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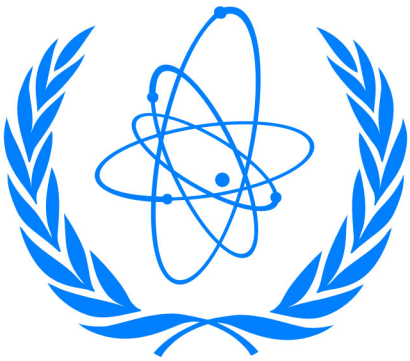
Report on the Proficiency Test Exercise for X-Ray Analytical Laboratories - PTXRFIAEA/02

Seibersdorf, August 2005

REPORT
ON
THE PROFICIENCY TEST EXERCISE
FOR
X-RAY ANALYTICAL LABORATORIES
ORGANIZED BY
INTERNATIONAL ATOMIC ENERGY AGENCY
PTXRFIAEA/02



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FOREWORD

The results of the worldwide PTXRFIAEA/02 proficiency test are presented. This proficiency test has been targeted to analytical laboratories applying X-ray spectrometry techniques for determination of element concentrations. The exercise has been organized by the XRF Group, Instrumentation Unit, the IAEA Laboratories Seibersdorf at no cost to the participating laboratories from the Agency's Member States. The results presented in this report should be examined carefully by the participants in order to control and eventually improve the performance of the applied analytical techniques. Regular participation in proficiency tests should be a "normal laboratory practice" for the laboratories performing routine analytical work. For any analytical laboratory participation in a proficiency test is the best way to get a reasonable assessment of its routine performance and to compare it with the performance of other analytical centers.

INTRODUCTION

Continuing the proficiency test scheme started by the XRF Group, Instrumentation Unit, the Agency's Laboratories Seibersdorf in 1997/98, followed by the PTXRFIAEA/01 exercise carried out in 2001/2002, the PTXRFIAEA/02 exercise was conducted in 2004/2005 and the results are presented in this report. This proficiency test (codenamed PTXRFIAEA/02) was carried out using a plant material, a lichen species. The well characterized material was distributed to 31 laboratories at the end of 2004 with a 3 months deadline for reporting back the analytical data. 17 laboratories reported 259 analytical results for 30 elements. A subset of 120 results for 10 elements, with well established property values (V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb), was selected and evaluated. The results of the evaluation are presented below.

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.

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 provided by the Chemistry Unit, the IAEA Laboratories, Seibersdorf, Austria. The test sample was a lichen species, identified as *Pseudevernia Furfuracea*, collected from the Bleiberg region of Kärnten, Austria in 1996. Approximately

24 kg of material was harvested and processed. The homogeneity of the bulk material was checked by neutron activation analysis (NAA) and was found to be acceptable at 10 mg and 100 mg levels. The details of the homogeneity testing can be found elsewhere [4].

Assigned Value and Target Standard Deviation

The property values established for the purpose of the IAEA-338 Proficiency Test [5] were used as the assigned values of the analytes, X_A. The property values for 10 trace elements were established for the IAEA-338 lichen material and were considered in this proficiency test round, including V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb. For each analyte a target value of the standard deviation has been assigned using a modified Horowitz function as proposed in the reference [6]:

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

In Eqn. (1) the assigned value of analyte, X_A, is expressed in terms of mass fraction. The target value of the standard deviation, σ_A was 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 was 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.

***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:

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

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

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

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:

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

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

The symbol '*L*' denotes the number of results provided by the laboratory/participant for all the analytes determined. The summing up in Eqns. (6) and (7) takes into account all *z*-scores for all analytes reported by the 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 standard uncertainty values were used to calculate the *u*-scores:

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

The symbol 'σ_x' denotes the standard uncertainty of the reported 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:

$$
\begin{aligned}
1.64 \ge u &\quad \text{- reported result does not differ from the assigned value,} \\
1.64 < u \le 1.95 &\quad \text{- reported result probably does not differ from the assigned value,} \\
1.95 < u \le 2.58 &\quad \text{- it is not clear whether the reported and assigned values differ,} \\
2.58 < u \le 3.29 &\quad \text{- reported result is probably different from the assigned value,} \\
3.29 < u &\quad \text{- reported result differs from the assigned value.}
\end{aligned} \tag{9}
$$

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*- and *z*-score the following inequality is fulfilled:

$$u < z \tag{10}$$

It implies that if the *u*-score falls outside the range $u < 3.29$ 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 within the range $u < 1.64$ but at the same time the *z*-score decision limit is triggered ($|z| > 3$) the laboratory should reevaluate its fit-for-purpose status for the particular analyte.

Consensus Values

In order to get a general overview of the performance of the techniques applied by the participants the reported consensus values have been estimated. The reported results for V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb were sorted and then tested for the presence of outliers using a set of seven outlier rejection tests:

description of symbols:

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

1. Coefficient of kurtosis [7], number of results: $5 \le n \le 100$, two-sided test, confidence level = 0.95:

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

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

2. Coefficient of skewness [7], 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 [8, 9], number of results: $4 \le n \le \infty$, two-sided test, confidence level = 0.95:

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

where:

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

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

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

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

4. Dixon's test [10], 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* ≤ critical value.

5. Outlier rejection test proposed in [7], number of results: $4 \le n \le 100$, 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 [11], number of results: $3 \le n < \infty$, 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 $B_4 \le$ critical value.

7. Outlier rejection test proposed in [12], number of results: $3 \le n \le 100$, two-sided test, confidence level = 0.95:

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

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

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

After outlier rejection procedure the remaining results 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 rejection 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 test material was distributed to 31 laboratories applying X-ray spectrometry techniques for elemental analysis. Out of the 31 laboratories 17 have provided the required analytical results. A list of the participating laboratories is presented in Table 1. One of the laboratories did not report the uncertainties of analytical results. The applied X-ray spectrometry techniques used by the participants for determination of element concentrations included: energy dispersive X-ray fluorescence spectrometry - radioisotope excitation (EDXRFS-R), energy dispersive X-ray fluorescence spectrometry - X-ray tube excitation (EDXRFS-T), total reflection X-ray fluorescence spectrometry (TXRFS), wavelength dispersive X-ray fluorescence spectrometry (WDXRFS), and particle induced X-ray emission (PIXE). The analytical technique codes are presented in Table 2. The participants provided 259 analytical results for 30 analytes out of which 120 results for the 10 analytes (V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb) were evaluated. Besides the analytes for which the assigned values were known the participants reported also results for the following analytes: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Co, Ni, Ga, Se, Br, Rb, Y, and Zr. These results were not evaluated in this proficiency test. 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 using Eqns. (19) and (20) based on a subset of 114 reported analytical results after exclusion of 7 results classified as outliers from the initial population of 120 results. The correlation between the assigned and the consensus values is shown in Fig. 2. As can be noticed there is a good overall agreement between the assigned and the consensus values, except for V, As, and Cd. The result for cadmium was reported only by one laboratory. The poor overall performance for arsenic was due to the presence of a relatively high content of lead. The biased consensus value for vanadium, determined by 4 laboratories, was due to its low content in the lichen material (3.68 $mg \cdot kg^{-1}$), close to the detection limit of the applied techniques. The remaining results correlated well with the assigned values of analytes. In Table 4 the reported values are listed together with *z*-scores and *u*-scores 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 have been shown. The data for analytes reported by at least 6 laboratories are presented in these graphs. In Fig. 3 the density distributions have been presented. Due to the rather low number of results, these graphs should only be used as indicators of the observed trends in the data.

In Fig. 4 the bar chart distributions of the reported results are presented. The results are shown sorted in ascending order and are plotted versus laboratory code. The technique codes are marked on a linked upper *X*-axis. The decision levels $|z| < 2$ for different fit-for-purpose ranges have also been marked on the graphs. For every participating laboratory its overall performance is presented in Fig. 5. The graphs presented in this figure relate all the *u*-scores and *z*-scores calculated for a given laboratory. The decision limits marked with black lines ($|z| < 3$, $u < 3.29$) divide the plot area into four quadrants. Due to inequality (10) all the points lay always below the line $u = z$. The smaller the laboratory estimated uncertainty is, the closer the related point lies to the $u = z$ line. In particular, the laboratory no. 10 did not report the uncertainty values and the plotted points overlap with the $u = z$ line completely. 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 ranges and that the laboratory provided too "optimistic" uncertainty estimate which requires some care and revision. 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 participants were also asked to report additional information about the analytical process, which included the data on the technique applied, methods of sample preparation, algorithms used for X-ray spectra deconvolution (for EDXRFS) and algorithms applied for calculating the concentrations of analytes. The summary of the collected data is presented in Fig. 6. As can be noticed the majority of the determinations were performed on samples prepared in the form of pressed pellets (about 45.9% of the reported results), the second most frequent sample preparation method was decomposition by means of digestion/acid dissolution (about 38.3%). The X-ray tube excitation (about 60.1% of the reported results) was in favor of radioisotope source excitation (26.7% of results). One laboratory applied also PIXE technique delivering a significant amount of results (13.3%). For X-ray spectra deconvolution the most frequently used software was the AXIL program (about 71.7%), which is included in the QXAS software package [13], and commercial software (about 22.5%). In the case of the software used for quantitative analysis the preferences of laboratories were more or less equally spread between QXAS software package (about 30.8%), QAES program [14, 15] (about 27.5%), and commercial + in house developed software (about 35.8%).

The organizers of the proficiency test scheme are grateful to the participants for providing the additional information on the analytical process. We would like to emphasize that in order to really benefit from proficiency testing a regular participation in the exercises, with a frequency of at least once per year, is required. The laboratories are invited to take part in the next PTXRFIAEA/03 round which will be announced soon.

Acknowledgement

The XRF Group/Instrumentation Unit, which carried out this proficiency test, is grateful to the Chemistry Unit for provision of the test samples as well as to Mr. Mike Campbell and Mr. Andreas Törvényi, both Chemistry Unit, for their kind assistance and provision of the data on the IAEA-338 lichen material.

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LITERATURE

1. M. Thompson, R. Wood, *J. AOAC International* **76**, 926 (1993).
2. ISO Guide 43, 2nd Edition, Geneva (1993).
3. E. Hund, D. L. Massart, J. Smeyers-Verbeke, *Anal. Chim. Acta* **423**, 145 (2000).
4. M. Makarewicz, IAEA Chemistry Unit Report, CU-96-017.
5. M. J. Campbell and A. Törvényi, IAEA/AL/148 Report, Overall Evaluation of the Proficiency Test on the determination of selected Trace Elements in a Lichen material, IAEA-338 (in preparation).
6. M. Thompson, *Analyst* **125**, 385 (2000).
7. F. E. Grubbs, *Technometrics* **11**, No. 1 (1969).
8. A. Veglia, International Atomic Energy Agency, Report No. IAEA/RL/84, August 1981.
9. L. Pszonicki, A. N. Hanna, O. Suschny, Report on Intercomparison IAEA/Soil-7 of the Determination of Trace Elements in Soil, IAEA/RL/112, May 1984.
10. M. G. Natrella, 'Experimental Statistic', National Bureau of Standards Handbook 91.
11. R. Zielinski, Statistical Tables, PWN Warszawa 1972.
12. F. E. Grubbs, *Annals of Mathematical Statistics* **21**, 27 (1950).
13. QXAS, Quantitative X-Ray Analysis System, Software Manual ver. 1.2, IAEA Laboratories, Seibersdorf, Austria.
14. P. Kump, Quantitative Analysis of Environmental Samples (QAES), Software Manual, unpublished.
15. J. Mellawati, M. Sumarti, Y. Menry, S. Surtipanti, P. Kump, *Appl. Radiat. Isotop.* **54**, 881 (2001).

APPENDIX I

Tables 1-5

Table 1. The names of the analysts and the laboratories participating in the proficiency test exercise.

Analyst name and contact e-mail address	Institution	Country
Ivone Mulako Sato, Marcos Antonio Scapin imsato@ipen.br	IPEN/CQMA - Instituto de Pesquisas Energéticas e Nucleares, LFX - Laboratório de Fluorescência de Raios X Av. Prof. Lineu Prestes, 2242 - Cidade Universitária, 05508-000 São Paulo, SP	**Brazil**
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Table 1 continued

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Table 2. The codes, the full and the abbreviated names of the X-ray spectrometry techniques applied by the participants of the proficiency test exercise.

Technique Code	Full name	Abbreviation
1.1	Energy dispersive X-ray fluorescence spectrometry, radioisotope excitation	EDXRFS-R
1.2	Energy dispersive X-ray fluorescence spectrometry, X-ray tube excitation	EDXRFS-T
1.3	Total reflection X-ray fluorescence spectrometry	TXRFS
2.0	Wavelength dispersive X-ray fluorescence spectrometry	WDXRFS
4.0	Particle induced X-ray emission	PIXE

Table 3. The assigned analyte values, the target values of the standard deviations, and the consensus values based on the results reported by the participants. The analytes marked in bold-red correspond to elements the consensus values of which showed a bias as compared to the assigned values.

Atomic number	Analyte symbol	Assigned value of the analyte, XA	Target value of standard deviation, σ_A			Consensus value of the analyte, XC	Consensus value of the standard deviation, σC	Number of results	Number of outliers	Normality test*
			$k = 0.5$	$k = 1.0$	$k = 1.5$					
			[mg/kg]							
23	**V**	**3.68**	**0.24**	**0.48**	**0.72**	**6.8**	**1.3**	**5**	**0**	**-**
25	Mn	52.8	2.3	4.6	6.9	53.4	1.9	19	1	passed
26	Fe	900	26	52	78	927	28	19	1	passed
29	Cu	8.00	0.47	0.94	1.41	8.71	0.59	16	2	passed
30	Zn	106	4	8	12	116	6	19	0	passed
33	**As**	**0.93**	**0.075**	**0.15**	**0.225**	**3.7**	**1.0**	**5**	**1**	**-**
38	Sr	5.45	0.34	0.68	1.02	5.64	0.32	16	0	passed
48	**Cd**	**0.57**	**0.05**	**0.10**	**0.15**	**6.70**	**0.45****	**1**	**0**	**-**
56	Ba	24.9	1.25	2.5	3.75	22.6	6.6	3	1	-
82	Pb	57.1	2.5	5.0	7.5	51.4	2.2	17	0	passed

*- the populations with at least 6 reported results were tested using Kolmogorov-Smirnov test, after rejecting the outliers all examined populations passed the test.

**- the standard deviation reported by the laboratory which submitted the result for cadmium.

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. For each analyte its assigned value and the target value of the standard deviation (for parameter $k = 1.0$) were shown in brackets next to the element symbol. The number of decimal digits in the analyte concentration and standard dev. columns has been shown as reported by the laboratory.

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
V (3.68 ± 0.48) [mg·kg^{-1}]										
3	1.3	3.723	0.5381	14.45	0.18	0.09	0.06	0.07	0.06	0.05
14	1.3	4.72	0.4	8.47	4.30	2.15	1.43	2.23	1.66	1.26
17	4	6.46	1.36	21.05	11.49	5.75	3.83	2.01	1.93	1.80
17	4	8.259	0.263	3.18	18.93	9.46	6.31	12.81	8.32	5.93
6	1.1	10.6	2.3	21.7	28.60	14.30	9.53	2.99	2.94	2.87
Mn (52.8 ± 4.6) [mg·kg^{-1}]										
1	2	40.478	0.589	1.46	-5.30	-2.65	-1.77	5.14	2.63	1.76
14	1.3	43.2	2.2	5.09	-4.13	-2.07	-1.38	3.00	1.87	1.31
9	1.3	46.1	0.5	1.08	-2.88	-1.44	-0.96	2.82	1.43	0.96
13	1.1	46.7	4.5	9.64	-2.62	-1.31	-0.87	1.20	0.94	0.73
15	1.2	47.07	3.97	8.43	-2.47	-1.23	-0.82	1.25	0.94	0.71
17	4	49.95	2.82	5.65	-1.23	-0.61	-0.41	0.78	0.52	0.38
17	4	50.49	1.77	3.51	-0.99	-0.50	-0.33	0.79	0.46	0.32
12	1.3	50.755	0.798	1.57	-0.88	-0.44	-0.29	0.83	0.43	0.29
11	1.2	50.8	5.3	10.43	-0.86	-0.43	-0.29	0.35	0.28	0.23
16	1.1	53.15	7.85	14.77	0.15	0.08	0.05	0.04	0.04	0.03
4	1.3	53.8	3.8	7.06	0.43	0.22	0.14	0.22	0.17	0.13
5	1.2	55	4	7.27	0.95	0.47	0.32	0.48	0.36	0.27
3	1.3	56.555	2.68	4.74	1.62	0.81	0.54	1.06	0.70	0.50
2	1.1	57	5	8.77	1.81	0.90	0.60	0.76	0.62	0.49
10	2	60	-	-	3.10	1.55	1.03	3.10	1.55	1.03
8	1.3	65	12	18.46	5.25	2.62	1.75	1.00	0.95	0.88
7	1.1	68	10	14.71	6.54	3.27	2.18	1.48	1.38	1.25
7	1.2	68	5	7.35	6.54	3.27	2.18	2.76	2.23	1.77
6	1.1	80*	8	10	11.70	5.85	3.90	3.27	2.94	2.56
Fe (900 ± 52) [mg·kg^{-1}]										
1	2	549.56*	1.55	0.28	-13.55	-6.78	-4.52	13.53	6.77	4.52
14	1.3	754	32	4.24	-5.65	-2.82	-1.88	3.55	2.40	1.74
9	1.3	783	3	0.38	-4.52	-2.26	-1.51	4.49	2.26	1.51
17	4	802.19	19.12	2.38	-3.78	-1.89	-1.26	3.04	1.77	1.22
17	4	807.63	32.46	4.02	-3.57	-1.79	-1.19	2.23	1.51	1.10
15	1.2	817	108	13.22	-3.21	-1.61	-1.07	0.75	0.69	0.62
11	1.2	849.7	49.2	5.79	-1.95	-0.97	-0.65	0.91	0.70	0.55
16	1.1	902	26.3	2.92	0.08	0.04	0.03	0.05	0.03	0.02
13	1.1	910	55	6.04	0.39	0.19	0.13	0.16	0.13	0.11
7	1.1	925	112	12.11	0.97	0.48	0.32	0.22	0.20	0.18
4	1.3	926	52	5.62	1.01	0.50	0.34	0.45	0.35	0.28

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
2	1.1	927	10	1.08	1.04	0.52	0.35	0.97	0.51	0.35
6	1.1	944	66	6.99	1.70	0.85	0.57	0.62	0.52	0.43
12	1.3	955.683	6.513	0.68	2.15	1.08	0.72	2.09	1.07	0.72
7	1.2	964	17	1.76	2.48	1.24	0.83	2.07	1.18	0.81
5	1.2	1081	54	5	7.00	3.50	2.33	3.02	2.42	1.92
10	2	1100	-	-	7.73	3.87	2.58	7.73	3.87	2.58
8	1.3	1100	70	6.36	7.73	3.87	2.58	2.68	2.30	1.91
3	1.3	1134.8	33.633	2.96	9.08	4.54	3.03	5.53	3.81	2.78
Cu (8.00 ± 0.94) [mg·kg^{-1}]										
13	1.1	3.83	0.6	15.67	-8.91	-4.46	-2.97	5.48	3.75	2.73
14	1.3	6.51	0.33	5.07	-3.18	-1.59	-1.06	2.60	1.50	1.03
9	1.3	7.6	0.3	3.95	-0.85	-0.43	-0.28	0.72	0.41	0.28
17	4	7.713	0.178	2.31	-0.61	-0.31	-0.20	0.57	0.30	0.20
15	1.2	7.744	0.748	9.66	-0.55	-0.27	-0.18	0.29	0.21	0.16
2	1.1	8	1	12.5	0.00	0.00	0.00	0.00	0.00	0.00
17	4	8.235	0.889	10.8	0.50	0.25	0.17	0.23	0.18	0.14
4	1.3	8.51	0.75	8.81	1.09	0.55	0.36	0.58	0.43	0.32
7	1.2	9.1	1.2	13.19	2.35	1.18	0.78	0.85	0.72	0.60
3	1.3	9.146	1.8033	19.72	2.45	1.23	0.82	0.62	0.56	0.50
6	1.1	11	1.4	12.73	6.41	3.21	2.14	2.03	1.78	1.51
5	1.2	11	1.5	13.64	6.41	3.21	2.14	1.91	1.70	1.46
11	1.2	11.5	1.4	12.17	7.48	3.74	2.49	2.37	2.08	1.77
7	1.1	12	2	16.67	8.55	4.27	2.85	1.95	1.81	1.64
12	1.3	14.938*	0.361	2.42	14.83	7.41	4.94	11.74	6.92	4.79
10	2	24*	-	-	34.19	17.10	11.40	34.19	17.10	11.40
Zn (106 ± 8) [mg·kg^{-1}]										
1	2	68.16	1.07	1.57	-9.00	-4.50	-3.00	8.73	4.47	2.99
13	1.1	76.8	7	9.11	-6.95	-3.47	-2.32	3.58	2.67	2.03
15	1.2	94.1	13	13.82	-2.83	-1.42	-0.94	0.87	0.77	0.66
5	1.2	97	5	5.15	-2.14	-1.07	-0.71	1.38	0.92	0.66
7	1.2	103	3	2.91	-0.71	-0.36	-0.24	0.58	0.34	0.23
14	1.3	103.1	4.2	4.07	-0.69	-0.35	-0.23	0.49	0.31	0.22
16	1.1	105	6.55	6.24	-0.24	-0.12	-0.08	0.13	0.09	0.07
17	4	108.5	3.62	3.34	0.59	0.30	0.20	0.45	0.27	0.19
17	4	108.83	5.18	4.76	0.67	0.34	0.22	0.42	0.29	0.21
11	1.2	110	6.7	6.09	0.95	0.48	0.32	0.51	0.37	0.28
7	1.1	114	7	6.14	1.90	0.95	0.63	0.98	0.73	0.55
4	1.3	117.5	6.7	5.7	2.74	1.37	0.91	1.45	1.07	0.81
9	1.3	121	1	0.83	3.57	1.79	1.19	3.47	1.77	1.19
6	1.1	128	10	7.81	5.24	2.62	1.75	2.03	1.68	1.37
3	1.3	133.92	4.8602	3.63	6.64	3.32	2.22	4.35	2.88	2.07
8	1.3	137	13	9.49	7.38	3.69	2.46	2.27	2.00	1.71
10	2	139	-	-	7.85	3.93	2.62	7.85	3.93	2.62
12	1.3	156.789	0.293	0.19	12.09	6.04	4.03	12.06	6.04	4.03
2	1.1	179	3	1.68	17.37	8.69	5.79	14.14	8.18	5.63

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
As (0.93 ± 0.15) [mg·kg^{-1}]										
14	1.3	1.6	0.17	10.62	8.91	4.46	2.97	3.60	2.95	2.37
17	4	2.594	0.394	15.19	22.13	11.06	7.38	4.15	3.95	3.67
17	4	4.71	1.49	31.63	50.26	25.13	16.75	2.53	2.52	2.51
5	1.2	6	1	16.67	67.42	33.71	22.47	5.06	5.01	4.95
2	1.1	27*	5	18.52	346.70	173.30	115.60	5.21	5.21	5.21
Sr (5.45 ± 0.68) [mg·kg^{-1}]										
7	1.1	3.6	0.4	11.11	-5.48	-2.74	-1.83	3.53	2.36	1.70
6	1.1	4	0.4	10	-4.29	-2.15	-1.43	2.77	1.85	1.33
7	1.2	4.2	0.3	7.14	-3.70	-1.85	-1.23	2.77	1.69	1.18
9	1.3	4.3	0.3	6.98	-3.41	-1.70	-1.14	2.55	1.56	1.09
10	2	5	-	-	-1.33	-0.67	-0.44	1.33	0.67	0.44
15	1.2	5	1.04	20.8	-1.33	-0.67	-0.44	0.41	0.36	0.31
11	1.2	5.4	0.7	12.96	-0.15	-0.07	-0.05	0.06	0.05	0.04
1	2	5.427	0.266	4.9	-0.07	-0.03	-0.02	0.05	0.03	0.02
14	1.3	5.44	0.26	4.78	-0.03	-0.01	-0.01	0.02	0.01	0.01
17	4	5.97	0.36	6.03	1.54	0.77	0.51	1.05	0.68	0.48
16	1.1	6.02	1.34	22.26	1.69	0.84	0.56	0.41	0.38	0.34
17	4	6.701	0.378	5.64	3.70	1.85	1.24	2.47	1.62	1.16
12	1.3	6.954	0.371	5.34	4.45	2.23	1.48	3.00	1.95	1.39
3	1.3	7.248	0.7566	10.44	5.32	2.66	1.77	2.17	1.77	1.42
4	1.3	7.25	0.58	8	5.33	2.67	1.78	2.68	2.02	1.54
13	1.1	7.67	0.65	8.47	6.57	3.29	2.19	3.03	2.37	1.84
Cd (0.57 ± 0.10) [mg·kg^{-1}]										
6	1.1	6.7	0.45	6.72	123.60	61.78	41.18	13.54	13.30	12.93
Ba (24.9 ± 2.5) [mg·kg^{-1}]										
2	1.1	16	2	12.5	-7.25	-3.63	-2.42	3.79	2.81	2.12
6	1.1	29.1	1.6	5.5	3.42	1.71	1.14	2.08	1.43	1.05
8	1.3	330*	70	21.21	248.50	124.30	82.84	4.36	4.36	4.35
Pb (57.1 ± 5.0) [mg·kg^{-1}]										
4	1.3	33.8	2.1	6.21	-9.38	-4.69	-3.13	7.16	4.32	3.01
17	4	39.85	3.36	8.43	-6.94	-3.47	-2.31	4.13	2.88	2.11
7	1.2	44.6	1.1	2.47	-5.03	-2.52	-1.68	4.60	2.46	1.66
9	1.3	46.4	0.1	0.22	-4.31	-2.15	-1.44	4.30	2.15	1.44
17	4	46.42	2.95	6.36	-4.30	-2.15	-1.43	2.77	1.85	1.33
14	1.3	48.2	2.4	4.98	-3.58	-1.79	-1.19	2.58	1.61	1.14
15	1.2	48.31	7.06	14.61	-3.54	-1.77	-1.18	1.17	1.02	0.86
8	1.3	50	7	14	-2.86	-1.43	-0.95	0.96	0.83	0.69
2	1.1	50	5	10	-2.86	-1.43	-0.95	1.27	1.01	0.79
7	1.1	50	3	6	-2.86	-1.43	-0.95	1.82	1.22	0.88
11	1.2	52.2	3.5	6.7	-1.97	-0.99	-0.66	1.14	0.81	0.60
5	1.2	54	5	9.26	-1.25	-0.62	-0.42	0.56	0.44	0.35
10	2	56	-	-	-0.44	-0.22	-0.15	0.44	0.22	0.15

Table 4 continued…

Laboratory code	Technique code	Analyte concentration	Standard dev.	Relative std. dev., [%]	*z*-scores			*u*-scores		
					$k = 0.5$	$k = 1.0$	$k = 1.5$	$k = 0.5$	$k = 1.0$	$k = 1.5$
16	1.1	57.9	6.12	10.57	0.32	0.16	0.11	0.12	0.10	0.08
6	1.1	62	4.7	7.58	1.97	0.99	0.66	0.92	0.72	0.56
3	1.3	62.732	1.8117	2.89	2.27	1.13	0.76	1.83	1.07	0.73
12	1.3	70.894	0.531	0.75	5.55	2.78	1.85	5.43	2.76	1.85

Table 5. The combined *z*-scores, critical values of the χ^2 distribution (significance level = 0.05, double sided test, number of the degrees of freedom in the "Number of analytes" column).

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	4	-13.96	-6.98	-4.65	293	73	33	11.14
2	7	134.90	67.43	44.95	120500	30140	13390	16.01
3	7	10.42	5.21	3.47	169	42	19	16.01
4	6	0.50	0.25	0.17	126	32	14	14.45
5	6	32.00	16.00	10.67	4642	1161	516	14.45
6	9	59.43	29.72	19.81	16330	4081	1814	19.02
7	12	3.33	1.67	1.11	253	63	28	23.34
8	5	119.00	59.49	39.66	61910	15480	6879	12.83
9	6	-5.06	-2.53	-1.69	72	18	8	14.45
10	6	20.86	10.43	6.95	1302	326	145	14.45
11	6	1.43	0.72	0.48	65	16	7	14.45
12	6	15.59	7.80	5.20	422	106	47	14.45
13	5	-5.15	-2.58	-1.72	178	44	20	12.83
14	8	-1.43	-0.72	-0.48	170	43	19	17.53
15	6	-5.68	-2.84	-1.90	39	10	4	14.45
16	5	0.89	0.45	0.30	3	1	0	12.83
17	16	22.10	11.05	7.37	3620	905	402	28.85

APPENDIX II

Figures 1-6

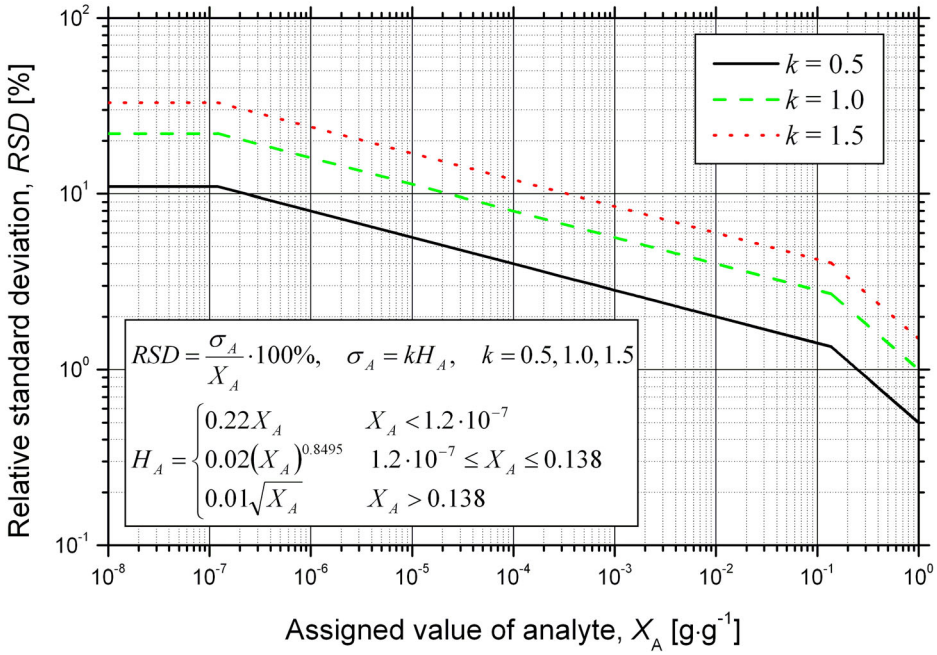


Fig. 1. Relative value of the target standard deviation, *RSD*, as a function of the assigned mass fraction of the analyte, X_A, calculated using a modified Horowitz function [5]. The target value of the standard deviation, σ_A, is related to H_A by a factor k and is recognized as fit-for-purpose at three levels of uncertainty: $k = 0.5$ (solid black line), appropriate for high precision analysis; $k = 1.0$ (dashed green line), appropriate for well established routine analysis; $k = 1.5$ (dot red line), satisfactory for common analytical tasks.

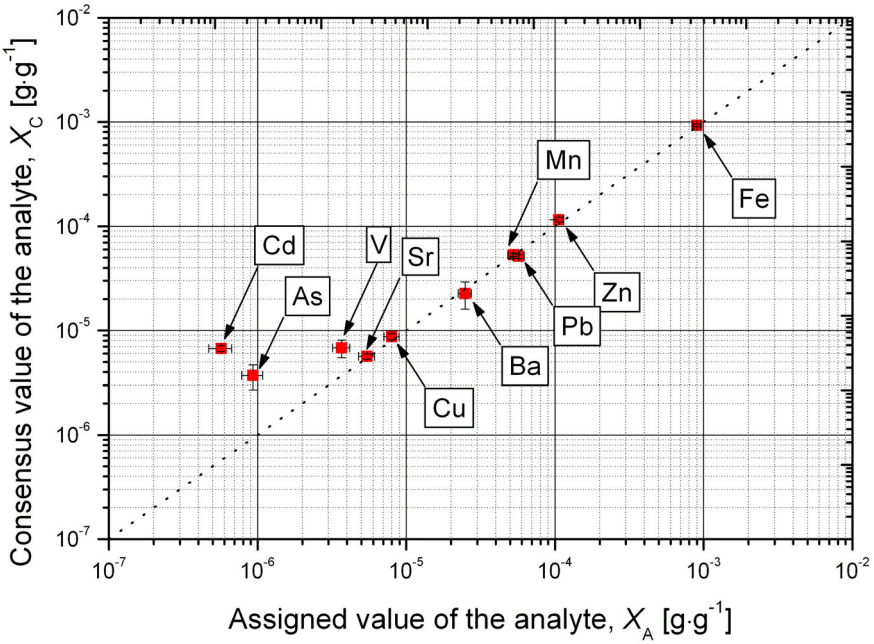


Fig. 2. The correlation between the assigned values of the analytes, X_A, and the consensus values, X_C, calculated based on the reported results (solid red squares - the analytes data, dashed line - the ideal correlation line). The uncertainties of the assigned values shown on the graph were calculated according to Eqn. (2) with $k = 1$. The uncertainties of the consensus values were calculated using Eqn.(20), except cadmium, reported by single laboratory, for which the laboratory estimate of the uncertainty was shown.

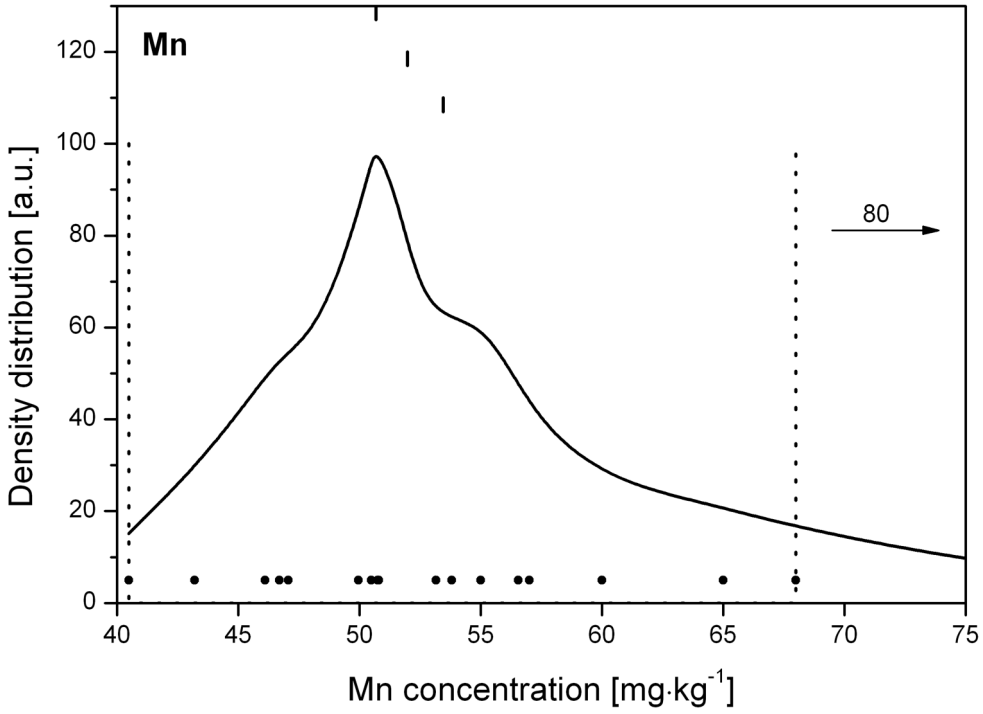
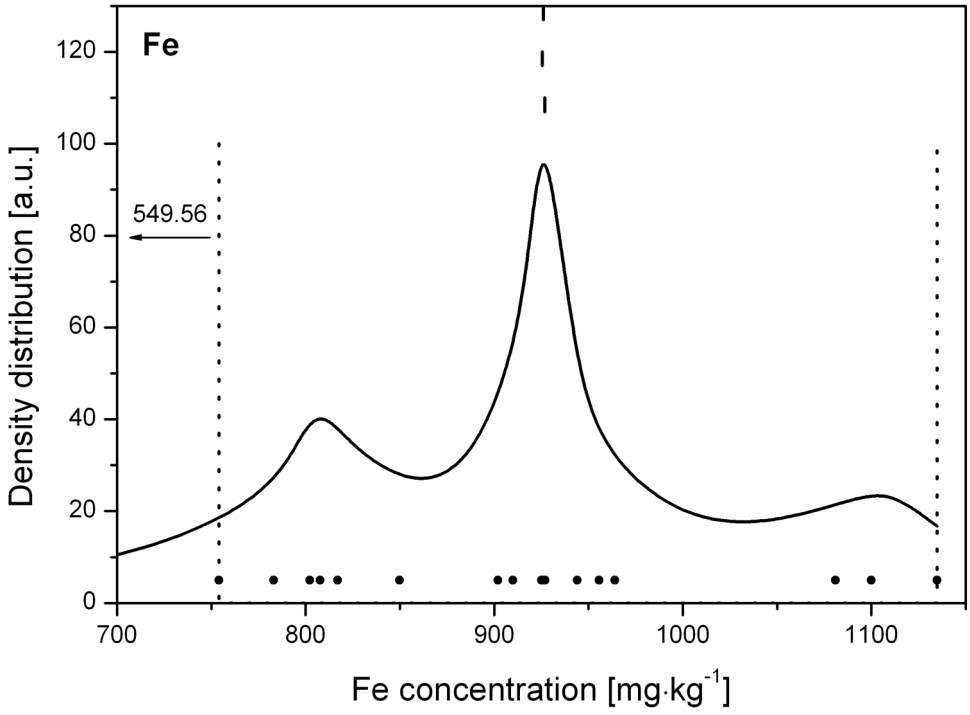


Fig. 3. The density distributions of the results for the analytes reported by at least 6 laboratories. The reported laboratory results were marked with filled circles. If outliers were present in the population the dotted lines were used to show the range of the accepted results taken for calculating the consensus values, the outlier values were shown and the outlier direction was marked with arrow. With markers positioned above the distribution curves, the estimated parameters of the distribution: mode, median, and mean value are also marked.

Fig. 3 continued…



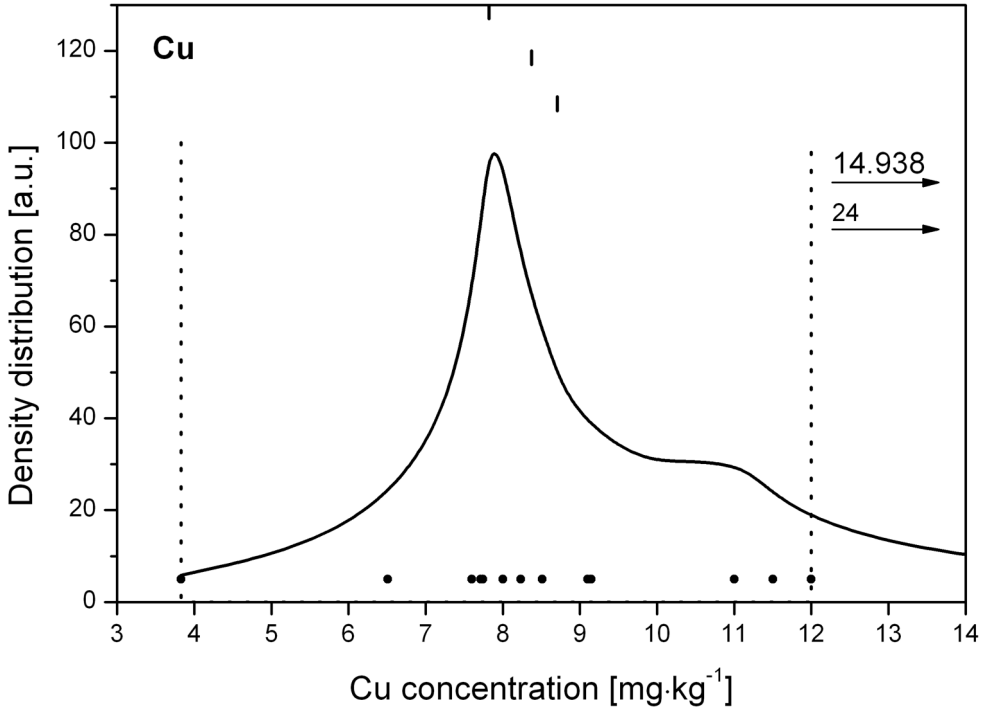
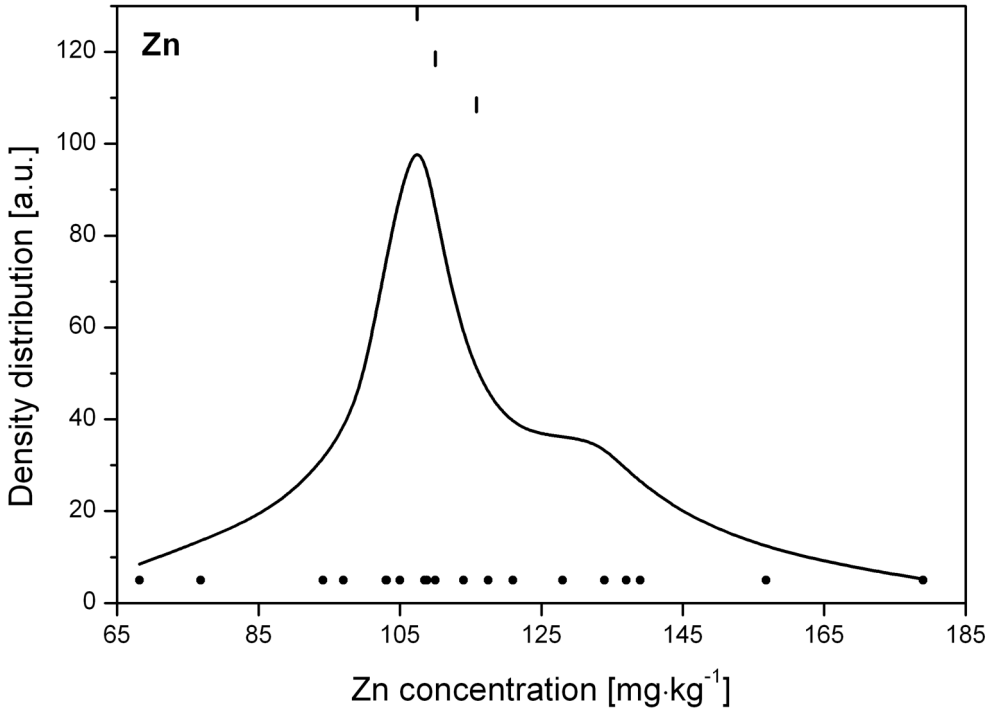


Fig. 3 continued…



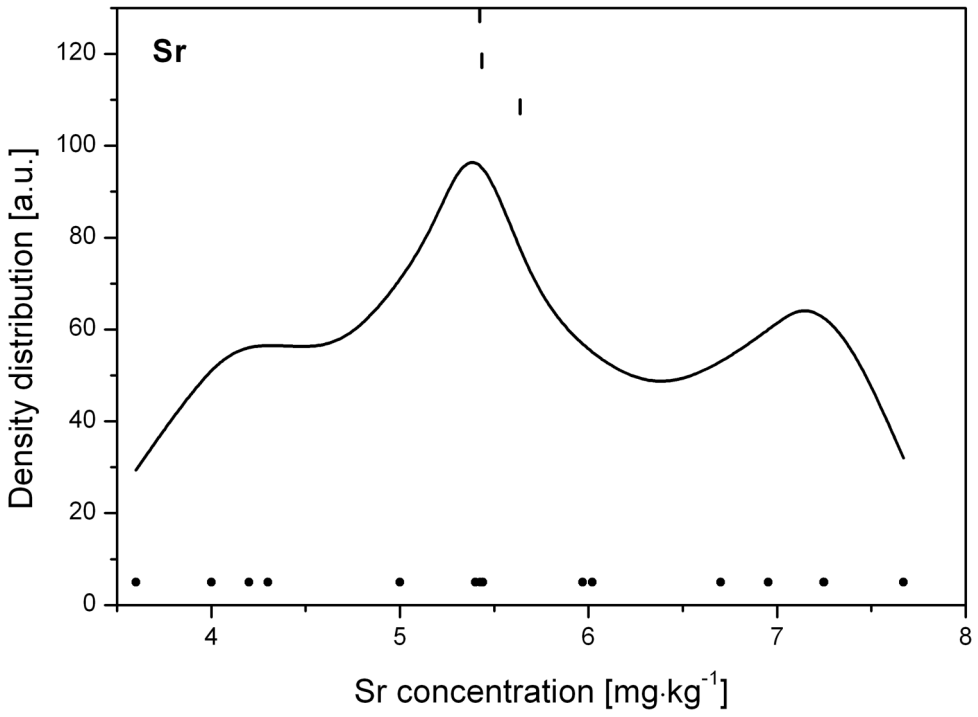
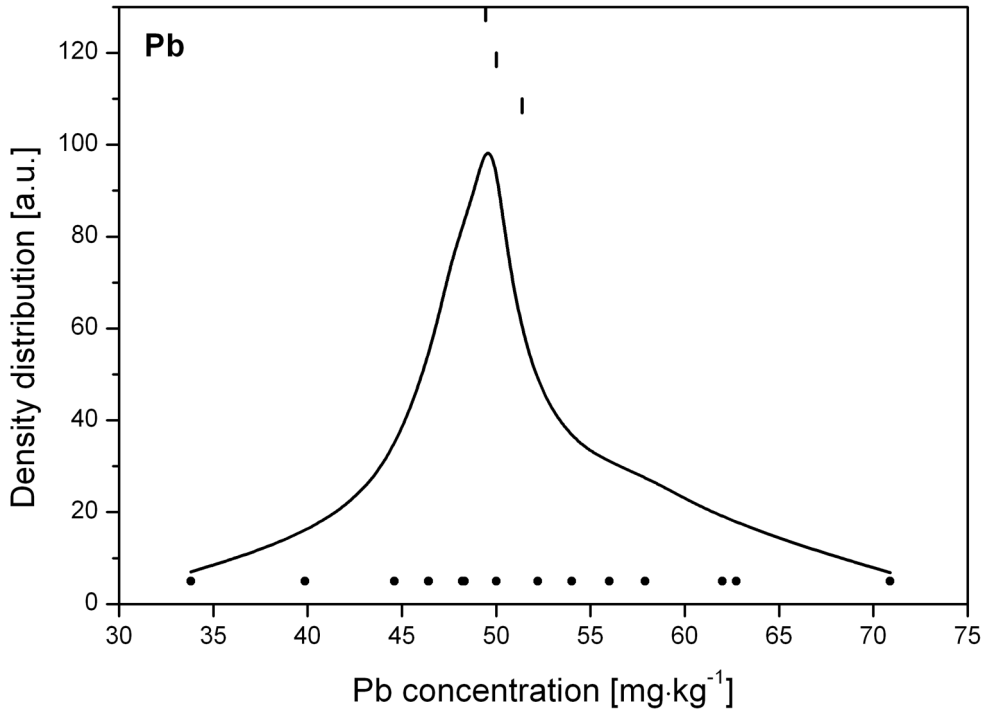


Fig. 3 continued…



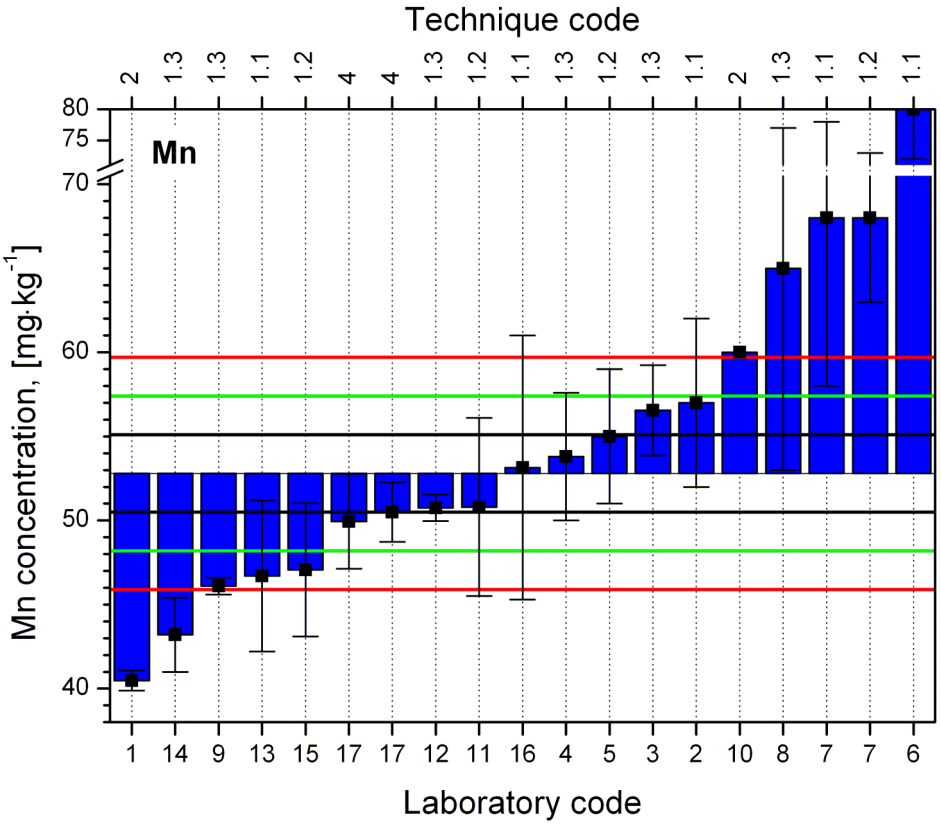
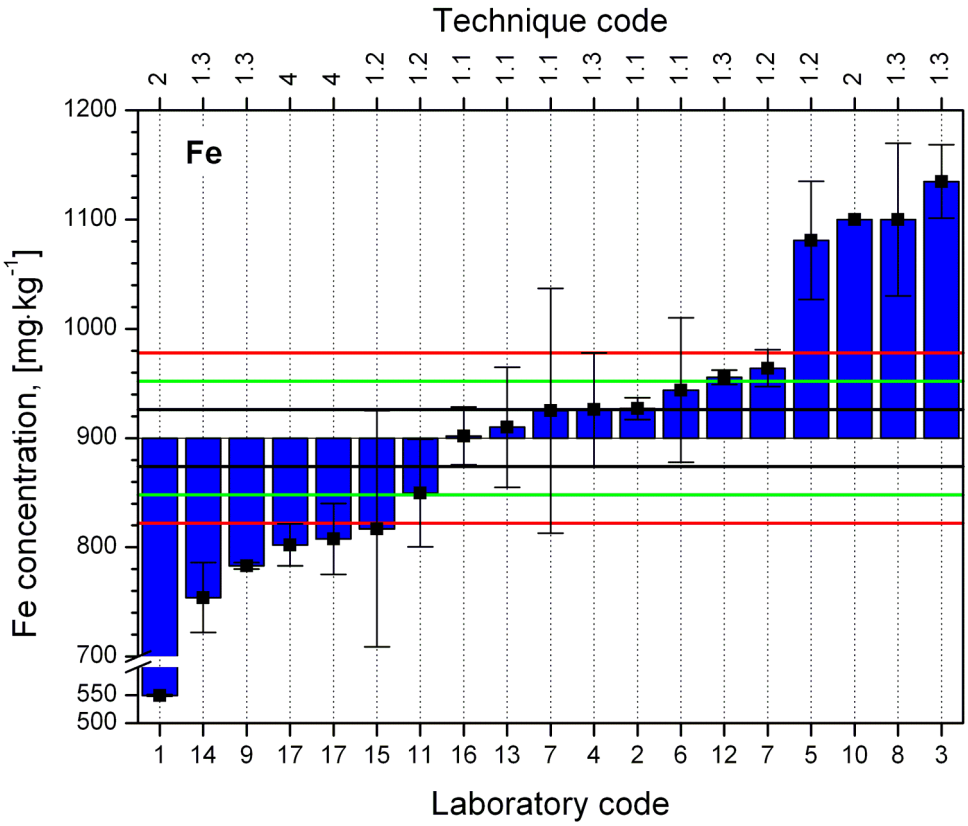


Fig. 4. The distributions of the results for analytes reported by at least 6 laboratories. The bar charts show the distance between the reported and the assigned value of the analyte. The reported values and their uncertainties, as provided by the analyst, are marked with the filled squares accompanied 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…



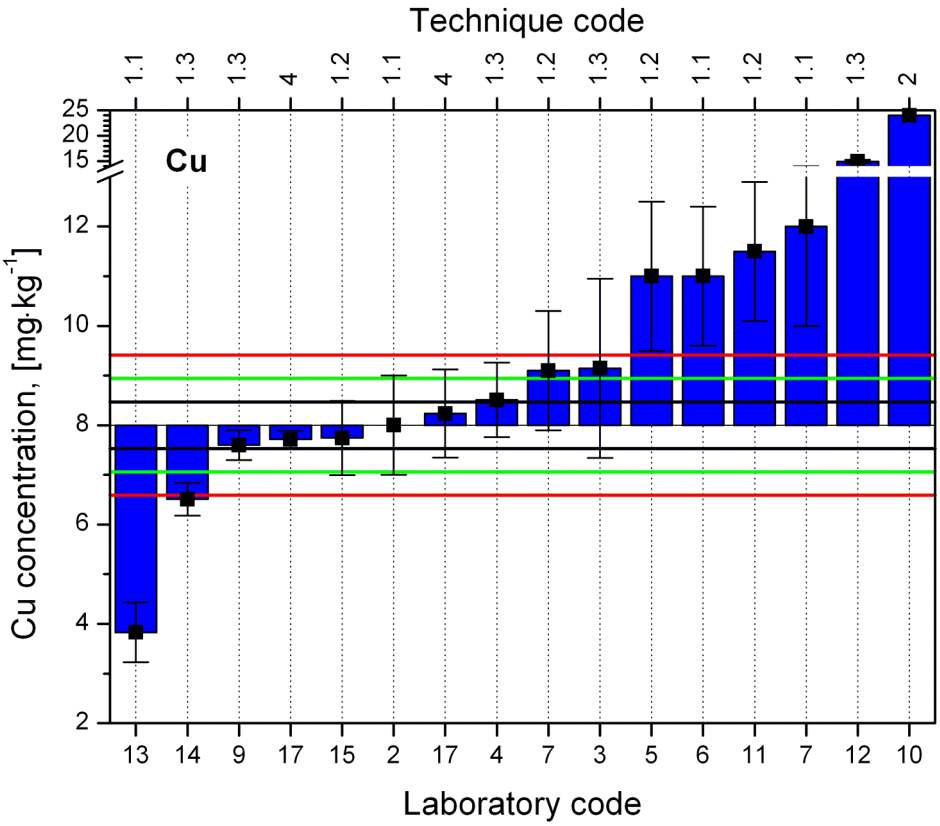
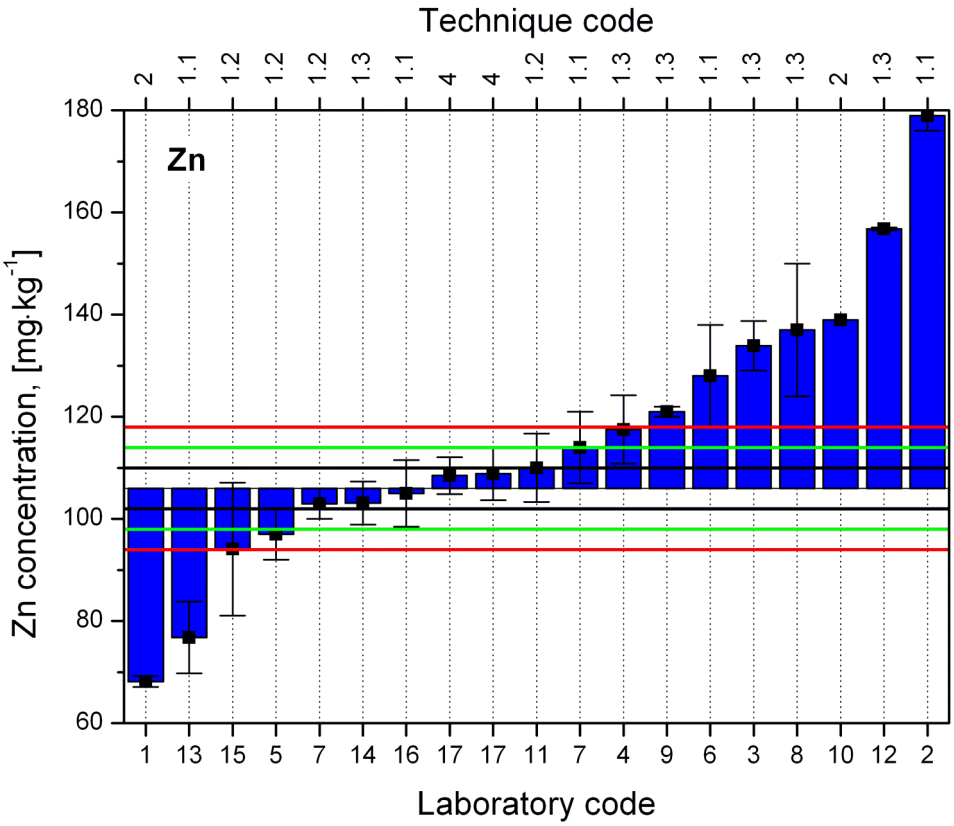


Fig. 4 continued…



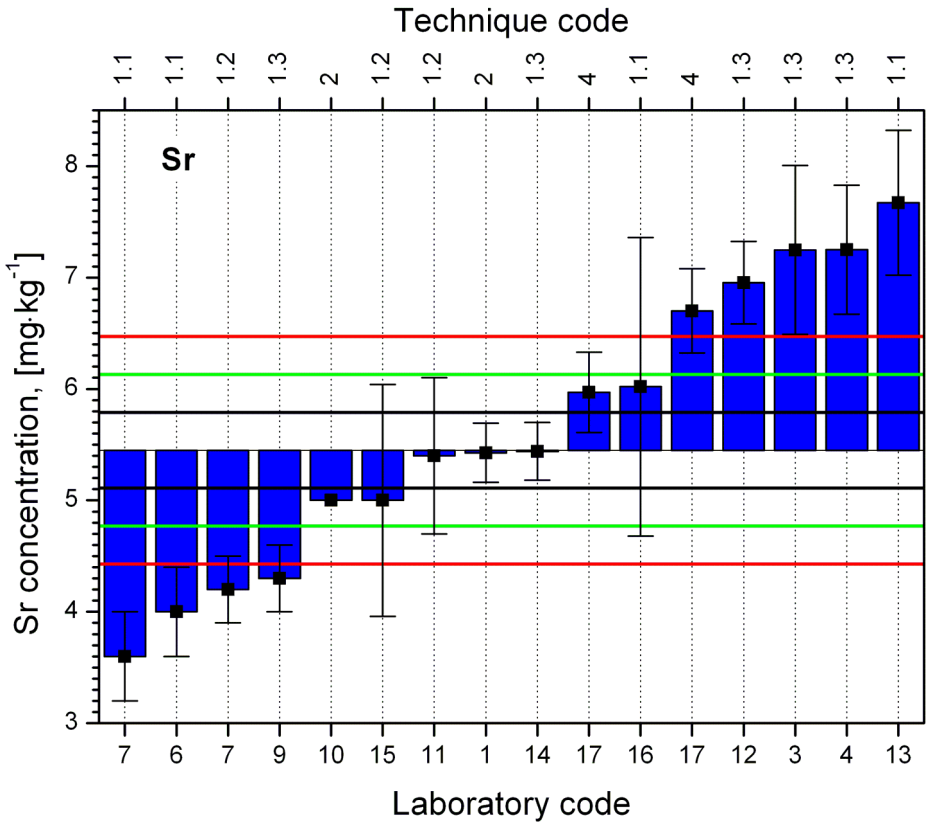
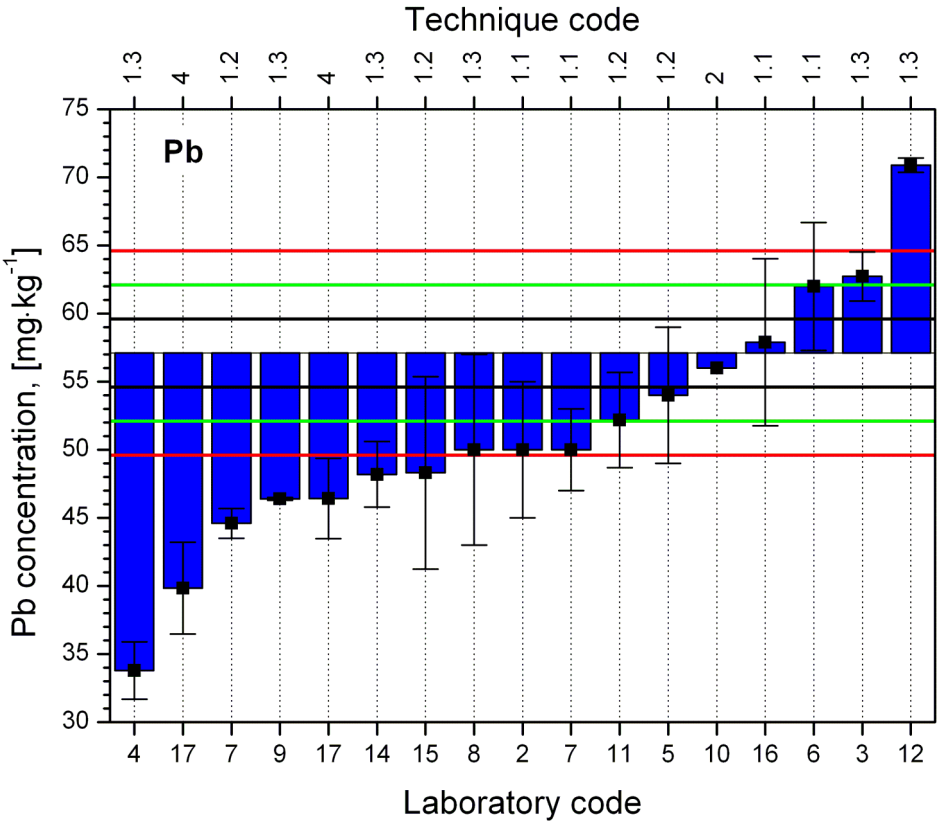


Fig. 4 continued…



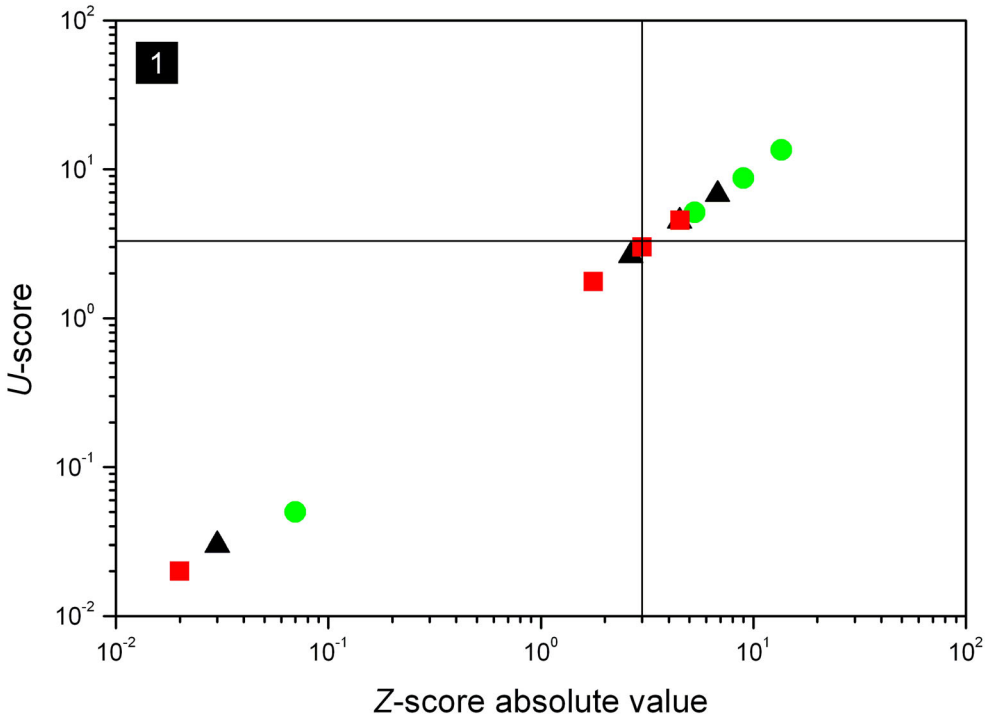
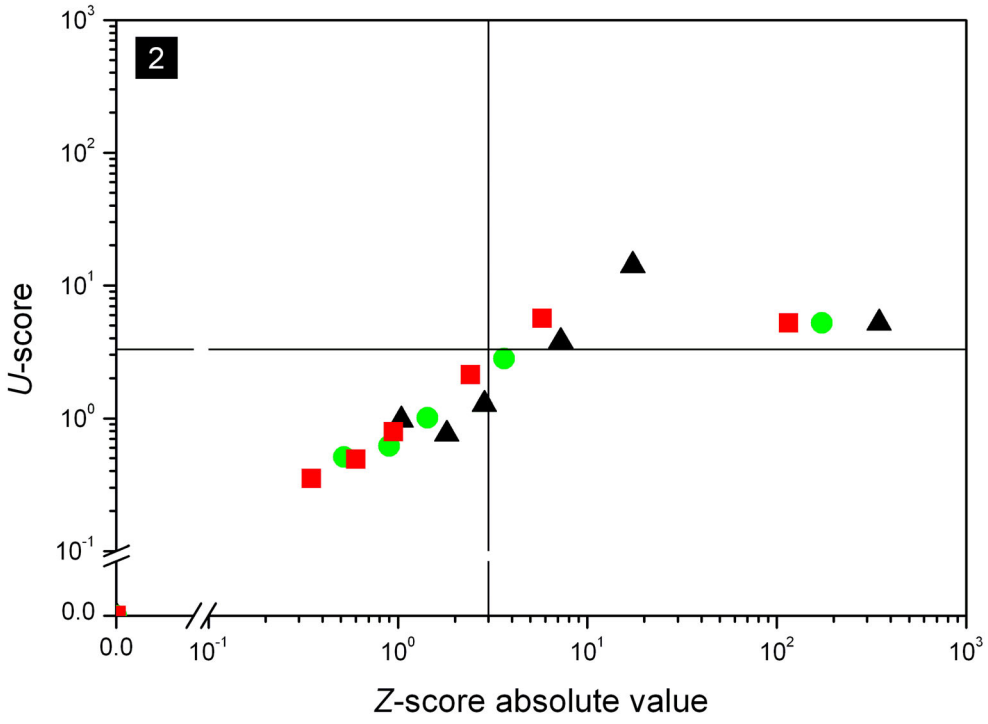


Fig. 5. Combined plots of *z*-scores and *u*-scores for participating laboratories. The laboratory code is shown in left upper corner of each plot. The hollow symbols denote the values calculated for specific fit-for-purpose levels as defined in Eqn. (2) with factor *k*, namely: $k = 0.5$ (black diamond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

Fig. 5 continued…



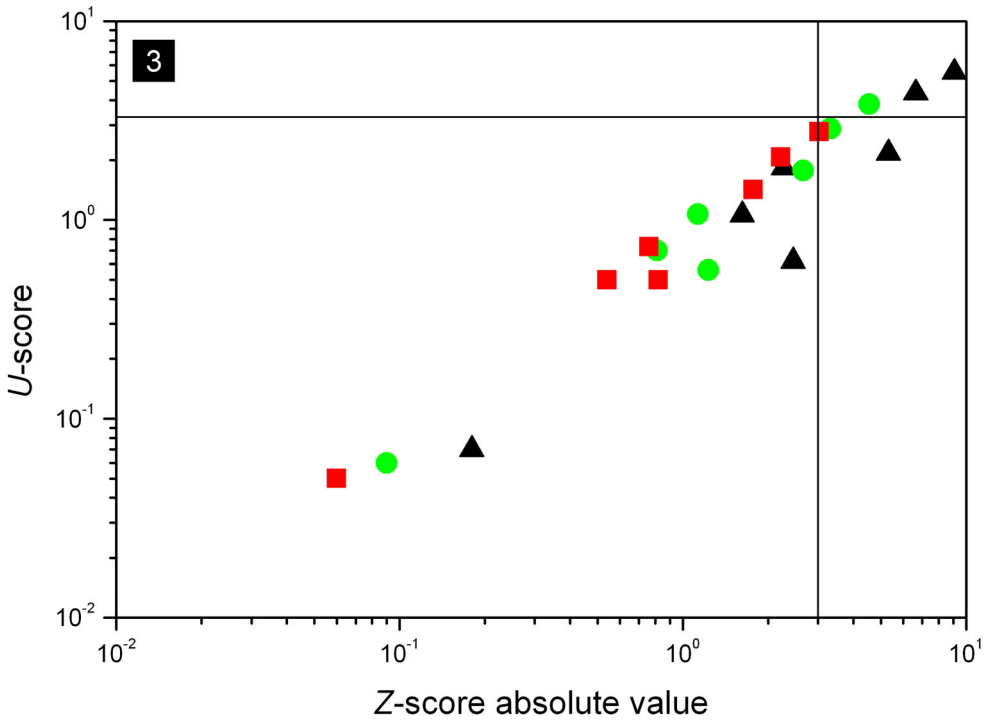


Fig. 5 continued…

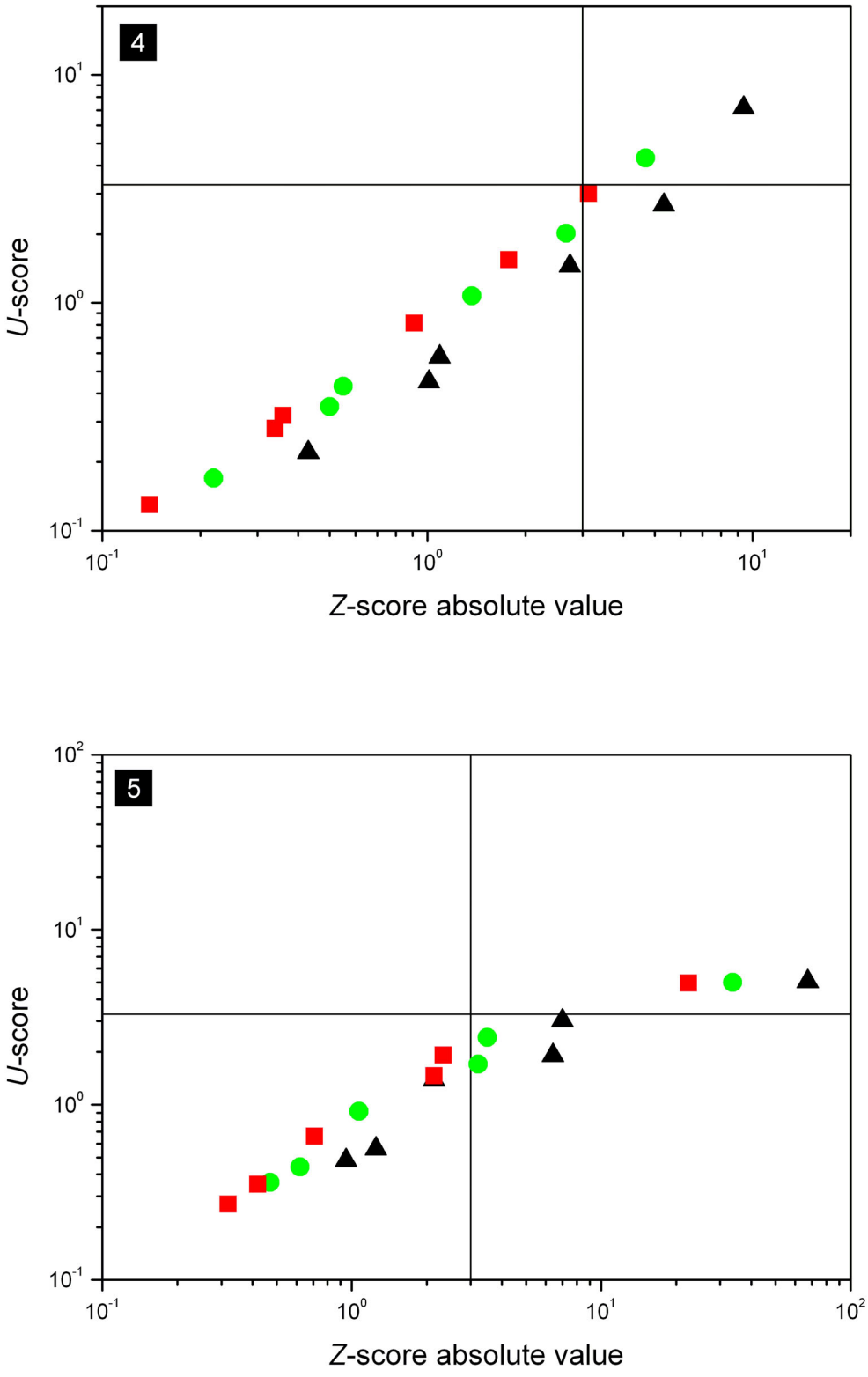
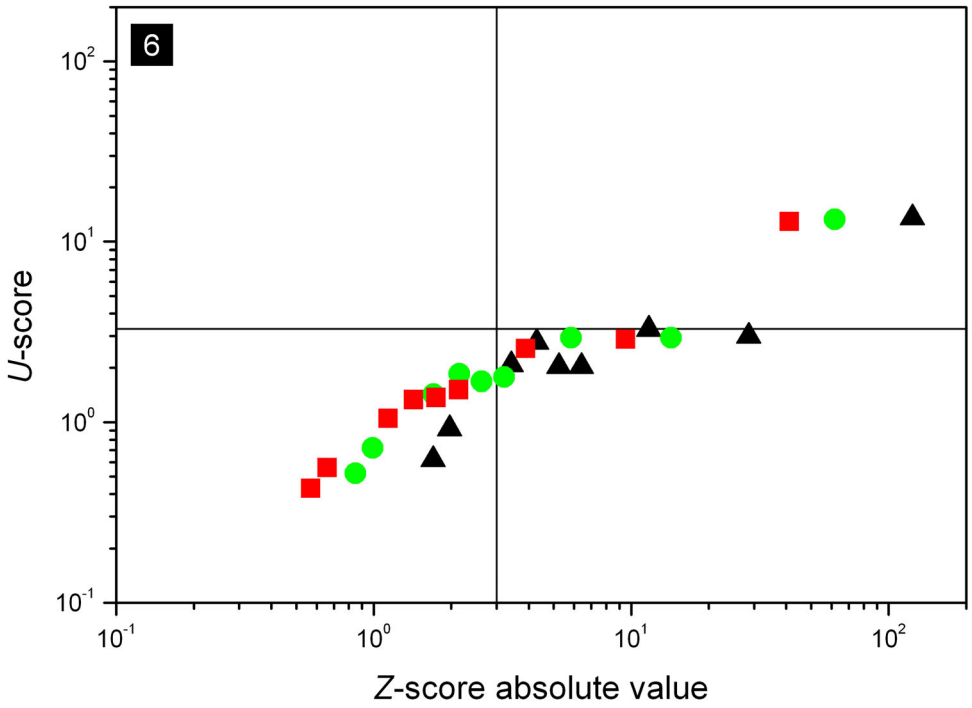


Fig. 5 continued…



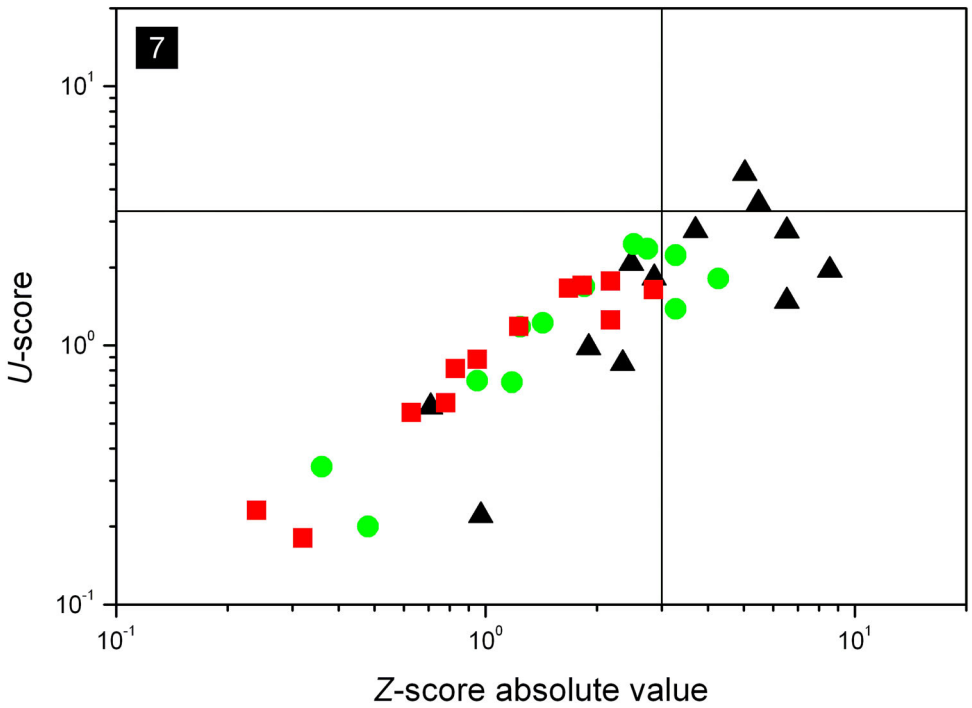
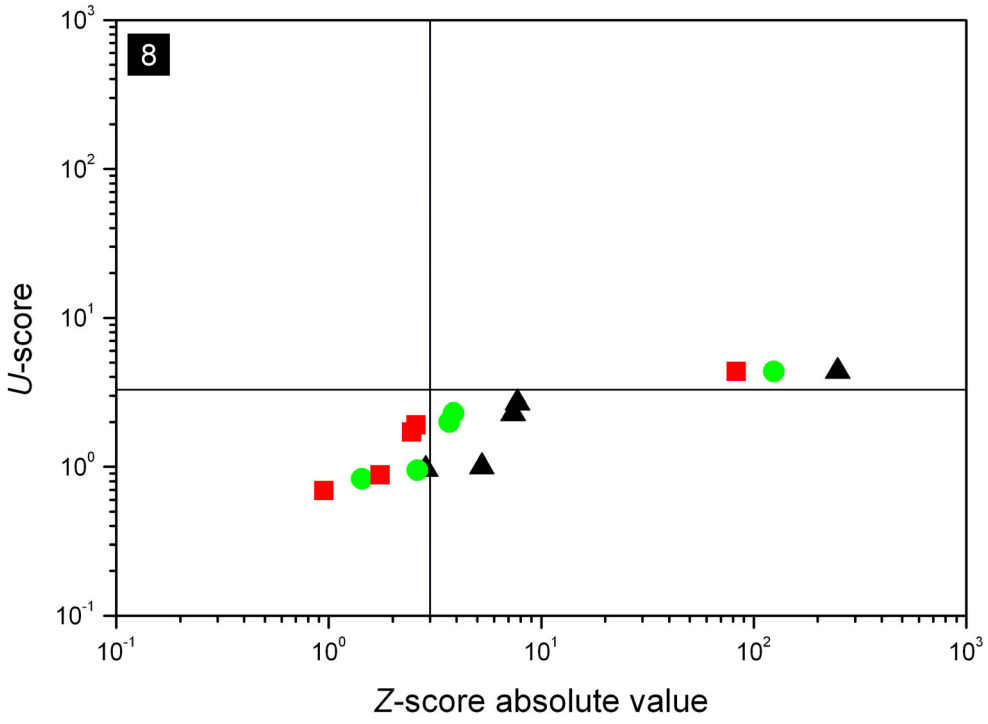


Fig. 5 continued…



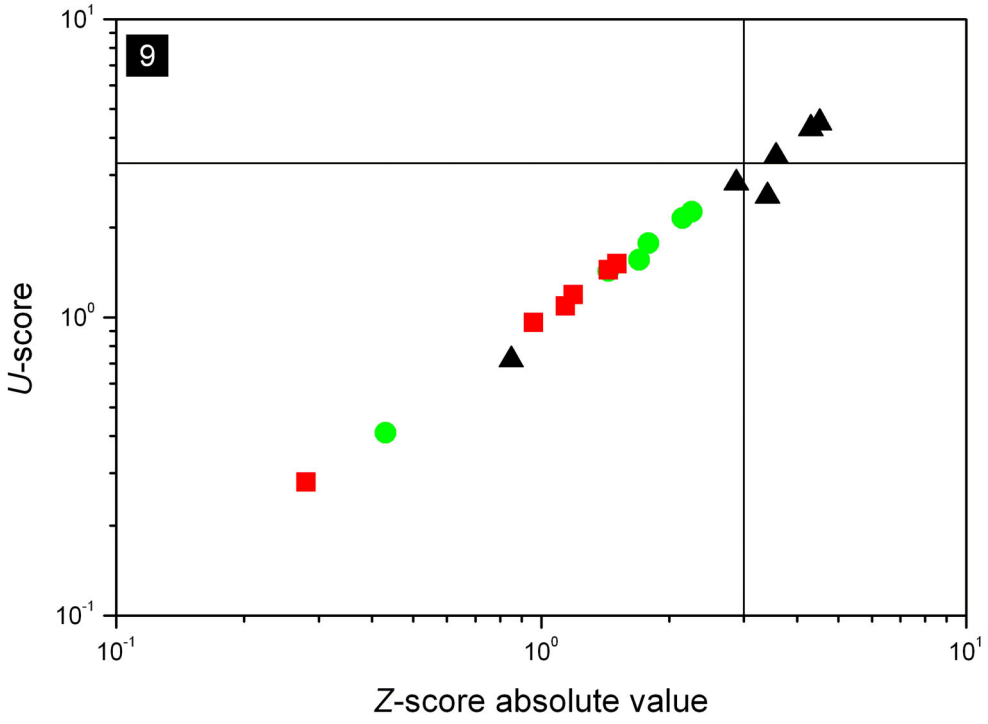
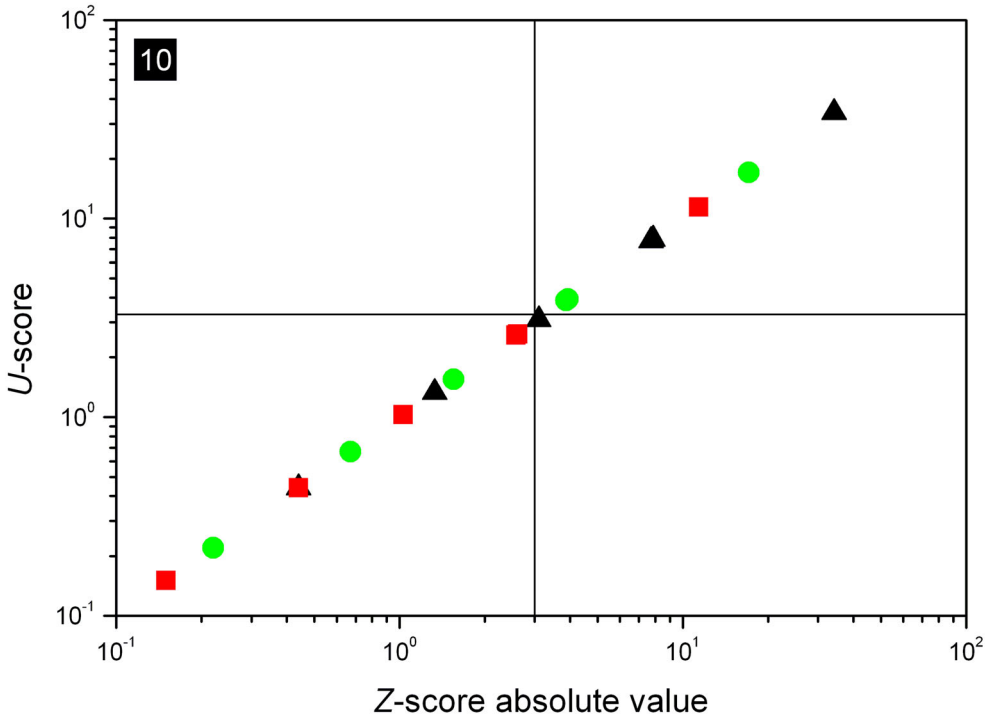
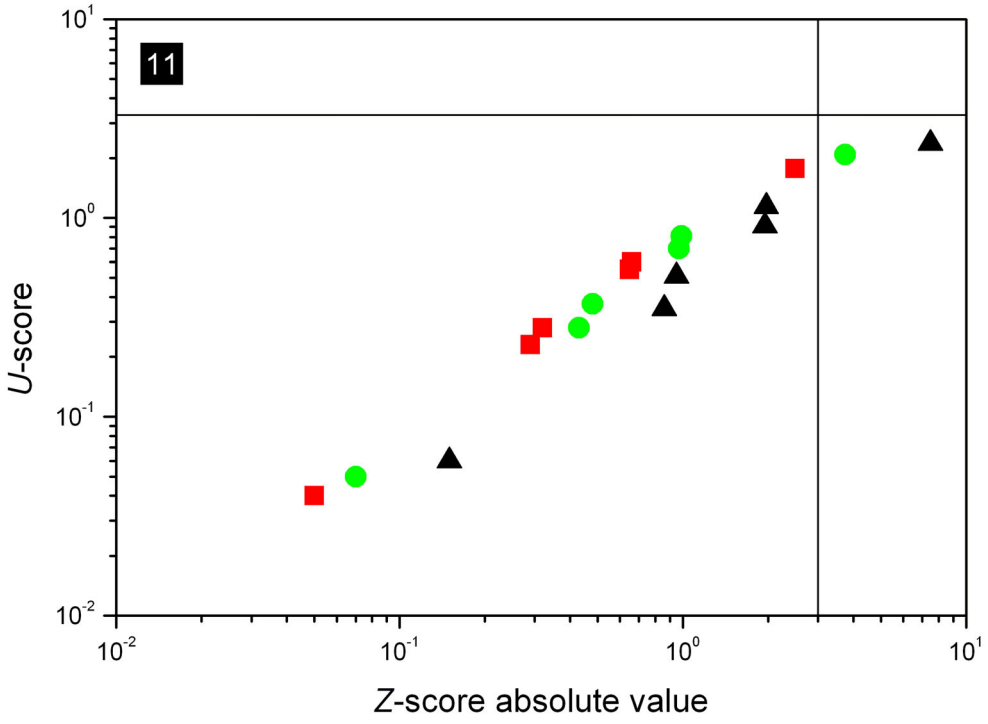


Fig. 5 continued…





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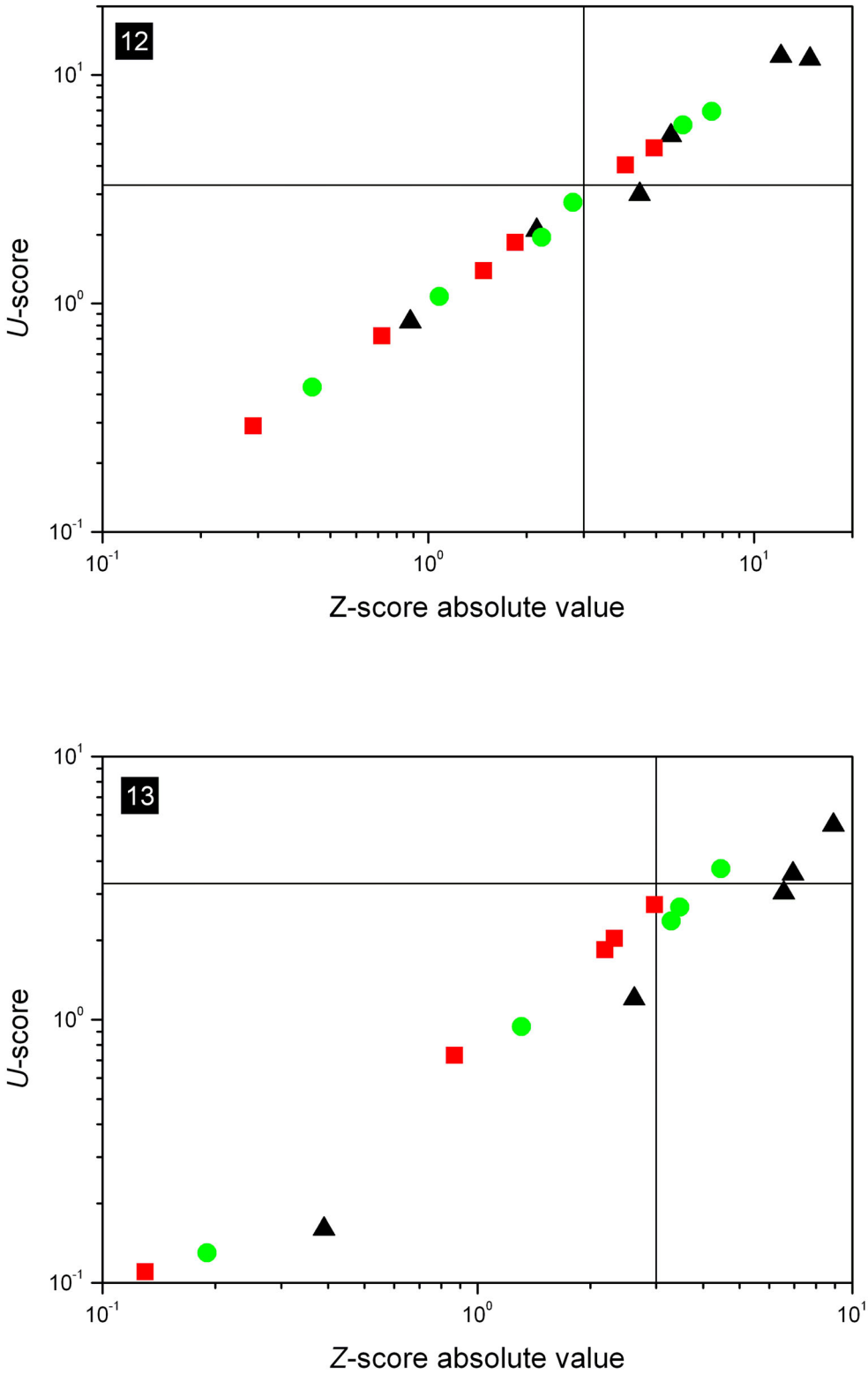

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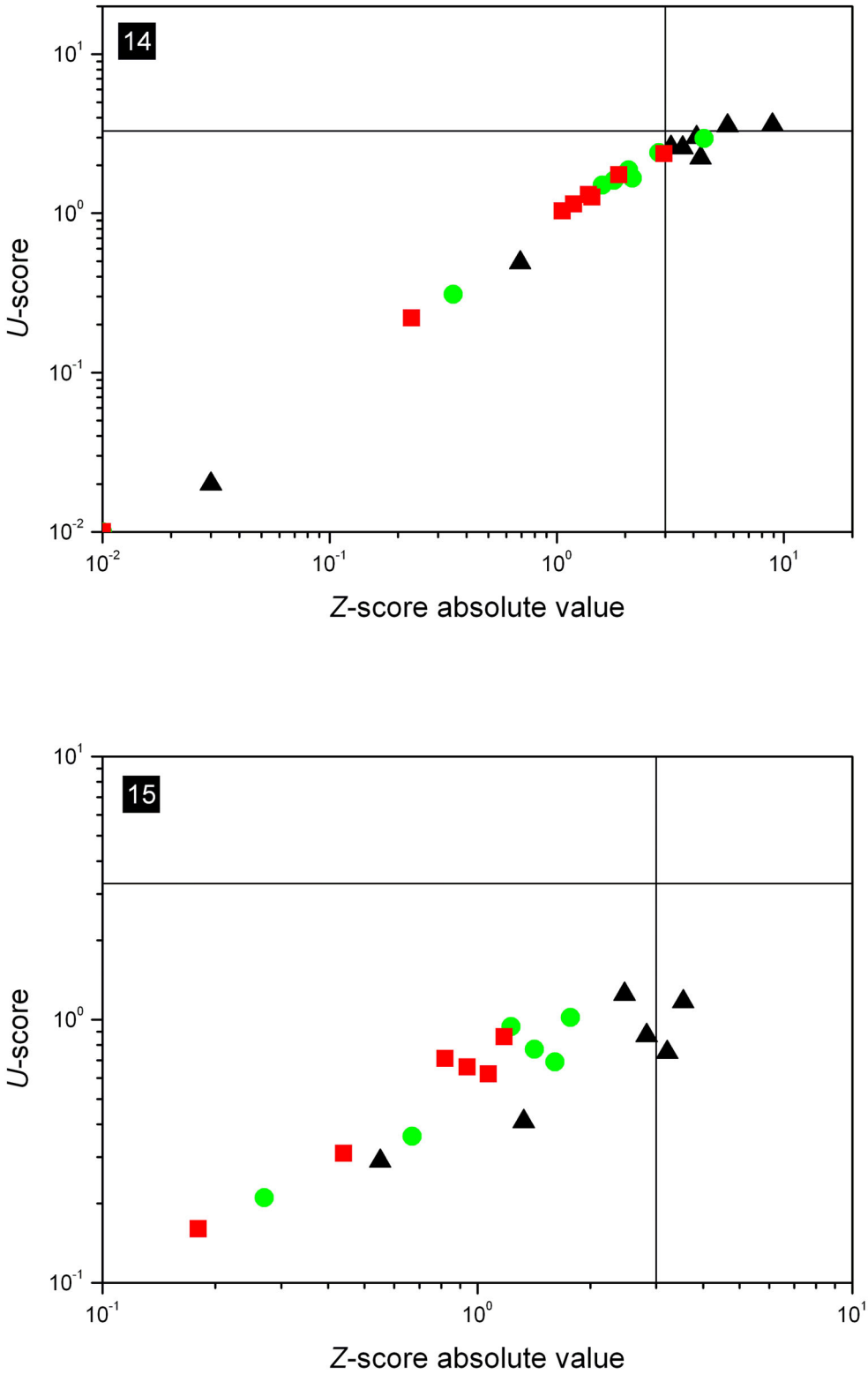
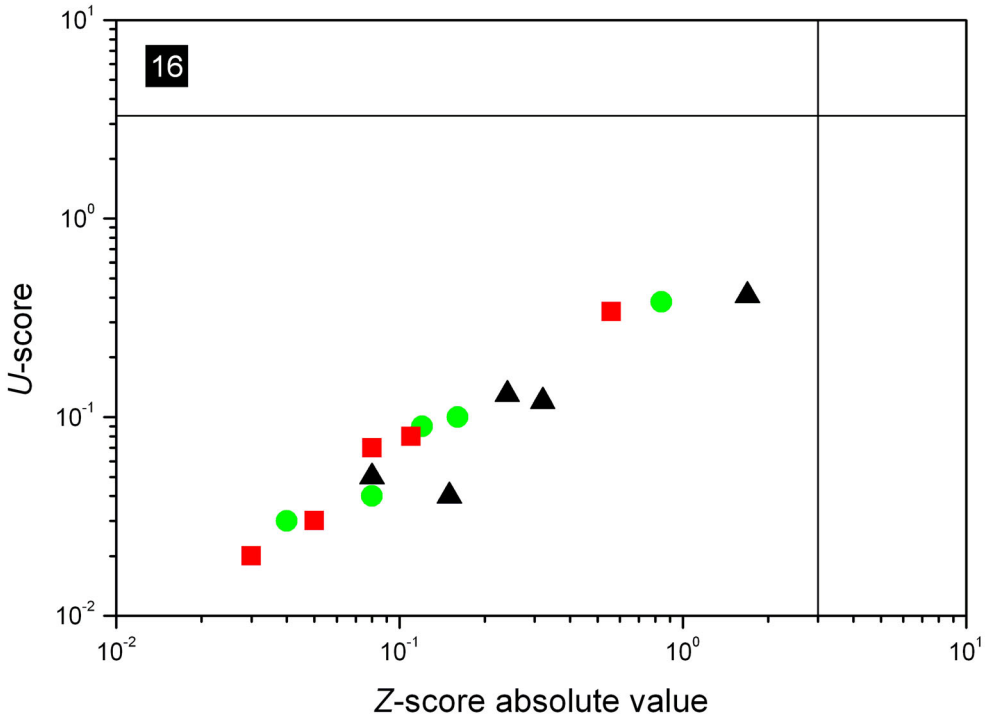
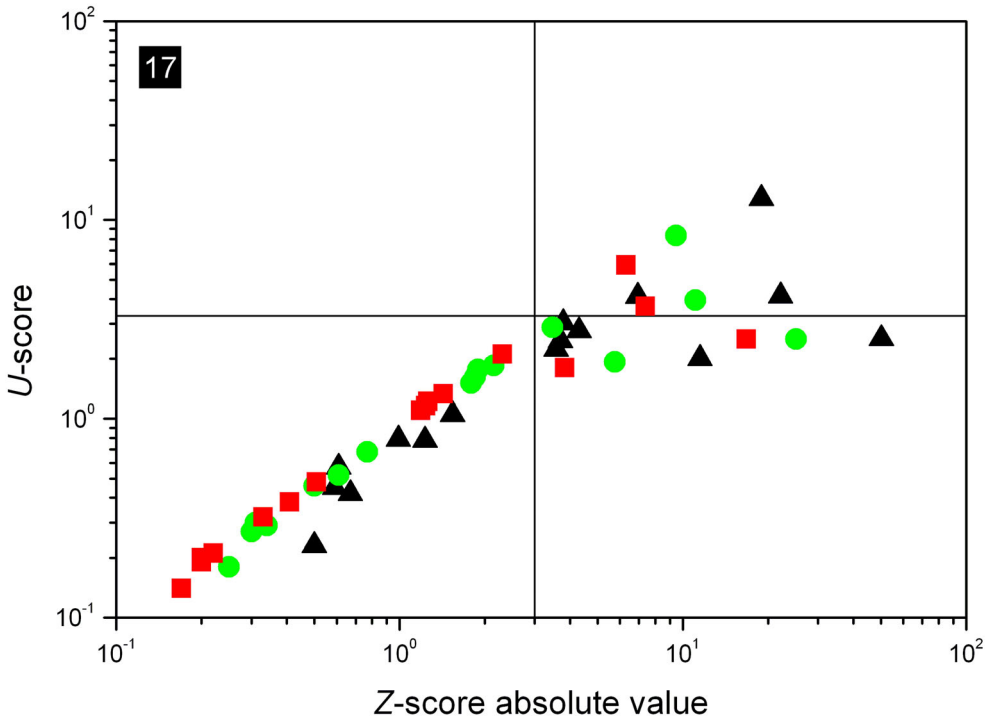


Fig. 5 continued…





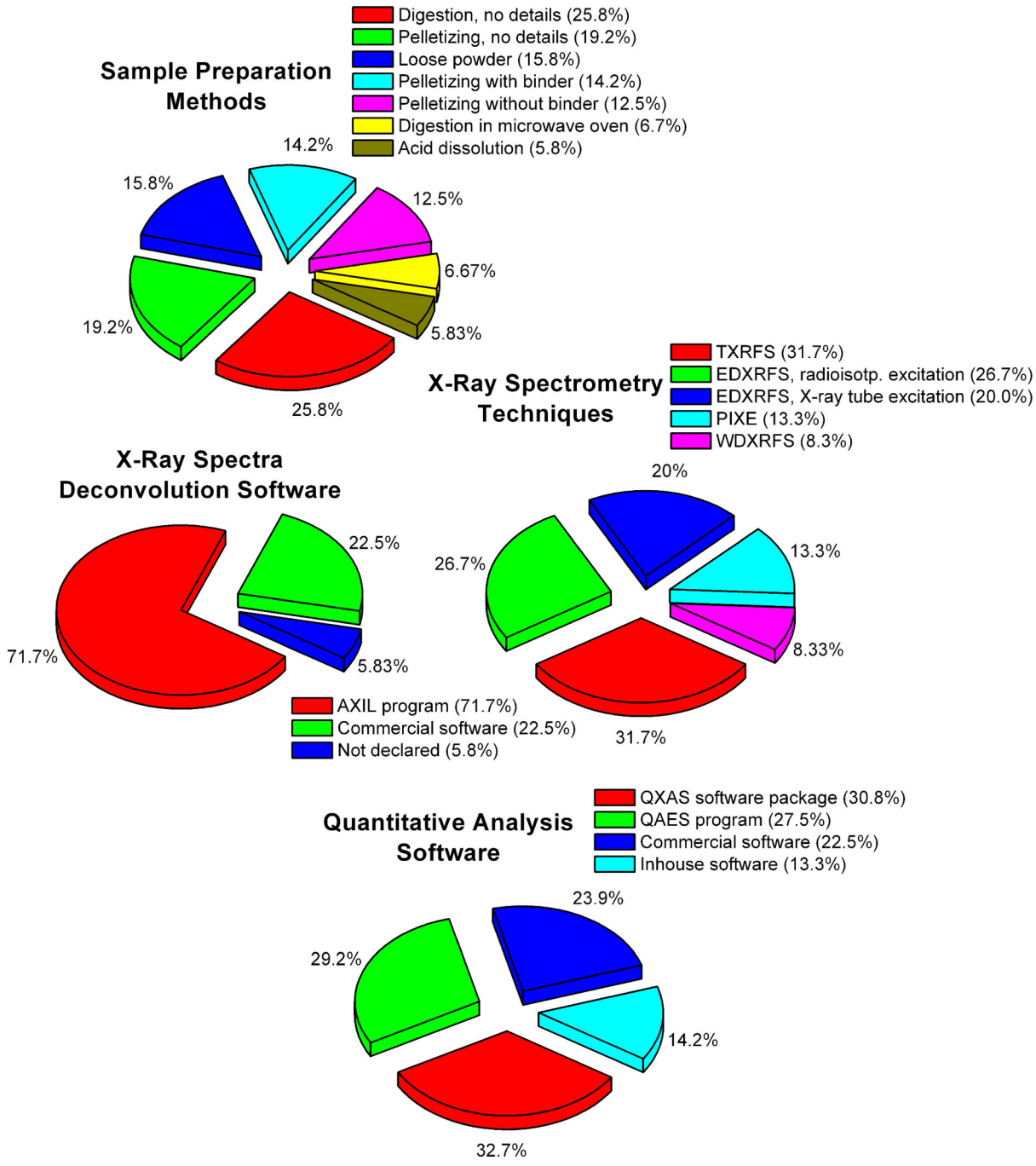


Fig. 6. Percentage utilization of the techniques, methods of sample preparation, X-ray spectra deconvolution and quantitative analysis software as reported by the participants of the proficiency test exercise. The per cent values refer to the total number (120) of the submitted results for the 10 elements: V, Mn, Fe, Cu, Zn, As, Sr, Cd, Ba, and Pb.