56 | 2.46 |

Table 5. The combined *z*-scores for the participating laboratories. The analytes without assigned values (Cl, Cs, Hf, Pd, Pr, and Sm) 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 | $\chi^2$ |
| 1 | 21 | 85.80 | 42.90 | 28.60 | 27890 | 6973 | 3099 | 35.48 |
| 2 | 11 | 30.82 | 15.41 | 10.27 | 3310 | 827 | 368 | 21.92 |
| 3 | 35 | 74.68 | 37.34 | 24.89 | 222000 | 55490 | 24660 | 53.20 |
| 4 | 17 | 16.63 | 8.32 | 5.54 | 2647 | 662 | 294 | 30.19 |
| 5 | 3 | 6.51 | 3.25 | 2.17 | 158 | 39 | 18 | 9.35 |
| 6 | 24 | 82.85 | 41.42 | 27.62 | 41450 | 10360 | 4606 | 39.36 |
| 7 | 17 | 43.28 | 21.64 | 14.43 | 33240 | 8310 | 3693 | 30.19 |
| 8 | 3 | 309.10 | 154.60 | 103.00 | 352300 | 88080 | 39150 | 9.35 |
| 9 | 13 | 97.12 | 48.56 | 32.37 | 57770 | 14440 | 6419 | 24.74 |
| 10 | 7 | 7.13 | 3.57 | 2.38 | 145 | 36 | 16 | 16.01 |
| 11 | 3 | 24.26 | 12.13 | 8.09 | 7626 | 1906 | 847 | 9.35 |
| 12 | 9 | -25.39 | -12.70 | -8.46 | 6637 | 1659 | 737 | 19.02 |
| 13 | 13 | 66.96 | 33.48 | 22.32 | 42480 | 10620 | 4720 | 24.74 |
| 14 | 14 | 2.69 | 1.34 | 0.90 | 3792 | 948 | 421 | 26.12 |
| 15 | 19 | 8.78 | 4.39 | 2.93 | 692 | 173 | 77 | 32.85 |
| 16 | 7 | 120.40 | 60.20 | 40.13 | 103900 | 25980 | 11550 | 16.01 |
| 17 | 17 | 53.75 | 26.87 | 17.92 | 19180 | 4795 | 2131 | 30.19 |
| 18 | 6 | 41.33 | 20.67 | 13.78 | 1958 | 490 | 218 | 14.45 |
| 19 | 10 | 2.56 | 1.28 | 0.85 | 356 | 89 | 40 | 20.48 |
| 20 | 26 | 8.88 | 4.44 | 2.96 | 432 | 108 | 48 | 41.92 |
| 21 | 32 | -22.75 | -11.37 | -7.58 | 12650 | 3162 | 1406 | 49.48 |
| 22 | 27 | 75.17 | 37.58 | 25.06 | 88600 | 22150 | 9844 | 43.19 |
| 23 | 6 | -14.32 | -7.16 | -4.77 | 255 | 64 | 28 | 14.45 |
| 24 | 15 | 4.73 | 2.37 | 1.58 | 186 | 46 | 21 | 27.49 |

## APPENDIX II
## Figures 1-6

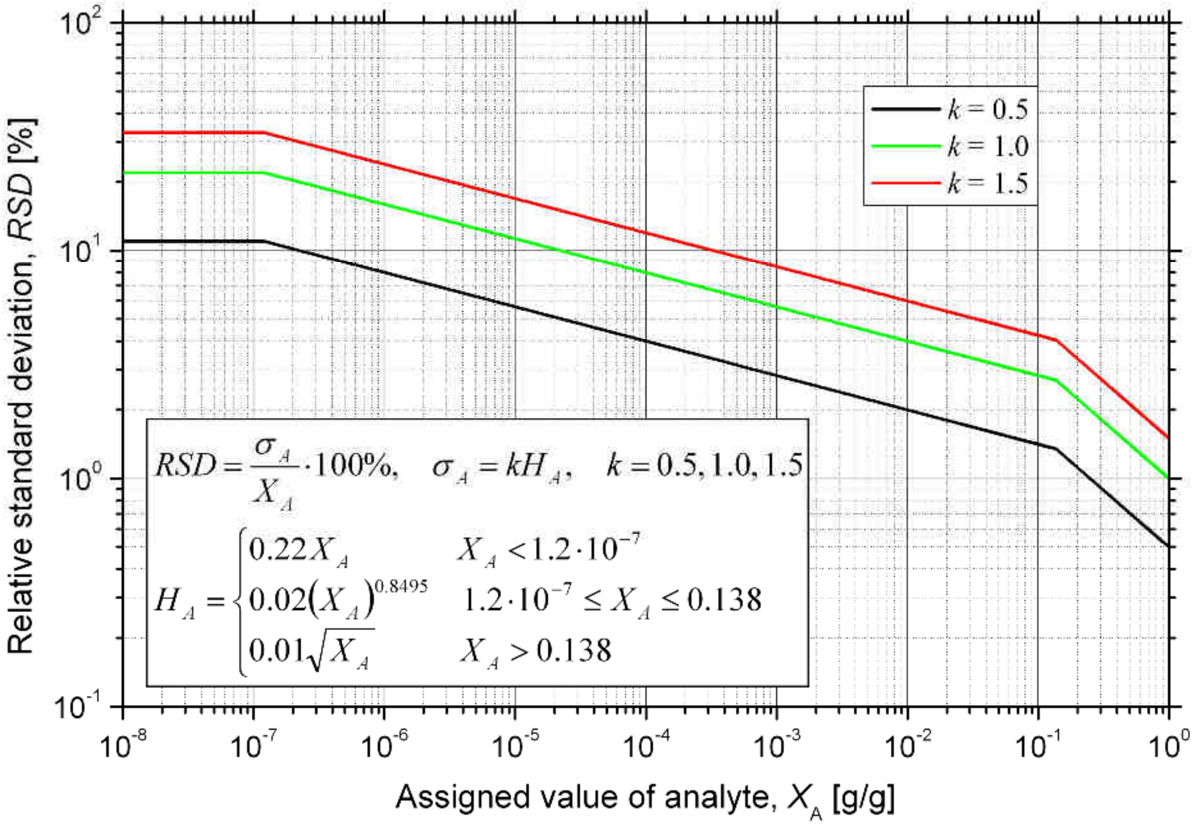



Fig. 1. Relative value of the target standard deviation, *RSD*, as a function of the assigned mass fraction of the analyte, $X_A$, calculated by using a modified Horowitz function, Eqn. (3). The target value, $\sigma_A$, is related to $H_A$ by a factor *k* and it is recognized as fit-for-purpose in three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

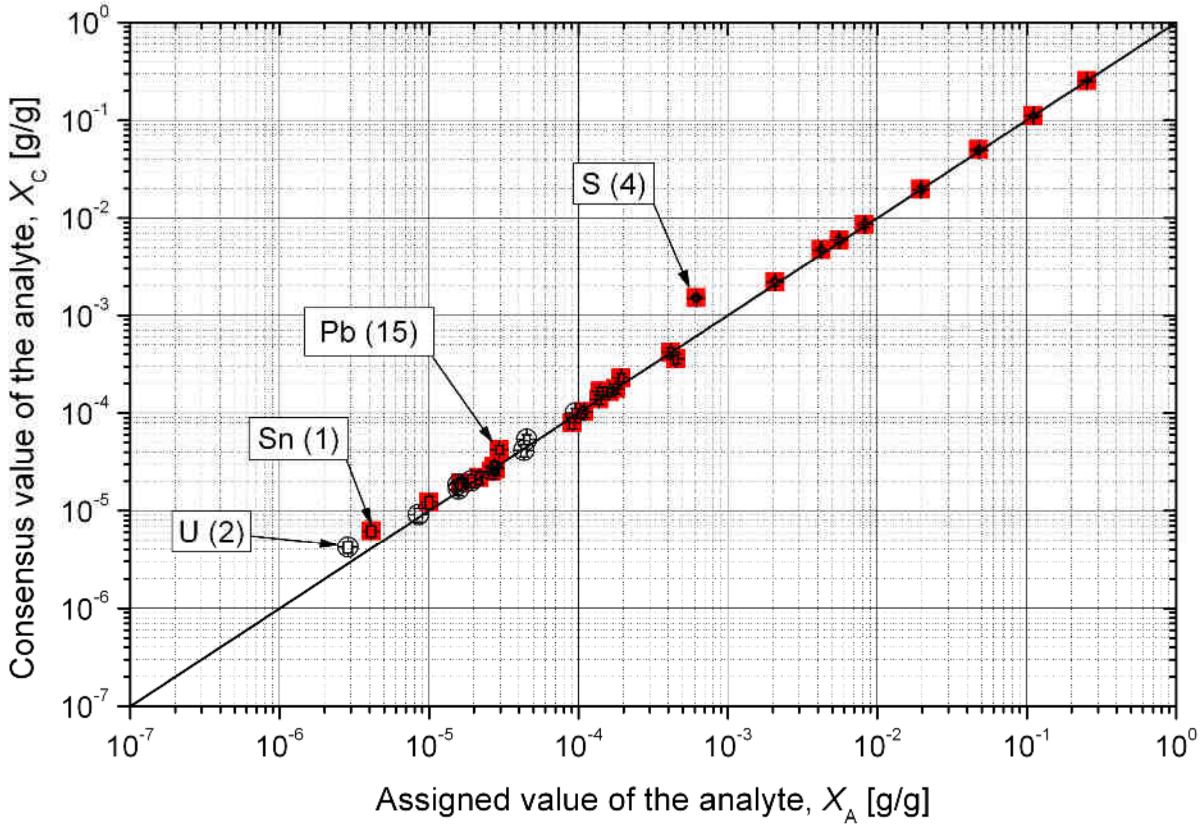
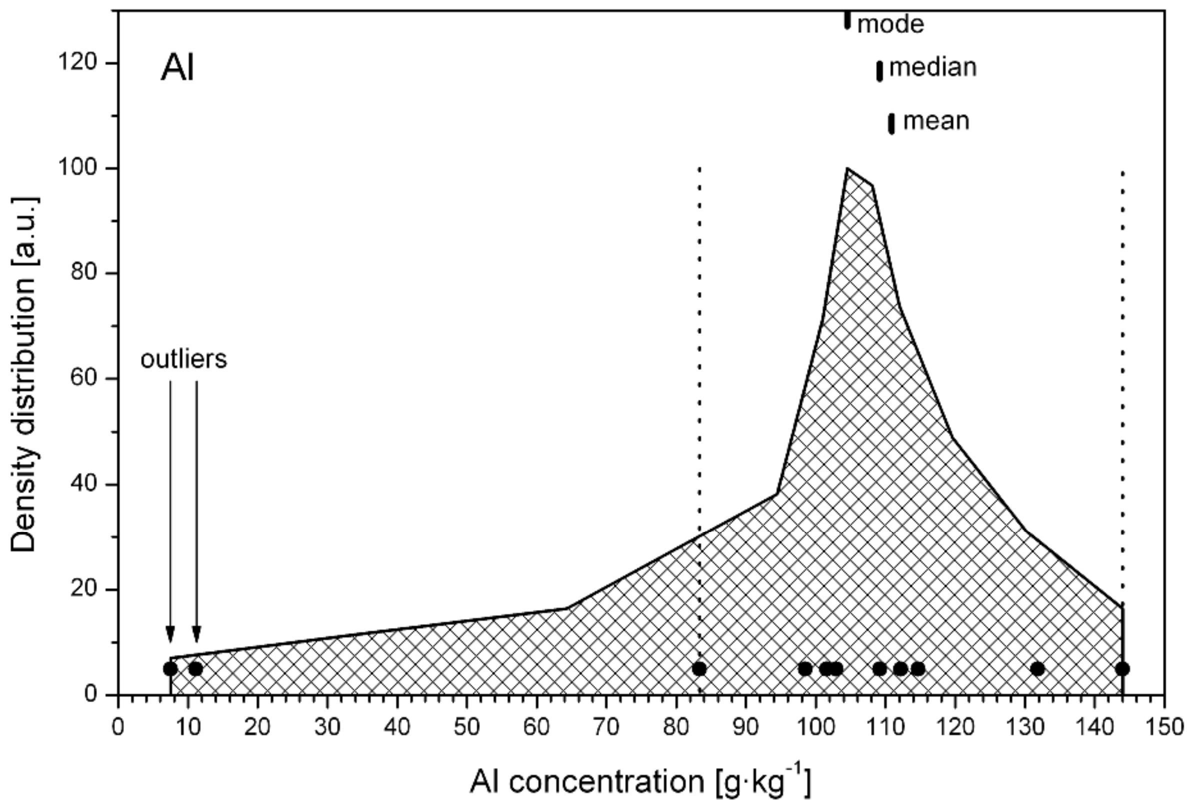



Fig. 2. Correlation between assigned values, $X_A$, and the consensus values of analytes, $X_C$. Solid red squares correspond to elements the assigned values of which were known with high degree of accuracy. Hollow black circles correspond to elements the assigned values of which can be considered as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



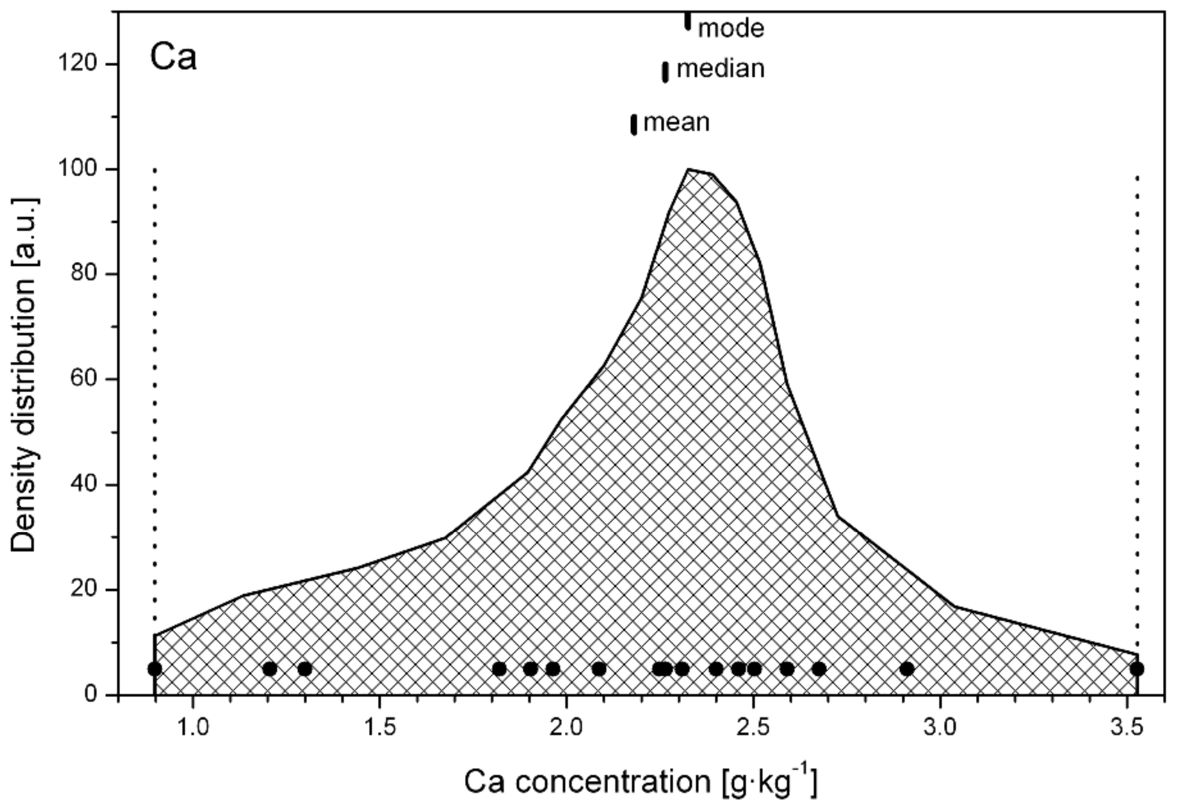




Fig. 3. The density distributions functions for the analytes for which at least 5 results passed the outlier rejection tests. The individual results are marked with filled circles. The dotted lines show the range of the accepted results – these results were used to calculate the consensus values. The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

Fig. 3 continued…

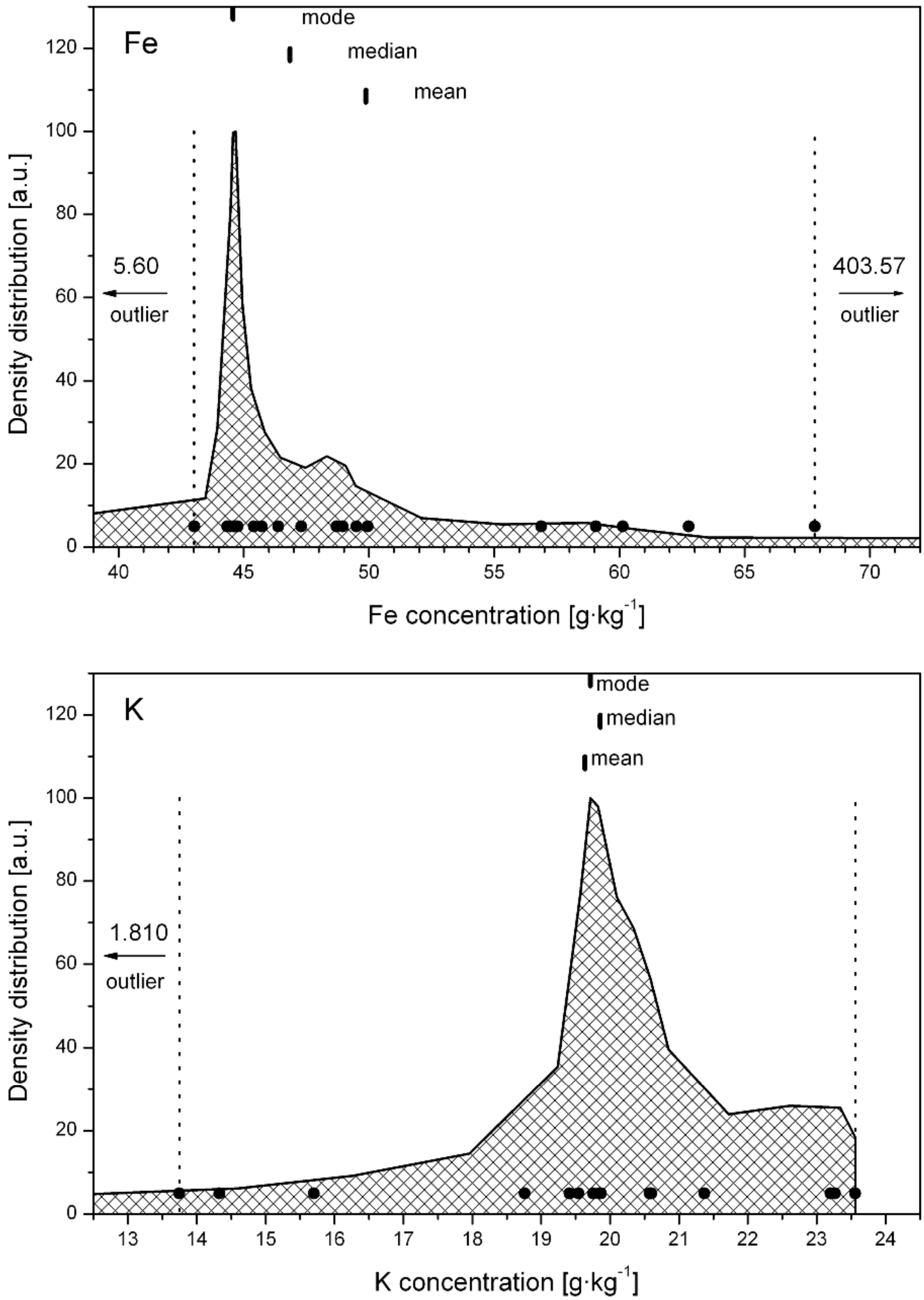
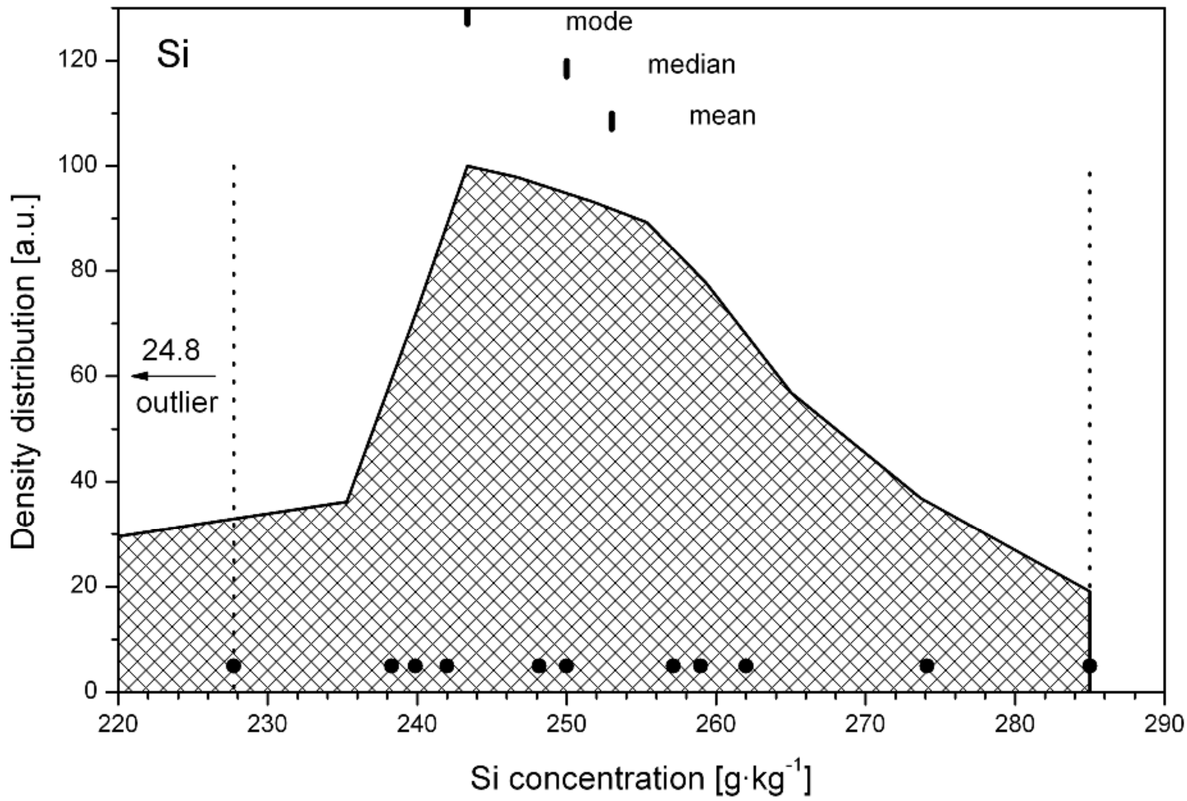


Fig. 3 continued…



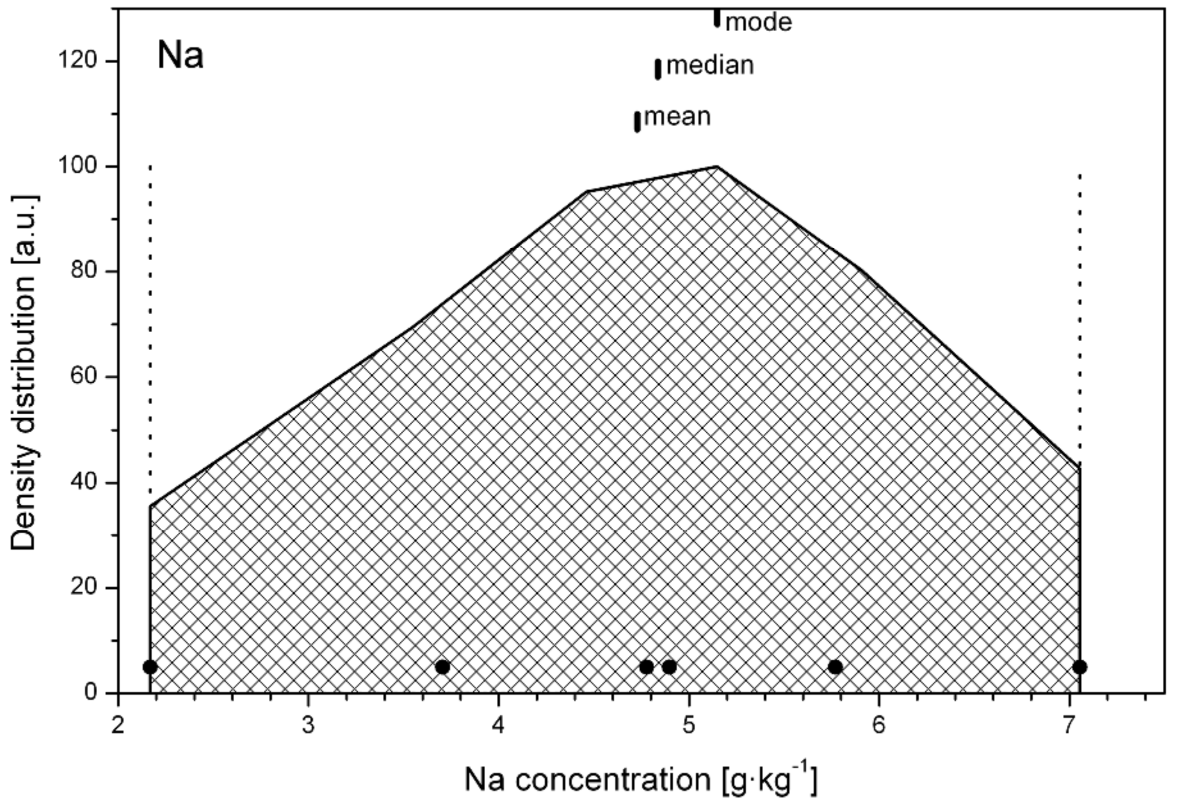
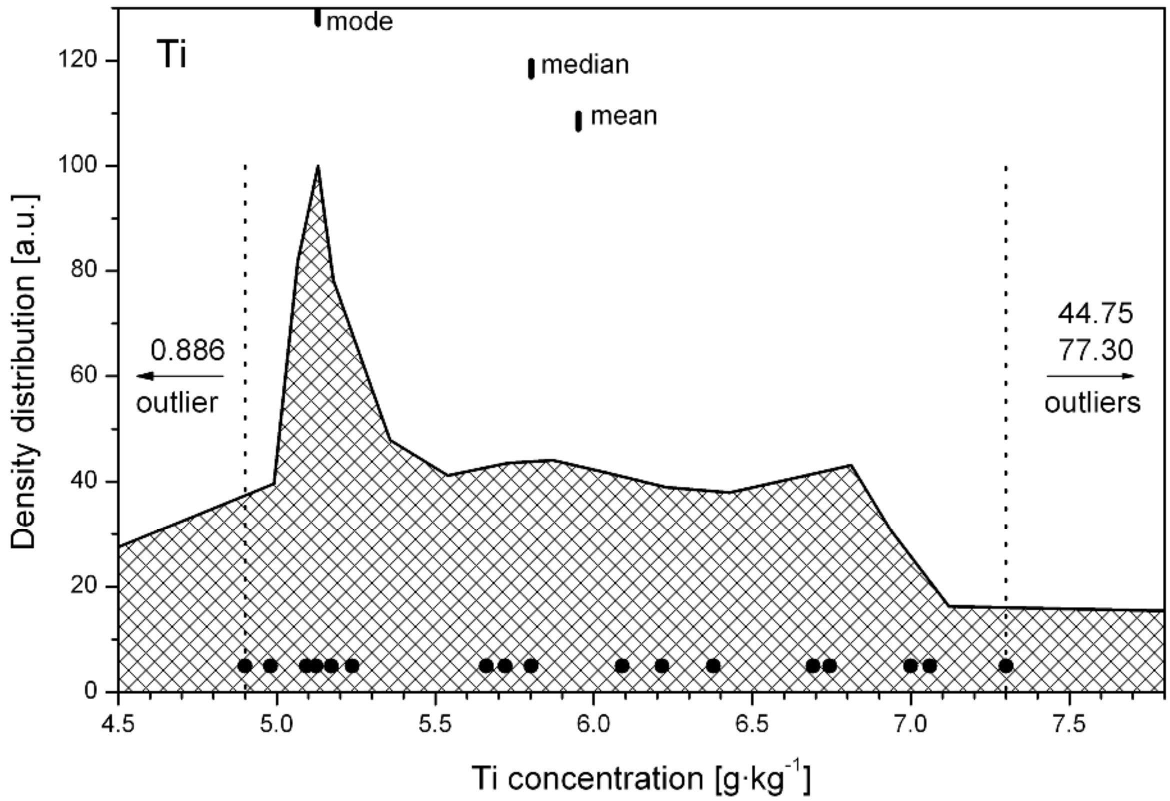



Fig. 3 continued…



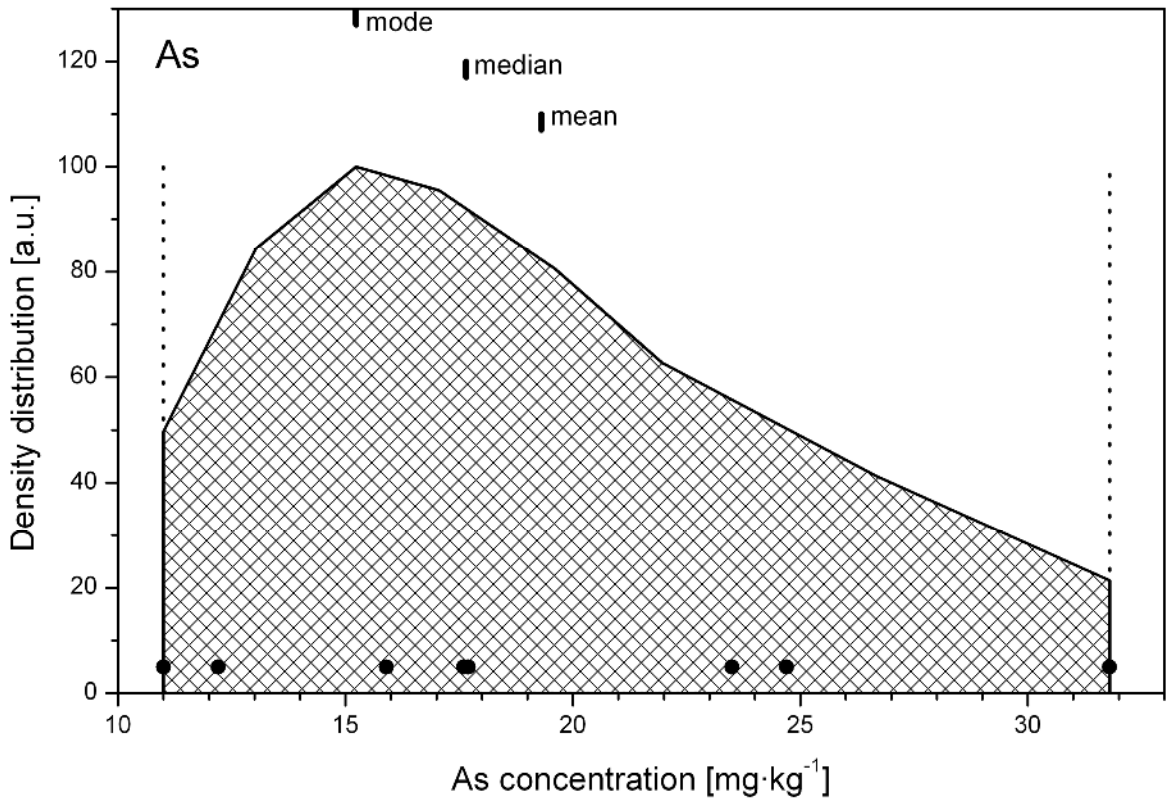
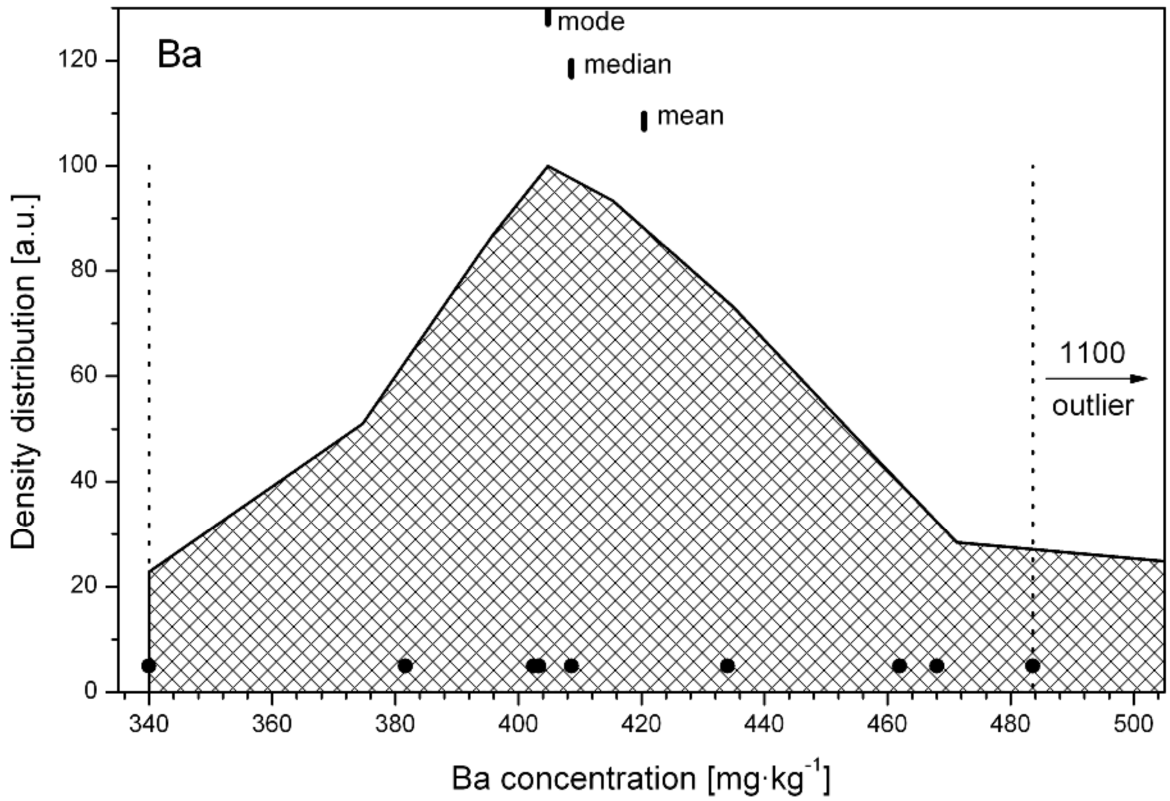



Fig. 3 continued…



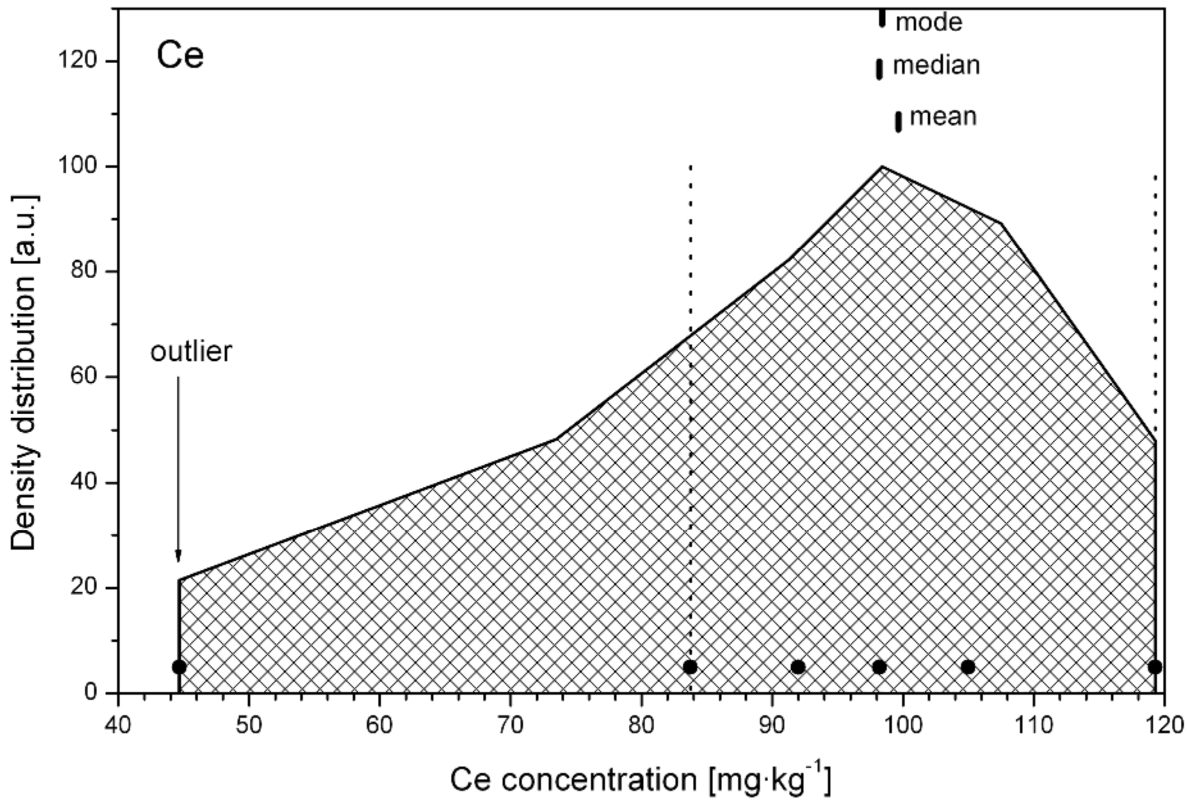
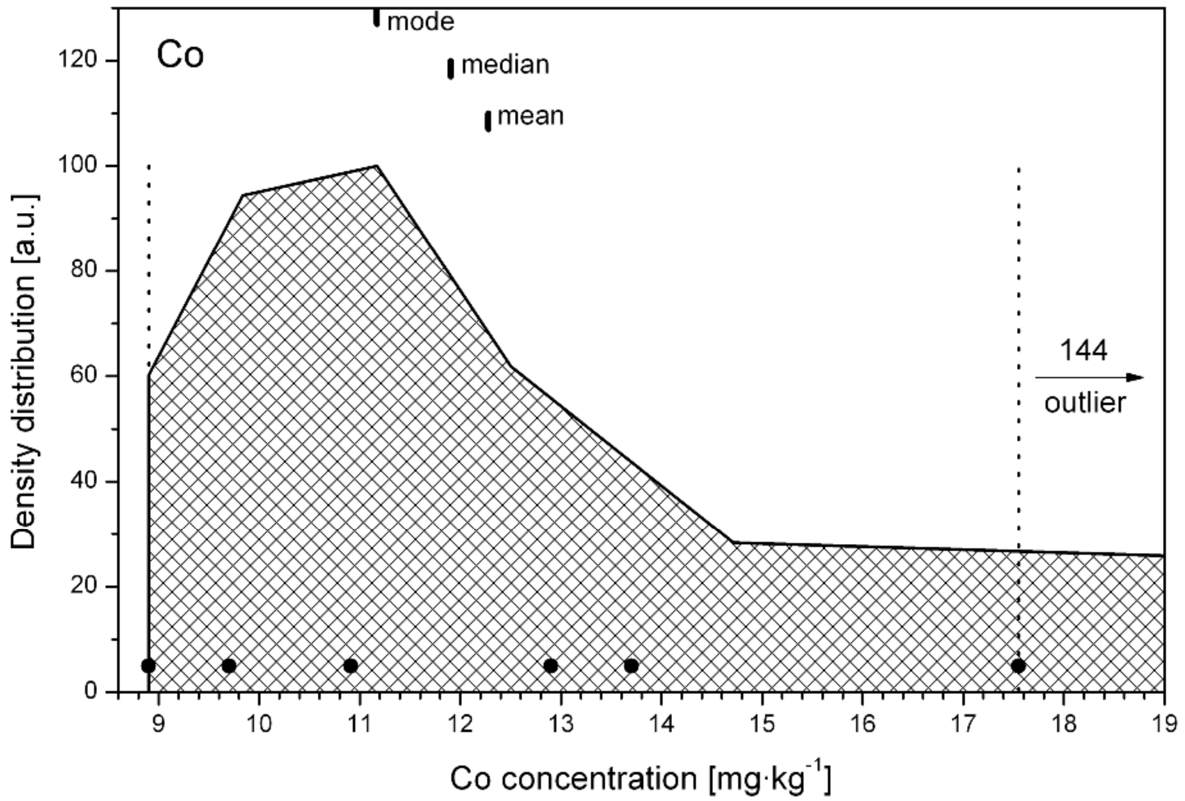



Fig. 3 continued…



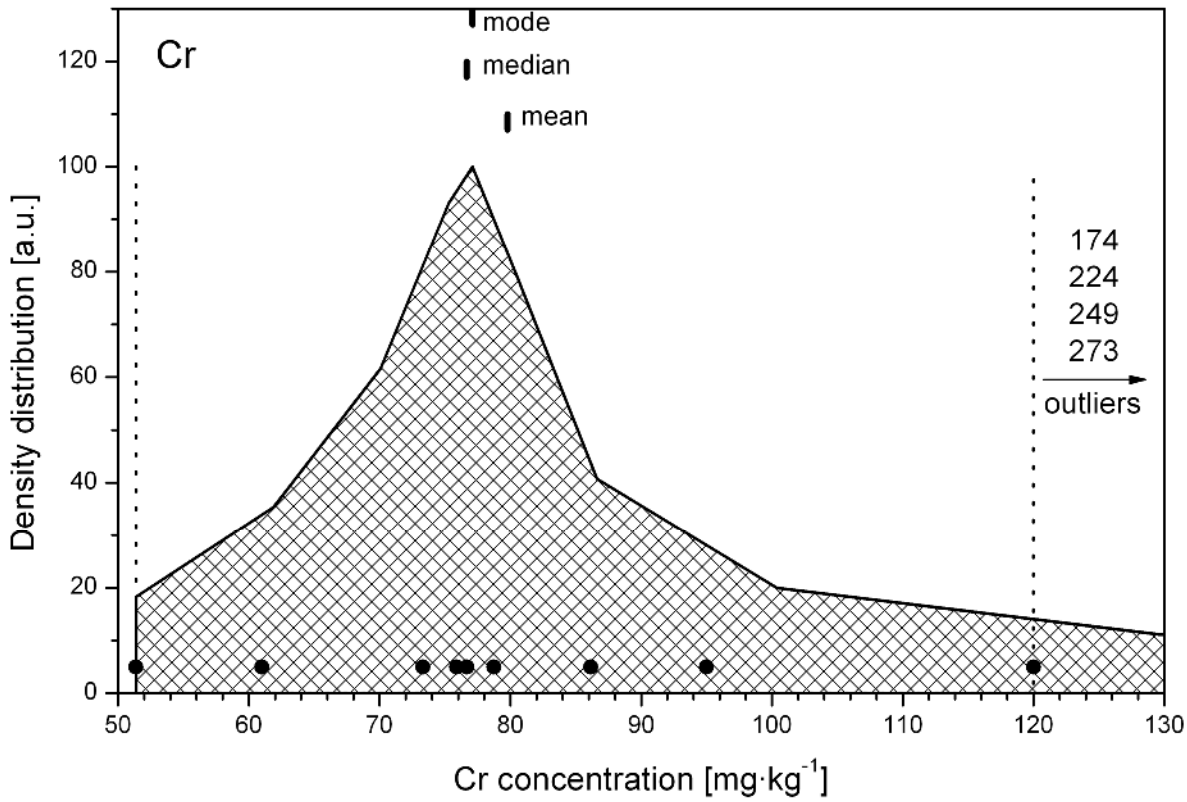
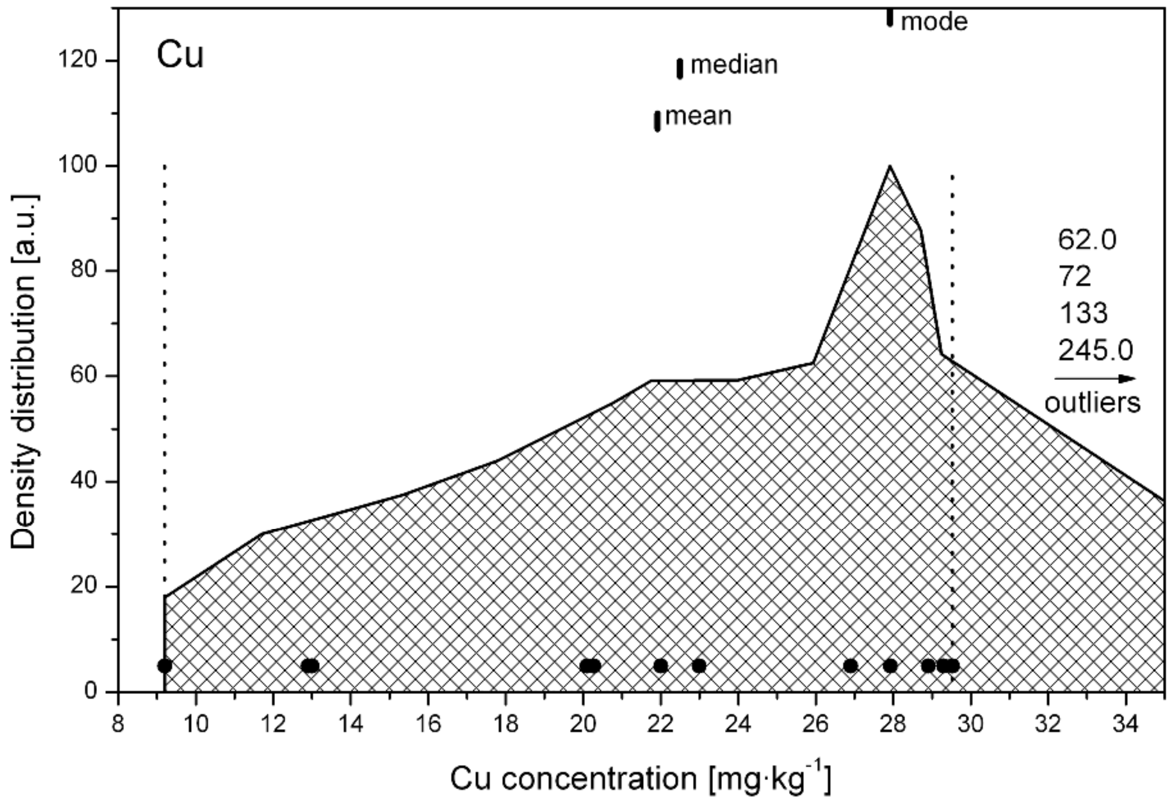



Fig. 3 continued…



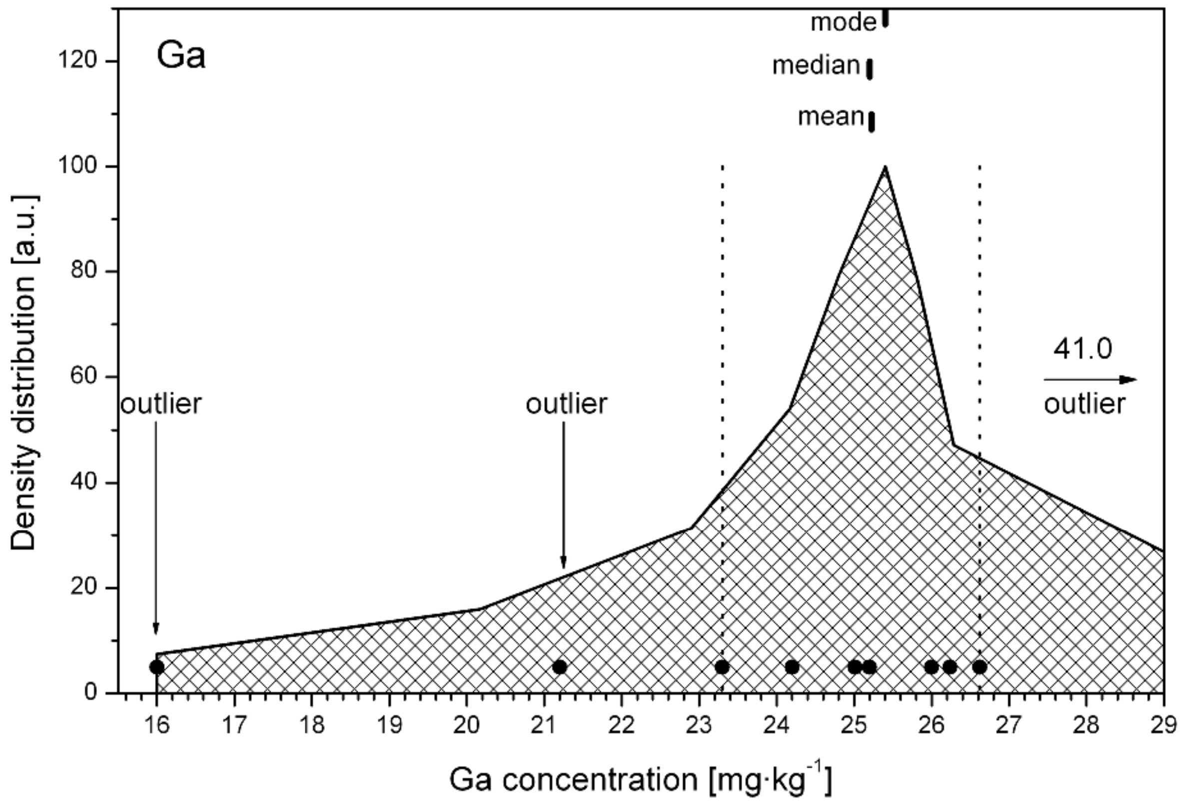
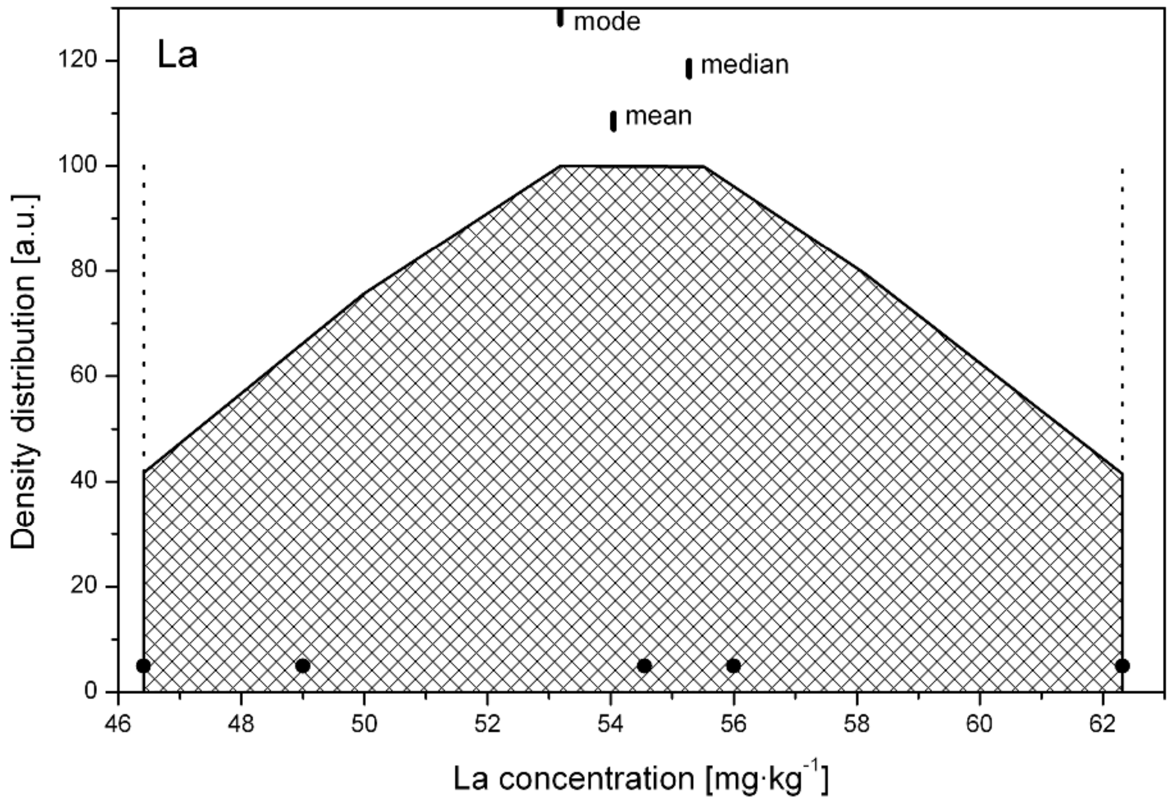
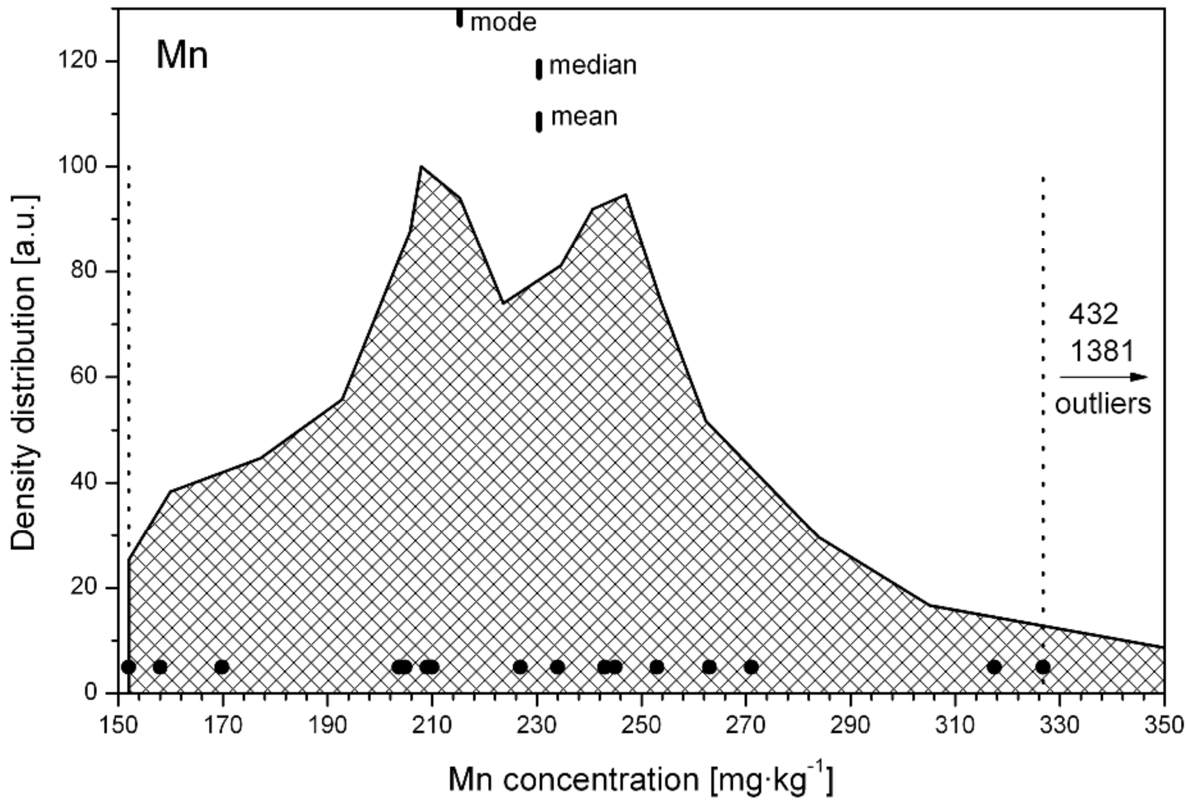



Fig. 3 continued…



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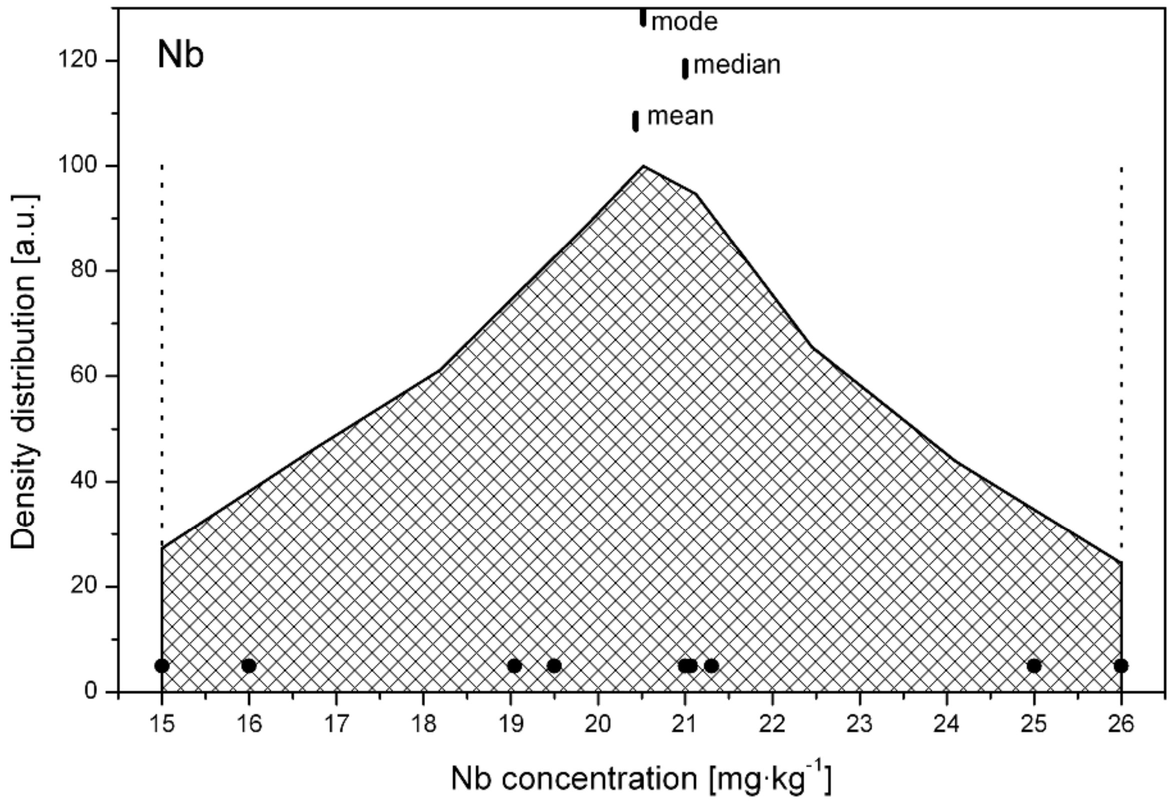


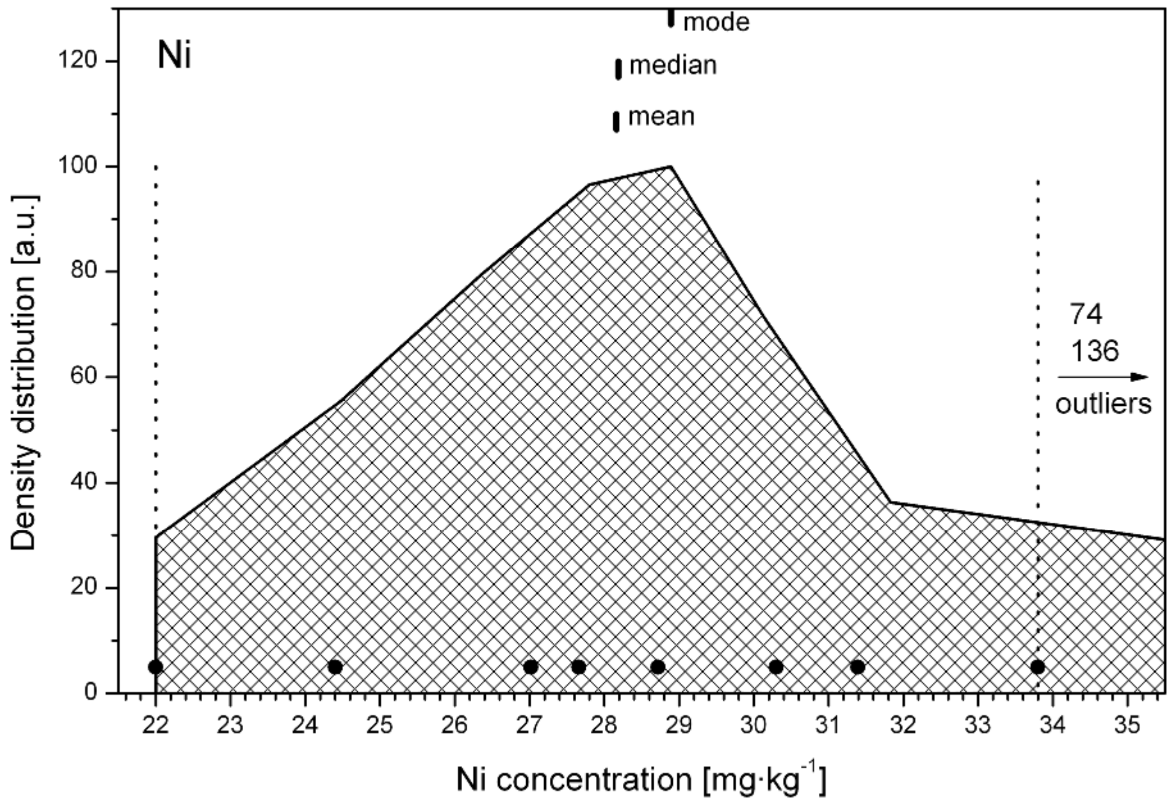

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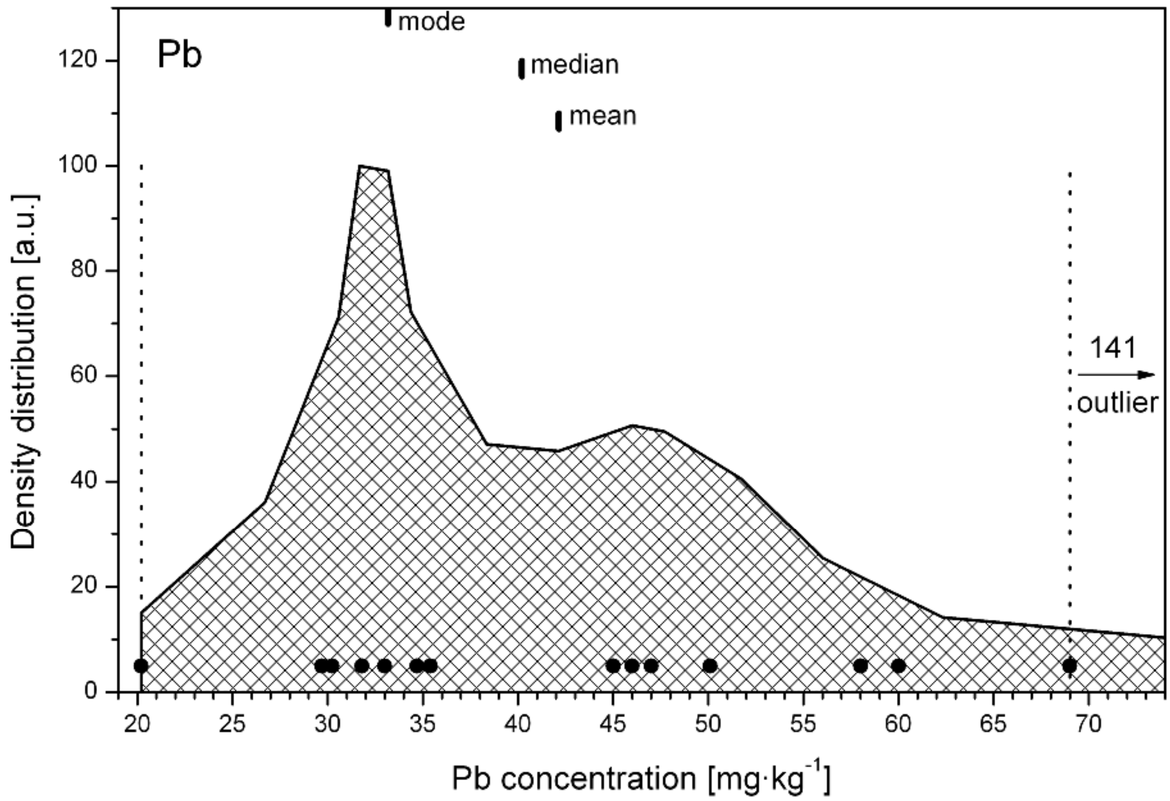


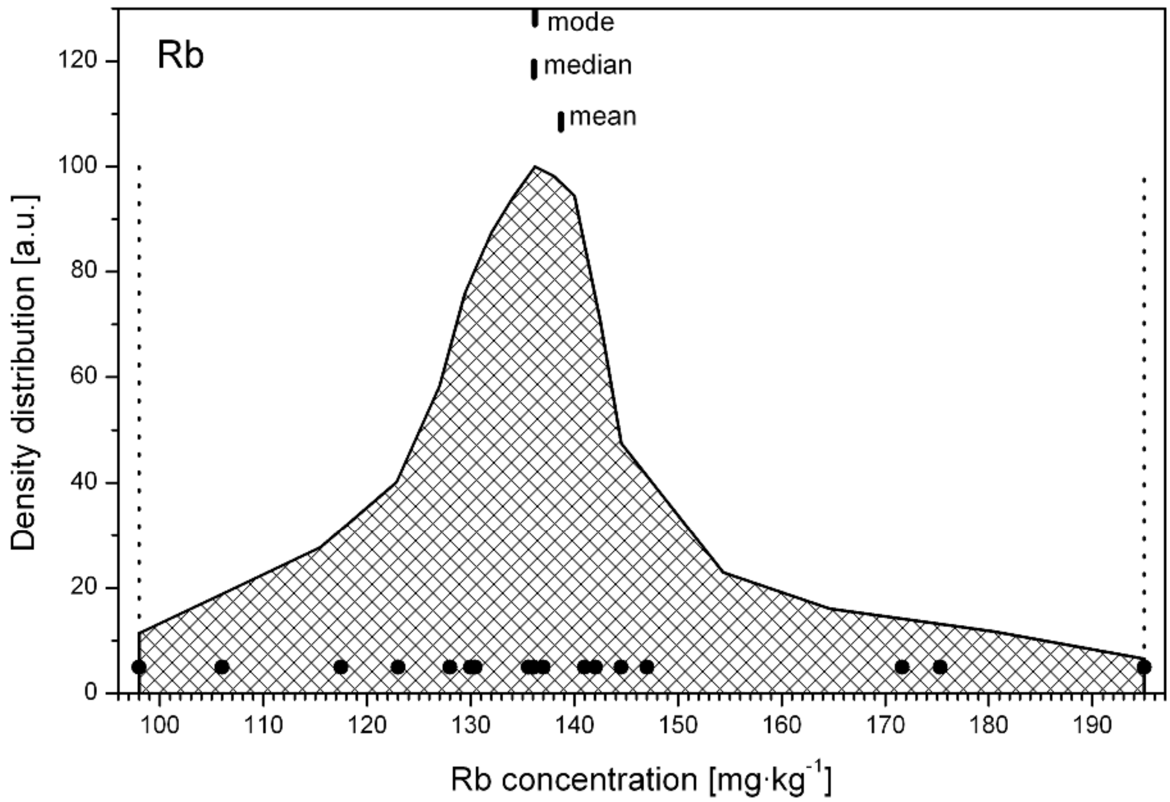

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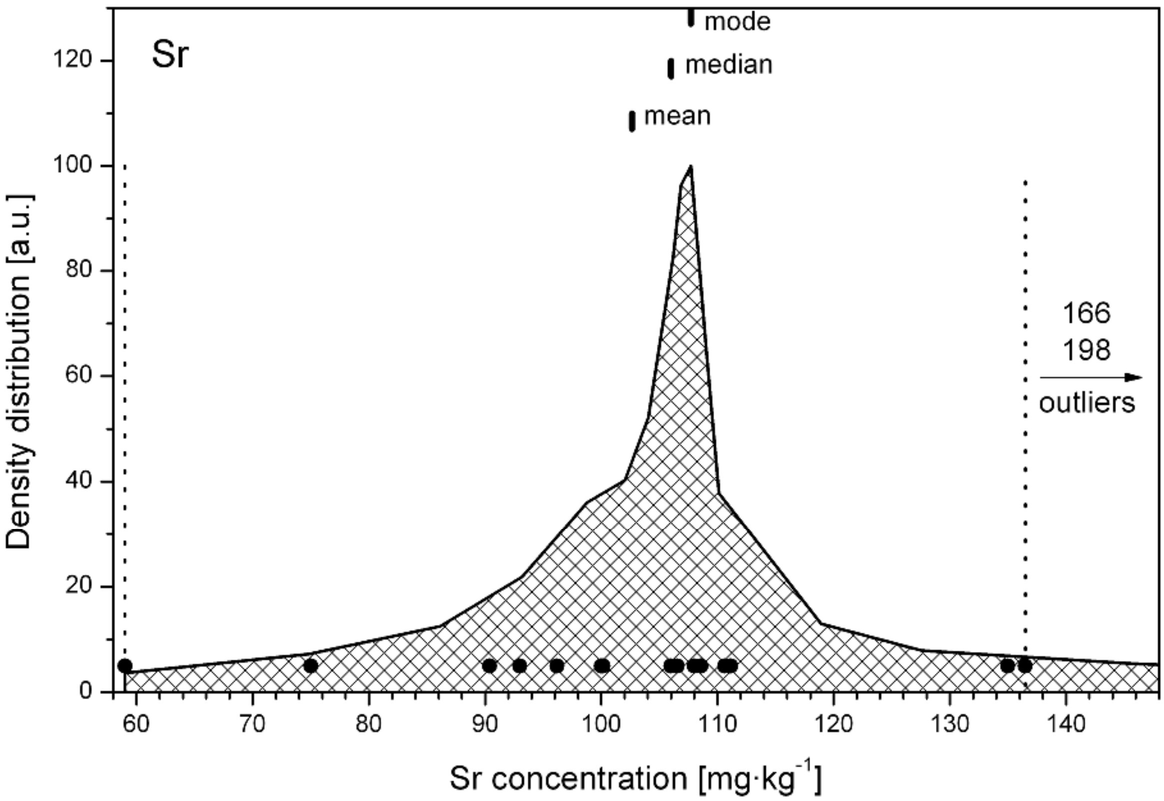


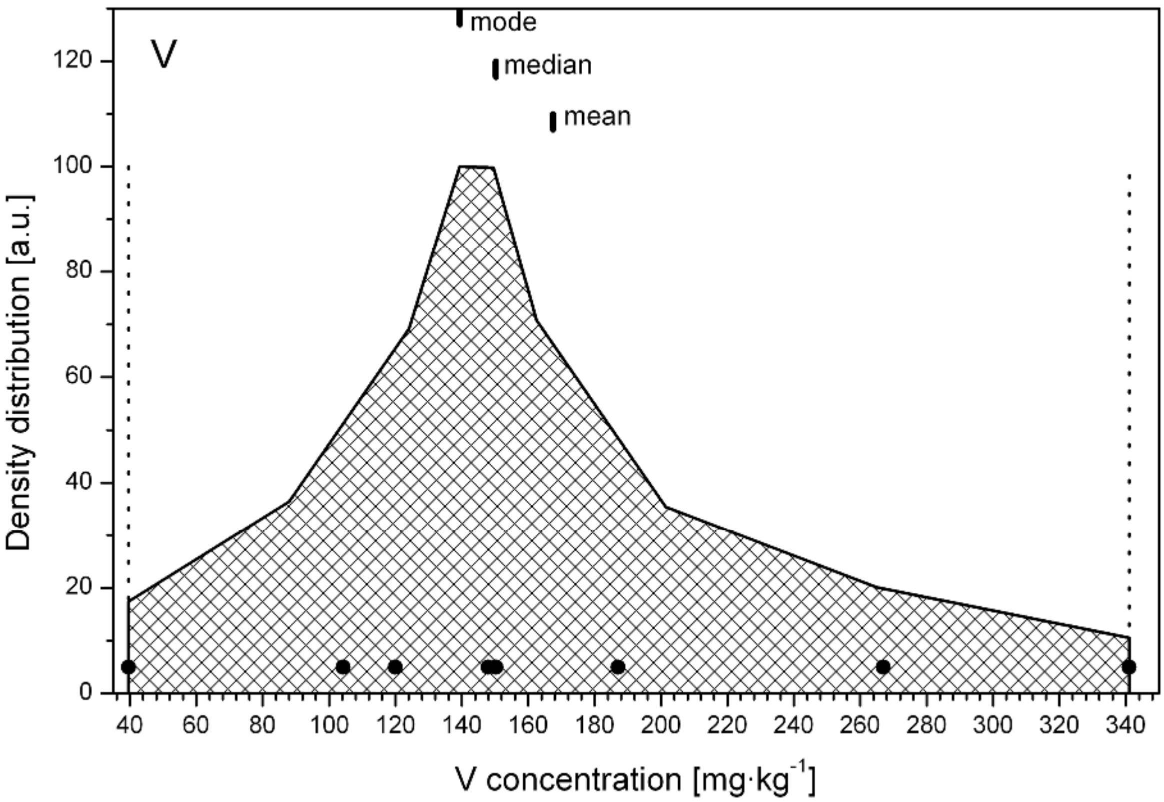

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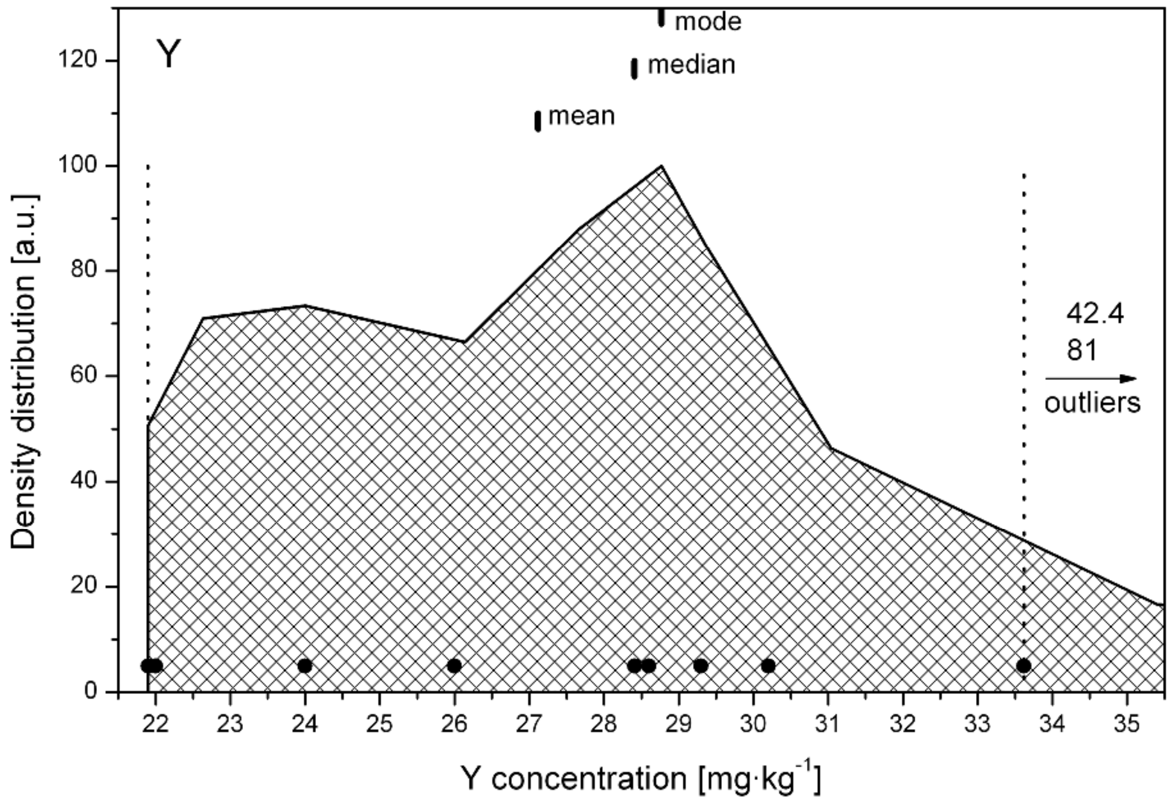


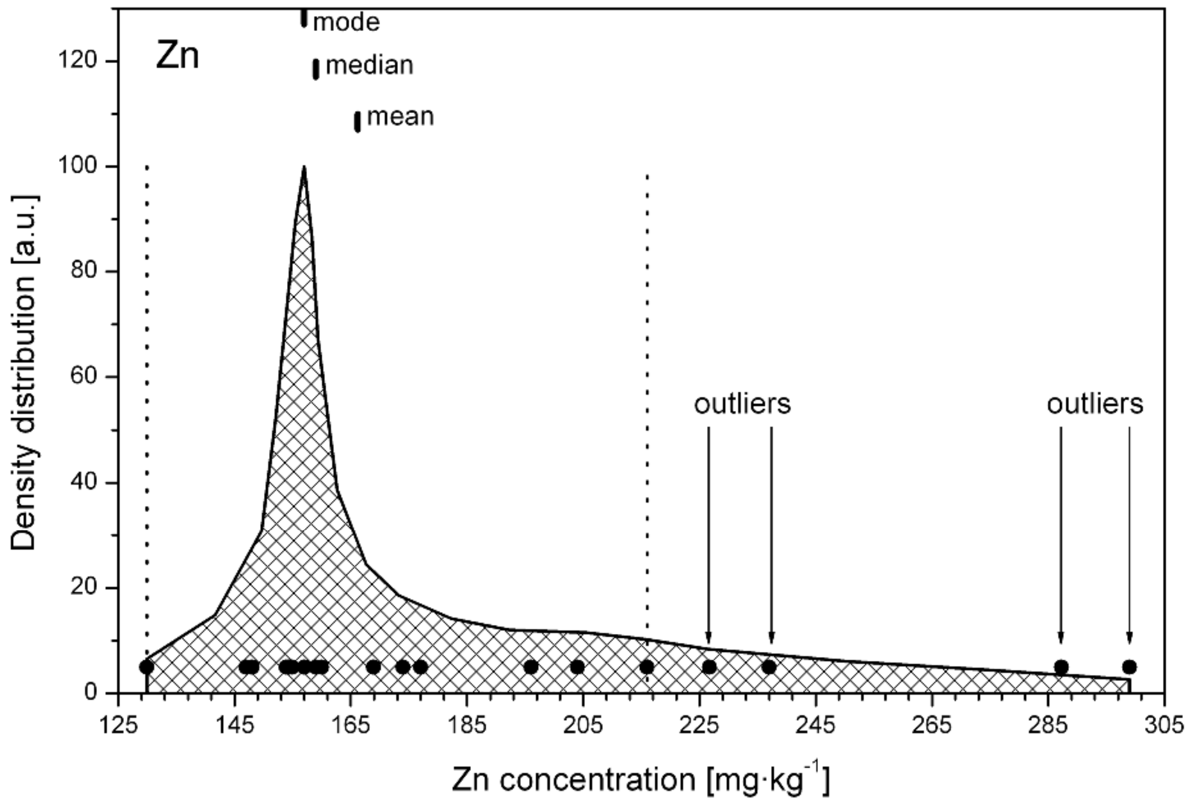

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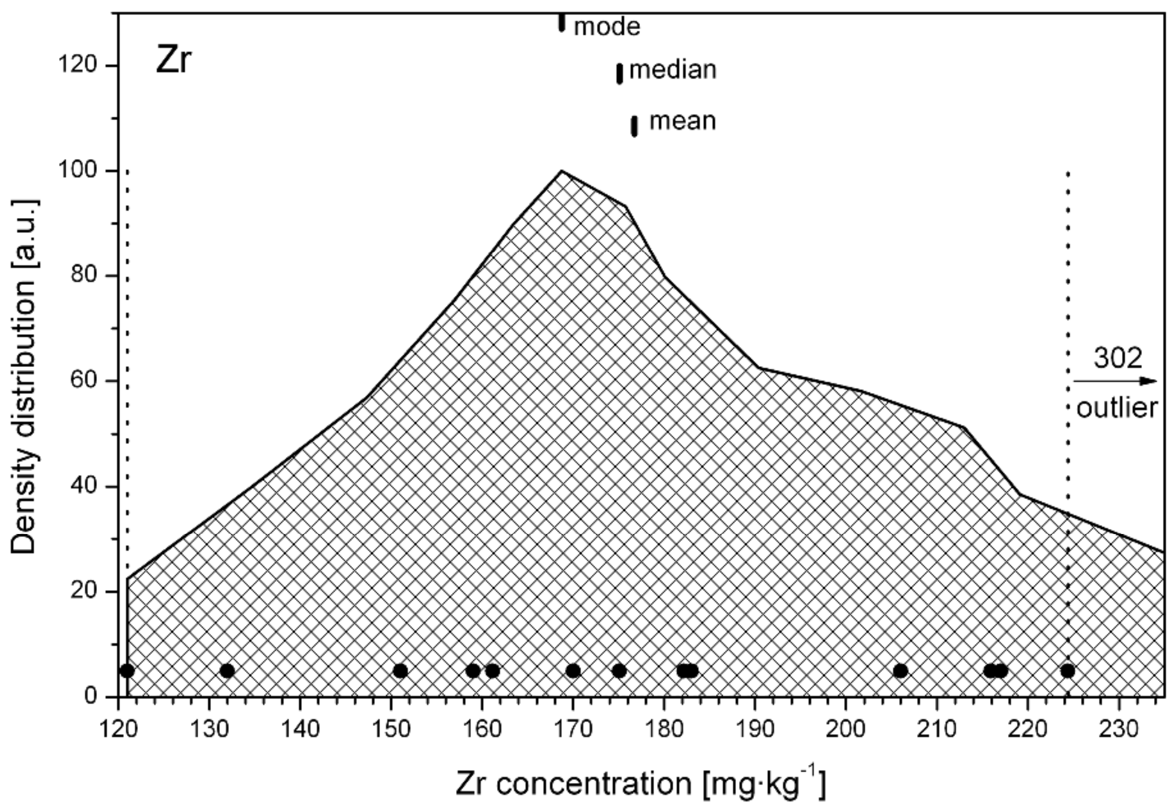


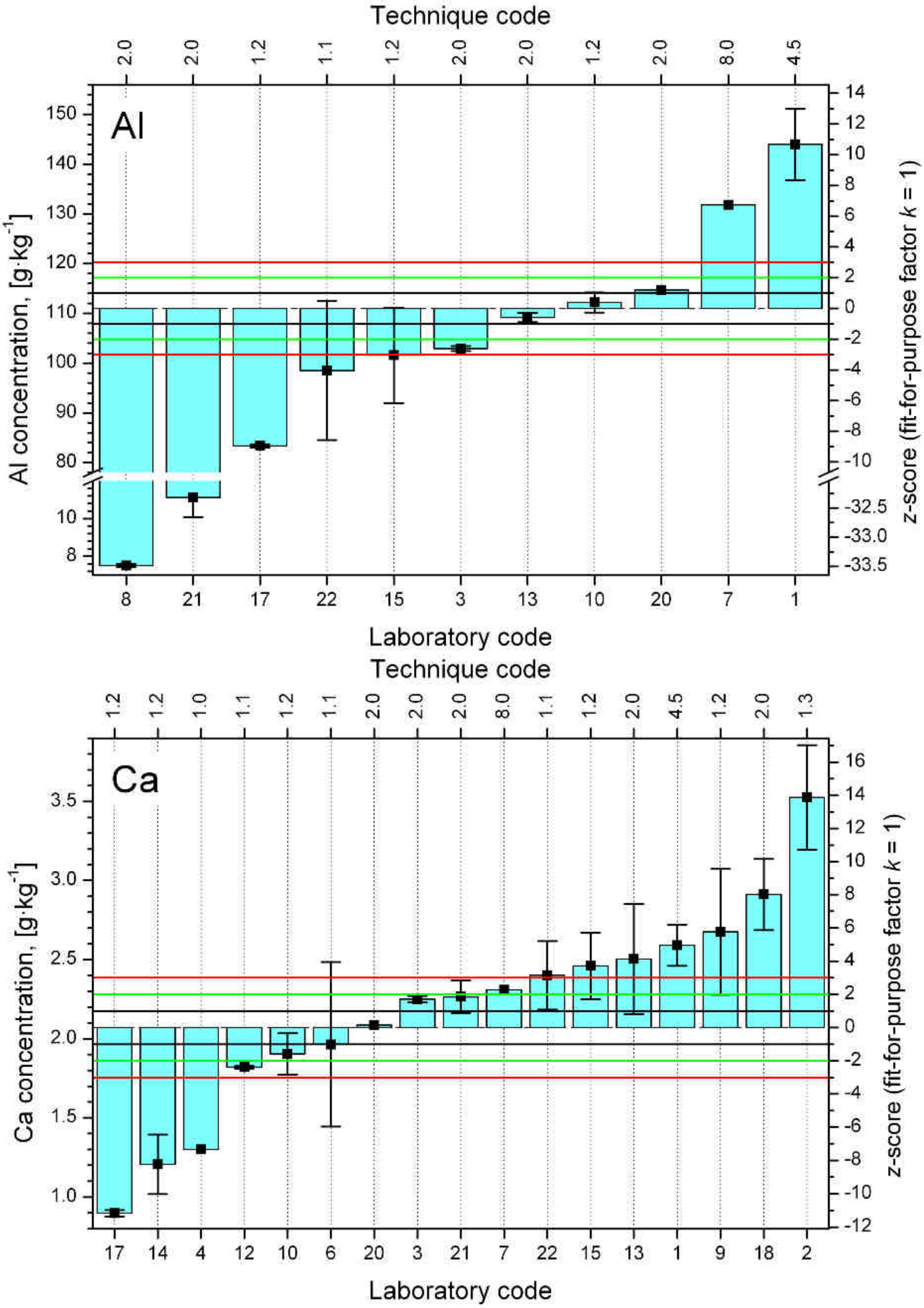
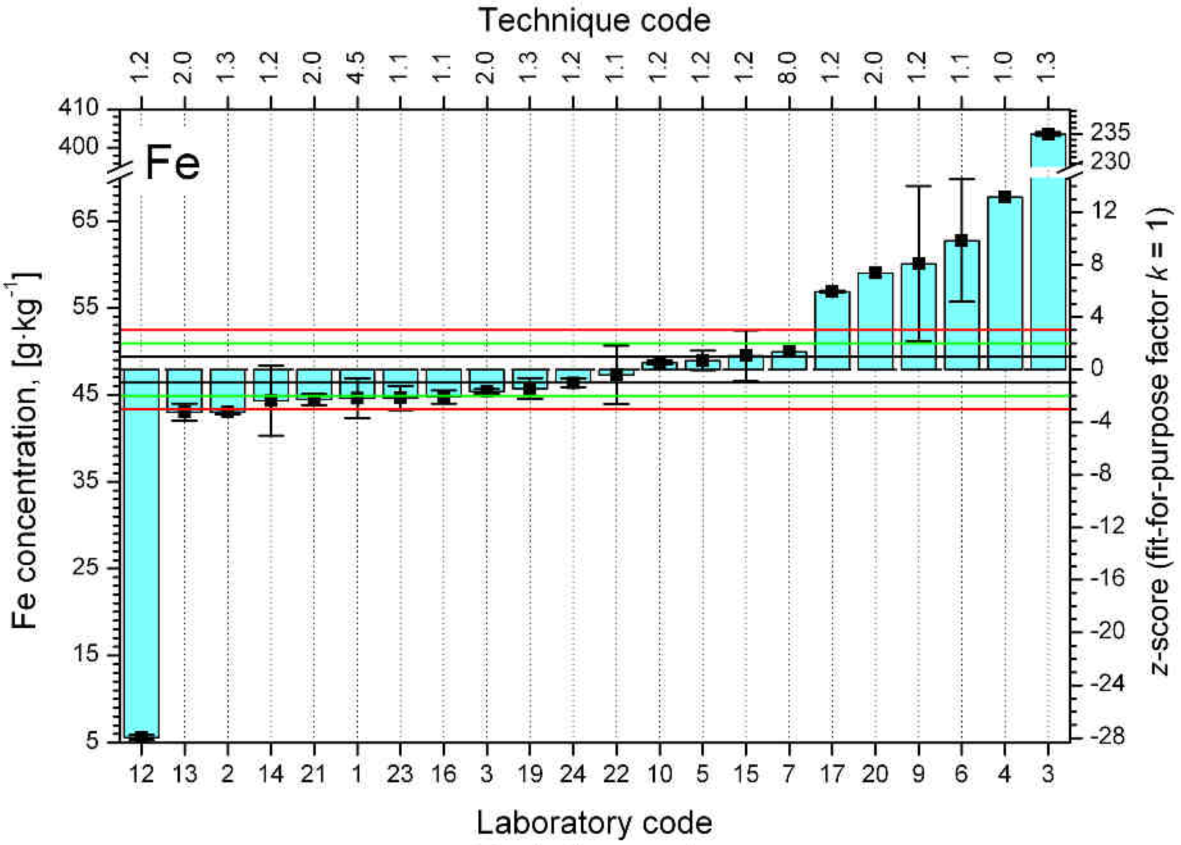



Fig. 4. Distributions of the *z*-scores for analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned values of the analyte. The submitted results and their uncertainties, as provided by the analysts, are marked with filled squares accompanied by uncertainty bars. The horizontal lines show the admissible levels of *z*-score, $|z| < 2$, for three different fit-for-purpose ranges defined by factor *k* in Eqn. (2): ***k* = 0.5 - solid black lines**, ***k* = 1.0 - solid green lines**, and ***k* = 1.5 - solid red lines**.

Fig. 4 continued…



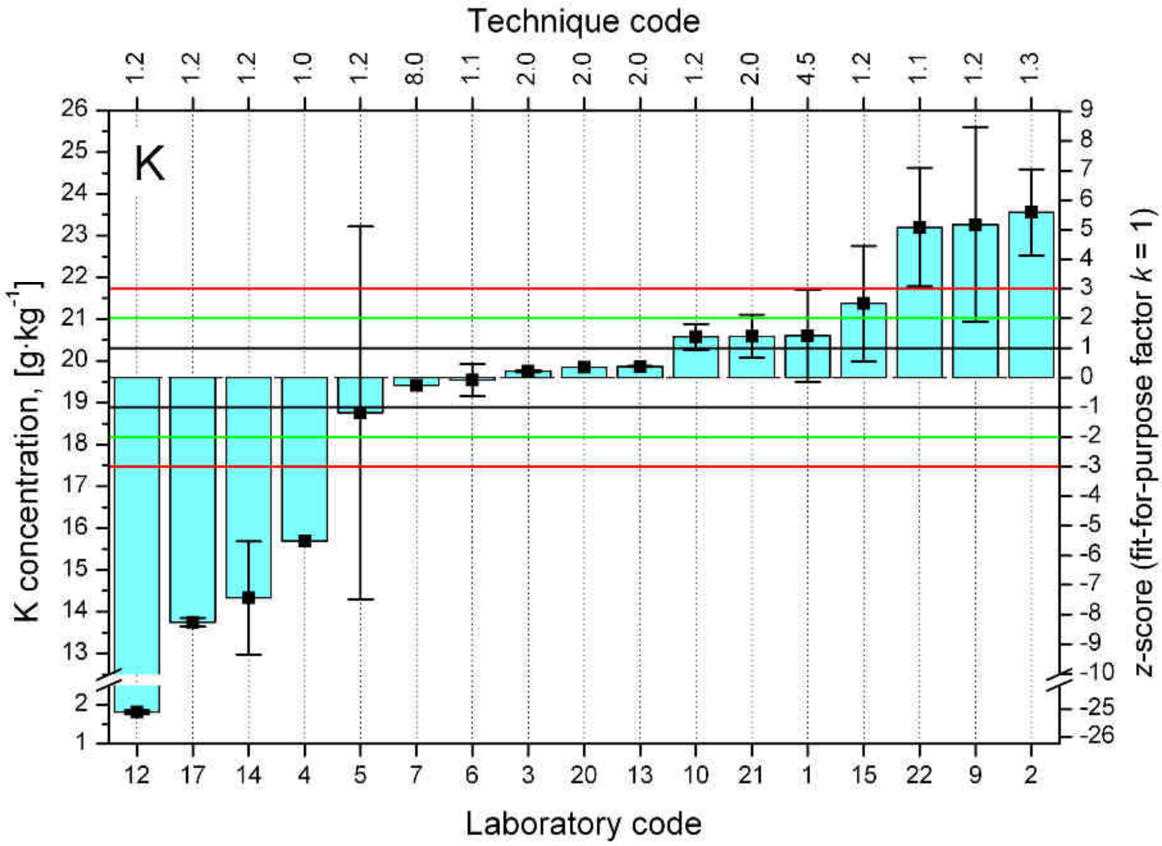
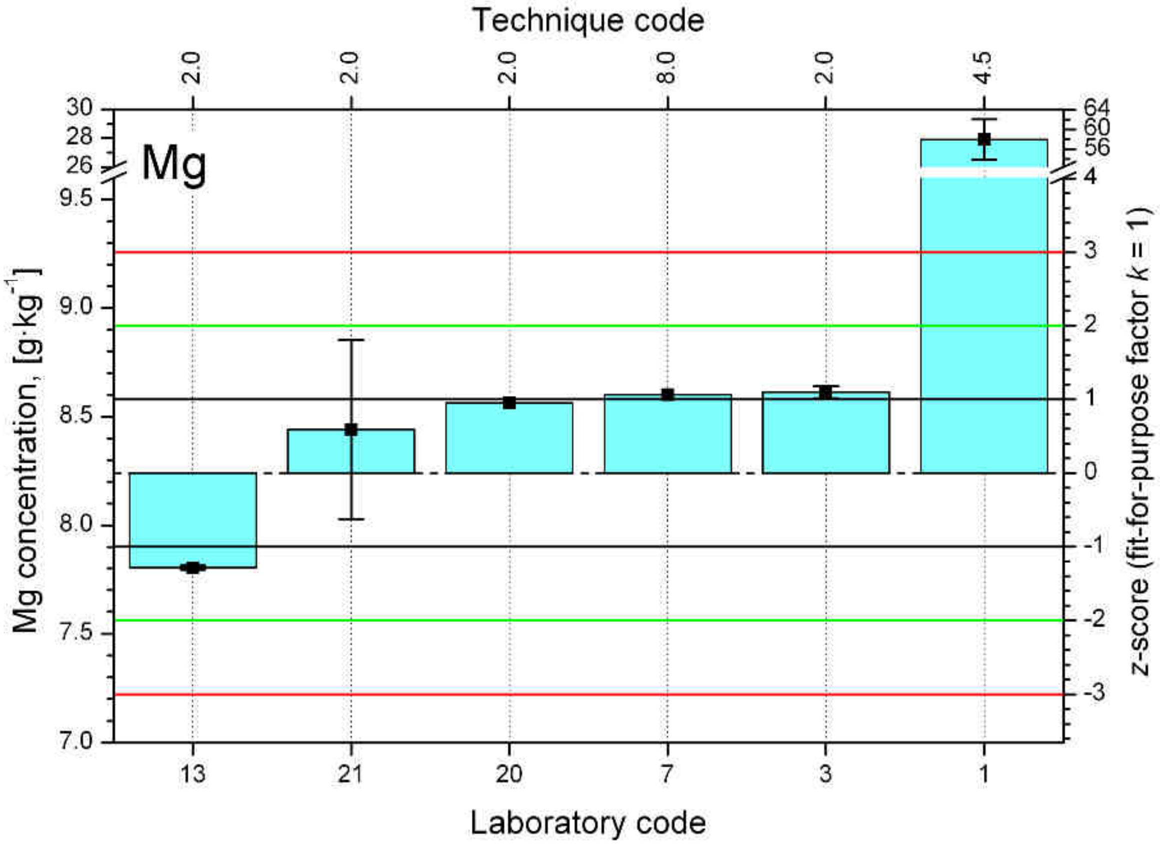
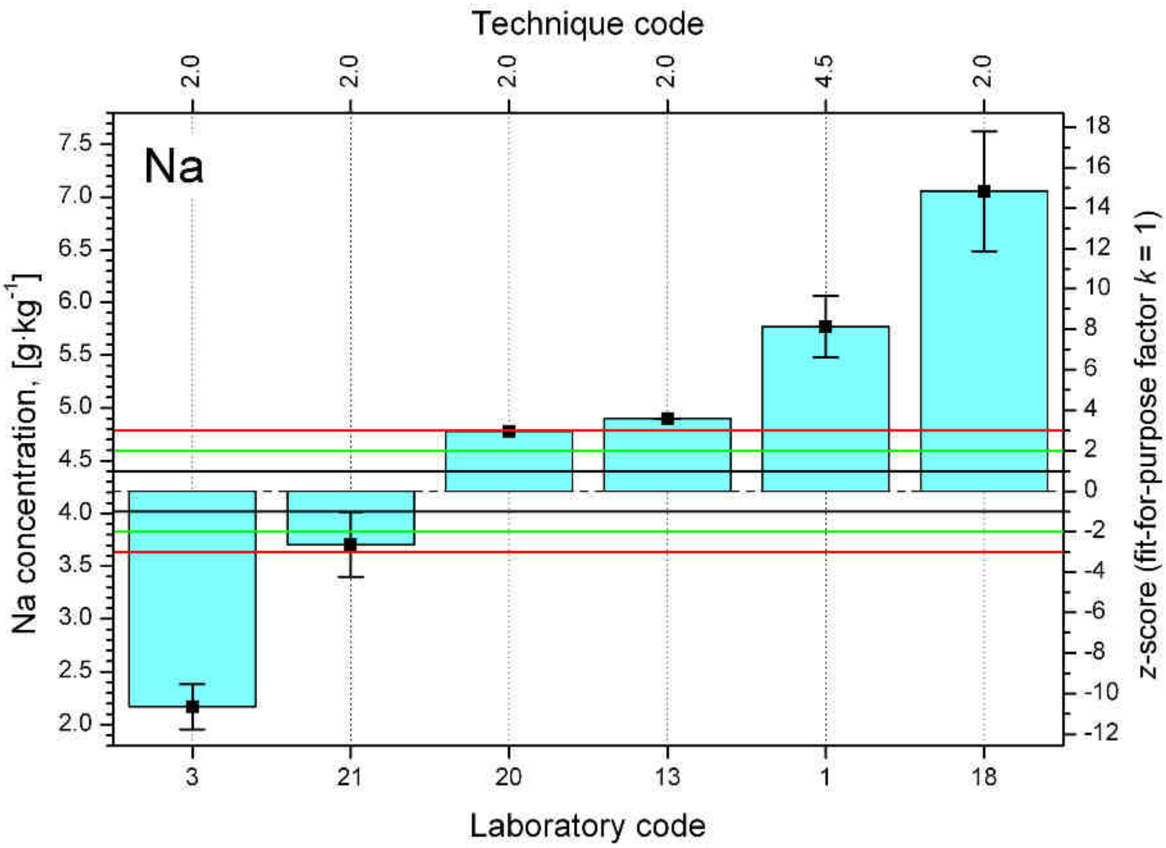



Fig. 4 continued…



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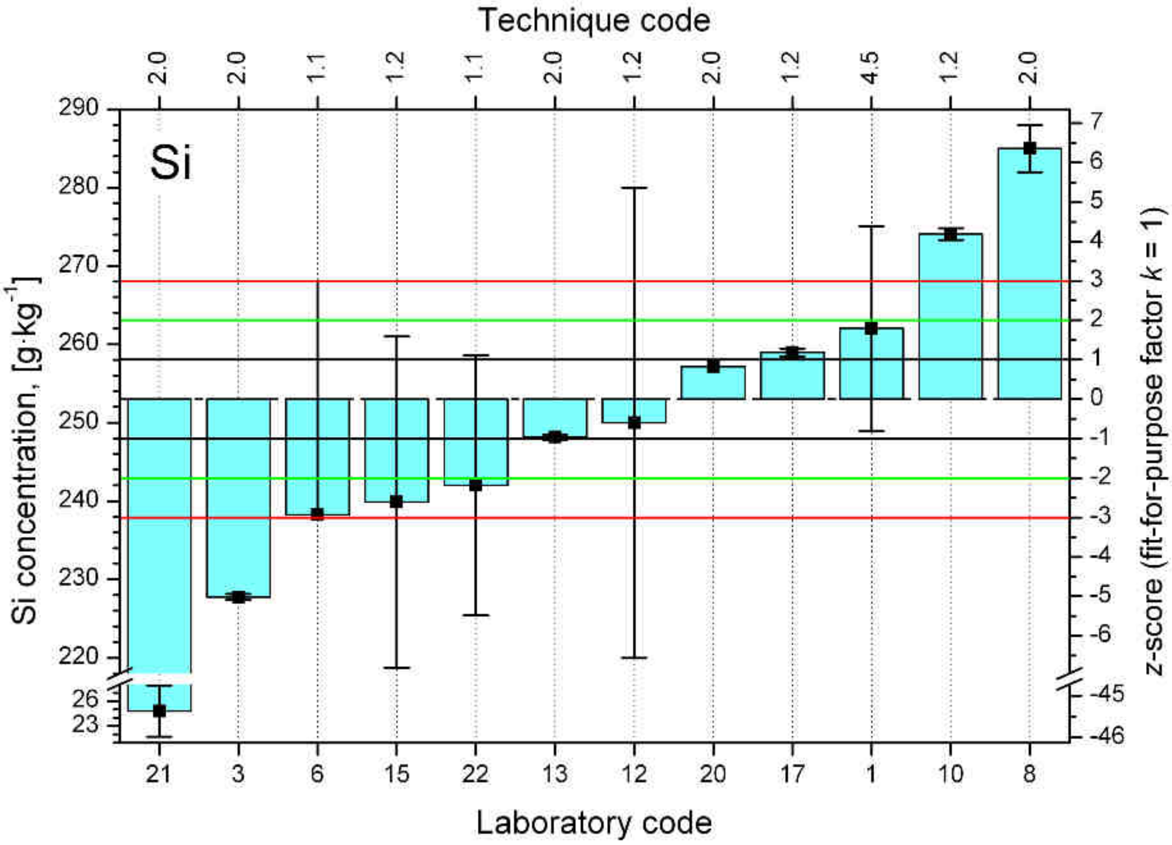


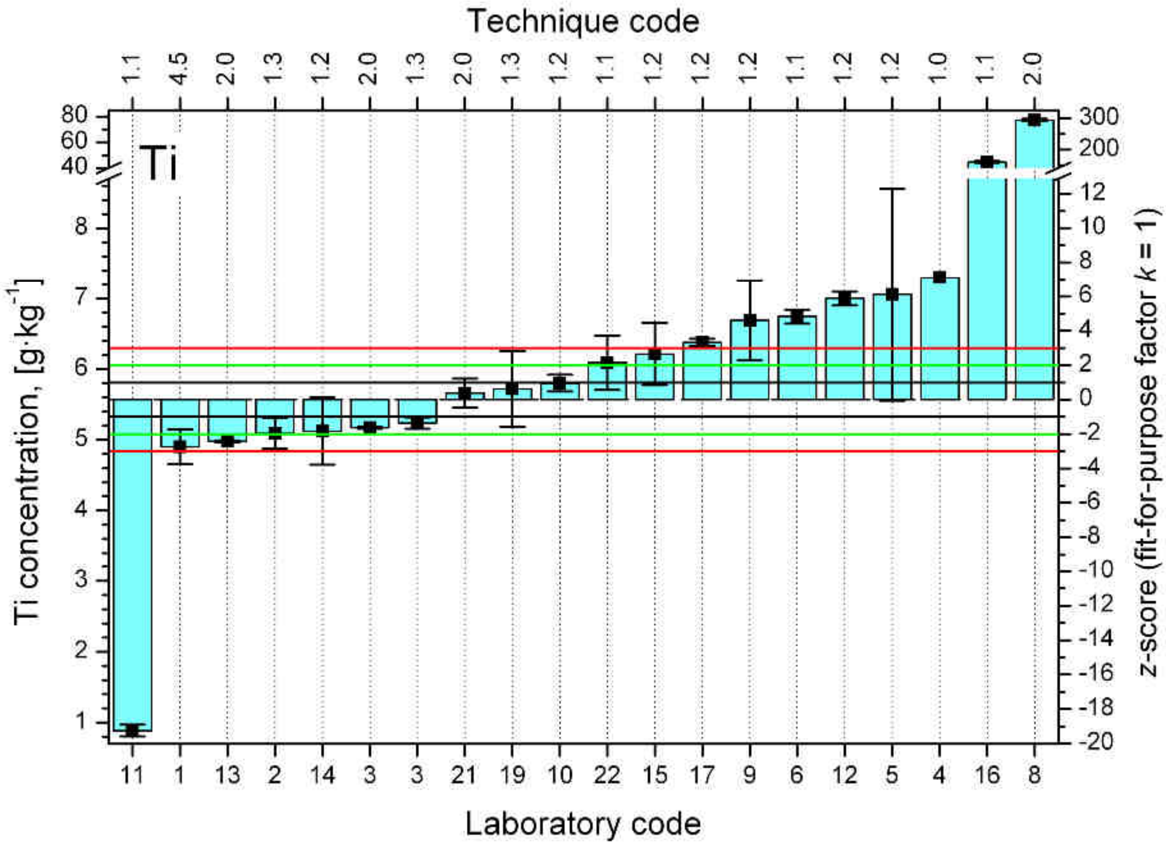

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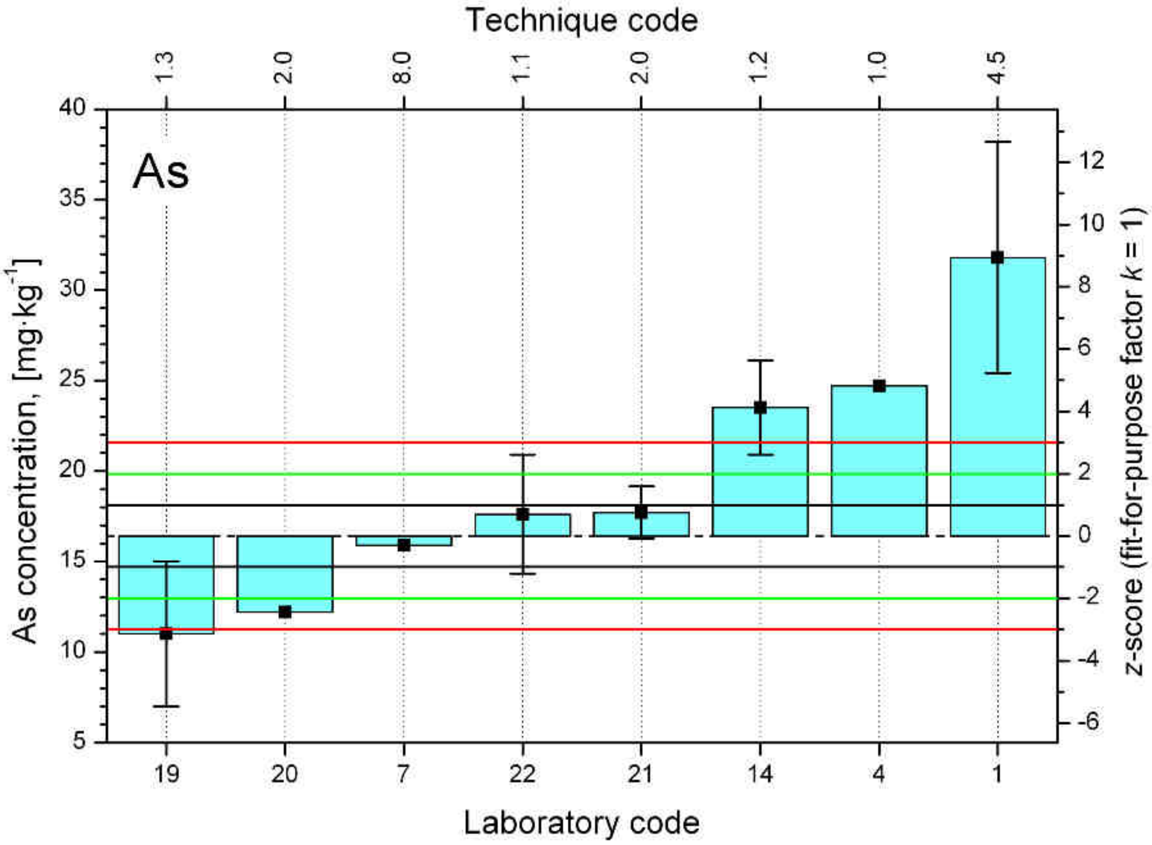


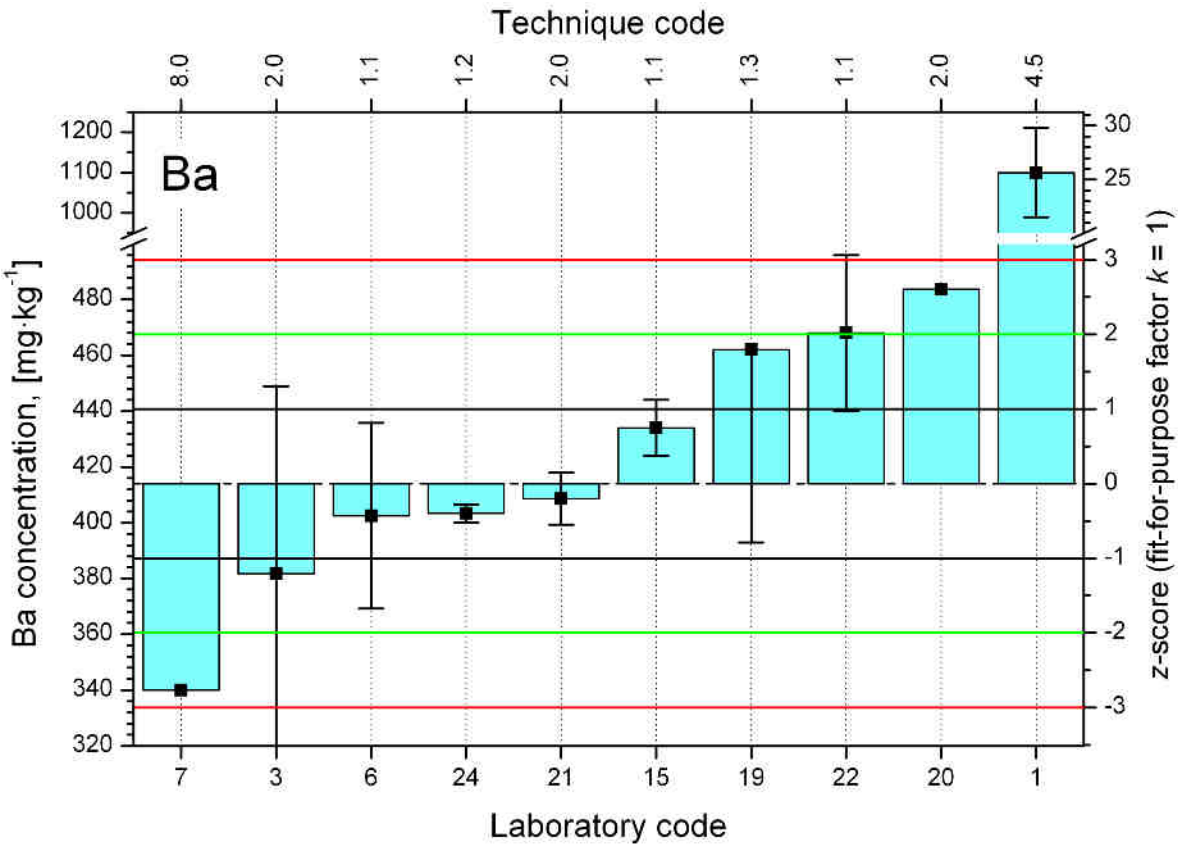

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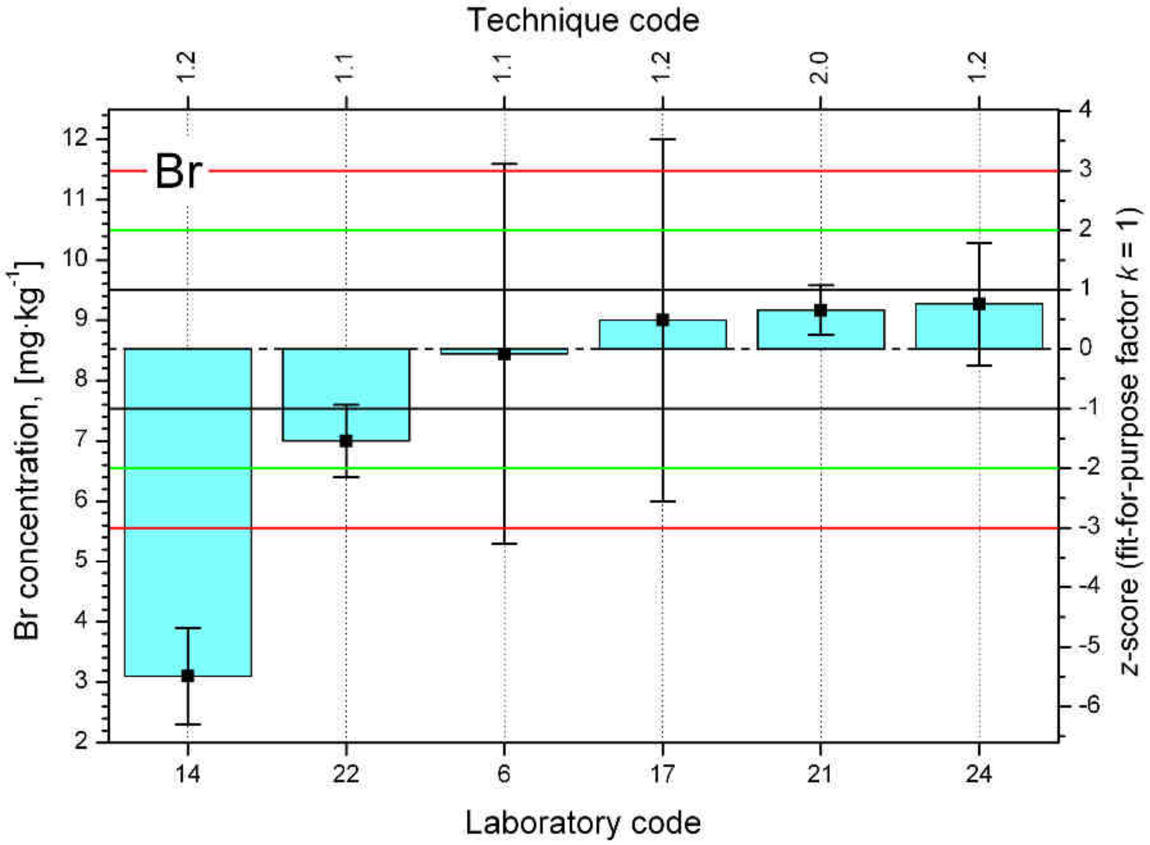


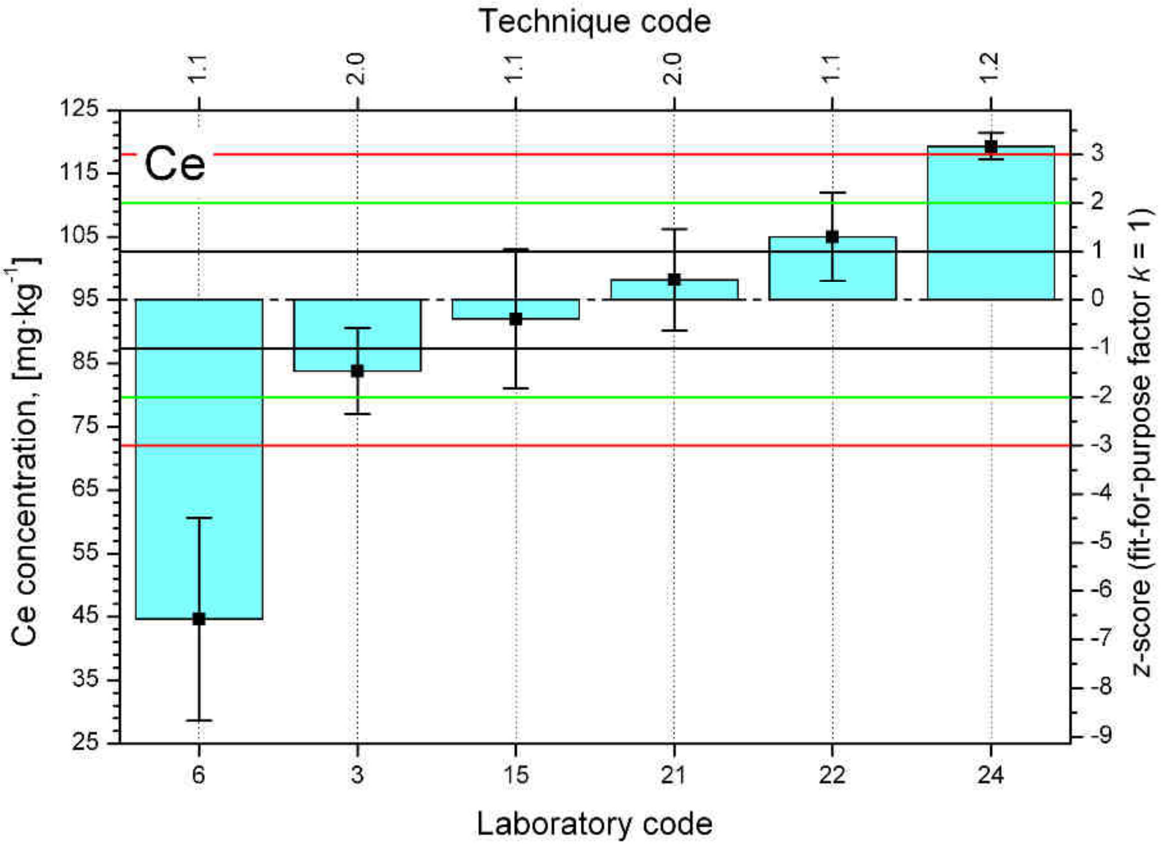

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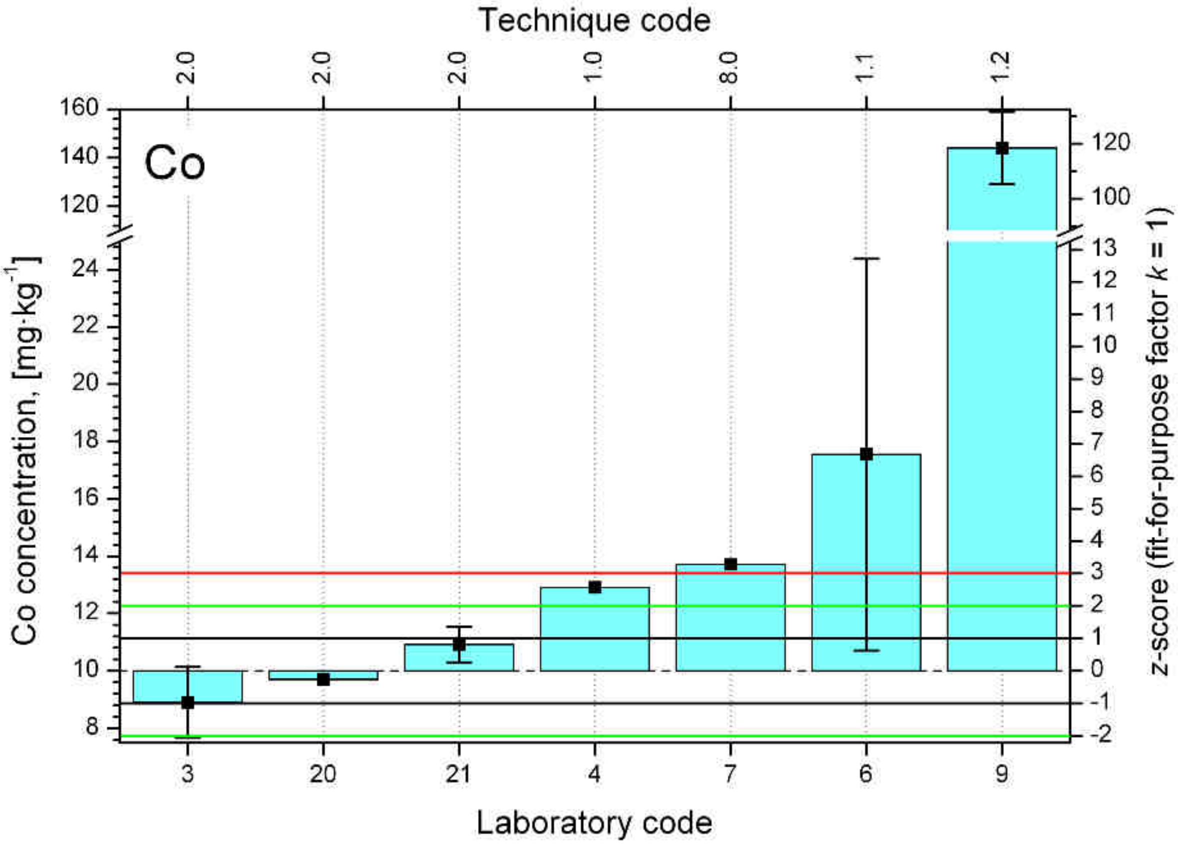


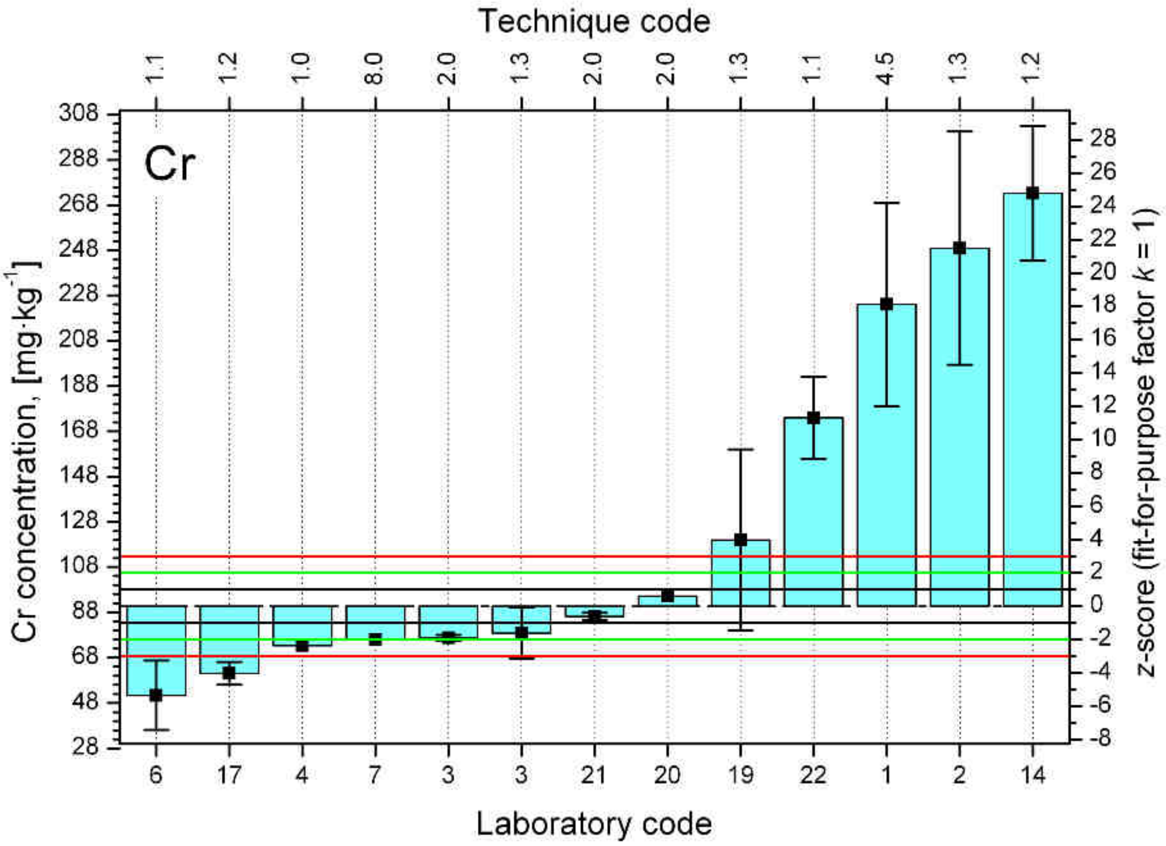

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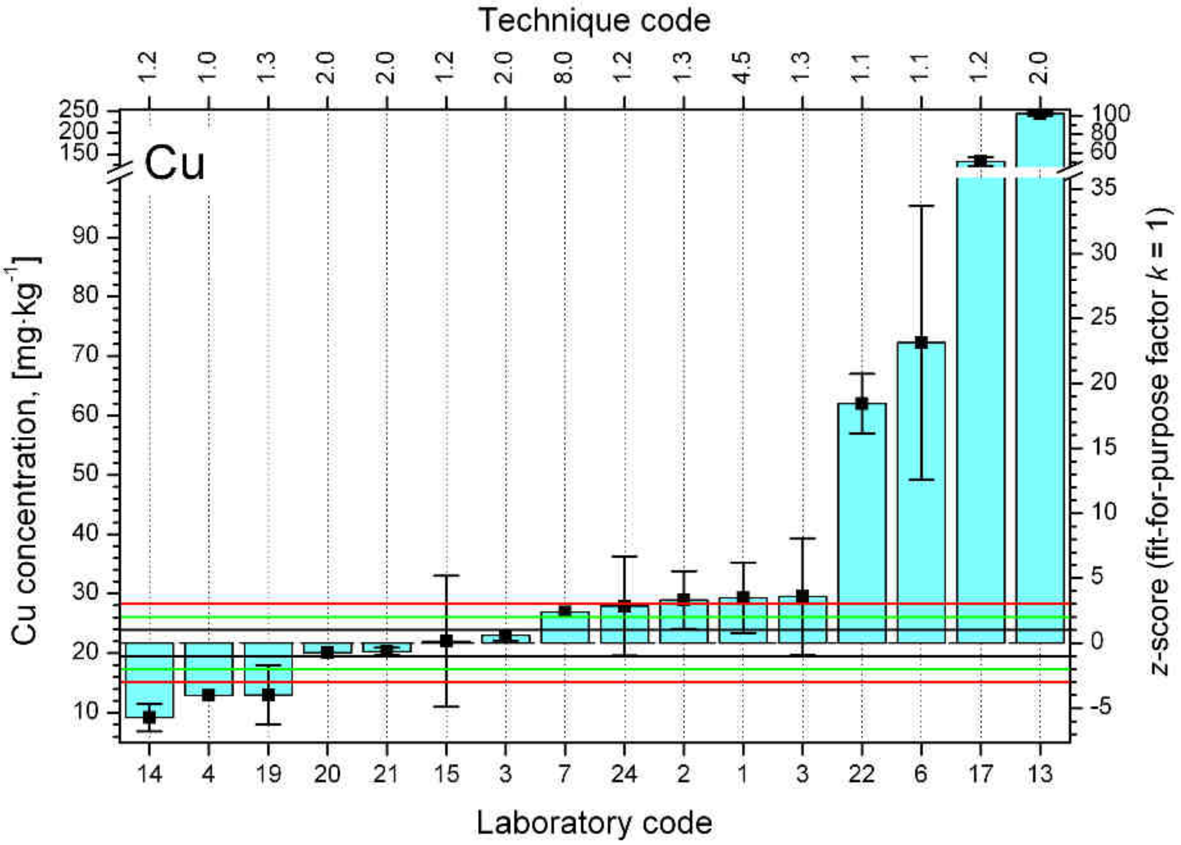


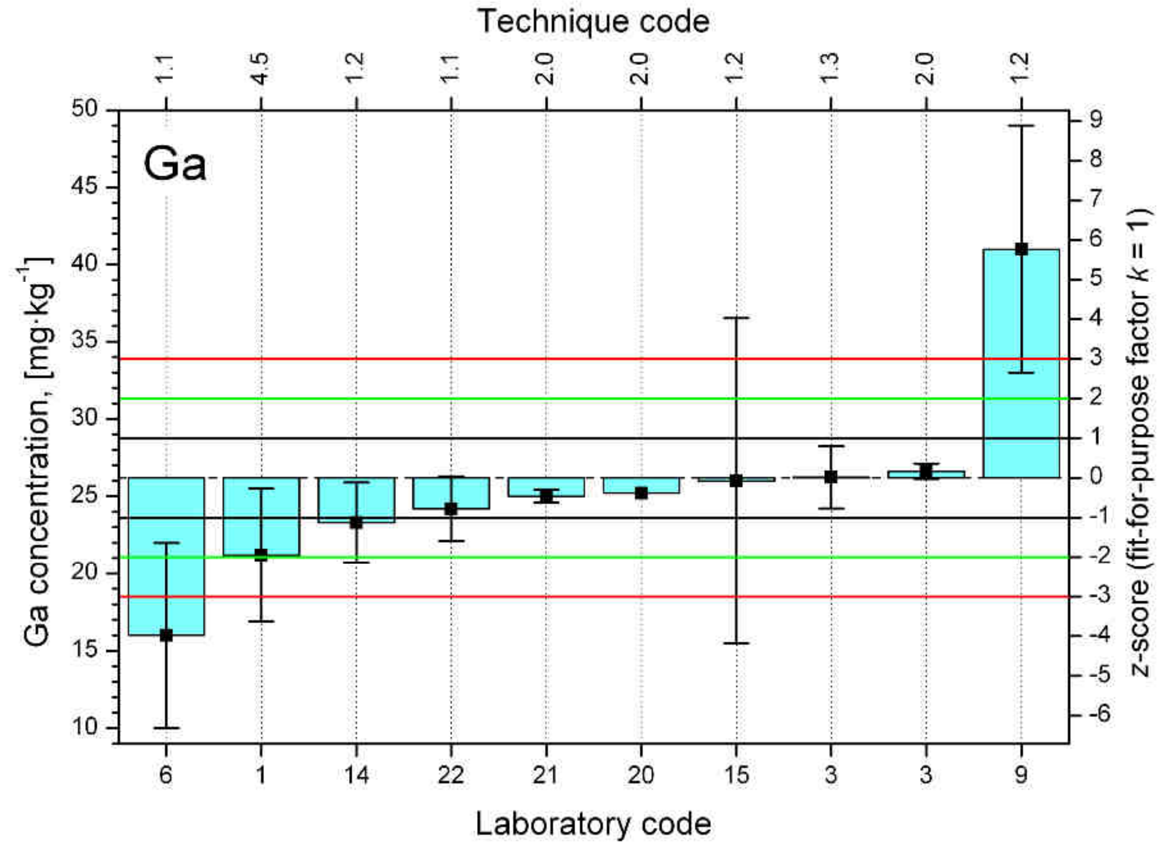

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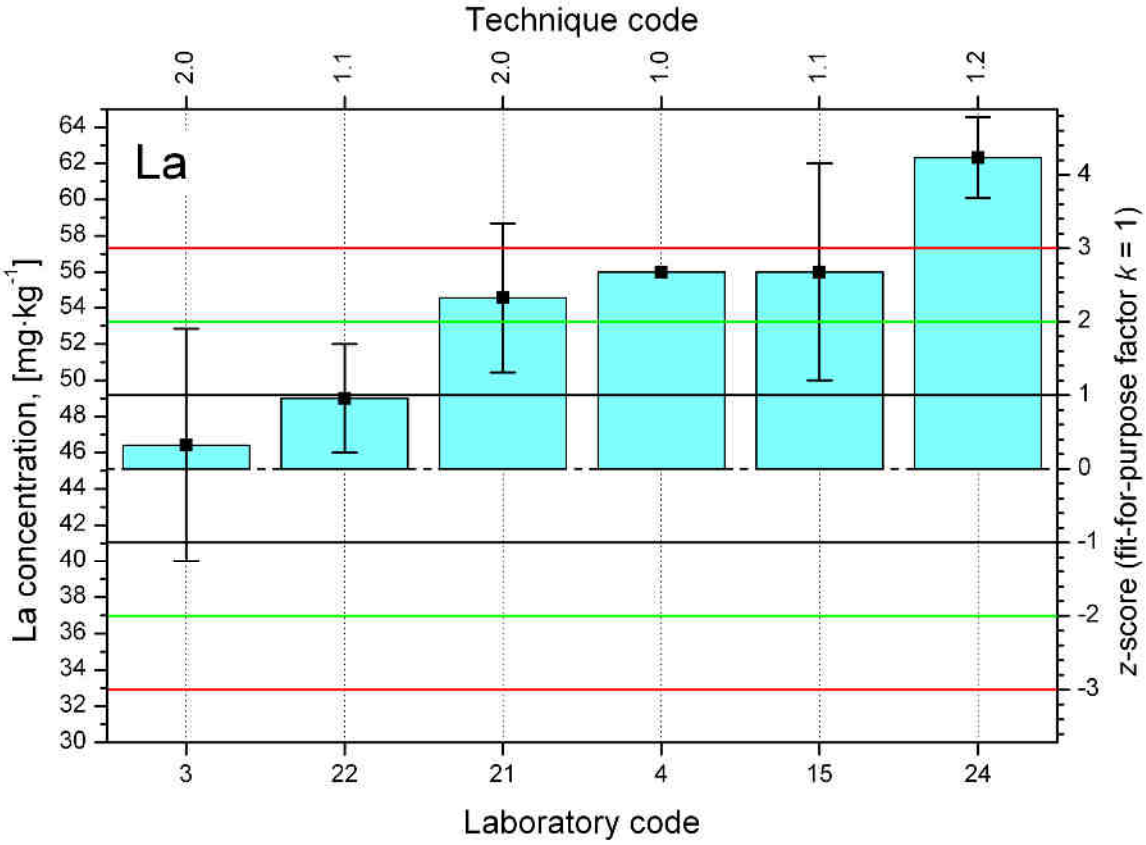


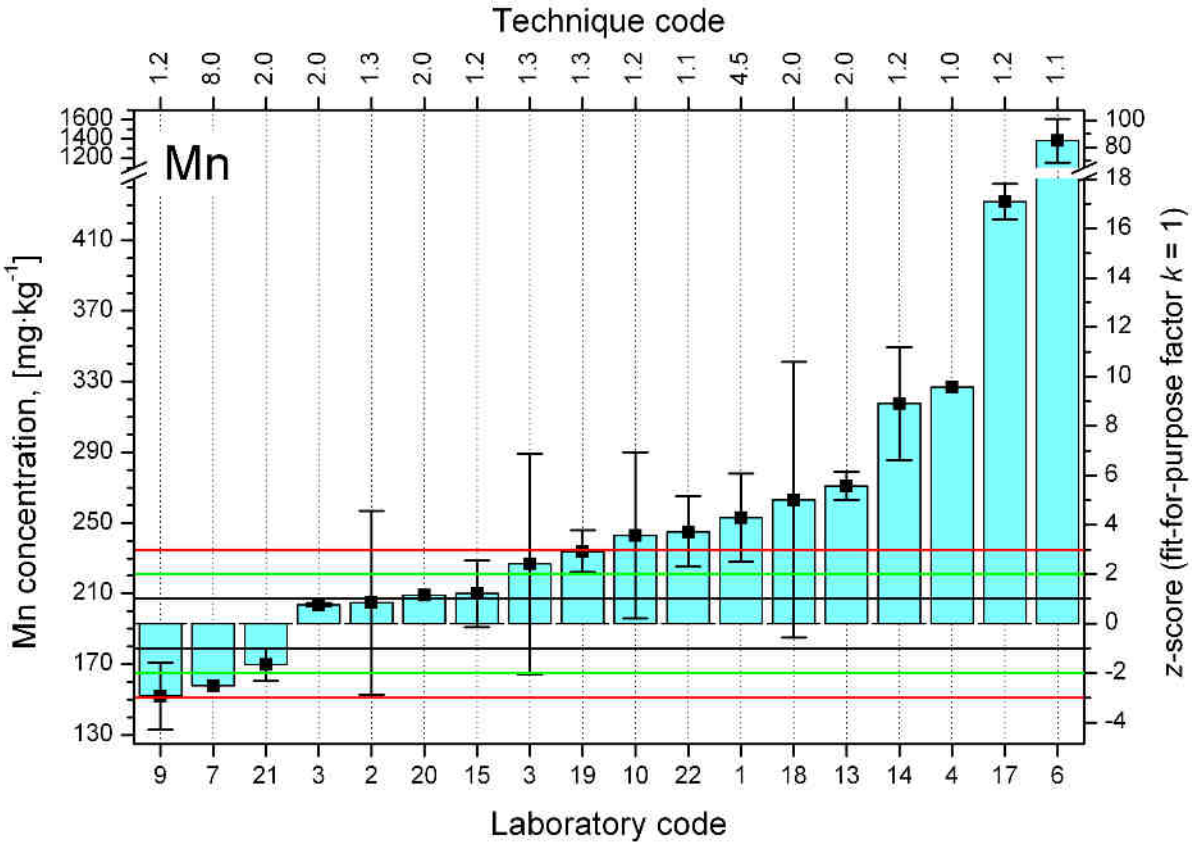

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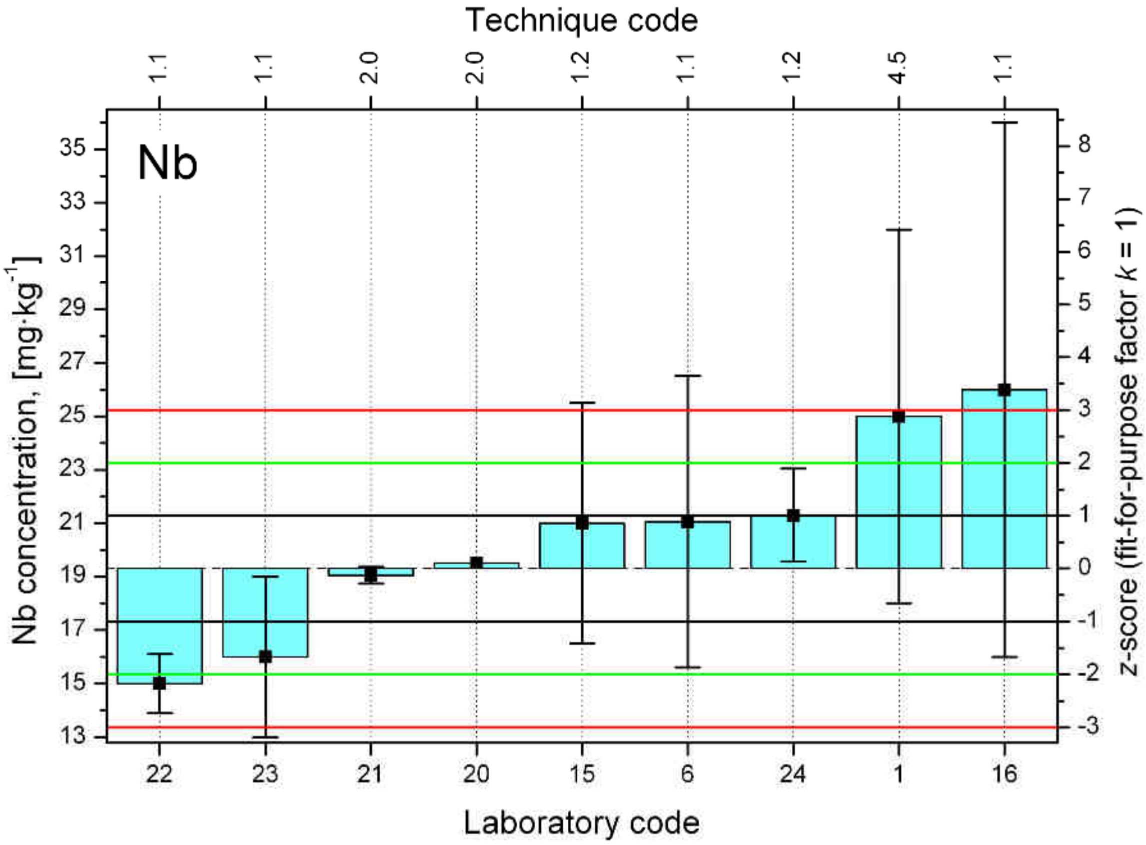


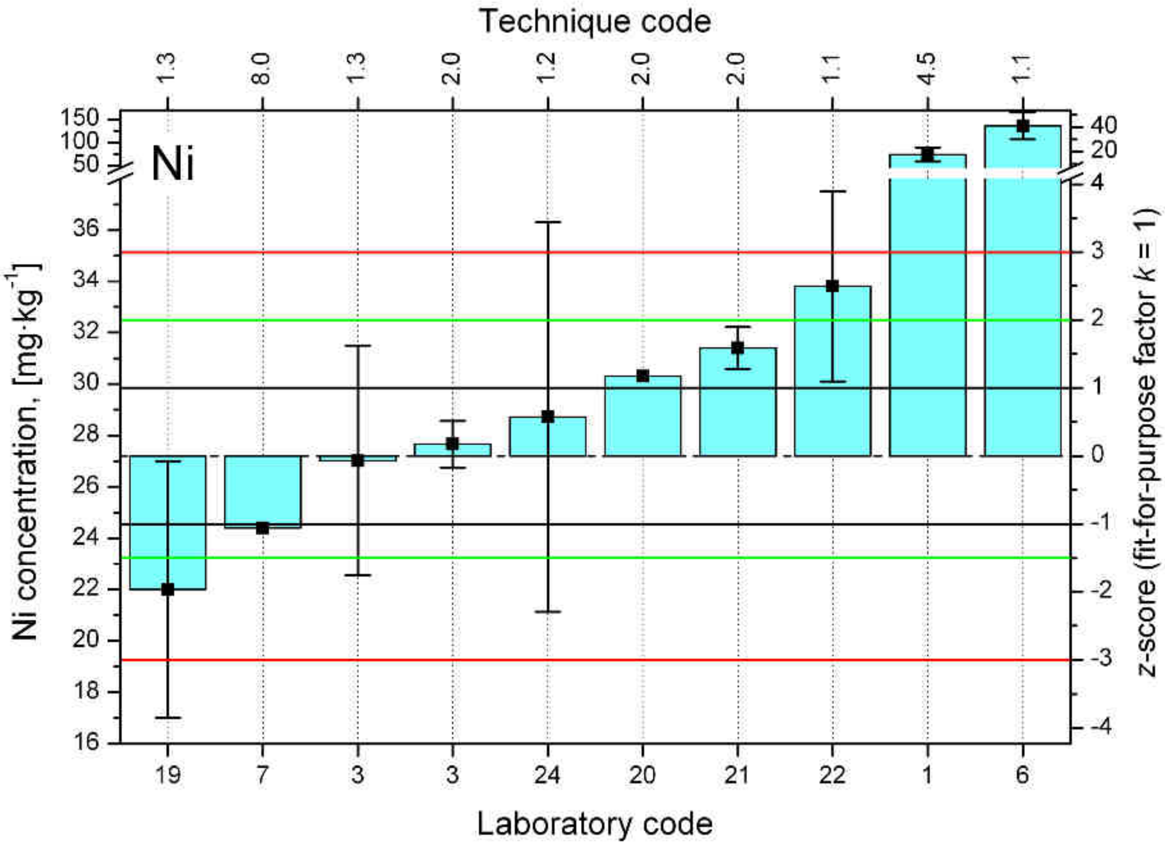

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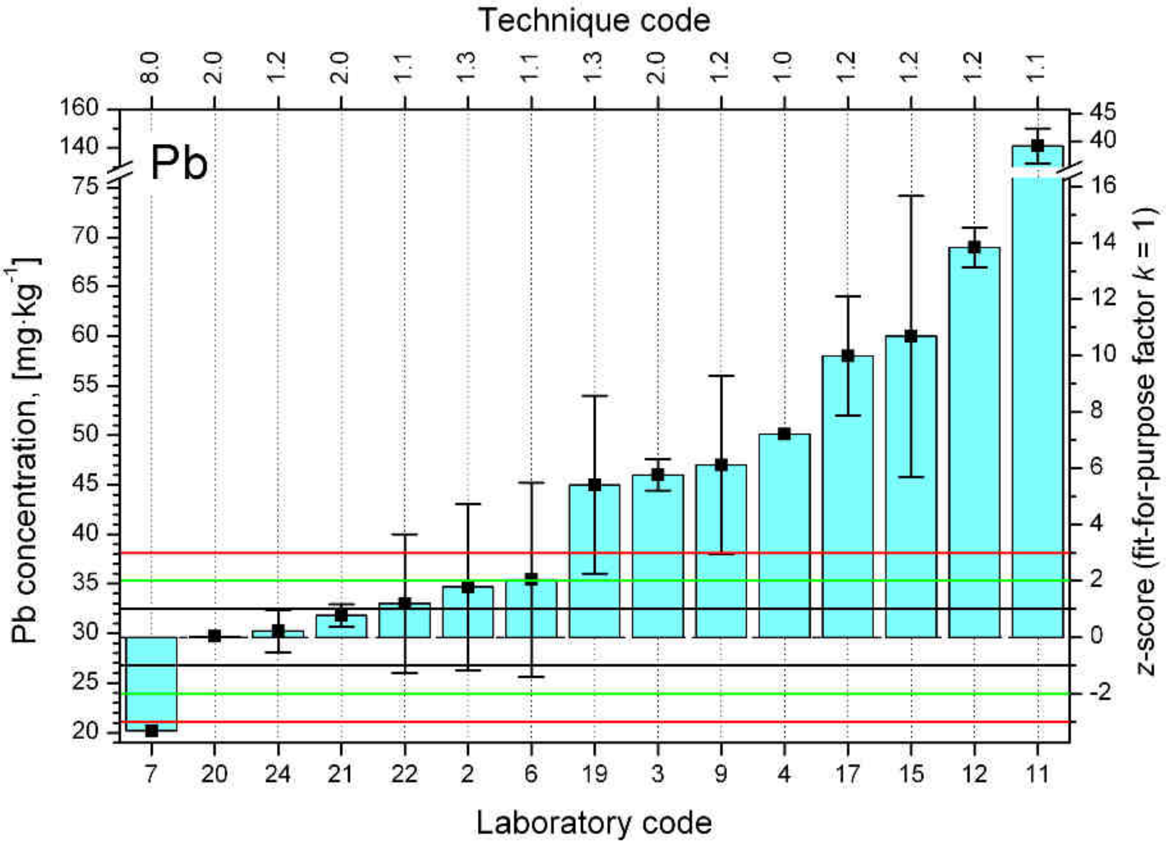


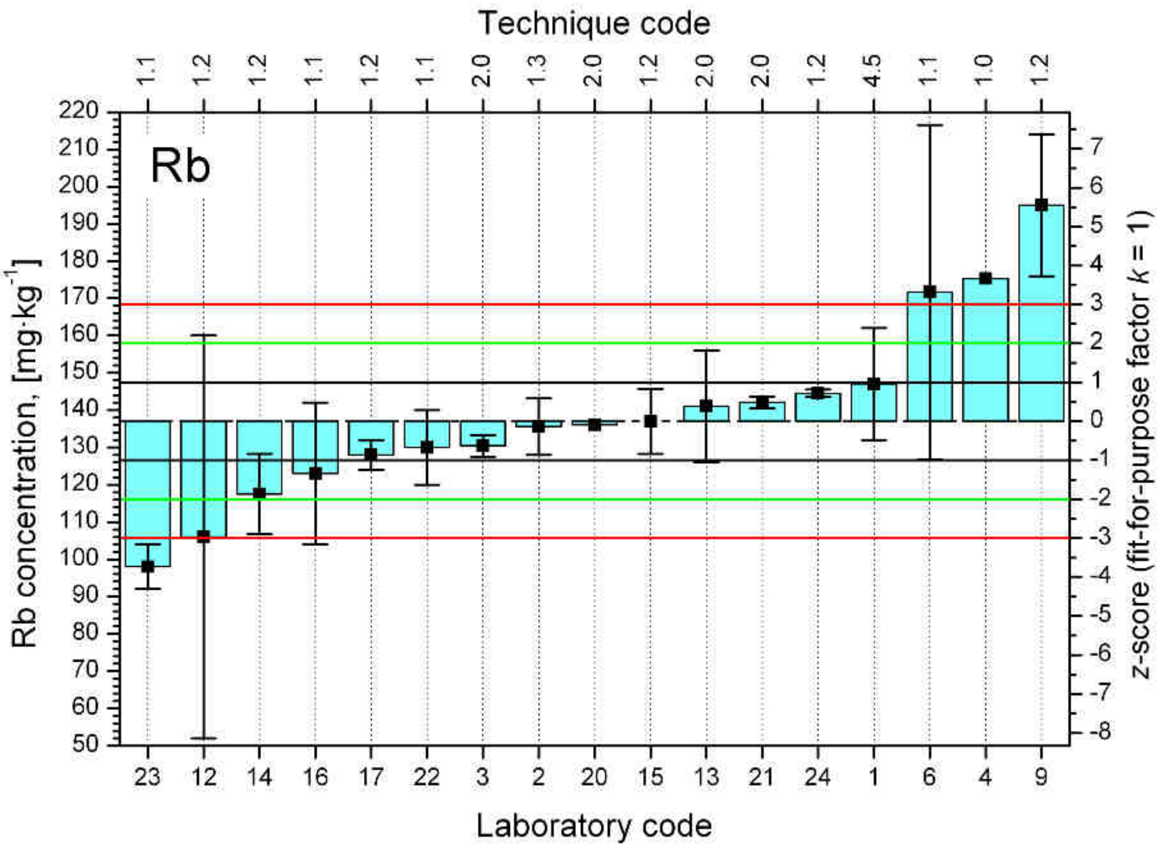

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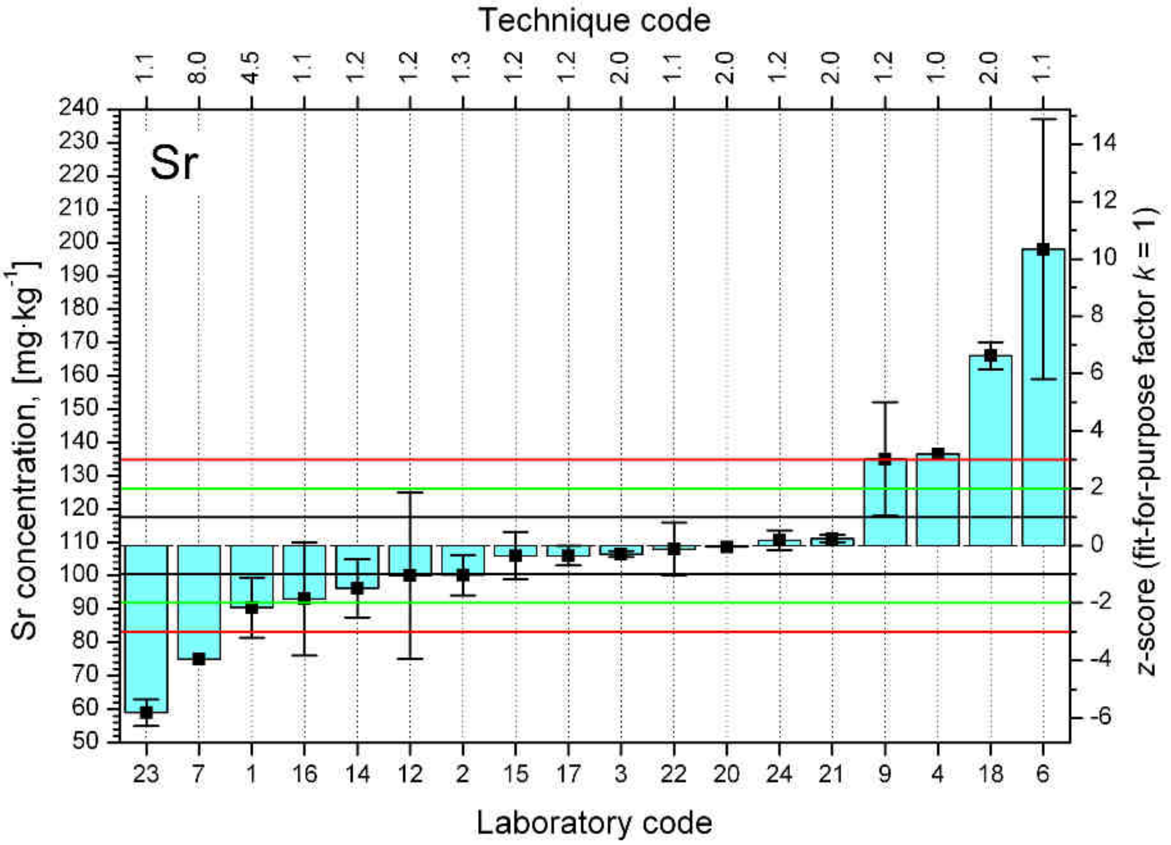


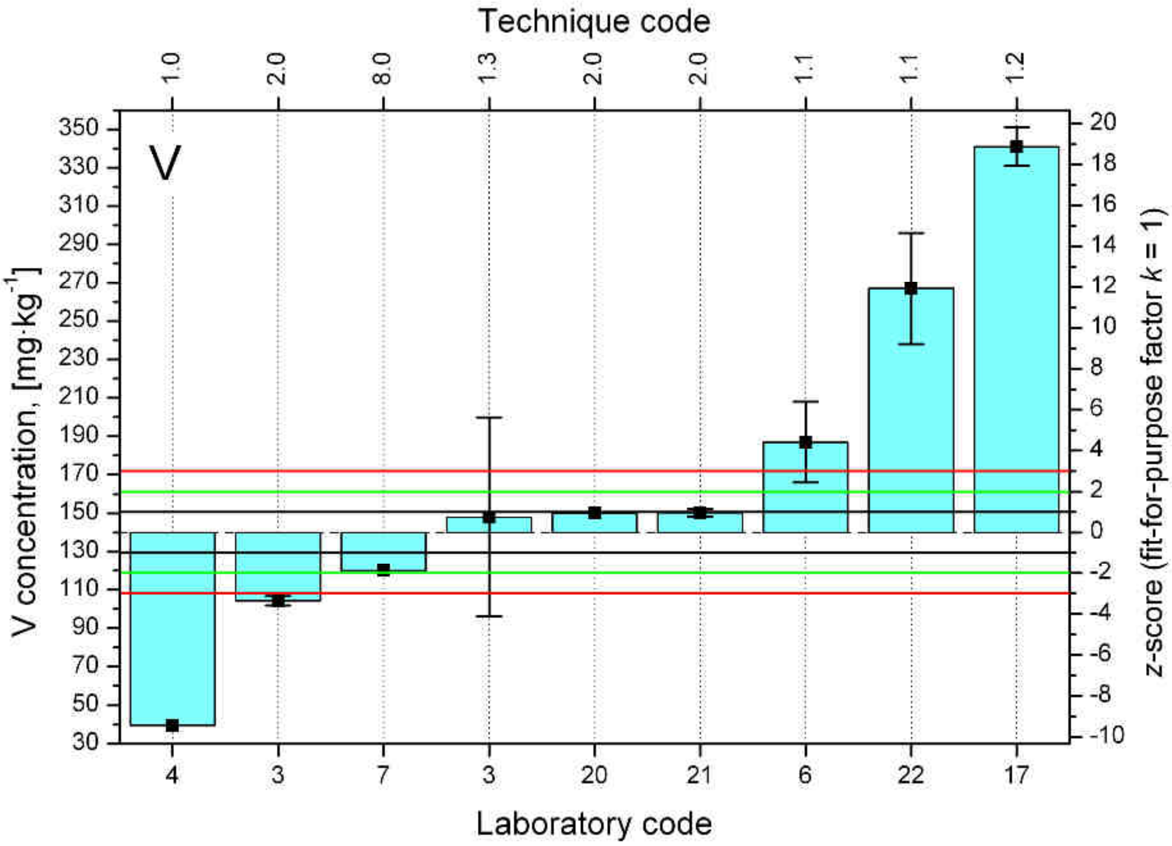

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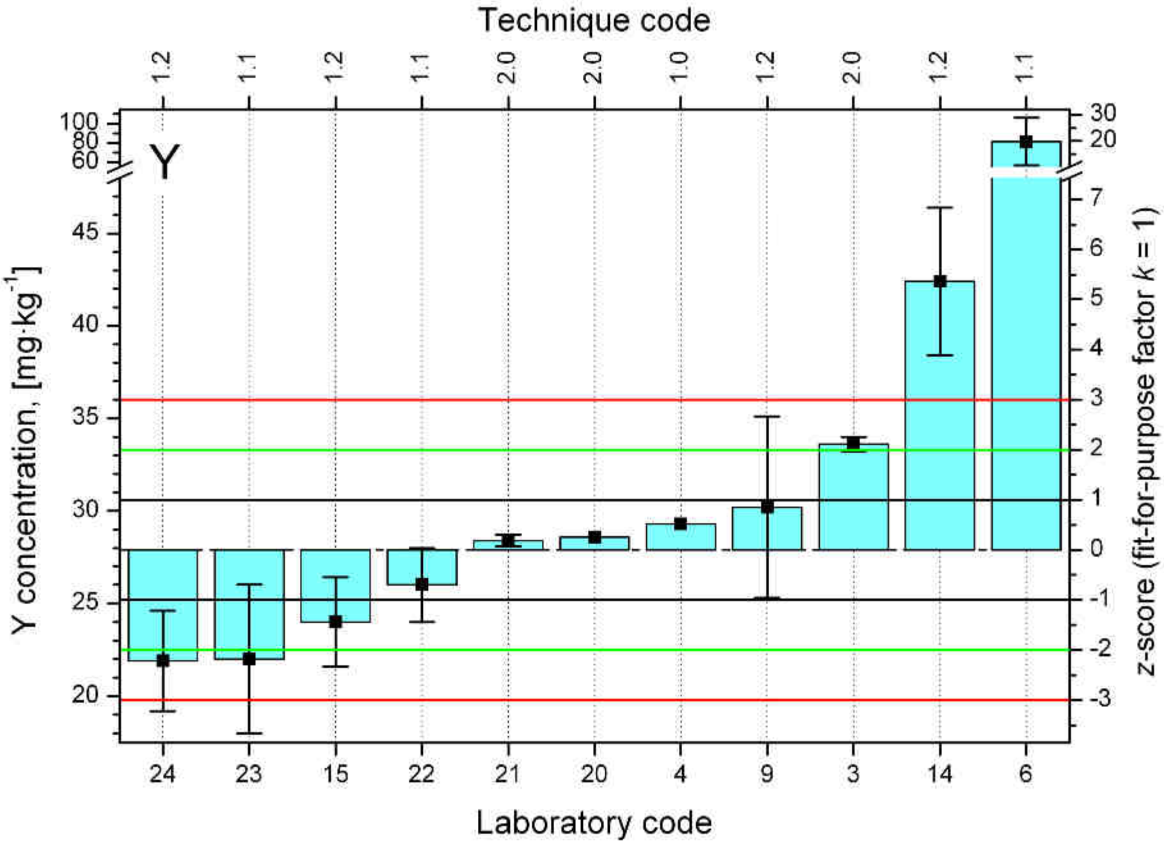


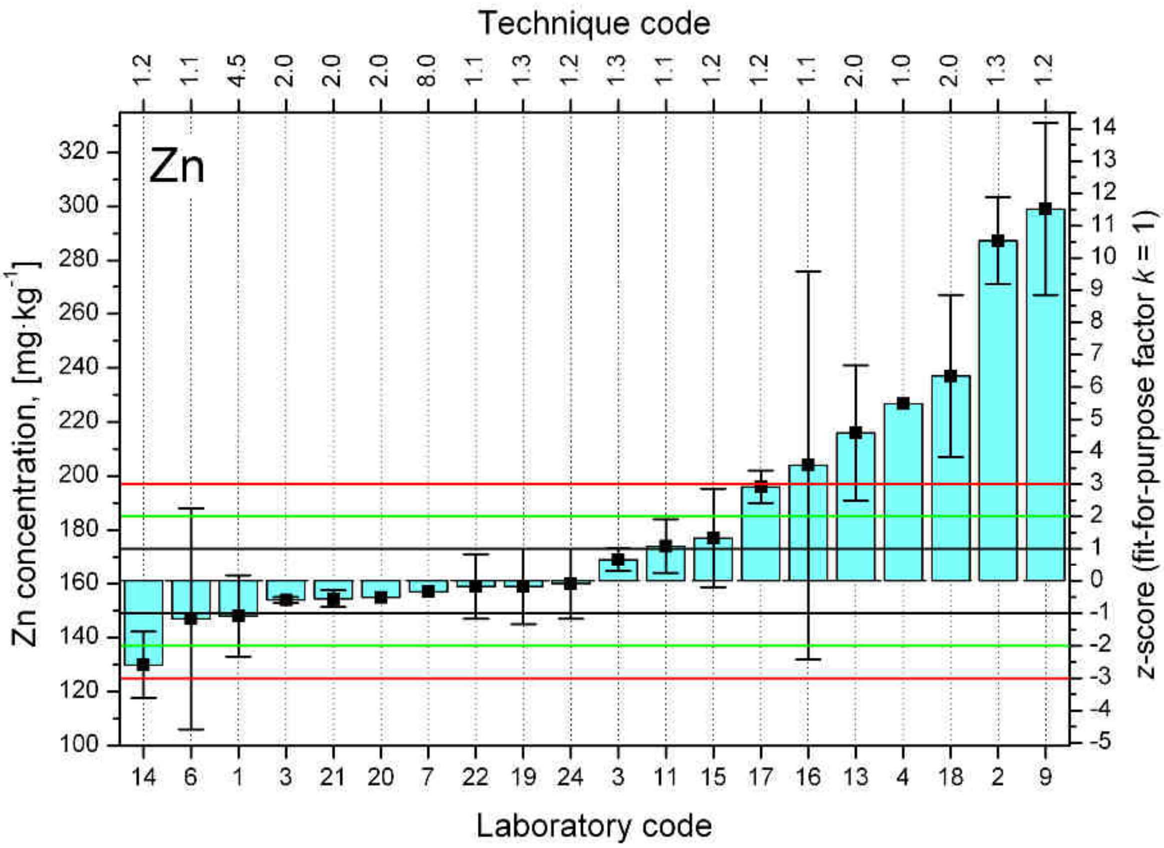

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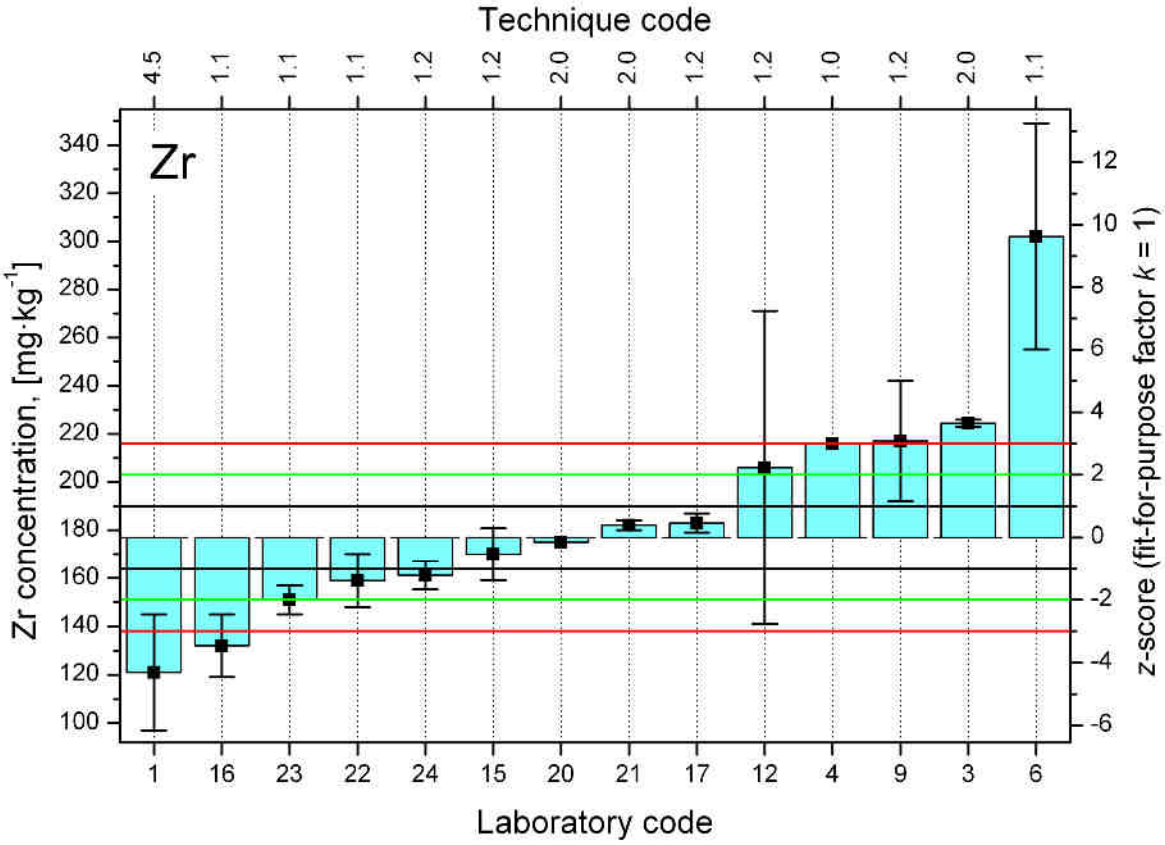


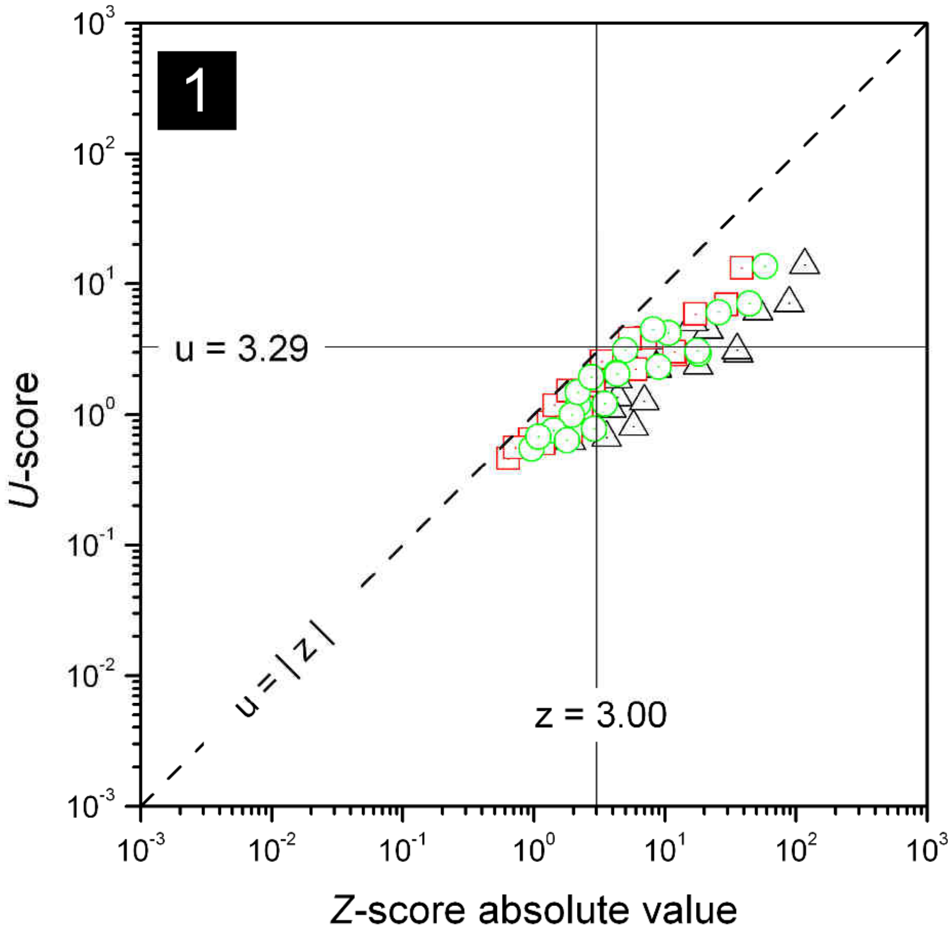



Fig. 5. Combined plots of *z*- and *u*-scores for participating laboratories. The laboratory code is shown in the left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2) with factor *k*, namely: ***k* = 0.5 - black triangles**,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

Fig. 5 continued…

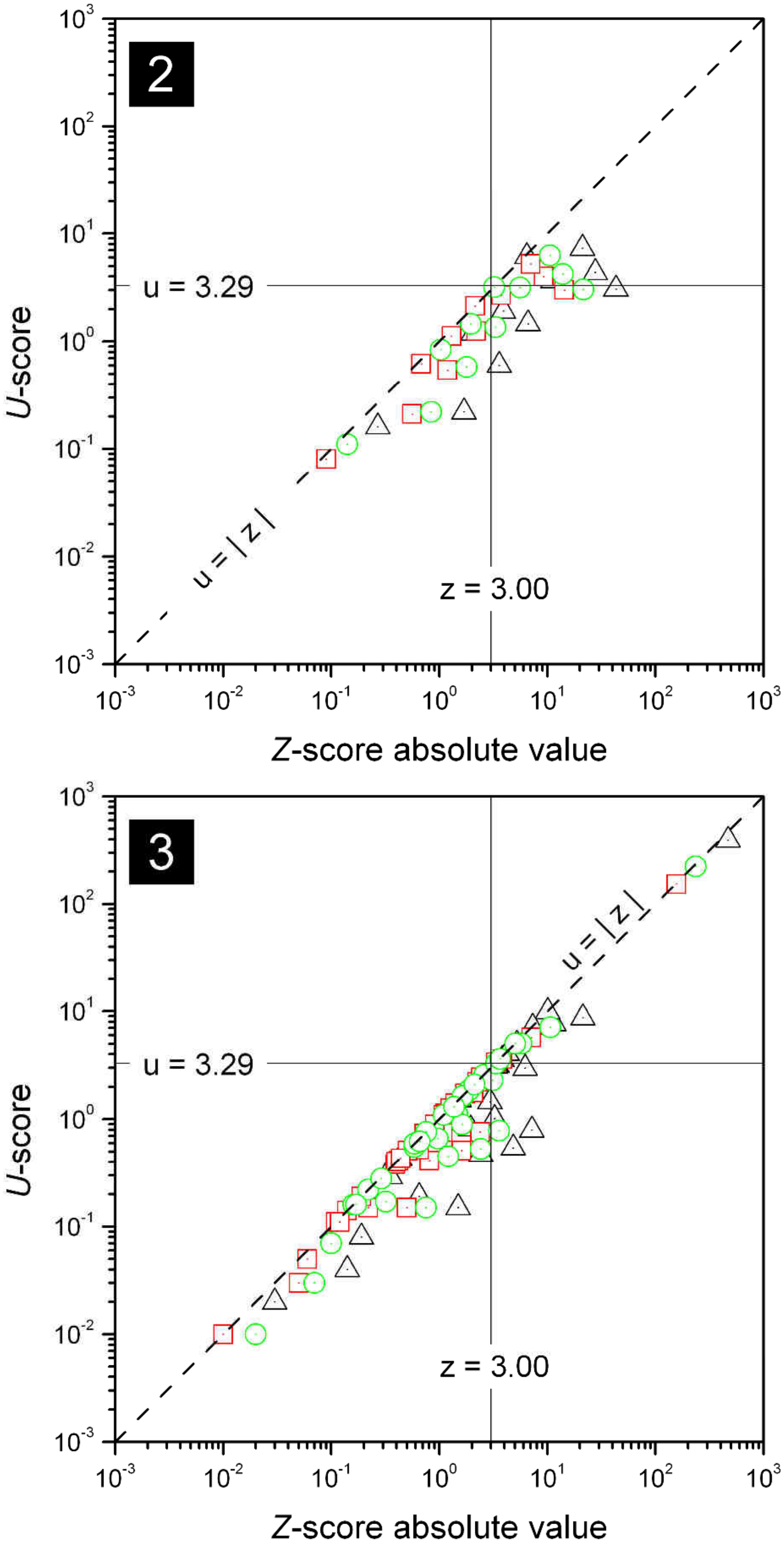
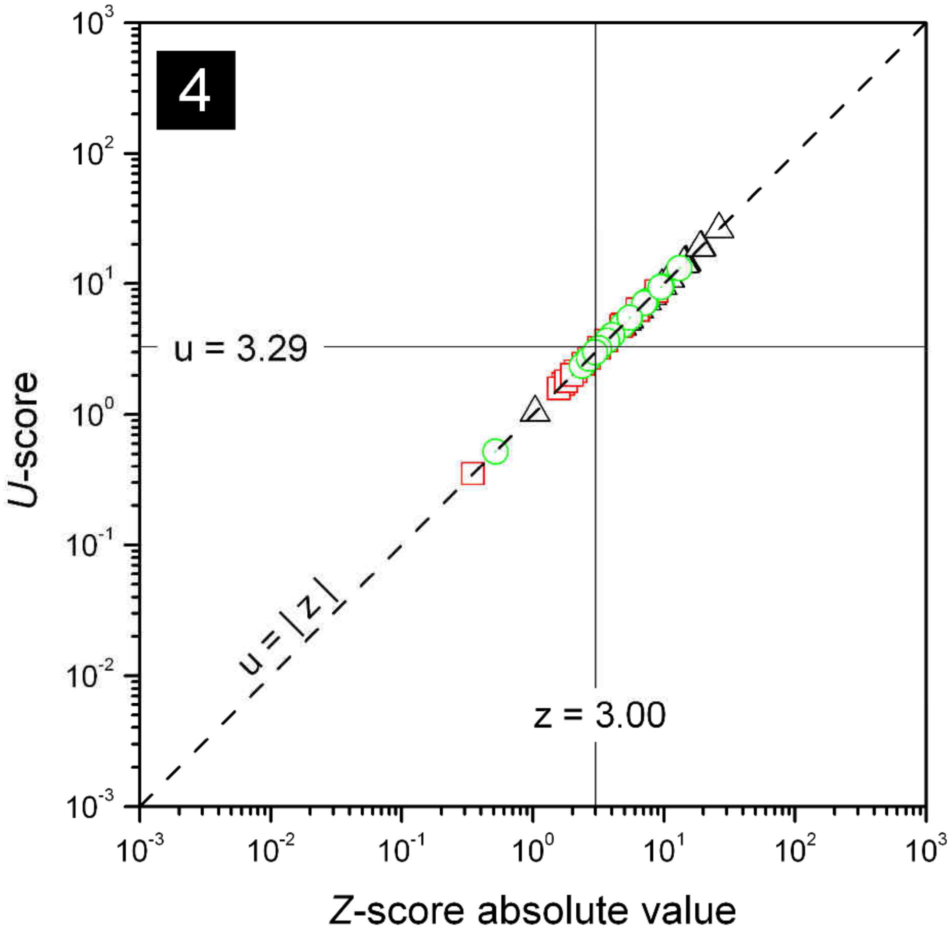
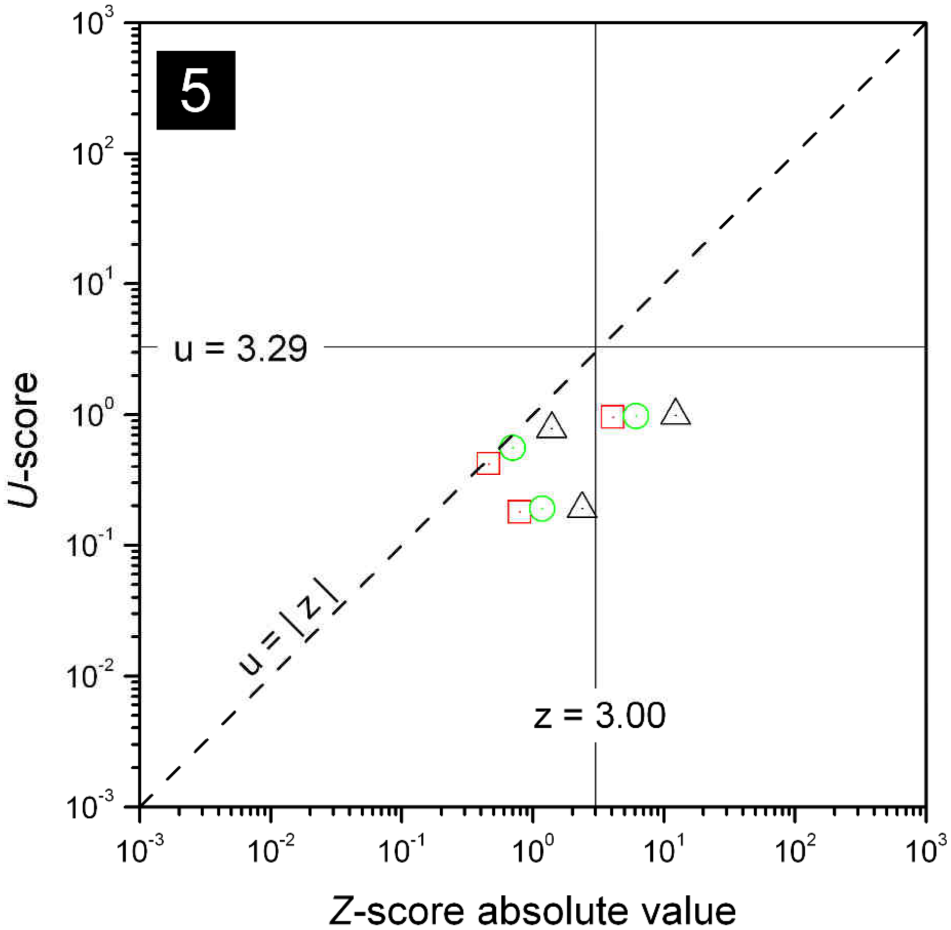


Fig. 5 continued…



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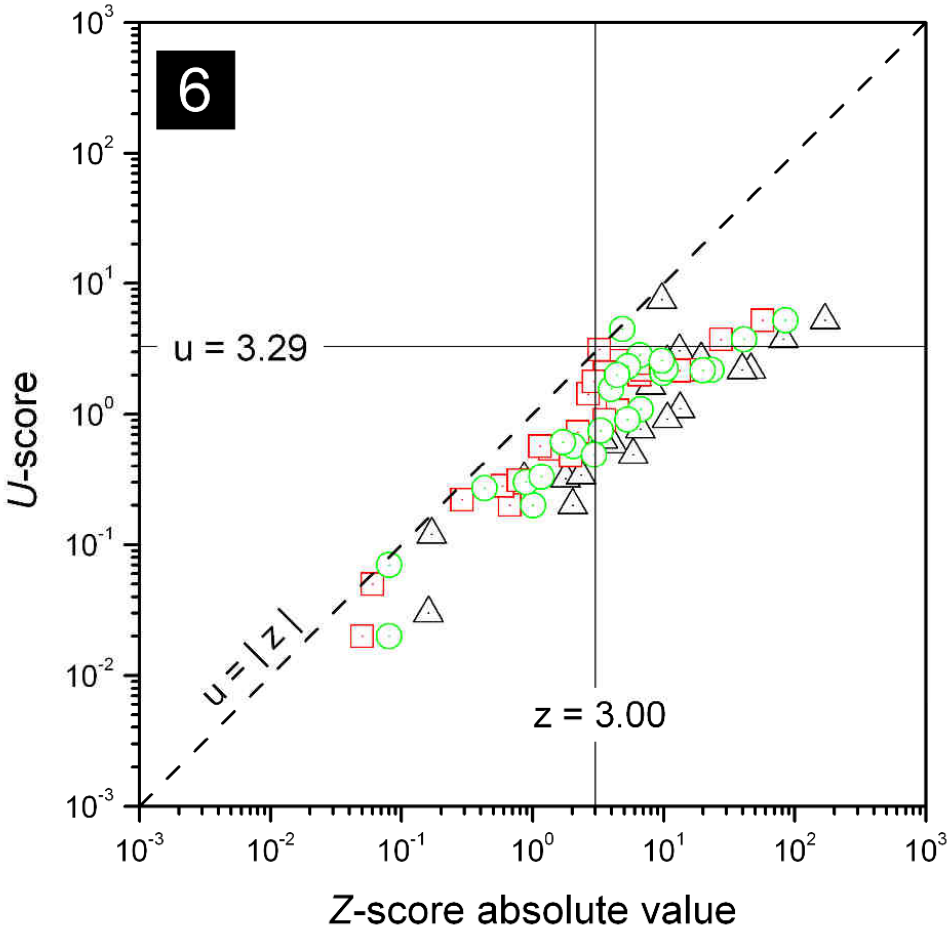


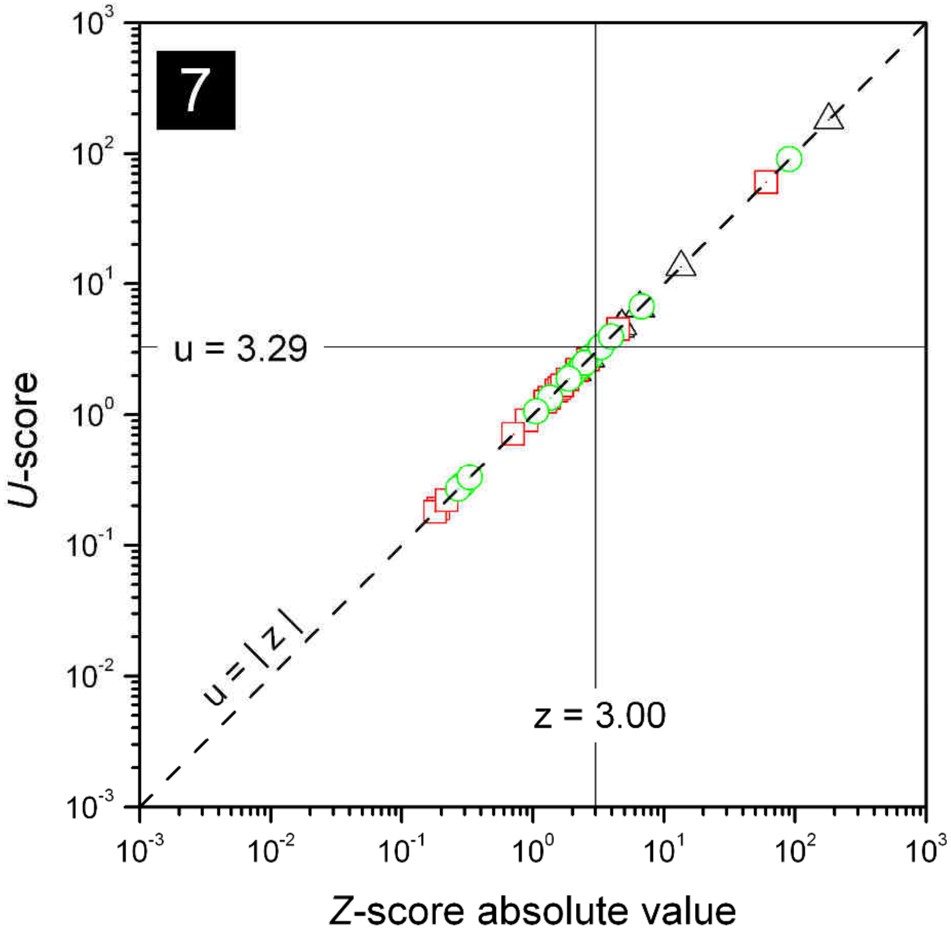

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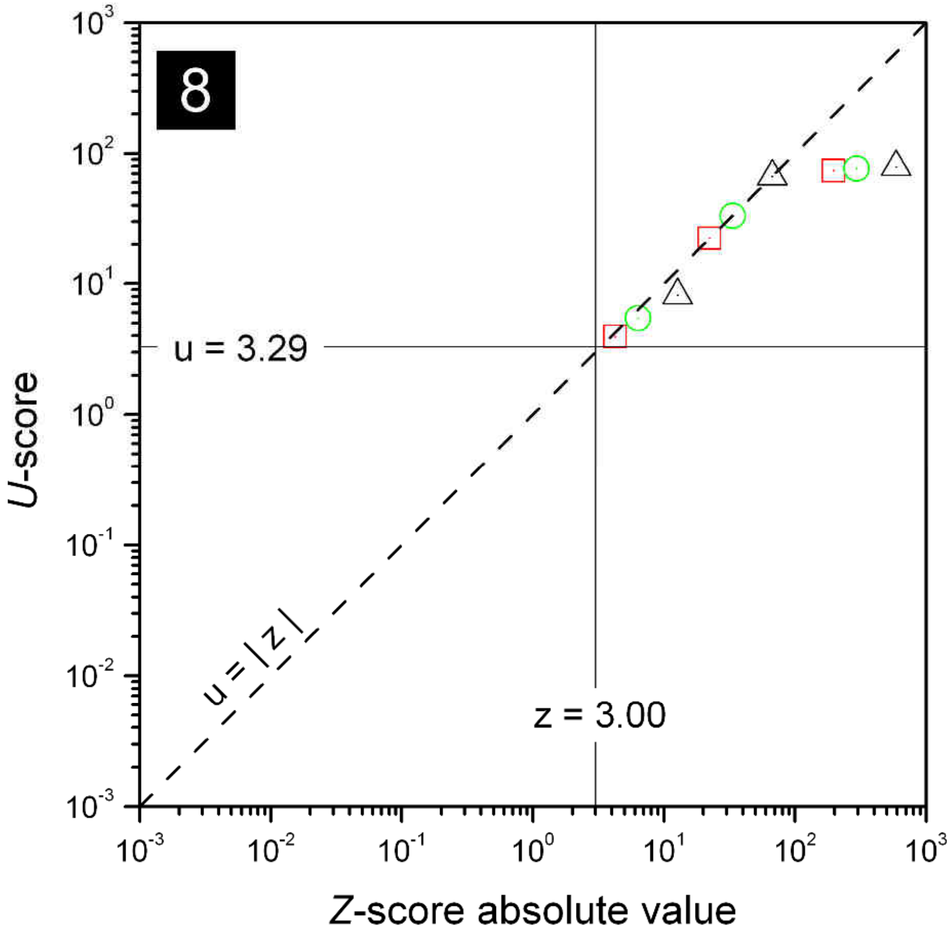


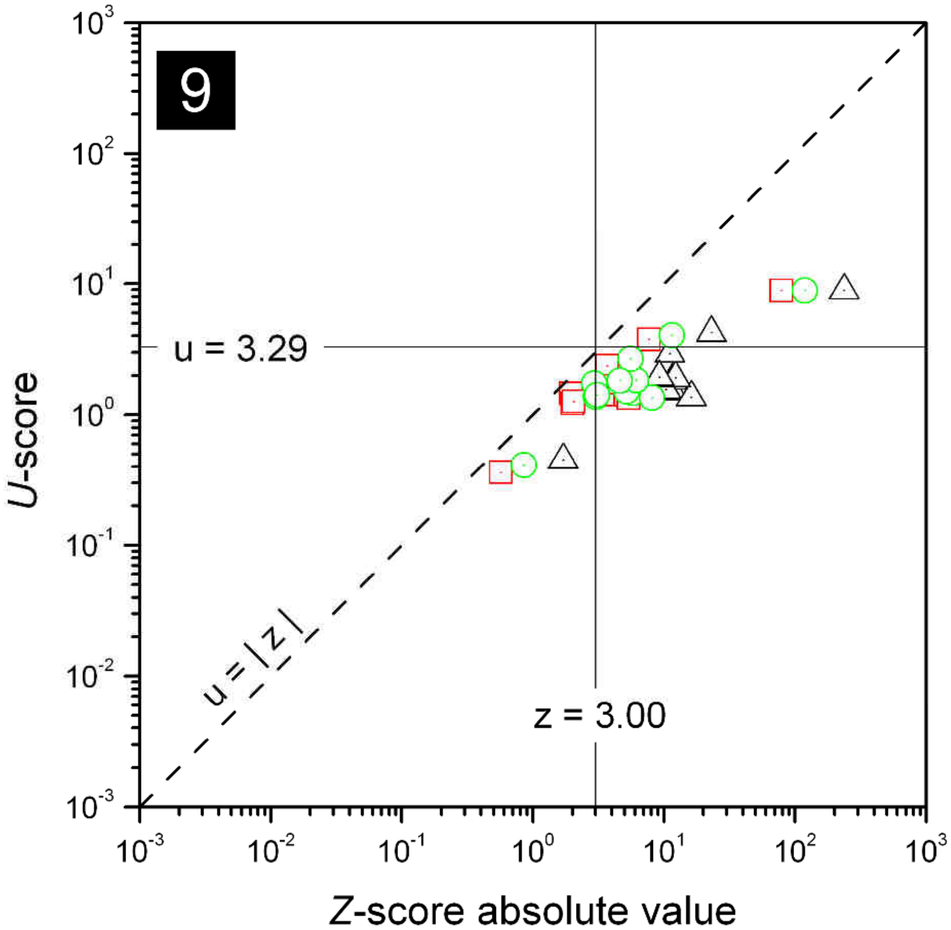

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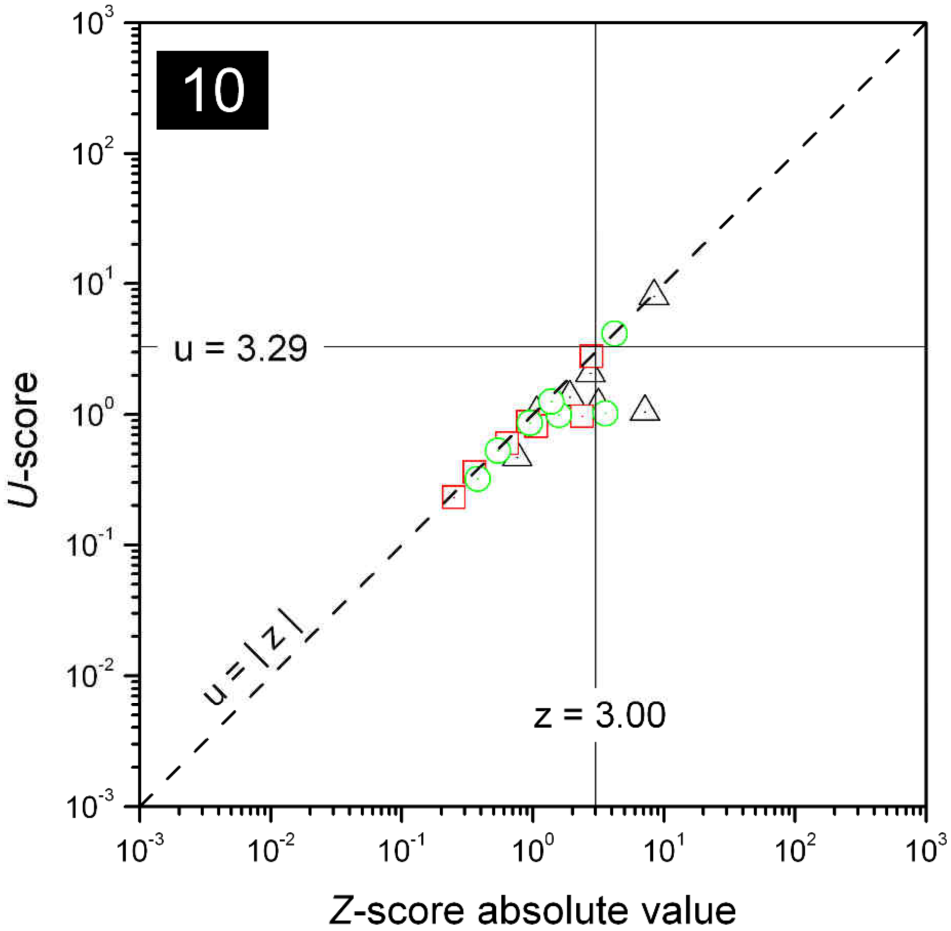


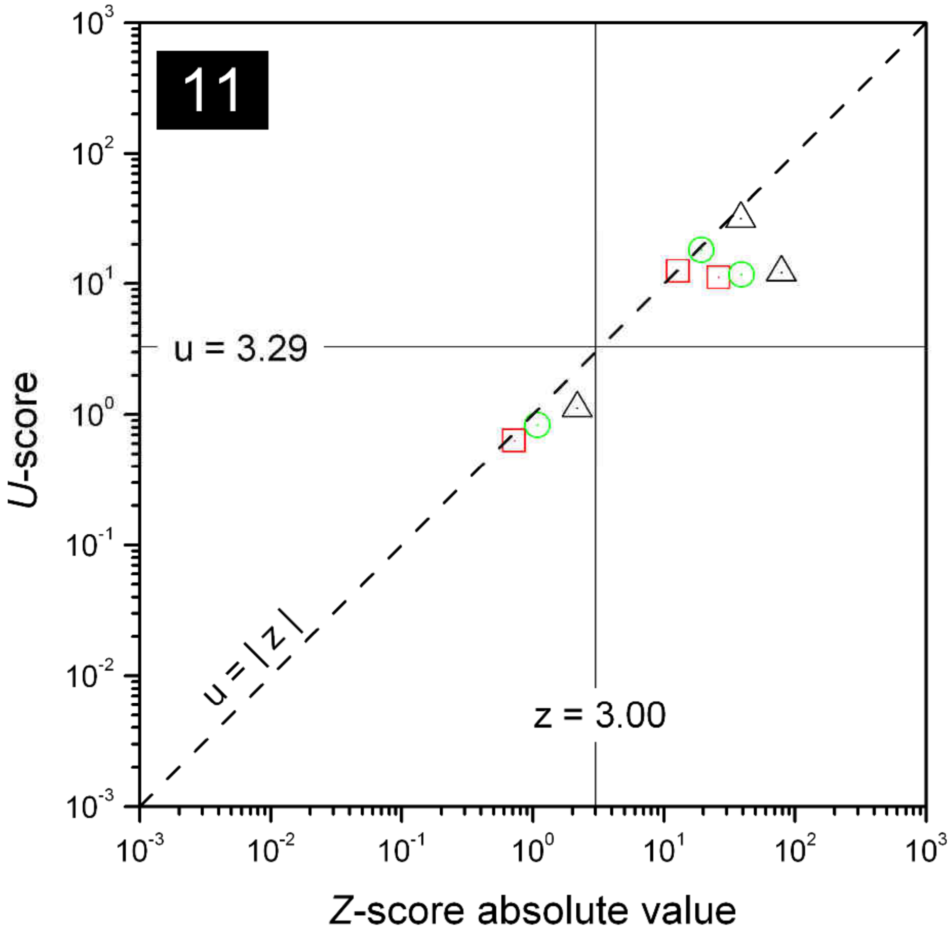

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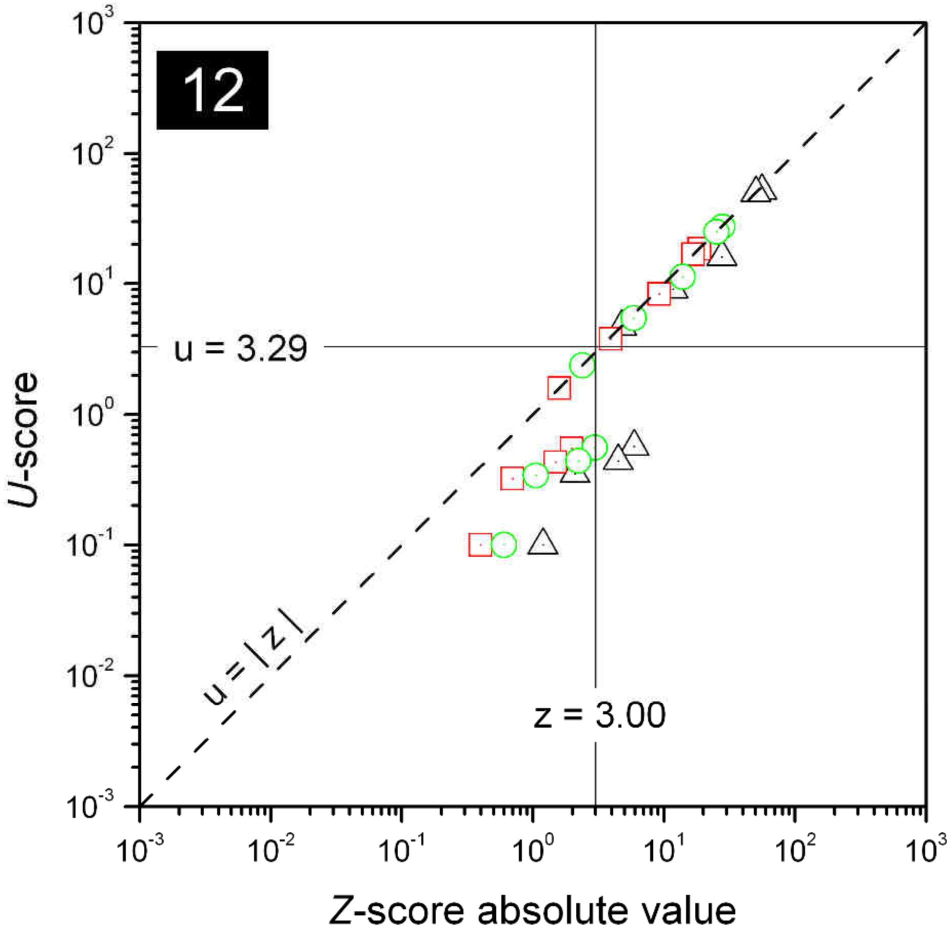


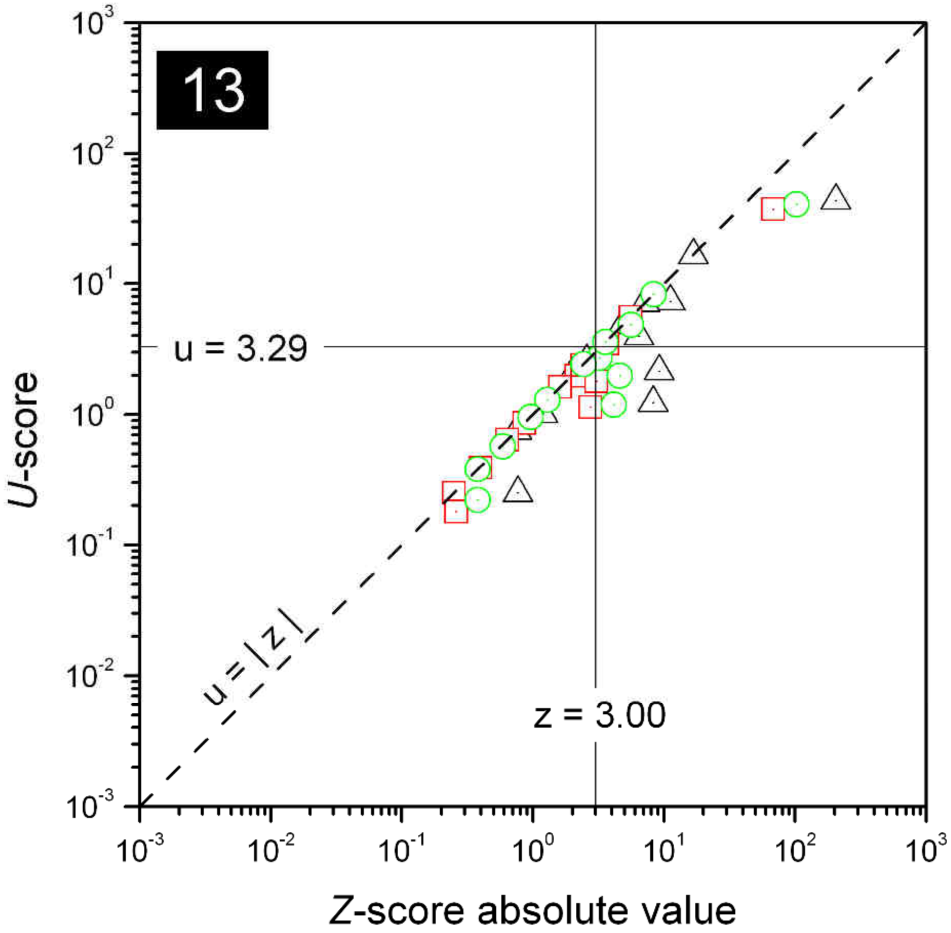

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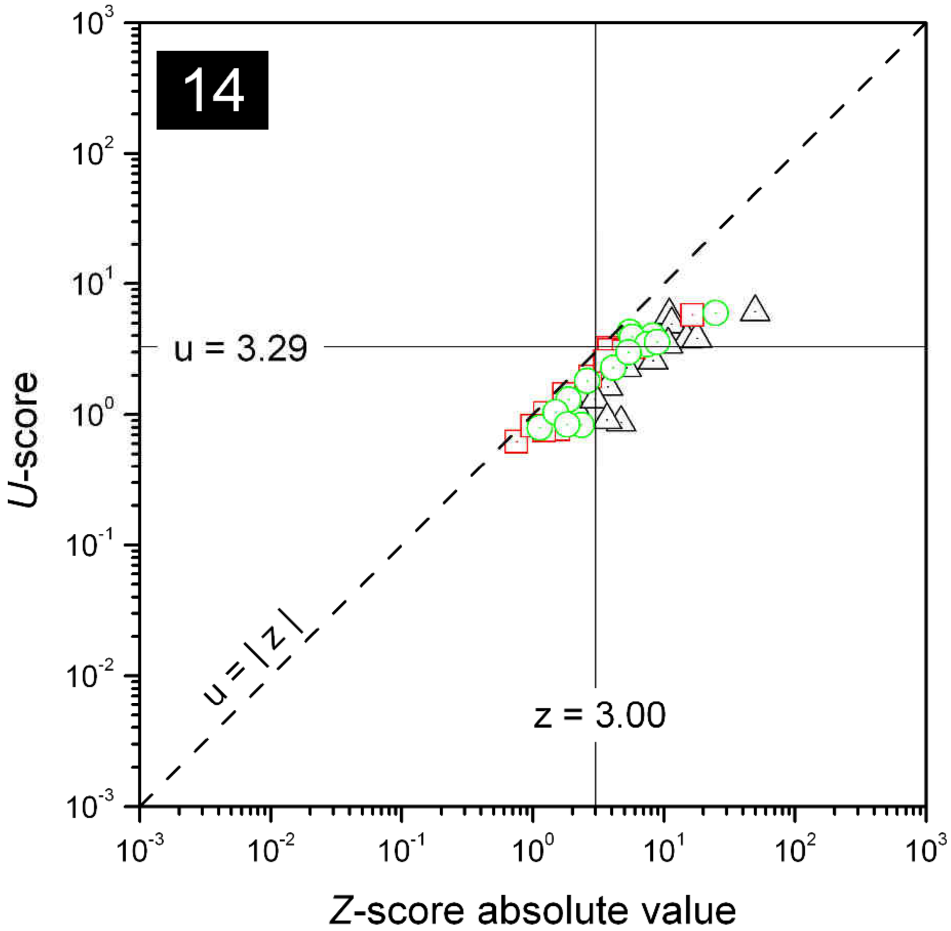


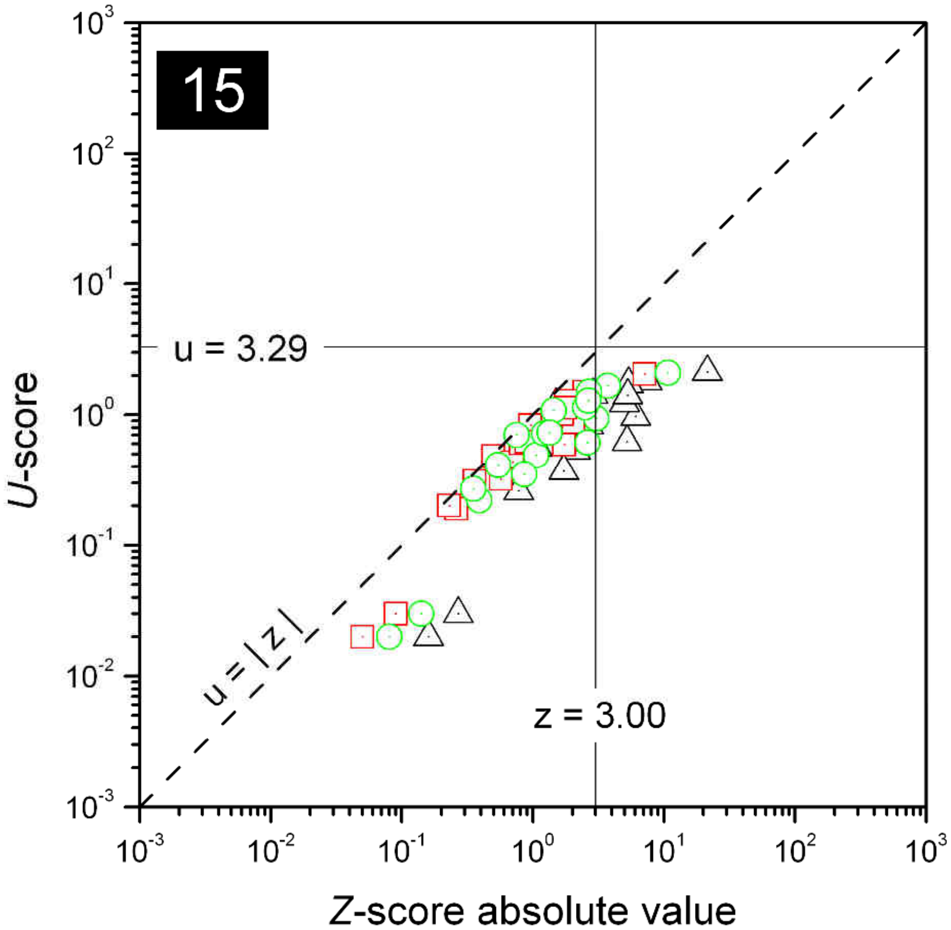

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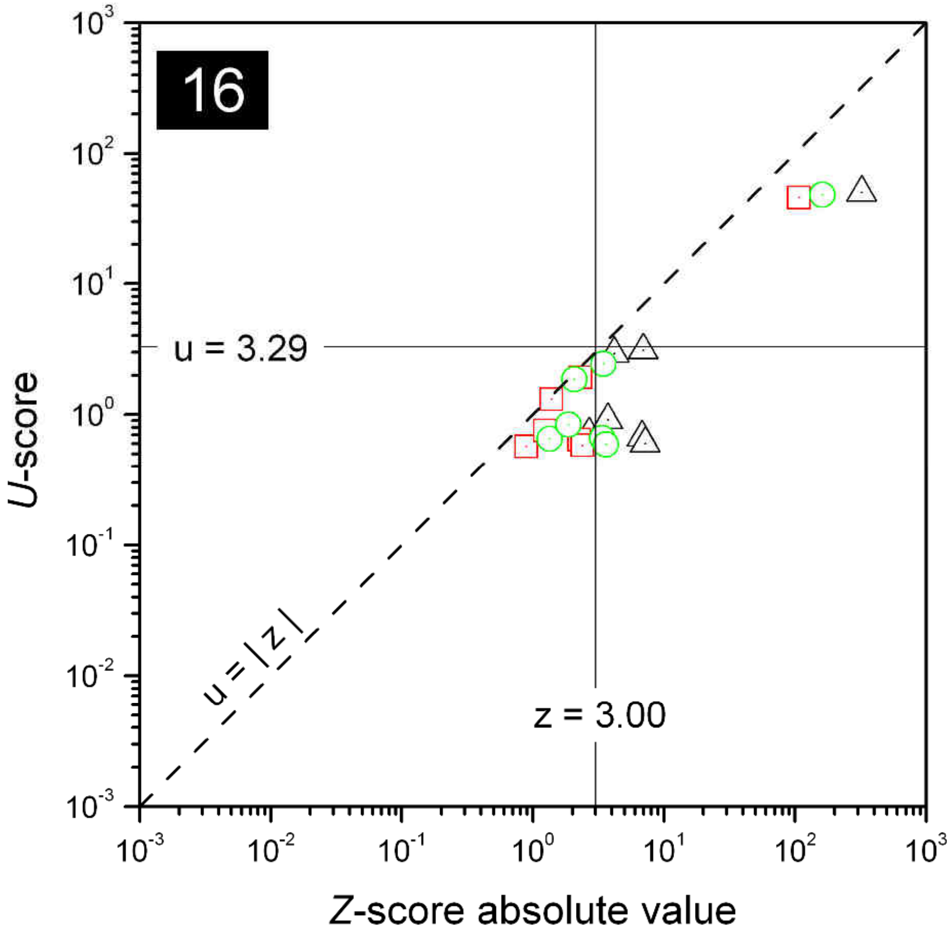


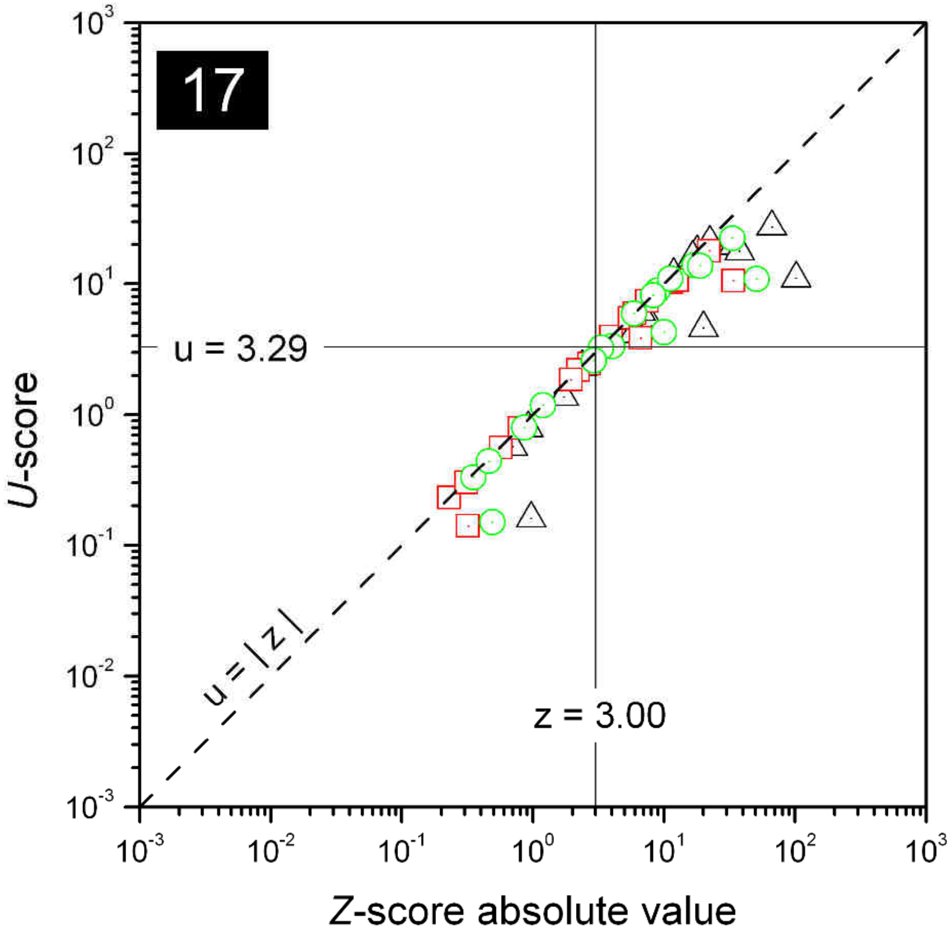

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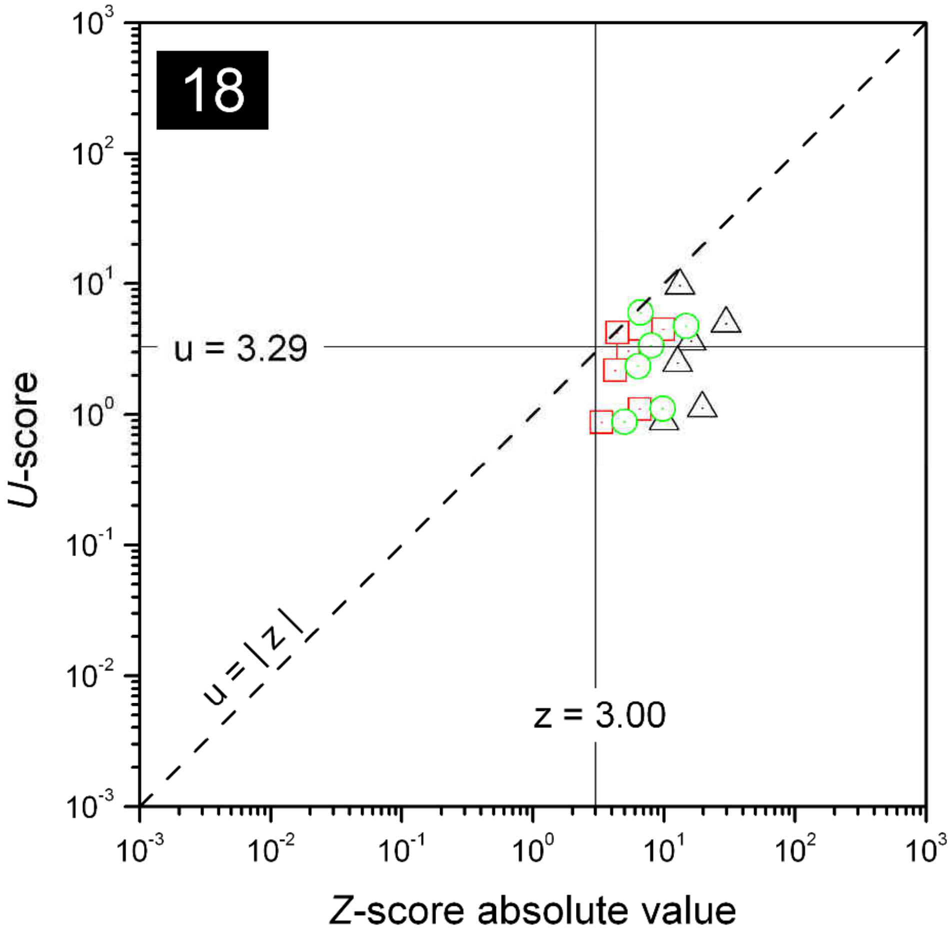


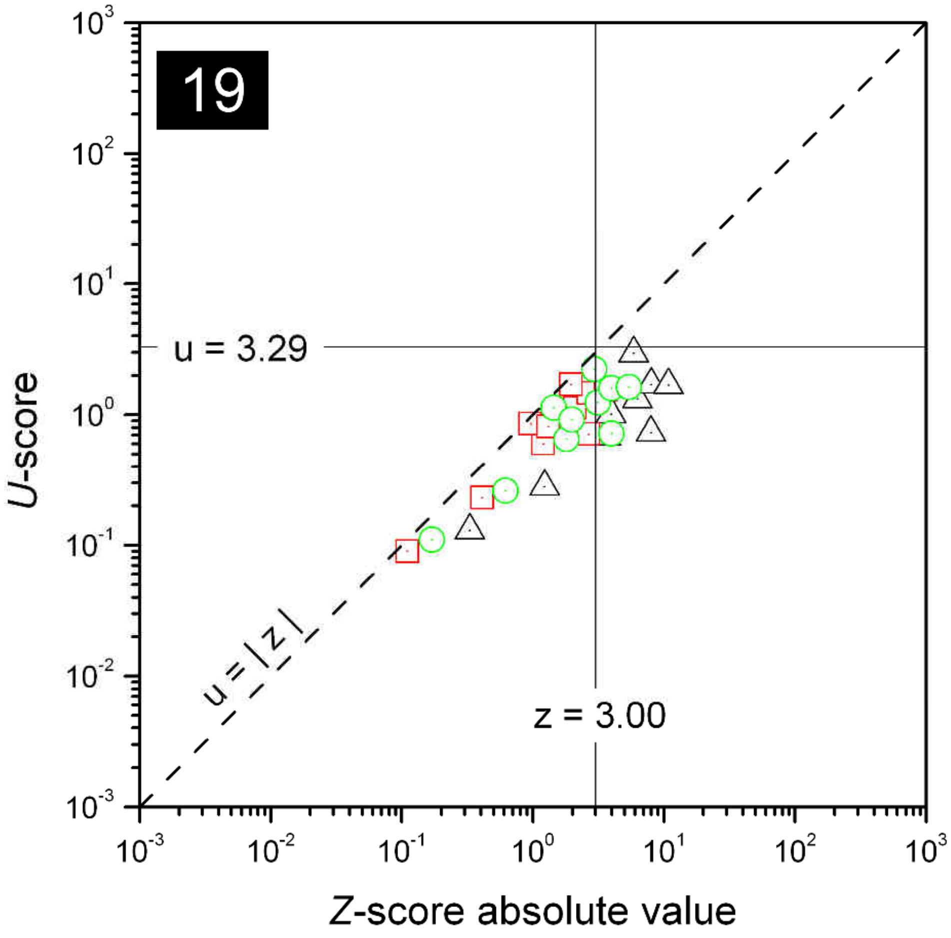

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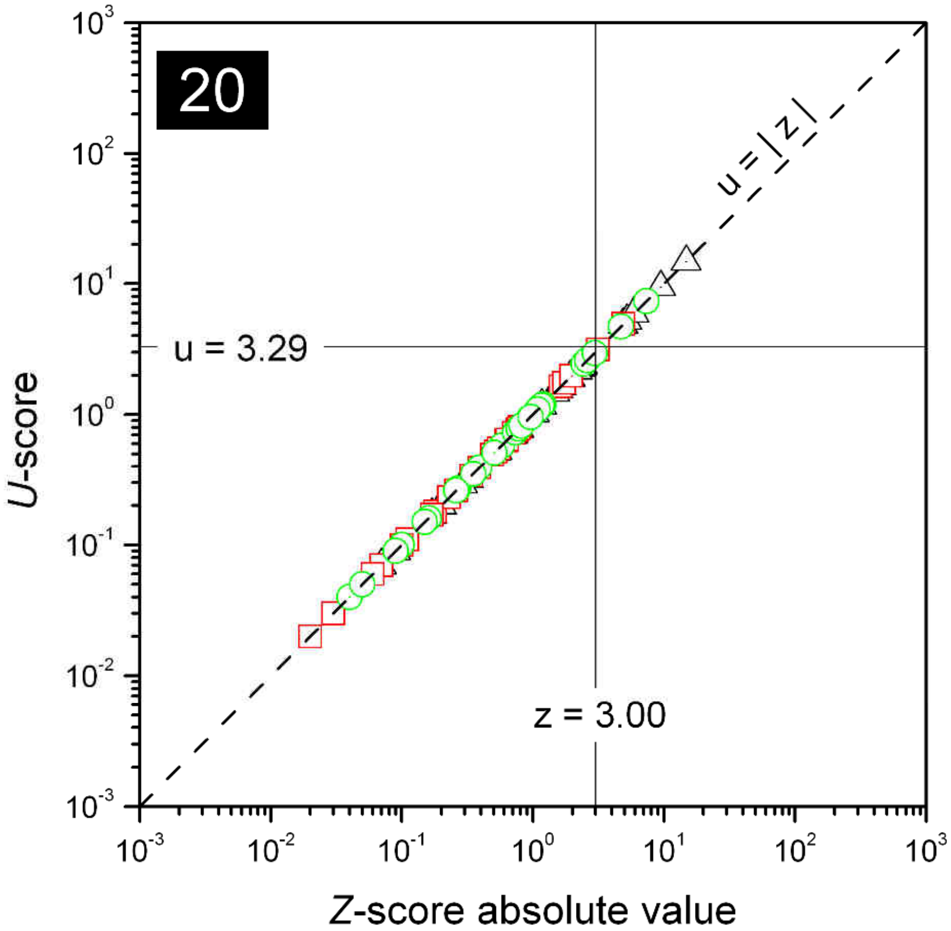


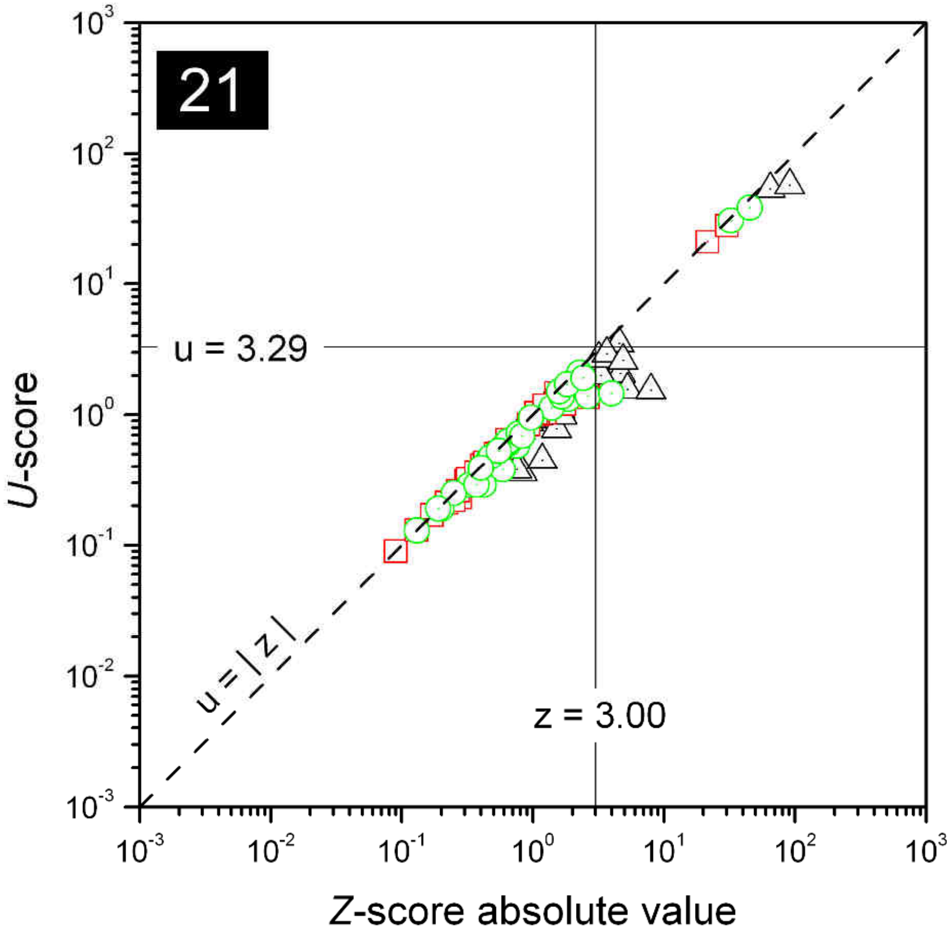

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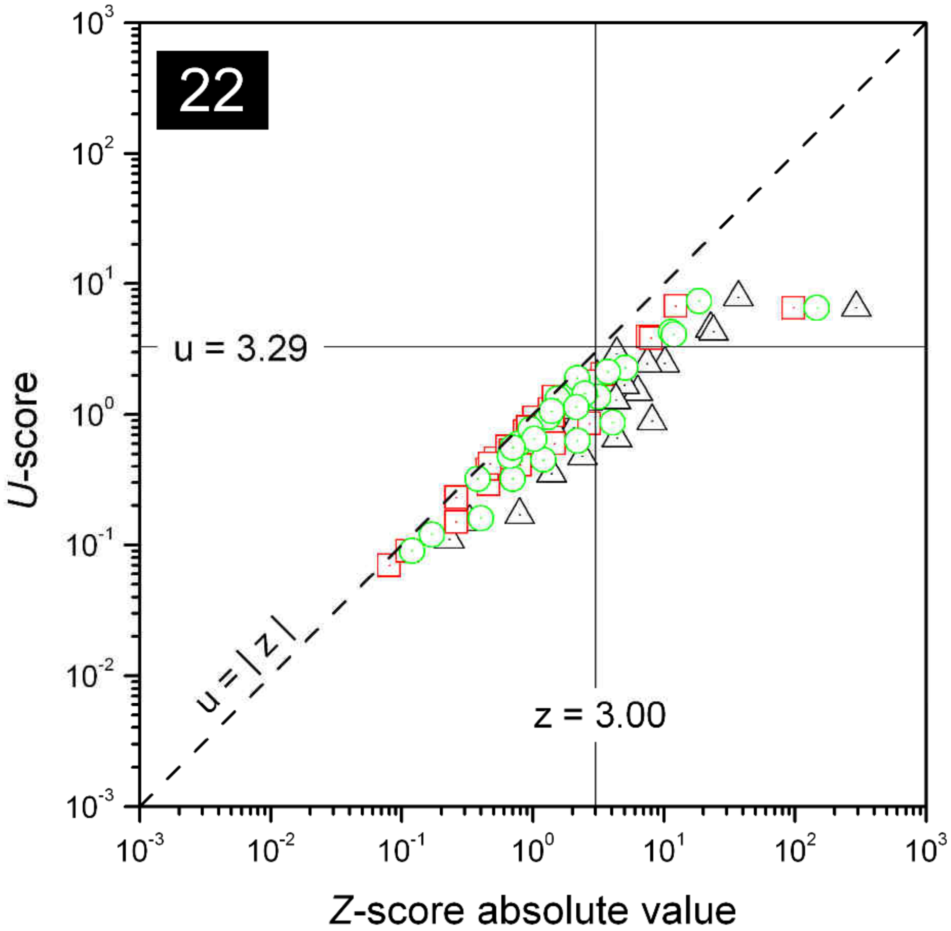


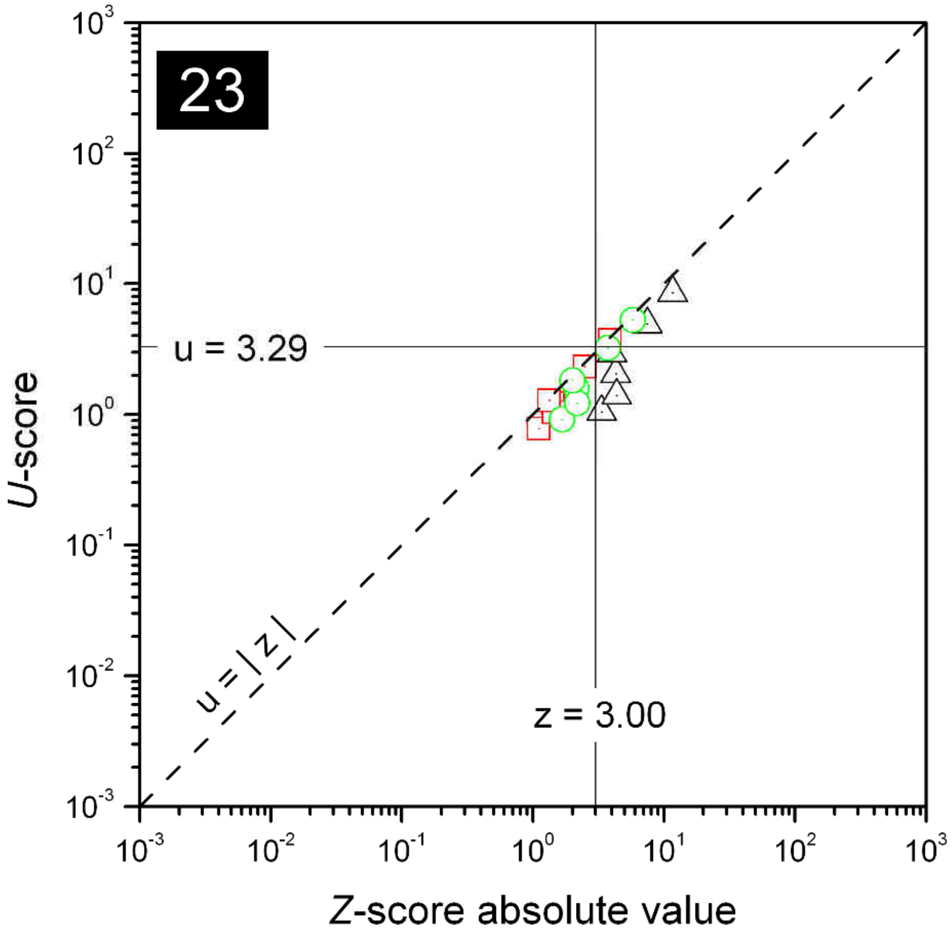

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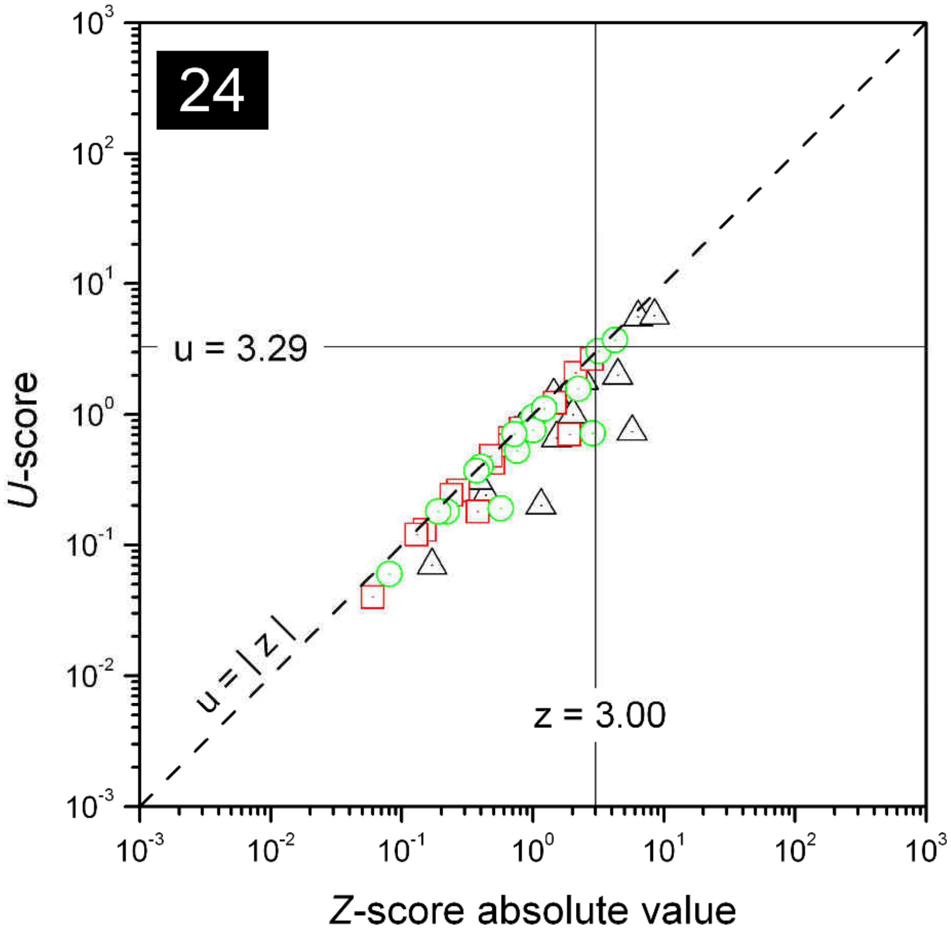

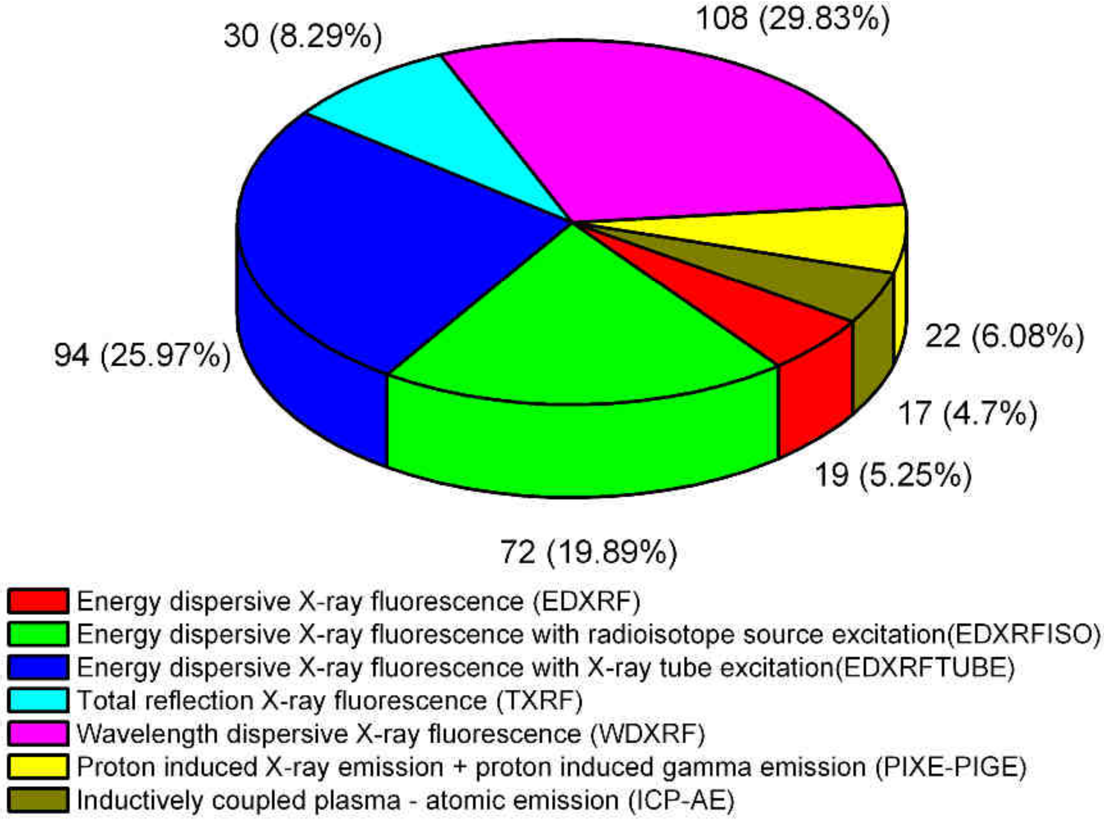


Fig. 6. Utilization of the analytical techniques. For each analytical technique the number of submitted results is shown. The percent values relate to the total number of 362 submitted results.