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PT01 (EN ISO/IEC 17043)

Helsinki 2017
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 8|2017
Finnish Environment Institute SYKE
Proftest SYKE

Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4667-1(PDF)
ISSN 1796-1726 (Online)

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Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2017

SYKE

ABSTRACT

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in waste waters and fly ash from wood and recycled fuel in October-November 2016. The measurands for synthetic sample as well as municipal and industrial waste water samples were: Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V and Zn. For the fly ash sample, the measurands were: As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V and Zn. In total 26 participants joined in the PT. In this proficiency test 92 % of the results were satisfactory when deviation of 10 – 25 % from the assigned value was accepted.

Basically, either the metrologically traceable concentration, calculated concentration, the robust mean or the mean of the results reported by the participants was used as the assigned value for the measurands. The evaluation of the performance of the participants was carried out using the z scores. In some cases the evaluation of the performance was not possible e.g. due to the low number of the participants. There, when possible, D% and E_n scores were calculated.
Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, metals, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, V, Zn, water, waste water, fly ash, recycled fuel, environmental laboratories, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Proftest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille loka-marraskuussa 2016. Pätevyyskokeessa määritettiin synteettisestä näytteestä, viemärilaitoksen ja teollisuuden jätevesistä Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V ja Zn sekä puun ja kierrätysmateriaalien polton lentotuhkasta As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V and Zn. Pätevyyskokeeseen osallistui yhteensä 26 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 92 %, kun vertailuarvosta sallittiin 10–25 %:n poikkeama.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Testisuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta, osallistujien ilmoittamien tulosten robustia keskiarvoa tai keskiarvoa. Joissain tapauksissa tulosten vähäisen määrän vuoksi pätevyyden arviointi ei ollut mahdollista. Tällöin, mikäli mahdollista, laskettiin D%- ja E_n- arvot.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, metallit, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, V, Zn, lentotuhka, kierrätysmateriaali jätevesi, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Proftest SYKE genomförde en provningsjämförelse i oktober-november 2016, som omfattade bestämningen av Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V, Zn i avloppssvatten och As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V, Zn bestämde i flygaska. Tillsammans 26 laboratorier deltog i jämförelsen. I jämförelsen var 92 % av alla resultaten tillfredsställande, när totalavvikelsen på 10–25 % från referensvärdet accepterades.

Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet, robust medelvärdet eller medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden eller beräknade D% och E_n värden.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, metaller, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, V, Zn, avloppssvatten, flygaska, återvunna bränslen, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in waste waters and fly ash in October - November 2016 (MET 10/16). The measurands for synthetic sample and waste water samples were: Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V and Zn. For the fly ash sample, the measurands were: As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V and Zn. In total 26 participants took part in the PT. In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed to participate in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/Documents/PT01_M08_2016.pdf). The organizing of this proficiency test is included in the accreditation scope with the exception of fly ash.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
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The responsibilities in organizing the proficiency test

Riitta Koivikko	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Timo Sara-Aho	analytical expert (metals, ID-ICP-MS)
Teemu Näykki	analytical expert (Hg, ID-ICP-MS)

Co-operation partner (Fly ash)	Analytical expert Suvi Pöyhönen, The Water Protection Association of the River Kokemäenjoki (KVVY), suvi.poyhonen@kvvy.fi
Subcontracting	Fly ash homogenization, sub-sample divining and analysis: KVVY (T064, www.finas.fi/Documents/T064_M32_2016.pdf)

2.2 Participants

In total 26 laboratories participated in this proficiency test (Appendix 1), 22 participants from Finland, one from Denmark, one from Sweden and two participants from Kyrgyzstan. Altogether 73 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the organizer has the codes 9 (SYKE, Helsinki, T003, www.finas.fi/Documents/T003_M34_2016.pdf) and 15 (KVVY, testing of fly ash sample) in the result tables.

2.3 Samples and delivery

Four types of samples were delivered to the participants: synthetic, municipal and industrial waste water as well as fly ash samples. The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The sample preparation is described in details in the Appendix 2. The synthetic sample A1M was acidified with nitric acid and the synthetic mercury sample A1Hg with the hydrochloric acid.

The samples V2M and V2Hg were municipal waste water with additions of single element standard solutions (AccuStandard for Hg and Merck CertiPUR® for other elements, Appendix 2). The industrial waste water samples T3M (after analysis: TN3 – no digestion / TY3 – digestion with acid or with acid mixture) and T3Hg for Hg measurements were prepared with additions of single element standard solutions (AccuStandard for Hg and Merck CertiPUR® for other elements, Appendix 2).

This PT used the fly ash sample from the previous PT SYKE 10/2012 [4], here sample F4M (after analysis: FC4 – oxygen combustion (only Hg) / FN4 – digestion with HNO_3 / FO4 – digestion with HNO_3 + HCl / FT4 – digestion with HNO_3 + HF). The material was fly ash from recycled fuel and wood from Southern Finland, no addition of metals was needed for the fly ash test material. The fly ash samples were rehomogenized and redivided in the laboratory of Proftest SYKE. The samples were tested at the laboratory of The Water Protection Association of the River Kokemäenjoki in Tampere (KVVY).

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after 3 days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 18 or 24 October 2016 to the international participants and on 25 October 2016 to the national participants. The samples arrived to the participants mainly on 27 October 2016. Participant 17 received the samples on 31 October 2016.

The samples were requested to be measured as follows:

Mercury (A1Hg, V2Hg and T3Hg)	latest on 4 November 2016
The other samples	latest on 23 November 2016

The results were requested to be reported latest on 23 November 2016 and mainly all participants delivered the results accordingly. One participant reported the results on 24 November 2016. The preliminary results were delivered to the participants via email and via the electronic client interface ProftestWEB on 2 December 2016.

2.4 Homogeneity and stability studies

The homogeneity of the waste water samples was tested by analyzing Cd, Cr, Hg, Pb, Se and Zn. More detailed information of homogeneity studies is shown in Appendix 3. According to the homogeneity test results, the samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials. However, homogeneity of these was checked by parallel measurements of three samples and they were considered homogenous. Based on the earlier similar proficiency tests the water samples are known to be stable over the given time period for the test.

The homogeneity and stability of the fly ash sample was studied by analyzing As, Ba, Cd, Cr, Cu, Hg, Mo, Pb and V. More detailed information of homogeneity studies is shown in Appendix 3. The difference of the results from the homogeneity study and the result of the organizing laboratory (KVVY) during the test were compared to the criterion $0.3 \times s_{pt}$ taking into account the total measurement uncertainties. The set criteria were fulfilled in all tested cases, thus the fly ash sample was considered homogenous and stable.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with missing information in the covering letter of sample. The comments from the provider are mainly focused to the lacking conversancy to the given information with the samples. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed more than 50 % or 5 times from the robust mean were rejected before the statistical results handling. The replicate results were tested using the Cochran-test. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values

For the synthetic sample A1M the NIST traceable calculated concentrations were used as the assigned value, with exception of Pb and Hg. The results based on isotope dilution (ID) ICP-MS technique were used as assigned value for Hg and Pb in samples A1Hg, T3Hg, V2Hg, A1M, TN3, and V2M. The assigned value for Hg in the synthetic sample A1Hg based on an average of 12 parallel ID-ICP-MS measurements, while the assigned value for the samples V2Hg and T3Hg based on an average of 21 parallel measurements. The assigned value for Pb in the synthetic sample A1M based on an average of 15 parallel ID-ICP-MS measurements, while the assigned value for the samples TN3 and V2M based on an average of 24 parallel measurements. The ID-ICP-MS method is accredited for soluble lead in synthetic and natural waters and for soluble mercury in synthetic, natural and waste water in the scope of calibration laboratory (K054; www.finas.fi/Documents/K054_M04_2015.pdf). For the other samples and measurands the robust mean was used as the assigned value. When the number of results was low, the mean value was reported as the assigned value (n<12, FC4, FN4, FO4, FT4, TY3, Appendix 5).

The robust mean or mean is not metrologically traceable assigned value. As it was not possible to have metrologically traceable assigned values, the robust means or means of the results were the best available values to be used as the assigned values. The reliability of the assigned value was statistically tested according to the IUPAC Technical report [3].

The expanded measurement uncertainty for the calculated assigned values was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method. When the robust mean or mean was used as the assigned value, the uncertainty was calculated using the robust standard deviation or standard deviation, respectively [2, 5].

The uncertainty of the calculated and metrologically traceable assigned values for metals in the synthetic samples varied between 0.6 and 3 %. When using the robust mean or mean of the participant results as the assigned value, the uncertainties of the assigned values were between 1.3 and 12 % (Appendix 5).

The assigned values **have not been changed** after reporting the preliminary results.

2.6.3 Standard deviation for proficiency assessment and results' evaluation

The target value for the standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. If the number of reported results was low or the deviation of the results was high (eg. FC4: Hg; FN4: As, Ba, Hg; FO4: Ba, Hg; FT4: As, Ba, Cd, Cr, Cu, Mo, Pb, V, Zn; TY3: As), the total standard deviation and the assigned value are not set, and the proficiency estimation is not given. The target value for the standard deviation for proficiency assessment ($2\times s_{pt}$, at the 95 % confidence interval) was set from 10 % to 25 % depending on the measurements. The standard deviations of the proficiency assessment values **have not been changed** after reporting the preliminary results.

When the number of reported results was low (n<6), the performance of the participant was estimated by means of D% values (*'Difference'*). D% values are calculated as the difference between the participant's result and the assigned value. D% value can be interpreted as the measurement error for that results to the extent to which the assigned value can be considered the reference quantity value.

$$D_i\% = \frac{100\,(x_i - x_{pt})}{x_{pt}}\%\text{ , where}$$

x_i = participant's result, x_{pt} = assigned value

Additionally, when the number of reported results was low and the uncertainty was set for the assigned value, the performance was estimated by means of E_n scores (*'Error, normalized'*). These are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}\text{ , where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

Scores of E_n $-1{,}0 < E_n < 1{,}0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1{,}0$ or $E_n \leq -1{,}0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

When using the robust mean as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the target value of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation of the reported results (s_{rob}, s) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value[1] and/or for the reliability of the target value for the deviation[2] was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurement
FO4	As[1,2], Cr[1,2], Mo[1,2], Zn[1,2]
FN4	Cd[1,2], Mo[1], V[1]
TN3	Cu[1]
TY3	Cu[1,2], Pb[1], Se[1]
V2M	Al[1]

3 Results and conclusions

3.1 Results

The terms used in the result tables are listed in Appendix 6. The results and the performance of each participant are presented in Appendix 7 and the summary of the results in Table 1. The results of the replicate determinations are presented in Table 2. The summary of the z scores is shown in Appendix 8 and in Appendix 9 the z scores are shown in the ascending order. The summary of D% and E_n scores are shown in Appendix 10. The reported results grouped by the used analytical methods with their expanded uncertainties (*k*=2) are presented in Appendix 11.

The robust standard deviations of the results mainly varied from 2.4 % to 68 % (Table 1). The robust standard deviation of results was lower than 10 % for 80 % of the results. Standard deviations higher than 10 % apply mainly to the fly ash sample. For the waste water samples the robust standard deviations of the results varied from 4.9 % to 17 % and for the fly ash sample the variation was from 2.4 % to 68% (Table 1). The robust standard deviations for waste water samples were approximately in the same range as in the previous similar proficiency test Proftest SYKE MET 08/2015 [6], where the deviations varied from 1.1 % to 17.5 %.

Table 1. The summary of the results in the proficiency test MET 10/2016.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Al	A1M	µg/l	659	666	664	656	40	6.1	10	23	91
	TN3	µg/l	1132	1133	1132	1120	76	6.7	15	18	94
	TY3	µg/l	1145	1145	1145	1100	98	8.6	15	7	100
	V2M	µg/l	121	120.9	121.1	121.3	13.9	11.5	20	19	89
As	A1M	µg/l	61.9	61.9	61.8	61.6	2.3	3.8	10	20	90
	FN4	mg/kg	18.2	18.2		18.4			-	6	-
	FO4	mg/kg	17.6	17.6	17.6	17.6	2.3	13.2	20	10	90
	FT4	mg/kg	17.6	17.6		17.6			-	2	-
	TN3	µg/l	105	104	105	103	6	5.5	15	17	82
	TY3	µg/l	106	105.9		104.5			-	6	-
	V2M	µg/l	8.58	8.50	8.58	8.52	0.58	6.8	20	18	94
Ba	FN4	mg/kg	2155	2155		2205			-	5	-
	FO4	mg/kg		1502	1502	2016	1027	68	-	7	-
	FT4	mg/kg	2300	2300		2300			-	2	-
Cd	A1M	µg/l	7.29	7.39	7.39	7.37	0.30	4.0	15	21	90
	FN4	mg/kg	20.0	20.0	20.0	19.9	3.1	15.5	20	7	86
	FO4	mg/kg	19.2	19.2	19.2	19.3	2.3	11.8	20	11	91
	FT4	mg/kg	19.8	19.8		19.8			-	2	-
	TN3	µg/l	28.2	28.1	28.2	28.4	1.4	4.9	15	18	100
	TY3	µg/l	29.4	29.4		29.7			20	6	100
	V2M	µg/l	4.48	4.45	4.48	4.52	0.25	5.6	15	19	89
Co	A1M	µg/l	37.0	37.3	37.2	37.0	1.4	3.7	10	22	95
	TN3	µg/l	79.1	79.3	79.1	79.9	5.5	7.0	15	18	94
	TY3	µg/l	77.8	77.8	77.8	78.2	4.0	5.1	15	7	100
	V2M	µg/l	11.0	11.0	11.0	11.0	0.7	6.4	15	18	100
Cr	A1M	µg/l	59.0	59.1	59.2	59.5	2.5	4.3	10	23	100
	FN4	mg/kg	108	108		111			20	7	86
	FO4	mg/kg	96.3	96.3	96.2	97.9	12.9	13.4	20	11	82
	FT4	mg/kg	139	139		139			-	2	-
	TN3	µg/l	160	160	160	159	11	7.0	15	19	95
	TY3	µg/l	161	161	161	159	8	5.1	15	7	100
	V2M	µg/l	12.3	12.3	12.3	12.4	0.9	7.2	15	18	100
Cu	A1M	µg/l	61.9	62.7	62.3	63.0	2.7	4.3	10	22	86
	FN4	mg/kg	175	175	176	175	4	2.4	15	8	100
	FO4	mg/kg	176	176	176	172	11	6.4	15	11	100
	FT4	mg/kg	195	195		195			-	2	-
	TN3	µg/l	97.8	97.8	97.8	98.7	8.6	8.8	15	19	95
	TY3	µg/l	103	103	103	106	10	10.2	15	8	100
	V2M	µg/l	10.1	10.1	10.1	10.1	1.0	9.9	20	21	100
Fe	A1M	µg/l	778	780	782	789	32	4.1	10	26	92
	TN3	µg/l	313	313	313	310	25	7.9	15	21	100
	TY3	µg/l	316	316	316	311	19	6.0	15	8	100
	V2M	µg/l	641	639	641	645	47	7.3	15	21	95

Table 1. The summary of the results in the proficiency test MET 10/2016.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Hg	A1Hg	µg/l	0.59	0.62	0.60	0.61	0.08	12.8	20	16	75
	FC4	mg/kg	0.081	0.081		0.084			-	3	-
	FN4	mg/kg	0.099	0.099		0.100			-	4	-
	FO4	mg/kg	0.13	0.13		0.10			-	7	-
	T3Hg	µg/l	3.33	3.27	3.30	3.30	0.55	16.7	20	17	76
	V2Hg	µg/l	5.34	5.39	5.48	5.30	0.45	8.2	20	17	88
Mn	A1M	µg/l	450	453	454	453	17	3.7	10	21	95
	TN3	µg/l	181	181	181	182	13	7.0	15	18	100
	TY3	µg/l	187	187		190			15	7	100
	V2M	µg/l	388	388	388	386	23	5.8	10	20	95
Mo	FN4	mg/kg	17.0	17.0		16.4			25	6	83
	FO4	mg/kg	16.1	16.1	16.1	16.3	2.8	17.7	25	9	100
	FT4	mg/kg	20.6	20.6		20.6			-	2	-
Ni	A1M	µg/l	71.9	72.3	71.9	73.0	2.3	3.1	10	23	96
	TN3	µg/l	91.8	91.9	91.8	91.1	7.3	7.9	15	19	95
	TY3	µg/l	91.9	91.9		91.8			15	6	100
	V2M	µg/l	8.54	8.53	8.54	8.53	0.58	6.8	20	18	94
Pb	A1M	µg/l	69.6	69.8	69.6	69.1	3.2	4.5	10	21	90
	FN4	mg/kg	239	239	239	242	15	6.4	15	7	100
	FO4	mg/kg	212	212	212	212	39	18.6	20	11	91
	FT4	mg/kg	275	275		275			-	2	-
	TN3	µg/l	82.2	76.7	76.6	77.9	6.0	7.8	15	18	83
	TY3	µg/l	78.5	78.5	77.9	75.4	6.6	8.5	15	7	86
	V2M	µg/l	4.64	4.47	4.46	4.50	0.29	6.4	15	19	89
Se	A1M	µg/l	62.9	62.8	63.3	63.2	3.6	5.7	10	18	89
	TN3	µg/l	40.2	40.6	40.2	40.0	2.7	6.6	15	15	80
	TY3	µg/l	40.6	40.6		38.9			15	6	83
	V2M	µg/l	7.64	7.64	7.64	7.62	0.59	7.7	15	17	82
V	A1M	µg/l	76.9	76.1	76.2	76.0	3.3	4.3	10	17	100
	FN4	mg/kg	84.0	84.0		82.2			20	6	100
	FO4	mg/kg	78.2	78.2	78.5	77.7	6.2	7.9	20	9	100
	FT4	mg/kg	81.0	81.0		81.0			-	2	-
	TN3	µg/l	107	107	107	104	11	10.2	20	14	86
	TY3	µg/l	107	107		107			15	6	100
	V2M	µg/l	13.7	13.7	13.7	13.4	1.0	7.3	15	17	94
Zn	A1M	µg/l	425	426	427	424	21	4.9	10	26	85
	FN4	mg/kg	3375	3375	3375	3360	135	4.0	10	8	88
	FO4	mg/kg	3203	3203	3217	3315	313	9.7	15	11	73
	FT4	mg/kg	3863	3863		3863			-	2	-
	TN3	µg/l	148	147	148	146	12	8.2	15	20	90
	TY3	µg/l	153	153		154			15	9	75
	V2M	µg/l	40.1	40.1	40.1	40.2	3.0	7.6	15	21	95

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the total standard deviation for proficiency assessment at the 95 % confidence interval, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

In this PT the participants were requested to report duplicate results for all measurements. The participants reported the replicates with the exception of the participant 3. The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w, which should not be exceeded 3 for robust methods. However, in many cases the robustness exceeded the value 3; varied between 0.35 and 15 (Table 2).

Table 2. The summary of repeatability on the basis of duplicate determinations (ANOVA) statistics.

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
Al	A1M	µg/l	659	666	17.4	38.8	42.5	2.6	5.8	6.4	2.2
	TN3	µg/l	1132	1133	15.6	67.8	69.5	1.4	6.0	6.1	4.3
	TY3	µg/l	1145	1145	17.3	85.9	87.6	1.5	7.5	7.6	5.0
	V2M	µg/l	121	120.9	1.86	12.5	12.7	1.5	10	10	6.7
As	A1M	µg/l	61.9	61.9	2.07	3.37	3.96	3.3	5.4	6.4	1.6
	FN4	mg/kg	18.2	18.2	1.35	2.30	2.67	7.0	12	14	1.7
	FO4	mg/kg	17.6	17.6	0.50	2.06	2.11	2.8	12	12	4.1
	TN3	µg/l	105	104	1.56	7.85	8.00	1.5	7.4	7.5	5.0
	TY3	µg/l	106	105.9	1.56	13.2	13.3	1.6	13	13	8.5
	V2M	µg/l	8.58	8.50	0.49	0.72	0.87	5.7	8.3	10	1.5
Ba	FN4	mg/kg	2155	2155	58.0	207	215	2.7	9.6	10	3.6
	FO4	mg/kg		1502	99.7	903	908	6.6	60	60	9.1
Cd	A1M	µg/l	7.29	7.39	0.12	0.48	0.49	1.6	6.4	6.6	4.1
	FN4	mg/kg	20.0	20.0	1.20	2.60	2.86	6.0	13	14	2.2
	FO4	mg/kg	19.2	19.2	0.26	2.03	2.05	1.3	11	11	7.9
	TN3	µg/l	28.2	28.1	0.32	1.27	1.31	1.1	4.5	4.6	4.0
	TY3	µg/l	29.4	29.4	0.41	3.46	3.49	1.4	12	12	8.4
	V2M	µg/l	4.48	4.45	0.22	0.28	0.35	4.6	6.3	7.8	1.4
Co	A1M	µg/l	37.0	37.3	0.87	1.53	1.76	2.4	4.1	4.8	1.8
	TN3	µg/l	79.1	79.3	1.51	5.13	5.35	1.9	6.5	6.7	3.4
	TY3	µg/l	77.8	77.8	1.41	3.46	3.74	1.8	4.5	4.8	2.5
	V2M	µg/l	11.0	11.0	0.28	0.63	0.69	2.5	5.7	6.3	2.3
Cr	A1M	µg/l	59.0	59.1	0.72	2.59	2.69	1.2	4.4	4.5	3.6
	FN4	mg/kg	108	108	3.22	5.54	6.41	3.0	5.1	5.9	1.7
	FO4	mg/kg	96.3	96.3	2.52	11.6	11.9	2.6	12	12	4.6
	TN3	µg/l	160	160	2.58	10.3	10.7	1.6	6.4	6.6	4.0
	TY3	µg/l	161	161	2.48	7.64	8.04	1.5	4.8	5.0	3.1
	V2M	µg/l	12.3	12.3	0.25	0.81	0.85	2.0	6.6	6.9	3.2
Cu	A1M	µg/l	61.9	62.7	0.92	3.13	3.27	1.5	5.1	5.3	3.4
	FN4	mg/kg	175	175	10.3	0	10.3	5.8	0	5.8	0
	FO4	mg/kg	176	176	12.9	4.54	13.7	7.3	2.6	7.8	0.35
	TN3	µg/l	97.8	97.8	1.06	7.57	7.64	1.1	7.7	7.8	7.1
	TY3	µg/l	103	103	2.45	9.02	9.35	2.4	8.8	9.1	3.7
	V2M	µg/l	10.1	10.1	0.33	0.92	0.97	3.3	9.1	9.7	2.8
Fe	A1M	µg/l	778	780	11.4	37.3	39.1	1.5	4.8	5.0	3.3
	TN3	µg/l	313	313	5.06	21.7	22.2	1.6	6.9	7.1	4.3
	TY3	µg/l	316	316	9.16	15.4	17.9	2.9	4.9	5.7	1.7
	V2M	µg/l	641	639	7.39	51.4	51.9	1.2	8.0	8.1	7.0

Table 2. The summary of repeatability on the basis of duplicate determinations (ANOVA) statistics.

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
Hg	A1Hg	µg/l	0.59	0.619	0.012	0.089	0.090	2.1	15	15	7.2
	FC4	mg/kg	0.081	0.081	0.002	0.014	0.0138	2.6	17	17	6.5
	FN4	mg/kg	0.099	0.099	0.004	0.007	0.0078	4.4	6.6	7.9	1.5
	FO4	mg/kg	0.13	0.13	0.013	0.040	0.0421	10	32	34	3.1
	T3Hg	µg/l	3.33	3.27	0.038	0.558	0.559	1.1	17	17	15
	V2Hg	µg/l	5.34	5.39	0.085	0.489	0.497	1.5	8.9	9.0	5.7
Mn	A1M	µg/l	450	453	4.30	16.8	17.4	0.95	3.7	3.8	3.9
	TN3	µg/l	181	181	2.79	11.6	11.9	1.5	6.4	6.6	4.1
	TY3	µg/l	187	187	3.24	9.18	9.73	1.7	4.9	5.2	2.8
	V2M	µg/l	388	388	5.08	20.7	21.3	1.3	5.3	5.5	4.1
Mo	FN4	mg/kg	17.0	17.0	0.78	2.55	2.67	4.6	15	16	3.3
	FO4	mg/kg	16.1	16.1	0.37	2.49	2.52	2.4	16	16	6.5
Ni	A1M	µg/l	71.9	72.3	0.66	3.07	3.14	0.92	4.3	4.4	4.6
	TN3	µg/l	91.8	91.9	0.89	6.41	6.48	0.97	7.0	7.1	7.2
	TY3	µg/l	91.9	91.9	1.46	4.58	4.80	1.6	5.0	5.2	3.1
	V2M	µg/l	8.54	8.53	0.20	0.78	0.80	2.3	9.1	9.4	4.0
Pb	A1M	µg/l	69.6	69.8	1.29	3.14	3.39	1.8	4.5	4.9	2.4
	FN4	mg/kg	239	239	9.57	11.7	15.1	4.0	4.9	6.3	1.2
	FN4	mg/kg	239	239	9.57	11.7	15.1	4.0	4.9	6.3	1.2
	FO4	mg/kg	212	212	6.51	34.5	35.1	3.1	16	17	5.3
	TN3	µg/l	82.2	76.7	2.99	5.56	6.31	3.9	7.3	8.2	1.9
	TY3	µg/l	78.5	78.5	1.93	7.10	7.35	2.5	9.0	9.4	3.7
	V2M	µg/l	4.64	4.47	0.13	0.27	0.30	3.0	6.1	6.8	2.0
Se	A1M	µg/l	62.9	62.8	1.77	4.68	5.00	2.8	7.3	7.9	2.6
	TN3	µg/l	40.2	40.6	0.95	2.99	3.14	2.3	7.4	7.7	3.2
	TY3	µg/l	40.6	40.6	1.48	3.31	3.62	3.6	8.1	8.9	2.2
	V2M	µg/l	7.64	7.64	0.20	0.55	0.58	2.6	7.2	7.6	2.8
V	A1M	µg/l	76.9	76.1	0.99	2.93	3.10	1.3	3.9	4.1	3.0
	FN4	mg/kg	84.0	84.0	3.27	7.94	8.59	3.9	9.5	10	2.4
	FO4	mg/kg	78.2	78.2	1.67	5.90	6.13	2.1	7.6	7.8	3.5
	TN3	µg/l	107	107	2.36	9.70	9.98	2.2	9.1	9.4	4.1
	TY3	µg/l	107	107	1.70	5.46	5.72	1.6	5.1	5.3	3.2
	V2M	µg/l	13.7	13.7	0.15	0.95	0.96	1.1	6.9	7.0	6.5
Zn	A1M	µg/l	425	426	5.67	21.8	22.6	1.3	5.1	5.3	3.8
	FN4	mg/kg	3375	3375	102	94.3	139	3.0	2.8	4.1	0.92
	FO4	mg/kg	3203	3203	82.8	300	311	2.6	9.4	9.7	3.6
	TN3	µg/l	148	147	2.01	13.1	13.3	1.4	8.9	9.0	6.5
	TY3	µg/l	153	153	4.42	3.26	5.50	2.9	2.1	3.6	0.74
	V2M	µg/l	40.1	40.1	1.08	2.56	2.78	2.7	6.4	6.9	2.4

Ass.val.: assigned value; s_w: repeatability standard error; s_b: between participants standard error; s_t: reproducibility standard error.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 11. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

Effect of sample pretreatment on elemental concentrations in waste waters
Elements in waste water were mainly measured from acidified samples without sample pretreatment with the exception of the industrial waste water sample (TN3/TY3). More than half of the participant measured the acidified industrial waste water without sample pretreatment (TN3), and the other participants measured the industrial waste water after acid digestion (TY3). The results of these samples were evaluated separately (Appendix 11).

The difference between the average concentrations of elements measured by different sample pretreatment methods was tested using the t-test. Statistically significant difference was not observed for metal analyses. For an unfiltered waste water sample the results are expected, acid digestion should give similar or in some cases higher results than without digestion.

Effect of sample pretreatment on elemental concentrations in fly ash sample
Elements in the fly ash sample were measured mainly after acid digestion (FN4/FO4). In average, 55 % of the participants measured the fly ash sample after aqua regia digestion (FO4), and the other participants measured the sample mainly after nitric acid digestion (FN4). Two participants measured the fly ash sample after nitric acid and hydrofluoric acid digestion (FT4). The results of these were evaluated separately (Appendix 11).

The difference between the average concentrations of elements measured by different acid digestion was tested using the t-test. Statistically significant difference was observed for Cr analyses. Nitric acid digestion gave significantly higher results compared to the aqua regia digestion approach (Appendix 12). Noticeable was also that digestion with hydrofluoric acid increase the concentration of chromium (Table 1, Appendix 12). This is evident also for copper, lead and zinc (Table 1). The digestion method in general can highly influence the recoveries depending on sample matrix, digestion temperature and hold times, as well the sample weight and acid amount ratio.

Effect of measurement methods on elemental results
The most commonly used analytical method was ICP-MS and ICP-OES. FAAS or GAAS techniques were used by one participant for some measurements (Appendix 11). The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. Statistically significant differences were observed for Al, Mn and Ni analysis of the synthetic sample A1M. For Al analysis ICP-MS technique gave higher results than ICP-OES technique, while for Mn and Ni ICP-MS technique gave smaller results than ICP-OES technique (Appendix 12).

ICP-MS is in most cases the technique of preference due to its superior detection capabilities compared to other techniques when low concentrations are to be measured. As a general note, a low recovery may be an indication of loss of analyte which can occur during sample pretreatment (e.g. volatilization during acid digestion) or measurement (e.g. GAAS analysis). It may also be caused by incorrect background correction (ICP-OES) or matrix effects. Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination. Matrix effects can often be overcome by matrix matching the calibration standards, however this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

Effect of measurement methods on mercury results

For the analysis of mercury, ICP-MS was the most often used method of analysis following by CV-AFS. CV-AAS or direct combustion technique was used one to two participants. One participant reported mercury results by CV-ICP-MS technique (Appendix 11).

For the fly ash sample, aqua regia digestion (FO4) was most commonly used, followed by nitric acid digestion (FN4). Three participant analysed mercury from the fly ash sample with direct oxygen combustion (FC4). Based on visual estimation no clear differences between the used methods of measurement or digestion could be concluded (Appendix 11).

Like most other metal determinations, mercury results are affected by the digestion procedures used (acids and oxidation reagents used, their concentration, amounts and purities, digestion temperature and time). For water samples hydrochloric acid is recommended for sample preservation and BrCl is recommended for oxidation of mercury species. Different cold vapour techniques usually give fairly similar results provided that the pretreatment is appropriate. CV-AFS and CV-ICP-MS have superior detection limits compared to CV-AAS.

3.3 Uncertainties of the results

In all 65 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 3, many of the participants have clearly under- or over-estimated their expanded ($k=2$) measurement uncertainty. Expanded measurement uncertainty below 5% is not common for routine laboratories. Also measurement uncertainty over 50% should not exist, unless the measured concentration is near to the limit of quantification.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into water quality registers have been published in Finland [7]. The recommendations for measurement uncertainties for most of the tested measurands in waste water are 20 %. In this proficiency test some of the participants had their measurement uncertainties within these limits, while some did not achieve them. Harmonization of the uncertainties estimation should be continued.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The most used approach was based on the data obtained from method validation, followed by the

Table 3. The range of the expanded measurement uncertainties (*k*=2, U%) reported by the participants.

Analyte	A1M / A1Hg %	FC4 / FN4 / FO4 / FT4 %	V2M / V2Hg %	TN3 / T3Hg %	TY3 %
Al	3-30	-	5-30	3-30	10-25
As	4-30	15-25	10-100	4-30	10-30
Ba	-	8-30	-	-	-
Cd	10-50	10-30	10-50	10-33	15-40
Co	10-30	-	10-100	5-30	14-30
Cr	10-30	15-40	10-50	5-35	15-30
Cu	10-30	10-32	10-50	7-34	7-34
Fe	3-33	-	3-33	3-40	14-33
Hg	10-46	10-50	10-40	10-40	-
Mn	3-30	-	3-30	4-30	11-20
Mo	-	10-30	-	-	-
Ni	10-30	-	10-100	10-30	15-27
Pb	10-30	10-35	10-100	10-30	15-30
Se	10-40	-	10-50	15-30	17-35
V	8-30	9-50	8-50	8-30	8-30
Zn	5-30	10-25	10-30	9-30	15-30

approach based on the internal quality data with sample replicates. At maximum four participants used MUkit measurement uncertainty software for the estimation of their uncertainties. The free software is available on the webpage: www.syke.fi/envical/en [8]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

4 Evaluation of the results

The evaluation of the participants was based on the z scores (Appendix 6). The evaluation of the participants was based on the z and E_n scores, which were interpreted as follows:

Criteria	Performance
$\| z \| \leq 2$	Satisfactory
$2 < \| z \| < 3$	Questionable
$\| z \| \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 92 % of the results were satisfactory, when deviation of 10–25 % from the assigned value was accepted (Appendix 8). Altogether 73 % of the participants used accredited analytical methods at least for a part of the measurements and 86 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 4. In the previous similar PT, Proftest SYKE MET 08/2015 [6], the performance was satisfactory for 90 % of the all participants. Based on E_n scores 82 % of arsenic results in the samples FN4 and TY3 was satisfactory (Appendix 10).

Table 4. Summary of the performance evaluation in the proficiency test MET 10/2016.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
A1M / A1Hg	92/75	10-20	• Generally good performance, but some difficulties in measurements for Hg, < 80% satisfactory results. • In the MET 08/2015 the performance was satisfactory for 89/85 % of the results [6].
FN4 / FO4 *FN4:As*	92/91 *E_n score: 80*	10-25	• Only approximate assessment for: FO4: As, Cr, Mo, Zn; FN4: Cd • High uncertainty of the assigned value: FN4: Mo, V • Due to low number of results FC4: Hg; FN4: As, Ba, Hg; FO4:Ba, Hg and FT4:all measurands were not evaluated based on z score. For As in the sample FN4 E_n score evaluation was performed. • Difficulties in measurements for FO4: Zn, < 80% satisfactory results.
TN3 / T3Hg	92/76	15-20	• Difficulties in measurements for Hg, < 80% satisfactory results. • Somewhat approximate performance evaluation for Cu. • In the MET 08/2015 the performance was satisfactory for 93/85 % of the results [6].
TY3 *TY3:As*	95 *E_n score: 83*	15-20	• Difficulties in measurements for Zn, < 80% satisfactory results. • Somewhat approximate performance evaluation for Cu, Pb, Se. • Due to low number of the results TY3: As was not evaluated based on z score, but based on E_n scores evaluation was performed. • In the MET 08/2015 the performance was satisfactory for 91 % of the results [6].
V2M / V2Hg	94/88	15-20	• Somewhat approximate performance evaluation for Al. • In the MET 08/2015 the performance was satisfactory for 89/83 % of the results [6].

D%-scores deviated between 0 and -34 %; 70 % of the values were below 10 % and 11 % of the values were between 10 and 20 %; 15 % of the values were higher than 20 % (bolded in Appendix 10). In average, the satisfactory results varied between 75 % and 95 % for the tested sample types (Table 4). The number of satisfactory results in the synthetic sample A1M was the lowest for Hg 75 %, which was lower than in 2015, when 85 % of results were satisfactory with the same accepted deviation (20 %) from the assigned value [6].

The fly ash sample turned out to be challenging for many measurands and the number of participants analysing the sample was low. The performance evaluation for some measurands of the fly ash sample F4M is only approximate due to the weakness of the reliability of the assigned value, the target value for total deviation and the reliability of the corresponding z score (Table 4). For the fly ash sample, standard deviations of 10–25 % from the assigned value were accepted. Of the results obtained after nitric acid digestion (FN4), 92 % of the results were satisfactory when the standard deviation of 10–25 % from the assigned value was accepted. The fly ash sample from recycled fuel and wood was not tested in the previous proficiency tests.

For the industrial waste water sample (TN3/TY3 and T3Hg) the satisfactory results varied between 76 and 95 %, when deviations of 10–20 % from the assigned value were accepted. Difficulties were noticed in measurements of Hg and Zn in the sample TY3. For Cd, Fe and Mn in the sample TN3 and for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, and V in the sample TY3 all the results were satisfactory. For the municipal waste water sample V2M all results for Co, Cr and Cu were satisfactory. For Hg in the waste water T3Hg the number of satisfactory results (76 %) was lower than in 2015, when 85 % of results were satisfactory with the same accepted deviation (20 %) from the assigned value [6].

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in waste waters and recycled fuel (fly ash) in October-November 2016 (MET 10/2016). The measurands for synthetic sample and waste water samples were: Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V, and Zn. For the fly ash sample, the measurands were: As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V, and Zn. Four sample types were: synthetic, municipal and industrial effluents as well as fly ash sample. In total 26 laboratories participated in the PT.

For the synthetic sample A1M the NIST traceable calculated concentrations were used as the assigned values with exception of Pb. For Hg and Pb (A1Hg, T3Hg, V2Hg, A1M, TN3, V2M, respectively) the assigned values based on the metrologically traceable isotope dilution technique (ID-ICP-MS) results were used. For other samples and measurements the robust mean or mean value was used as the assigned value. The uncertainty for the assigned value was estimated at the 95 % confidence interval and it was between 0.6 and 3 % for the calculated and metrologically traceable assigned values and for assigned values based on the robust mean or mean it was between 1.3–12 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In this proficiency test 92 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value 10 to 25 %. About 73 % of the participants used accredited methods and 86 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti jätevesiä ja kierrätysmateriaalien polton lentotuhkasta analysoiville laboratorioille pätevyyskokeen loka-marraskuussa 2016 (MET 10/2016). Pätevyyskokeessa määritettiin synteettisestä näytteestä, viemärilaitoksen ja teollisuuden jätevesistä Al, As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, V ja Zn sekä kierrätysmateriaalien polton lentotuhkasta As, Ba, Cd, Cr, Cu, Hg, Mo, Pb, V and Zn. Pätevyyskokeeseen osallistui yhteensä 26 laboratoriota.

Mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa tai keskiarvoa. Lyijylle ja elohopealle käytettiin metrologisesti jäljitettävää tavoitearvoa osassa testinäytteistä. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,6 – 3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 1,3 – 12 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 10 – 25 %. Koko aineistossa hyväksyttäviä tuloksia oli 92 %. Noin 73 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 86 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Denmark	Force Technology, Holstebro, Denmark
Finland	Ahma ympäristö Oy, Oulu
	Boliden Harjavalta Oy
	Boliden Kokkola Oy
	Ekokem Oy Ab, Riihimäki
	Freeport Cobalt Oy
	Huntsman P&A Finland Oy, Analyyttinen laboratorio Pori
	KCL Kymen Laboratorio Oy
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere
	Labtium Oy, Jyväskylä
	Labtium Oy, Kuopio
	Lounais-Suomen vesi- ja ympäristötukimus Oy, Turku
	Metropolilab Oy
	Nab Labs Oy / Ambiotica Jyväskylä
	Norilsk Nickel Harjavalta Oy
	Novalab Oy
	Outokumpu Stainless Oy, Tutkimuskeskus, Tornio
	Ramboll Finland Oy, Ramboll Analytics, Lahti
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SGS Inspection Services Oy, Kotka
	SSAB Europe Oy, Analyysilaboratorio, Hämeenlinna
	SYKE Ympäristökemia Helsinki
	UPM Tutkimuskeskus, Lappeenranta
Kyrgyz Republic	SAEPF, EMA Laboratory, Bishkek, Kyrgyz Republic
	SAEPF, Issyk-Kul-Naryn, Cholpon-Ata City, Kyrgyz Republic
Sweden	Eurofins Environment testing Sweden AB, Lidköping

APPENDIX 2: Preparation of the samples

The synthetic samples A1M was prepared by diluting from the NIST traceable certified reference materials produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The water samples V2M, T3M (TN3/TY3), V2Hg and T3Hg were prepared by adding some separate metal solutions (Merck CertiPUR® or AccuStandard) into the original water sample, if the original concentration was not high enough.

Analyte		A1M µg/l	V2M µg/l	TN3/TY3 µg/l
Al	Original	6600 000	6	860
	Dilution	10 000	-	-
	Addition	-	110	-
	Ass. value	659	121	1132/ 1145
As	Original	620 000	0.41	2.0
	Dilution	10 000	-	-
	Addition	-	8	105
	Ass. value	61.9	8.58	105/ 106
Ba	Original	-	-	-
	Dilution	-	-	-
	Addition	-	-	-
	Ass. value	-	-	-
Cd	Original	73 000	0.03	0.34
	Dilution	10 000	-	-
	Addition	-	4.5	28
	Ass. value	7.29	4.48	28.2/ 29.4
Co	Original	370 000	4.6	0.99
	Dilution	10 000	-	-
	Addition	-	5	80
	Ass. value	37.0	11.0	79.1/ 77.8
Cr	Original	590 000	0.29	76
	Dilution	10 000	-	-
	Addition	-	12	74
	Ass. value	59.0	12.3	160/ 161
Cu	Original	620 000	9.6	11
	Dilution	10 000	-	-
	Addition	-	-	87
	Ass. value	61.9	10.1	97.8/ 103
Fe	Original	7 800 000	280	130
	Dilution	10 000	-	-
	Addition	-	270	-
	Ass. value	778	641	313/ 316
Mn	Original	4 500 000	150	150
	Dilution	10 000	-	-
	Addition	-	175	-
	Ass. value	450	388	181/ 187

Measurand		A1M µg/l	V2M µg/l	TN3/TY3 µg/l
Mo	Original	-	-	-
	Dilution	-	-	-
	Addition	-	-	-
	Ass. value	-	-	-
Ni	Original	720 000	8,5	14
	Dilution	10 000	-	-
	Addition	-	-	80
	Ass. value	71,9	8,54	91,8/ 91,9
Pb	Original	690 000	0,34	0,76
	Dilution	10 000	-	-
	Addition	-	4,2	80
	Ass. value	69,6	4,64	82,2/ 78,5
Se	Original	630 000	0,2	3,3
	Dilution	10 000	-	-
	Addition	-	7,3	37
	Ass. value	62,9	7,64	40,2/ 40,6
V	Original	770 000	0,33	7,4
	Dilution	10 000	-	-
	Addition	-	13	98
	Ass. value	76,9	13,7	107/ 107
Zn	Original	4 250 000	31	130
	Dilution	10 000	-	-
	Addition	-	8	-
	Ass. value	425	40,1	148/ 153

Measurand		A1Hg µg/l	V2Hg µg/l	T3Hg µg/l
Hg	Original	-	0,64	0,032
	Dilution	-	-	-
	Addition	0.6	1,86	3,3
	Ass. value	0,59	5,34	3,33

Original = the original concentration
Dilution = the ratio of dilution
Addition = the addition concentration
Ass. value = the assigned value

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of selected measurement from three to six samples of each sample types (see table below).

Criteria for homogeneity

$s_a/s_h<0.5$ and $s_{sam}^2<c$, where

s_h = standard deviation for testing of homogeneity
s_a = analytical deviation, standard deviation of the results within sub samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_a^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurement/ sample	Concentration [µg/l] [mg/kg]	n	s_h %	s_h	s_a	s_a/s_h	Is $s_a/s_h<0.5$?	s_{sam}^2	c	Is $s_{sam}^2<c$?
Cd/V2M	4.82	6	2.0	0.10	0.04	0.39	Yes	0.00002	0.004	Yes
Cr/V2M	12.9	6	1.5	0.19	0.08	0.42	Yes	0	0.02	Yes
Se/ V2M	8.27	6	2.0	0.17	0.08	0.46	Yes	0	0.02	Yes
Zn/ V2M	40.6	6	1.0	0.41	0.16	0.39	Yes	0	0.08	Yes
Cd/T3M	29.5	6	1.5	0.44	0.17	0.39	Yes	0.02	0.09	Yes
Cr/ T3M	164	6	1.5	2.46	0.97	0.39	Yes	0.20	2.79	Yes
Se/ T3M	42.6	6	2.0	0.85	0.37	0.43	Yes	0.09	0.37	Yes
Zn/T3M	151	6	1.0	1.51	0.29	0.19	Yes	0.39	0.60	Yes
As/F4M	17.7	3	7	1.24	0.58	0.47	Yes	0	1.84	Yes
Ba/F4M	2017	3	5	101	40.8	0.40	Yes	0	9869	Yes
Cd/F4M	20.2	3	5	1.01	0.41	0.40	Yes	0	0.99	Yes
Cr/F4M	101	3	10	10.4	4.64	0.46	Yes	5	119	Yes
Cu/F4M	172	3	5	8.58	4.09	0.48	Yes	0	91.1	Yes
Hg/F4M	0.09	3	2.5	0.002	0.001	0.42	Yes	0	0	Yes
Mo/F4M	17.2	3	5	0.86	0.41	0.48	Yes	0	0.91	Yes
Pb/F4M	238	3	4	9.53	4.08	0.43	Yes	0	95.8	Yes
V/F4M	80.7	3	2	1.61	1.15	0.72	Yes	0	6.40	Yes
ID-ICP-MS testing										
Hg/V2Hg*	5.30	6	1.5	0.08	0.02	0.26	Yes	0.002	0.002	Yes
Hg/T3Hg*	3.33	6	1.0	0.03	0.01	0.40	Yes	0.0003	0.0005	Yes
Pb/V2M*	4.65	6	2.0	0.09	0.02	0.21	Yes	0.002	0.002	Yes
Pb/T3M*	82.3	6	1.5	1.23	0.42	0.34	Yes	0.45	0.60	Yes

*) result based on the ID-ICP-MS measurement

Conclusion: The criteria were fulfilled for the tested measurands and the samples were regarded as homogenous

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest
All	The sample codes for sample T3M were missing in the sample letter.	The codes were informed later. In the future PTs the provider will be more careful with the given information.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
6	The participant reported only one result in their dataset for some samples and measurands, though replicate results were requested. These results were not included in the calculation of assigned values and z scores were not calculated. The provider recommends the participant to follow the given guidelines.
1,3, 5, 10, 11,14, 17, 18, 20, 21, 22, 26	For these participants the deviation of replicate measurements for some measurands and samples were high and their results were Cochran outliers. The provider recommends the participants to validate their deviation of replicate measurements.

APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Al	A1M	µg/l	659	5	0.7	Calculated value	0.07
	TN3	µg/l	1132	46	4.1	Robust mean	0.27
	TY3	µg/l	1145	65	5.7	Mean	0.38
	V2M	µg/l	121	9	7.0	Robust mean	0.35
As	A1M	µg/l	61.9	0.6	1.0	Calculated value	0.10
	FN4	mg/kg	18.2	0.6	3.3	Mean	
	FO4	mg/kg	17.6	1.3	7.5	Mean	0.38
	FT4	mg/kg	17.6			Mean	
	TN3	µg/l	105	4	3.4	Robust mean	0.23
	TY3	µg/l	106	3	3.0	Mean	
	V2M	µg/l	8.58	0.35	4.1	Robust mean	0.21
Ba	FN4	mg/kg	2155			Mean	
	FO4	mg/kg				Mean	
	FT4	mg/kg	2300			Mean	
Cd	A1M	µg/l	7.29	0.05	0.7	Calculated value	0.05
	FN4	mg/kg	20.0	2.0	10.0	Mean	0.50
	FO4	mg/kg	19.2	1.3	6.7	Mean	0.34
	FT4	mg/kg	19.8			Mean	
	TN3	µg/l	28.2	0.8	2.9	Robust mean	0.19
	TY3	µg/l	29.4	2.9	9.7	Mean	0.49
	V2M	µg/l	4.48	0.15	3.3	Robust mean	0.22
Co	A1M	µg/l	37.0	0.2	0.6	Calculated value	0.06
	TN3	µg/l	79.1	3.3	4.2	Robust mean	0.28
	TY3	µg/l	77.8	2.7	3.5	Mean	0.23
	V2M	µg/l	11.0	0.4	3.7	Robust mean	0.25
Cr	A1M	µg/l	59.0	0.4	0.7	Calculated value	0.07
	FN4	mg/kg	108	5	4.5	Mean	0.23
	FO4	mg/kg	96.3	7.4	7.7	Mean	0.39
	FT4	mg/kg	139			Mean	
	TN3	µg/l	160	6	4.0	Robust mean	0.27
	TY3	µg/l	161	6	3.7	Mean	0.25
	V2M	µg/l	12.3	0.5	4.2	Robust mean	0.28
Cu	A1M	µg/l	61.9	0.4	0.6	Calculated value	0.06
	FN4	mg/kg	175	2	1.3	Mean	0.09
	FO4	mg/kg	176	6	3.5	Mean	0.23
	FT4	mg/kg	195			Mean	
	TN3	µg/l	97.8	5.1	5.2	Robust mean	0.35
	TY3	µg/l	103	7	6.8	Mean	0.45
	V2M	µg/l	10.1	0.6	5.5	Robust mean	0.28
Fe	A1M	µg/l	778	5	0.6	Calculated value	0.06
	TN3	µg/l	313	14	4.4	Robust mean	0.29
	TY3	µg/l	316	13	4.0	Mean	0.27
	V2M	µg/l	641	26	4.0	Robust mean	0.27
Hg	A1Hg	µg/l	0.59	0.02	3.0	ID-ICP-MS	0.15
	FC4	mg/kg	0.081			Mean	
	FN4	mg/kg	0.099			Mean	

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Hg	FO4	mg/kg	0.13			Mean	
	T3Hg	µg/l	3.33	0.10	3.0	ID-ICP-MS	0.15
	V2Hg	µg/l	5.34	0.16	3.0	ID-ICP-MS	0.15
Mn	A1M	µg/l	450	3	0.6	Calculated value	0.06
	TN3	µg/l	181	7	4.0	Robust mean	0.27
	TY3	µg/l	187	7	4.0	Mean	0.27
	V2M	µg/l	388	13	3.4	Robust mean	0.34
Mo	FN4	mg/kg	17.0	2.0	12.0	Mean	0.48
	FO4	mg/kg	16.1	1.6	10.0	Mean	0.40
	FT4	mg/kg	20.6			Mean	
	FT4	mg/kg	20.6			Mean	
Ni	A1M	µg/l	71.9	0.4	0.6	Calculated value	0.06
	TN3	µg/l	91.8	4.3	4.7	Robust mean	0.31
	TY3	µg/l	91.9	3.9	4.2	Mean	0.28
	V2M	µg/l	8.54	0.34	4.0	Robust mean	0.20
Pb	A1M	µg/l	69.6	2.1	3.0	ID-ICP-MS	0.30
	FN4	mg/kg	239	10	4.0	Mean	0.27
	FO4	mg/kg	212	21	10.0	Mean	0.50
	FT4	mg/kg	275			Mean	
	TN3	µg/l	82.2	2.5	3.0	ID-ICP-MS	0.20
	TY3	µg/l	78.5	5.5	7.0	Mean	0.47
	V2M	µg/l	4.64	0.14	3.0	ID-ICP-MS	0.20
Se	A1M	µg/l	62.9	0.5	0.8	Calculated value	0.08
	TN3	µg/l	40.2	1.8	4.4	Robust mean	0.29
	TY3	µg/l	40.6	3.1	7.6	Mean	0.51
	V2M	µg/l	7.64	0.40	5.2	Robust mean	0.35
V	A1M	µg/l	76.9	0.5	0.6	Calculated value	0.06
	FN4	mg/kg	84.0	6.7	8.0	Mean	0.40
	FO4	mg/kg	78.2	3.9	5.0	Mean	0.25
	FT4	mg/kg	81.0			Mean	
	TN3	µg/l	107	7	7.0	Robust mean	0.35
	TY3	µg/l	107	4	4.0	Mean	0.27
	V2M	µg/l	13.7	0.6	4.4	Robust mean	0.29
Zn	A1M	µg/l	425	3	0.6	Calculated value	0.06
	FN4	mg/kg	3375	101	3.0	Mean	0.30
	FO4	mg/kg	3203	192	6.0	Mean	0.40
	FT4	mg/kg	3863			Mean	
	TN3	µg/l	148	7	5.0	Robust mean	0.33
	TY3	µg/l	153	3	2.0	Mean	0.13
	V2M	µg/l	40.1	1.7	4.3	Robust mean	0.29

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= target value of the standard deviation for proficiency assessment
u_{pt}= standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 6: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the reference value (*the assigned value*) s_{pt} = the standard deviation for proficiency assessment
Assigned value	The reference value
$2\times s_{pt}$ %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2< z < 3$), positive error, the result deviates more than $2 \times s_{pt}$ from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than $2 \times s_{pt}$ from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \times s_{pt}$ from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \times s_{pt}$ from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i,\ldots,x_p$.
Initial values for x^* *and* s^* are calculated as*:*
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows*:*
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i *(i = 1, 2 …p)*:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.70	659	10	636	656	666	41	6.1	23
	µg/l	TN3		0.42	1132	15	1168	1120	1133	69	6.1	17
As	µg/l	A1M		1.00	61.9	10	65.0	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		-1.31	17.6	20	15.3	17.6	17.6	2.1	11.8	10
	µg/l	TN3		0.38	105	15	108	103	104	4	4.0	16
Cd	µg/l	A1M		-0.07	7.29	15	7.25	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-3.72	19.2	20	12.1	19.3	19.2	2.0	10.6	10
	µg/l	TN3		-0.33	28.2	15	27.5	28.4	28.1	1.3	4.6	18
Co	µg/l	A1M		1.35	37.0	10	39.5	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.15	79.1	15	80.0	79.9	79.3	5.2	6.6	17
Cr	µg/l	A1M		0.51	59.0	10	60.5	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		-1.47	96.3	20	82.1	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-0.04	160	15	160	159	160	11	6.5	18
Cu	µg/l	A1M		0.52	61.9	10	63.5	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.34	176	15	172	172	176	10	5.8	11
	µg/l	TN3		0.50	97.8	15	101.5	98.7	97.8	7.6	7.8	18
Fe	µg/l	A1M		0.87	778	10	812	789	780	30	3.9	24
	µg/l	TN3		-0.13	313	15	310	310	313	22	7.0	20
Mn	µg/l	A1M		0.80	450	10	468	453	453	17	3.8	20
	µg/l	TN3		0.29	181	15	185	182	181	12	6.5	18
Mo	mg/kg	FO4		-1.84	16.1	25	12.4	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		-1.92	71.9	10	65.0	73.0	72.3	1.8	2.4	21
Pb	µg/l	A1M		2.41	69.6	10	78.0	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-2.46	212	20	160	212	212	35	16.4	11
	µg/l	TN3		0.86	82.2	15	87.5	77.9	76.7	5.9	7.8	17
Zn	µg/l	A1M		0.92	425	10	445	424	426	22	5.2	25
	mg/kg	FO4		-7.42	3203	15	1421	3315	3203	306	9.5	9
	µg/l	TN3		0.32	148	15	152	146	147	13	9.0	19

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.14	659	10	655	656	666	41	6.1	23
	µg/l	TN3		0.89	1132	15	1208	1120	1133	69	6.1	17
As	µg/l	A1M		-0.62	61.9	10	60.0	61.6	61.9	1.9	3.1	18
	µg/l	TN3		2.71	105	15	126	103	104	4	4.0	16
Cd	µg/l	A1M		0.89	7.29	15	7.78	7.37	7.39	0.23	3.1	18
	µg/l	TN3		0.38	28.2	15	29.0	28.4	28.1	1.3	4.6	18
Co	µg/l	A1M		0.87	37.0	10	38.6	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.61	79.1	15	82.7	79.9	79.3	5.2	6.6	17
Cr	µg/l	A1M		1.91	59.0	10	64.6	59.5	59.1	2.6	4.5	23
	µg/l	TN3		1.42	160	15	177	159	160	11	6.5	18
Cu	µg/l	A1M		0.45	61.9	10	63.3	63.0	62.7	2.2	3.4	19
	µg/l	TN3		0.38	97.8	15	100.6	98.7	97.8	7.6	7.8	18
Fe	µg/l	A1M		0.41	778	10	794	789	780	30	3.9	24
	µg/l	TN3		1.26	313	15	343	310	313	22	7.0	20

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Mn	µg/l	A1M		1.30	450	10	479	453	453	17	3.8	20
	µg/l	TN3		1.19	181	15	197	182	181	12	6.5	18
Ni	µg/l	A1M		0.72	71.9	10	74.5	73.0	72.3	1.8	2.4	21
	µg/l	TN3		0.54	91.8	15	95.5	91.1	91.9	6.4	7.0	18
Pb	µg/l	A1M		1.56	69.6	10	75.0	69.1	69.8	3.3	4.7	20
	µg/l	TN3		0.79	82.2	15	87.1	77.9	76.7	5.9	7.8	17
Se	µg/l	A1M		-0.88	62.9	10	60.1	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.03	40.2	15	40.1	40.0	40.6	3.1	7.6	14
V	µg/l	A1M		-1.36	76.9	10	71.7	76.0	76.1	3.0	4.0	17
	µg/l	TN3		0.79	107	20	115	104	107	10	9.2	12
Zn	µg/l	A1M		-0.16	425	10	422	424	426	22	5.2	25
	µg/l	TN3		1.28	148	15	162	146	147	13	9.0	19

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cd	µg/l	A1M		-4.13	7.29	15	5.03	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		1.85	19.2	20	22.8	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.85	28.2	15	30.0	28.4	28.1	1.3	4.6	18
	µg/l	V2M		8.06	4.48	15	7.19	4.52	4.45	0.21	4.7	18
Co	µg/l	TN3		13.64	79.1	15	160.0	79.9	79.3	5.2	6.6	17
Cr	mg/kg	FO4		-5.95	96.3	20	39.0	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-5.42	160	15	95	159	160	11	6.5	18
Cu	µg/l	A1M		-12.91	61.9	10	22.0	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.22	176	15	173	172	176	10	5.8	11
	µg/l	TN3		4.39	97.8	15	130.0	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-0.21	10.1	20	9.9	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		1.85	778	10	850	789	780	30	3.9	24
	µg/l	TN3		1.58	313	15	350	310	313	22	7.0	20
Ni	µg/l	A1M		-0.53	71.9	10	70.0	73.0	72.3	1.8	2.4	21
	µg/l	TN3		2.64	91.8	15	110.0	91.1	91.9	6.4	7.0	18
Pb	µg/l	A1M		-14.02	69.6	10	20.8	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		1.99	212	20	254	212	212	35	16.4	11
	µg/l	TN3		4.51	82.2	15	110.0	77.9	76.7	5.9	7.8	17
	µg/l	V2M		43.91	4.64	15	19.92	4.50	4.47	0.29	6.5	16
Zn	µg/l	A1M		-1.18	425	10	400	424	426	22	5.2	25
	mg/kg	FO4		-12.64	3203	15	168	3315	3203	306	9.5	9
	µg/l	TN3		0.63	148	15	155	146	147	13	9.0	19
	µg/l	V2M		1.42	40.1	15	44.4	40.2	40.1	2.7	6.7	19

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.03	659	10	660	656	666	41	6.1	23
	µg/l	TN3		-0.15	1132	15	1120	1120	1133	69	6.1	17
As	µg/l	A1M		0.39	61.9	10	63.1	61.6	61.9	1.9	3.1	18
	µg/l	TN3		0.51	105	15	109	103	104	4	4.0	16
Cd	µg/l	A1M		0.75	7.29	15	7.70	7.37	7.39	0.23	3.1	18
	µg/l	TN3		0.50	28.2	15	29.3	28.4	28.1	1.3	4.6	18
Co	µg/l	A1M		0.97	37.0	10	38.8	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.91	79.1	15	84.5	79.9	79.3	5.2	6.6	17
Cr	µg/l	A1M		0.54	59.0	10	60.6	59.5	59.1	2.6	4.5	23
	µg/l	TN3		0.42	160	15	165	159	160	11	6.5	18
Cu	µg/l	A1M		-2.34	61.9	10	54.7	63.0	62.7	2.2	3.4	19
	µg/l	TN3		-0.07	97.8	15	97.3	98.7	97.8	7.6	7.8	18
Fe	µg/l	A1M		0.24	778	10	788	789	780	30	3.9	24
	µg/l	TN3		0.55	313	15	326	310	313	22	7.0	20
Hg	µg/l	A1Hg		-0.76	0.59	20	0.55	0.61	0.62	0.05	8.6	13
	µg/l	T3Hg		-2.27	3.33	20	2.58	3.30	3.27	0.56	17.1	16
Mn	µg/l	A1M		0.58	450	10	463	453	453	17	3.8	20
	µg/l	TN3		0.41	181	15	187	182	181	12	6.5	18
Ni	µg/l	A1M		0.54	71.9	10	73.9	73.0	72.3	1.8	2.4	21
	µg/l	TN3		1.63	91.8	15	103.0	91.1	91.9	6.4	7.0	18
Pb	µg/l	A1M		0.55	69.6	10	71.5	69.1	69.8	3.3	4.7	20
	µg/l	TN3		-0.15	82.2	15	81.3	77.9	76.7	5.9	7.8	17
Se	µg/l	A1M		0.41	62.9	10	64.2	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.12	40.2	15	39.9	40.0	40.6	3.1	7.6	14
Zn	µg/l	A1M		2.24	425	10	473	424	426	22	5.2	25
	µg/l	TN3		-0.27	148	15	145	146	147	13	9.0	19

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.91	659	10	629	656	666	41	6.1	23
	µg/l	TN3		-1.02	1132	15	1045	1120	1133	69	6.1	17
	µg/l	V2M		-1.57	121	20	102	121	121	13	10.4	17
As	µg/l	A1M		0.11	61.9	10	62.3	61.6	61.9	1.9	3.1	18
	mg/kg	FN4			18.2		24.2	18.4	18.2	0.7	3.7	5
	µg/l	TN3		-0.32	105	15	103	103	104	4	4.0	16
	µg/l	V2M		0.16	8.58	20	8.72	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FN4			2155		1800	2205	2155	211	9.8	5
Cd	µg/l	A1M		-0.07	7.29	15	7.25	7.37	7.39	0.23	3.1	18
	mg/kg	FN4		2.05	20.0	20	24.1	19.9	20.0	2.7	13.6	7
	µg/l	TN3		0.12	28.2	15	28.5	28.4	28.1	1.3	4.6	18
	µg/l	V2M		-0.04	4.48	15	4.47	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.11	37.0	10	36.8	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.41	79.1	15	76.7	79.9	79.3	5.2	6.6	17
	µg/l	V2M		0.18	11.0	15	11.2	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.29	59.0	10	59.9	59.5	59.1	2.6	4.5	23
	mg/kg	FN4		-4.32	108	20	61	111	108	6	5.5	6
	µg/l	TN3		-0.50	160	15	154	159	160	11	6.5	18
	µg/l	V2M		0.92	12.3	15	13.2	12.4	12.3	0.8	6.7	18

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cu	µg/l	A1M		-0.32	61.9	10	60.9	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		-0.42	175	15	170	175	175	3	1.7	7
	µg/l	TN3		-0.71	97.8	15	92.6	98.7	97.8	7.6	7.8	18
	µg/l	V2M		1.73	10.1	20	11.9	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.68	778	10	752	789	780	30	3.9	24
	µg/l	TN3		-0.70	313	15	297	310	313	22	7.0	20
	µg/l	V2M		-0.48	641	15	618	645	639	52	8.1	20
Hg	µg/l	A1Hg		-3.72	0.59	20	0.37	0.61	0.62	0.05	8.6	13
	mg/kg	FC4			0.081		0.067	0.084	0.081	0.014	16.9	3
	µg/l	T3Hg		-4.04	3.33	20	1.99	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.26	5.34	20	5.20	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.44	450	10	440	453	453	17	3.8	20
	µg/l	TN3		-0.55	181	15	174	182	181	12	6.5	18
	µg/l	V2M		-0.72	388	10	374	386	388	21	5.4	19
Mo	mg/kg	FN4		2.02	17.0	25	21.3	16.4	17.0	2.6	15.4	6
Ni	µg/l	A1M		-0.24	71.9	10	71.1	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.25	91.8	15	90.1	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.67	8.54	20	9.11	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-1.09	69.6	10	65.8	69.1	69.8	3.3	4.7	20
	mg/kg	FN4		-1.14	239	15	219	242	239	14	5.7	7
	µg/l	TN3		-0.39	82.2	15	79.8	77.9	76.7	5.9	7.8	17
	µg/l	V2M		1.44	4.64	15	5.14	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		0.19	62.9	10	63.5	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.73	40.2	15	38.0	40.0	40.6	3.1	7.6	14
	µg/l	V2M		-0.10	7.64	15	7.59	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.72	76.9	10	74.2	76.0	76.1	3.0	4.0	17
	mg/kg	FN4		-1.01	84.0	20	75.6	82.2	84.0	8.3	9.8	6
	µg/l	TN3		-0.61	107	20	100	104	107	10	9.2	12
	µg/l	V2M		-0.29	13.7	15	13.4	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.80	425	10	408	424	426	22	5.2	25
	mg/kg	FN4		-1.13	3375	10	3185	3360	3375	119	3.5	7
	µg/l	TN3		-0.27	148	15	145	146	147	13	9.0	19
	µg/l	V2M		1.00	40.1	15	43.1	40.2	40.1	2.7	6.7	19

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cu	µg/l	TY3			103	15	*105,4*	106	103	9	9.0	7
	µg/l	V2M			10.1	20	*10,7*	10.1	10.1	0.9	9.4	20
Fe	µg/l	TY3			316	15	*272*	311	316	17	5.3	7
	µg/l	V2M			641	15	*632,0*	645	639	52	8.1	20
Hg	µg/l	T3Hg		-0.66	3.33	20	3.11	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		0.17	5.34	20	5.43	5.30	5.39	0.32	5.9	14
Mn	µg/l	TY3			187	15	*173*	190	187	9	5.1	6
	µg/l	V2M			388	10	*363*	386	388	21	5.4	19
Zn	µg/l	TY3			153	15	*132,7*	154	153	5	2.9	6
	µg/l	V2M			40.1	15	*34,3*	40.2	40.1	2.7	6.7	19

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.09	659	10	656	656	666	41	6.1	23
	µg/l	TN3		-0.48	1132	15	1092	1120	1133	69	6.1	17
	µg/l	TY3		-0.75	1145	15	1081	1100	1145	87	7.6	7
	µg/l	V2M		-0.25	121	20	118	121	121	13	10.4	17
As	µg/l	A1M		-0.02	61.9	10	61.9	61.6	61.9	1.9	3.1	18
	mg/kg	FN4			18.2		17.8	18.4	18.2	0.7	3.7	5
	µg/l	TN3		-0.46	105	15	101	103	104	4	4.0	16
	µg/l	TY3			106		105	105	106	4	3.4	5
	µg/l	V2M		-0.23	8.58	20	8.39	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FN4			2155		2324	2205	2155	211	9.8	5
Cd	µg/l	A1M		0.60	7.29	15	7.62	7.37	7.39	0.23	3.1	18
	mg/kg	FN4		-0.02	20.0	20	20.0	19.9	20.0	2.7	13.6	7
	µg/l	TN3		-0.07	28.2	15	28.1	28.4	28.1	1.3	4.6	18
	µg/l	TY3		-0.12	29.4	20	29.1	29.7	29.4	3.5	11.8	6
	µg/l	V2M		0.34	4.48	15	4.60	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.27	37.0	10	36.5	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.65	79.1	15	75.3	79.9	79.3	5.2	6.6	17
	µg/l	TY3		0.05	77.8	15	78.1	78.2	77.8	3.6	4.6	7
	µg/l	V2M		-0.67	11.0	15	10.5	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.44	59.0	10	60.3	59.5	59.1	2.6	4.5	23
	mg/kg	FN4		0.68	108	20	115	111	108	6	5.5	6
	µg/l	TN3		-0.08	160	15	159	159	160	11	6.5	18
	µg/l	TY3		0.00	161	15	161	159	161	8	4.9	7
	µg/l	V2M		0.05	12.3	15	12.4	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.18	61.9	10	62.5	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		0.16	175	15	177	175	175	3	1.7	7
	µg/l	TN3		-1.10	97.8	15	89.8	98.7	97.8	7.6	7.8	18
	µg/l	TY3		-0.99	103	15	95	106	103	9	9.0	7
	µg/l	V2M		-0.94	10.1	20	9.2	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.45	778	10	796	789	780	30	3.9	24
	µg/l	TN3		-0.19	313	15	309	310	313	22	7.0	20
	µg/l	TY3		0.36	316	15	325	311	316	17	5.3	7
	µg/l	V2M		0.26	641	15	654	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.30	0.59	20	0.61	0.61	0.62	0.05	8.6	13
	mg/kg	FN4			0.099		0.100	0.100	0.099	0.007	7.3	4
	µg/l	T3Hg		-0.12	3.33	20	3.29	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		0.45	5.34	20	5.58	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		0.13	450	10	453	453	453	17	3.8	20
	µg/l	TN3		-0.29	181	15	177	182	181	12	6.5	18
	µg/l	TY3		-0.36	187	15	182	190	187	9	5.1	6
	µg/l	V2M		-0.39	388	10	381	386	388	21	5.4	19
Mo	mg/kg	FN4		-0.33	17.0	25	16.3	16.4	17.0	2.6	15.4	6
Ni	µg/l	A1M		0.00	71.9	10	71.9	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.38	91.8	15	89.2	91.1	91.9	6.4	7.0	18
	µg/l	TY3		0.15	91.9	15	92.9	91.8	91.9	4.7	5.1	6
	µg/l	V2M		-0.23	8.54	20	8.35	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		0.40	69.6	10	71.0	69.1	69.8	3.3	4.7	20
	mg/kg	FN4		0.24	239	15	243	242	239	14	5.7	7

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Pb	µg/l	TN3		-0.60	82.2	15	78.5	77.9	76.7	5.9	7.8	17
	µg/l	TY3		-0.63	78.5	15	74.8	75.4	78.5	7.2	9.2	7
	µg/l	V2M		-0.24	4.64	15	4.56	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-0.02	62.9	10	62.9	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-1.18	40.2	15	36.7	40.0	40.6	3.1	7.6	14
	µg/l	TY3		0.59	40.6	15	42.4	38.9	40.6	3.5	8.5	5
	µg/l	V2M		-0.21	7.64	15	7.52	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.48	76.9	10	75.1	76.0	76.1	3.0	4.0	17
	mg/kg	FN4		-0.54	84.0	20	79.5	82.2	84.0	8.3	9.8	6
	µg/l	TN3		-0.23	107	20	105	104	107	10	9.2	12
	µg/l	TY3		-0.12	107	15	106	107	107	6	5.2	6
	µg/l	V2M		-0.34	13.7	15	13.4	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		0.38	425	10	433	424	426	22	5.2	25
	mg/kg	FN4		0.71	3375	10	3495	3360	3375	119	3.5	7
	µg/l	TN3		-1.17	148	15	135	146	147	13	9.0	19
	µg/l	TY3		-0.26	153	15	150	154	153	5	2.9	6
	µg/l	V2M		-0.28	40.1	15	39.3	40.2	40.1	2.7	6.7	19

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.09	659	10	656	656	666	41	6.1	23
	µg/l	TN3		-0.08	1132	15	1125	1120	1133	69	6.1	17
	µg/l	V2M		0.02	121	20	121	121	121	13	10.4	17
As	µg/l	A1M		-0.26	61.9	10	61.1	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		0.26	17.6	20	18.1	17.6	17.6	2.1	11.8	10
	µg/l	TN3		0.17	105	15	106	103	104	4	4.0	16
	µg/l	V2M		-0.47	8.58	20	8.18	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					2160	2016	1502	906	60.3	7
Cd	µg/l	A1M		0.26	7.29	15	7.43	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		0.39	19.2	20	20.0	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.19	28.2	15	28.6	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.36	4.48	15	4.60	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.03	37.0	10	37.0	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.13	79.1	15	79.9	79.9	79.3	5.2	6.6	17
	µg/l	V2M		0.06	11.0	15	11.1	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-0.08	59.0	10	58.8	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		2.18	96.3	20	117.3	97.9	96.3	11.7	12.2	10
	µg/l	TN3		0.08	160	15	161	159	160	11	6.5	18
	µg/l	V2M		-0.05	12.3	15	12.3	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-0.11	61.9	10	61.6	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.04	176	15	176	172	176	10	5.8	11
	µg/l	TN3		0.41	97.8	15	100.8	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-0.17	10.1	20	9.9	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.17	778	10	785	789	780	30	3.9	24
	µg/l	TN3		0.11	313	15	316	310	313	22	7.0	20
	µg/l	V2M		0.24	641	15	653	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.23	0.59	20	0.60	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		0.09	0.10	0.13	0.04	32.9	5

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Hg	µg/l	T3Hg		0.39	3.33	20	3.46	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.08	5.34	20	5.30	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.47	450	10	440	453	453	17	3.8	20
	µg/l	TN3		0.04	181	15	182	182	181	12	6.5	18
	µg/l	V2M		-0.39	388	10	381	386	388	21	5.4	19
Mo	mg/kg	FO4		0.94	16.1	25	18.0	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		0.45	71.9	10	73.5	73.0	72.3	1.8	2.4	21
	µg/l	TN3		0.57	91.8	15	95.7	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.25	8.54	20	8.75	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.42	69.6	10	68.2	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		1.92	212	20	253	212	212	35	16.4	11
	µg/l	TN3		-0.58	82.2	15	78.7	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-0.16	4.64	15	4.59	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		0.27	62.9	10	63.8	63.2	62.8	3.2	5.1	17
	µg/l	TN3		0.27	40.2	15	41.0	40.0	40.6	3.1	7.6	14
	µg/l	V2M		0.03	7.64	15	7.66	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.49	76.9	10	75.0	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		0.73	78.2	20	83.9	77.7	78.2	6.0	7.7	9
	µg/l	TN3		0.02	107	20	107	104	107	10	9.2	12
	µg/l	V2M		-0.34	13.7	15	13.4	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.19	425	10	421	424	426	22	5.2	25
	mg/kg	FO4		1.07	3203	15	3460	3315	3203	306	9.5	9
	µg/l	TN3		0.32	148	15	152	146	147	13	9.0	19
	µg/l	V2M		0.38	40.1	15	41.3	40.2	40.1	2.7	6.7	19

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.49	659	10	675	656	666	41	6.1	23
	µg/l	TN3		-0.27	1132	15	1109	1120	1133	69	6.1	17
	µg/l	V2M		0.09	121	20	122	121	121	13	10.4	17
As	µg/l	A1M		0.05	61.9	10	62.1	61.6	61.9	1.9	3.1	18
	µg/l	TN3		0.53	105	15	109	103	104	4	4.0	16
	µg/l	V2M		0.29	8.58	20	8.83	8.52	8.50	0.53	6.3	17
Cd	µg/l	A1M		0.10	7.29	15	7.34	7.37	7.39	0.23	3.1	18
	µg/l	TN3		0.38	28.2	15	29.0	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.43	4.48	15	4.62	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.01	37.0	10	37.0	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.17	79.1	15	80.1	79.9	79.3	5.2	6.6	17
	µg/l	V2M		0.01	11.0	15	11.0	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.08	59.0	10	59.2	59.5	59.1	2.6	4.5	23
	µg/l	TN3		0.19	160	15	162	159	160	11	6.5	18
	µg/l	V2M		0.25	12.3	15	12.5	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-0.10	61.9	10	61.6	63.0	62.7	2.2	3.4	19
	µg/l	TN3		0.33	97.8	15	100.2	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-0.22	10.1	20	9.9	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.74	778	10	807	789	780	30	3.9	24
	µg/l	TN3		-0.22	313	15	308	310	313	22	7.0	20
	µg/l	V2M		0.32	641	15	657	645	639	52	8.1	20

Participant 9

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Hg	µg/l	A1Hg		0.23	0.59	20	0.60	0.61	0.62	0.05	8.6	13
	µg/l	T3Hg		-0.03	3.33	20	3.32	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.16	5.34	20	5.25	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		0.76	450	10	467	453	453	17	3.8	20
	µg/l	TN3		0.13	181	15	183	182	181	12	6.5	18
	µg/l	V2M		0.41	388	10	396	386	388	21	5.4	19
Ni	µg/l	A1M		-0.03	71.9	10	71.8	73.0	72.3	1.8	2.4	21
	µg/l	TN3		0.39	91.8	15	94.5	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.37	8.54	20	8.86	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.06	69.6	10	69.4	69.1	69.8	3.3	4.7	20
	µg/l	TN3		-0.67	82.2	15	78.1	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-0.59	4.64	15	4.44	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-0.05	62.9	10	62.7	63.2	62.8	3.2	5.1	17
	µg/l	TN3		0.55	40.2	15	41.9	40.0	40.6	3.1	7.6	14
	µg/l	V2M		0.78	7.64	15	8.09	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.23	76.9	10	76.0	76.0	76.1	3.0	4.0	17
	µg/l	TN3		0.38	107	20	111	104	107	10	9.2	12
	µg/l	V2M		0.29	13.7	15	14.0	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.14	425	10	422	424	426	22	5.2	25
	µg/l	TN3		0.73	148	15	156	146	147	13	9.0	19
	µg/l	V2M		0.32	40.1	15	41.1	40.2	40.1	2.7	6.7	19

Participant 10

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.84	659	10	720	656	666	41	6.1	23
	µg/l	TN3		0.84	1132	15	1203	1120	1133	69	6.1	17
	µg/l	V2M		1.37	121	20	138	121	121	13	10.4	17
As	µg/l	A1M		-0.51	61.9	10	60.3	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		2.10	17.6	20	21.3	17.6	17.6	2.1	11.8	10
	µg/l	TN3		-0.64	105	15	100	103	104	4	4.0	16
	µg/l	V2M		-0.57	8.58	20	8.09	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					2397	2016	1502	906	60.3	7
Cd	µg/l	A1M		0.20	7.29	15	7.40	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		1.02	19.2	20	21.2	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.26	28.2	15	28.8	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.39	4.48	15	4.61	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.26	37.0	10	36.5	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-1.24	79.1	15	71.7	79.9	79.3	5.2	6.6	17
	µg/l	V2M		-0.42	11.0	15	10.7	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-0.77	59.0	10	56.7	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		0.33	96.3	20	99.5	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-1.15	160	15	146	159	160	11	6.5	18
	µg/l	V2M		-0.96	12.3	15	11.4	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-0.76	61.9	10	59.5	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		1.39	176	15	194	172	176	10	5.8	11
	µg/l	TN3		-1.63	97.8	15	85.8	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-1.12	10.1	20	9.0	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.62	778	10	754	789	780	30	3.9	24

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Fe	µg/l	TN3		-1.28	313	15	283	310	313	22	7.0	20
	µg/l	V2M		-0.34	641	15	625	645	639	52	8.1	20
Hg	µg/l	A1Hg		2.11	0.59	20	0.71	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		0.17	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		1.23	3.33	20	3.74	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		0.94	5.34	20	5.84	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.05	450	10	449	453	453	17	3.8	20
	µg/l	TN3		-0.59	181	15	173	182	181	12	6.5	18
	µg/l	V2M		-0.17	388	10	385	386	388	21	5.4	19
Mo	mg/kg	FO4		0.10	16.1	25	16.3	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		-0.63	71.9	10	69.7	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-1.57	91.8	15	81.0	91.1	91.9	6.4	7.0	18
	µg/l	V2M		-0.67	8.54	20	7.97	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		0.38	69.6	10	70.9	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		1.24	212	20	238	212	212	35	16.4	11
	µg/l	TN3		-1.08	82.2	15	75.6	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-0.23	4.64	15	4.56	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		0.35	62.9	10	64.0	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.91	40.2	15	37.5	40.0	40.6	3.1	7.6	14
	µg/l	V2M		-0.87	7.64	15	7.14	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.30	76.9	10	78.1	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		0.71	78.2	20	83.8	77.7	78.2	6.0	7.7	9
	µg/l	TN3		-2.34	107	20	82	104	107	10	9.2	12
	µg/l	V2M		0.10	13.7	15	13.8	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.17	425	10	421	424	426	22	5.2	25
	mg/kg	FO4		-0.06	3203	15	3189	3315	3203	306	9.5	9
	µg/l	TN3		-1.76	148	15	128	146	147	13	9.0	19
	µg/l	V2M		-0.45	40.1	15	38.8	40.2	40.1	2.7	6.7	19

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.16	659	10	654	656	666	41	6.1	23
	µg/l	TY3		1.05	1145	15	1236	1100	1145	87	7.6	7
	µg/l	V2M		0.82	121	20	131	121	121	13	10.4	17
As	µg/l	A1M		-0.47	61.9	10	60.4	61.6	61.9	1.9	3.1	18
	mg/kg	FT4			17.6		17.0	17.6	17.6	0.9	4.9	2
	µg/l	TY3			106		102	105	106	4	3.4	5
	µg/l	V2M		-0.91	8.58	20	7.80	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FT4			2300		2266	2300	2300	49	2.1	2
Cd	µg/l	A1M		-0.44	7.29	15	7.05	7.37	7.39	0.23	3.1	18
	mg/kg	FT4			19.8		20.0	19.8	19.8	0.3	1.7	2
	µg/l	TY3		-0.53	29.4	20	27.9	29.7	29.4	3.5	11.8	6
	µg/l	V2M		-0.64	4.48	15	4.27	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.19	37.0	10	36.6	37.0	37.3	1.3	3.5	21
	µg/l	TY3		0.07	77.8	15	78.2	78.2	77.8	3.6	4.6	7
	µg/l	V2M		0.45	11.0	15	11.4	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		1.41	59.0	10	63.2	59.5	59.1	2.6	4.5	23
	mg/kg	FT4			139		122	139	139	24	17.3	2

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cr	µg/l	TY3		1.17	161	15	175	159	161	8	4.9	7
	µg/l	V2M		0.26	12.3	15	12.5	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.11	61.9	10	62.3	63.0	62.7	2.2	3.4	19
	mg/kg	FT4			195		190	195	195	7	3.5	2
	µg/l	TY3		1.25	103	15	113	106	103	9	9.0	7
	µg/l	V2M		0.00	10.1	20	10.1	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-19.98	778	10	1	789	780	30	3.9	24
	µg/l	TY3		1.03	316	15	341	311	316	17	5.3	7
	µg/l	V2M		1.43	641	15	710	645	639	52	8.1	20
Hg	µg/l	A1Hg		1.61	0.59	20	0.69	0.61	0.62	0.05	8.6	13
	mg/kg	FN4			0.099		0.099	0.100	0.099	0.007	7.3	4
	µg/l	T3Hg		1.83	3.33	20	3.94	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		2.65	5.34	20	6.76	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-19.98	450	10	0	453	453	17	3.8	20
	µg/l	TY3		0.71	187	15	197	190	187	9	5.1	6
	µg/l	V2M		1.29	388	10	413	386	388	21	5.4	19
Mo	mg/kg	FT4			20.6		21.6	20.6	20.6	1.4	6.7	2
Ni	µg/l	A1M		0.75	71.9	10	74.6	73.0	72.3	1.8	2.4	21
	µg/l	TY3		0.83	91.9	15	97.7	91.8	91.9	4.7	5.1	6
	µg/l	V2M		-0.11	8.54	20	8.45	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-1.06	69.6	10	65.9	69.1	69.8	3.3	4.7	20
	mg/kg	FT4			275		271	275	275	6	2.2	2
	µg/l	TY3		0.06	78.5	15	78.9	75.4	78.5	7.2	9.2	7
	µg/l	V2M		-0.65	4.64	15	4.41	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-1.48	62.9	10	58.3	63.2	62.8	3.2	5.1	17
	µg/l	TY3		-0.95	40.6	15	37.7	38.9	40.6	3.5	8.5	5
	µg/l	V2M		-1.38	7.64	15	6.85	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		1.00	76.9	10	80.8	76.0	76.1	3.0	4.0	17
	mg/kg	FT4			81.0		77.6	81.0	81.0	4.9	6.1	2
	µg/l	TY3		1.25	107	15	117	107	107	6	5.2	6
	µg/l	V2M		1.17	13.7	15	14.9	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		0.41	425	10	434	424	426	22	5.2	25
	mg/kg	FT4			3863		3852	3863	3863	17	0.4	2
	µg/l	TY3		0.15	153	15	155	154	153	5	2.9	6
	µg/l	V2M		-1.40	40.1	15	35.9	40.2	40.1	2.7	6.7	19

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.90	659	10	630	656	666	41	6.1	23
	µg/l	TN3		-1.18	1132	15	1032	1120	1133	69	6.1	17
	µg/l	V2M		-1.98	121	20	97	121	121	13	10.4	17
As	µg/l	A1M		-0.61	61.9	10	60.0	61.6	61.9	1.9	3.1	18
	mg/kg	FN4			18.2		17.4	18.4	18.2	0.7	3.7	5
	µg/l	TN3		-0.72	105	15	99	103	104	4	4.0	16
	µg/l	V2M		-1.52	8.58	20	7.28	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FN4			2155		2148	2205	2155	211	9.8	5
Cd	µg/l	A1M		0.27	7.29	15	7.44	7.37	7.39	0.23	3.1	18
	mg/kg	FN4		-0.88	20.0	20	18.3	19.9	20.0	2.7	13.6	7

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cd	µg/l	TN3		-0.95	28.2	15	26.2	28.4	28.1	1.3	4.6	18
	µg/l	V2M		-0.37	4.48	15	4.36	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.76	37.0	10	38.4	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.97	79.1	15	73.4	79.9	79.3	5.2	6.6	17
	µg/l	V2M		-0.48	11.0	15	10.6	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.54	59.0	10	60.6	59.5	59.1	2.6	4.5	23
	mg/kg	FN4		-0.82	108	20	99	111	108	6	5.5	6
	µg/l	TN3		-1.33	160	15	144	159	160	11	6.5	18
	µg/l	V2M		-0.38	12.3	15	12.0	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.34	61.9	10	63.0	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		0.19	175	15	178	175	175	3	1.7	7
	µg/l	TN3		-0.84	97.8	15	91.7	98.7	97.8	7.6	7.8	18
	µg/l	V2M		0.16	10.1	20	10.3	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.49	778	10	797	789	780	30	3.9	24
	µg/l	TN3		-1.55	313	15	277	310	313	22	7.0	20
	µg/l	V2M		-0.64	641	15	610	645	639	52	8.1	20
Mn	µg/l	A1M		0.36	450	10	458	453	453	17	3.8	20
	µg/l	TN3		-1.55	181	15	160	182	181	12	6.5	18
	µg/l	V2M		-1.39	388	10	361	386	388	21	5.4	19
Mo	mg/kg	FN4		-1.41	17.0	25	14.0	16.4	17.0	2.6	15.4	6
Ni	µg/l	A1M		0.50	71.9	10	73.7	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.92	91.8	15	85.5	91.1	91.9	6.4	7.0	18
	µg/l	V2M		-0.05	8.54	20	8.50	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.19	69.6	10	69.0	69.1	69.8	3.3	4.7	20
	mg/kg	FN4		-0.42	239	15	232	242	239	14	5.7	7
	µg/l	TN3		-2.09	82.2	15	69.3	77.9	76.7	5.9	7.8	17
	µg/l	V2M		0.45	4.64	15	4.80	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-0.10	62.9	10	62.6	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.58	40.2	15	38.5	40.0	40.6	3.1	7.6	14
	µg/l	V2M		-1.87	7.64	15	6.57	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.46	76.9	10	78.7	76.0	76.1	3.0	4.0	17
	mg/kg	FN4		1.83	84.0	20	99.4	82.2	84.0	8.3	9.8	6
	µg/l	TN3		-1.20	107	20	94	104	107	10	9.2	12
	µg/l	V2M		-1.02	13.7	15	12.7	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.40	425	10	417	424	426	22	5.2	25
	mg/kg	FN4		-0.52	3375	10	3288	3360	3375	119	3.5	7
	µg/l	TN3		-0.23	148	15	146	146	147	13	9.0	19
	µg/l	V2M		-0.67	40.1	15	38.1	40.2	40.1	2.7	6.7	19

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.65	659	10	638	656	666	41	6.1	23
	µg/l	TN3		-0.77	1132	15	1067	1120	1133	69	6.1	17
	µg/l	V2M		0.42	121	20	126	121	121	13	10.4	17
As	µg/l	A1M		-0.23	61.9	10	61.2	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		-0.37	17.6	20	17.0	17.6	17.6	2.1	11.8	10
	µg/l	TN3		-0.62	105	15	100	103	104	4	4.0	16
	µg/l	V2M		0.23	8.58	20	8.78	8.52	8.50	0.53	6.3	17

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ba	mg/kg	FO4					2116	2016	1502	906	60.3	7
Cd	µg/l	A1M		-0.26	7.29	15	7.15	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-0.44	19.2	20	18.4	19.3	19.2	2.0	10.6	10
	µg/l	TN3		-0.76	28.2	15	26.6	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.25	4.48	15	4.57	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		1.11	37.0	10	39.1	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.13	79.1	15	78.3	79.9	79.3	5.2	6.6	17
	µg/l	V2M		-0.05	11.0	15	11.0	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.46	59.0	10	60.4	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		0.90	96.3	20	105.0	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-0.17	160	15	158	159	160	11	6.5	18
	µg/l	V2M		0.07	12.3	15	12.4	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.08	61.9	10	62.2	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.83	176	15	165	172	176	10	5.8	11
	µg/l	TN3		-0.83	97.8	15	91.7	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-0.03	10.1	20	10.1	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.67	778	10	804	789	780	30	3.9	24
	µg/l	TN3		-1.51	313	15	278	310	313	22	7.0	20
	µg/l	V2M		-0.73	641	15	606	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.74	0.59	20	0.63	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		0.10	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		0.03	3.33	20	3.34	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.07	5.34	20	5.31	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		0.13	450	10	453	453	453	17	3.8	20
	µg/l	TN3		-0.15	181	15	179	182	181	12	6.5	18
	µg/l	V2M		0.61	388	10	400	386	388	21	5.4	19
Mo	mg/kg	FO4		0.35	16.1	25	16.8	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		0.32	71.9	10	73.1	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.78	91.8	15	86.5	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.09	8.54	20	8.62	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.09	69.6	10	69.3	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-0.21	212	20	208	212	212	35	16.4	11
	µg/l	TN3		-0.67	82.2	15	78.1	77.9	76.7	5.9	7.8	17
	µg/l	V2M		0.23	4.64	15	4.72	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-0.70	62.9	10	60.7	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.13	40.2	15	39.8	40.0	40.6	3.1	7.6	14
	µg/l	V2M		0.86	7.64	15	8.13	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.29	76.9	10	78.0	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		0.19	78.2	20	79.7	77.7	78.2	6.0	7.7	9
	µg/l	TN3		-0.70	107	20	100	104	107	10	9.2	12
	µg/l	V2M		0.39	13.7	15	14.1	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		0.09	425	10	427	424	426	22	5.2	25
	mg/kg	FO4		-1.27	3203	15	2899	3315	3203	306	9.5	9
	µg/l	TN3		-0.41	148	15	144	146	147	13	9.0	19
	µg/l	V2M		0.02	40.1	15	40.2	40.2	40.1	2.7	6.7	19

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-1.79	659	10	600	656	666	41	6.1	23
	µg/l	TN3		-0.14	1132	15	1120	1120	1133	69	6.1	17
	µg/l	V2M		-1.65	121	20	101	121	121	13	10.4	17
As	µg/l	A1M		-0.45	61.9	10	60.5	61.6	61.9	1.9	3.1	18
	µg/l	TN3		-0.83	105	15	99	103	104	4	4.0	16
	µg/l	V2M		0.61	8.58	20	9.10	8.52	8.50	0.53	6.3	17
Cd	µg/l	A1M		-0.07	7.29	15	7.25	7.37	7.39	0.23	3.1	18
	µg/l	TN3		-0.95	28.2	15	26.2	28.4	28.1	1.3	4.6	18
	µg/l	V2M		-1.13	4.48	15	4.10	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.27	37.0	10	36.5	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-1.45	79.1	15	70.5	79.9	79.3	5.2	6.6	17
	µg/l	V2M		-1.64	11.0	15	9.7	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-1.19	59.0	10	55.5	59.5	59.1	2.6	4.5	23
	µg/l	TN3		-0.21	160	15	158	159	160	11	6.5	18
	µg/l	V2M		-1.41	12.3	15	11.0	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-1.42	61.9	10	57.5	63.0	62.7	2.2	3.4	19
	µg/l	TN3		-0.59	97.8	15	93.5	98.7	97.8	7.6	7.8	18
	µg/l	V2M		-1.83	10.1	20	8.3	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.98	778	10	740	789	780	30	3.9	24
	µg/l	TN3		-0.66	313	15	298	310	313	22	7.0	20
	µg/l	V2M		-1.68	641	15	560	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.50	0.59	20	0.62	0.61	0.62	0.05	8.6	13
	µg/l	T3Hg		0.41	3.33	20	3.47	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		0.84	5.34	20	5.79	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.56	450	10	438	453	453	17	3.8	20
	µg/l	TN3		-0.41	181	15	176	182	181	12	6.5	18
	µg/l	V2M		-1.44	388	10	360	386	388	21	5.4	19
Ni	µg/l	A1M		-0.67	71.9	10	69.5	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-1.13	91.8	15	84.0	91.1	91.9	6.4	7.0	18
	µg/l	V2M		-2.21	8.54	20	6.65	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.75	69.6	10	67.0	69.1	69.8	3.3	4.7	20
	µg/l	TN3		-2.79	82.2	15	65.0	77.9	76.7	5.9	7.8	17
	µg/l	V2M		4.48	4.64	15	6.20	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		1.30	62.9	10	67.0	63.2	62.8	3.2	5.1	17
	µg/l	TN3		0.10	40.2	15	40.5	40.0	40.6	3.1	7.6	14
	µg/l	V2M		3.94	7.64	15	9.90	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.23	76.9	10	76.0	76.0	76.1	3.0	4.0	17
	µg/l	TN3		-0.42	107	20	103	104	107	10	9.2	12
	µg/l	V2M		-0.68	13.7	15	13.0	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		0.24	425	10	430	424	426	22	5.2	25
	µg/l	TN3		0.18	148	15	150	146	147	13	9.0	19
	µg/l	V2M		-1.03	40.1	15	37.0	40.2	40.1	2.7	6.7	19

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.17	659	10	665	656	666	41	6.1	23
	µg/l	TN3		-0.61	1132	15	1080	1120	1133	69	6.1	17
	µg/l	TY3		-0.52	1145	15	1100	1100	1145	87	7.6	7
	µg/l	V2M		-0.08	121	20	120	121	121	13	10.4	17
As	µg/l	A1M		0.57	61.9	10	63.7	61.6	61.9	1.9	3.1	18
	mg/kg	FN4			18.2		18.4	18.4	18.2	0.7	3.7	5
	mg/kg	FO4		0.23	17.6	20	18.0	17.6	17.6	2.1	11.8	10
	µg/l	TN3		-0.25	105	15	103	103	104	4	4.0	16
	µg/l	TY3			106		108	105	106	4	3.4	5
	µg/l	V2M		-0.42	8.58	20	8.22	8.52	8.50	0.53	6.3	17
Cd	µg/l	A1M		-0.37	7.29	15	7.09	7.37	7.39	0.23	3.1	18
	mg/kg	FN4		-0.05	20.0	20	19.9	19.9	20.0	2.7	13.6	7
	mg/kg	FO4		0.44	19.2	20	20.1	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.07	28.2	15	28.4	28.4	28.1	1.3	4.6	18
	µg/l	TY3		0.48	29.4	20	30.8	29.7	29.4	3.5	11.8	6
	µg/l	V2M		-0.55	4.48	15	4.30	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.05	37.0	10	37.1	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.44	79.1	15	76.5	79.9	79.3	5.2	6.6	17
	µg/l	TY3		0.26	77.8	15	79.3	78.2	77.8	3.6	4.6	7
	µg/l	V2M		-0.61	11.0	15	10.5	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.64	59.0	10	60.9	59.5	59.1	2.6	4.5	23
	mg/kg	FN4		0.37	108	20	112	111	108	6	5.5	6
	mg/kg	FO4		0.59	96.3	20	102.0	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-0.50	160	15	154	159	160	11	6.5	18
	µg/l	TY3		-0.46	161	15	156	159	161	8	4.9	7
	µg/l	V2M		-1.01	12.3	15	11.4	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-0.63	61.9	10	60.0	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		0.27	175	15	179	175	175	3	1.7	7
	mg/kg	FO4		-0.45	176	15	170	172	176	10	5.8	11
	µg/l	TN3		-0.43	97.8	15	94.7	98.7	97.8	7.6	7.8	18
	µg/l	TY3		-1.13	103	15	94	106	103	9	9.0	7
	µg/l	V2M		-1.02	10.1	20	9.1	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.64	778	10	753	789	780	30	3.9	24
	µg/l	TN3		0.26	313	15	319	310	313	22	7.0	20
	µg/l	TY3		-0.57	316	15	303	311	316	17	5.3	7
	µg/l	V2M		-0.55	641	15	615	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.15	0.59	20	0.60	0.61	0.62	0.05	8.6	13
	mg/kg	FC4			0.081		0.084	0.084	0.081	0.014	16.9	3
	µg/l	T3Hg		-0.41	3.33	20	3.20	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		0.57	5.34	20	5.65	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.42	450	10	441	453	453	17	3.8	20
	µg/l	TN3		-0.96	181	15	168	182	181	12	6.5	18
	µg/l	TY3		-1.14	187	15	171	190	187	9	5.1	6
	µg/l	V2M		-0.75	388	10	374	386	388	21	5.4	19
Mo	mg/kg	FN4		0.73	17.0	25	18.6	16.4	17.0	2.6	15.4	6
	mg/kg	FO4		1.44	16.1	25	19.0	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		-0.67	71.9	10	69.5	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.28	91.8	15	89.9	91.1	91.9	6.4	7.0	18

Participant 15

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ni	µg/l	TY3		-0.17	91.9	15	90.7	91.8	91.9	4.7	5.1	6
	µg/l	V2M		-0.40	8.54	20	8.20	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.82	69.6	10	66.8	69.1	69.8	3.3	4.7	20
	mg/kg	FN4		0.75	239	15	253	242	239	14	5.7	7
	mg/kg	FO4		1.72	212	20	249	212	212	35	16.4	11
	µg/l	TN3		-0.95	82.2	15	76.4	77.9	76.7	5.9	7.8	17
	µg/l	TY3		-0.53	78.5	15	75.4	75.4	78.5	7.2	9.2	7
	µg/l	V2M		-1.11	4.64	15	4.26	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		0.08	62.9	10	63.2	63.2	62.8	3.2	5.1	17
	µg/l	TN3		-0.58	40.2	15	38.5	40.0	40.6	3.1	7.6	14
	µg/l	TY3		-0.77	40.6	15	38.3	38.9	40.6	3.5	8.5	5
	µg/l	V2M		-0.63	7.64	15	7.28	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-0.33	76.9	10	75.7	76.0	76.1	3.0	4.0	17
	mg/kg	FN4		-0.04	84.0	20	83.7	82.2	84.0	8.3	9.8	6
	mg/kg	FO4		1.03	78.2	20	86.3	77.7	78.2	6.0	7.7	9
	µg/l	TN3		-0.37	107	20	103	104	107	10	9.2	12
	µg/l	TY3		-0.31	107	15	105	107	107	6	5.2	6
	µg/l	V2M		-0.68	13.7	15	13.0	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		-0.28	425	10	419	424	426	22	5.2	25
	mg/kg	FN4		0.68	3375	10	3490	3360	3375	119	3.5	7
	mg/kg	FO4		0.47	3203	15	3315	3315	3203	306	9.5	9
	µg/l	TN3		-0.95	148	15	138	146	147	13	9.0	19
	µg/l	TY3		-0.57	153	15	147	154	153	5	2.9	6
	µg/l	V2M		-0.85	40.1	15	37.6	40.2	40.1	2.7	6.7	19

Participant 16

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.38	659	10	647	656	666	41	6.1	23
	µg/l	TN3		1.51	1132	15	1260	1120	1133	69	6.1	17
	µg/l	V2M		0.79	121	20	131	121	121	13	10.4	17
As	µg/l	A1M		0.55	61.9	10	63.6	61.6	61.9	1.9	3.1	18
	mg/kg	FN4			18.2		19.2	18.4	18.2	0.7	3.7	5
	µg/l	TN3		2.10	105	15	122	103	104	4	4.0	16
	µg/l	V2M		0.92	8.58	20	9.37	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FN4			2155		2300	2205	2155	211	9.8	5
Cd	µg/l	A1M		0.08	7.29	15	7.34	7.37	7.39	0.23	3.1	18
	mg/kg	FN4		-1.80	20.0	20	16.4	19.9	20.0	2.7	13.6	7
	µg/l	TN3		-0.07	28.2	15	28.1	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.12	4.48	15	4.52	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.65	37.0	10	38.2	37.0	37.3	1.3	3.5	21
	µg/l	TN3		1.44	79.1	15	87.7	79.9	79.3	5.2	6.6	17
	µg/l	V2M		0.67	11.0	15	11.6	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.69	59.0	10	61.1	59.5	59.1	2.6	4.5	23
	mg/kg	FN4		-0.42	108	20	104	111	108	6	5.5	6
	µg/l	TN3		1.83	160	15	182	159	160	11	6.5	18
	µg/l	V2M		1.14	12.3	15	13.4	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.47	61.9	10	63.4	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		-0.11	175	15	174	175	175	3	1.7	7

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cu	µg/l	TN3		1.05	97.8	15	105.5	98.7	97.8	7.6	7.8	18
	µg/l	V2M		0.30	10.1	20	10.4	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.54	778	10	799	789	780	30	3.9	24
	µg/l	TN3		1.70	313	15	353	310	313	22	7.0	20
	µg/l	V2M		1.04	641	15	691	645	639	52	8.1	20
Hg	µg/l	A1Hg		-0.51	0.59	20	0.56	0.61	0.62	0.05	8.6	13
	mg/kg	FN4			0.099		0.090	0.100	0.099	0.007	7.3	4
	µg/l	T3Hg		-1.95	3.33	20	2.68	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.85	5.34	20	4.89	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.44	450	10	440	453	453	17	3.8	20
	µg/l	TN3		1.29	181	15	199	182	181	12	6.5	18
	µg/l	V2M		0.75	388	10	403	386	388	21	5.4	19
Mo	mg/kg	FN4		-0.87	17.0	25	15.2	16.4	17.0	2.6	15.4	6
Ni	µg/l	A1M		0.46	71.9	10	73.6	73.0	72.3	1.8	2.4	21
	µg/l	TN3		1.14	91.8	15	99.7	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.26	8.54	20	8.76	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.45	69.6	10	68.1	69.1	69.8	3.3	4.7	20
	mg/kg	FN4		-0.59	239	15	229	242	239	14	5.7	7
	µg/l	TN3		-0.75	82.2	15	77.6	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-1.03	4.64	15	4.28	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		0.57	62.9	10	64.7	63.2	62.8	3.2	5.1	17
	µg/l	TN3		2.09	40.2	15	46.5	40.0	40.6	3.1	7.6	14
	µg/l	V2M		1.82	7.64	15	8.68	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.09	76.9	10	77.3	76.0	76.1	3.0	4.0	17
	mg/kg	FN4		0.16	84.0	20	85.4	82.2	84.0	8.3	9.8	6
	µg/l	TN3		1.45	107	20	123	104	107	10	9.2	12
	µg/l	V2M		0.92	13.7	15	14.7	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		1.06	425	10	448	424	426	22	5.2	25
	mg/kg	FN4		-0.30	3375	10	3325	3360	3375	119	3.5	7
	µg/l	TN3		1.62	148	15	166	146	147	13	9.0	19
	µg/l	V2M		1.23	40.1	15	43.8	40.2	40.1	2.7	6.7	19

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		3.03	659	10	759	656	666	41	6.1	23
	µg/l	TN3		2.39	1132	15	1335	1120	1133	69	6.1	17
	µg/l	V2M		11.03	121	20	255	121	121	13	10.4	17
As	µg/l	A1M		3.91	61.9	10	74.0	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		1.14	17.6	20	19.6	17.6	17.6	2.1	11.8	10
	µg/l	TN3		4.76	105	15	143	103	104	4	4.0	16
	µg/l	V2M		2.82	8.58	20	11.00	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					101	2016	1502	906	60.3	7
Cd	µg/l	A1M		3.13	7.29	15	9.00	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		0.49	19.2	20	20.2	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.85	28.2	15	30.0	28.4	28.1	1.3	4.6	18
	µg/l	V2M		3.04	4.48	15	5.50	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.54	37.0	10	38.0	37.0	37.3	1.3	3.5	21
	µg/l	TN3		1.84	79.1	15	90.0	79.9	79.3	5.2	6.6	17

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Co	µg/l	V2M		1.21	11.0	15	12.0	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.00	59.0	10	59.0	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		-0.52	96.3	20	91.3	97.9	96.3	11.7	12.2	10
	µg/l	TN3		1.25	160	15	175	159	160	11	6.5	18
	µg/l	V2M		0.76	12.3	15	13.0	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		1.00	61.9	10	65.0	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		0.74	176	15	186	172	176	10	5.8	11
	µg/l	TN3		1.66	97.8	15	110.0	98.7	97.8	7.6	7.8	18
	µg/l	V2M		0.89	10.1	20	11.0	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		3.19	778	10	902	789	780	30	3.9	24
	µg/l	TN3			313	15	*< 500*	310	313	22	7.0	20
	µg/l	V2M		2.00	641	15	737	645	639	52	8.1	20
Hg	µg/l	A1Hg		846	0.59	20	50.50	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		0.10	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		831	3.33	20	280.00	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		681	5.34	20	369.00	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		1.27	450	10	479	453	453	17	3.8	20
	µg/l	TN3		1.03	181	15	195	182	181	12	6.5	18
	µg/l	V2M		1.11	388	10	410	386	388	21	5.4	19
Mo	mg/kg	FO4		1.59	16.1	25	19.3	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		-0.53	71.9	10	70.0	73.0	72.3	1.8	2.4	21
	µg/l	TN3		1.19	91.8	15	100.0	91.1	91.9	6.4	7.0	18
	µg/l	V2M		0.54	8.54	20	9.00	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.46	69.6	10	68.0	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		0.91	212	20	231	212	212	35	16.4	11
	µg/l	TN3		-1.98	82.2	15	70.0	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-1.84	4.64	15	4.00	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		4.96	62.9	10	78.5	63.2	62.8	3.2	5.1	17
	µg/l	TN3		3.25	40.2	15	50.0	40.0	40.6	3.1	7.6	14
	µg/l	V2M		4.12	7.64	15	10.00	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.68	76.9	10	79.5	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		-0.07	78.2	20	77.7	77.7	78.2	6.0	7.7	9
	µg/l	TN3		2.15	107	20	130	104	107	10	9.2	12
	µg/l	V2M		1.27	13.7	15	15.0	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		10.40	425	10	646	424	426	22	5.2	25
	mg/kg	FO4		0.75	3203	15	3384	3315	3203	306	9.5	9
	µg/l	TN3		6.94	148	15	225	146	147	13	9.0	19
	µg/l	V2M		7.45	40.1	15	62.5	40.2	40.1	2.7	6.7	19

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-1.79	659	10	600	656	666	41	6.1	23
	µg/l	TN3		-0.86	1132	15	1059	1120	1133	69	6.1	17
	µg/l	TY3		-0.89	1145	15	1069	1100	1145	87	7.6	7
	µg/l	V2M		0.08	121	20	122	121	121	13	10.4	17
As	µg/l	A1M		-0.19	61.9	10	61.3	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		-0.26	17.6	20	17.2	17.6	17.6	2.1	11.8	10
	µg/l	TN3		-0.68	105	15	100	103	104	4	4.0	16

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
As	µg/l	TY3			106		74	105	106	4	3.4	5
	µg/l	V2M		-0.38	8.58	20	8.26	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					1224	2016	1502	906	60.3	7
Cd	µg/l	A1M		-0.29	7.29	15	7.13	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-0.26	19.2	20	18.7	19.3	19.2	2.0	10.6	10
	µg/l	TN3		-1.25	28.2	15	25.6	28.4	28.1	1.3	4.6	18
	µg/l	TY3		-1.89	29.4	20	23.9	29.7	29.4	3.5	11.8	6
	µg/l	V2M		-0.70	4.48	15	4.25	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.14	37.0	10	36.8	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.15	79.1	15	80.0	79.9	79.3	5.2	6.6	17
	µg/l	TY3		-0.37	77.8	15	75.7	78.2	77.8	3.6	4.6	7
	µg/l	V2M		-0.48	11.0	15	10.6	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-1.08	59.0	10	55.8	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		-0.01	96.3	20	96.3	97.9	96.3	11.7	12.2	10
	µg/l	TN3		-1.13	160	15	146	159	160	11	6.5	18
	µg/l	TY3		-0.19	161	15	159	159	161	8	4.9	7
	µg/l	V2M		-0.87	12.3	15	11.5	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.81	61.9	10	64.4	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		1.27	176	15	193	172	176	10	5.8	11
	µg/l	TN3		-1.62	97.8	15	85.9	98.7	97.8	7.6	7.8	18
	µg/l	TY3		-1.70	103	15	90	106	103	9	9.0	7
	µg/l	V2M		-0.34	10.1	20	9.8	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.69	778	10	751	789	780	30	3.9	24
	µg/l	TN3		-0.49	313	15	302	310	313	22	7.0	20
	µg/l	TY3		-0.21	316	15	311	311	316	17	5.3	7
	µg/l	V2M		-0.02	641	15	640	645	639	52	8.1	20
Hg	µg/l	A1Hg		0.34	0.59	20	0.61	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		0.17	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		-0.29	3.33	20	3.24	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.23	5.34	20	5.22	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-1.80	450	10	410	453	453	17	3.8	20
	µg/l	TN3		-1.18	181	15	165	182	181	12	6.5	18
	µg/l	TY3		0.07	187	15	188	190	187	9	5.1	6
	µg/l	V2M		-1.47	388	10	360	386	388	21	5.4	19
Mo	mg/kg	FO4		-0.15	16.1	25	15.8	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		-0.33	71.9	10	70.7	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-1.28	91.8	15	83.0	91.1	91.9	6.4	7.0	18
	µg/l	TY3		-0.89	91.9	15	85.7	91.8	91.9	4.7	5.1	6
	µg/l	V2M		-0.42	8.54	20	8.18	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.90	69.6	10	66.5	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-1.46	212	20	181	212	212	35	16.4	11
	µg/l	TN3		-1.64	82.2	15	72.1	77.9	76.7	5.9	7.8	17
	µg/l	TY3		-1.04	78.5	15	72.4	75.4	78.5	7.2	9.2	7
	µg/l	V2M		-1.05	4.64	15	4.28	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		1.21	62.9	10	66.7	63.2	62.8	3.2	5.1	17
	µg/l	TN3		2.22	40.2	15	46.9	40.0	40.6	3.1	7.6	14
	µg/l	TY3		-4.71	40.6	15	26.3	38.9	40.6	3.5	8.5	5
	µg/l	V2M		-0.30	7.64	15	7.47	7.62	7.64	0.57	7.4	14

Participant 18													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
V	µg/l	A1M		-1.64	76.9	10	70.6	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		-0.38	78.2	20	75.3	77.7	78.2	6.0	7.7	9
	µg/l	TN3		-1.04	107	20	96	104	107	10	9.2	12
	µg/l	TY3		0.02	107	15	107	107	107	6	5.2	6
	µg/l	V2M		-1.13	13.7	15	12.5	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		0.56	425	10	437	424	426	22	5.2	25
	mg/kg	FO4		-2.44	3203	15	2616	3315	3203	306	9.5	9
	µg/l	TN3		-3.34	148	15	111	146	147	13	9.0	19
	µg/l	TY3		-4.27	153	15	104	154	153	5	2.9	6
	µg/l	V2M		-1.25	40.1	15	36.3	40.2	40.1	2.7	6.7	19

Participant 19													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.38	659	10	647	656	666	41	6.1	23
	µg/l	TN3		0.11	1132	15	1141	1120	1133	69	6.1	17
	µg/l	V2M		1.48	121	20	139	121	121	13	10.4	17
As	µg/l	A1M		-1.07	61.9	10	58.6	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		1.00	17.6	20	19.4	17.6	17.6	2.1	11.8	10
	µg/l	TN3		0.50	105	15	109	103	104	4	4.0	16
	µg/l	V2M		0.68	8.58	20	9.16	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					2016	2016	1502	906	60.3	7
Cd	µg/l	A1M		0.35	7.29	15	7.48	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-1.26	19.2	20	16.8	19.3	19.2	2.0	10.6	10
	µg/l	TN3		0.37	28.2	15	29.0	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.42	4.48	15	4.62	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-0.16	37.0	10	36.7	37.0	37.3	1.3	3.5	21
	µg/l	TN3		0.56	79.1	15	82.4	79.9	79.3	5.2	6.6	17
	µg/l	V2M		1.27	11.0	15	12.1	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-0.05	59.0	10	58.8	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		-1.55	96.3	20	81.4	97.9	96.3	11.7	12.2	10
	µg/l	TN3		0.91	160	15	171	159	160	11	6.5	18
	µg/l	V2M		1.91	12.3	15	14.1	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.97	61.9	10	64.9	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.44	176	15	170	172	176	10	5.8	11
	µg/l	TN3		1.38	97.8	15	107.9	98.7	97.8	7.6	7.8	18
	µg/l	V2M		1.00	10.1	20	11.1	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.60	778	10	755	789	780	30	3.9	24
	µg/l	TN3		0.96	313	15	335	310	313	22	7.0	20
	µg/l	V2M		1.30	641	15	704	645	639	52	8.1	20
Hg	µg/l	A1Hg		1.95	0.59	20	0.71	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		*< 0,50*	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		1.85	3.33	20	3.95	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		1.02	5.34	20	5.89	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.08	450	10	448	453	453	17	3.8	20
	µg/l	TN3		1.62	181	15	203	182	181	12	6.5	18
	µg/l	V2M		2.25	388	10	432	386	388	21	5.4	19
Mo	mg/kg	FO4		-1.45	16.1	25	13.2	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		0.34	71.9	10	73.1	73.0	72.3	1.8	2.4	21

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ni	µg/l	TN3		1.23	91.8	15	100.3	91.1	91.9	6.4	7.0	18
	µg/l	V2M		1.42	8.54	20	9.76	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		-0.65	69.6	10	67.4	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-1.61	212	20	178	212	212	35	16.4	11
	µg/l	TN3		-0.70	82.2	15	77.9	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-1.25	4.64	15	4.21	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-1.07	62.9	10	59.5	63.2	62.8	3.2	5.1	17
	µg/l	TN3		0.73	40.2	15	42.4	40.0	40.6	3.1	7.6	14
	µg/l	V2M		1.01	7.64	15	8.22	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.66	76.9	10	79.4	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		-1.47	78.2	20	66.7	77.7	78.2	6.0	7.7	9
	µg/l	TN3		1.65	107	20	125	104	107	10	9.2	12
	µg/l	V2M		2.04	13.7	15	15.8	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		1.20	425	10	451	424	426	22	5.2	25
	mg/kg	FO4		-0.78	3203	15	3016	3315	3203	306	9.5	9
	µg/l	TN3		1.45	148	15	164	146	147	13	9.0	19
	µg/l	V2M		1.32	40.1	15	44.1	40.2	40.1	2.7	6.7	19

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cd	mg/kg	FN4		1.57	20.0	20	23.1	19.9	20.0	2.7	13.6	7
Cu	mg/kg	FN4		0.04	175	15	175	175	175	3	1.7	7
	µg/l	TY3		1.10	103	15	112	106	103	9	9.0	7
Fe	µg/l	A1M		-0.89	778	10	744	789	780	30	3.9	24
	µg/l	TN3		0.77	313	15	331	310	313	22	7.0	20
	µg/l	V2M		-2.75	641	15	509	645	639	52	8.1	20
Pb	mg/kg	FN4		0.97	239	15	256	242	239	14	5.7	7
	µg/l	TY3		-1.02	78.5	15	72.5	75.4	78.5	7.2	9.2	7
Zn	µg/l	A1M		-2.26	425	10	377	424	426	22	5.2	25
	mg/kg	FN4		-19.04	3375	10	162	3360	3375	119	3.5	7
	µg/l	TY3		0.44	153	15	158	154	153	5	2.9	6

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		2.55	659	10	743	656	666	41	6.1	23
	µg/l	TY3		-1.04	1145	15	1056	1100	1145	87	7.6	7
Co	µg/l	A1M		-0.81	37.0	10	35.5	37.0	37.3	1.3	3.5	21
	µg/l	TY3		-1.08	77.8	15	71.5	78.2	77.8	3.6	4.6	7
Cr	µg/l	A1M		-0.51	59.0	10	57.5	59.5	59.1	2.6	4.5	23
	µg/l	TY3		-0.66	161	15	153	159	161	8	4.9	7
Fe	µg/l	A1M		0.37	778	10	793	789	780	30	3.9	24
	µg/l	TY3		-0.38	316	15	307	311	316	17	5.3	7
Zn	µg/l	A1M		-1.22	425	10	399	424	426	22	5.2	25
	µg/l	TY3		-4.23	153	15	105	154	153	5	2.9	6

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.21	659	10	666	656	666	41	6.1	23
	µg/l	TN3		0.97	1132	15	1215	1120	1133	69	6.1	17
	µg/l	V2M		5.33	121	20	186	121	121	13	10.4	17
As	µg/l	A1M		1.32	61.9	10	66.0	61.6	61.9	1.9	3.1	18
	µg/l	TN3		0.25	105	15	107	103	104	4	4.0	16
	µg/l	V2M		0.26	8.58	20	8.80	8.52	8.50	0.53	6.3	17
Cd	µg/l	A1M		0.38	7.29	15	7.50	7.37	7.39	0.23	3.1	18
	µg/l	TN3		-0.09	28.2	15	28.0	28.4	28.1	1.3	4.6	18
	µg/l	V2M		0.51	4.48	15	4.65	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.00	37.0	10	37.0	37.0	37.3	1.3	3.5	21
	µg/l	TN3		-0.19	79.1	15	78.0	79.9	79.3	5.2	6.6	17
	µg/l	V2M		0.61	11.0	15	11.5	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.17	59.0	10	59.5	59.5	59.1	2.6	4.5	23
	µg/l	TN3		-0.21	160	15	158	159	160	11	6.5	18
	µg/l	V2M		0.22	12.3	15	12.5	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		0.84	61.9	10	64.5	63.0	62.7	2.2	3.4	19
	µg/l	TN3		0.37	97.8	15	100.5	98.7	97.8	7.6	7.8	18
	µg/l	V2M		0.40	10.1	20	10.5	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.12	778	10	783	789	780	30	3.9	24
	µg/l	TN3		-0.28	313	15	307	310	313	22	7.0	20
	µg/l	V2M		0.36	641	15	659	645	639	52	8.1	20
Mn	µg/l	A1M		0.22	450	10	455	453	453	17	3.8	20
	µg/l	TN3		0.22	181	15	184	182	181	12	6.5	18
	µg/l	V2M		0.54	388	10	399	386	388	21	5.4	19
Ni	µg/l	A1M		0.31	71.9	10	73.0	73.0	72.3	1.8	2.4	21
	µg/l	TN3		0.25	91.8	15	93.5	91.1	91.9	6.4	7.0	18
	µg/l	V2M		-0.34	8.54	20	8.25	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		0.83	69.6	10	72.5	69.1	69.8	3.3	4.7	20
	µg/l	TN3		-1.90	82.2	15	70.5	77.9	76.7	5.9	7.8	17
	µg/l	V2M		-1.55	4.64	15	4.10	4.50	4.47	0.29	6.5	16
Zn	µg/l	A1M		0.68	425	10	440	424	426	22	5.2	25
	µg/l	TN3		0.77	148	15	157	146	147	13	9.0	19
	µg/l	V2M		0.63	40.1	15	42.0	40.2	40.1	2.7	6.7	19

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cr	µg/l	A1M		-0.17	59.0	10	58.5	59.5	59.1	2.6	4.5	23
	µg/l	TN3		-0.22	160	15	157	159	160	11	6.5	18
Fe	µg/l	A1M		0.31	778	10	790	789	780	30	3.9	24
	µg/l	TN3		0.26	313	15	319	310	313	22	7.0	20
Ni	µg/l	A1M		0.25	71.9	10	72.8	73.0	72.3	1.8	2.4	21
	µg/l	TN3		-0.28	91.8	15	89.9	91.1	91.9	6.4	7.0	18
Zn	µg/l	A1M		-0.20	425	10	421	424	426	22	5.2	25
	µg/l	TN3		-0.69	148	15	140	146	147	13	9.0	19

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	V2M		-0.37	121	20	117	121	121	13	10.4	17
As	mg/kg	FN4			18.2		18.4	18.4	18.2	0.7	3.7	5
	mg/kg	FT4			17.6		18.3	17.6	17.6	0.9	4.9	2
	µg/l	V2M		-0.10	8.58	20	8.50	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FN4			2155		2205	2205	2155	211	9.8	5
	mg/kg	FT4			2300		2335	2300	2300	49	2.1	2
Cd	mg/kg	FN4		-0.73	20.0	20	18.6	19.9	20.0	2.7	13.6	7
	mg/kg	FT4			19.8		19.6	19.8	19.8	0.3	1.7	2
	µg/l	V2M		-0.71	4.48	15	4.24	4.52	4.45	0.21	4.7	18
Co	µg/l	V2M		0.24	11.0	15	11.2	11.0	11.0	0.7	6.0	18
Cr	mg/kg	FN4		0.19	108	20	110	111	108	6	5.5	6
	mg/kg	FT4			139		156	139	139	24	17.3	2
	µg/l	V2M		0.98	12.3	15	13.2	12.4	12.3	0.8	6.7	18
Cu	mg/kg	FN4		0.00	175	15	175	175	175	3	1.7	7
	mg/kg	FT4			195		200	195	195	7	3.5	2
	µg/l	V2M		0.01	10.1	20	10.1	10.1	10.1	0.9	9.4	20
Fe	µg/l	V2M		0.24	641	15	653	645	639	52	8.1	20
Hg	mg/kg	FC4			0.081		0.094	0.084	0.081	0.014	16.9	3
	mg/kg	FN4			0.099		0.107	0.100	0.099	0.007	7.3	4
	µg/l	V2Hg		1.73	5.34	20	6.27	5.30	5.39	0.32	5.9	14
Mn	µg/l	V2M		0.00	388	10	388	386	388	21	5.4	19
Mo	mg/kg	FN4		-0.24	17.0	25	16.5	16.4	17.0	2.6	15.4	6
	mg/kg	FT4			20.6		19.7	20.6	20.6	1.4	6.7	2
Ni	µg/l	V2M		0.03	8.54	20	8.57	8.53	8.53	0.79	9.3	18
Pb	mg/kg	FN4		0.14	239	15	242	242	239	14	5.7	7
	mg/kg	FT4			275		280	275	275	6	2.2	2
	µg/l	V2M		0.03	4.64	15	4.65	4.50	4.47	0.29	6.5	16
Se	µg/l	V2M		0.52	7.64	15	7.94	7.62	7.64	0.57	7.4	14
V	mg/kg	FN4		-0.40	84.0	20	80.7	82.2	84.0	8.3	9.8	6
	mg/kg	FT4			81.0		84.5	81.0	81.0	4.9	6.1	2
	µg/l	V2M		0.44	13.7	15	14.2	13.4	13.7	1.0	7.0	17
Zn	mg/kg	FN4		-0.09	3375	10	3360	3360	3375	119	3.5	7
	mg/kg	FT4			3863		3875	3863	3863	17	0.4	2
	µg/l	V2M		-0.78	40.1	15	37.8	40.2	40.1	2.7	6.7	19

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.43	659	10	706	656	666	41	6.1	23
	µg/l	TY3		1.05	1145	15	1235	1100	1145	87	7.6	7
	µg/l	V2M		1.49	121	20	139	121	121	13	10.4	17
As	µg/l	A1M		0.26	61.9	10	62.7	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		-1.82	17.6	20	14.4	17.6	17.6	2.1	11.8	10
	µg/l	TY3			106		105	105	106	4	3.4	5
	µg/l	V2M			8.58	20	<13	8.52	8.50	0.53	6.3	17
Ba	mg/kg	FO4					499	2016	1502	906	60.3	7
Cd	µg/l	A1M		0.99	7.29	15	7.83	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-1.67	19.2	20	16.0	19.3	19.2	2.0	10.6	10
	µg/l	TY3		0.34	29.4	20	30.4	29.7	29.4	3.5	11.8	6

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cd	µg/l	V2M		1.03	4.48	15	4.83	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		0.78	37.0	10	38.5	37.0	37.3	1.3	3.5	21
	µg/l	TY3		0.95	77.8	15	83.4	78.2	77.8	3.6	4.6	7
	µg/l	V2M		0.85	11.0	15	11.7	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		0.61	59.0	10	60.8	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		-1.30	96.3	20	83.8	97.9	96.3	11.7	12.2	10
	µg/l	TY3		0.54	161	15	168	159	161	8	4.9	7
	µg/l	V2M		0.16	12.3	15	12.5	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		1.31	61.9	10	66.0	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.34	176	15	172	172	176	10	5.8	11
	µg/l	TY3		0.39	103	15	106	106	103	9	9.0	7
	µg/l	V2M		1.29	10.1	20	11.4	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.66	778	10	804	789	780	30	3.9	24
	µg/l	TY3		-0.89	316	15	295	311	316	17	5.3	7
	µg/l	V2M		-0.20	641	15	632	645	639	52	8.1	20
Hg	µg/l	A1Hg		-2.33	0.59	20	0.45	0.61	0.62	0.05	8.6	13
	mg/kg	FO4			0.13		*<0,10*	0.10	0.13	0.04	32.9	5
	µg/l	T3Hg		-1.26	3.33	20	2.91	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.49	5.34	20	5.08	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		1.13	450	10	476	453	453	17	3.8	20
	µg/l	TY3		0.50	187	15	194	190	187	9	5.1	6
	µg/l	V2M		1.44	388	10	416	386	388	21	5.4	19
Mo	mg/kg	FO4		-1.14	16.1	25	13.8	16.3	16.1	2.5	15.6	9
Ni	µg/l	A1M		0.60	71.9	10	74.1	73.0	72.3	1.8	2.4	21
	µg/l	TY3		0.65	91.9	15	96.4	91.8	91.9	4.7	5.1	6
	µg/l	V2M		1.97	8.54	20	10.23	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		0.56	69.6	10	71.6	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-1.79	212	20	174	212	212	35	16.4	11
	µg/l	TY3		0.82	78.5	15	83.4	75.4	78.5	7.2	9.2	7
	µg/l	V2M			4.64	15	*<13*	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		1.76	62.9	10	68.5	63.2	62.8	3.2	5.1	17
	µg/l	TY3		1.74	40.6	15	45.9	38.9	40.6	3.5	8.5	5
	µg/l	V2M		13.54	7.64	15	15.40	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		0.05	76.9	10	77.1	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		-0.34	78.2	20	75.6	77.7	78.2	6.0	7.7	9
	µg/l	TY3		-0.87	107	15	100	107	107	6	5.2	6
	µg/l	V2M		-1.02	13.7	15	12.7	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		1.36	425	10	454	424	426	22	5.2	25
	mg/kg	FO4		0.72	3203	15	3375	3315	3203	306	9.5	9
	µg/l	TY3		0.04	153	15	154	154	153	5	2.9	6
	µg/l	V2M		0.32	40.1	15	41.1	40.2	40.1	2.7	6.7	19

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.41	659	10	673	656	666	41	6.1	23
	µg/l	TN3		1.04	1132	15	1220	1120	1133	69	6.1	17
	µg/l	V2M		-0.45	121	20	116	121	121	13	10.4	17
Cr	mg/kg	FN4		0.28	108	20	111	111	108	6	5.5	6
Cu	µg/l	A1M		0.95	61.9	10	64.9	63.0	62.7	2.2	3.4	19
	mg/kg	FN4		1.23	175	15	191	175	175	3	1.7	7
	µg/l	TN3		1.66	97.8	15	110.0	98.7	97.8	7.6	7.8	18
	µg/l	V2M		0.74	10.1	20	10.9	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		0.77	778	10	808	789	780	30	3.9	24
	µg/l	TN3		-0.11	313	15	311	310	313	22	7.0	20
	µg/l	V2M		0.19	641	15	650	645	639	52	8.1	20
Mn	µg/l	A1M		0.51	450	10	462	453	453	17	3.8	20
	µg/l	TN3		0.07	181	15	182	182	181	12	6.5	18
	µg/l	V2M		-0.10	388	10	386	386	388	21	5.4	19
Ni	µg/l	A1M		0.49	71.9	10	73.7	73.0	72.3	1.8	2.4	21
	µg/l	TN3		0.06	91.8	15	92.2	91.1	91.9	6.4	7.0	18
Zn	µg/l	A1M		-0.07	425	10	424	424	426	22	5.2	25
	mg/kg	FN4		0.61	3375	10	3479	3360	3375	119	3.5	7
	µg/l	TN3		-0.32	148	15	145	146	147	13	9.0	19
	µg/l	V2M		-0.53	40.1	15	38.5	40.2	40.1	2.7	6.7	19

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.16	659	10	697	656	666	41	6.1	23
	µg/l	TY3		1.10	1145	15	1239	1100	1145	87	7.6	7
	µg/l	V2M		-0.31	121	20	117	121	121	13	10.4	17
As	µg/l	A1M		-2.29	61.9	10	54.8	61.6	61.9	1.9	3.1	18
	mg/kg	FO4		-0.78	17.6	20	16.2	17.6	17.6	2.1	11.8	10
	µg/l	TY3			106		111	105	106	4	3.4	5
	µg/l	V2M		-0.03	8.58	20	8.55	8.52	8.50	0.53	6.3	17
Cd	µg/l	A1M		-1.57	7.29	15	6.43	7.37	7.39	0.23	3.1	18
	mg/kg	FO4		-0.67	19.2	20	17.9	19.3	19.2	2.0	10.6	10
	µg/l	TY3		1.67	29.4	20	34.3	29.7	29.4	3.5	11.8	6
	µg/l	V2M		-0.97	4.48	15	4.16	4.52	4.45	0.21	4.7	18
Co	µg/l	A1M		-2.56	37.0	10	32.3	37.0	37.3	1.3	3.5	21
	µg/l	TY3		0.07	77.8	15	78.2	78.2	77.8	3.6	4.6	7
	µg/l	V2M		-1.35	11.0	15	9.9	11.0	11.0	0.7	6.0	18
Cr	µg/l	A1M		-1.56	59.0	10	54.4	59.5	59.1	2.6	4.5	23
	mg/kg	FO4		0.89	96.3	20	104.8	97.9	96.3	11.7	12.2	10
	µg/l	TY3		-0.44	161	15	156	159	161	8	4.9	7
	µg/l	V2M		-1.18	12.3	15	11.2	12.4	12.3	0.8	6.7	18
Cu	µg/l	A1M		-2.44	61.9	10	54.3	63.0	62.7	2.2	3.4	19
	mg/kg	FO4		-0.70	176	15	167	172	176	10	5.8	11
	µg/l	TY3		0.68	103	15	108	106	103	9	9.0	7
	µg/l	V2M		-1.61	10.1	20	8.5	10.1	10.1	0.9	9.4	20
Fe	µg/l	A1M		-0.60	778	10	755	789	780	30	3.9	24
	µg/l	TY3		0.70	316	15	333	311	316	17	5.3	7
	µg/l	V2M		-0.83	641	15	601	645	639	52	8.1	20

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Hg	µg/l	A1Hg		-0.40	0.59	20	0.57	0.61	0.62	0.05	8.6	13
	µg/l	T3Hg		2.55	3.33	20	4.18	3.30	3.27	0.56	17.1	16
	µg/l	V2Hg		-0.62	5.34	20	5.01	5.30	5.39	0.32	5.9	14
Mn	µg/l	A1M		-0.54	450	10	438	453	453	17	3.8	20
	µg/l	TY3		0.30	187	15	191	190	187	9	5.1	6
	µg/l	V2M		-1.46	388	10	360	386	388	21	5.4	19
Ni	µg/l	A1M		-2.83	71.9	10	61.7	73.0	72.3	1.8	2.4	21
	µg/l	TY3		-0.58	91.9	15	87.9	91.8	91.9	4.7	5.1	6
	µg/l	V2M		-1.32	8.54	20	7.41	8.53	8.53	0.79	9.3	18
Pb	µg/l	A1M		1.24	69.6	10	73.9	69.1	69.8	3.3	4.7	20
	mg/kg	FO4		-0.01	212	20	212	212	212	35	16.4	11
	µg/l	TY3		2.36	78.5	15	92.4	75.4	78.5	7.2	9.2	7
	µg/l	V2M		-0.06	4.64	15	4.62	4.50	4.47	0.29	6.5	16
Se	µg/l	A1M		-2.29	62.9	10	55.7	63.2	62.8	3.2	5.1	17
	µg/l	TY3		-0.56	40.6	15	38.9	38.9	40.6	3.5	8.5	5
	µg/l	V2M		0.36	7.64	15	7.85	7.62	7.64	0.57	7.4	14
V	µg/l	A1M		-1.60	76.9	10	70.8	76.0	76.1	3.0	4.0	17
	mg/kg	FO4		-0.42	78.2	20	74.9	77.7	78.2	6.0	7.7	9
	µg/l	TY3		0.06	107	15	107	107	107	6	5.2	6
	µg/l	V2M		-0.90	13.7	15	12.8	13.4	13.7	1.0	7.0	17
Zn	µg/l	A1M		1.23	425	10	451	424	426	22	5.2	25
	mg/kg	FO4		1.53	3203	15	3570	3315	3203	306	9.5	9
	µg/l	TY3		0.42	153	15	158	154	153	5	2.9	6
	µg/l	V2M		0.52	40.1	15	41.7	40.2	40.1	2.7	6.7	19

Participant 29												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s$_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.53	659	10	710	656	666	41	6.1	23
Co	µg/l	A1M		-1.62	37.0	10	34.0	37.0	37.3	1.3	3.5	21
Cr	µg/l	A1M		-1.86	59.0	10	53.5	59.5	59.1	2.6	4.5	23
Fe	µg/l	A1M		-1.49	778	10	720	789	780	30	3.9	24
Zn	µg/l	A1M		-2.07	425	10	381	424	426	22	5.2	25

APPENDIX 8: Summary of the z scores

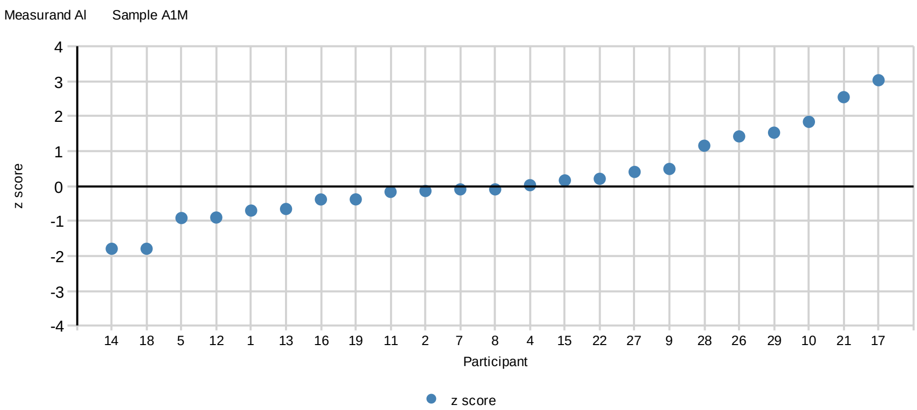
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	24	25	26	27	28	29	%
Al	A1M	S	S	.	S	S	.	S	S	S	S	S	S	S	S	S	S	U	S	S	.	Q	S	.	.	S	S	S	S	91.3
	TN3	S	S	.	S	S	.	S	S	S	S	.	S	S	S	S	S	Q	S	S	.	.	S	.	.	.	S	.	.	94.4
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	.	S	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	S	S	S	S	S	S	S	U	S	S	.	.	U	.	S	S	S	S	.	89.5
As	A1M	S	S	.	S	S	.	S	S	S	S	S	S	S	S	S	S	U	S	S	.	.	S	.	.	S	.	q	.	90.0
	FN4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FO4	S	.	.	.	.	.	.	S	.	Q	.	.	S	.	S	.	S	S	S	.	.	.	.	.	S	.	S	.	90.0
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	S	Q	.	S	S	.	S	S	S	S	.	S	S	S	S	Q	U	S	S	.	.	S	.	.	.	.	.	.	82.4
	TY3	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	V2M	.	.	.	.	S	.	S	S	S	S	S	S	S	S	S	S	Q	S	S	.	.	S	.	S	.	.	S	.	94.1
Ba	FN4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FO4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Cd	A1M	S	S	u	S	S	.	S	S	S	S	S	S	S	S	S	S	U	S	S	.	.	S	.	.	S	.	S	.	90.5
	FN4	.	.	.	.	Q	.	S	.	.	.	.	S	.	.	S	S	.	.	.	S	.	.	.	S	.	.	.	.	85.7
	FO4	u	.	S	.	.	.	.	S	.	S	.	.	S	.	S	.	S	S	S	.	.	.	.	.	S	.	S	.	90.9
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	S	S	S	S	S	.	S	S	S	S	.	S	S	S	S	S	S	S	S	.	.	S	.	.	.	.	.	.	100
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	.	.	.	.	.	S	.	S	.	100
	V2M	.	.	U	.	S	.	S	S	S	S	S	S	S	S	S	S	U	S	S	.	.	S	.	S	S	.	S	.	89.5
Co	A1M	S	S	.	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	S	.	.	S	.	q	S	95.5
	TN3	S	S	U	S	S	.	S	S	S	S	.	S	S	S	S	S	S	S	S	.	.	S	.	.	.	.	.	.	94.4
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	.	S	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	.	S	.	S	S	.	S	.	100
Cr	A1M	S	S	.	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	.	S	S	100
	FN4	.	.	.	.	u	.	S	.	.	.	.	S	.	.	S	S	.	.	.	.	.	.	.	S	.	S	.	.	85.7
	FO4	S	.	u	.	.	.	.	Q	.	S	.	.	S	.	S	.	S	S	S	.	.	.	.	.	S	.	S	.	81.8
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	S	S	u	S	S	.	S	S	S	S	.	S	S	S	S	S	S	S	S	.	.	S	S	.	.	.	.	.	94.7
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	.	S	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	.	S	.	S	S	.	S	.	100
Cu	A1M	S	S	u	q	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	.	S	.	.	S	S	q	.	86.4
	FN4	.	.	.	.	S	.	S	.	.	.	.	S	.	.	S	S	.	.	.	S	.	.	.	S	.	S	.	.	100
	FO4	S	.	S	.	.	.	.	S	.	S	.	.	S	.	S	.	S	S	S	.	.	.	.	.	S	.	S	.	100
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	S	S	U	S	S	.	S	S	S	S	.	S	S	S	S	S	S	S	S	.	.	S	.	.	.	S	.	.	94.7
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	S	.	.	.	.	S	.	S	.	100
	V2M	.	.	S	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	.	.	S	.	S	S	S	S	.	100
Fe	A1M	S	S	S	S	S	.	S	S	S	S	u	S	S	S	S	S	U	S	S	S	S	S	S	.	S	S	S	S	92.3
	TN3	S	S	S	S	S	.	S	S	S	S	.	S	S	S	S	S	.	S	S	S	.	S	S	.	.	S	.	.	100
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	.	S	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	q	.	S	.	S	S	S	S	.	95.0

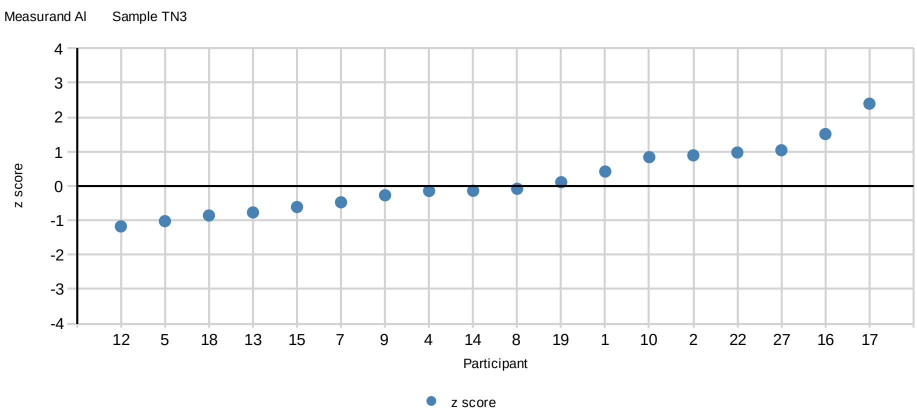
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	24	25	26	27	28	29	%
Hg	A1Hg	.	.	.	*S*	u	.	S	S	S	*Q*	S	.	S	*S*	S	S	*U*	S	S	.	.	.	.	.	q	.	S	.	75.0
	FC4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FN4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FO4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	T3Hg	.	.	.	*q*	u	S	S	S	S	*S*	S	.	S	*S*	S	S	*U*	S	S	.	.	.	.	.	S	.	Q	.	76.5
	V2Hg	.	.	.	.	S	S	S	S	S	*S*	Q	.	S	*S*	S	S	*U*	S	S	.	.	.	.	S	S	.	S	.	88.2
Mn	A1M	*S*	*S*	.	*S*	S	.	S	S	S	*S*	u	*S*	S	*S*	S	S	*S*	S	S	.	.	*S*	.	.	S	S	S	.	95.2
	TN3	*S*	*S*	.	*S*	*S*	.	S	S	S	*S*	.	*S*	S	*S*	S	S	*S*	*S*	S	.	.	*S*	.	.	.	S	.	.	100
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	*S*	.	.	.	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	*S*	*S*	S	*S*	S	*S*	S	S	*S*	*S*	Q	.	.	*S*	.	*S*	S	S	S	.	94.7
Mo	FN4	.	.	.	.	*Q*	.	*S*	.	.	.	.	*S*	.	.	S	S	.	.	.	.	.	.	.	*S*	.	.	.	.	83.3
	FO4	*S*	.	.	.	.	.	.	*S*	.	*S*	.	.	S	.	*S*	.	S	*S*	*S*	.	.	.	.	.	S	.	.	.	100
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Ni	A1M	*S*	*S*	*S*	*S*	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*S*	S	S	.	.	*S*	*S*	.	S	S	q	.	95.7
	TN3	.	*S*	*Q*	*S*	S	.	S	S	S	*S*	.	*S*	S	*S*	S	S	*S*	*S*	S	.	.	*S*	*S*	.	.	S	.	.	94.7
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	*S*	.	.	.	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	*S*	S	*S*	S	*q*	S	S	*S*	S	S	.	.	*S*	.	S	S	.	S	.	94.4
Pb	A1M	*Q*	*S*	*u*	*S*	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*S*	S	S	.	.	*S*	.	.	S	.	S	.	90.5
	FN4	.	.	.	.	S	.	*S*	.	.	.	.	*S*	.	.	S	*S*	.	.	.	*S*	.	.	.	S	.	.	.	.	100
	FO4	*q*	.	*S*	.	.	.	.	S	.	*S*	.	.	S	.	S	.	S	*S*	*S*	.	.	.	.	.	S	.	S	.	90.9
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	*S*	*S*	*U*	*S*	S	.	S	S	S	*S*	.	*q*	S	*q*	S	S	*S*	S	S	.	.	*S*	.	.	.	.	.	.	83.3
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	S	.	*S*	.	.	.	.	S	.	Q	.	85.7
	V2M	.	.	*U*	.	S	.	S	S	S	*S*	S	*S*	S	*U*	S	S	*S*	S	S	.	.	*S*	.	S	.	.	S	.	88.9
Se	A1M	.	*S*	.	*S*	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*U*	S	S	.	.	.	.	.	S	.	q	.	88.9
	TN3	.	*S*	.	*S*	S	.	S	S	S	*S*	.	*S*	S	*S*	S	Q	*U*	Q	S	.	.	.	.	.	.	.	.	.	80.0
	TY3	.	.	.	.	.	.	*S*	.	.	.	S	.	.	.	S	.	.	u	.	.	.	.	.	.	S	.	S	.	83.3
	V2M	.	.	.	.	S	.	S	S	S	*S*	S	*S*	S	*U*	S	S	*U*	S	S	.	.	.	.	S	U	.	S	.	82.4
V	A1M	.	*S*	.	.	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*S*	S	S	.	.	.	.	.	S	.	S	.	100
	FN4	.	.	.	.	*S*	.	*S*	.	.	.	.	*S*	.	.	S	*S*	.	.	.	.	.	.	.	*S*	.	.	.	.	100
	FO4	.	.	.	.	.	.	.	S	.	*S*	.	.	S	.	S	.	S	*S*	*S*	.	.	.	.	.	S	.	S	.	100
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	.	*S*	.	.	S	.	S	S	S	*q*	.	*S*	S	*S*	S	S	*Q*	*S*	S	.	.	.	.	.	.	.	.	.	85.7
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	*S*	.	.	.	.	.	.	S	.	S	.	100
	V2M	.	.	.	.	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*S*	*S*	Q	.	.	.	.	S	S	.	S	.	94.1
Zn	A1M	*S*	*S*	*S*	*Q*	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*U*	S	S	*q*	*S*	*S*	*S*	.	S	S	S	*q*	84.6
	FN4	.	.	.	.	*S*	.	*S*	.	.	.	.	*S*	.	.	S	*S*	.	.	.	*u*	.	.	.	S	.	*S*	.	.	87.5
	FO4	*u*	.	*u*	.	.	.	.	S	.	*S*	.	.	S	.	S	.	S	*q*	*S*	.	.	.	.	.	S	.	S	.	72.7
	FT4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	TN3	*S*	*S*	*S*	*S*	S	.	S	S	S	*S*	.	*S*	S	*S*	S	S	*U*	*u*	S	.	.	*S*	*S*	.	.	S	.	.	90.0
	TY3	.	.	.	.	.	.	S	.	.	.	S	.	.	.	S	.	.	*u*	.	*S*	*u*	.	.	.	S	.	S	.	75.0
	V2M	.	.	*S*	.	S	.	S	S	S	*S*	S	*S*	S	*S*	S	S	*U*	*S*	S	.	.	*S*	.	S	S	S	S	.	95.0
%		86	96	48	88	90	100	100	98	100	94	93	98	100	90	100	96	61	92	96	73	80	97	100	100	96	100	85	80	
accredited						44	2	53	48	36		41		50		68	43	8	36	42					16	46	17	48		

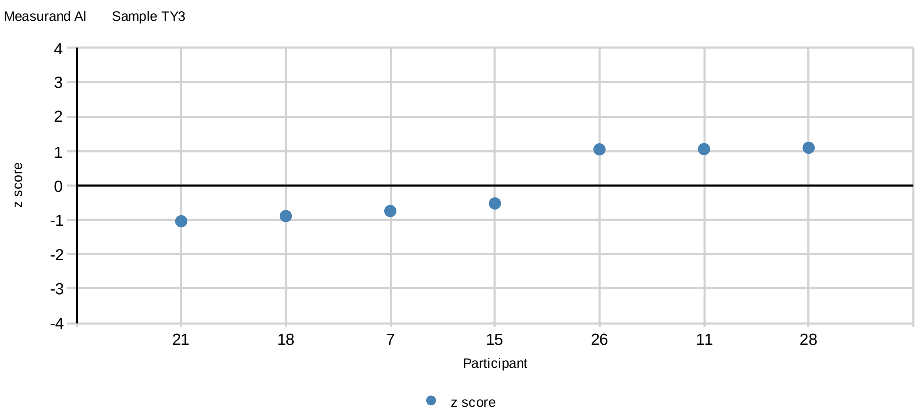
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

Totally satisfactory, % in all: 92 % in accredited: 96 % in non-accredited: 86

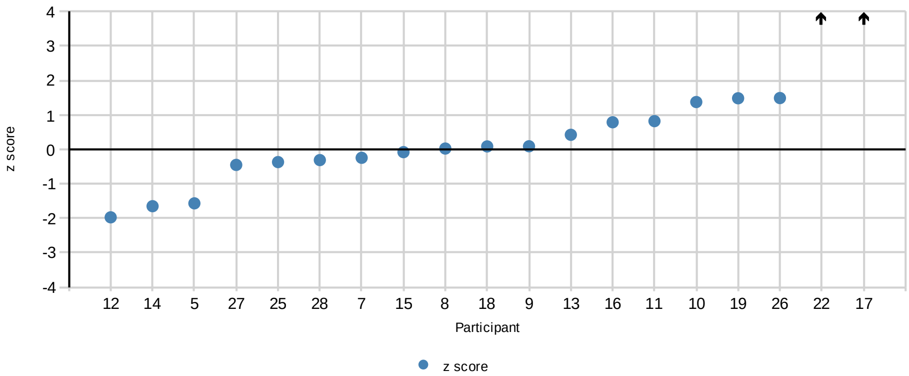
APPENDIX 9: z scores in ascending order



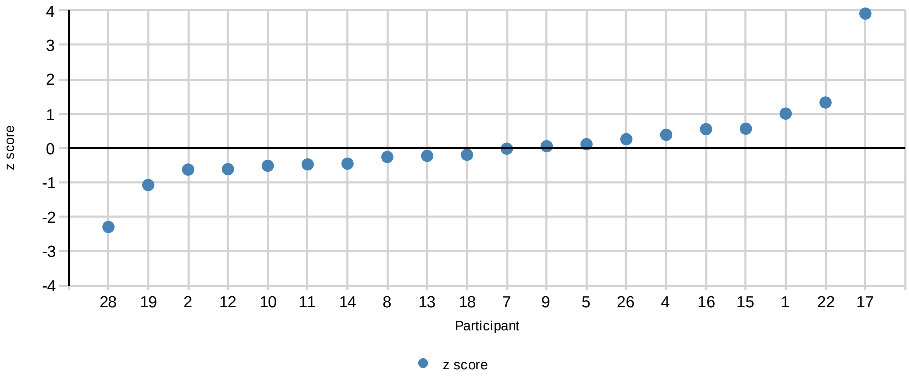




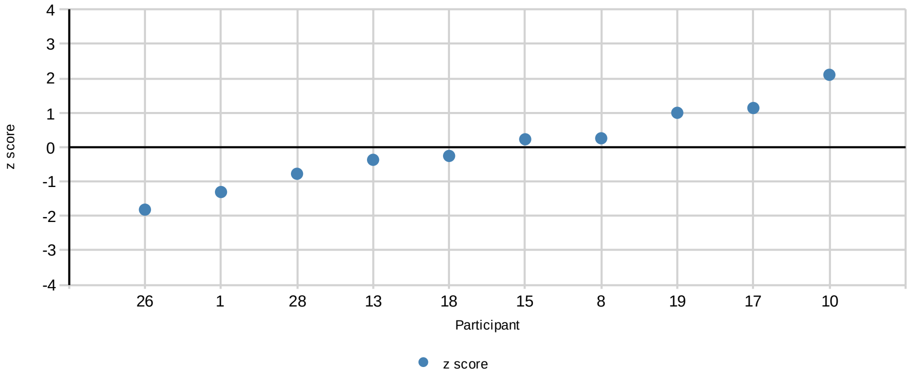
Measurand Al Sample V2M

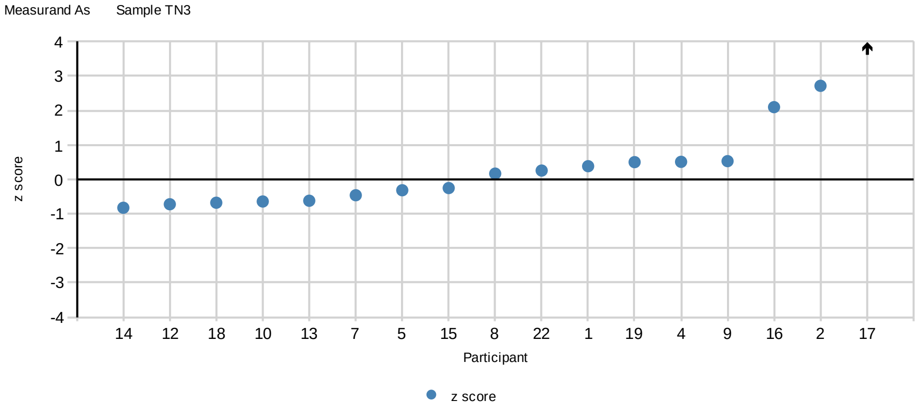


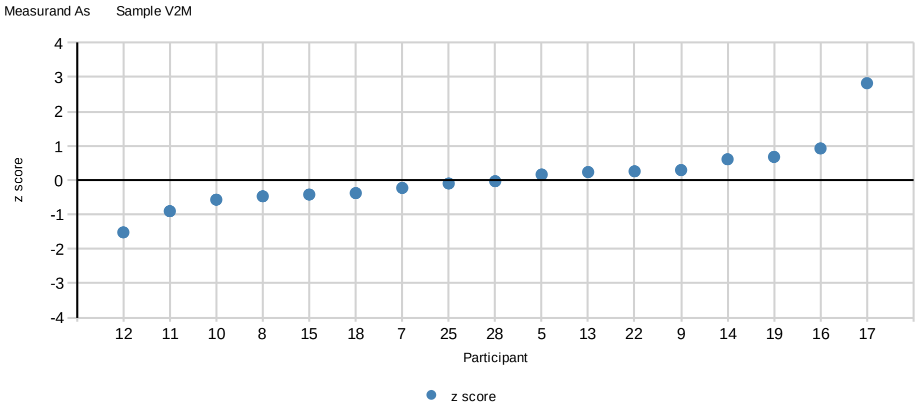
Measurand As Sample A1M

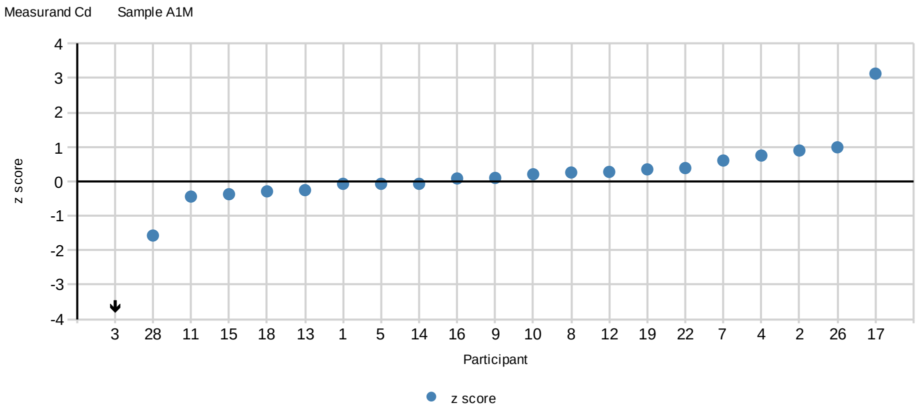


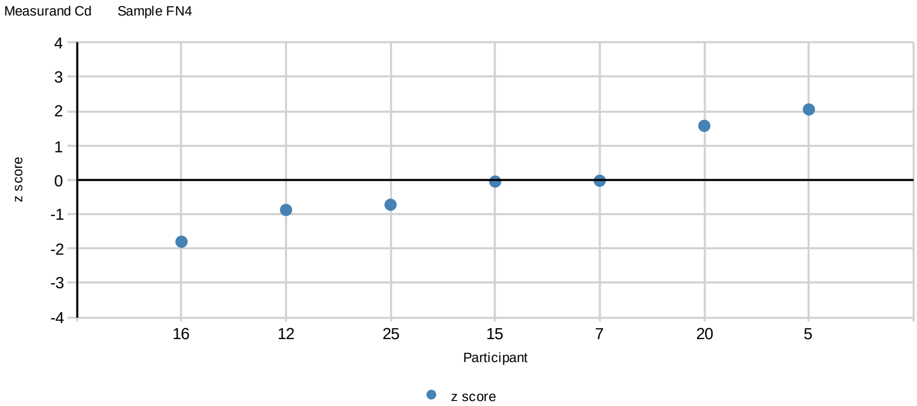
Measurand As Sample FO4

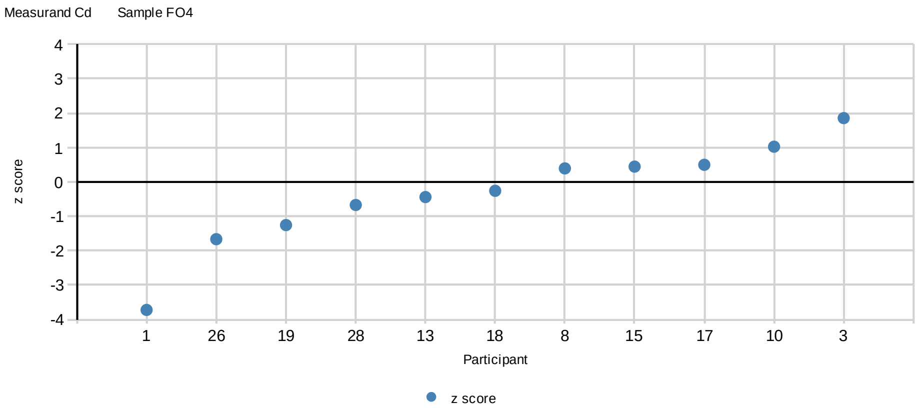


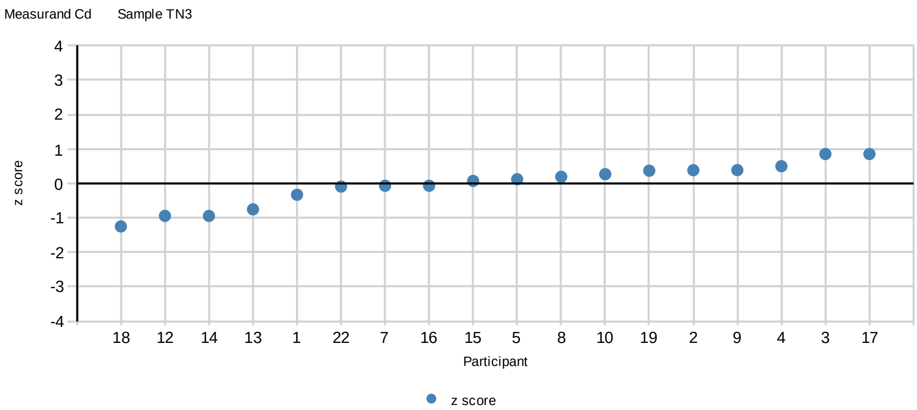

Measurand As
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
14
12
18
10
13
7
5
15
8
22
1
19
4
9
16
2
17
Participant
z score

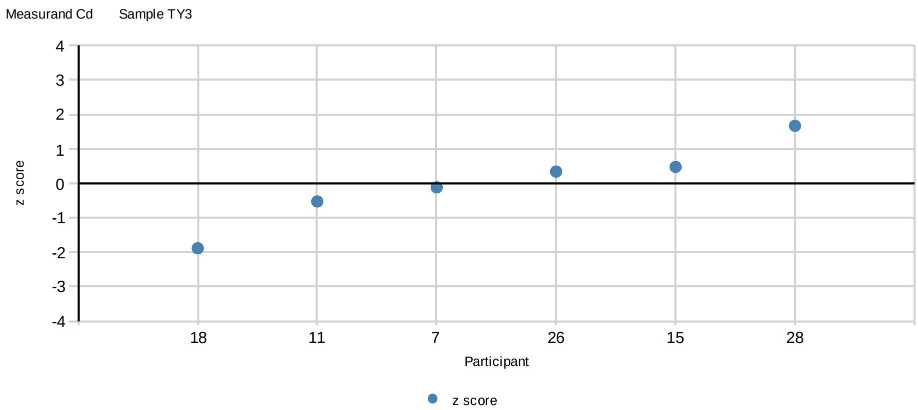

Measurand As
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
12
11
10
8
15
18
7
25
28
5
13
22
9
14
19
16
17
Participant
z score

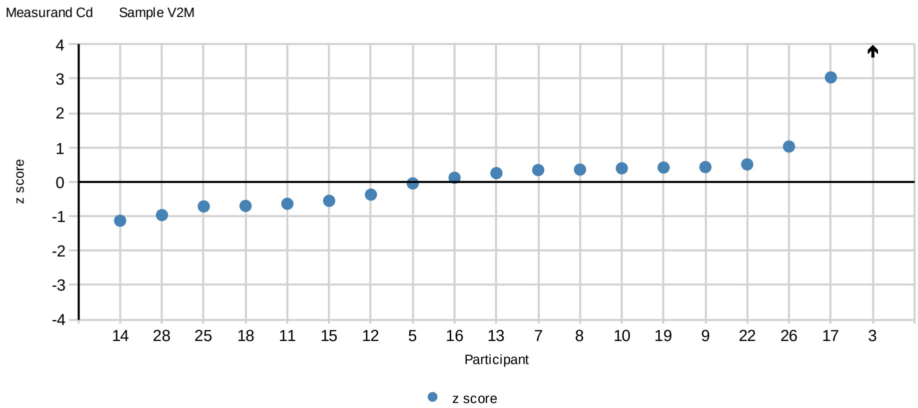

Measurand Cd
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
3
28
11
15
18
13
1
5
14
16
9
10
8
12
19
22
7
4
2
26
17
Participant
z score

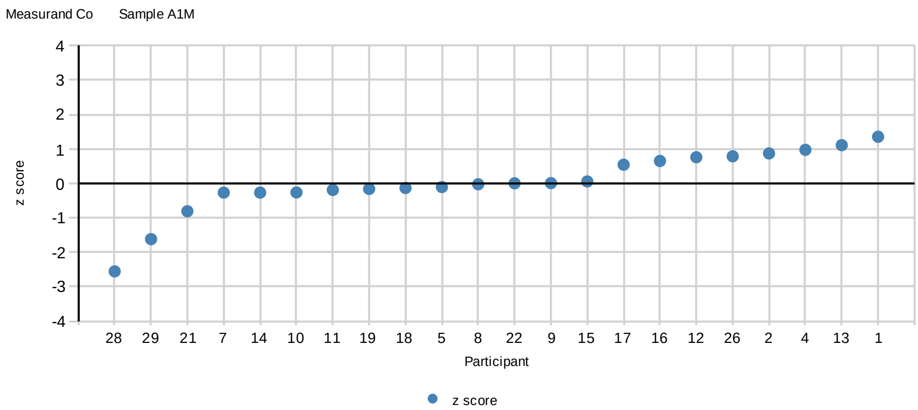

Measurand Cd
Sample FN4
z score
4
3
2
1
0
-1
-2
-3
-4
16
12
25
15
7
20
5
Participant
z score

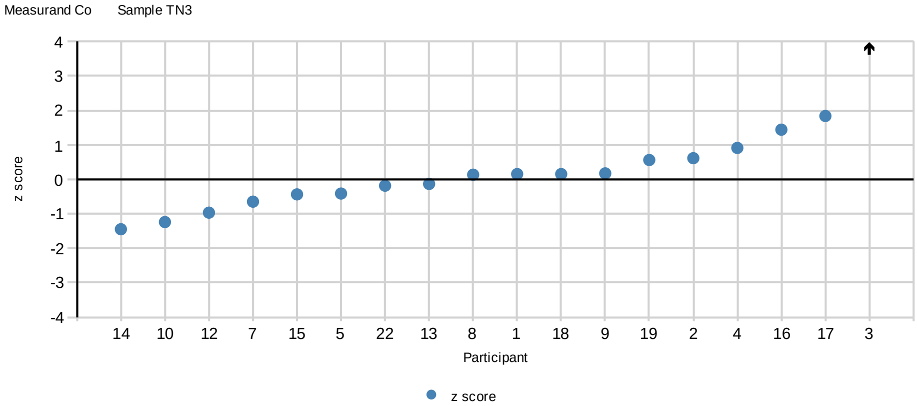

Measurand Cd
Sample FO4
z score
4
3
2
1
0
-1
-2
-3
-4
1
26
19
28
13
18
8
15
17
10
3
Participant
z score

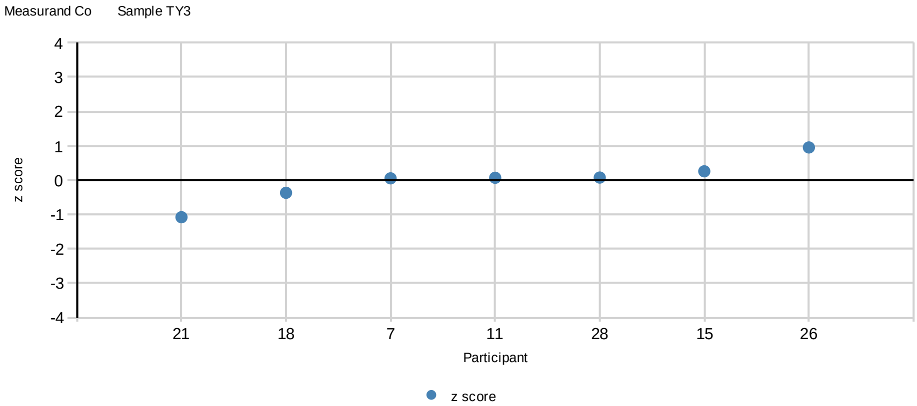

Measurand Cd
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
18
12
14
13
1
22
7
16
15
5
8
10
19
2
9
4
3
17
Participant
z score

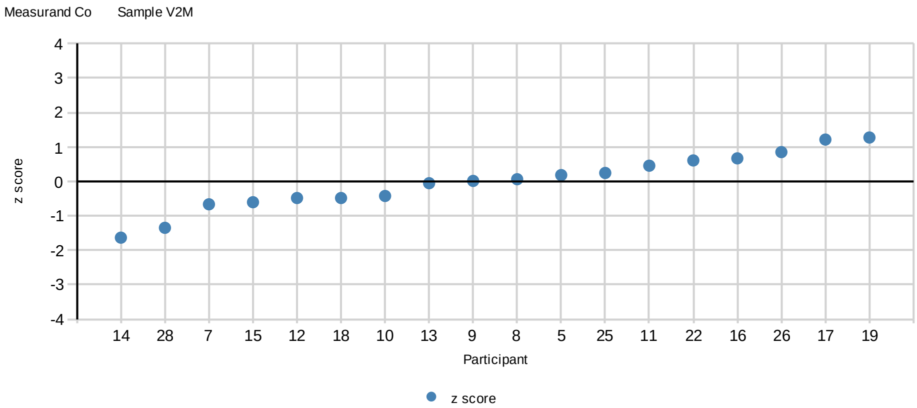

Measurand Cd
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
18
11
7
26
15
28
Participant
z score

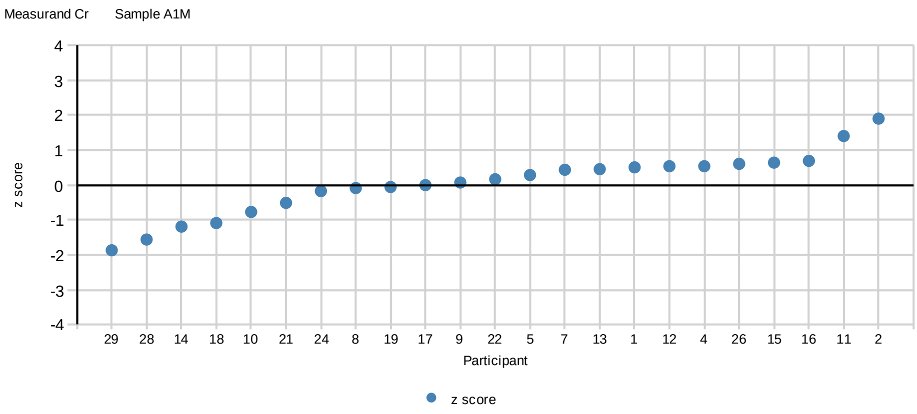

Measurand Cd
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
14
28
25
18
11
15
12
5
16
13
7
8
10
19
9
22
26
17
3
Participant
z score

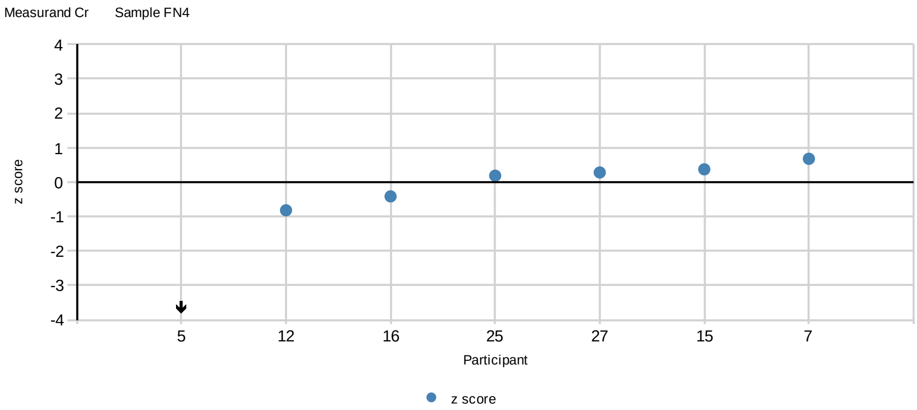

Measurand Co
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
28
29
21
7
14
10
11
19
18
5
8
22
9
15
17
16
12
26
2
4
13
1
Participant
z score

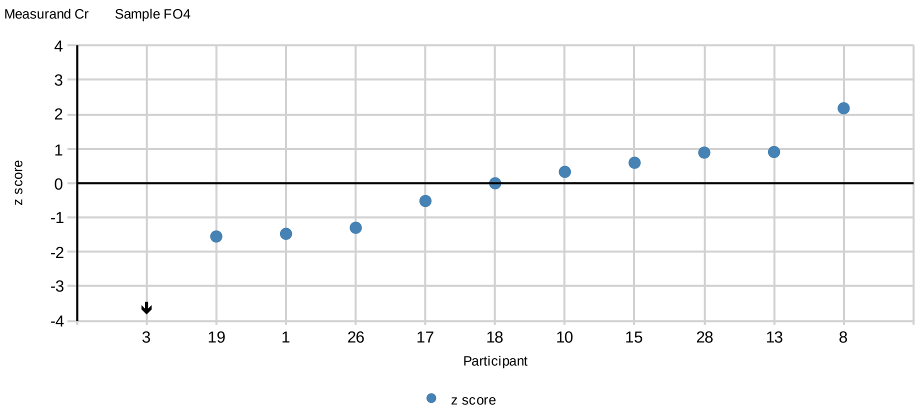

Measurand Co
Sample TN3
4
3
2
1
0
-1
-2
-3
-4
z score
14 10 12 7 15 5 22 13 8 1 18 9 19 2 4 16 17 3
Participant
z score

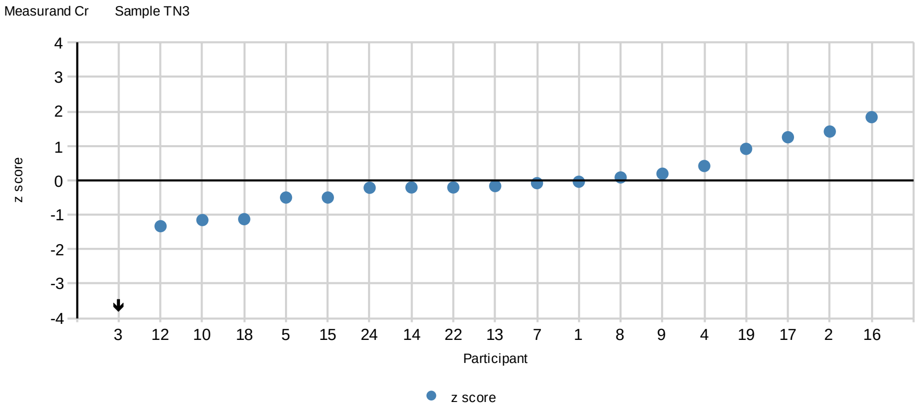

Measurand Co
Sample TY3
4
3
2
1
0
-1
-2
-3
-4
z score
21 18 7 11 28 15 26
Participant
z score

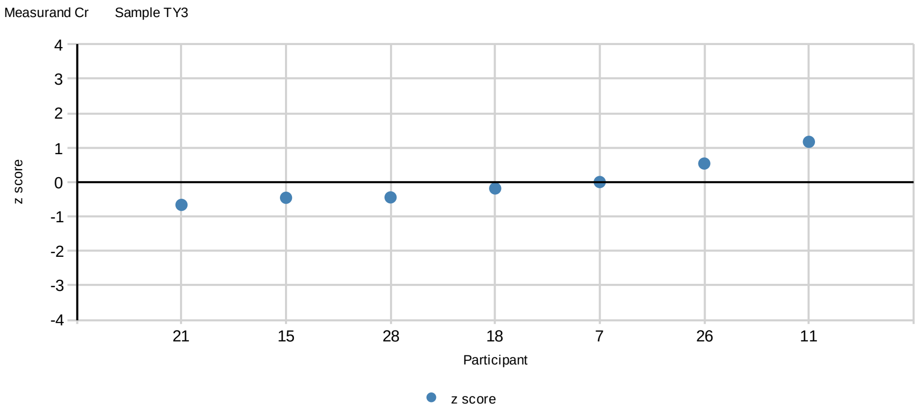

Measurand Co
Sample V2M
4
3
2
1
0
-1
-2
-3
-4
z score
14 28 7 15 12 18 10 13 9 8 5 25 11 22 16 26 17 19
Participant
z score

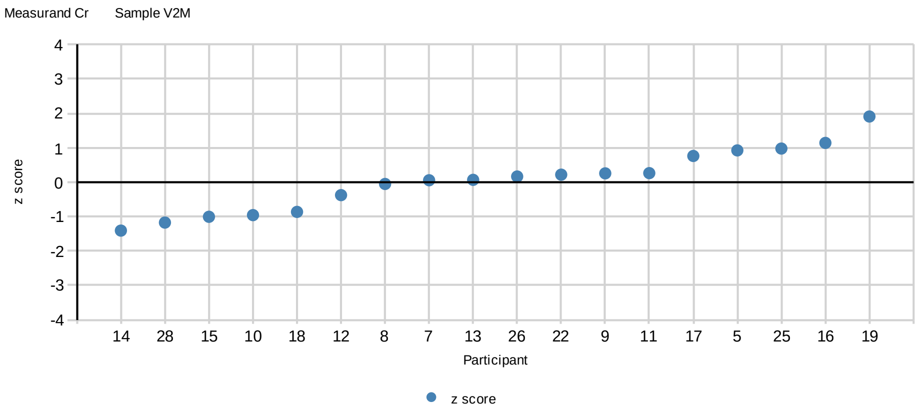

Measurand Cr
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
29 28 14 18 10 21 24 8 19 17 9 22 5 7 13 1 12 4 26 15 16 11 2
Participant
z score

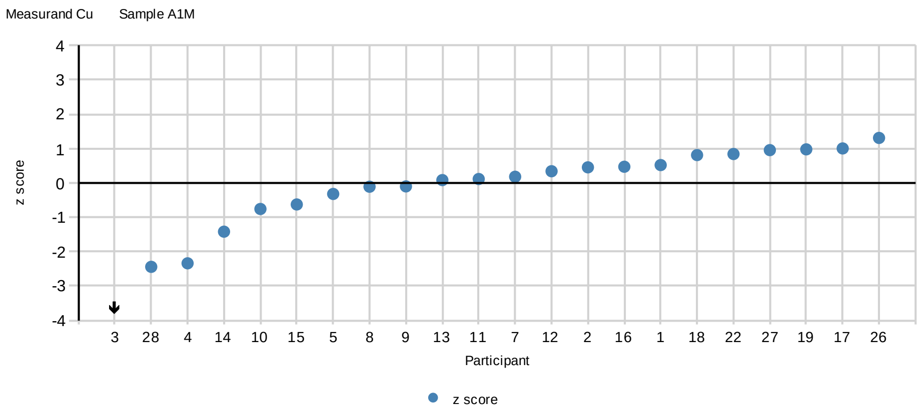

Measurand Cr
Sample FN4
z score
4
3
2
1
0
-1
-2
-3
-4
5 12 16 25 27 15 7
Participant
z score

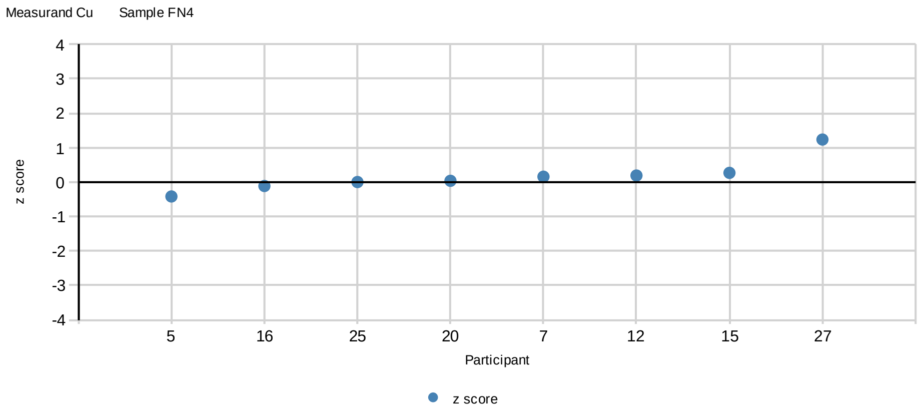

Measurand Cr
Sample FO4
z score
4
3
2
1
0
-1
-2
-3
-4
3 19 1 26 17 18 10 15 28 13 8
Participant
z score

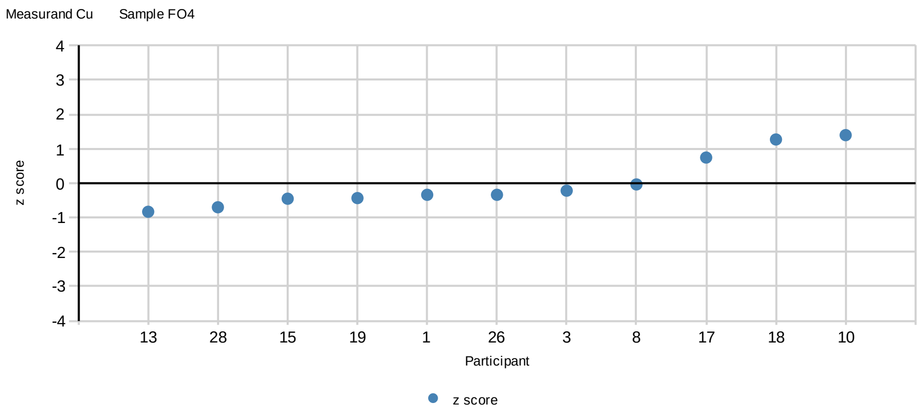

Measurand Cr
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
3 12 10 18 5 15 24 14 22 13 7 1 8 9 4 19 17 2 16
Participant
z score

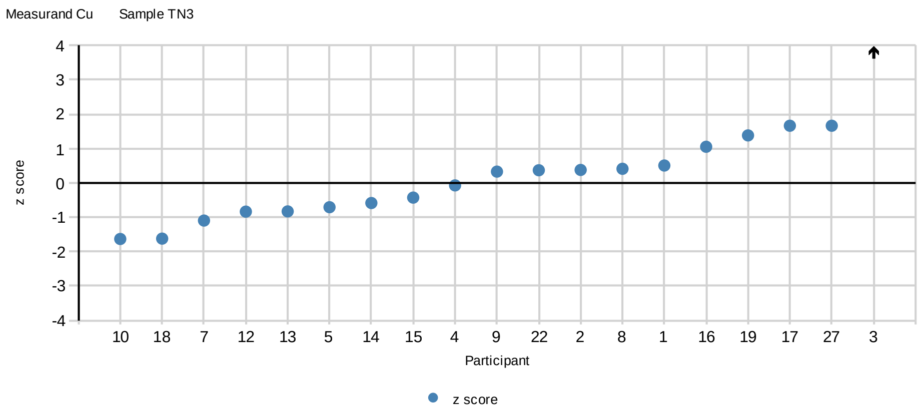

Measurand Cr
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
21 15 28 18 7 26 11
Participant
z score

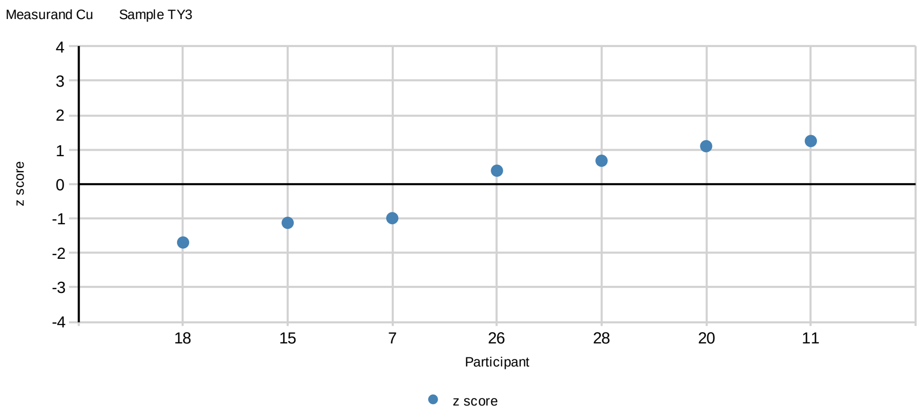

Measurand Cr
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
14 28 15 10 18 12 8 7 13 26 22 9 11 17 5 25 16 19
Participant
z score

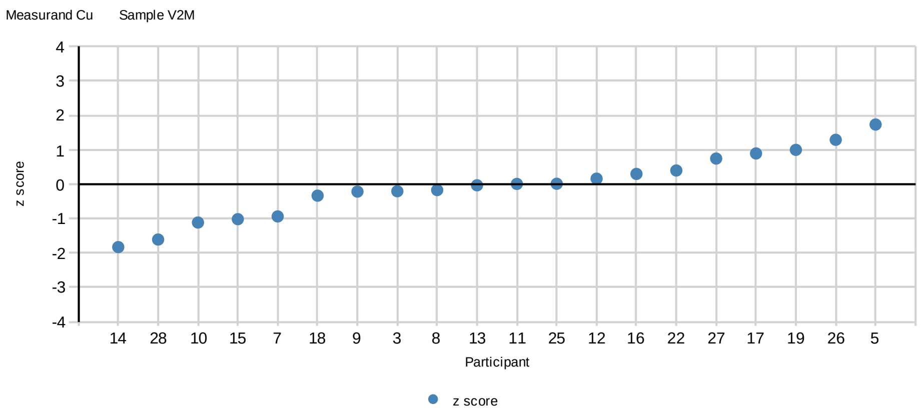

Measurand Cu
Sample A1M
z score
Participant
3 28 4 14 10 15 5 8 9 13 11 7 12 2 16 1 18 22 27 19 17 26
4 3 2 1 0 -1 -2 -3 -4
z score

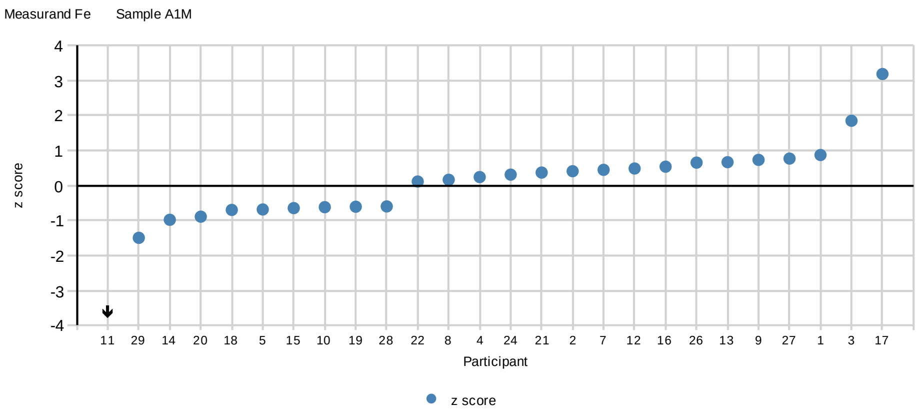

Measurand Cu
Sample FN4
z score
Participant
5 16 25 20 7 12 15 27
4 3 2 1 0 -1 -2 -3 -4
z score


Measurand Cu
Sample FO4
z score
Participant
13 28 15 19 1 26 3 8 17 18 10
4 3 2 1 0 -1 -2 -3 -4
z score

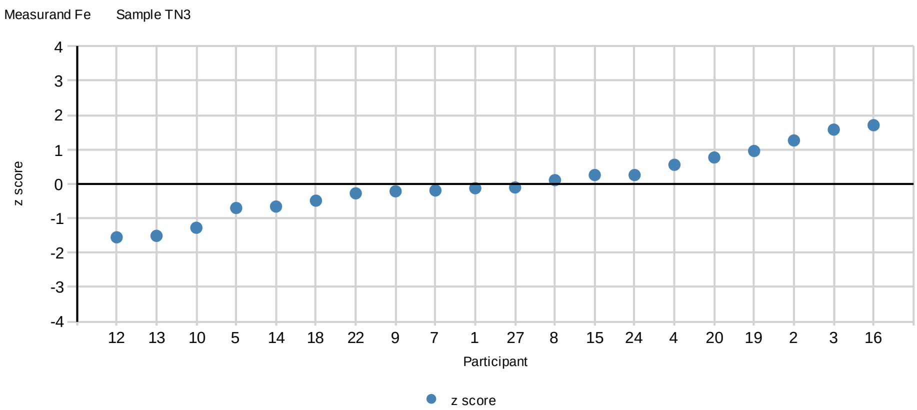

Measurand Cu
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
10
18
7
12
13
5
14
15
4
9
22
2
8
1
16
19
17
27
3
Participant
z score


Measurand Cu
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
18
15
7
26
28
20
11
Participant
z score

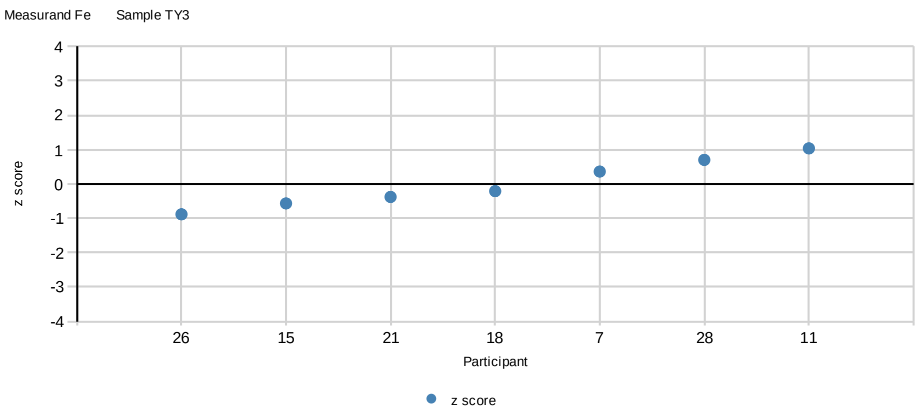

Measurand Cu
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
14
28
10
15
7
18
9
3
8
13
11
25
12
16
22
27
17
19
26
5
Participant
z score



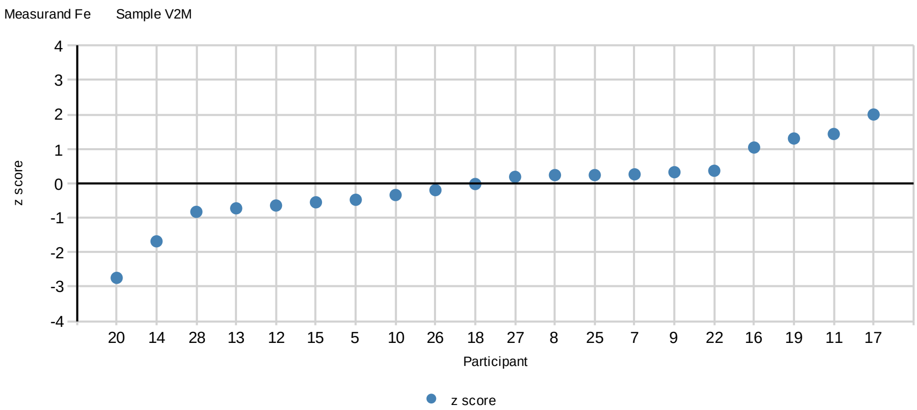
Measurand Fe
Sample A1M
z score
Participant
11 29 14 20 18 5 15 10 19 28 22 8 4 24 21 2 7 12 16 26 13 9 27 1 3 17
4 3 2 1 0 -1 -2 -3 -4

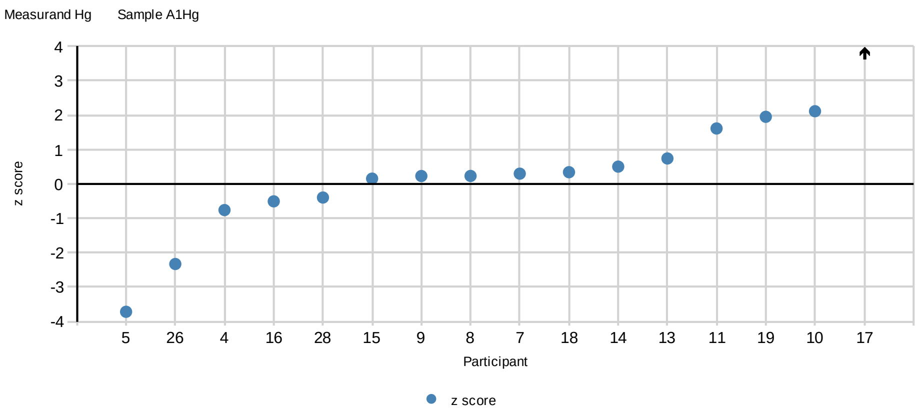


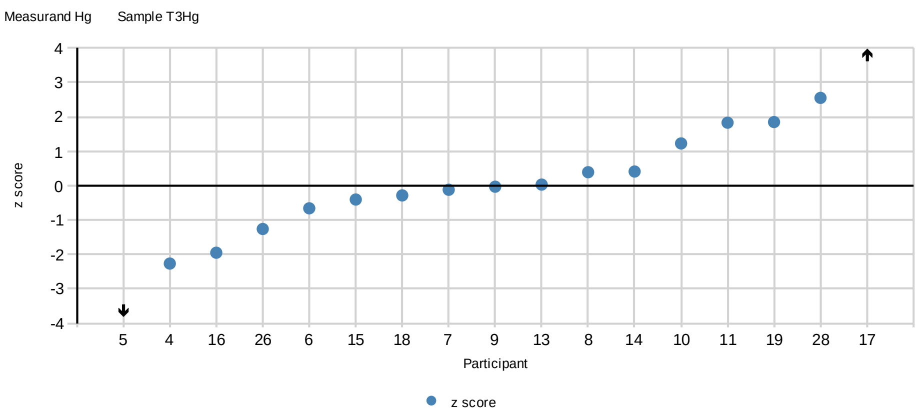
Measurand Fe
Sample TN3
z score
Participant
12 13 10 5 14 18 22 9 7 1 27 8 15 24 4 20 19 2 3 16
4 3 2 1 0 -1 -2 -3 -4

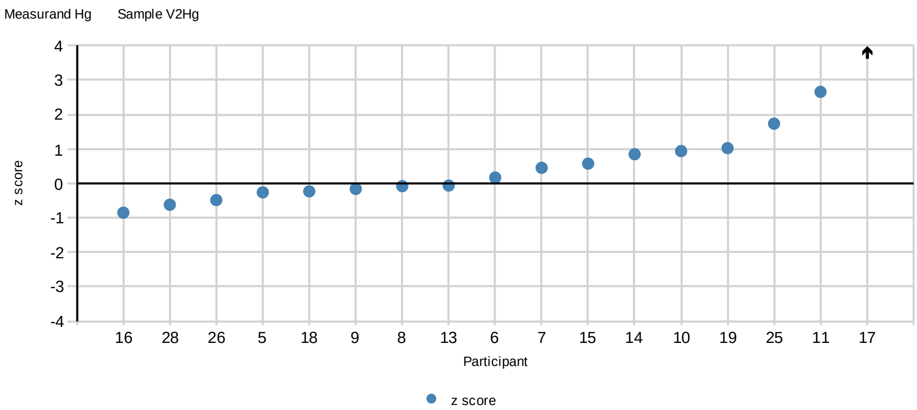


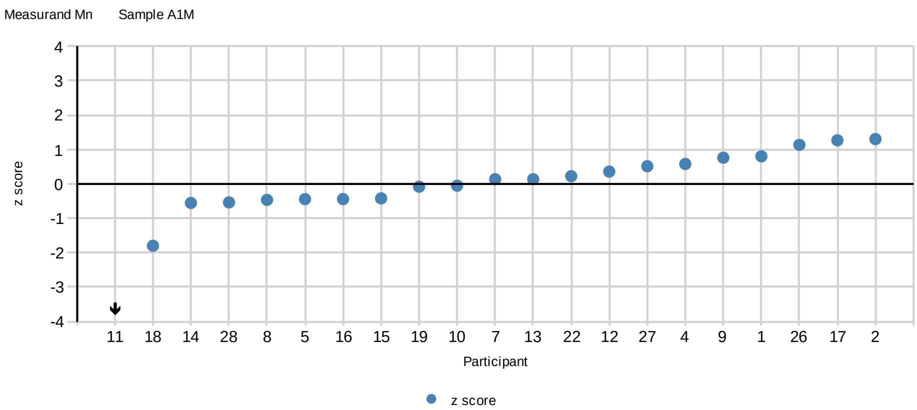
Measurand Fe
Sample TY3
z score
Participant
26 15 21 18 7 28 11
4 3 2 1 0 -1 -2 -3 -4

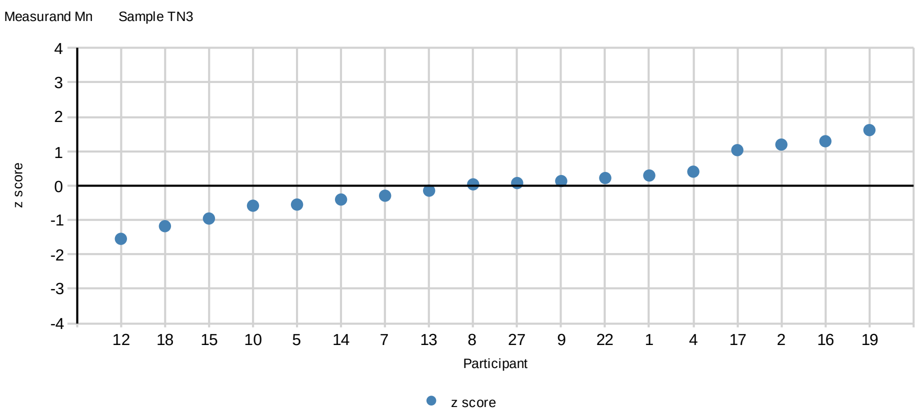

Measurand Fe
Sample V2M
z score
Participant
20 14 28 13 12 15 5 10 26 18 27 8 25 7 9 22 16 19 11 17
z score

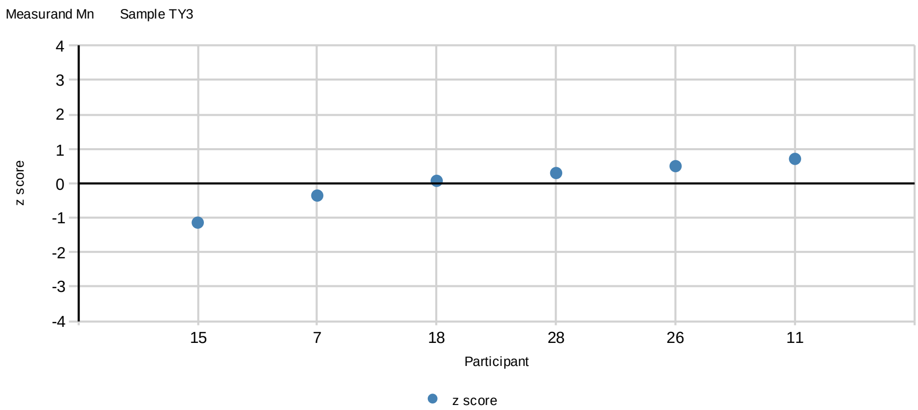

Measurand Hg
Sample A1Hg
z score
Participant
5 26 4 16 28 15 9 8 7 18 14 13 11 19 10 17
z score

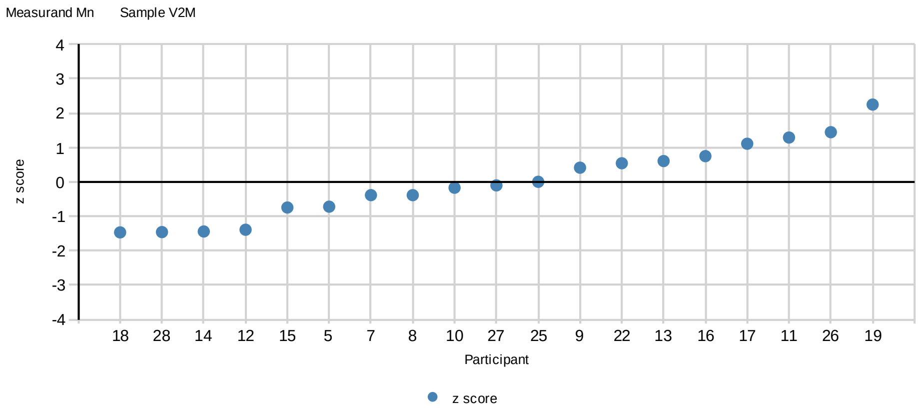

Measurand Hg
Sample T3Hg
z score
Participant
5 4 16 26 6 15 18 7 9 13 8 14 10 11 19 28 17
z score

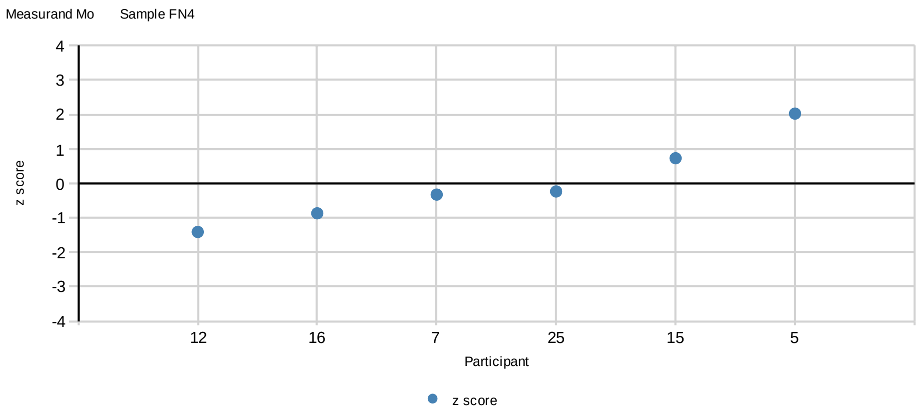

Measurand Hg
Sample V2Hg
z score
4
3
2
1
0
-1
-2
-3
-4
16
28
26
5
18
9
8
13
6
7
15
14
10
19
25
11
17
Participant
z score

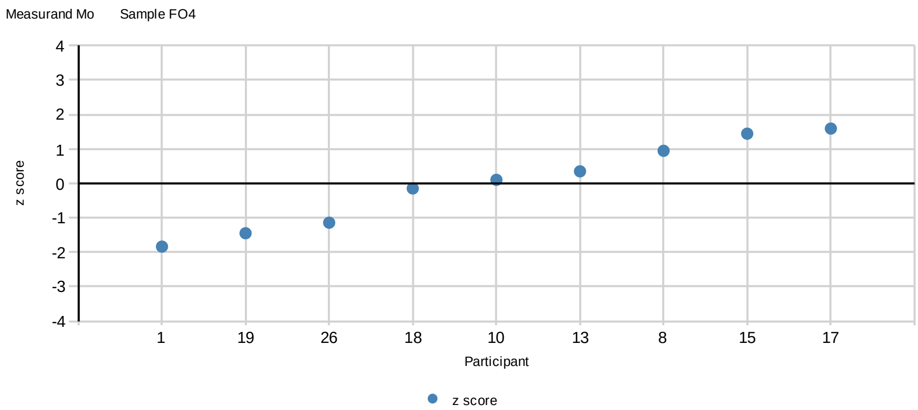

Measurand Mn
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
11
18
14
28
8
5
16
15
19
10
7
13
22
12
27
4
9
1
26
17
2
Participant
z score

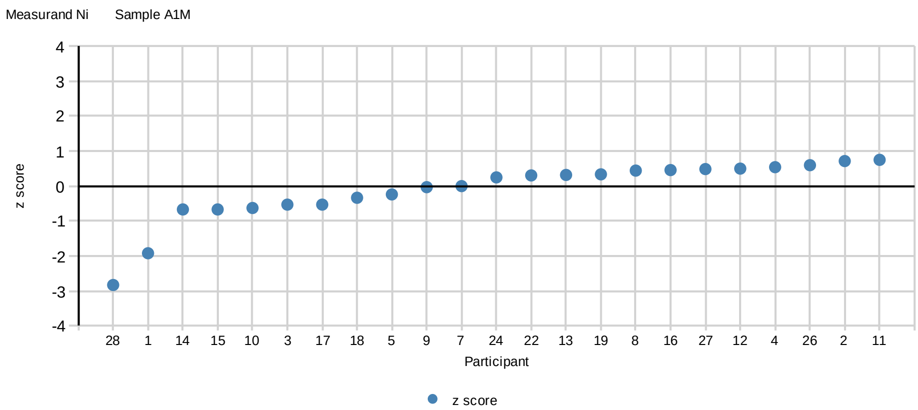

Measurand Mn
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
12
18
15
10
5
14
7
13
8
27
9
22
1
4
17
2
16
19
Participant
z score

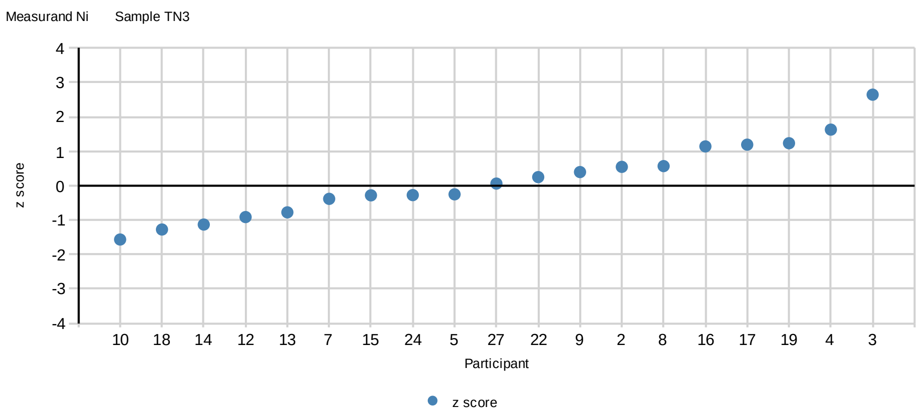

Measurand Mn
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
15
7
18
28
26
11
Participant
z score


Measurand Mn
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
18
28
14
12
15
5
7
8
10
27
25
9
22
13
16
17
11
26
19
Participant
z score

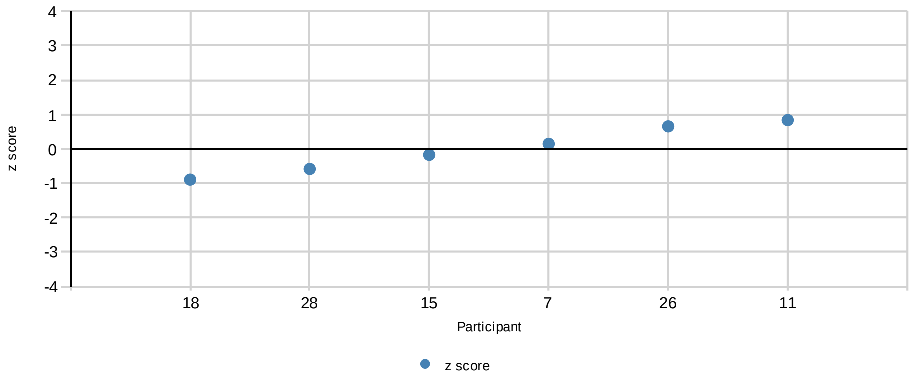

Measurand Mo
Sample FN4
z score
4
3
2
1
0
-1
-2
-3
-4
12
16
7
25
15
5
Participant
z score


Measurand Mo
Sample FO4
z score
4
3
2
1
0
-1
-2
-3
-4
1
19
26
18
10
13
8
15
17
Participant
z score

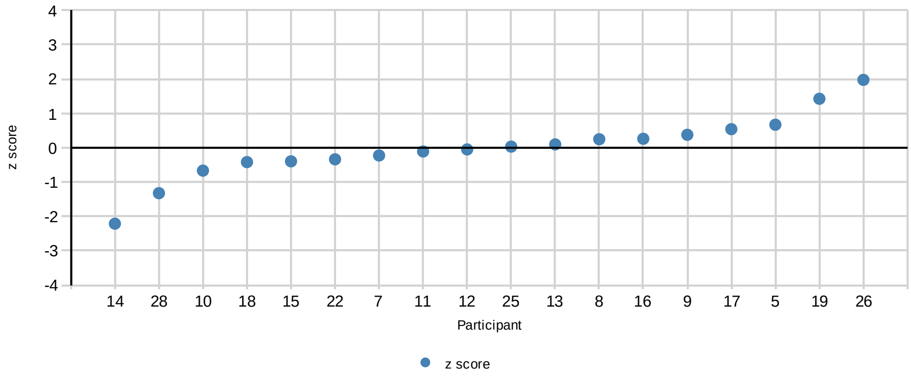

Measurand Ni
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
28
1
14
15
10
3
17
18
5
9
7
24
22
13
19
8
16
27
12
4
26
2
11
Participant
z score


Measurand Ni
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
10
18
14
12
13
7
15
24
5
27
22
9
2
8
16
17
19
4
3
Participant
z score

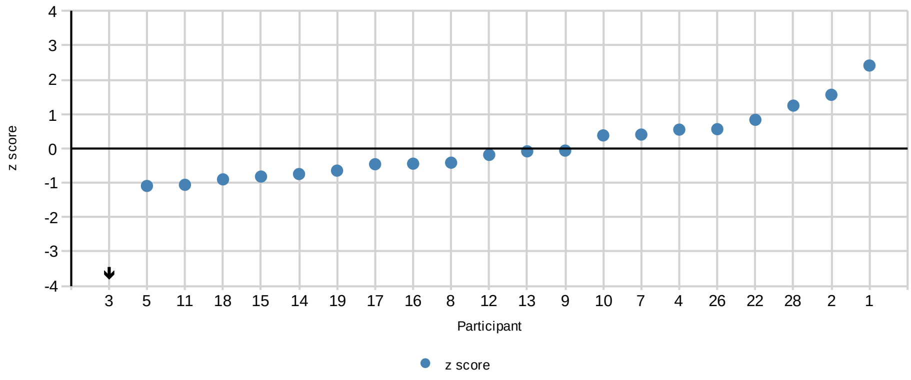
Measurand Ni Sample TY3

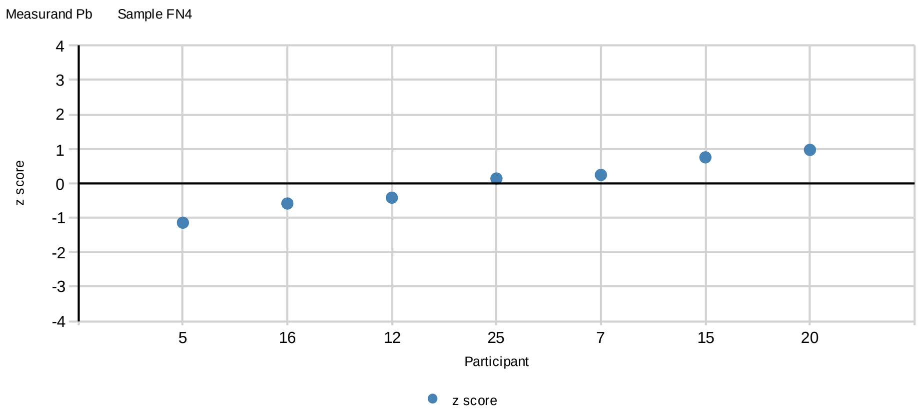


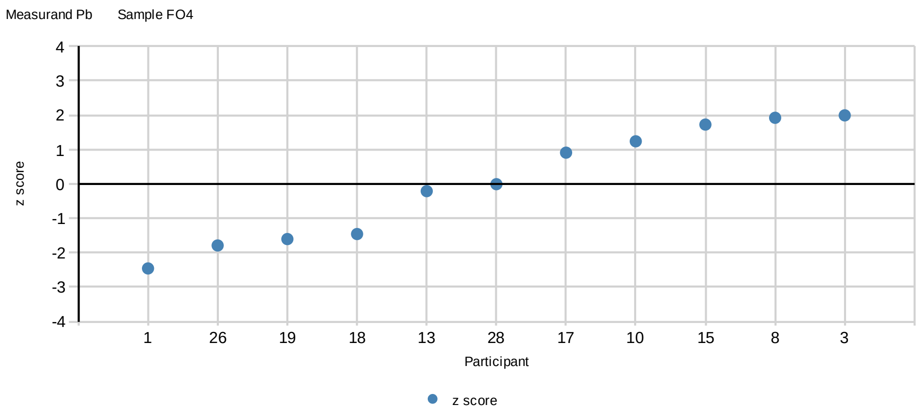
Measurand Ni Sample V2M

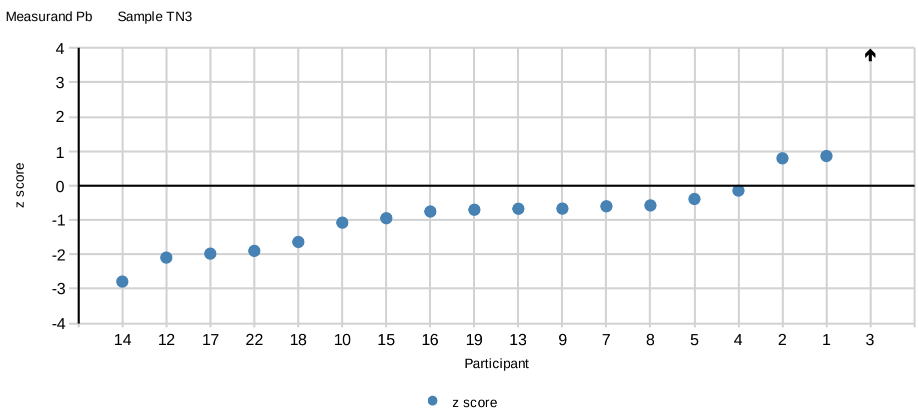


Measurand Pb Sample A1M

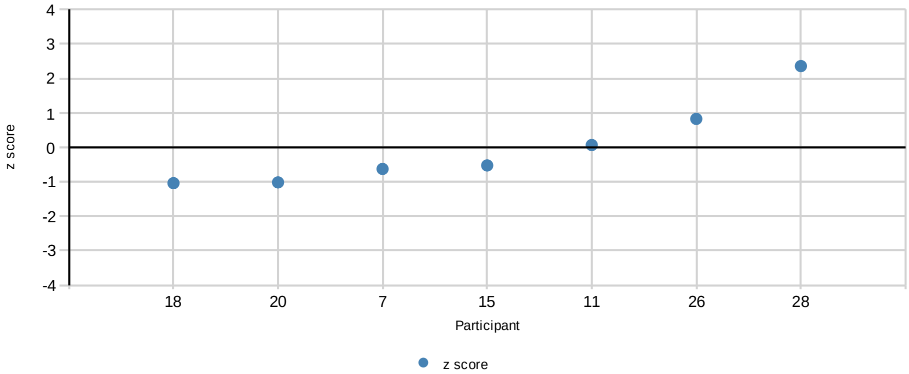



Measurand Pb
Sample FN4
z score
4
3
2
1
0
-1
-2
-3
-4
5
16
12
25
7
15
20
Participant
z score

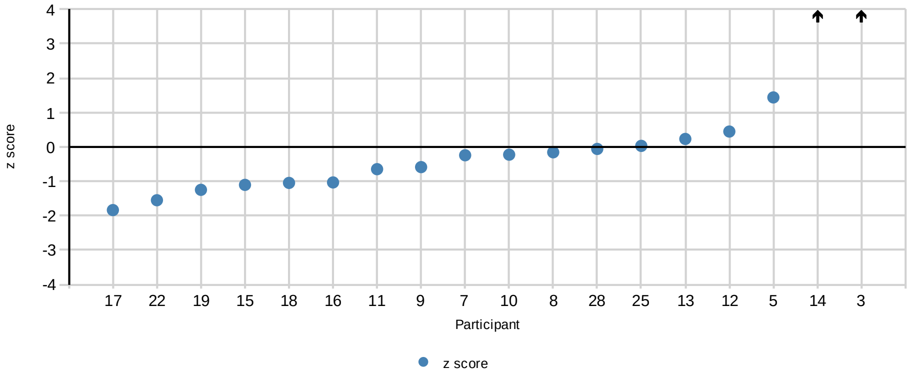

Measurand Pb
Sample FO4
z score
4
3
2
1
0
-1
-2
-3
-4
1
26
19
18
13
28
17
10
15
8
3
Participant
z score


Measurand Pb
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
14
12
17
22
18
10
15
16
19
13
9
7
8
5
4
2
1
3
Participant
z score

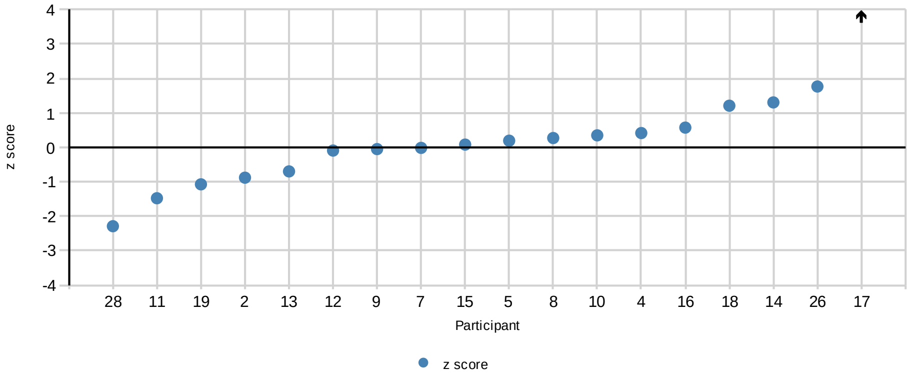
Measurand Pb Sample TY3



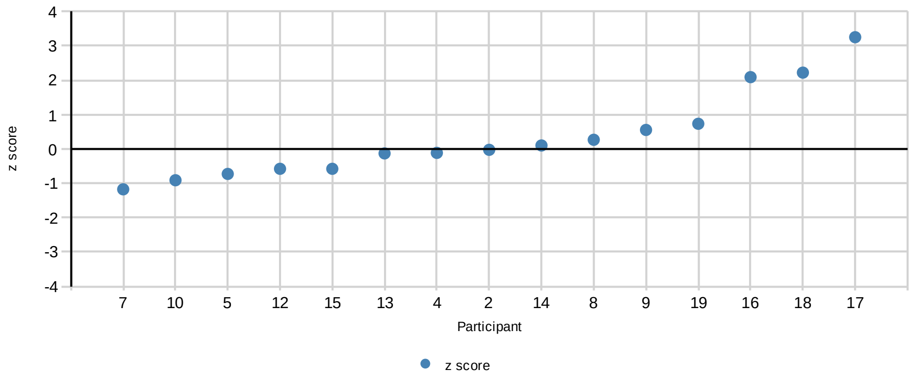
Measurand Pb Sample V2M



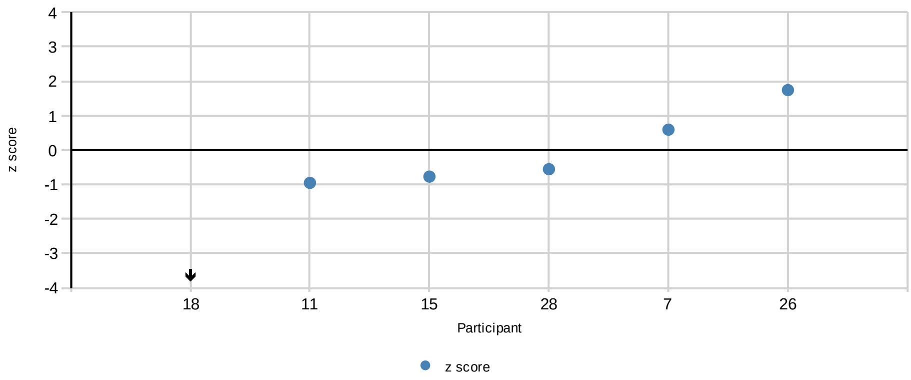
Measurand Se Sample A1M



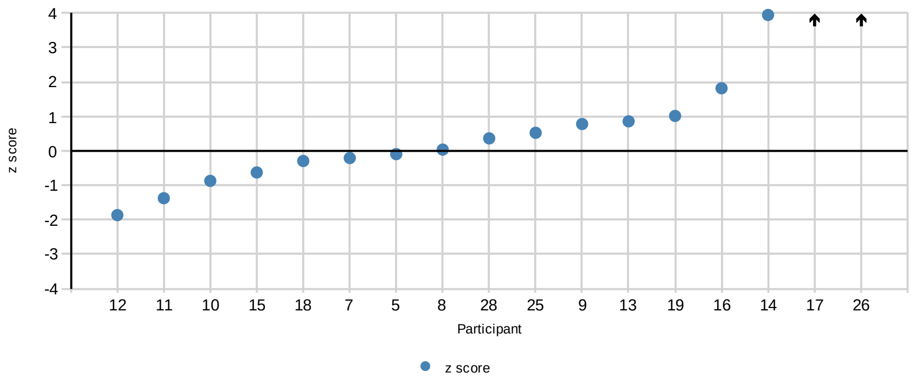
Measurand Se Sample TN3

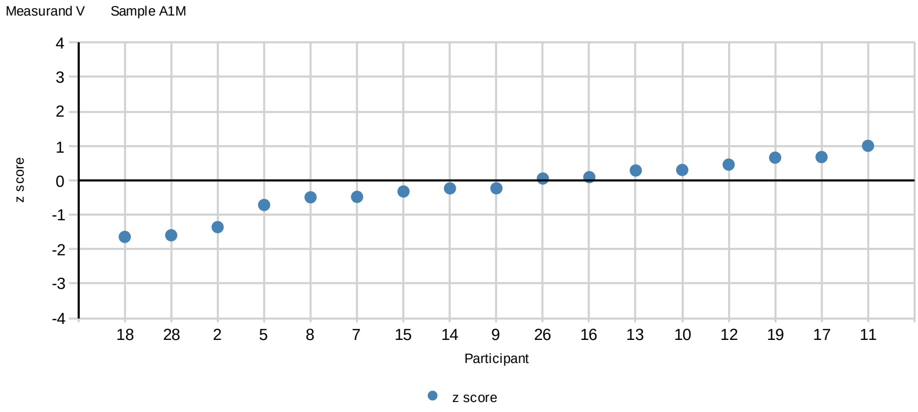


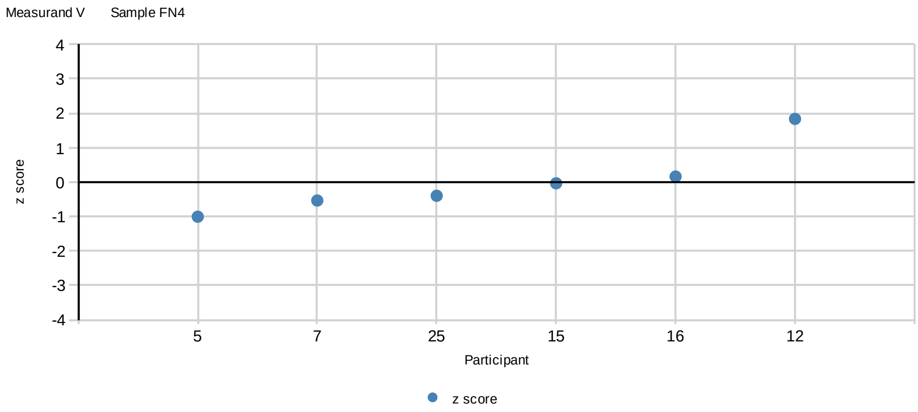
Measurand Se Sample TY3

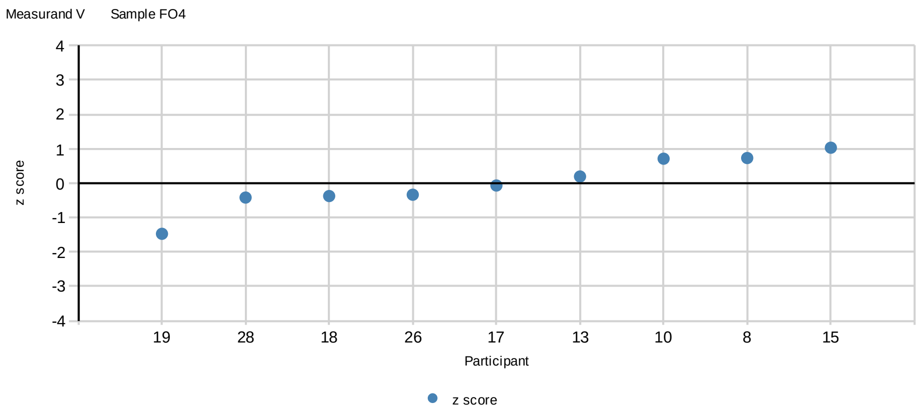


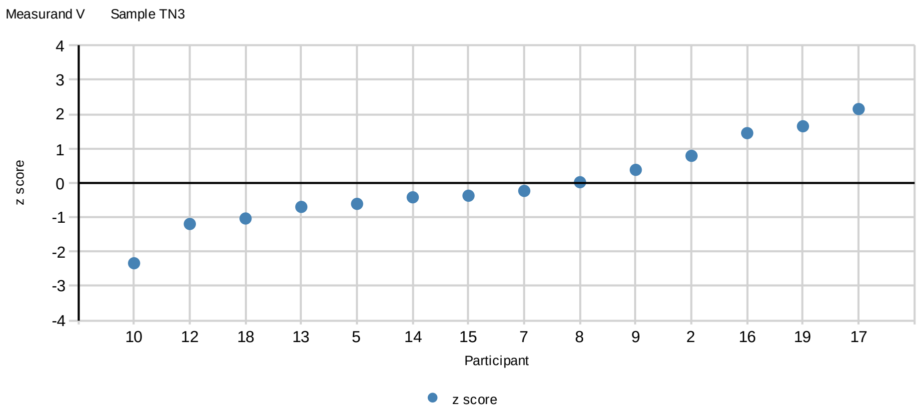
Measurand Se Sample V2M

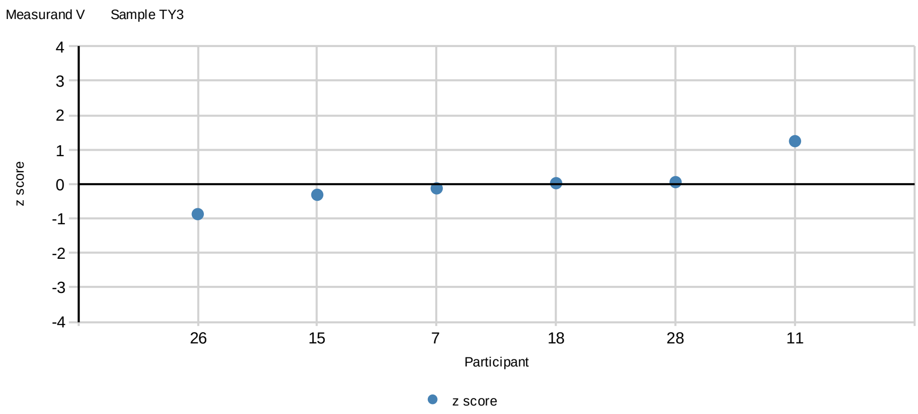


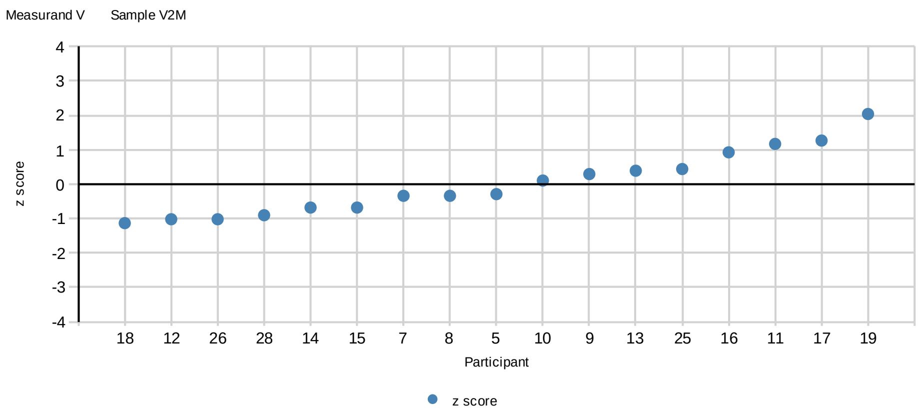

Measurand V
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
18
28
2
5
8
7
15
14
9
26
16
13
10
12
19
17
11
Participant
z score

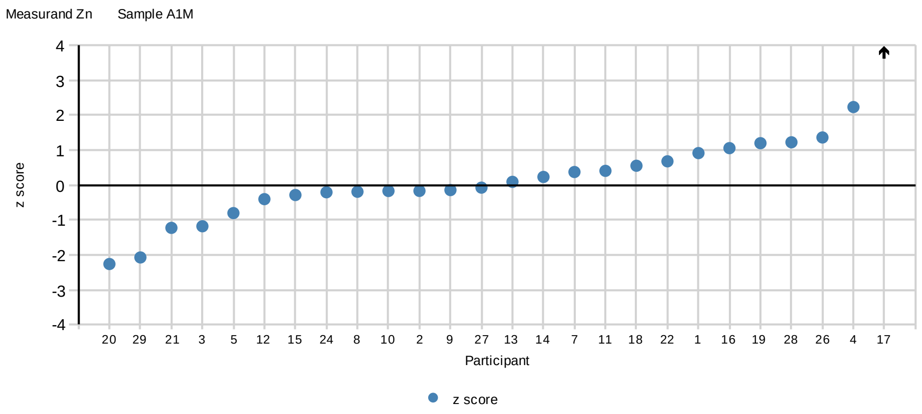

Measurand V
Sample FN4
z score
4
3
2
1
0
-1
-2
-3
-4
5
7
25
15
16
12
Participant
z score

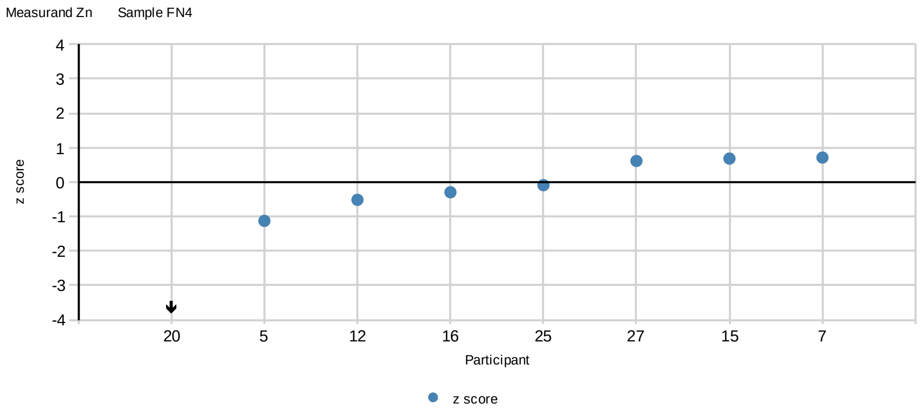

Measurand V
Sample FO4
z score
4
3
2
1
0
-1
-2
-3
-4
19
28
18
26
17
13
10
8
15
Participant
z score

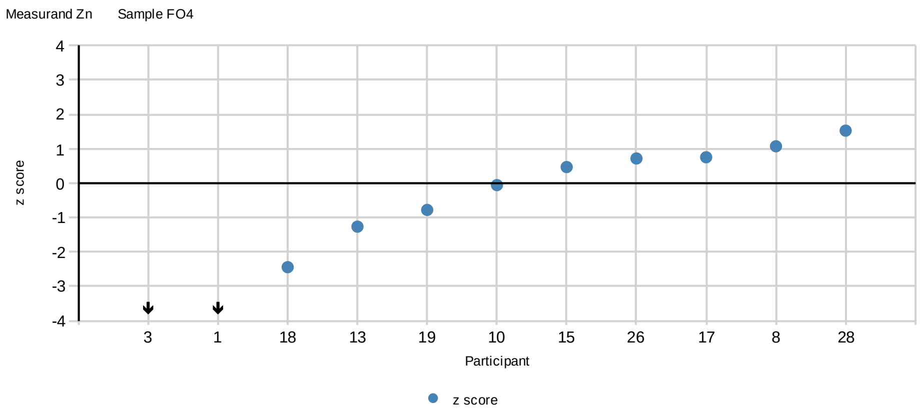

Measurand V
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
10
12
18
13
5
14
15
7
8
9
2
16
19
17
Participant
z score

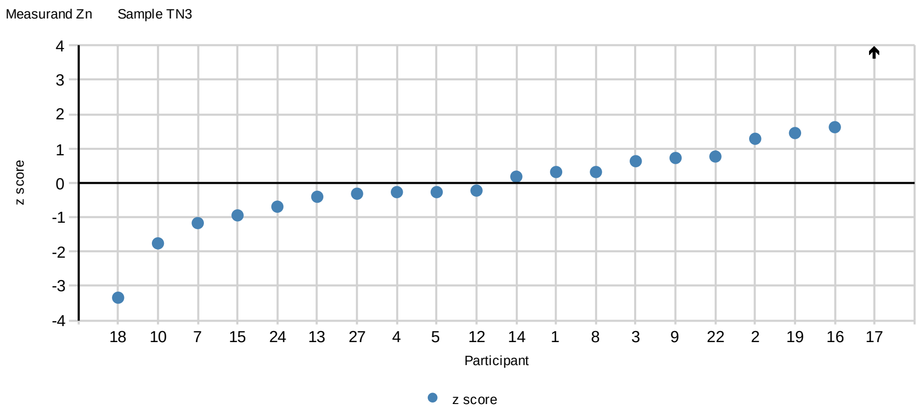

Measurand V
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
26
15
7
18
28
11
Participant
z score

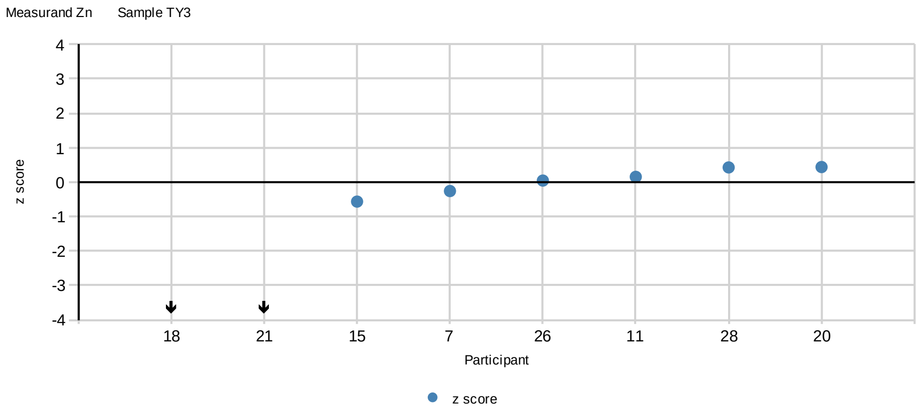

Measurand V
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
18
12
26
28
14
15
7
8
5
10
9
13
25
16
11
17
19
Participant
z score

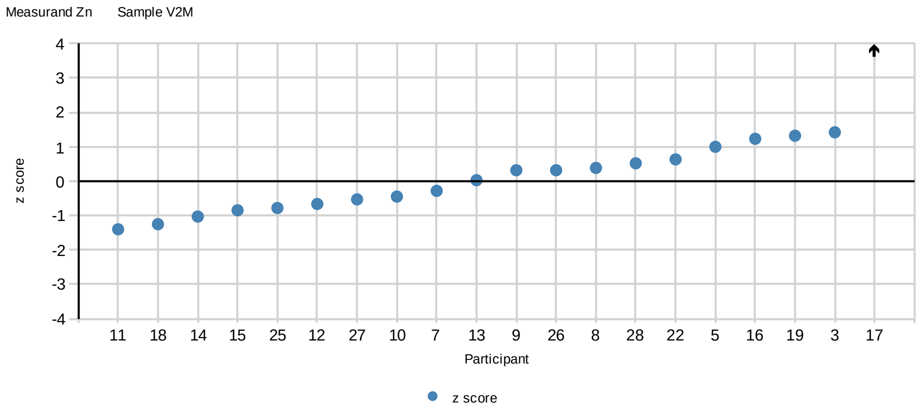

Measurand Zn
Sample A1M
4
3
2
1
0
-1
-2
-3
-4
z score
20 29 21 3 5 12 15 24 8 10 2 9 27 13 14 7 11 18 22 1 16 19 28 26 4 17
Participant
z score


Measurand Zn
Sample FN4
4
3
2
1
0
-1
-2
-3
-4
z score
20 5 12 16 25 27 15 7
Participant
z score


Measurand Zn
Sample FO4
4
3
2
1
0
-1
-2
-3
-4
z score
3 1 18 13 19 10 15 26 17 8 28
Participant
z score


Measurand Zn
Sample TN3
z score
Participant
18 10 7 15 24 13 27 4 5 12 14 1 8 3 9 22 2 19 16 17
z score


Measurand Zn
Sample TY3
z score
Participant
18 21 15 7 26 11 28 20
z score


Measurand Zn
Sample V2M
z score
Participant
11 18 14 15 25 12 27 10 7 13 9 26 8 28 22 5 16 19 3 17
z score

APPENDIX 10: Summary of D% and E_n scores

D% scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
As	FN4	.	.	.	.	33	.	-2.1	.	.	.	.	-4.4	.	.	0.82	5.5	.	.	.	.	.	.	.	.	0.82	.	.	.	.
	FT4	.	.	.	.	.	.	.	.	.	.	-3.2	.	.	.	.	.	.	.	.	.	.	.	.	.	3.7	.	.	.	.
	TY3	.	.	.	.	.	.	-1.4	.	.	.	-4.0	.	.	.	1.9	.	.	-30	.	.	.	.	.	.	.	-1.4	.	4.7	.
Ba	FN4	.	.	.	.	-17	.	7.8	.	.	.	.	-0.32	.	.	.	6.7	.	.	.	.	.	.	.	.	2.3	.	.	.	.
	FO4	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
	FT4	.	.	.	.	.	.	.	.	.	.	-1.5	.	.	.	.	.	.	.	.	.	.	.	.	.	1.5	.	.	.	.
Cd	FT4	.	.	.	.	.	.	.	.	.	.	1.2	.	.	.	.	.	.	.	.	.	.	.	.	.	-1.3	.	.	.	.
Cr	FT4	.	.	.	.	.	.	.	.	.	.	-13	.	.	.	.	.	.	.	.	.	.	.	.	.	12	.	.	.	.
Hg	FC4	.	.	.	.	-18	.	.	.	.	.	.	.	.	.	3.1	.	.	.	.	.	.	.	.	.	16	.	.	.	.
	FN4	.	.	.	.	.	.	1.01	.	.	.	0.0	.	.	.	.	-9.6	.	.	.	.	.	.	.	.	8.1	.	.	.	.
	FO4	.	.	.	.	.	.	.	-34	.	31	.	.	-24	.	.	.	-22	31	.	.	.	.	.	.	.	.	.	.	.
Mo	FT4	.	.	.	.	.	.	.	.	.	.	4.8	.	.	.	.	.	.	.	.	.	.	.	.	.	-4.6	.	.	.	.
Pb	FT4	.	.	.	.	.	.	.	.	.	.	-1.5	.	.	.	.	.	.	.	.	.	.	.	.	.	1.6	.	.	.	.
V	FT4	.	.	.	.	.	.	.	.	.	.	-4.3	.	.	.	.	.	.	.	.	.	.	.	.	.	4.3	.	.	.	.
Zn	FT4	.	.	.	.	.	.	.	.	.	.	-0.3	.	.	.	.	.	.	.	.	.	.	.	.	.	0.3	.	.	.	.

D can be interpreted as the measurement error for the result, to the extent to which
assigned value can be considered a reference quantity value

E_n scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	%
As	FN4	.	.	.	.	1.2	.	-0.1	.	.	.	.	.	.	.	0.0	0.3	.	.	.	.	.	.	.	.	0.1	.	.	.	.	80.0
	TY3	.	.	.	.	.	.	-0.1	.	.	.	-0.1	.	.	.	0.2	.	.	-1.7	.	.	.	.	.	.	.	-0.1	.	0.2	.	83.3

E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty

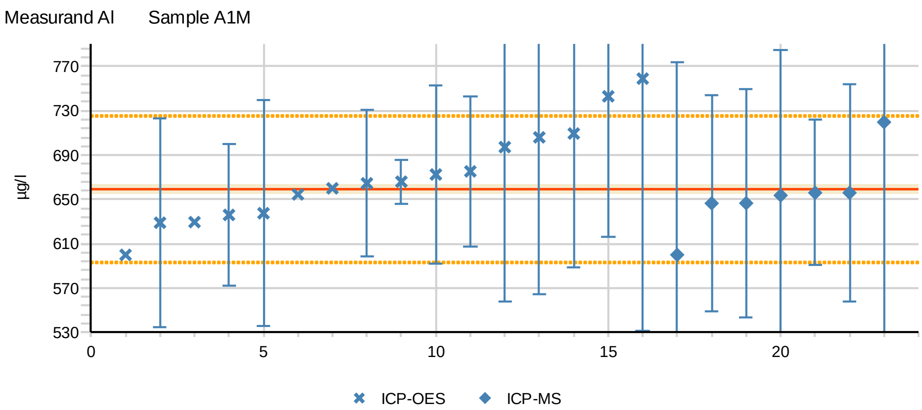
Scores of $-1.0 < E_n < 1.0$ indicate successful performance

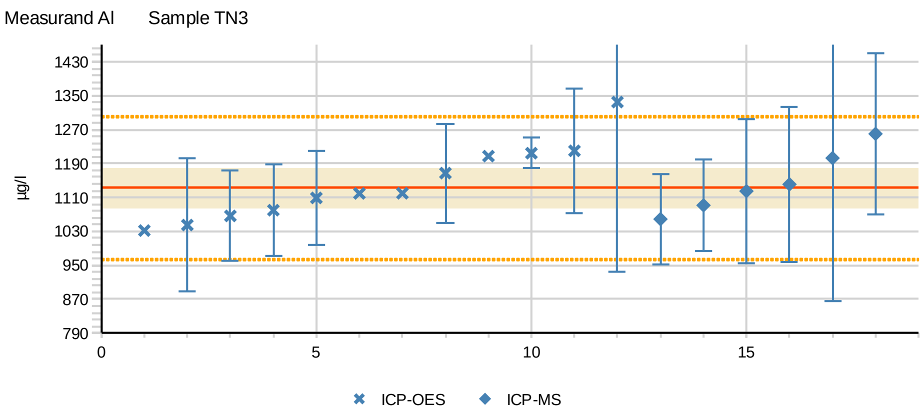
Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

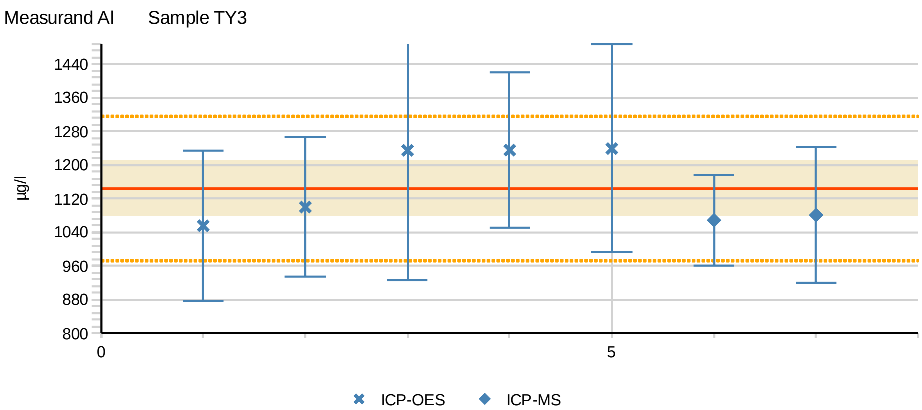
APPENDIX 11: Results grouped according to the methods

In figures:

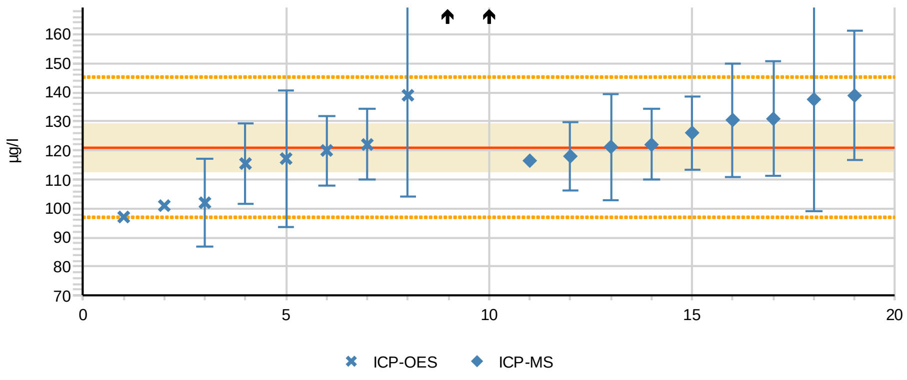
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



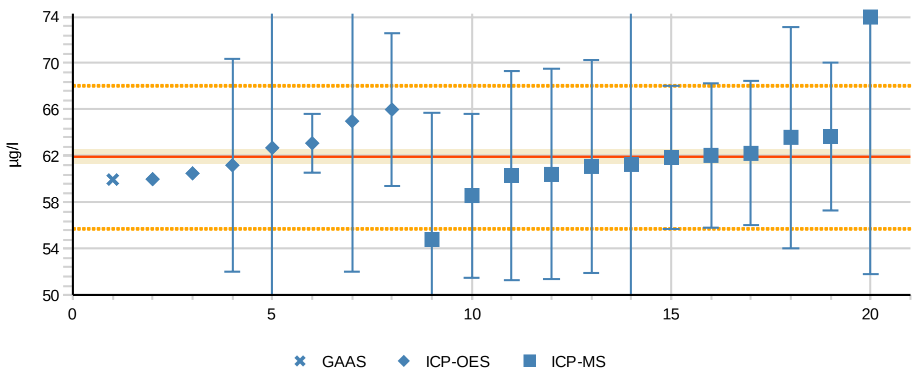




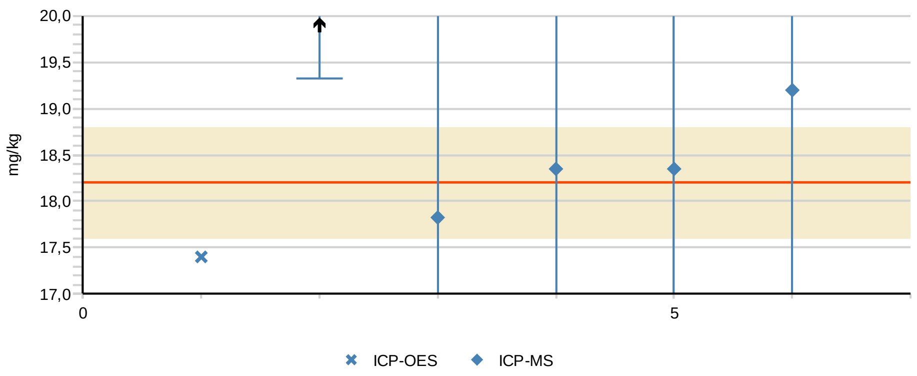
Measurand Al Sample V2M



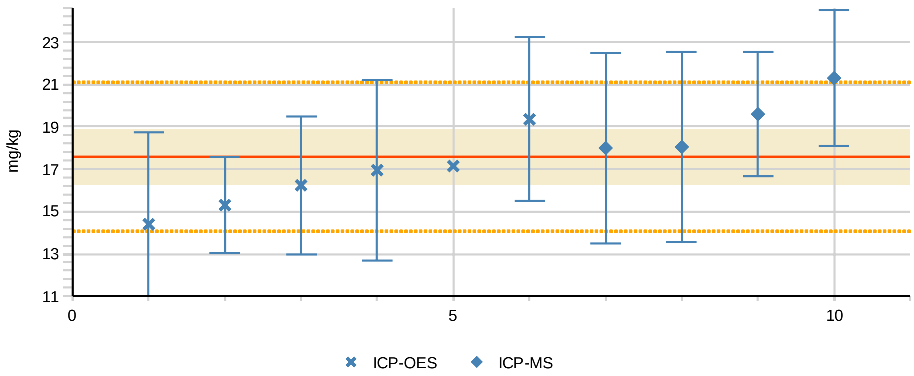
Measurand As Sample A1M



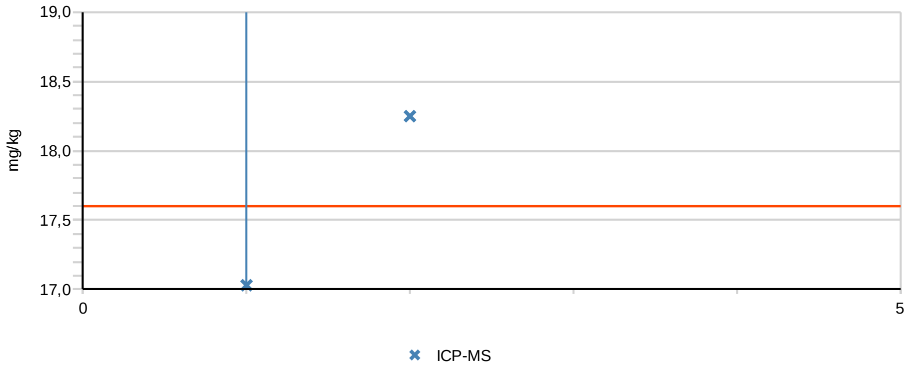
Measurand As Sample FN4



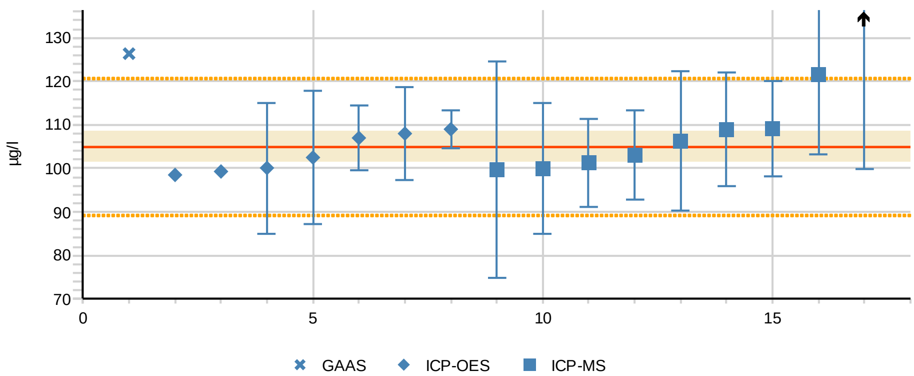
Measurand As Sample FO4



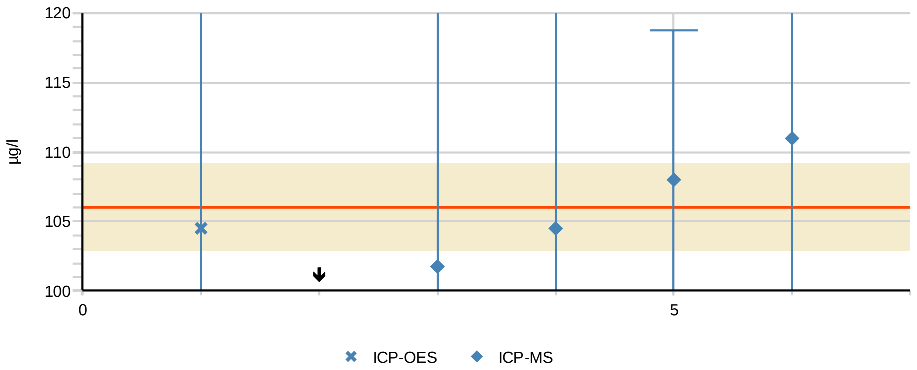
Measurand As Sample FT4



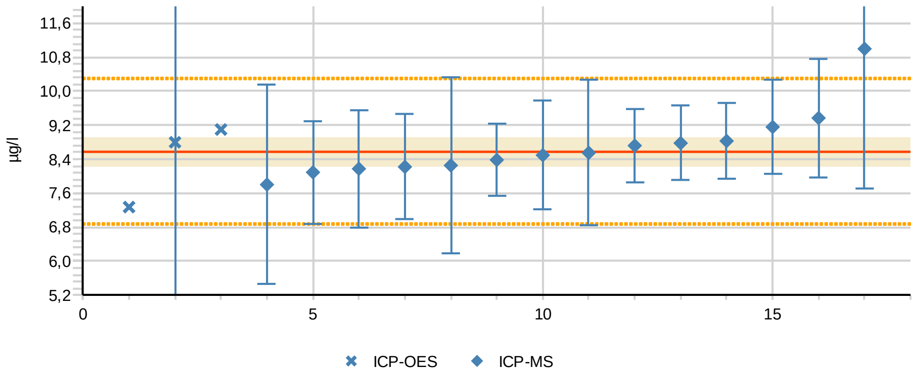
Measurand As Sample TN3



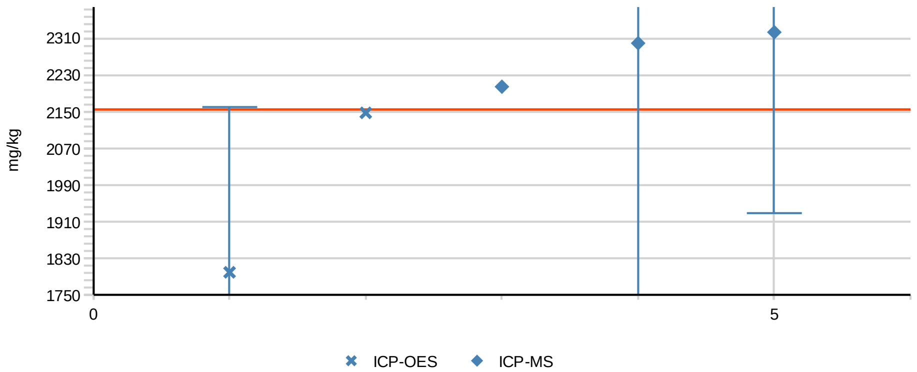
Measurand As Sample TY3

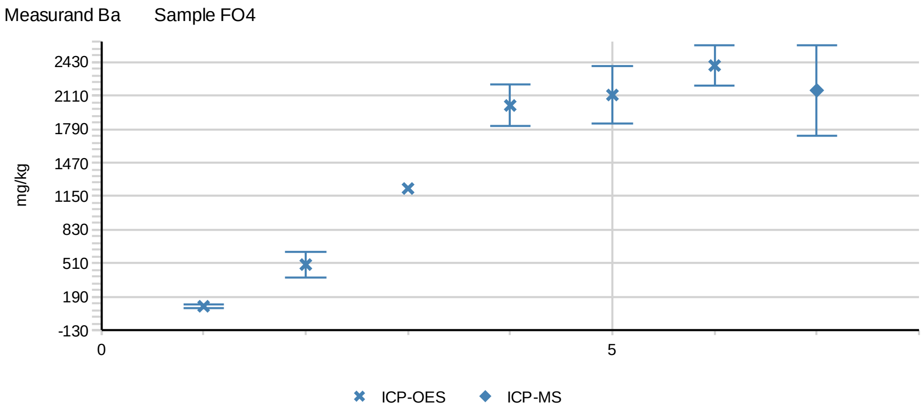


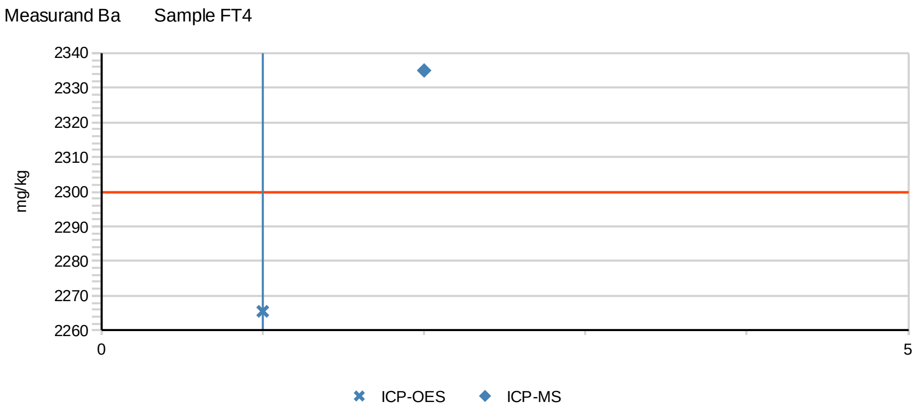
Measurand As Sample V2M

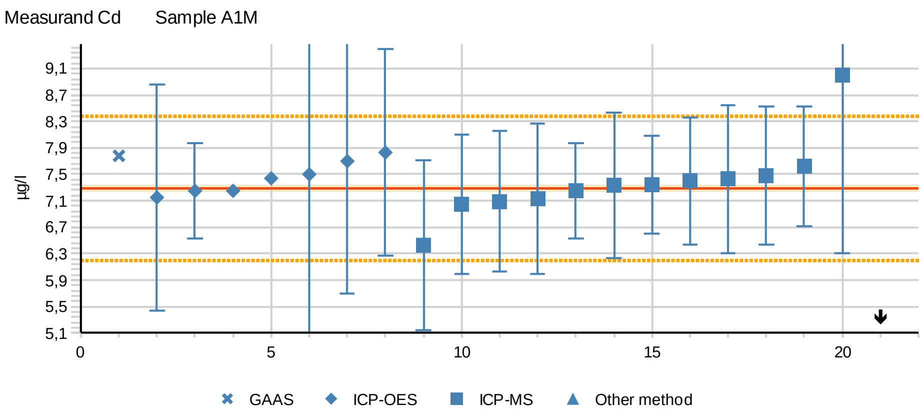


Measurand Ba Sample FN4

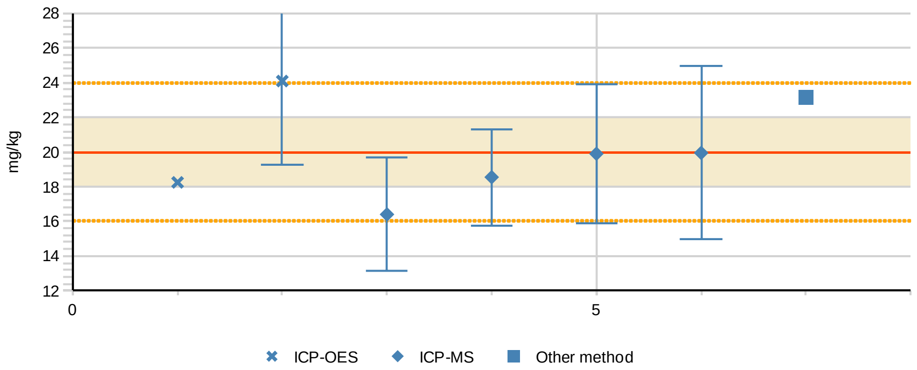



Measurand Ba
Sample FO4
mg/kg
2430
2110
1790
1470
1150
830
510
190
-130
0
5
ICP-OES
ICP-MS

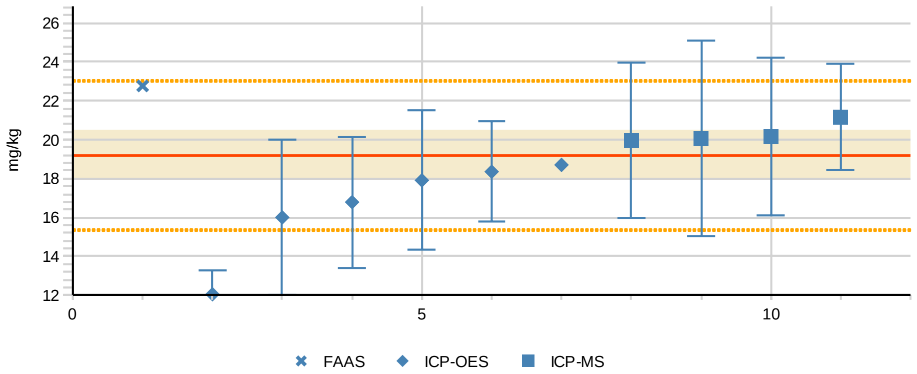

Measurand Ba
Sample FT4
mg/kg
2340
2330
2320
2310
2300
2290
2280
2270
2260
0
5
ICP-OES
ICP-MS


Measurand Cd
Sample A1M
µg/l
9,1
8,7
8,3
7,9
7,5
7,1
6,7
6,3
5,9
5,5
5,1
0
5
10
15
20
GAAS
ICP-OES
ICP-MS
Other method

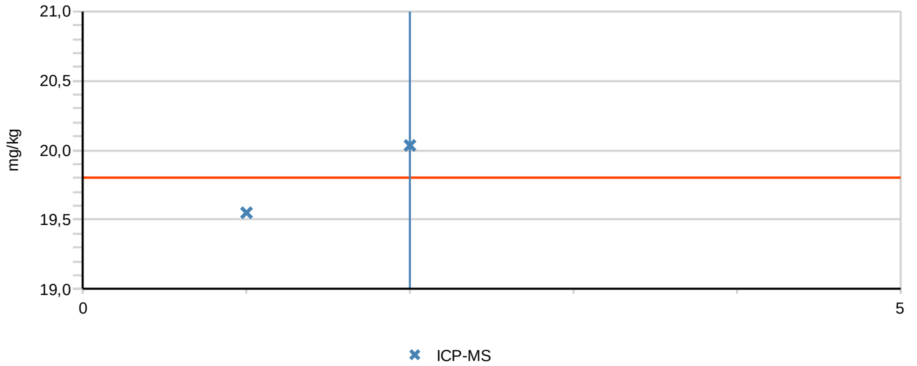
Measurand Cd   Sample FN4

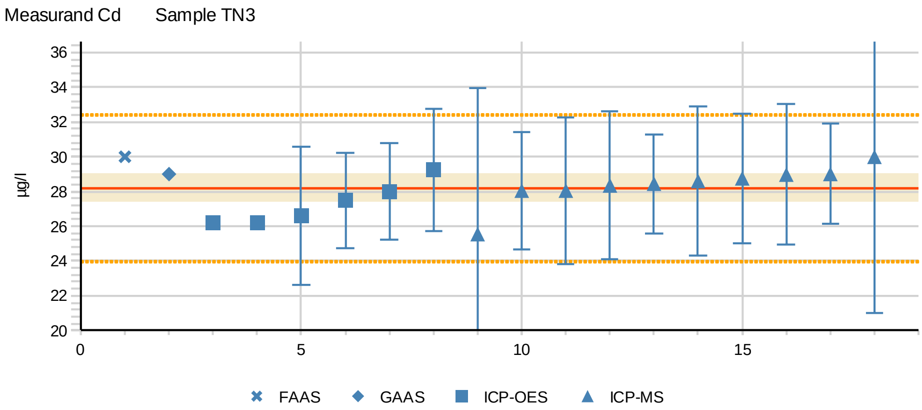


Measurand Cd   Sample FO4

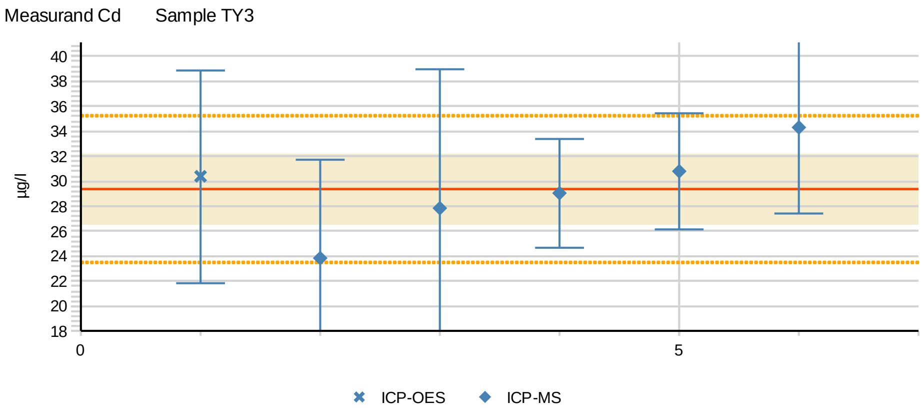


Measurand Cd   Sample FT4

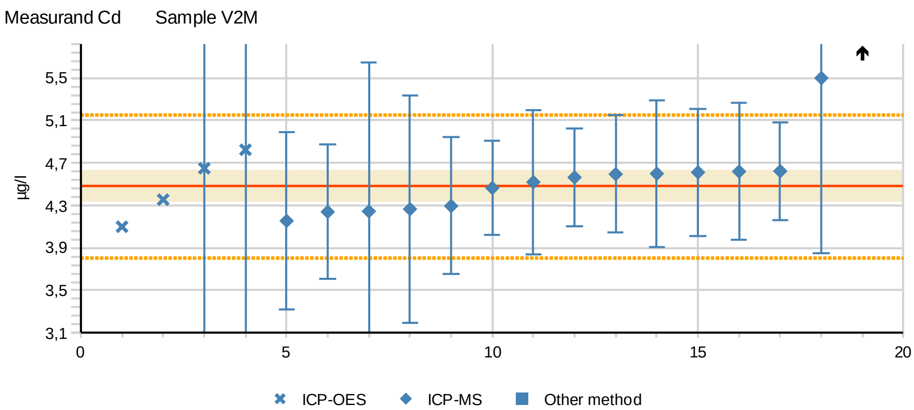




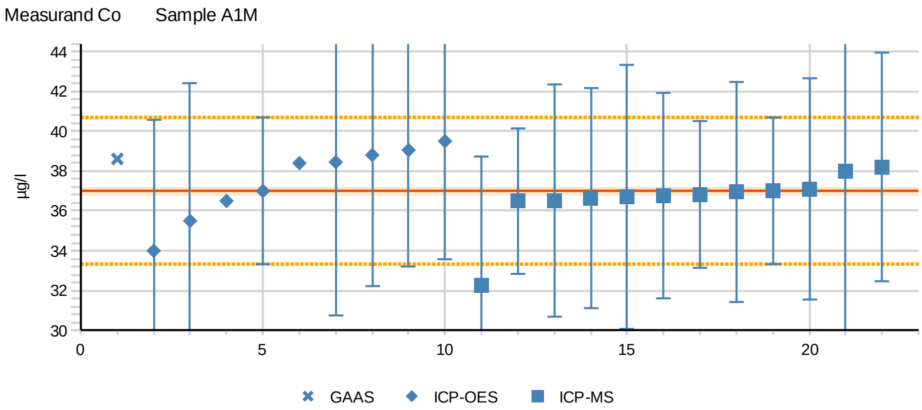
Measurand Cd
Sample TN3
µg/l
36
34
32
30
28
26
24
22
20
0
5
10
15
FAAS
GAAS
ICP-OES
ICP-MS

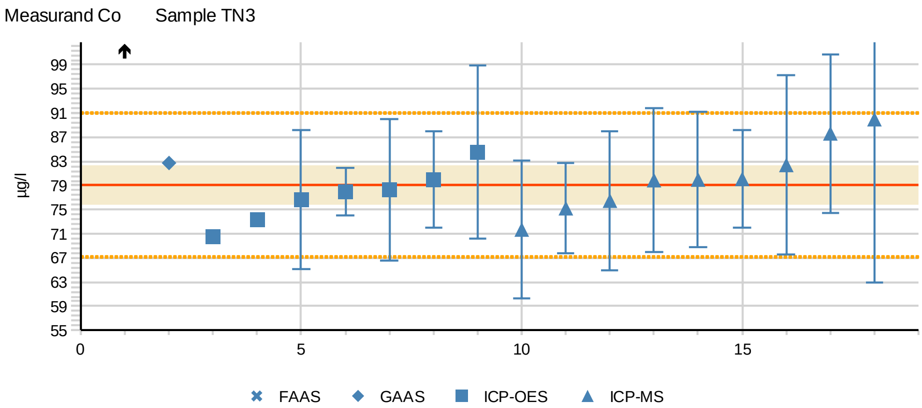


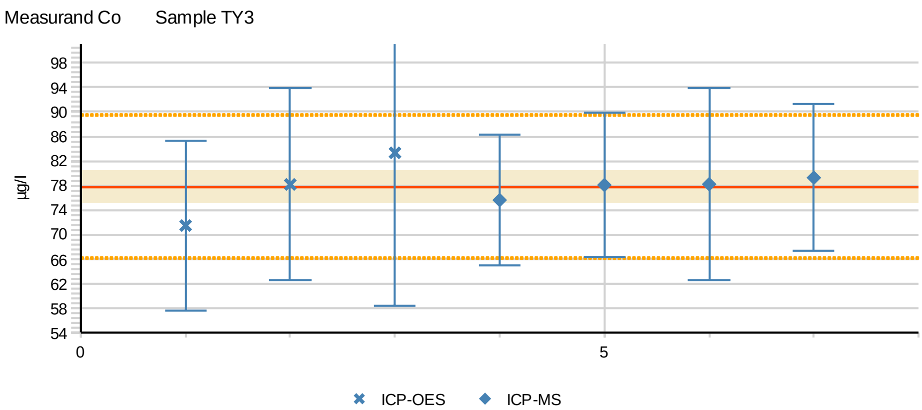
Measurand Cd
Sample TY3
µg/l
40
38
36
34
32
30
28
26
24
22
20
18
0
5
ICP-OES
ICP-MS

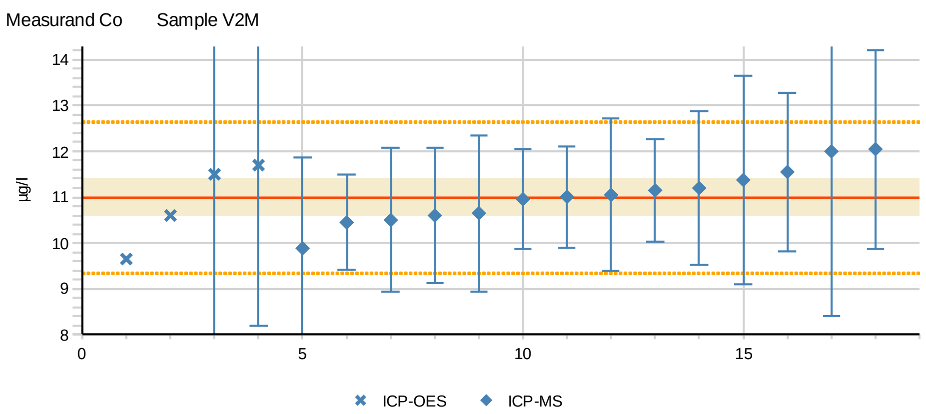


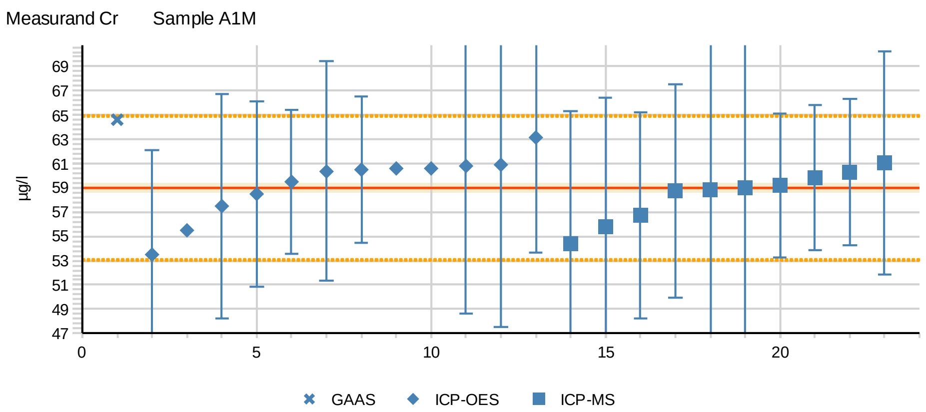
Measurand Cd
Sample V2M
µg/l
5,5
5,1
4,7
4,3
3,9
3,5
3,1
0
5
10
15
20
ICP-OES
ICP-MS
Other method

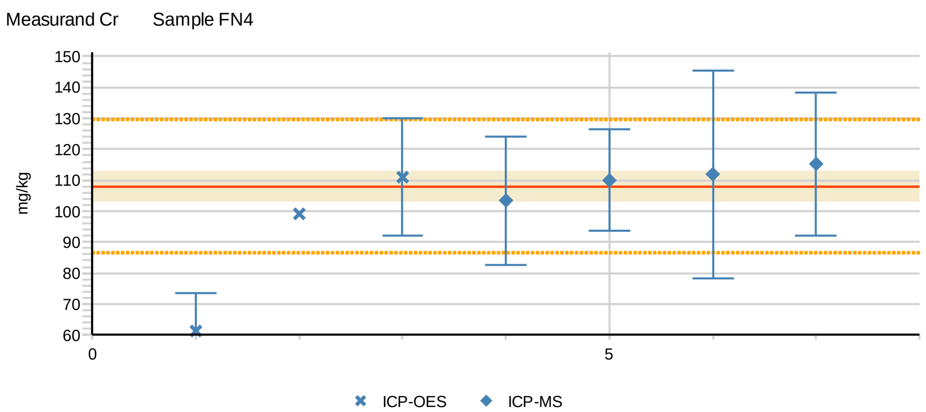

Measurand Co
Sample A1M
µg/l
44
42
40
38
36
34
32
30
0
5
10
15
20
GAAS
ICP-OES
ICP-MS


Measurand Co
Sample TN3
µg/l
99
95
91
87
83
79
75
71
67
63
59
55
0
5
10
15
FAAS
GAAS
ICP-OES
ICP-MS

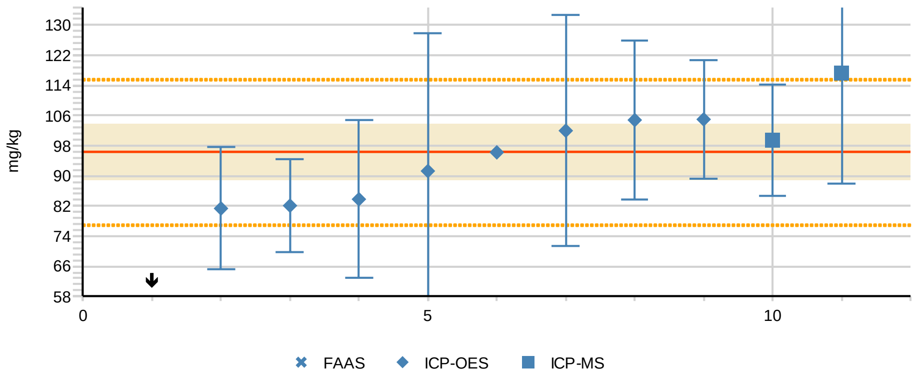

Measurand Co
Sample TY3
µg/l
98
94
90
86
82
78
74
70
66
62
58
54
0
5
ICP-OES
ICP-MS


Measurand Co
Sample V2M
µg/l
14
13
12
11
10
9
8
0
5
10
15
ICP-OES
ICP-MS

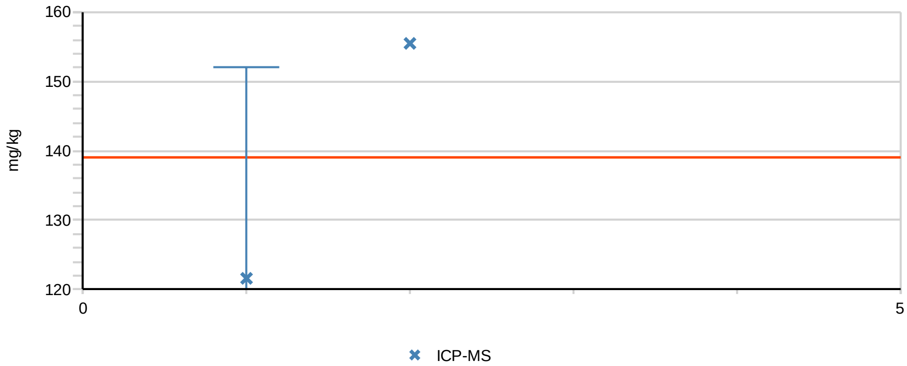

Measurand Cr
Sample A1M
µg/l
69
67
65
63
61
59
57
55
53
51
49
47
0
5
10
15
20
GAAS
ICP-OES
ICP-MS


Measurand Cr
Sample FN4
mg/kg
150
140
130
120
110
100
90
80
70
60
0
5
ICP-OES
ICP-MS

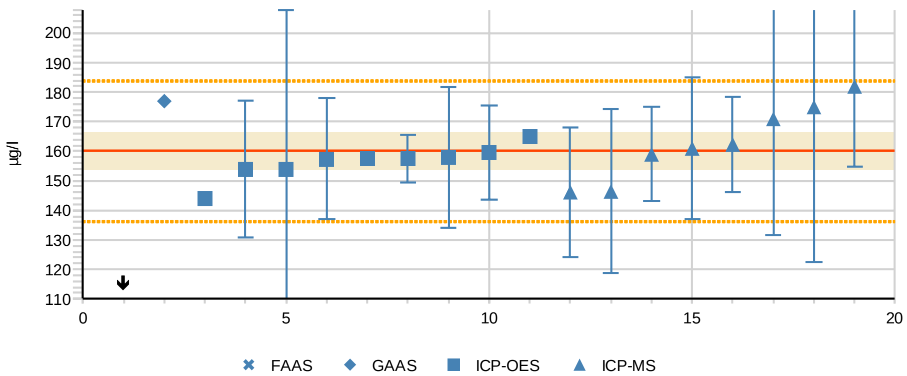
Measurand Cr Sample FO4

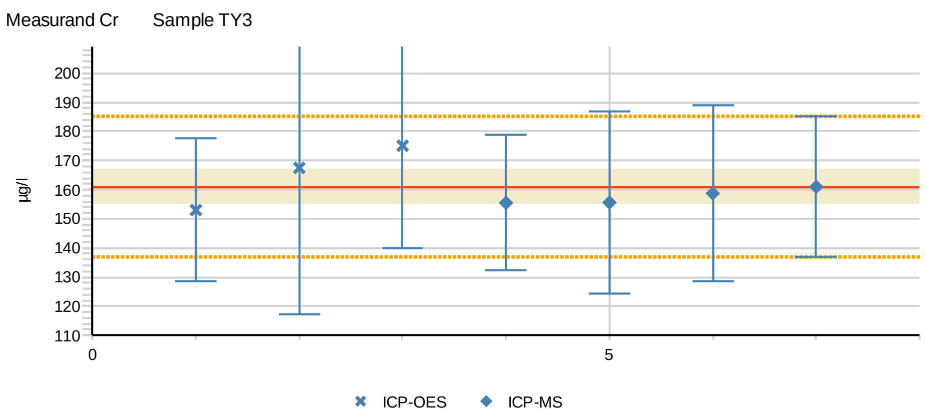


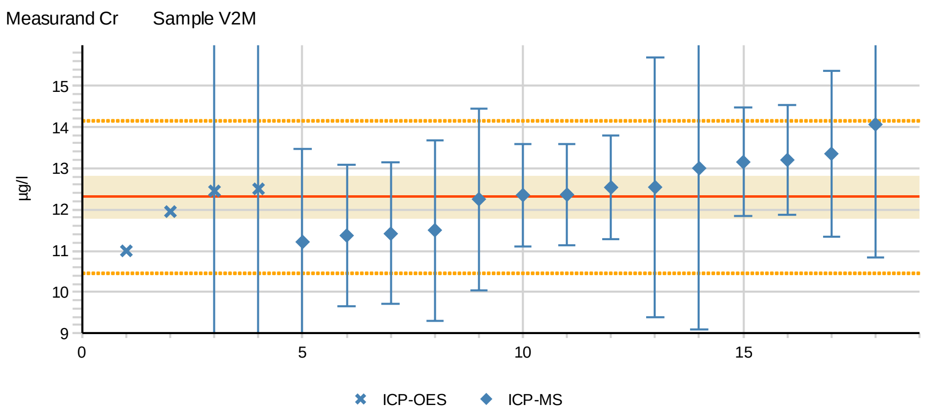
Measurand Cr Sample FT4

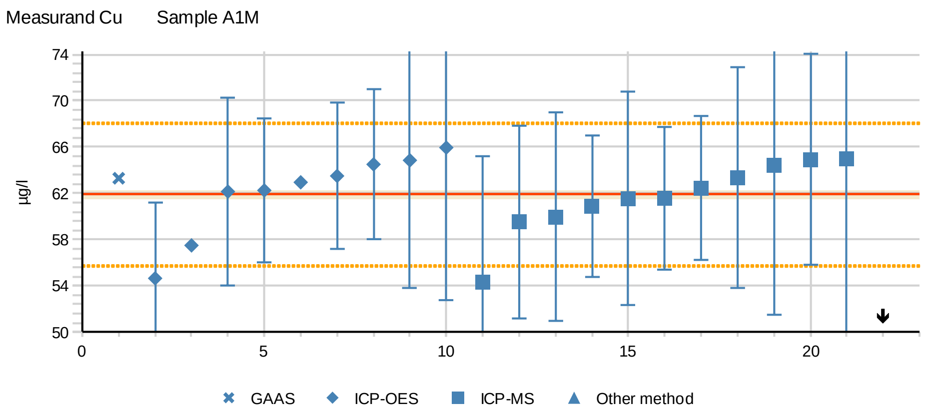


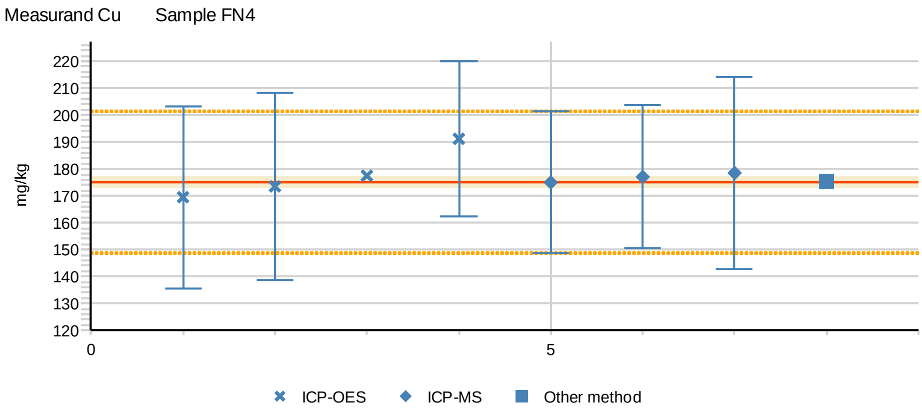
Measurand Cr Sample TN3

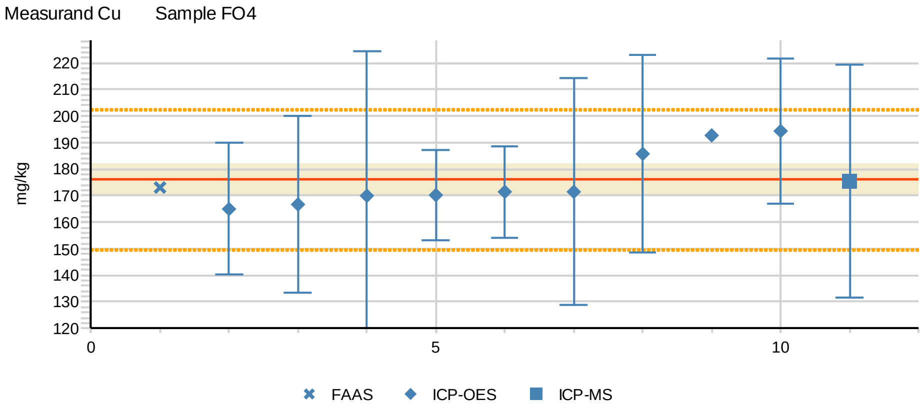


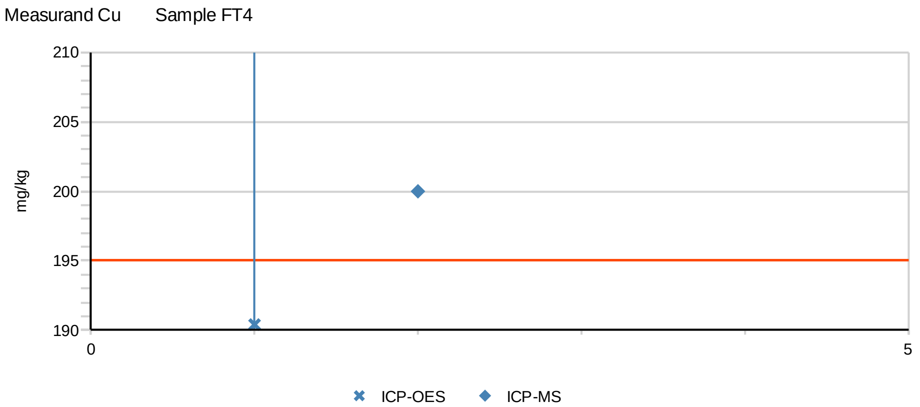

Measurand Cr
Sample TY3
µg/l
200
190
180
170
160
150
140
130
120
110
0
5
ICP-OES
ICP-MS

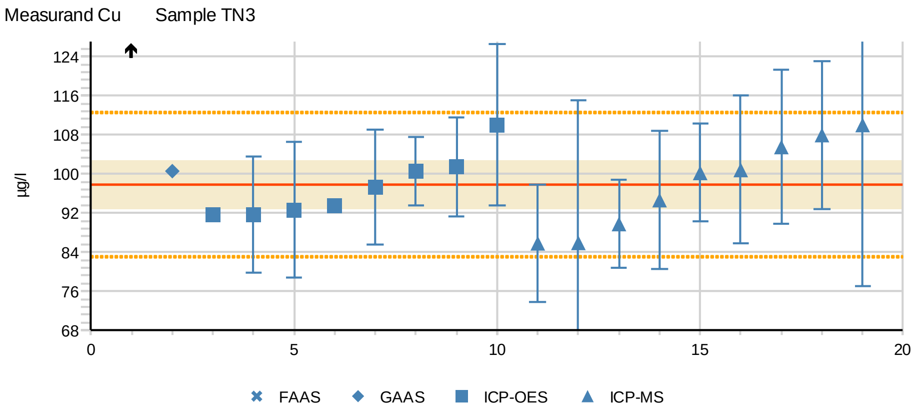

Measurand Cr
Sample V2M
µg/l
15
14
13
12
11
10
9
0
5
10
15
ICP-OES
ICP-MS

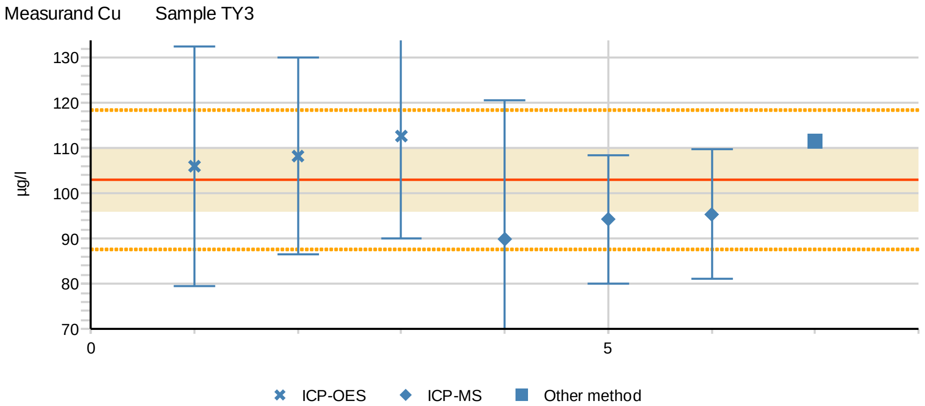

Measurand Cu
Sample A1M
µg/l
74
70
66
62
58
54
50
0
5
10
15
20
GAAS
ICP-OES
ICP-MS
Other method

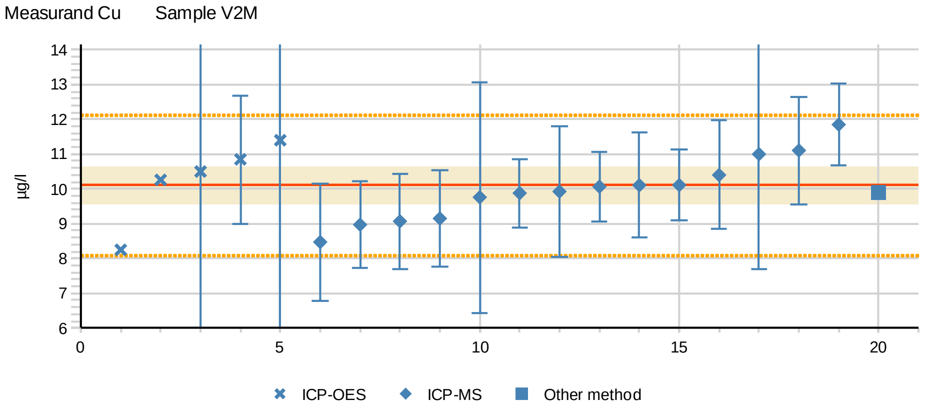

Measurand Cu
Sample FN4
mg/kg
220
210
200
190
180
170
160
150
140
130
120
0
5
ICP-OES
ICP-MS
Other method


Measurand Cu
Sample FO4
mg/kg
220
210
200
190
180
170
160
150
140
130
120
0
5
10
FAAS
ICP-OES
ICP-MS

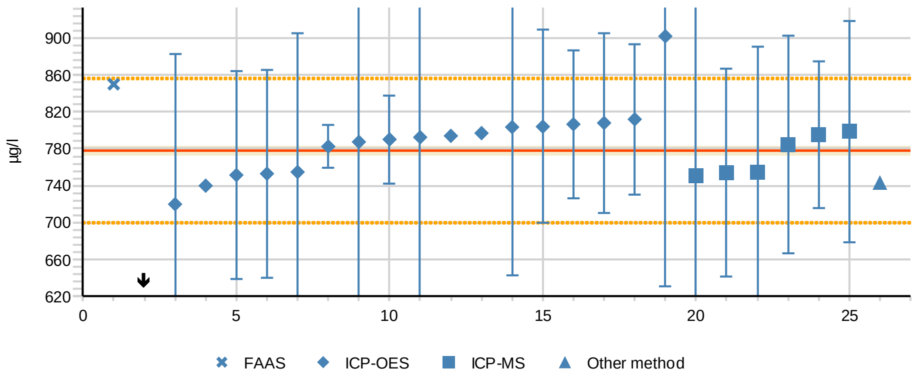

Measurand Cu
Sample FT4
mg/kg
210
205
200
195
190
0
5
ICP-OES
ICP-MS


Measurand Cu
Sample TN3
µg/l
124
116
108
100
92
84
76
68
0
5
10
15
20
FAAS
GAAS
ICP-OES
ICP-MS

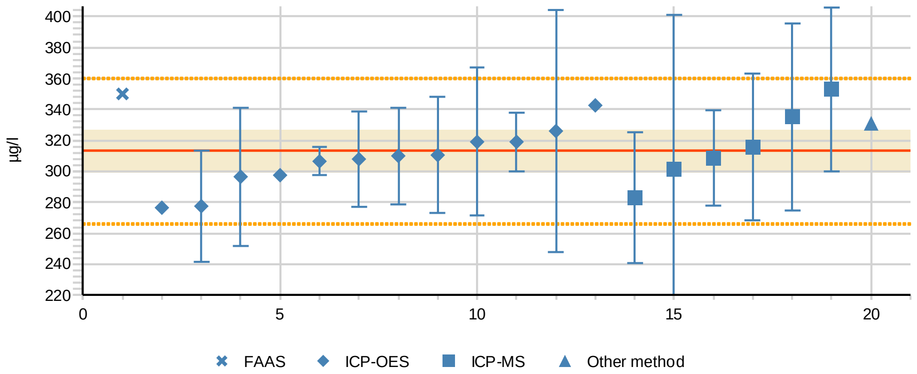

Measurand Cu
Sample TY3
µg/l
130
120
110
100
90
80
70
0
5
ICP-OES
ICP-MS
Other method


Measurand Cu
Sample V2M
µg/l
14
13
12
11
10
9
8
7
6
0
5
10
15
20
ICP-OES
ICP-MS
Other method

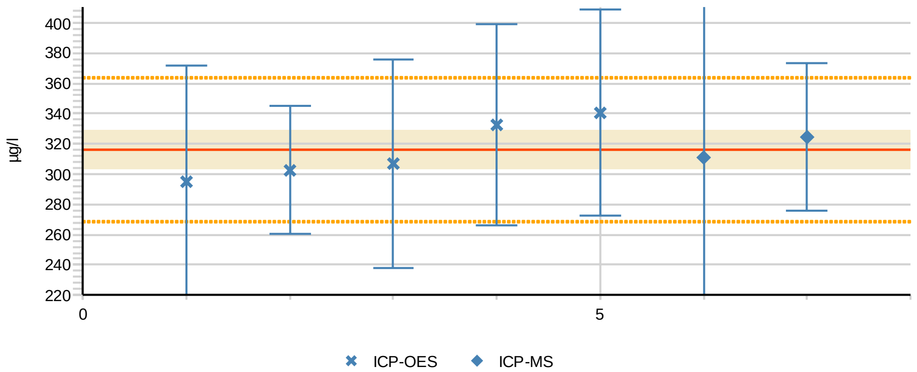
Measurand Fe Sample A1M



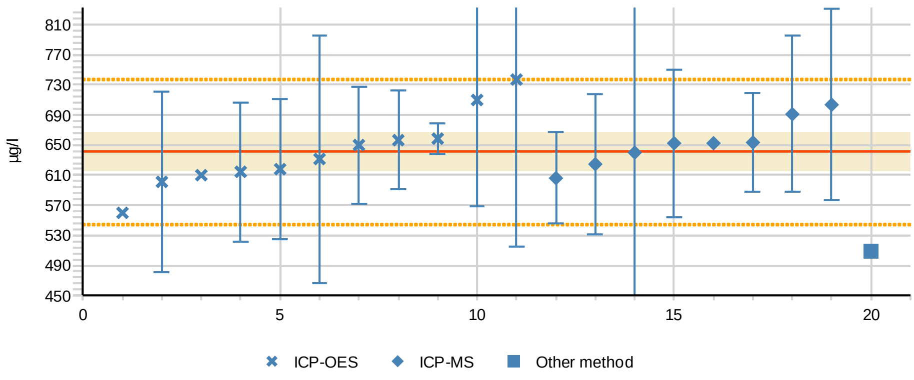
Measurand Fe Sample TN3



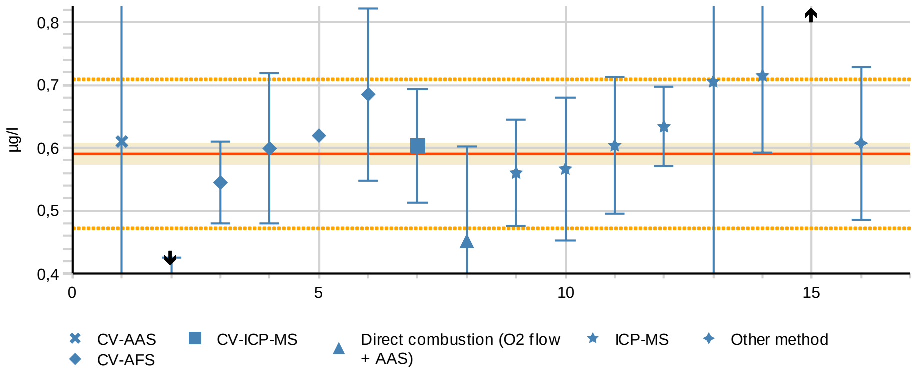
Measurand Fe Sample TY3



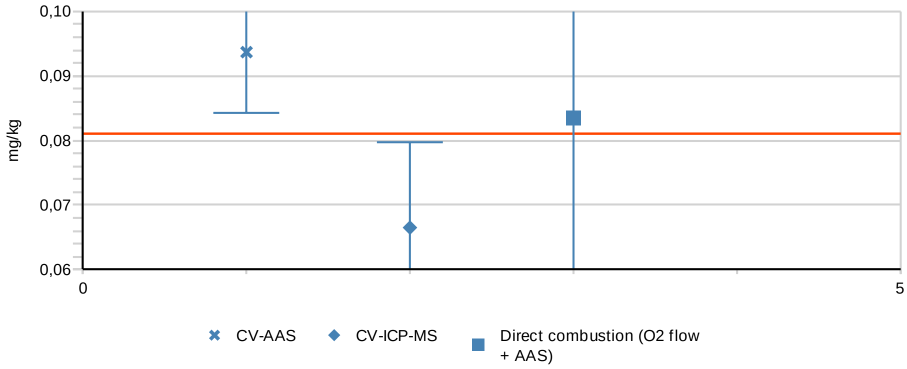
Measurand Fe Sample V2M



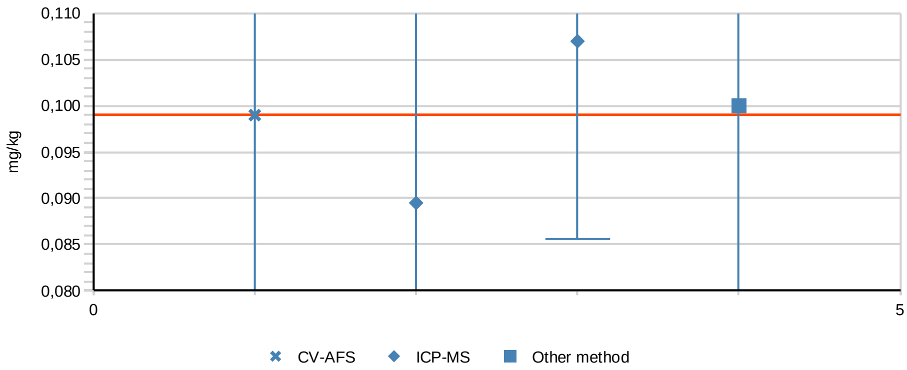
Measurand Hg Sample A1Hg



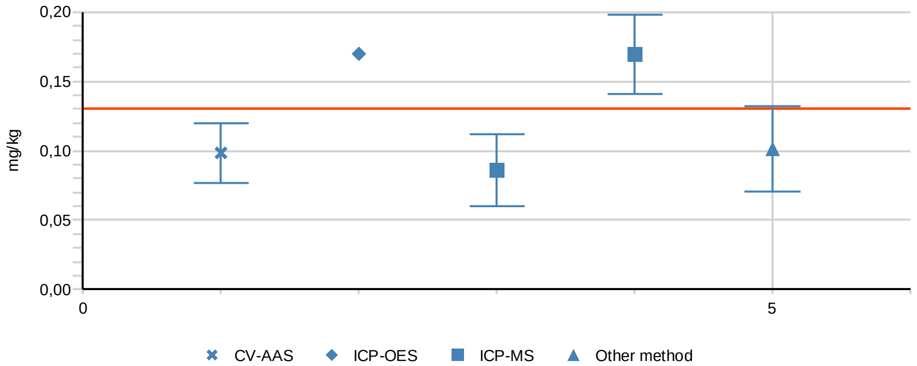
Measurand Hg Sample FC4



Measurand Hg Sample FN4

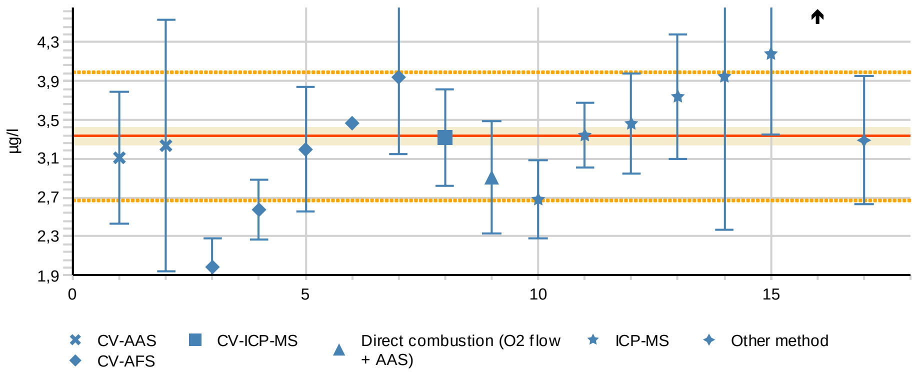


Measurand Hg Sample FO4

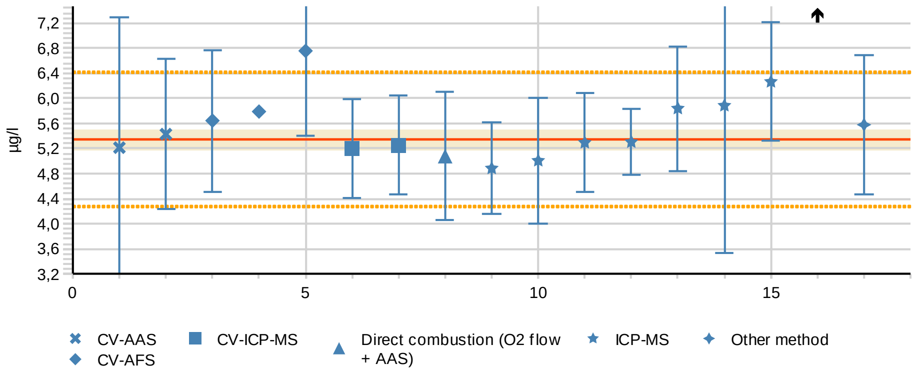


Measurand Hg Sample FT4

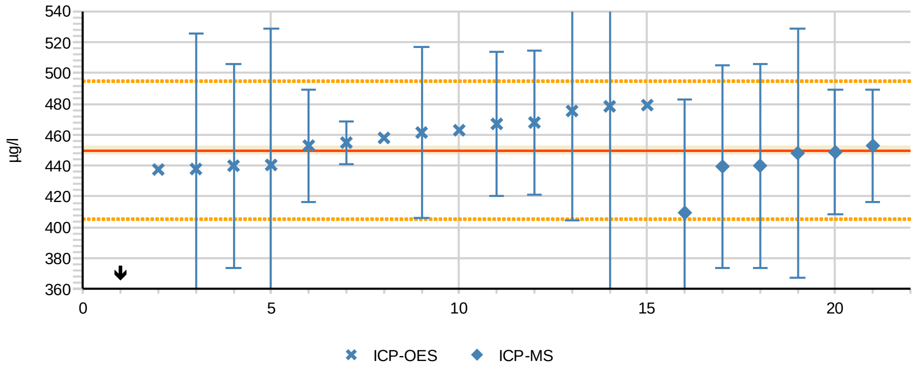
Measurand Hg   Sample T3Hg

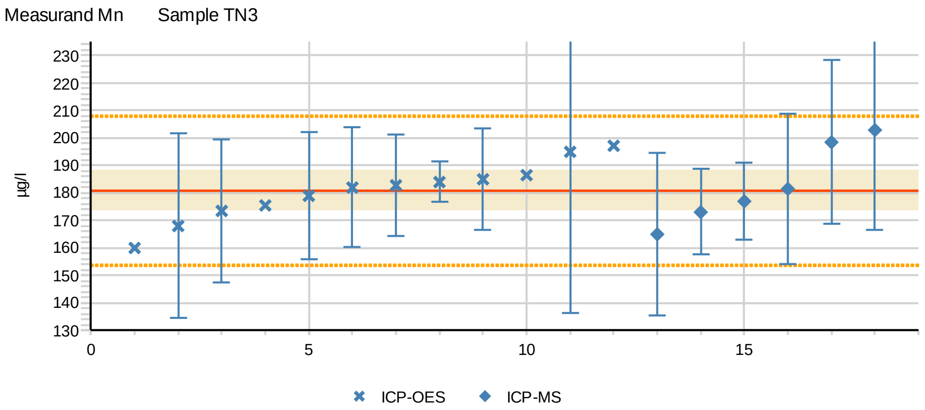


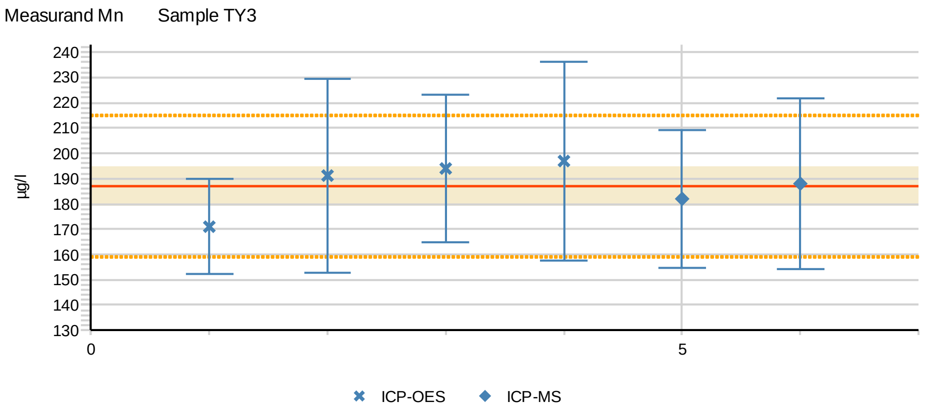
Measurand Hg   Sample V2Hg

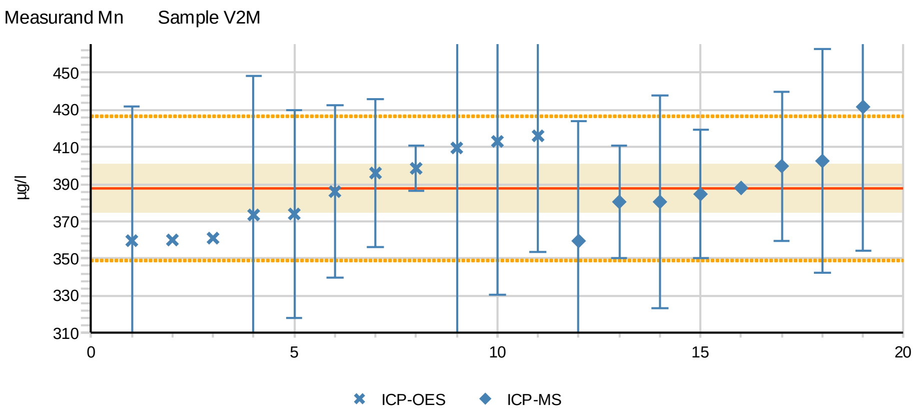


Measurand Mn   Sample A1M

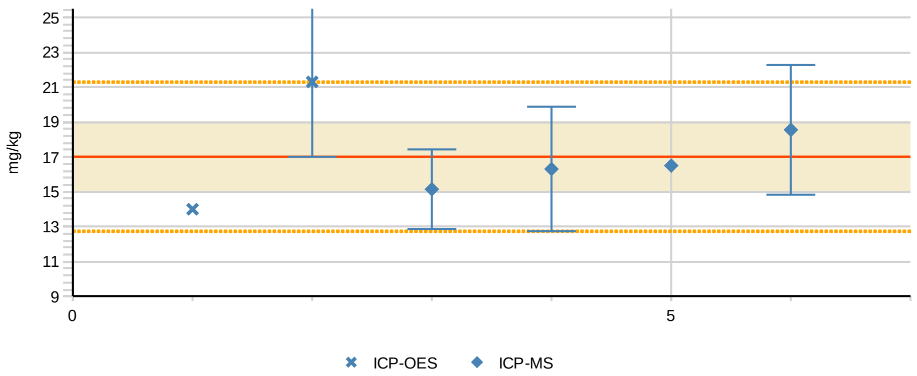



Measurand Mn
Sample TN3
µg/l
ICP-OES
ICP-MS

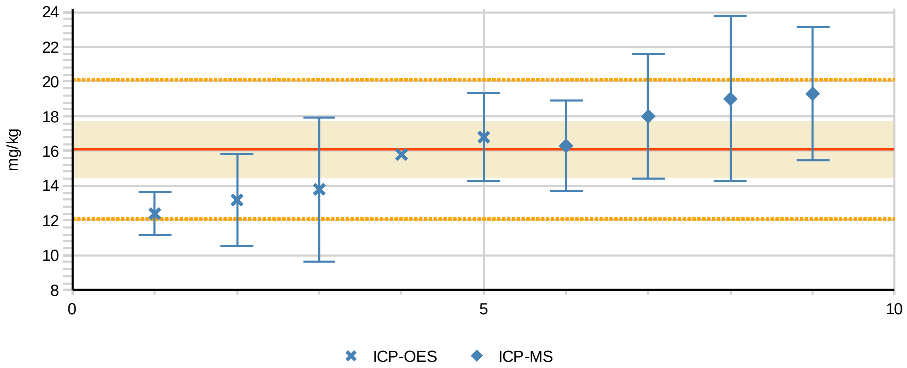

Measurand Mn
Sample TY3
µg/l
ICP-OES
ICP-MS


Measurand Mn
Sample V2M
µg/l
ICP-OES
ICP-MS

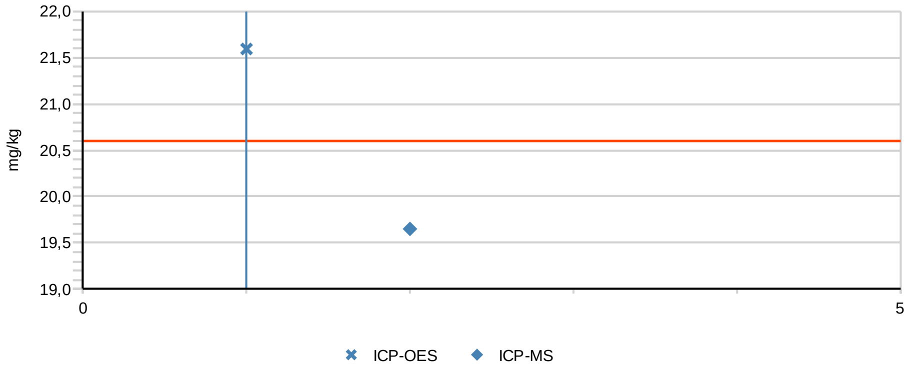
Measurand Mo Sample FN4



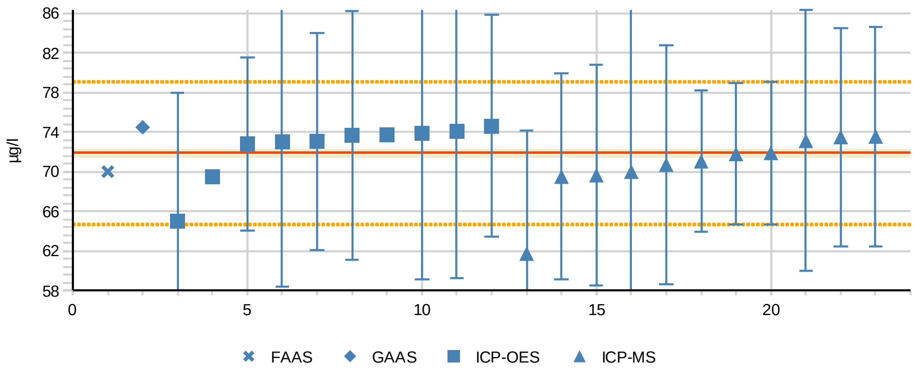
Measurand Mo Sample FO4



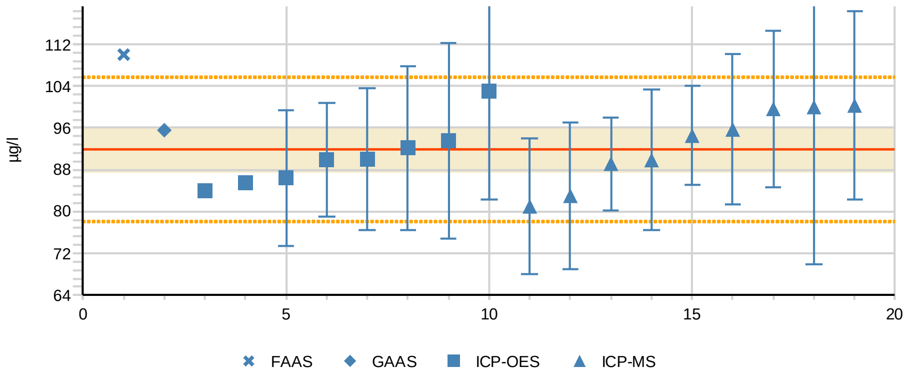
Measurand Mo Sample FT4



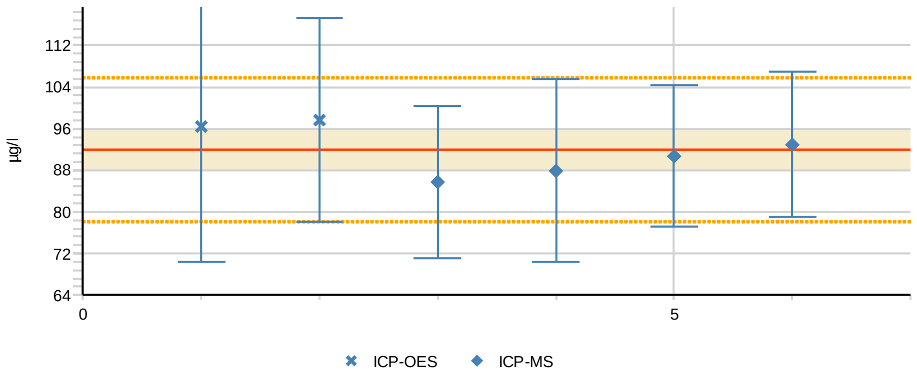
Measurand Ni Sample A1M



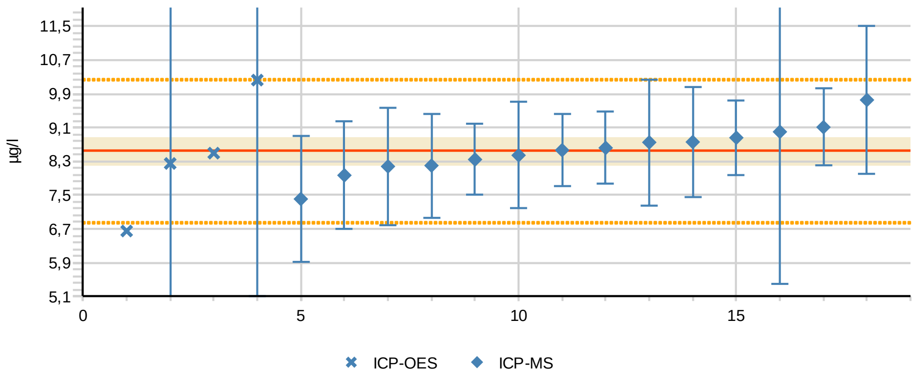
Measurand Ni Sample TN3



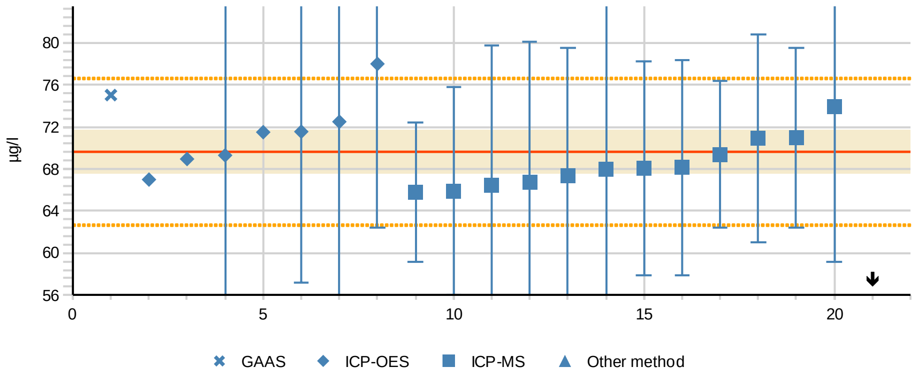
Measurand Ni Sample TY3



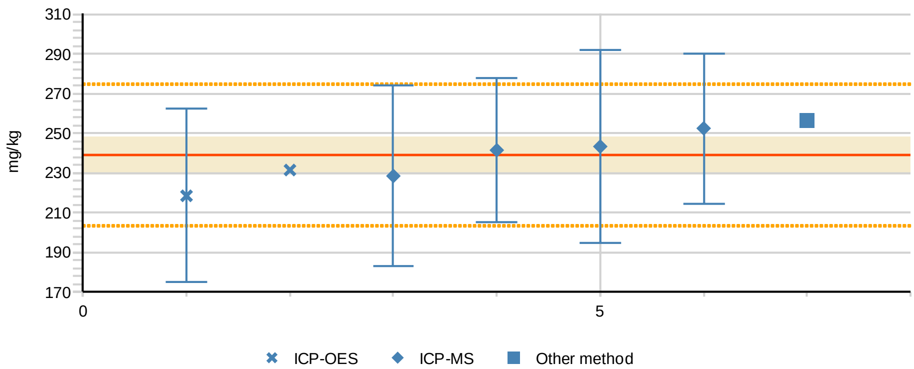
Measurand Ni Sample V2M



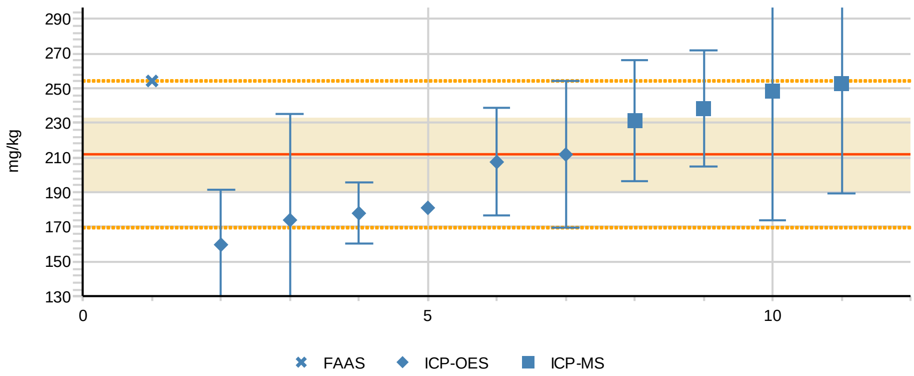
Measurand Pb Sample A1M



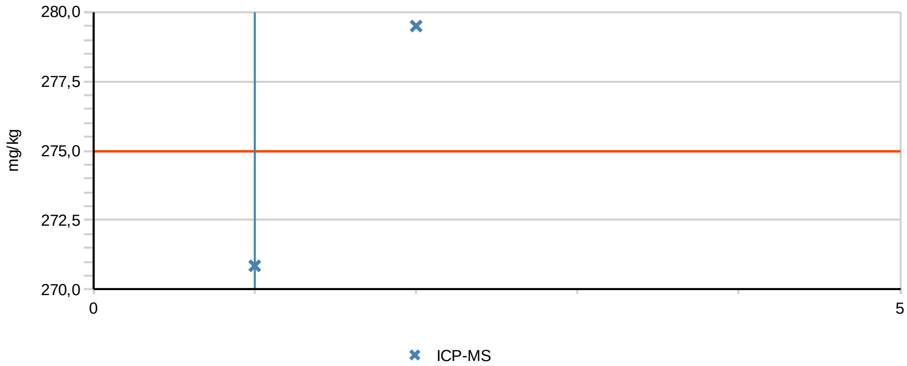
Measurand Pb Sample FN4



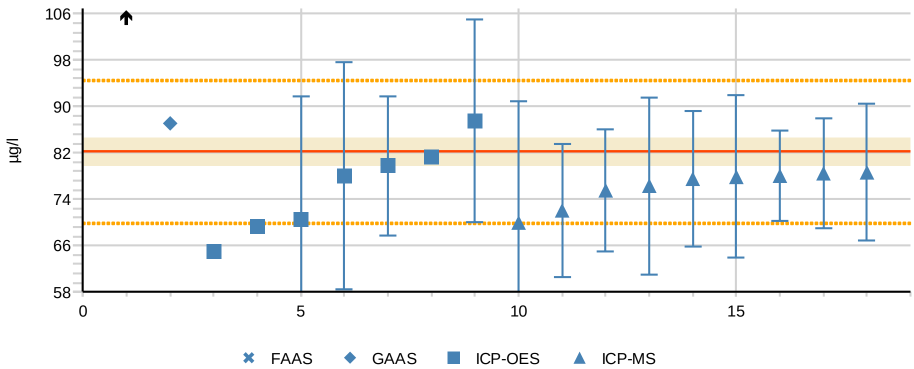
Measurand Pb   Sample FO4

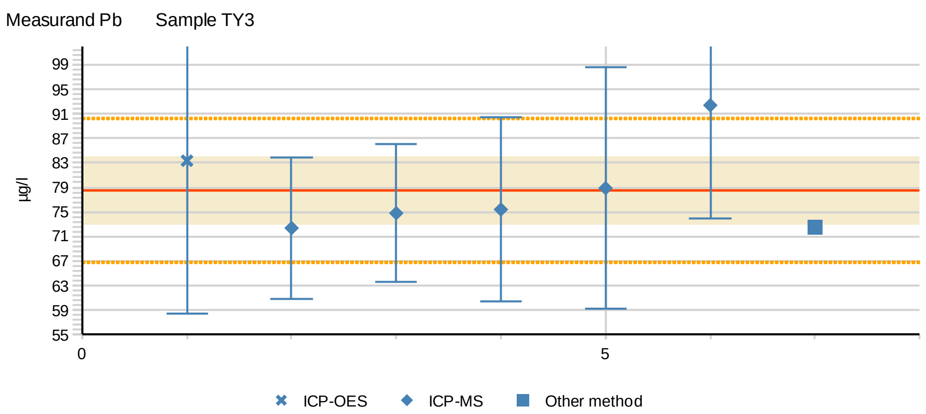


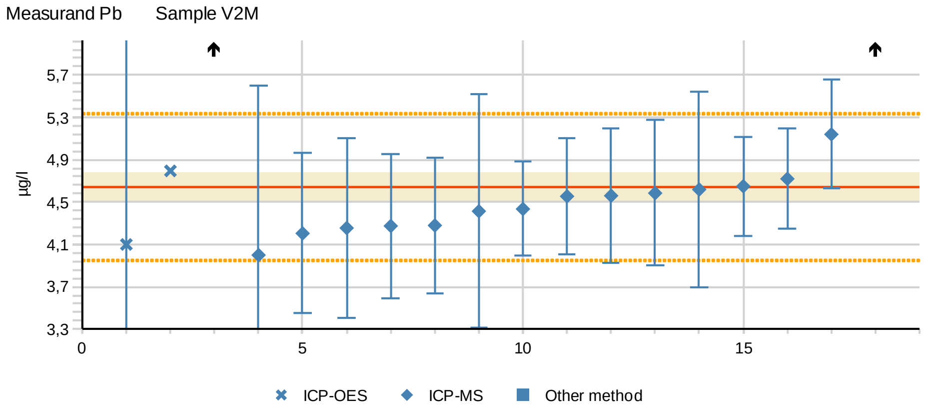
Measurand Pb   Sample FT4

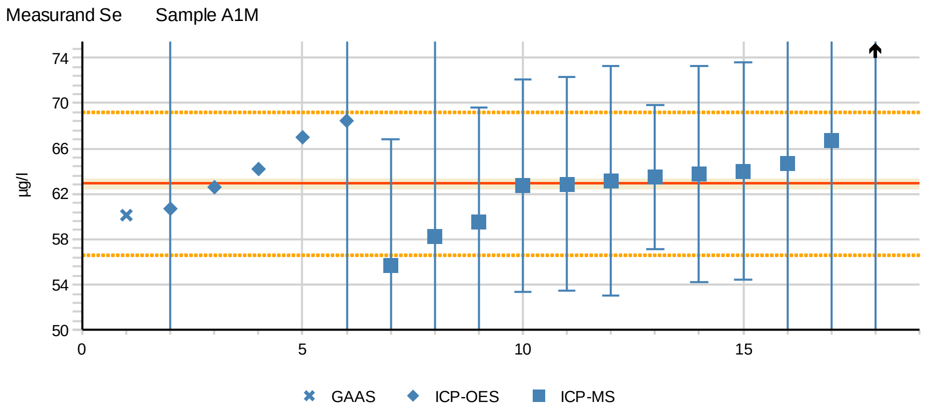


Measurand Pb   Sample TN3

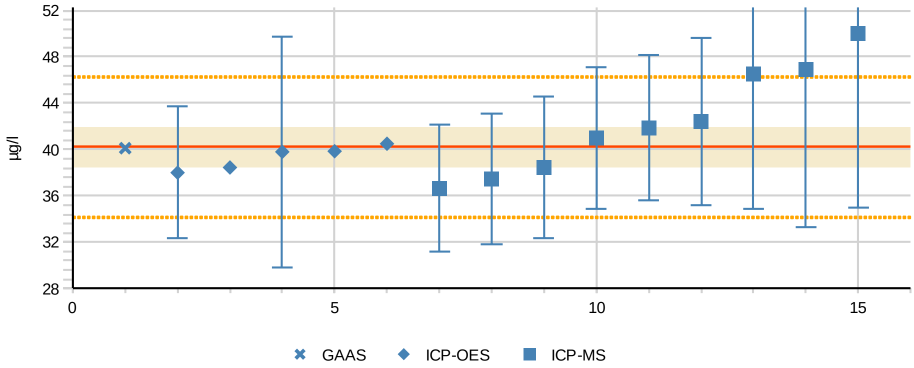



Measurand Pb
Sample TY3
µg/l
99
95
91
87
83
79
75
71
67
63
59
55
0
5
ICP-OES
ICP-MS
Other method

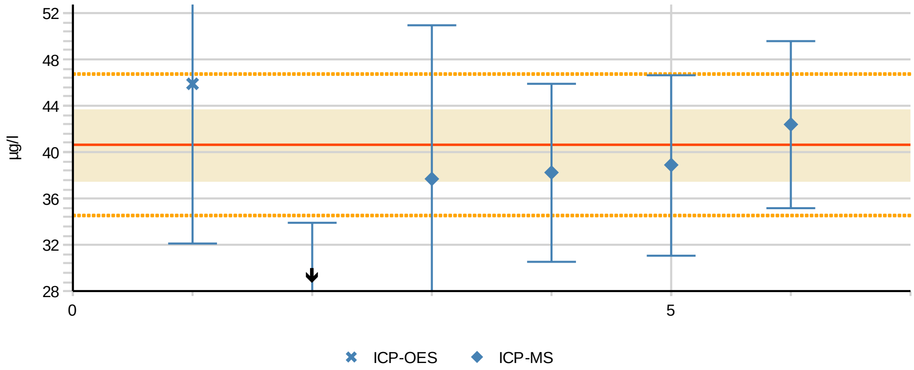

Measurand Pb
Sample V2M
µg/l
5,7
5,3
4,9
4,5
4,1
3,7
3,3
0
5
10
15
ICP-OES
ICP-MS
Other method


Measurand Se
Sample A1M
µg/l
74
70
66
62
58
54
50
0
5
10
15
GAAS
ICP-OES
ICP-MS

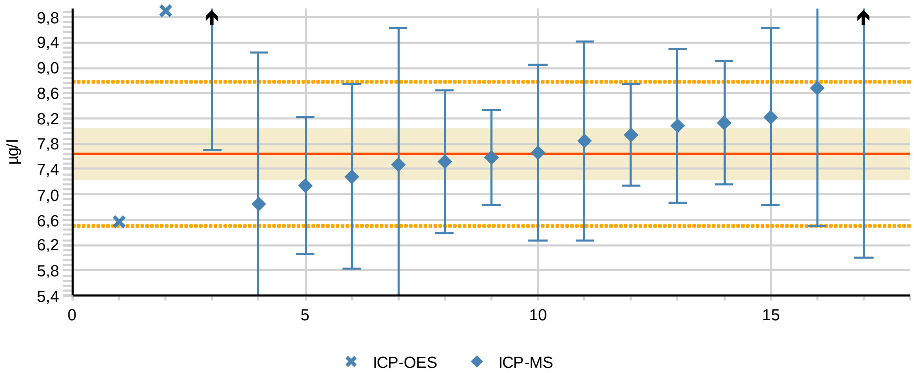
Measurand Se Sample TN3

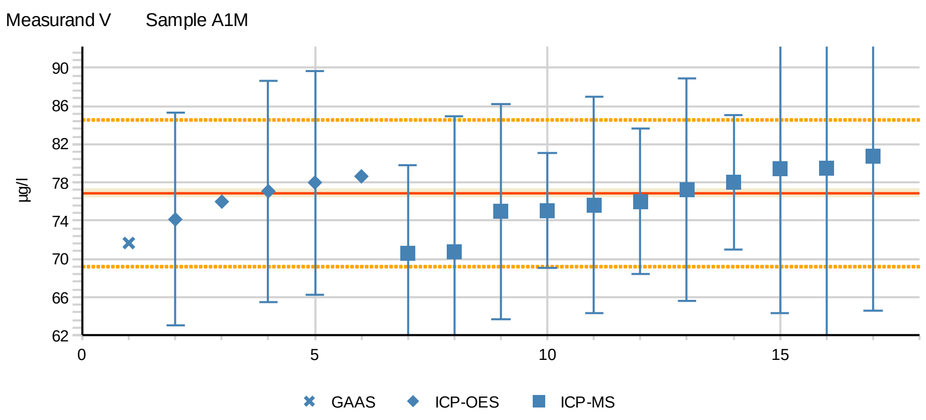


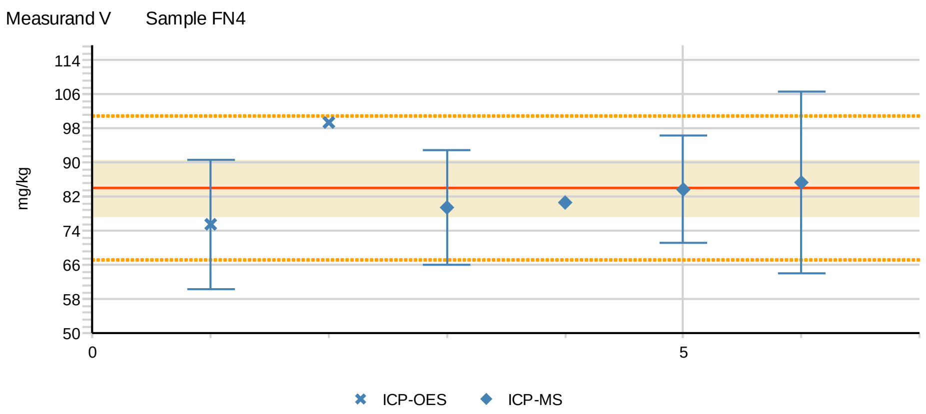
Measurand Se Sample TY3

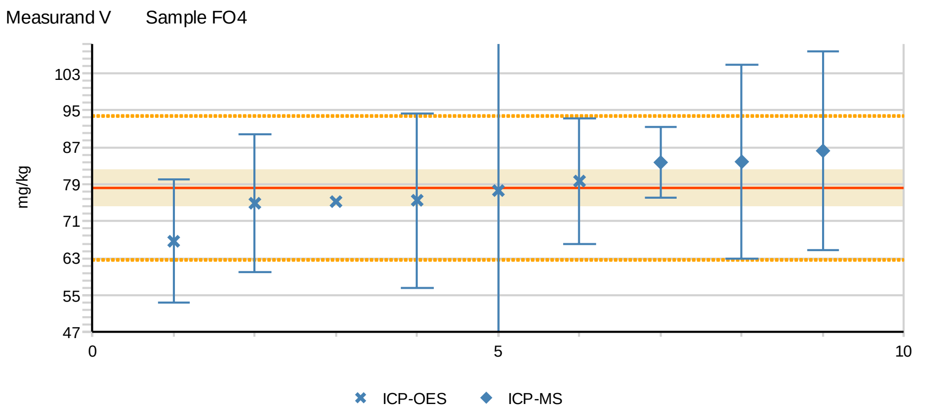


Measurand Se Sample V2M

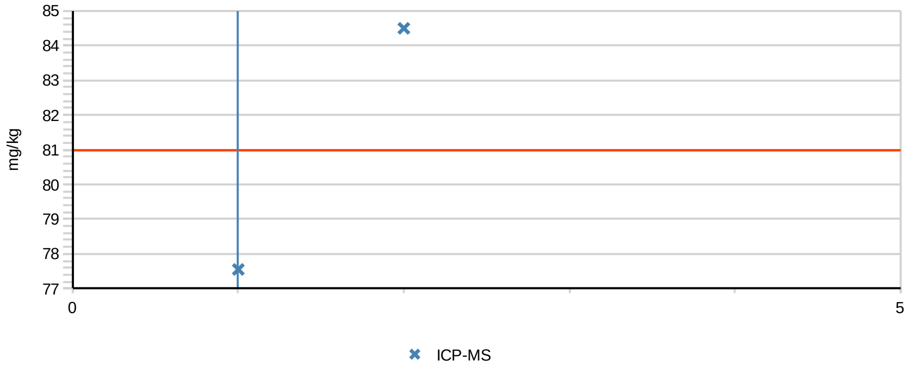



Measurand V
Sample A1M
µg/l
90
86
82
78
74
70
66
62
0
5
10
15
GAAS
ICP-OES
ICP-MS

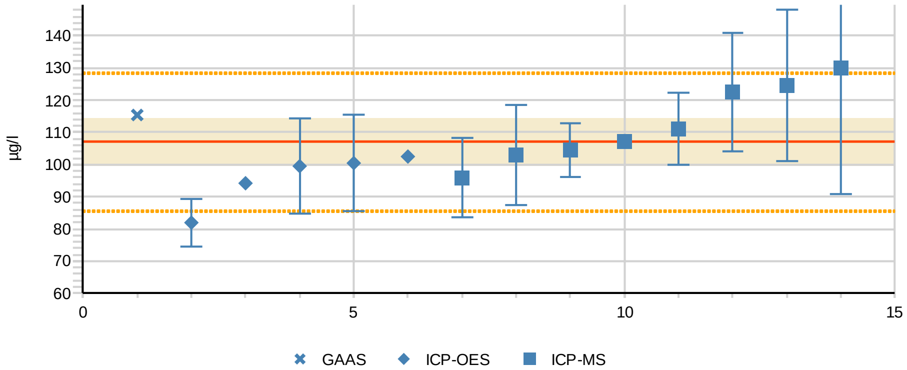

Measurand V
Sample FN4
mg/kg
114
106
98
90
82
74
66
58
50
0
5
ICP-OES
ICP-MS


Measurand V
Sample FO4
mg/kg
103
95
87
79
71
63
55
47
0
5
10
ICP-OES
ICP-MS

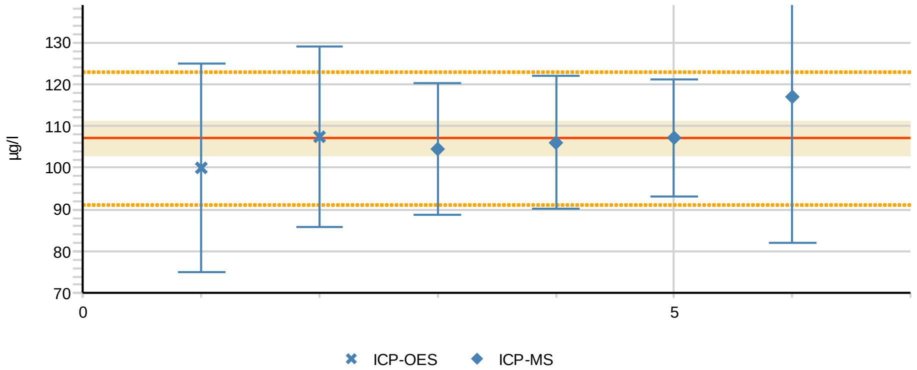
Measurand V Sample FT4

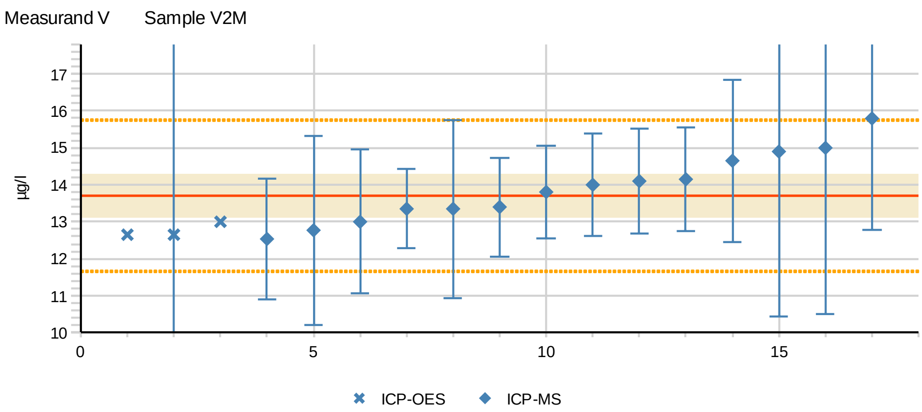


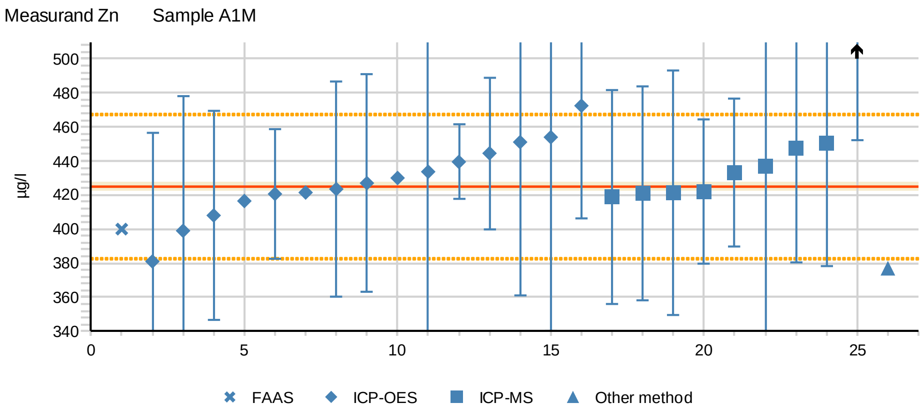
Measurand V Sample TN3

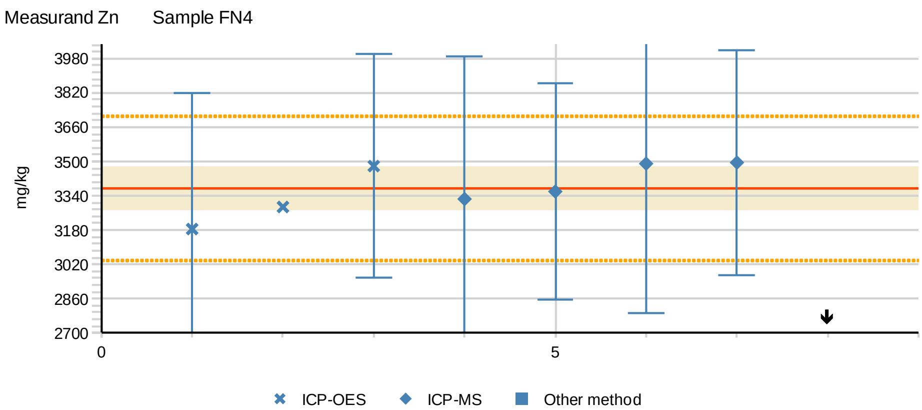


Measurand V Sample TY3

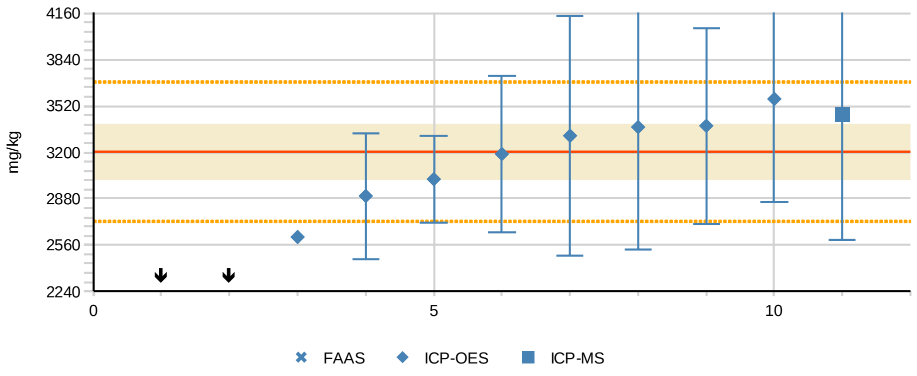



Measurand V
Sample V2M
µg/l
17
16
15
14
13
12
11
10
0
5
10
15
ICP-OES
ICP-MS

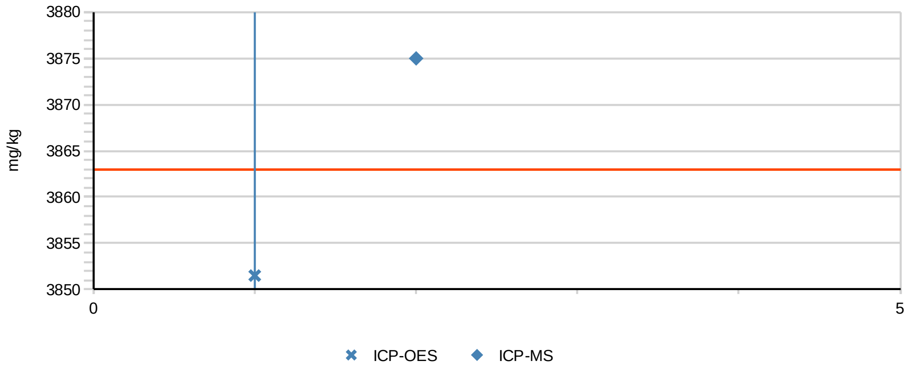

Measurand Zn
Sample A1M
µg/l
500
480
460
440
420
400
380
360
340
0
5
10
15
20
25
FAAS
ICP-OES
ICP-MS
Other method


Measurand Zn
Sample FN4
mg/kg
3980
3820
3660
3500
3340
3180
3020
2860
2700
0
5
ICP-OES
ICP-MS
Other method

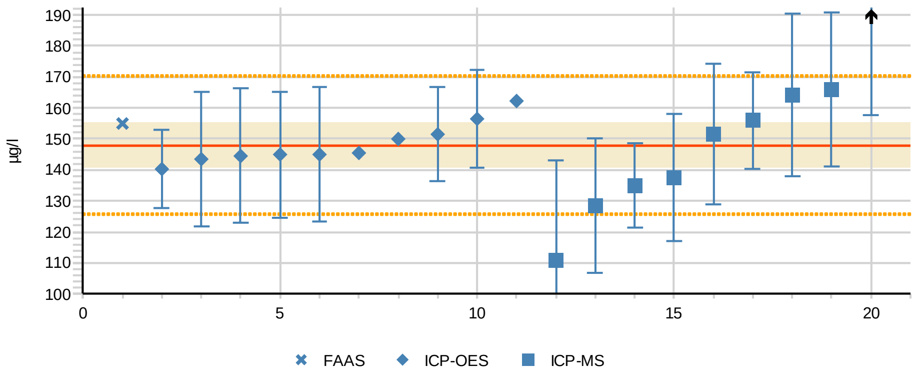
Measurand Zn Sample FO4



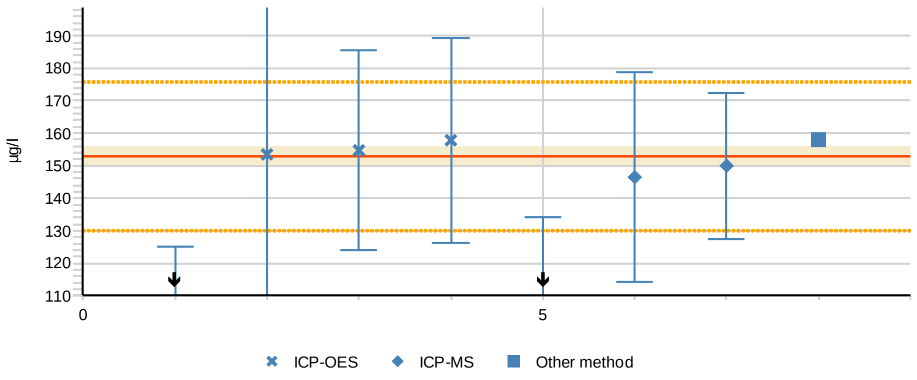
Measurand Zn Sample FT4



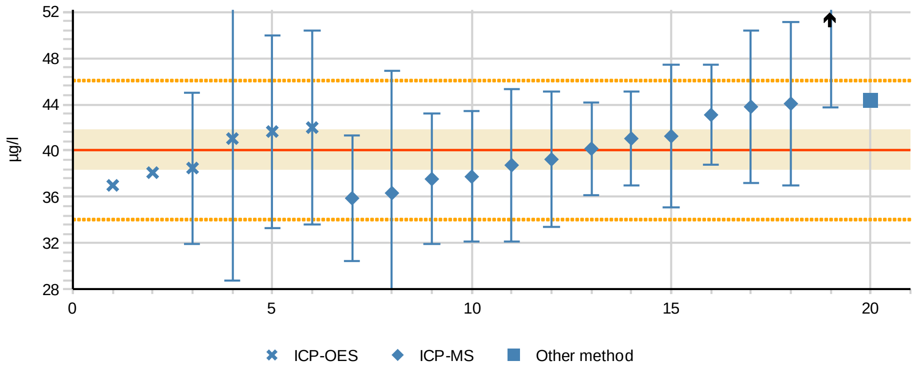
Measurand Zn Sample TN3



Measurand Zn Sample TY3



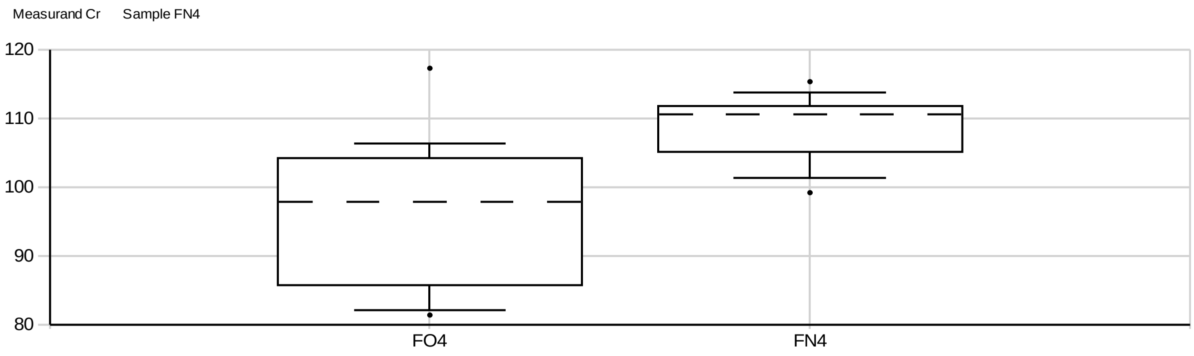
Measurand Zn Sample V2M



APPENDIX 12: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

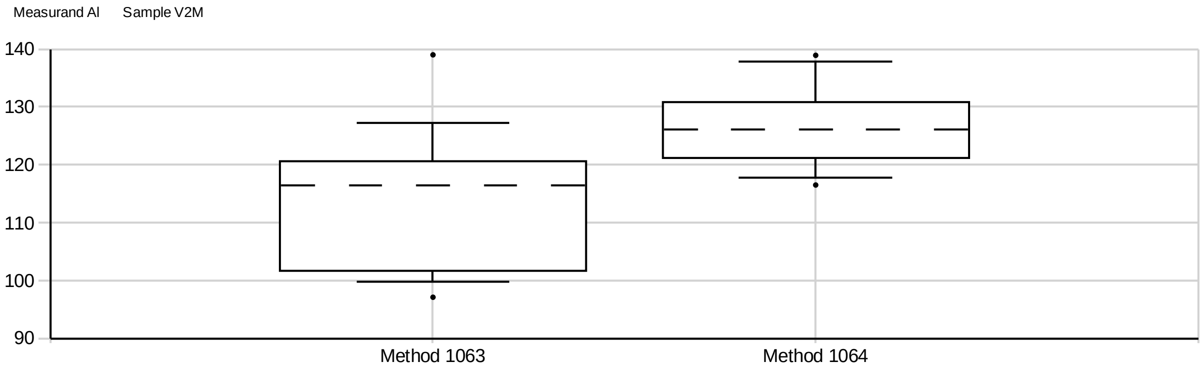
Statistically significant differences between different acid digestions (fly ash)



Method	n	Mean (mg/kg)	SD (mg/kg)
FN4: digestion with HNO_3	6	108	6
FO4: digestion with HNO_3+HCl	10	96	12
FT4: digestion with HNO_3+HF	2	139	24

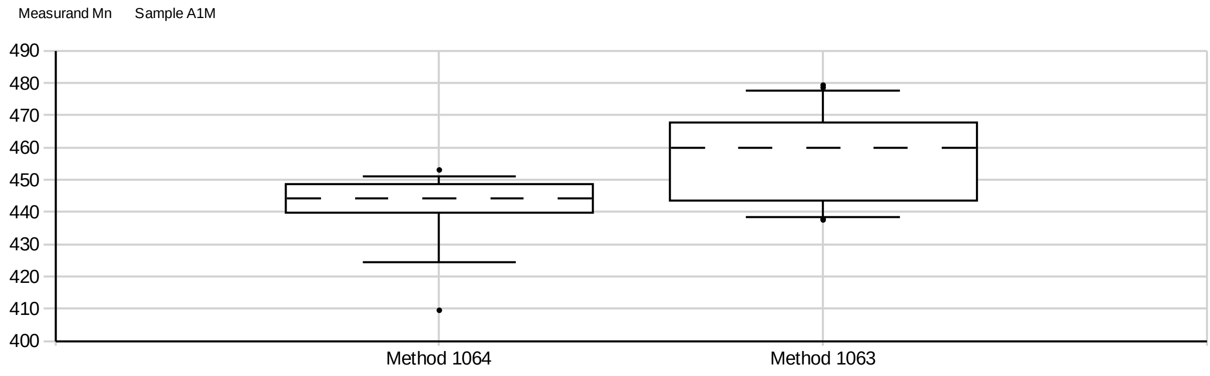
n = number of results; SD = standard deviation

Statistically significant differences between analytical methods



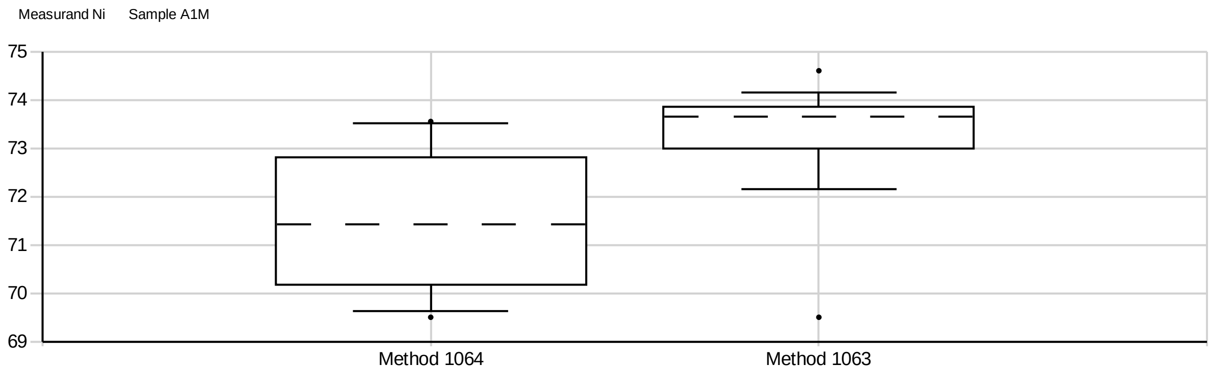
Method	n	Mean (µg/l)	SD (µg/l)
Method 1063: ICP-OES	8	114	14
Method 1064: ICP-MS	9	127	8.2

n = number of results; SD = standard deviation



Method	n	Mean (µg/l)	SD (µg/l)
Method 1063: ICP-OES	14	458	15
Method 1064: ICP-MS	6	440	16

n = number of results; SD = standard deviation

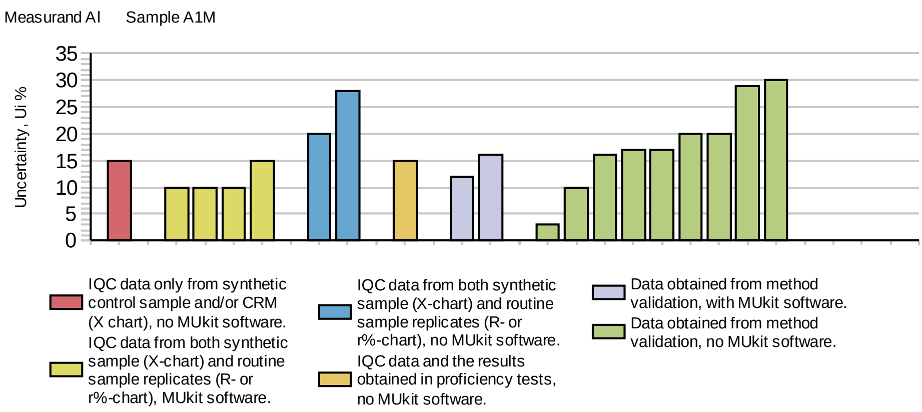


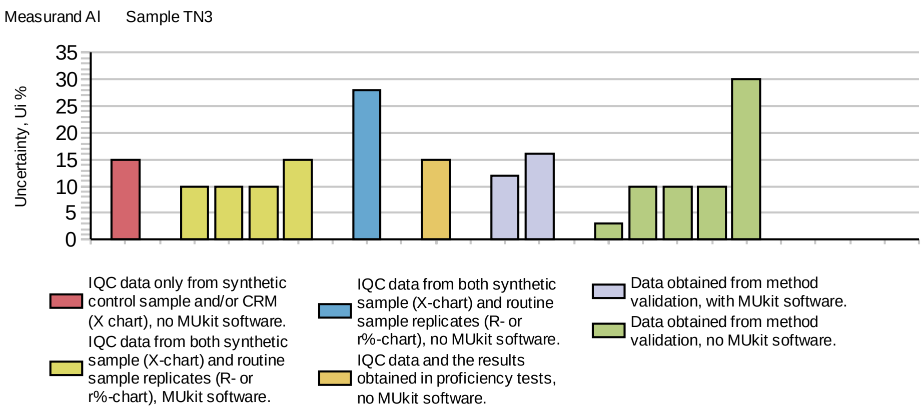
Method	n	Mean (µg/l)	SD (µg/l)
Method 1063: ICP-OES	9	73.1	1.5
Method 1064: ICP-MS	10	71.5	1.5

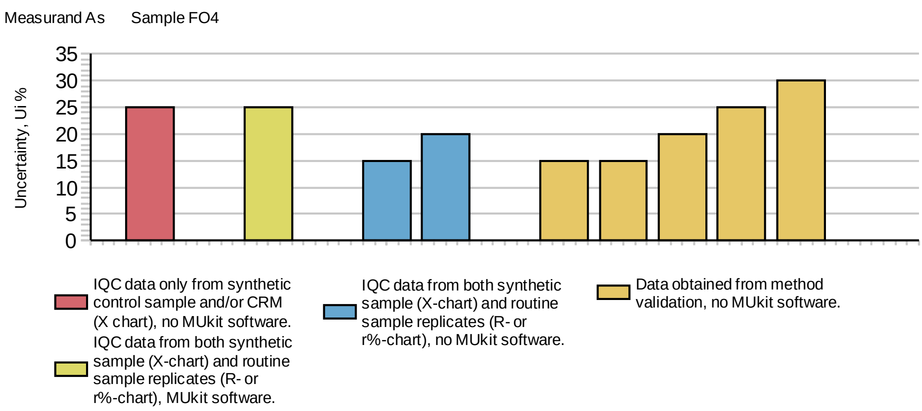
n = number of results; SD = standard deviation

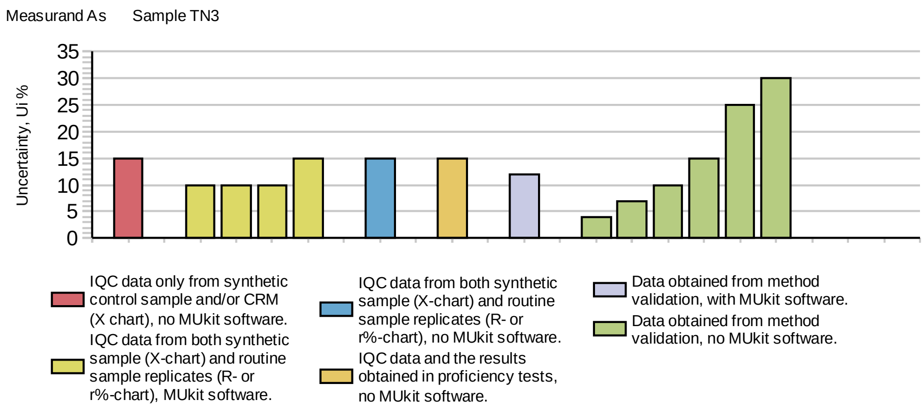
APPENDIX 13: Estimation of the measurement uncertainties reported by the participants

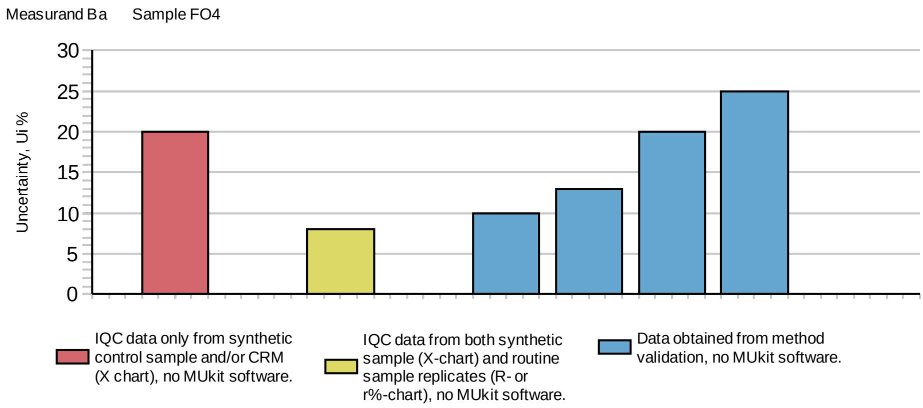
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [8, 9] or using a modelling approach based [10, 11].

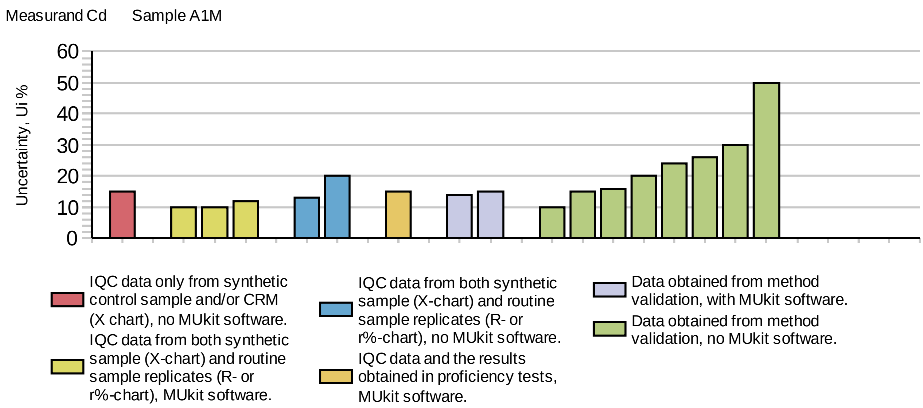




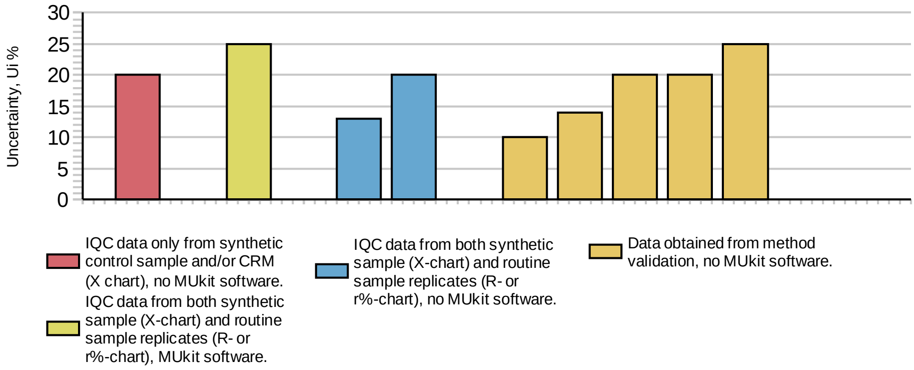



Measurand As
Sample TN3
35
30
25
20
15
10
5
0
Uncertainty, Ui %
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

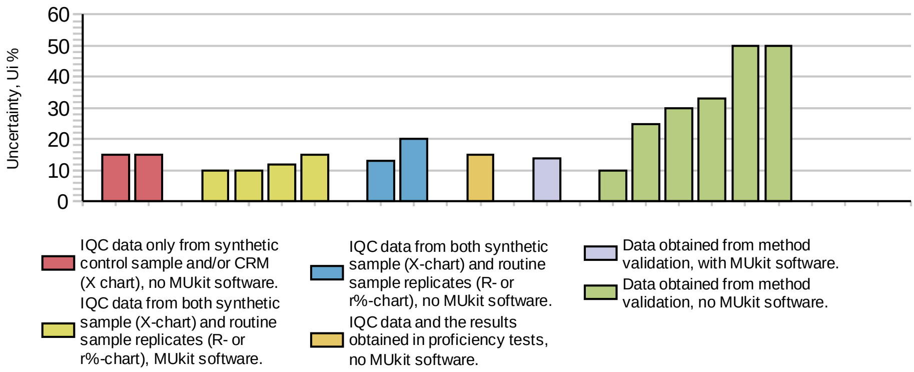

Measurand Ba
Sample FO4
30
25
20
15
10
5
0
Uncertainty, Ui %
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Cd
Sample A1M
60
50
40
30
20
10
0
Uncertainty, Ui %
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

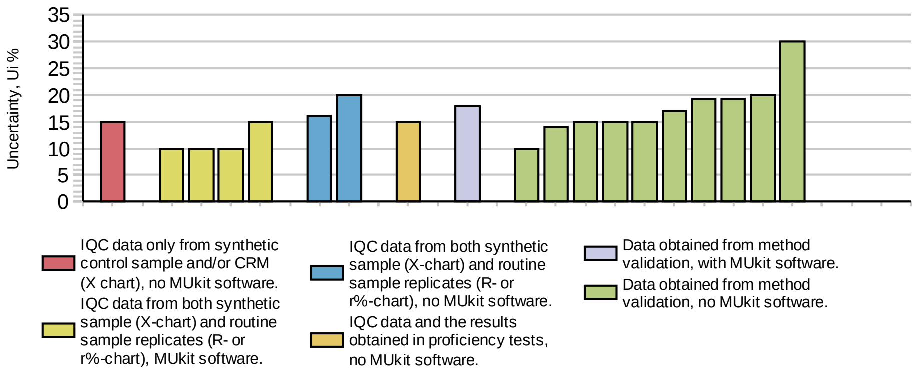
Measurand Cd Sample FO4



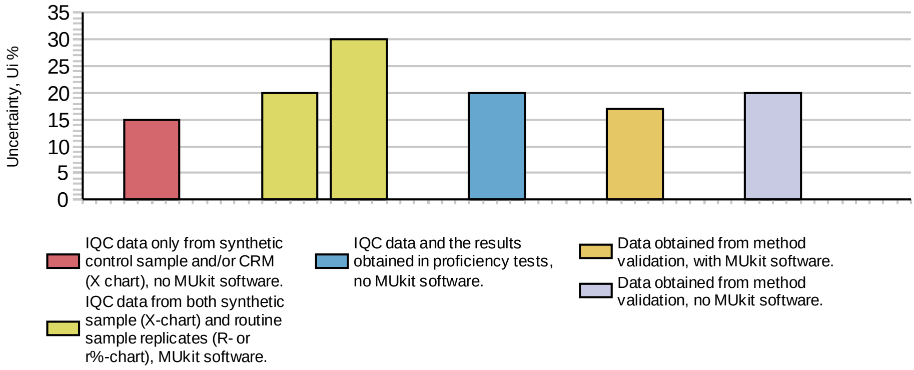
Measurand Cd Sample V2M



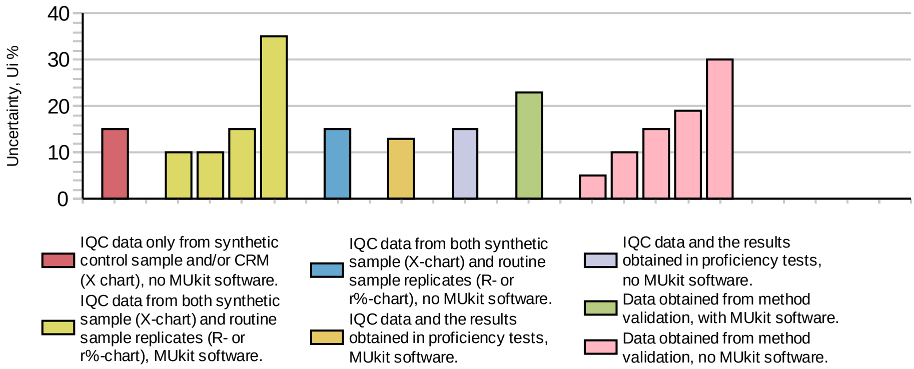
Measurand Co Sample A1M



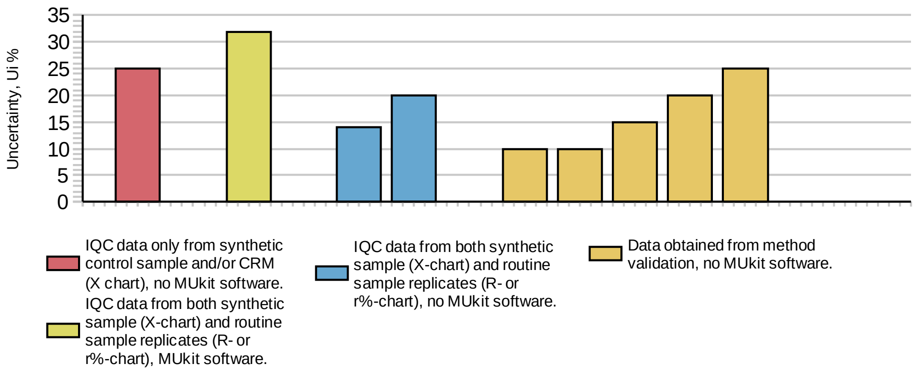
Measurand Cr Sample FN4

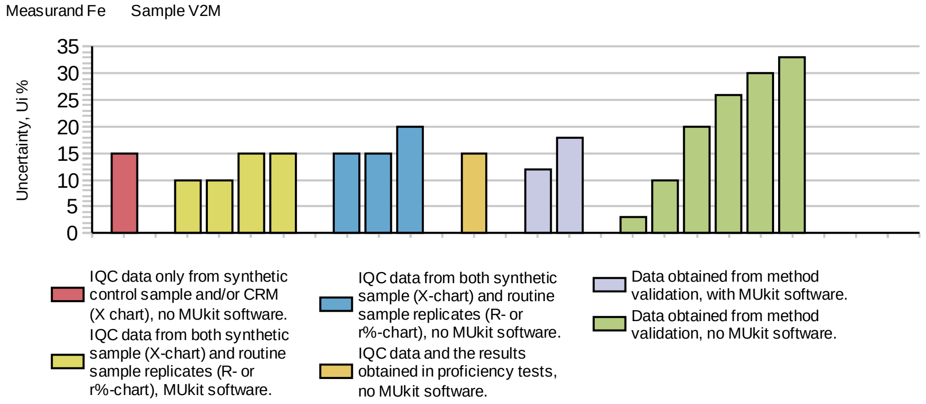


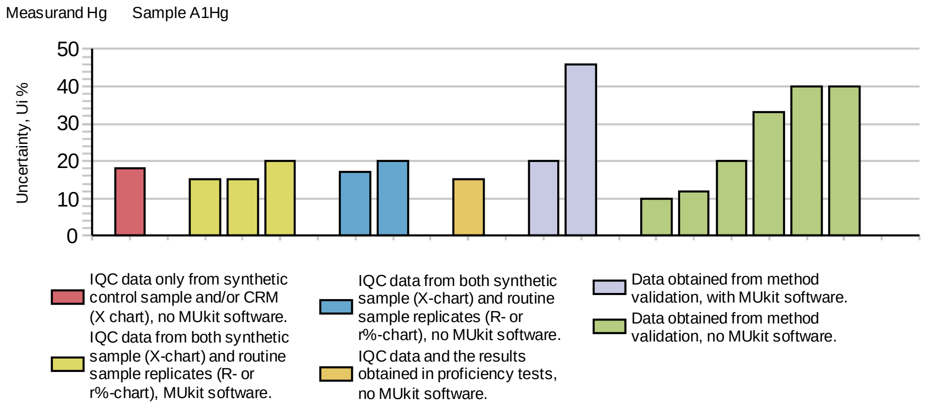
Measurand Cr Sample TN3

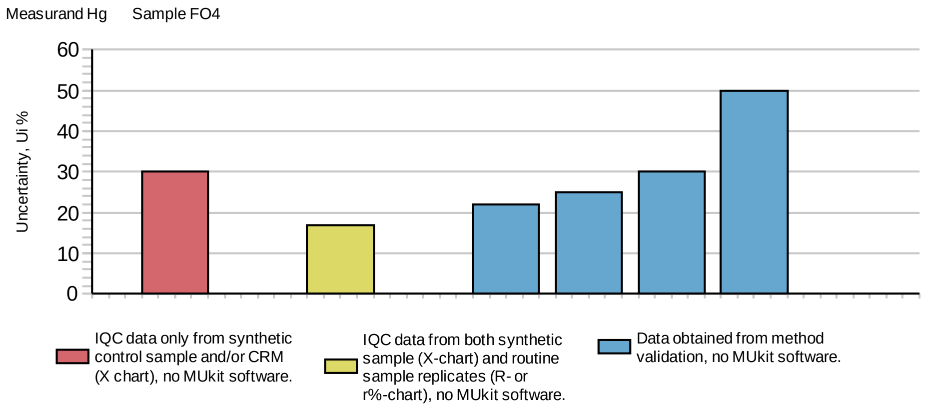


Measurand Cu Sample FO4

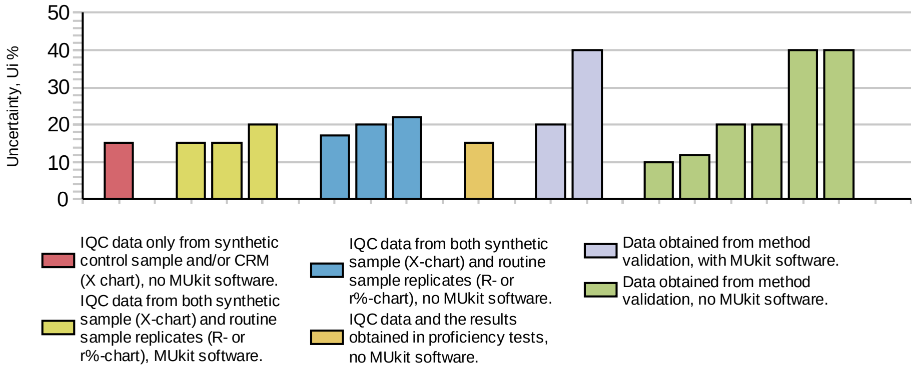



Measurand Fe
Sample V2M
Uncertainty, Ui %
0
5
10
15
20
25
30
35
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

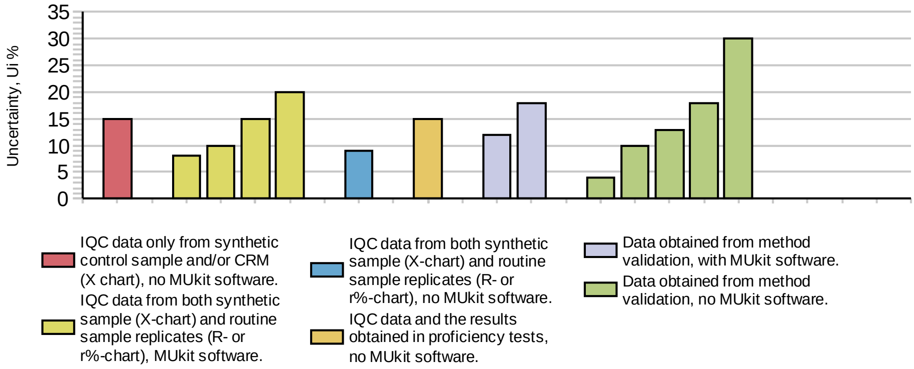

Measurand Hg
Sample A1Hg
Uncertainty, Ui %
0
10
20
30
40
50
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Hg
Sample FO4
Uncertainty, Ui %
0
10
20
30
40
50
60
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, no MUkit software.

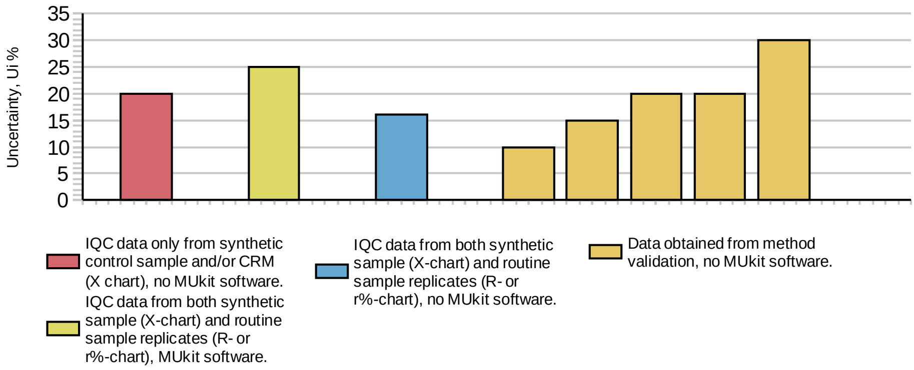
Measurand Hg   Sample T3Hg



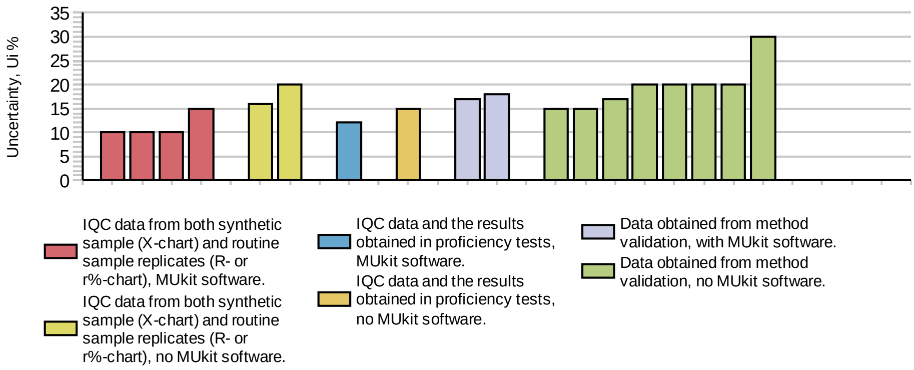
Measurand Mn   Sample TN3



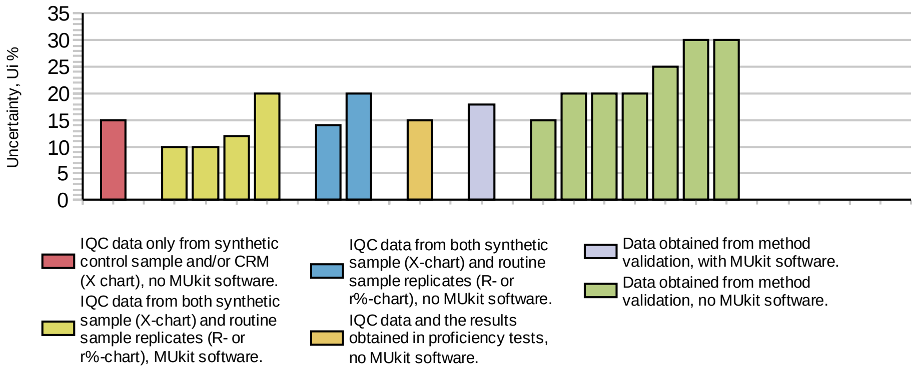
Measurand Mo   Sample FO4



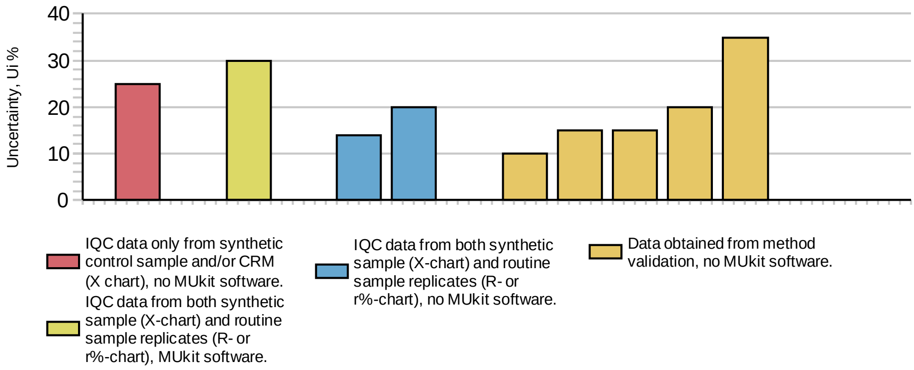
Measurand Ni Sample A1M



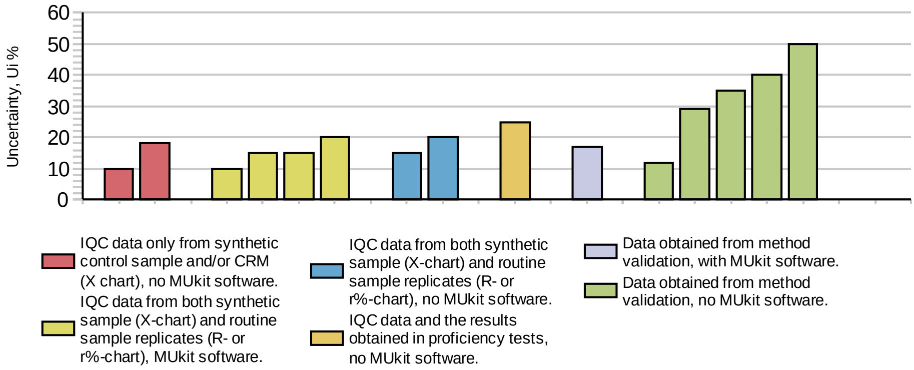
Measurand Pb Sample A1M



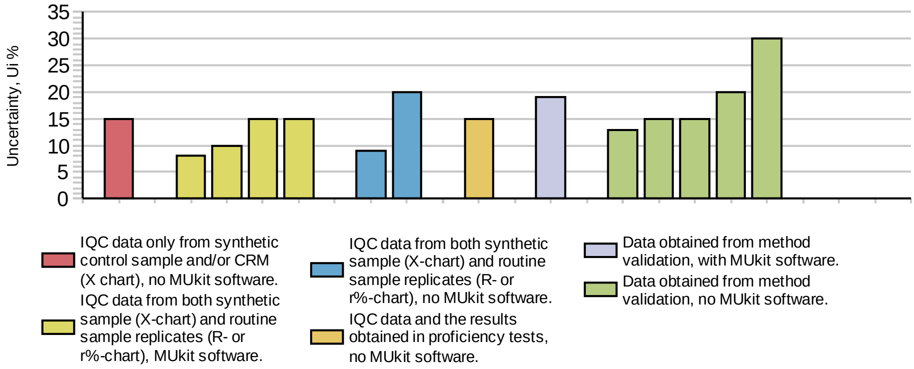
Measurand Pb Sample FO4



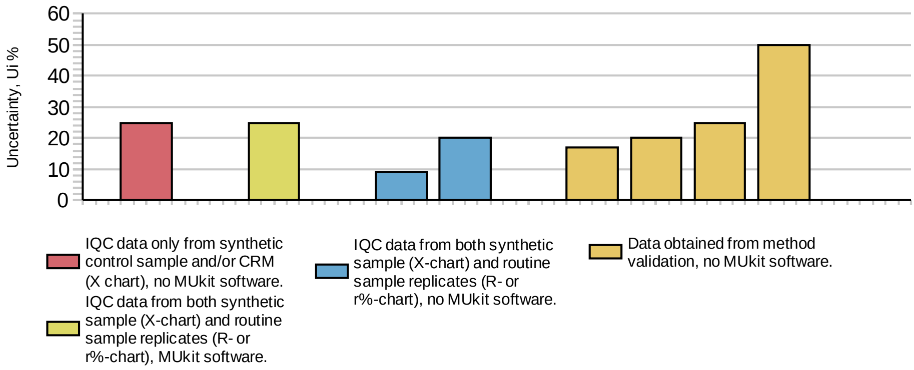
Measurand Se Sample V2M

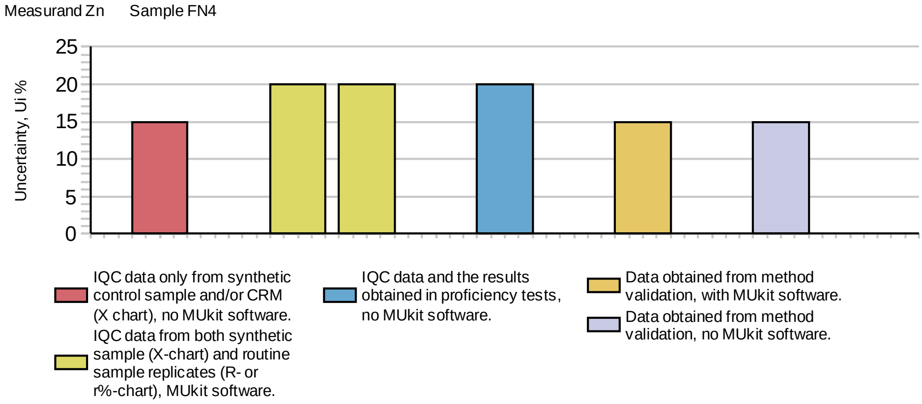


Measurand V Sample A1M



Measurand V Sample FO4




Measurand Zn
Sample FN4
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
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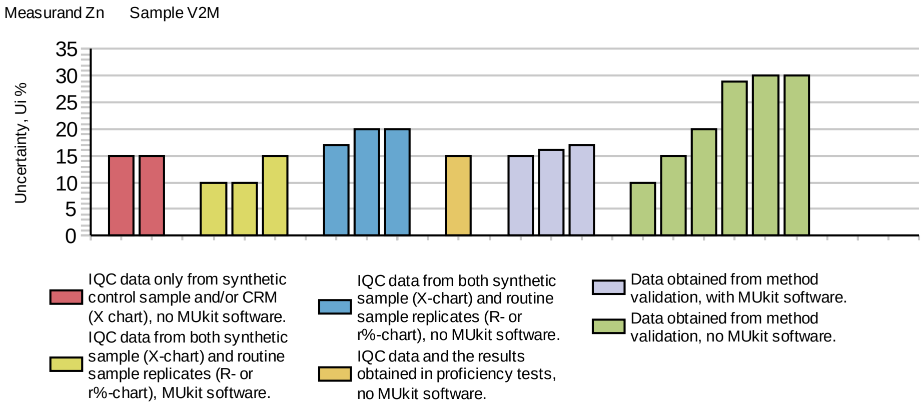
Measurand Zn
Sample V2M
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
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PROFICIENCY TEST SYKE 10/2016

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-4667-1 (PDF)
ISSN 1796-1726 (online)