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Proftest SYKE

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ABSTRACT

Interlaboratory Proficiency Test 10/2018

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in waters and compost material in October-November 2018. The measurands for the synthetic and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V, and Zn. For the compost sample the measurands were: As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V, and Zn. In total 21 laboratories participated in the PT.

In total, 90 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted. From the results evaluated with E_n scores, 72 % were satisfactory. Basically, either the metrologically traceable concentration, calculated concentration, the robust mean, the mean or the median of the results reported by the participants was used as the assigned value for measurands.
Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, compost, metals, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, Sb, Se, Sn, Sr, S_{tot}, V, Zn, water and environmental laboratories, proficiency test, interlaboratory comparison

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 10/2018

Proftest SYKE järjesti loka-marraskuussa 2018 pätevyyskokeen laboratorioille, jotka määrittävät metalleja ja elohopeaa viemärilaitos- ja teollisuusjätevesistä sekä lannoitteena käytettävästä kompostimateriaalista (MET 10/2018). Pätevyyskokeessa määritettiin synteettisestä sekä jätevesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V ja Zn. Kompostinäytteestä määritettiin testisuureet As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V ja Zn. Pätevyyskokeeseen osallistui yhteensä 21 laboratoriota.

Koko aineistossa hyväksyttäviä z-arvolla arvioituja tuloksia oli 90 %, kun tulosten sallittiin poiketa vertailuarvosta 10–25 %. Tuloksista, jotka arvioitiin E_n-arvolla, hyväksyttyjä oli 72 %. Testisuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta, osallistujien ilmoittamien tulosten robustia keskiarvoa, keskiarvoa tai mediaania.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, komposti, metallit, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, Sb, Se, Sn, Sr, S_{tot}, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 10/2018

Proftest SYKE genomförde en provningsjämförelse i oktober-november 2018, som omfattade bestämningen av Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V och Zn i syntetiska provet och avloppsvatten. Från kompost provet bestämdes As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V och Zn . Tillsammans 21 laboratorier deltog i jämförelsen.

I jämförelsen 90 % av resultaten som värderas med hjälp z värdet var acceptabla, när total deviation på10–25 % från referensvärdet tillåten. Resultaten som värderades med hjälp E_n värdet var 72 % acceptabla. Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet eller robust medelvärdet, medelvärdet eller median av deltagarnas resultat.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, kompost, metaller, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, Sb, Se, Sn, Sr, S_{tot}, V, Zn, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out a proficiency test (PT) for analysis of metals and mercury in waste waters and compost material to be used as fertilizer in October - November 2018 (MET 10/2018). 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. In this PT it was also possible to test metals and nutrients from the composted sludge material to be used as fertilizer based on the national decree of the Ministry of Agriculture and Forestry 24/11 [1].

The measurands for the synthetic and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V, and Zn. For the compost sample the measurands were: As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V, and Zn.

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 standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4, FI-00430 Helsinki, Finland
Phone: +358 295 251 000, email: proftest@environment.fi

The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

Cooperation partner	Finnish Food Safety Authority, Aija Pelkonen, compost sample
Analytical experts	Timo Sara-Aho (SYKE): metals, ID-ICP-MS Teemu Näykki (SYKE): Hg, ID-ICP-MS Compost sample: Aija Pelkonen, firstname.lastname@foodauthority.fi
Subcontracting	Homogenization and dividing of the compost into subsamples: KVVY Tutkimus Oy, accredited by FINAS (T064, www.finas.fi/sites/en) Analytical services for the compost sample: Finnish Food Safety Authority, Research and Analytical Department accredited by FINAS (T014, www.finas.fi/sites/en)

2.2 Participants

In total 21 laboratories participated in this proficiency test (Appendix 1), 19 participants from Finland and two from other European countries. One participant reported two sets of results. Altogether 64 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the sample testing laboratories have the codes 12 and 23 (SYKE, Helsinki, T003, www.finas.fi/sites/en) and 6 (Finnish Food Safety Authority, Research and Analytical Department, T014, www.finas.fi/sites/en, compost 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 compost 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).

The tested compost sample K4M (after analysis: KN4 – digestion with HNO_3 / KO4 – digestion with HNO_3 + HCl / KX4 – other digestion) was composted sludge collected from the sewage

treatment plant in Southern Finland. The composted sludge was freeze-dried and sieved to particle size of 0.25 mm. The sample was homogenized and divided into sub-samples using a vibrating feeder distributor at the laboratory of KVVY Tutkimus Oy in Tampere.

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 8 October 2018 to the participants abroad and on 9 October 2018 to the national participants. The samples arrived to the participants mainly on 10 October 2018. The samples were requested to be measured as follows:

Mercury in water samples	latest on 19 October 2018
The other measurands and samples	latest on 2 November 2018

The results were requested to be reported latest on 2 November 2018. The participants delivered the results mainly accordingly, two participants reported their results on 5 November 2018. The preliminary results were delivered to the participants via email on 14 November 2018.

2.4 Homogeneity and stability studies

The homogeneity of the water samples was tested by analyzing Cd, Cr, Cu, Hg, Pb, Se, and Zn. More detailed information of homogeneity study is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials, and thus known to be homogenous. However, homogeneity of these was checked by parallel measurements of two 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 of the compost sample was studied by analyzing Cu, Mn, Pb, P_{tot}, and Zn in the laboratory of the Finnish Food Safety Authority (T014, www.finas.fi/sites/en). The difference of the results from the homogeneity study and the result of the organizing laboratory (SYKE and KVVY) during the test were compared to the criterion $0.3 \times s_{pt}$ taking into account the total measurement uncertainties (data not shown). The criterion was fulfilled in each case, thus the compost sample was considered 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 their result reporting errors. The comment from the provider is about the zero results. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean were rejected before the statistical results handling. If the result was reported as below detection limit, it was not 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 A1M, TN3, V2M, A1Hg, T3Hg and V2Hg. The assigned value based on the ID-ICP-MS method is the mean of the homogeneity results and the test result (9-12 results). 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/sites/en). For the other samples and measurands either the robust mean or, when the number of reported results was low (n(stat)<12), the mean or the median of the results reported by the participants was used as the assigned value (Appendix 5). If only one result was reported to the sample, the assigned value is not set (Hg, P_{tot}: KX4).

The robust mean, the mean and the median are not metrologically traceable assigned values. As it was not possible to have metrologically traceable assigned values for all measurands, in those cases the robust mean, the mean or the median of the results was the best available value to be used as the assigned value. The reliability of the assigned value was statistically tested [3, 4].

The expanded uncertainty for the calculated assigned values ($k=2$) 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.

When the robust mean, the mean or the median was used as the assigned value, the uncertainty was calculated using the robust standard deviation or standard deviation, respectively [3, 5]. For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method.

The expanded uncertainty of the calculated and metrologically traceable assigned values for metals in the synthetic samples varied between 0.4 and 3 %. When using the robust mean, the mean or the median of the participant results as the assigned value, the expanded uncertainties of the assigned values were between 1.3 and 29 % (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 standard deviation for proficiency assessment was estimated on the basis of the uncertainty of the assigned value, the concentration of the measurand, the results of homogeneity and stability tests, and the long-term variation in the former proficiency tests. If the number of reported results was low (Hg: KC4, P_{tot}, N_{tot}: KN4) the standard deviation for proficiency assessment was not set, and the proficiency estimation was not given. The standard deviation for the proficiency assessment ($2\times s_{pt}$, at the 95 % confidence level) was set to 10–25 % depending on the measurement.

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*', Appendix 8). 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 [5]:

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

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, the mean or the median 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 [4]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability 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 (s_{rob}) or standard deviation (s) of the reported results [3]. The criterion s_{rob} (or s) / $s_{pt} < 1.2$ 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	Measurand
TN3	Cd[1], Cu[1,2]
TY3	As[1], Cr[1], Ni[1,2], Zn[1]
KO4	Cd[1], Cr[1], Ni[1], V[1,2]

3 Results and conclusions

3.1 Results

The terms used in the result tables are show 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 and E_n scores is shown in Appendix 8 and z scores in the ascending order in Appendix 9. The reported results grouped by the used analytical methods with their expanded uncertainties (k=2) are presented in Appendix 10.

The robust standard deviations of the results varied from 2.8 % to 34.7 % and the standard deviations varied from 1.3 % to 43.4 % (Table 1). The robust standard deviation or the standard deviation of results was lower than 10 % for 81 % and for 40 % of the results, respectively. For the waste water samples the robust standard deviations of the results varied from 2.8 % to 19.7 % and for the compost sample the variation was from 4.8 % to 34.7 % (Table 1). The robust standard deviations for waste water samples were approximately in the same range as in the previous similar proficiency test, where the deviations varied from 3.1 % to 15.5 % [6].

Table 1. The summary of the results in the proficiency test MET 10/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} %/ s %	2 x s_{pt} %	n (all)	Acc z %
Al	A1M	µg/l	850	873	859	869	46	5.3	10	18	89
	TN3	µg/l	975	964	975	979	59	6.0	15	14	86
	TY3	µg/l	1018	1020	-	1018	*36*	*3.5*	-	7	-
	V2M	µg/l	261	264	261	260	22	8.3	20	15	80
As	A1M	µg/l	35.0	34.7	34.7	35.0	1.6	4.8	10	16	100
	KN4	mg/kg	7.36	7.07	-	7.36	*1.00*	*13.6*	-	5	-
	KO4	mg/kg	7.83	7.83	7.80	7.83	1.01	13.0	25	8	100
	TN3	µg/l	100	101	100	101	6	5.7	15	12	100
	TY3	µg/l	106	106	-	106	*11*	*10.6*	20	8	75
	V2M	µg/l	10.7	10.7	10.7	10.6	0.9	8.2	20	14	85
B	A1M	µg/l	52.0	51.3	51.2	51.9	6.8	13.4	10	13	69
	TN3	µg/l	246	246	243	246	19	7.9	20	9	89
	TY3	µg/l	280	275	-	280	*38*	*13.7*	-	7	-
	V2M	µg/l	71.3	71.3	71.3	70.4	7.9	11.1	20	12	92
Ba	A1M	µg/l	77.0	77.7	77.5	78.0	4.5	5.8	10	12	83
	TN3	µg/l	33.1	33.0	33.0	33.1	2.0	5.9	15	8	100
	TY3	µg/l	33.9	34.7	-	33.9	*2.7*	*8.0*	-	7	-
	V2M	µg/l	6.74	6.74	6.74	6.69	0.35	5.3	15	12	91
Ca	A1M	mg/l	2.20	2.23	2.27	2.23	0.14	6.0	10	16	75
	KN4	g/kg	32.8	32.8	32.8	32.3	2.1	6.3	15	7	100
	KO4	g/kg	33.7	33.7	33.5	33.2	2.3	6.8	15	10	100
	TN3	mg/l	68.3	68.3	68.1	68.3	2.8	4.1	10	11	91
	TY3	mg/l	70.4	71.0	-	70.4	*7.1*	*10.1*	-	7	-
	V2M	mg/l	32.9	32.6	32.5	32.9	1.5	4.5	10	15	87
Cd	A1M	µg/l	8.50	8.67	8.68	8.63	0.56	6.4	15	16	100
	KN4	mg/kg	0.89	1.10	-	0.89	*0.36*	*40.6*	-	5	-
	KO4	mg/kg	0.85	0.88	0.87	0.85	0.11	12.1	25	8	75
	TN3	µg/l	15.0	15.0	15.0	15.0	1.2	8.3	15	12	100
	TY3	µg/l	15.5	15.5	-	15.0	*1.3*	*8.2*	20	8	75
	V2M	µg/l	2.10	2.09	2.10	2.10	0.14	6.7	15	14	86
Co	A1M	µg/l	55.5	56.4	56.4	56.0	3.1	5.5	10	15	100
	TN3	µg/l	30.3	30.3	30.3	30.5	2.6	8.7	15	11	100
	TY3	µg/l	30.6	32.2	-	30.6	*3.7*	*12.1*	-	8	-
	V2M	µg/l	10.5	10.5	10.5	10.5	0.8	7.4	20	13	92
Cr	A1M	µg/l	85.5	85.7	85.8	85.7	3.9	4.5	10	18	94
	KN4	mg/kg	31.4	33.1	-	31.4	*3.1*	*9.7*	-	5	-
	KO4	mg/kg	35.5	35.0	34.8	35.5	5.0	14.5	25	9	89
	TN3	µg/l	77.1	76.9	77.1	77.9	4.0	5.2	15	13	100
	TY3	µg/l	83.6	83.6	83.6	80.7	10.4	12.4	20	9	78
	V2M	µg/l	10.5	10.5	10.5	10.2	0.7	6.8	15	14	93
Cu	A1M	µg/l	68.0	68.1	68.0	67.4	4.4	6.4	10	17	94
	KN4	mg/kg	330	330	330	345	29	8.9	20	7	100
	KO4	mg/kg	329	329	329	330	16	4.8	20	10	100
	TN3	µg/l	12.7	12.7	12.7	12.6	2.1	16.2	25	13	83
	TY3	µg/l	13.0	12.6	12.6	13.0	2.5	19.7	-	9	-
	V2M	µg/l	4.07	4.07	4.07	4.15	0.54	13.2	25	14	83

Table 1. The summary of the results in the proficiency test MET 10/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} %/ s %	2 x s_{pt} %	n (all)	Acc z %
Fe	A1M	µg/l	925	936	936	932	42	4.5	10	20	100
	KN4	g/kg	125	103	103	125	36	34.7	-	7	-
	KO4	g/kg	130	130	130	130	7	5.1	20	9	100
	TN3	µg/l	705	704	705	708	42	6.0	15	15	100
	TY3	µg/l	713	713	726	724	51	7.1	15	9	67
	V2M	µg/l	119	119	119	119	10	8.8	20	16	94
Hg	A1Hg	µg/l	0.45	0.45	0.44	0.44	0.04	9.8	20	15	80
	KC4	mg/kg	0.40	0.40	-	0.40	*0.02*	*4.2*	-	2	-
	KN4	mg/kg	0.39	0.39	-	0.39	*0.04*	*9.3*	-	4	-
	KO4	mg/kg	0.31	0.32	-	0.31	*0.10*	*33.6*	-	6	-
	KX4	mg/kg	-	0.34	-	0.34	-	-	-	1	-
	T3Hg	µg/l	1.82	1.86	1.91	1.88	0.21	11.1	20	15	80
	V2Hg	µg/l	2.84	2.84	2.85	2.83	0.17	6.0	20	13	85
K	KN4	mg/kg	9090	9297	-	9090	*302*	*3.3*	-	7	-
	KO4	mg/kg	9115	9115	9115	9050	567	6.2	15	10	90
Mg	A1M	mg/l	1.20	1.23	1.23	1.22	0.05	3.9	10	16	100
	KN4	mg/kg	4020	3995	-	4020	*220*	*5.5*	15	7	86
	KO4	mg/kg	3985	3985	3985	3980	261	6.6	15	9	100
	TN3	mg/l	22.4	22.4	22.3	22.3	0.9	4.0	10	11	100
	TY3	mg/l	21.4	22.4	-	21.4	*2.3*	*10.6*	-	7	-
	V2M	mg/l	6.80	6.80	6.80	6.83	0.19	2.8	10	15	93
Mn	A1M	µg/l	95.5	96.8	96.5	95.3	4.5	4.6	10	17	94
	KN4	mg/kg	406	406	406	412	31	7.5	20	7	100
	KO4	mg/kg	405	405	407	404	35	8.6	20	10	100
	TN3	µg/l	159	159	159	157	8	5.2	10	13	100
	TY3	µg/l	157	158	-	157	*4.6*	*2.9*	-	8	-
	V2M	µg/l	83.5	83.5	83.5	83.0	3.9	4.7	15	15	93
Mo	A1M	µg/l	73.5	74.1	74.1	73.9	2.3	3.1	10	16	94
	KN4	mg/kg	5.32	5.11	-	5.32	*0.92*	*17.4*	-	6	-
	KO4	mg/kg	5.75	5.75	5.72	5.46	0.65	11.3	25	8	88
	TN3	µg/l	1688	1695	1688	1689	92	5.5	10	12	83
	TY3	µg/l	1733	1766	-	1733	*172*	*9.9*	-	8	-
	V2M	µg/l	16.4	16.4	16.3	16.5	0.7	4.3	15	13	83
Ni	A1M	µg/l	85.5	86.5	86.4	86.2	4.3	5.0	10	18	94
	KN4	mg/kg	30.4	30.4	-	30.4	*3.5*	*11.4*	-	5	-
	KO4	mg/kg	27.1	27.1	27.1	26.7	3.9	14.5	25	7	100
	TN3	µg/l	63.9	63.9	63.9	64.4	4.6	7.1	15	13	92
	TY3	µg/l	64.9	64.9	64.5	62.8	5.6	8.7	15	9	67
	V2M	µg/l	4.35	4.35	4.35	4.33	0.26	5.9	15	12	91
N_{tot}	KN4	mg/kg	24000	24000	-	24000	*1273*	*5.3*	-	2	-
	KX4	mg/kg	23350	22936	-	23350	*1919*	*8.2*	20	6	100
Pb	A1M	µg/l	73.6	72.6	73.1	73.0	4.9	6.7	10.0	16	88
	KN4	mg/kg	26.1	26.5	-	26.1	*2.7*	*10.2*	-	5	-
	KO4	mg/kg	22.7	22.7	22.7	23.0	2.5	10.8	20	9	100
	TN3	µg/l	51.9	48.6	48.9	48.4	3.3	6.6	15	11	91
	TY3	µg/l	49.0	49.0	48.7	47.6	4.2	8.6	20	9	78
	V2M	µg/l	5.17	4.83	4.84	4.99	0.36	7.3	15	12	73

Table 1. The summary of the results in the proficiency test MET 10/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} %/ s %	2 x s_{pt} %	n (all)	Acc z %
P_{tot}	KN4	g/kg	32.4	32.4	-	32.4	*0.66*	*2.0*	-	5	-
	KO4	g/kg	32.4	32.2	32.7	32.4	2.4	7.2	15	9	89
	KX4	g/kg		32.8	-	32.8	-	-	-	1	-
Sb	A1M	µg/l	75.1	74.4	74.4	74.3	3.1	4.1	10	13	92
	TN3	µg/l	57.2	57.2	57.6	58.6	3.9	6.7	15	9	89
	TY3	µg/l	57.1	57.2	-	57.1	*2.7*	*4.7*	-	8	-
	V2M	µg/l	5.17	5.17	5.21	5.15	0.25	4.8	15	11	80
Se	A1M	µg/l	35.5	36.5	36.6	36.3	2.6	7.1	10	13	77
	TN3	µg/l	23.3	23.3	23.1	23.0	1.3	5.7	15	9	100
	TY3	µg/l	24.3	25.0	-	24.3	*4.3*	*17.7*	-	7	-
	V2M	µg/l	5.11	5.09	5.40	5.11	0.61	11.3	15	11	50
Sn	A1M	µg/l	22.5	23.1	22.9	23.1	1.3	5.7	10	12	82
	TN3	µg/l	24.5	24.6	-	24.5	*1.48*	*6.3*	20	8	86
	TY3	µg/l	25.9	25.7	-	25.9	*1.58*	*6.1*	-	7	-
	V2M	µg/l	3.55	3.55	3.55	3.60	0.18	5.2	15	11	89
Sr	A1M	µg/l	89.5	90.6	90.6	90.7	3.7	4.0	10	12	100
	TN3	µg/l	226	226	225	224	8	3.4	15	9	100
	TY3	µg/l	234	240	-	234	*25.9*	*11.1*	-	6	-
	V2M	µg/l	91.0	91.0	90.9	90.6	4.0	4.3	10	11	91
S_{tot}	A1M	mg/l	3.20	3.12	3.18	3.12	0.20	6.2	10	13	92
	KN4	mg/kg	7132	7174	-	7132	3097	*43.4*	-	6	-
	KO4	mg/kg	10093	10114	10271	10093	838	8.2	15	9	89
	TN3	µg/l	167000	169466	169466	167000	6050	3.6	10	10	90
	TY3	µg/l	170000	170667	-	170000	*4042*	*2.4*	-	5	-
	V2M	µg/l	23973	24208	24181	23973	1002	4.1	10	12	92
V	A1M	µg/l	45.5	45.3	45.3	45.4	2.6	5.8	10	11	100
	KN4	mg/kg	31.6	31.5	-	31.6	*0.42*	*1.3*	-	5	-
	KO4	mg/kg	31.6	30.1	30.2	31.6	5.3	17.7	25	7	86
	TN3	µg/l	57.9	57.4	57.4	57.9	2.4	4.2	15	7	100
	TY3	µg/l	60.6	61.2	-	60.6	*13.6*	*22.5*	-	7	-
	V2M	µg/l	10.4	10.5	10.5	10.4	1.1	10.5	20	11	90
Zn	A1M	µg/l	121	125	125	123	8	6.5	10	19	84
	KN4	mg/kg	614	603	603	614	40	6.7	15	7	100
	KO4	mg/kg	574	574	574	574	51	8.9	15	10	100
	TN3	µg/l	134	134	134	137	11	8.2	15	15	100
	TY3	µg/l	134	136	136	134	16	12.0	20	9	78
	V2M	µg/l	46.4	46.4	46.4	46.0	3.6	7.8	15	16	88

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

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 10. 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). Mostly the participants measured the acidified industrial waste water without sample pretreatment (TN3), and a smaller part of the participants measured the industrial waste water after acid digestion (TY3). The results of these samples were evaluated separately (Table 1).

The difference between the average concentrations of elements measured by different sample pretreatment methods was tested using the t-test. Statistically significant difference was observed for chromium analyses. For Cr no pretreatment approach gave statistically significantly lower results compared to the pretreatment with acid digestion (Appendix 11). For an unfiltered waste water sample the results are expected, acid digestion should give similar or higher results than without digestion.

Effect of sample pretreatment on elemental concentrations in compost sample
Elements in the compost sample were measured mainly after nitric acid digestion (KN4) or after aqua regia digestion (KO4). The results of these were evaluated separately (Table 1). Both treatments can be considered as partial digestions.

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 Fe, Pb and S_{tot} analyses. In both cases, nitric acid digestion gave significantly lower results compared to the aqua regia digestion approach (Appendix 11).

The digestion method in general can highly influence the recoveries depending on digestion temperature and hold times as can the sample weight and acid amount ratio.

Effect of measurement methods on elemental results
The most commonly used analytical method was ICP-MS, followed by ICP-OES. FAAS or GAAS technique was used by one participant for some measurements. Hydride generation ICP-OES and AAS techniques were both used by one participant for some measurements (Appendix 10).

The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. Statistically significant differences or visual differences were not observed between the results.

As a general note, a low recovery may be an indication of loss of measurand 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. That was followed by CV-AFS. Also some participants (1-2) reported to measure mercury with CV-AAS, CV-ICP-OES and CV-ICP-MS technique. Also ICP-OES or direct combustion (O_2 flow + AAS) method was used by some participants for mercury analyses of the compost sample (Appendix 10).

For the compost sample quite few mercury results were reported, aqua regia digestion (KO4) was most commonly used, followed by nitric acid digestion (KN4). Two participants analysed mercury from the compost sample with direct oxygen combustion (LC4, Table 1). Based on the visual comparison no differences between the used measuring or digestion methods were found (Appendix 10).

As for the other metal determinations, also mercury results are affected by digestion procedures used (acids and oxidation reagents used, their concentration, amounts and purities, digestion temperature and time).

Analytical techniques does not have so much effect on the results, but the fact is that for example using CV-AFS lower detection limits can be achieved compared to CV-AAS. CV-ICP-MS technique is known to have very competent detection limits as well.

3.3 Uncertainties of the results

At maximum 82 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 12). Several approaches were used for estimating the measurement uncertainty (Appendix 12). The most commonly used approach was based on the method validation data or using the internal quality data in different ways [7]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum five participants (Appendix 12) [8]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 2, some of the participants have over-estimated their expanded (k=2)

measurement uncertainty. Very high measurement uncertainties (i.e. 50 % or higher) 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 [9]. 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.

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

Measurand	A1M/A1Hg %	TN3/T3Hg %	TY3 %	V2M/V2Hg %	KC4/KN4/KO4/KX4 %
Al	3-30	3-30	10-25	5-40	-
As	10-50	4-25	10-27	10-100	18-30
B	15-50	5-40	20-25	12-50	-
Ba	10-20	10-20	10-50	10-50	-
Ca	5-32	5-20	6-25	5-25	10-35
Cd	10-50	10-33	14-33	10-100	15-26
Co	7-20	10-20	14-30	9-100	-
Cr	9-26	9-26	14-30	10-50	15-30
Cu	10-40	10-50	14-50	10-100	15-30
Fe	3-33	3-33	13-33	10-40	15-30
Hg	6-46	6-40	-	6-40	15-50
K	-	-	-	-	10-35
Mg	5-38	5-20	10-30	5-30	15-40
Mn	6-20	4-20	11-20	6-40	15-30
Mo	5-40	5-20	12-35	10-50	18-50
Ni	9-25	9-20	14-27	10-100	15-35
N_{tot}	-	-	-	-	10-30
Pb	10-30	10-30	12-50	10-50	15-35
P_{tot}	-	-	-	-	10-30
Sb	10-20	10-26	15-50	10-50	-
Se	15-50	15-29	17-50	12-50	-
Sn	15-50	15-20	15-50	10-50	-
Sr	10-20	5-20	15-20	9-20	-
S_{tot}	10-20	5-15	10-25	10-25	15-30
V	10-50	10-20	13-50	10-50	20-30
Zn	10-29	10-29	10-30	10-40	15-25

4 Evaluation of the results

The evaluation of the participants was based on the z and E_n scores and they were interpreted as follows:

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

In total, 90 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted. From the results evaluated with E_n scores, 72 % were satisfactory (Appendix 8).

Table 3. Summary of the performance evaluation in the proficiency test MET 10/2018.

Sample	Satisfactory results (mean, %)	Accepted deviation from the assigned value (%)	Remarks
A1M / A1Hg	91 / 80	10-20	- Mainly good performance in the sample A1M. - Difficulties in measurements for B, Ca and Se, < 80% satisfactory results. - In the MET 10/2017 the performance was satisfactory for 92/75 % of the results [6].
KN4 / KO4	z score: 97 / 89 E_n score KN4: 83	15-25	- Somewhat approximate assessment for: Cd, Cr, Ni, V. - Mainly good performance in the sample KN4. - Difficulties in measurements for Cd in the sample KO4, < 80% satisfactory results. - E_n score for Hg in the sample KO4 was 60 %. - Due to low number of results P_{tot} and N_{tot} was not evaluated in the sample KN4.
TN3 / T3Hg	95 / 80	10-25	- Somewhat approximate performance evaluation for Cd, Cu. - Mainly good performance in the sample TN3. - In the MET 10/2017 the performance was satisfactory for 90 / 94 % of the results [6].
TY3	z score: 74 E_n score: 64	10-20	- Somewhat approximate performance evaluation for As, Cr, Ni, Zn. - Many results were evaluated based on E_n scores due to low number of results. - In the MET 10/2017 the performance was satisfactory based on z scores for 96 % of the results when accepting deviation of 15-25 % from the assigned value [6]. - Totally the performance was remarkable lower in this PT than in the MET 10/2017.
V2M / V2Hg	86 / 85	10-25	- Difficulties in measurements for Pb, Se, < 80% satisfactory results. - In the MET 10/2017 the performance was satisfactory for 89 / 88 % of the results when accepting deviation of 10-20 % from the assigned value [6].

Altogether 64 % of the participants used accredited analytical methods at least for a part of the measurements and 89 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, Proftest SYKE MET 10/2017, the performance was satisfactory for 90 % of the all participants when standard deviation of 5–30 % from the assigned values were accepted [6].

In average, the satisfactory results varied between 74 % and 95 %, based on evaluation with z scores, for the tested sample types (Table 3). The share of satisfactory results in the synthetic sample A1M was the lowest for B, about 69 %. In total the share was at the same level as in the previous similar proficiency test in 2017 (Table 3) [6].

For the compost sample digested with nitric acid (KN4) the number of results for some measurands was low, and thus the performance was evaluated based on the E_n scores (Appendix 8). For the sample KN4, 83 % of the E_n scores were satisfactory (Table 3). Further, 97 % of the results evaluated with z scores were satisfactory when the deviation of 15–20 % from the assigned value was accepted (Table 3).

The compost sample results obtained after aqua regia digestion (HNO_3+HCl, KO4) were evaluated with z scores and the performance was satisfactory for 97 % of the results when accepting the deviation of 15–25 % from the assigned value (Table 3).

For the industrial waste water sample (TN3 (no digestion) and T3Hg) 88 % of the results were satisfactory, when deviation of 10–25 % from the assigned value was accepted (Table 3). For As, Ba, Cd, Co, Cr, Fe, Mg, Mn, Se, Sr, V, and Zn in the sample TN3 all the results were satisfactory. For the industrial waste water sample digested with acid or with acid mixture, TY3, the performance evaluation was done with z scores and was weaker than in the previous similar PT, Proftest SYKE MET 10/2017 (74 % vs. 96 %, respectively, Table 3) [6]. Also for the sample TY3 the number of results for some measurands was low, and thus the performance of those was evaluated based on the E_n scores (Appendix 8). In total, 64 % of the results evaluated with E_n scores were satisfactory (Table 3). For the municipal waste water samples V2M and V2Hg the number of satisfactory results was in the same level than in 2017, with accepting standard deviation 15–25 % from the assigned value (Table 3) [6].

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in waste waters and compost material in October - November 2018 (MET 10/2018). The measurands for the synthetic and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V, and Zn. For the compost sample the measurands were: As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V, and Zn. In total 21 laboratories participated in the PT.

The calculated concentration (the NIST traceable), the robust mean, the mean or the median of the results reported by the participants was chosen to be the assigned value for the measurand,

with the exception of Pb and Hg where the used assigned values were based on the metrologically traceable isotope dilution (ID) ICP-MS technique for some samples. The uncertainty for the assigned value was estimated at the 95 % confidence level (*k=2*) and it was between 0.4 and 3 % for the calculated and metrologically traceable assigned values and for assigned values based on the robust mean, the mean or the median it was between 1.3 and 29 %.

The evaluation of the performance was based on the z or E_n scores. In total, 90 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted. From the results evaluated with E_n scores, 72 % were satisfactory. Altogether 64 % of the participants used accredited analytical methods at least for a part of the measurements and 89 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti loka-marraskuussa 2018 pätevyyskokeen laboratorioille, jotka määrittävät metalleja ja elohopeaa viemärilaitos- ja teollisuusjätevesistä sekä lannoitteena käytettävästä kompostimateriaalista (MET 10/2018). Pätevyyskokeessa määritettiin synteettisestä sekä jätevesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, V ja Zn. Kompostinäytteestä määritettiin testisuureet As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N_{tot}, Ni, P_{tot}, Pb, S_{tot}, V ja Zn. Pätevyyskokeeseen osallistui yhteensä 21 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Lyijylle ja elohopealle käytettiin metrologisesti jäljitettävää vertailuarvoa osassa testinäytteistä. Vertailuarvolle laskettiin epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,4 – 3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 1,3 – 29 %.

Pätevyyden arviointi tehtiin z- tai E_n-arvojen avulla. Koko aineistossa hyväksyttäviä z-arvoilla arvioituja tuloksia oli 90 %, kun tulosten sallittiin poiketa vertailuarvosta 10 – 25 %. Tuloksista, jotka arvioitiin E_n-arvoilla, hyväksyttyjä oli 72 %. Noin 64 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 89 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Boliden Harjavalta Oy
	Boliden Kokkola Oy
	Eurofins Ahma Oy, Oulu
	Eurofins Environment Testing Finland Oy, Lahti
	Finnish Food Security Authority, Laboratory and Research
	Fortum Waste Solutions Oy, Riihimäki
	Freeport Cobalt Oy
	Hortilab Ab Oy
	KVVY Tutkimus Oy, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	MetropoliLab Oy
	Norilsk Nickel Harjavalta Oy
	Outokumpu Stainless Oy, Tutkimuskeskus, Tornio
	SGS Finland Oy, Kotka
	SSAB Europe Raahe, Raahe
	SYKE, Helsingin toimipaikka
	SYNLAB Analytics & Services Finland Oy
	UPM Tutkimuskeskus, Lappeenranta
Luxembourg	Laboratoire National de Sante
Sweden	INOVYN Sverige Ab

APPENDIX 2: Preparation of the samples

The synthetic sample A1M was prepared by diluting the NIST traceable certified reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting 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. The compost sample K4M (KN4/KO4/KX4) was composted sewage treatment plant sludge collected from southern Finland.

Measurand		A1M µg/l	V2M µg/l	TN3/TY3 µg/l	KN4/KO4/ KX4 mg/kg	Measurand		A1M µg/l	V2M µg/l	TN3/TY3 µg/l	KN4/KO4/ KX4 mg/kg
Al	Original	8 500	-	1 000	-	Cu	Original	680	4	13	309
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	250	-	-		Addition	-	-	13	-
	Ass. value	850	261	975/1018	-		Ass. value	68.0	4.07	12.7/13.0	330/329/-
As	Original	350	0.1	2	10	Fe	Original	9250	16	200	130 g/kg
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	10	100	-		Addition	-	100	500	-
	Ass. value	35.0	10.7	100/106	7.36/7.83/-		Ass. value	925	119	705/713	125/130/-
B	Original	520	88	290	-	K	Original	-	-	-	7 900
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	-	-	-		Addition	-	-	-	-
	Ass. value	52.0	71.3	246/280	-		Ass. value	-	-	-	9090/9115/-
Ba	Original	770	7.1	31	-	Mg	Original	12 000	6 900	22 300	3 800
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	-		Addition	-	-	-	-
	Ass. value	77.0	6.74	33.1/33.9	-		Ass. value	12 000	6 800	22 400/ 21 400	4020/3985/-
Ca	Original	22 000	33 200	69 500	30 g/kg	Mn	Original	955	1.2	120	375
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	-		Addition	-	80	-	-
	Ass. value	22 000	32 900	68 300/ 70 400	32.8/33.7/-		Ass. value	95.5	83.5	159/157	406/405/-
Cd	Original	85	-	0.32	0.9	Mo	Original	735	0.8	1 700	not meas.
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	2	15	-		Addition	-	15	-	-
	Ass. value	8.50	2.10	15.0/15.5	0.89/0.85/-		Ass. value	73.5	16.4	1 688/ 1 733	5.32/5.75/-
Co	Original	555	0.3	1	-	Ni	Original	855	4.5	15	30
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	10	30	-		Addition	-	-	50	-
	Ass. value	55.5	10.5	30.3/30.6	-		Ass. value	85.5	4.35	63.9/64.9	30.4/27.1
Cr	Original	855	0.2	84	40	N_{tot}	Original	-	-	-	24 g/kg
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	10	-	-		Addition	-	-	-	-
	Ass. value	85.5	10.5	77.1/83.6	31.4/35.5/-		Ass. value	-	-	-	24/-/23.35

Measurand		A1M µg/l	V2M µg/l	TN3/TY3 µg/l	KN4/KO4/ KX4 mg/kg
Pb	Original	735	0.02	1.1	25
	Dilution	10	-	-	-
	Addition	-	5	50	-
	Ass. value	73.6	5.17	51.9/49.0	26.1/22.7
P_{tot}	Original	-	-	-	30.4 g/kg
	Dilution	-	-	-	-
	Addition	-	-	-	-
	Ass. value	-	-	-	32.4/32.4/-
Sb	Original	751	0.19	7.1	-
	Dilution	10	-	-	-
	Addition	-	5	50	-
	Ass. value	75.1	5.17	57.2/57.1	-
Se	Original	355	-	2.6	-
	Dilution	10	-	-	-
	Addition	-	5	20	-
	Ass. value	35.5	5.11	23.3/24.3	-
Sn	Original	225	-	-	-
	Dilution	10	-	-	-
	Addition	-	3.5	25	-
	Ass. value	22.5	3.55	24.5/25.9	-
Sr	Original	895	91	220	-
	Dilution	10	-	-	-
	Addition	-	-	-	-
	Ass. value	89.5	91.0	226/234	-

Measurand		A1M µg/l	V2M µg/l	TN3/TY3 µg/l	KN4/KO4/ KX4 mg/kg
S_{tot}	Original	32 000	24 000	160 000	9 500
	Dilution	10	-	-	-
	Addition	-	-	-	-
	Ass. value	32 000	23 973	167 000/ 170 000	7 132/ 10 093/-
V	Original	455	0.08	8.2	not meas.
	Dilution	10	-	-	-
	Addition	-	10	50	-
	Ass. value	45,5	10,4	57,9/60,6	31,6/31,6/-
Zn	Original	1210	49	150	526
	Dilution	10	-	-	-
	Addition	-	-	-	-
	Ass. value	121	49	134/134	614/574
Measurand		A1Hg µg/l	V2Hg µg/l	T3Hg µg/l	KN4/KO4/ KX4/KC4 mg/kg
Hg	Original	0.45	0.001	0.003	0.35
	Dilution	-	-	-	-
	Addition	-	3	1.80	-
	Ass. value	0.45	2.84	1.82	0.39/0.31/ -/0.40

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 measurands from three to five (n) samples of each sample type (see table below).

Criteria for homogeneity

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

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

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, 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 [3, 4].

Measurement/ sample	Concentration [µg/l] [mg/kg] [g/kg]	n	s_{pt} %	s_h%	s_h	s_{anal}	s_{anal}/s_h	Is s_{anal}/s_h<0.5?	s_{sam}^2	c	Is s_{sam}^2<c?
Cd/V2M	2.11	3	7.5	1.3	0.03	0.01	0.49	Yes	0.0006	0.001	Yes
Cr/V2M	10.1	3	7.5	0.6	0.06	0.03	0.46	Yes	0.0008	0.004	Yes
Cu/V2M	3.74	3	12.5	3.1	0.12	0.06	0.50	Yes	0	0.02	Yes
Se/V2M	5.12	3	7.5	2.4	0.12	0.06	0.48	Yes	0	0.02	Yes
Zn/V2M	47.8	3	7.5	1.8	0.86	0.42	0.49	Yes	0	0.99	Yes
Cd/T3M	16.1	3	10	0.3	0.05	0.02	0.42	Yes	0.001	0.002	Yes
Cr/T3M	74.8	3	10	0.7	0.52	0.25	0.48	Yes	0.16	0.34	Yes
Cu/T3M	11.5	3	12.5	1.7	0.20	0.10	0.49	Yes	0.02	0.05	Yes
Se/T3M	22.4	3	7.5	1.9	0.43	0.20	0.48	Yes	0.02	0.23	Yes
Zn/T3M	148	3	10	0.8	1.18	0.56	0.47	Yes	0.42	1.72	Yes
Cu/K4M	309	5	10	1.3	4.01	1.96	0.49	Yes	0	11.5	Yes
Mn/K4M	375	5	10	3.1	11.6	5.70	0.49	Yes	0	96.8	Yes
Pb/K4M	25.0	5	10	1.5	0.38	0.18	0.49	Yes	0.06	0.10	Yes
P_{tot}/K4M	30.4	5	7.5	2.0	0.61	0.29	0.48	Yes	0	0.26	Yes
Zn/K4M	526	5	7.5	2.7	14.2	6.85	0.48	Yes	0	141	Yes
Hg/V2Hg*	2.85	3	10	1.1	0.03	0.006	0.18	Yes	0.0004	0.0004	Yes
Hg/T3Hg*	1.83	3	10	1.1	0.02	0	0	Yes	0.0001	0.0001	Yes
Pb/V2M*	5.16	3	7.5	0.8	0.04	0.02	0.44	Yes	0	0.002	Yes
Pb/T3M*	51.7	3	10	1.1	0.57	0.27	0.48	Yes	0	0.41	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 SYKE
All	In the registration the measurands were not correct on the electronic client interface (ProftestWEB) for the compost sample.	The provider corrected the mistake after the participant's note.

Participant	Comments to the results	Action / Proftest SYKE
19	The participant reported laboratory's results erroneously for the samples TY3 and V2M (vice versa). The result for S_{tot} in the sample A1M reported in the wrong unit. The corrected result was: Sample A1M: 3.122 mg/l.	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the results would have been satisfactory based on evaluation with z score, with the exception of questionable result for Sn in the sample V2M. The participant can re-calculate the z and E_n scores according to the Guide for participants [5].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
2	The participant reported zero value results for Hg in the water samples. These results were treated as outliers in the statistical result handling. In the analytical measurements there is always a detection limit. Thus, the correct way to inform these low values is to report result as 'lower than' or 'equal to detection limit'. The provider strongly recommends participant to update the reporting procedure for low concentration results.

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	850	4	0.5	Calculated value	0.05
	TN3	µg/l	975	41	4.2	Robust mean	0.28
	TY3	µg/l	1018	36	3.5	Median	
	V2M	µg/l	261	15	5.7	Robust mean	0.29
As	A1M	µg/l	35.0	0.3	0.8	Calculated value	0.08
	KN4	mg/kg	7.36	1.03	14.0	Median	
	KO4	mg/kg	7.83	0.67	8.5	Mean	0.34
	TN3	µg/l	100	4	4.1	Robust mean	0.27
	TY3	µg/l	106	9	8.7	Median	0.44
	V2M	µg/l	10.7	0.5	4.4	Mean	0.22
B	A1M	µg/l	52.0	0.5	1.0	Calculated value	0.10
	TN3	µg/l	246	15	6.3	Mean	0.32
	TY3	µg/l	280	34	12.0	Median	
	V2M	µg/l	71.3	4.2	5.9	Mean	0.30
Ba	A1M	µg/l	77.0	0.4	0.5	Calculated value	0.05
	TN3	µg/l	33.1	1.2	3.7	Median	0.25
	TY3	µg/l	33.9	2.4	7.0	Median	
	V2M	µg/l	6.74	0.23	3.4	Mean	0.23
Ca	A1M	mg/l	2.20	0.01	0.4	Calculated value	0.04
	KN4	g/kg	32.8	1.4	4.2	Mean	0.28
	KO4	g/kg	33.7	1.5	4.5	Mean	0.30
	TN3	mg/l	68.3	1.8	2.7	Mean	0.27
	TY3	mg/l	70.4	6.3	8.9	Median	
	V2M	mg/l	32.9	0.7	2.2	Median	0.22
Cd	A1M	µg/l	8.50	0.06	0.7	Calculated value	0.05
	KN4	mg/kg	0.89	0.26	29.0	Median	
	KO4	mg/kg	0.85	0.08	9.8	Median	0.39
	TN3	µg/l	15.0	0.9	6.0	Robust mean	0.40
	TY3	µg/l	15.5	1.0	6.7	Mean	0.34
	V2M	µg/l	2.10	0.10	4.8	Robust mean	0.32
Co	A1M	µg/l	55.5	0.3	0.6	Calculated value	0.06
	TN3	µg/l	30.3	1.5	4.8	Mean	0.32
	TY3	µg/l	30.6	2.9	9.4	Median	
	V2M	µg/l	10.5	0.6	5.3	Robust mean	0.27
Cr	A1M	µg/l	85.5	0.6	0.7	Calculated value	0.07
	KN4	mg/kg	31.4	2.6	8.3	Median	
	KO4	mg/kg	35.5	3.3	9.3	Median	0.37
	TN3	µg/l	77.1	2.8	3.6	Robust mean	0.24
	TY3	µg/l	83.6	6.9	8.3	Mean	0.42
	V2M	µg/l	10.5	0.5	4.7	Robust mean	0.31
Cu	A1M	µg/l	68.0	0.3	0.5	Calculated value	0.05
	KN4	mg/kg	330	19	5.9	Mean	0.30
	KO4	mg/kg	329	10	3.0	Mean	0.15
	TN3	µg/l	12.7	1.1	8.8	Mean	0.35
	TY3	µg/l	13.0	1.7	13.1	Median	
	V2M	µg/l	4.07	0.31	7.5	Mean	0.30

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/S_{pt}
Fe	A1M	µg/l	925	6	0.6	Calculated value	0.06
	KN4	g/kg	125	29	23.0	Median	
	KO4	g/kg	130	4	3.0	Mean	0.15
	TN3	µg/l	705	27	3.8	Robust mean	0.25
	TY3	µg/l	713	26	3.7	Mean	0.25
	V2M	µg/l	119	7	5.7	Robust mean	0.29
Hg	A1Hg	µg/l	0.45	0.01	3.0	ID-ICP-MS	0.15
	KC4	mg/kg	0.40			Median	
	KN4	mg/kg	0.39	0.04	9.3	Median	
	KO4	mg/kg	0.31	0.08	26.0	Median	
	T3Hg	µg/l	1.82	0.05	3.0	ID-ICP-MS	0.15
	V2Hg	µg/l	2.84	0.09	3.0	ID-ICP-MS	0.15
K	KN4	mg/kg	9090	264	2.9	Median	
	KO4	mg/kg	9115	337	3.7	Mean	0.25
Mg	A1M	mg/l	1.20	0.01	0.6	Calculated value	0.06
	KN4	mg/kg	4020	181	4.5	Median	0.30
	KO4	mg/kg	3985	155	3.9	Mean	0.26
	TN3	mg/l	22.4	0.6	2.5	Mean	0.25
	TY3	mg/l	21.4	1.8	8.3	Median	
	V2M	mg/l	6.80	0.13	1.9	Robust mean	0.19
Mn	A1M	µg/l	95.5	0.4	0.4	Calculated value	0.04
	KN4	mg/kg	406	20	5.0	Mean	0.25
	KO4	mg/kg	405	21	5.2	Mean	0.26
	TN3	µg/l	159	6	3.6	Robust mean	0.36
	TY3	µg/l	157	4	2.5	Median	
	V2M	µg/l	83.5	2.6	3.1	Robust mean	0.21
Mo	A1M	µg/l	73.5	0.4	0.6	Calculated value	0.06
	KN4	mg/kg	5.32	0.80	15.0	Median	
	KO4	mg/kg	5.75	0.48	8.3	Mean	0.33
	TN3	µg/l	1688	66	3.9	Robust mean	0.39
	TY3	µg/l	1733	137	7.9	Median	
	V2M	µg/l	16.4	0.3	2.1	Mean	0.14
Ni	A1M	µg/l	85.5	0.4	0.5	Calculated value	0.05
	KN4	mg/kg	30.4	3.0	10.0	Median	
	KO4	mg/kg	27.1	2.6	9.7	Mean	0.39
	TN3	µg/l	63.9	3.3	5.1	Robust mean	0.34
	TY3	µg/l	64.9	4.5	6.9	Mean	0.46
	V2M	µg/l	4.35	0.14	3.3	Mean	0.22
N_{tot}	KN4	mg/kg	24000			Mean	
	KX4	mg/kg	23350	1588	6.8	Median	0.34
Pb	A1M	µg/l	73.6	1.8	2.5	ID-ICP-MS	0.25
	KN4	mg/kg	26.1	2.3	9.0	Median	
	KO4	mg/kg	22.7	1.5	6.4	Mean	0.32
	TN3	µg/l	51.9	1.3	2.5	ID-ICP-MS	0.17
	TY3	µg/l	49.0	3.2	6.6	Mean	0.33
	V2M	µg/l	5.17	0.13	2.5	ID-ICP-MS	0.17
P_{tot}	KN4	g/kg	32.4	0.7	2.3	Median	
	KO4	g/kg	32.4	1.3	3.9	Median	0.26

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Sb	A1M	µg/l	75.1	0.5	0.7	Calculated value	0.07
	TN3	µg/l	57.2	2.9	5.1	Mean	0.34
	TY3	µg/l	57.1	2.4	4.2	Median	
	V2M	µg/l	5.17	0.13	2.5	Mean	0.17
Se	A1M	µg/l	35.5	0.2	0.6	Calculated value	0.06
	TN3	µg/l	23.3	1.0	4.2	Mean	0.28
	TY3	µg/l	24.3	3.6	15.0	Median	
	V2M	µg/l	5.11	0.12	2.3	Median	0.15
Sn	A1M	µg/l	22.5	0.1	0.6	Calculated value	0.06
	TN3	µg/l	24.5	1.5	6.3	Median	0.32
	TY3	µg/l	25.9	1.6	6.1	Median	
	V2M	µg/l	3.55	0.12	3.3	Mean	0.22
Sr	A1M	µg/l	89.5	0.5	0.6	Calculated value	0.06
	TN3	µg/l	226	5	2.4	Mean	0.16
	TY3	µg/l	234	25	10.8	Median	
	V2M	µg/l	91.0	2.3	2.5	Mean	0.25
S_{tot}	A1M	mg/l	3.20	0.02	0.5	Calculated value	0.05
	KN4	mg/kg	7132	2496	35.0	Median	
	KO4	mg/kg	10093	434	4.3	Median	0.29
	TN3	µg/l	167000	3507	2.1	Median	0.21
	TY3	µg/l	170000	4590	2.7	Median	
	V2M	µg/l	23973	551	2.3	Median	0.23
V	A1M	µg/l	45.5	0.3	0.6	Calculated value	0.06
	KN4	mg/kg	31.6	0.4	1.3	Median	
	KO4	mg/kg	31.6	3.8	12.0	Median	0.48
	TN3	µg/l	57.9	1.6	2.8	Median	0.19
	TY3	µg/l	60.6	12.1	20.0	Median	
	V2M	µg/l	10.4	0.6	6.1	Median	0.31
Zn	A1M	µg/l	121	1	0.6	Calculated value	0.06
	KN4	mg/kg	614	28	4.5	Median	0.30
	KO4	mg/kg	574	29	5.0	Median	0.33
	TN3	µg/l	134	7	5.3	Robust mean	0.35
	TY3	µg/l	134	11	8.0	Median	0.40
	V2M	µg/l	46.4	2.4	5.2	Robust mean	0.35

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}= the standard deviation for proficiency assessment
u_{pt}= the 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 assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The reference value
2×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
s	Standard deviation
s %	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
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 ($z \ge 3$), positive error, the result deviates more than $3 \times s_{pt}$ from the assigned value
u – unsatisfactory ($z \le -3$), 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 ($i = 1, 2 \ldots p$):

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

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	s	s %	n (stat)
Al	µg/l	A1M		-2.00	850	10	765	869	873	28	3.2	15
	µg/l	TN3		-3.08	975	15	750	979	964	80	8.3	13
	µg/l	V2M		-1.07	261	20	233	260	264	27	10.0	13
As	µg/l	A1M		0.17	35.0	10	35.3	35.0	34.7	1.5	4.2	16
	µg/l	TN3		-0.72	100	15	95	101	101	5	5.2	12
	µg/l	V2M		-0.47	10.7	20	10.2	10.6	10.7	0.8	7.3	11
Ca	g/kg	KO4		0.71	33.7	15	35.5	33.2	33.7	2.4	7.1	10
	mg/l	V2M		1.22	32.9	10	34.9	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		-1.00	8.50	15	7.86	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		-0.35	0.85	25	0.81	0.85	0.88	0.11	12.9	7
	µg/l	TN3		-0.98	15.0	15	13.9	15.0	15.0	1.1	7.5	12
	µg/l	V2M		-1.97	2.10	15	1.79	2.10	2.09	0.14	6.7	12
Cr	µg/l	A1M		1.01	85.5	10	89.8	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		-1.55	35.5	25	28.6	35.5	35.0	4.9	14.0	9
	µg/l	TN3		0.19	77.1	15	78.2	77.9	76.9	4.0	5.2	13
	µg/l	V2M		-0.83	10.5	15	9.9	10.2	10.5	0.7	6.7	13
Cu	mg/kg	KO4		0.12	329	20	333	330	329	15	4.7	10
	µg/l	TN3		8.00	12.7	25	25.4	12.6	12.7	1.8	14.5	11
	µg/l	V2M		24.04	4.07	25	16.30	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		-0.45	925	10	904	932	936	38	4.0	20
	µg/l	TN3		-1.19	705	15	642	708	704	47	6.6	15
	µg/l	V2M		-1.26	119	20	104	119	119	10	8.0	15
Hg	µg/l	A1Hg		-1.16	0.45	20	0.40	0.44	0.45	0.04	9.8	13
	mg/kg	KX4					0.34	0.34	0.34	0.00	0.0	1
	µg/l	T3Hg		-0.93	1.82	20	1.65	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-1.30	2.84	20	2.47	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		-0.72	9115	15	8622	9050	9115	500	5.5	9
Mg	mg/l	V2M		0.26	6.80	10	6.89	6.83	6.80	0.17	2.5	14
Mn	mg/kg	KO4		-0.67	405	20	378	404	405	34	8.3	10
	µg/l	TN3		-0.29	159	10	157	157	159	7	4.7	13
	µg/l	V2M		-1.41	83.5	15	74.7	83.0	83.5	4.4	5.2	14
Ni	µg/l	A1M		1.08	85.5	10	90.1	86.2	86.5	4.7	5.5	18
	µg/l	TN3		-0.56	63.9	15	61.2	64.4	63.9	4.0	6.3	12
N_{tot}	mg/kg	KX4		-0.06	23350	20	23200	23350	22936	1919	8.4	6
Pb	µg/l	A1M		3.97	73.6	10	88.2	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		-1.23	22.7	20	19.9	23.0	22.7	2.2	9.5	9
	µg/l	TN3		-1.16	51.9	15	47.4	48.4	48.6	3.5	7.2	11
	µg/l	V2M		-1.50	5.17	15	4.59	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KX4					32.8	32.8	32.8	0.0	0.0	1
Zn	mg/kg	KO4		0.60	574	15	600	574	574	45	7.9	10
	µg/l	TN3		0.80	134	15	142	137	134	11	7.8	15
	µg/l	V2M		0.75	46.4	15	49.0	46.0	46.4	3.4	7.3	14

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		1.57	850	10	917	869	873	28	3.2	15
	µg/l	TN3		1.25	975	15	1067	979	964	80	8.3	13
	µg/l	TY3			1018		2	1018	1020	36	3.5	4
	µg/l	V2M		0.32	261	20	269	260	264	27	10.0	13
As	µg/l	A1M		0.06	35.0	10	35.1	35.0	34.7	1.5	4.2	16
	µg/l	TN3		1.01	100	15	108	101	101	5	5.2	12
	µg/l	TY3		-9.99	106	20	0	106	106	11	10.6	6
	µg/l	V2M		-0.12	10.7	20	10.6	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-4.98	52.0	10	39.1	51.9	51.3	7.0	13.6	13
	µg/l	TN3		-0.49	246	20	234	246	246	23	9.5	9
	µg/l	TY3			280		0	280	275	38	13.9	5
	µg/l	V2M		-0.51	71.3	20	67.7	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		0.52	77.0	10	79.0	78.0	77.7	5.8	7.4	12
	µg/l	TN3		1.06	33.1	15	35.7	33.1	33.0	1.7	5.2	8
	µg/l	TY3			33.9		0.0	33.9	34.7	2.7	7.8	5
	µg/l	V2M		0.82	6.74	15	7.16	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		-9.74	2.20	10	1.13	2.23	2.23	0.06	2.6	12
	mg/l	TN3		-10.22	68.3	10	33.4	68.3	68.3	2.9	4.2	10
	mg/l	TY3			70.4		0.0	70.4	71.0	7.1	10.0	5
	mg/l	V2M		-10.47	32.9	10	15.7	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		0.21	8.50	15	8.63	8.63	8.67	0.50	5.8	16
	µg/l	TN3		1.64	15.0	15	16.9	15.0	15.0	1.1	7.5	12
	µg/l	TY3		-9.99	15.5	20	0.0	15.0	15.5	1.3	8.2	6
	µg/l	V2M		0.16	2.10	15	2.13	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		1.11	55.5	10	58.6	56.0	56.4	2.7	4.9	15
	µg/l	TN3		1.27	30.3	15	33.2	30.5	30.3	2.4	7.9	11
	µg/l	TY3			30.6		0.0	30.6	32.2	3.7	11.5	6
	µg/l	V2M		0.37	10.5	20	10.9	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		0.78	85.5	10	88.8	85.7	85.7	4.1	4.8	18
	µg/l	TN3		0.95	77.1	15	82.6	77.9	76.9	4.0	5.2	13
	µg/l	TY3		-9.99	83.6	20	0.1	80.7	83.6	9.1	10.9	7
	µg/l	V2M		0.29	10.5	15	10.7	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		1.74	68.0	10	73.9	67.4	68.1	3.9	5.8	17
	µg/l	TN3		0.74	12.7	25	13.9	12.6	12.7	1.8	14.5	11
	µg/l	TY3			13.0		0.0	13.0	12.6	2.2	17.4	7
	µg/l	V2M		0.94	4.07	25	4.55	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		1.66	925	10	1002	932	936	38	4.0	20
	µg/l	TN3		1.79	705	15	800	708	704	47	6.6	15
	µg/l	TY3		-13.31	713	15	1	724	713	33	4.6	6
	µg/l	V2M		1.27	119	20	134	119	119	10	8.0	15
Hg	µg/l	A1Hg		-10.00	0.45	20	0.00	0.44	0.45	0.04	9.8	13
	µg/l	T3Hg		-10.00	1.82	20	0.00	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-10.00	2.84	20	0.00	2.83	2.84	0.17	6.1	11
Mg	mg/l	A1M		0.27	1.20	10	1.22	1.22	1.23	0.05	3.7	16
	mg/l	TN3		-0.06	22.4	10	22.3	22.3	22.4	0.9	4.2	11
	mg/l	TY3			21.4		24.0	21.4	22.4	2.3	10.1	6
	mg/l	V2M		0.53	6.80	10	6.98	6.83	6.80	0.17	2.5	14

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Mn	µg/l	A1M		1.11	95.5	10	100.8	95.3	96.8	4.6	4.7	17
	µg/l	TN3		1.62	159	10	172	157	159	7	4.7	13
	µg/l	TY3			157		0	157	158	5	2.9	5
	µg/l	V2M		0.74	83.5	15	88.1	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		1.65	73.5	10	79.6	73.9	74.1	1.1	1.5	12
	µg/l	TN3		2.03	1688	10	1860	1689	1695	93	5.5	12
	µg/l	TY3			1733		2	1733	1766	172	9.7	6
	µg/l	V2M		0.18	16.4	15	16.6	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		2.87	85.5	10	97.8	86.2	86.5	4.7	5.5	18
	µg/l	TN3		1.19	63.9	15	69.6	64.4	63.9	4.0	6.3	12
	µg/l	TY3		-13.31	64.9	15	0.1	62.8	64.9	5.9	9.1	7
	µg/l	V2M		0.72	4.35	15	4.58	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-0.91	73.6	10	70.3	73.0	72.6	4.0	5.5	15
	µg/l	TN3		-0.44	51.9	15	50.2	48.4	48.6	3.5	7.2	11
	µg/l	TY3		-9.99	49.0	20	0.1	47.6	49.0	4.3	8.7	7
	µg/l	V2M		-0.48	5.17	15	4.99	4.99	4.83	0.34	7.0	9
Sb	µg/l	A1M		-0.49	75.1	10	73.3	74.3	74.4	3.7	5.0	13
	µg/l	TN3		0.32	57.2	15	58.6	58.6	57.2	4.3	7.6	9
	µg/l	TY3			57.1		0.1	57.1	57.2	2.7	4.7	5
	µg/l	V2M		0.50	5.17	15	5.37	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		0.46	35.5	10	36.3	36.3	36.5	3.0	8.3	13
	µg/l	TN3		0.02	23.3	15	23.3	23.0	23.3	1.5	6.3	9
	µg/l	TY3			24.3		0.0	24.3	25.0	4.3	17.3	5
	µg/l	V2M		-3.62	5.11	15	3.72	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		1.01	22.5	10	23.6	23.1	23.1	1.0	4.3	10
	µg/l	TN3		1.10	24.5	20	27.2	24.5	24.6	1.9	7.8	6
	µg/l	TY3			25.9		0.0	25.9	25.7	1.6	6.1	4
	µg/l	V2M		0.77	3.55	15	3.76	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		1.25	89.5	10	95.1	90.7	90.6	3.2	3.6	12
	µg/l	TN3		1.01	226	15	243	224	226	8	3.7	9
	µg/l	TY3			234		0	234	240	26	10.8	4
	µg/l	V2M		1.05	91.0	10	95.8	90.6	91.0	3.6	4.0	10
V	µg/l	A1M		0.61	45.5	10	46.9	45.4	45.3	2.4	5.3	11
	µg/l	TN3		0.64	57.9	15	60.7	57.9	57.4	2.1	3.7	7
	µg/l	TY3			60.6		0.1	60.6	61.2	13.6	22.3	5
	µg/l	V2M		0.69	10.4	20	11.1	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		2.76	121	10	138	123	125	7	5.7	19
	µg/l	TN3		1.95	134	15	154	137	134	11	7.8	15
	µg/l	TY3		-9.98	134	20	0	134	136	14	10.5	7
	µg/l	V2M		2.86	46.4	15	56.4	46.0	46.4	3.4	7.3	14

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		-0.02	850	10	849	869	873	28	3.2	15
	µg/l	TN3		0.36	975	15	1001	979	964	80	8.3	13
	µg/l	V2M		-1.15	261	20	231	260	264	27	10.0	13
As	µg/l	A1M		0.34	35.0	10	35.6	35.0	34.7	1.5	4.2	16
	mg/kg	KN4			7.36		2.99	7.36	7.07	1.00	14.2	4
	µg/l	TN3		1.33	100	15	110	101	101	5	5.2	12
	µg/l	V2M		0.65	10.7	20	11.4	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-1.92	52.0	10	47.0	51.9	51.3	7.0	13.6	13
	µg/l	TN3		0.00	246	20	246	246	246	23	9.5	9
	µg/l	V2M		-0.97	71.3	20	64.4	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		3.51	77.0	10	90.5	78.0	77.7	5.8	7.4	12
	µg/l	TN3		0.48	33.1	15	34.3	33.1	33.0	1.7	5.2	8
	µg/l	V2M		-0.49	6.74	15	6.49	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		1.09	2.20	10	2.32	2.23	2.23	0.06	2.6	12
	g/kg	KN4		0.28	32.8	15	33.5	32.3	32.8	1.8	5.5	7
	mg/l	TN3		0.15	68.3	10	68.8	68.3	68.3	2.9	4.2	10
	mg/l	V2M		0.06	32.9	10	33.0	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		1.10	8.50	15	9.20	8.63	8.67	0.50	5.8	16
	mg/kg	KN4			0.89		1.71	0.89	1.10	0.36	32.8	5
	µg/l	TN3		1.42	15.0	15	16.6	15.0	15.0	1.1	7.5	12
	µg/l	V2M		1.08	2.10	15	2.27	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		1.95	55.5	10	60.9	56.0	56.4	2.7	4.9	15
	µg/l	TN3		-0.44	30.3	15	29.3	30.5	30.3	2.4	7.9	11
	µg/l	V2M		0.38	10.5	20	10.9	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		1.87	85.5	10	93.5	85.7	85.7	4.1	4.8	18
	mg/kg	KN4			31.4		31.0	31.4	33.1	3.1	9.2	5
	µg/l	TN3		0.24	77.1	15	78.5	77.9	76.9	4.0	5.2	13
	µg/l	V2M		1.02	10.5	15	11.3	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		1.68	68.0	10	73.7	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		-0.82	330	20	303	345	330	26	7.8	7
	µg/l	TN3		1.51	12.7	25	15.1	12.6	12.7	1.8	14.5	11
	µg/l	V2M		0.79	4.07	25	4.47	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		1.30	925	10	985	932	936	38	4.0	20
	g/kg	KN4			125		126	125	103	32	30.6	7
	µg/l	TN3		-0.09	705	15	700	708	704	47	6.6	15
	µg/l	V2M		0.17	119	20	121	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.22	0.45	20	0.44	0.44	0.45	0.04	9.8	13
	mg/kg	KN4			0.39		0.35	0.39	0.39	0.04	9.3	4
	µg/l	T3Hg		0.33	1.82	20	1.88	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-0.04	2.84	20	2.83	2.83	2.84	0.17	6.1	11
K	mg/kg	KN4			9090		9709	9090	9297	301	3.2	5
Mg	mg/l	A1M		1.83	1.20	10	1.31	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		0.61	4020	15	4203	4020	3995	220	5.5	6
	mg/l	TN3		1.79	22.4	10	24.4	22.3	22.4	0.9	4.2	11
	mg/l	V2M		0.74	6.80	10	7.05	6.83	6.80	0.17	2.5	14

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Mn	µg/l	A1M		1.15	95.5	10	101.0	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		-1.06	406	20	363	412	406	27	6.6	7
	µg/l	TN3		-0.63	159	10	154	157	159	7	4.7	13
	µg/l	V2M		-0.02	83.5	15	83.4	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		1.61	73.5	10	79.4	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		4.62	5.32	5.11	0.92	18.1	6
	µg/l	TN3		0.18	1688	10	1703	1689	1695	93	5.5	12
	µg/l	V2M		0.24	16.4	15	16.7	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		1.36	85.5	10	91.3	86.2	86.5	4.7	5.5	18
	mg/kg	KN4			30.4		35.8	30.4	30.4	3.5	11.4	5
	µg/l	TN3		0.04	63.9	15	64.1	64.4	63.9	4.0	6.3	12
	µg/l	V2M		0.09	4.35	15	4.38	4.33	4.35	0.23	5.2	10
N_{tot}	mg/kg	KN4			24000		24900	24000	24000	1273	5.3	2
Pb	µg/l	A1M		1.82	73.6	10	80.3	73.0	72.6	4.0	5.5	15
	mg/kg	KN4			26.1		31.1	26.1	26.5	2.7	10.0	5
	µg/l	TN3		0.28	51.9	15	53.0	48.4	48.6	3.5	7.2	11
	µg/l	V2M		11.32	5.17	15	9.56	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KN4			32.4		32.4	32.4	32.4	0.7	2.0	3
Sb	µg/l	A1M		1.38	75.1	10	80.3	74.3	74.4	3.7	5.0	13
	µg/l	TN3		1.28	57.2	15	62.7	58.6	57.2	4.3	7.6	9
	µg/l	V2M		-0.05	5.17	15	5.15	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		1.24	35.5	10	37.7	36.3	36.5	3.0	8.3	13
	µg/l	TN3		1.77	23.3	15	26.4	23.0	23.3	1.5	6.3	9
	µg/l	V2M		2.37	5.11	15	6.02	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		2.13	22.5	10	24.9	23.1	23.1	1.0	4.3	10
	µg/l	TN3		12.57	24.5	20	55.3	24.5	24.6	1.9	7.8	6
	µg/l	V2M		-0.60	3.55	15	3.39	3.60	3.55	0.16	4.6	8
S_{tot}	mg/l	A1M		1.56	3.20	10	3.45	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		9533	7132	7174	3097	43.2	6
	µg/l	TN3		1.15	167000	10	176600	167000	169466	5335	3.1	9
	µg/l	V2M		1.67	23973	10	25980	23973	24208	937	3.9	11
V	µg/l	A1M		1.71	45.5	10	49.4	45.4	45.3	2.4	5.3	11
	mg/kg	KN4			31.6		39.8	31.6	31.5	0.4	1.3	4
	µg/l	TN3		0.25	57.9	15	59.0	57.9	57.4	2.1	3.7	7
	µg/l	V2M		0.38	10.4	20	10.8	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		1.82	121	10	132	123	125	7	5.7	19
	mg/kg	KN4		-1.11	614	15	563	614	603	36	5.9	7
	µg/l	TN3		1.29	134	15	147	137	134	11	7.8	15
	µg/l	V2M		0.89	46.4	15	49.5	46.0	46.4	3.4	7.3	14

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
As	µg/l	A1M		0.57	35.0	10	36.0	35.0	34.7	1.5	4.2	16
	µg/l	TN3		-0.13	100	15	99	101	101	5	5.2	12
	µg/l	TY3		-0.38	106	20	102	106	106	11	10.6	6
	µg/l	V2M		-0.28	10.7	20	10.4	10.6	10.7	0.8	7.3	11
Cd	µg/l	A1M		0.31	8.50	15	8.70	8.63	8.67	0.50	5.8	16
	µg/l	TN3		-1.78	15.0	15	13.0	15.0	15.0	1.1	7.5	12
	µg/l	TY3		-0.97	15.5	20	14.0	15.0	15.5	1.3	8.2	6
	µg/l	V2M		-1.27	2.10	15	1.90	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		0.18	55.5	10	56.0	56.0	56.4	2.7	4.9	15
	µg/l	TN3		-1.89	30.3	15	26.0	30.5	30.3	2.4	7.9	11
	µg/l	TY3			30.6		29.0	30.6	32.2	3.7	11.5	6
	µg/l	V2M		-0.86	10.5	20	9.6	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-0.58	85.5	10	83.0	85.7	85.7	4.1	4.8	18
	µg/l	TN3		-1.57	77.1	15	68.0	77.9	76.9	4.0	5.2	13
	µg/l	TY3		-1.03	83.6	20	75.0	80.7	83.6	9.1	10.9	7
	µg/l	V2M		-1.02	10.5	15	9.7	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-0.59	68.0	10	66.0	67.4	68.1	3.9	5.8	17
	µg/l	TN3		-0.69	12.7	25	11.6	12.6	12.7	1.8	14.5	11
	µg/l	TY3			13.0		14.3	13.0	12.6	2.2	17.4	7
Fe	µg/l	A1M		-0.71	925	10	892	932	936	38	4.0	20
	µg/l	TN3		-1.93	705	15	603	708	704	47	6.6	15
	µg/l	TY3		-0.82	713	15	669	724	713	33	4.6	6
	µg/l	V2M		-1.18	119	20	105	119	119	10	8.0	15
Hg	µg/l	A1Hg		0.44	0.45	20	0.47	0.44	0.45	0.04	9.8	13
	µg/l	T3Hg		0.99	1.82	20	2.00	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		0.56	2.84	20	3.00	2.83	2.84	0.17	6.1	11
Mo	µg/l	A1M		-0.41	73.5	10	72.0	73.9	74.1	1.1	1.5	12
	µg/l	TN3		-0.94	1688	10	1609	1689	1695	93	5.5	12
	µg/l	TY3			1733		1523	1733	1766	172	9.7	6
	µg/l	V2M		-2.11	16.4	15	13.8	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-0.12	85.5	10	85.0	86.2	86.5	4.7	5.5	18
	µg/l	TN3		-2.07	63.9	15	54.0	64.4	63.9	4.0	6.3	12
	µg/l	TY3		-1.01	64.9	15	60.0	62.8	64.9	5.9	9.1	7
Pb	µg/l	A1M		-0.16	73.6	10	73.0	73.0	72.6	4.0	5.5	15
	µg/l	TN3		-2.80	51.9	15	41.0	48.4	48.6	3.5	7.2	11
	µg/l	TY3		-0.41	49.0	20	47.0	47.6	49.0	4.3	8.7	7
Sb	µg/l	A1M		-0.56	75.1	10	73.0	74.3	74.4	3.7	5.0	13
	µg/l	TN3		-2.14	57.2	15	48.0	58.6	57.2	4.3	7.6	9
	µg/l	TY3			57.1		58.0	57.1	57.2	2.7	4.7	5
Se	µg/l	A1M		1.41	35.5	10	38.0	36.3	36.5	3.0	8.3	13
	µg/l	TN3		-0.17	23.3	15	23.0	23.0	23.3	1.5	6.3	9
Zn	µg/l	A1M		0.33	121	10	123	123	125	7	5.7	19
	µg/l	TN3		-1.39	134	15	120	137	134	11	7.8	15
	µg/l	TY3		-0.67	134	20	125	134	136	14	10.5	7
	µg/l	V2M		-0.98	46.4	15	43.0	46.0	46.4	3.4	7.3	14

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		-2.19	850	10	757	869	873	28	3.2	15
	µg/l	TN3		-0.56	975	15	934	979	964	80	8.3	13
	µg/l	V2M		-2.30	261	20	201	260	264	27	10.0	13
B	µg/l	A1M		-1.19	52.0	10	48.9	51.9	51.3	7.0	13.6	13
	µg/l	TN3		-0.77	246	20	227	246	246	23	9.5	9
	µg/l	V2M		-0.63	71.3	20	66.8	70.4	71.3	7.0	9.8	11
Ca	mg/l	A1M		-0.09	2.20	10	2.19	2.23	2.23	0.06	2.6	12
	g/kg	KN4		-0.28	32.8	15	32.1	32.3	32.8	1.8	5.5	7
	mg/l	TN3		-1.20	68.3	10	64.2	68.3	68.3	2.9	4.2	10
	mg/l	V2M		-1.03	32.9	10	31.2	32.9	32.6	1.3	4.0	13
Cu	µg/l	A1M		-0.59	68.0	10	66.0	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		-0.36	330	20	318	345	330	26	7.8	7
	µg/l	TN3			12.7	25	*<20*	12.6	12.7	1.8	14.5	11
	µg/l	V2M			4.07	25	*<20*	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		0.19	925	10	934	932	936	38	4.0	20
	g/kg	KN4			125		66	125	103	32	30.6	7
	µg/l	TN3		0.06	705	15	708	708	704	47	6.6	15
	µg/l	V2M		1.51	119	20	137	119	119	10	8.0	15
K	mg/kg	KN4			9090		9090	9090	9297	301	3.2	5
Mg	mg/l	A1M		1.17	1.20	10	1.27	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		-0.03	4020	15	4010	4020	3995	220	5.5	6
	mg/l	TN3		-0.18	22.4	10	22.2	22.3	22.4	0.9	4.2	11
	mg/l	V2M		0.29	6.80	10	6.90	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		2.62	95.5	10	108.0	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		0.15	406	20	412	412	406	27	6.6	7
	µg/l	TN3		1.51	159	10	171	157	159	7	4.7	13
	µg/l	V2M		1.44	83.5	15	92.5	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		-0.08	73.5	10	73.2	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		3.62	5.32	5.11	0.92	18.1	6
	µg/l	TN3		-0.81	1688	10	1620	1689	1695	93	5.5	12
	µg/l	V2M			16.4	15	*<20*	16.5	16.4	0.5	3.3	10
N_{tot}	mg/kg	KX4		0.32	23350	20	24100	23350	22936	1919	8.4	6
P_{tot}	g/kg	KN4			32.4		5.3	32.4	32.4	0.7	2.0	3
S_{tot}	mg/l	A1M		-1.25	3.20	10	3.00	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		3890	7132	7174	3097	43.2	6
	µg/l	TN3		0.00	167000	10	167000	167000	169466	5335	3.1	9
	µg/l	V2M		-0.39	23973	10	23500	23973	24208	937	3.9	11
Zn	µg/l	A1M		1.16	121	10	128	123	125	7	5.7	19
	mg/kg	KN4		0.00	614	15	614	614	603	36	5.9	7
	µg/l	TN3		0.60	134	15	140	137	134	11	7.8	15
	µg/l	V2M		0.60	46.4	15	48.5	46.0	46.4	3.4	7.3	14

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
As	mg/kg	KO4		-0.28	7.83	25	7.56	7.83	7.83	0.94	12.1	8
Ca	g/kg	KO4		-0.55	33.7	15	32.3	33.2	33.7	2.4	7.1	10
Cr	mg/kg	KO4		0.90	35.5	25	39.5	35.5	35.0	4.9	14.0	9
Cu	mg/kg	KO4		-0.15	329	20	324	330	329	15	4.7	10
Fe	g/kg	KO4		-0.31	130	20	126	130	130	6	4.5	9
Hg	mg/kg	KC4			0.40		0.41	0.40	0.40	0.02	4.3	2
K	mg/kg	KO4		-0.10	9115	15	9050	9050	9115	500	5.5	9
Mg	mg/kg	KO4		-0.02	3985	15	3980	3980	3985	230	5.8	9
Mn	mg/kg	KO4		0.07	405	20	408	404	405	34	8.3	10
Mo	mg/kg	KO4		0.51	5.75	25	6.12	5.46	5.75	0.63	11.0	7
N_{tot}	mg/kg	KX4		-0.69	23350	20	21750	23350	22936	1919	8.4	6
Pb	mg/kg	KO4		1.41	22.7	20	25.9	23.0	22.7	2.2	9.5	9
P_{tot}	g/kg	KO4		0.00	32.4	15	32.4	32.4	32.2	1.8	5.5	8
S_{tot}	mg/kg	KO4		-0.39	10093	15	9800	10093	10114	609	6.0	8
Zn	mg/kg	KO4		0.49	574	15	595	574	574	45	7.9	10

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.45	850	10	869	869	873	28	3.2	15
	µg/l	TY3			1018		1040	1018	1020	36	3.5	4
Cr	µg/l	A1M		0.47	85.5	10	87.5	85.7	85.7	4.1	4.8	18
	µg/l	TY3		-0.35	83.6	20	80.7	80.7	83.6	9.1	10.9	7
Cu	µg/l	A1M		0.18	68.0	10	68.6	67.4	68.1	3.9	5.8	17
	µg/l	TY3			13.0		10.1	13.0	12.6	2.2	17.4	7
Fe	µg/l	A1M		1.02	925	10	972	932	936	38	4.0	20
	µg/l	TY3		0.47	713	15	738	724	713	33	4.6	6
Mn	µg/l	A1M		0.71	95.5	10	98.9	95.3	96.8	4.6	4.7	17
	µg/l	TY3			157		157	157	158	5	2.9	5
Ni	µg/l	A1M		0.23	85.5	10	86.5	86.2	86.5	4.7	5.5	18
	µg/l	TY3		-0.43	64.9	15	62.8	62.8	64.9	5.9	9.1	7
Pb	µg/l	A1M		-1.03	73.6	10	69.8	73.0	72.6	4.0	5.5	15
	µg/l	TY3		-1.04	49.0	20	43.9	47.6	49.0	4.3	8.7	7
Zn	µg/l	A1M		0.83	121	10	126	123	125	7	5.7	19
	µg/l	TY3		0.00	134	20	134	134	136	14	10.5	7

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		1.53	850	10	915	869	873	28	3.2	15
	µg/l	TY3			1018		1060	1018	1020	36	3.5	4
	µg/l	V2M		0.77	261	20	281	260	264	27	10.0	13
As	µg/l	A1M		0.34	35.0	10	35.6	35.0	34.7	1.5	4.2	16
	mg/kg	KO4		-0.58	7.83	25	7.26	7.83	7.83	0.94	12.1	8
	µg/l	TY3		-0.92	106	20	96	106	106	11	10.6	6
	µg/l	V2M			10.7	20	*<13*	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		1.42	52.0	10	55.7	51.9	51.3	7.0	13.6	13
	µg/l	TY3			280		213	280	275	38	13.9	5
	µg/l	V2M		0.42	71.3	20	74.3	70.4	71.3	7.0	9.8	11

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ba	µg/l	A1M		0.62	77.0	10	79.4	78.0	77.7	5.8	7.4	12
	µg/l	TY3			33.9		34.6	33.9	34.7	2.7	7.8	5
	µg/l	V2M			6.74	15	*<13*	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.45	2.20	10	2.25	2.23	2.23	0.06	2.6	12
	g/kg	KO4		0.12	33.7	15	34.0	33.2	33.7	2.4	7.1	10
	mg/l	TY3			70.4		71.1	70.4	71.0	7.1	10.0	5
	mg/l	V2M		-0.06	32.9	10	32.8	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		1.60	8.50	15	9.52	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		-0.19	0.85	25	0.83	0.85	0.88	0.11	12.9	7
	µg/l	TY3		-0.39	15.5	20	14.9	15.0	15.5	1.3	8.2	6
	µg/l	V2M		-0.13	2.10	15	2.08	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		1.55	55.5	10	59.8	56.0	56.4	2.7	4.9	15
	µg/l	TY3			30.6		30.5	30.6	32.2	3.7	11.5	6
	µg/l	V2M		-0.10	10.5	20	10.4	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		1.22	85.5	10	90.7	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		0.18	35.5	25	36.3	35.5	35.0	4.9	14.0	9
	µg/l	TY3		-0.19	83.6	20	82.0	80.7	83.6	9.1	10.9	7
	µg/l	V2M		-0.51	10.5	15	10.1	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		0.74	68.0	10	70.5	67.4	68.1	3.9	5.8	17
	mg/kg	KO4		0.00	329	20	329	330	329	15	4.7	10
	µg/l	TY3			13.0		14.1	13.0	12.6	2.2	17.4	7
	µg/l	V2M			4.07	25	*<6,3*	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		1.06	925	10	974	932	936	38	4.0	20
	g/kg	KO4		-0.46	130	20	124	130	130	6	4.5	9
	µg/l	TY3		0.04	713	15	715	724	713	33	4.6	6
	µg/l	V2M		-0.50	119	20	113	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.49	0.45	20	0.43	0.44	0.45	0.04	9.8	13
	mg/kg	KO4			0.31		0.21	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		0.77	1.82	20	1.96	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-0.28	2.84	20	2.76	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		-0.18	9115	15	8990	9050	9115	500	5.5	9
Mg	mg/l	A1M		1.33	1.20	10	1.28	1.22	1.23	0.05	3.7	16
	mg/kg	KO4		0.69	3985	15	4190	3980	3985	230	5.8	9
	mg/l	TY3			21.4		21.0	21.4	22.4	2.3	10.1	6
	mg/l	V2M		-0.53	6.80	10	6.62	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		1.57	95.5	10	103.0	95.3	96.8	4.6	4.7	17
	mg/kg	KO4		0.64	405	20	431	404	405	34	8.3	10
	µg/l	TY3			157		166	157	158	5	2.9	5
	µg/l	V2M		0.08	83.5	15	84.0	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.46	73.5	10	75.2	73.9	74.1	1.1	1.5	12
	mg/kg	KO4		-0.99	5.75	25	5.04	5.46	5.75	0.63	11.0	7
	µg/l	TY3			1733		1740	1733	1766	172	9.7	6
	µg/l	V2M		-0.57	16.4	15	15.7	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		1.36	85.5	10	91.3	86.2	86.5	4.7	5.5	18
	mg/kg	KO4		0.44	27.1	25	28.6	26.7	27.1	3.5	12.8	7
	µg/l	TY3		-0.27	64.9	15	63.6	62.8	64.9	5.9	9.1	7
	µg/l	V2M			4.35	15	*<6,3*	4.33	4.35	0.23	5.2	10

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Pb	µg/l	A1M		-0.16	73.6	10	73.0	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		-0.66	22.7	20	21.2	23.0	22.7	2.2	9.5	9
	µg/l	TY3		0.45	49.0	20	51.2	47.6	49.0	4.3	8.7	7
	µg/l	V2M			5.17	15	*<13*	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		3.54	32.4	15	41.0	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		0.53	75.1	10	77.1	74.3	74.4	3.7	5.0	13
	µg/l	TY3			57.1		57.1	57.1	57.2	2.7	4.7	5
	µg/l	V2M			5.17	15	*<13*	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		3.55	35.5	10	41.8	36.3	36.5	3.0	8.3	13
	µg/l	TY3			24.3		29.6	24.3	25.0	4.3	17.3	5
	µg/l	V2M			5.11	15	*<13*	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		1.60	22.5	10	24.3	23.1	23.1	1.0	4.3	10
	µg/l	TY3			25.9		23.7	25.9	25.7	1.6	6.1	4
	µg/l	V2M			3.55	15	*<13*	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		1.50	89.5	10	96.2	90.7	90.6	3.2	3.6	12
	µg/l	TY3			234		225	234	240	26	10.8	4
	µg/l	V2M		0.48	91.0	10	93.2	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		-0.64	3.20	10	3.10	3.12	3.12	0.13	4.0	10
	mg/kg	KO4		0.14	10093	15	10200	10093	10114	609	6.0	8
	µg/l	TY3			170000		175000	170000	170667	4041	2.4	3
	µg/l	V2M		-0.31	23973	10	23600	23973	24208	937	3.9	11
V	µg/l	A1M		0.18	45.5	10	45.9	45.4	45.3	2.4	5.3	11
	mg/kg	KO4		0.33	31.6	25	32.9	31.6	30.1	4.9	16.3	7
	µg/l	TY3			60.6		40.3	60.6	61.2	13.6	22.3	5
	µg/l	V2M			10.4	20	*<13*	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		2.64	121	10	137	123	125	7	5.7	19
	mg/kg	KO4		-1.46	574	15	511	574	574	45	7.9	10
	µg/l	TY3		0.07	134	20	135	134	136	14	10.5	7
	µg/l	V2M		-0.11	46.4	15	46.0	46.0	46.4	3.4	7.3	14

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.24	850	10	860	869	873	28	3.2	15
	µg/l	TN3		0.21	975	15	990	979	964	80	8.3	13
As	µg/l	A1M		-1.20	35.0	10	32.9	35.0	34.7	1.5	4.2	16
	µg/l	TN3		0.27	100	15	102	101	101	5	5.2	12
Ca	mg/l	A1M		0.09	2.20	10	2.21	2.23	2.23	0.06	2.6	12
Cd	µg/l	A1M		0.00	8.50	15	8.50	8.63	8.67	0.50	5.8	16
	µg/l	TN3		-0.09	15.0	15	14.9	15.0	15.0	1.1	7.5	12
Co	µg/l	A1M		0.65	55.5	10	57.3	56.0	56.4	2.7	4.9	15
	µg/l	TN3		1.41	30.3	15	33.5	30.5	30.3	2.4	7.9	11
Cr	µg/l	A1M		0.35	85.5	10	87.0	85.7	85.7	4.1	4.8	18
	µg/l	TN3		0.76	77.1	15	81.5	77.9	76.9	4.0	5.2	13
Cu	µg/l	A1M		0.21	68.0	10	68.7	67.4	68.1	3.9	5.8	17
	µg/l	TN3		2.08	12.7	25	16.0	12.6	12.7	1.8	14.5	11
Fe	µg/l	A1M		0.11	925	10	930	932	936	38	4.0	20
	µg/l	TN3		0.36	705	15	724	708	704	47	6.6	15

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Mg	mg/l	A1M		0.00	1.20	10	1.20	1.22	1.23	0.05	3.7	16
Mn	µg/l	A1M		-0.04	95.5	10	95.3	95.3	96.8	4.6	4.7	17
	µg/l	TN3		0.38	159	10	162	157	159	7	4.7	13
Mo	µg/l	A1M		0.08	73.5	10	73.8	73.9	74.1	1.1	1.5	12
	µg/l	TN3		-0.09	1688	10	1680	1689	1695	93	5.5	12
Ni	µg/l	A1M		0.42	85.5	10	87.3	86.2	86.5	4.7	5.5	18
	µg/l	TN3		1.09	63.9	15	69.1	64.4	63.9	4.0	6.3	12
Zn	µg/l	A1M		0.17	121	10	122	123	125	7	5.7	19
	µg/l	TN3		0.30	134	15	137	137	134	11	7.8	15

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		-0.09	850	10	846	869	873	28	3.2	15
	µg/l	TN3		-0.05	975	15	971	979	964	80	8.3	13
	µg/l	TY3			1018		984	1018	1020	36	3.5	4
	µg/l	V2M		0.31	261	20	269	260	264	27	10.0	13
As	µg/l	A1M		-0.23	35.0	10	34.6	35.0	34.7	1.5	4.2	16
	mg/kg	KN4			7.36		7.28	7.36	7.07	1.00	14.2	4
	mg/kg	KO4		-0.69	7.83	25	7.15	7.83	7.83	0.94	12.1	8
	µg/l	TN3		0.27	100	15	102	101	101	5	5.2	12
	µg/l	TY3		0.28	106	20	109	106	106	11	10.6	6
	µg/l	V2M		-0.72	10.7	20	9.9	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-0.42	52.0	10	50.9	51.9	51.3	7.0	13.6	13
	µg/l	TN3		0.08	246	20	248	246	246	23	9.5	9
	µg/l	TY3			280		309	280	275	38	13.9	5
	µg/l	V2M		-0.65	71.3	20	66.7	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		-1.27	77.0	10	72.1	78.0	77.7	5.8	7.4	12
	µg/l	TN3		-1.09	33.1	15	30.4	33.1	33.0	1.7	5.2	8
	µg/l	TY3			33.9		33.9	33.9	34.7	2.7	7.8	5
	µg/l	V2M		-1.27	6.74	15	6.10	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.82	2.20	10	2.29	2.23	2.23	0.06	2.6	12
	g/kg	KN4		-0.69	32.8	15	31.1	32.3	32.8	1.8	5.5	7
	g/kg	KO4		-1.11	33.7	15	30.9	33.2	33.7	2.4	7.1	10
	mg/l	TN3		1.73	68.3	10	74.2	68.3	68.3	2.9	4.2	10
	mg/l	TY3			70.4		70.4	70.4	71.0	7.1	10.0	5
	mg/l	V2M		0.61	32.9	10	33.9	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		-0.28	8.50	15	8.32	8.63	8.67	0.50	5.8	16
	mg/kg	KN4			0.89		0.86	0.89	1.10	0.36	32.8	5
	mg/kg	KO4		-0.02	0.85	25	0.85	0.85	0.88	0.11	12.9	7
	µg/l	TN3		-0.44	15.0	15	14.5	15.0	15.0	1.1	7.5	12
	µg/l	TY3		-0.32	15.5	20	15.0	15.0	15.5	1.3	8.2	6
	µg/l	V2M		-0.44	2.10	15	2.03	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		-1.01	55.5	10	52.7	56.0	56.4	2.7	4.9	15
	µg/l	TN3		-0.35	30.3	15	29.5	30.5	30.3	2.4	7.9	11
	µg/l	TY3			30.6		30.6	30.6	32.2	3.7	11.5	6
	µg/l	V2M		-1.21	10.5	20	9.2	10.5	10.5	0.7	6.7	12

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Cr	µg/l	A1M		-1.01	85.5	10	81.2	85.7	85.7	4.1	4.8	18
	mg/kg	KN4			31.4		31.4	31.4	33.1	3.1	9.2	5
	mg/kg	KO4		0.00	35.5	25	35.5	35.5	35.0	4.9	14.0	9
	µg/l	TN3		-0.31	77.1	15	75.3	77.9	76.9	4.0	5.2	13
	µg/l	TY3		-0.53	83.6	20	79.2	80.7	83.6	9.1	10.9	7
	µg/l	V2M		-0.65	10.5	15	10.0	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-1.53	68.0	10	62.8	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		-1.18	330	20	291	345	330	26	7.8	7
	mg/kg	KO4		-0.91	329	20	299	330	329	15	4.7	10
	µg/l	TN3		-1.64	12.7	25	10.1	12.6	12.7	1.8	14.5	11
	µg/l	TY3			13.0		12.1	13.0	12.6	2.2	17.4	7
	µg/l	V2M		-1.40	4.07	25	3.36	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		0.35	925	10	941	932	936	38	4.0	20
	g/kg	KN4			125		125	125	103	32	30.6	7
	g/kg	KO4		-0.77	130	20	120	130	130	6	4.5	9
	µg/l	TN3		0.40	705	15	726	708	704	47	6.6	15
	µg/l	TY3		0.37	713	15	733	724	713	33	4.6	6
	µg/l	V2M		0.00	119	20	119	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.38	0.45	20	0.43	0.44	0.45	0.04	9.8	13
	mg/kg	KC4			0.40		0.38	0.40	0.40	0.02	4.3	2
	µg/l	T3Hg		-0.60	1.82	20	1.71	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-0.49	2.84	20	2.70	2.83	2.84	0.17	6.1	11
K	mg/kg	KN4			9090		8	9090	9297	301	3.2	5
	mg/kg	KO4		-13.32	9115	15	8	9050	9115	500	5.5	9
Mg	mg/l	A1M		0.00	1.20	10	1.20	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		-1.29	4020	15	3630	4020	3995	220	5.5	6
	mg/kg	KO4		-0.79	3985	15	3750	3980	3985	230	5.8	9
	mg/l	TN3		0.89	22.4	10	23.4	22.3	22.4	0.9	4.2	11
	mg/l	TY3			21.4		20.5	21.4	22.4	2.3	10.1	6
	mg/l	V2M		-0.56	6.80	10	6.61	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.36	95.5	10	93.8	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		-0.52	406	20	385	412	406	27	6.6	7
	mg/kg	KO4		-0.52	405	20	384	404	405	34	8.3	10
	µg/l	TN3		-0.25	159	10	157	157	159	7	4.7	13
	µg/l	TY3			157		156	157	158	5	2.9	5
	µg/l	V2M		-0.48	83.5	15	80.5	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.08	73.5	10	73.8	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		5.81	5.32	5.11	0.92	18.1	6
	mg/kg	KO4		0.33	5.75	25	5.99	5.46	5.75	0.63	11.0	7
	µg/l	TN3		0.36	1688	10	1718	1689	1695	93	5.5	12
	µg/l	TY3			1733		1713	1733	1766	172	9.7	6
	µg/l	V2M		-0.89	16.4	15	15.3	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-1.15	85.5	10	80.6	86.2	86.5	4.7	5.5	18
	mg/kg	KN4			30.4		27.5	30.4	30.4	3.5	11.4	5
	mg/kg	KO4		-0.12	27.1	25	26.7	26.7	27.1	3.5	12.8	7
	µg/l	TN3		-0.69	63.9	15	60.6	64.4	63.9	4.0	6.3	12
	µg/l	TY3		-0.72	64.9	15	61.4	62.8	64.9	5.9	9.1	7
	µg/l	V2M		-0.83	4.35	15	4.08	4.33	4.35	0.23	5.2	10

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
N_{tot}	mg/kg	KX4		-1.52	23350	20	19800	23350	22936	1919	8.4	6
Pb	µg/l	A1M		-1.20	73.6	10	69.2	73.0	72.6	4.0	5.5	15
	mg/kg	KN4			26.1		24.4	26.1	26.5	2.7	10.0	5
	mg/kg	KO4		0.48	22.7	20	23.8	23.0	22.7	2.2	9.5	9
	µg/l	TN3		-1.26	51.9	15	47.0	48.4	48.6	3.5	7.2	11
	µg/l	TY3		0.24	49.0	20	50.2	47.6	49.0	4.3	8.7	7
	µg/l	V2M		-1.78	5.17	15	4.48	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KN4			32.4		33.1	32.4	32.4	0.7	2.0	3
	g/kg	KO4		-0.37	32.4	15	31.5	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		-0.56	75.1	10	73.0	74.3	74.4	3.7	5.0	13
	µg/l	TN3		0.63	57.2	15	59.9	58.6	57.2	4.3	7.6	9
	µg/l	TY3			57.1		61.1	57.1	57.2	2.7	4.7	5
	µg/l	V2M		-0.08	5.17	15	5.14	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		-0.51	35.5	10	34.6	36.3	36.5	3.0	8.3	13
	µg/l	TN3		-1.20	23.3	15	21.2	23.0	23.3	1.5	6.3	9
	µg/l	TY3			24.3		24.3	24.3	25.0	4.3	17.3	5
	µg/l	V2M		-0.50	5.11	15	4.92	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		-0.09	22.5	10	22.4	23.1	23.1	1.0	4.3	10
	µg/l	TN3		0.41	24.5	20	25.5	24.5	24.6	1.9	7.8	6
	µg/l	TY3			25.9		25.2	25.9	25.7	1.6	6.1	4
	µg/l	V2M		-0.30	3.55	15	3.47	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		-0.47	89.5	10	87.4	90.7	90.6	3.2	3.6	12
	µg/l	TN3		0.47	226	15	234	224	226	8	3.7	9
	µg/l	TY3			234		242	234	240	26	10.8	4
	µg/l	V2M		-0.75	91.0	10	87.6	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		1.13	3.20	10	3.38	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		9710	7132	7174	3097	43.2	6
	mg/kg	KO4		-0.43	10093	15	9770	10093	10114	609	6.0	8
	µg/l	TN3		0.72	167000	10	173000	167000	169466	5335	3.1	9
	µg/l	TY3			170000		167000	170000	170667	4041	2.4	3
	µg/l	V2M		1.19	23973	10	25400	23973	24208	937	3.9	11
V	µg/l	A1M		-1.41	45.5	10	42.3	45.4	45.3	2.4	5.3	11
	mg/kg	KN4			31.6		31.3	31.6	31.5	0.4	1.3	4
	mg/kg	KO4		0.00	31.6	25	31.6	31.6	30.1	4.9	16.3	7
	µg/l	TN3		-0.58	57.9	15	55.4	57.9	57.4	2.1	3.7	7
	µg/l	TY3			60.6		60.6	60.6	61.2	13.6	22.3	5
	µg/l	V2M		-1.08	10.4	20	9.3	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		-0.99	121	10	115	123	125	7	5.7	19
	mg/kg	KN4		-1.45	614	15	547	614	603	36	5.9	7
	mg/kg	KO4		-0.86	574	15	537	574	574	45	7.9	10
	µg/l	TN3		-0.70	134	15	127	137	134	11	7.8	15
	µg/l	TY3		0.00	134	20	134	134	136	14	10.5	7
	µg/l	V2M		-1.75	46.4	15	40.3	46.0	46.4	3.4	7.3	14

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Cr	µg/l	A1M		-0.35	85.5	10	84.0	85.7	85.7	4.1	4.8	18
	µg/l	TN3		-0.88	77.1	15	72.0	77.9	76.9	4.0	5.2	13
Fe	µg/l	A1M		-0.13	925	10	919	932	936	38	4.0	20
	µg/l	TN3		-0.51	705	15	678	708	704	47	6.6	15
Mo	µg/l	A1M		-0.14	73.5	10	73.0	73.9	74.1	1.1	1.5	12
	µg/l	TN3		-1.18	1688	10	1588	1689	1695	93	5.5	12
Ni	µg/l	A1M		-0.35	85.5	10	84.0	86.2	86.5	4.7	5.5	18
	µg/l	TN3		-0.81	63.9	15	60.0	64.4	63.9	4.0	6.3	12
Zn	µg/l	A1M		-0.50	121	10	118	123	125	7	5.7	19
	µg/l	TN3		-1.00	134	15	124	137	134	11	7.8	15

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.45	850	10	869	869	873	28	3.2	15
	µg/l	TN3		0.62	975	15	1020	979	964	80	8.3	13
	µg/l	V2M		-0.08	261	20	259	260	264	27	10.0	13
As	µg/l	A1M		-0.11	35.0	10	34.8	35.0	34.7	1.5	4.2	16
	mg/kg	KN4			7.36		5.62	7.36	7.07	1.00	14.2	4
	mg/kg	KO4		0.27	7.83	25	8.09	7.83	7.83	0.94	12.1	8
	µg/l	TN3		0.67	100	15	105	101	101	5	5.2	12
	µg/l	V2M		-0.09	10.7	20	10.6	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		0.73	52.0	10	53.9	51.9	51.3	7.0	13.6	13
	µg/l	TN3		0.16	246	20	250	246	246	23	9.5	9
	µg/l	V2M		0.15	71.3	20	72.4	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		0.34	77.0	10	78.3	78.0	77.7	5.8	7.4	12
	µg/l	TN3		-0.73	33.1	15	31.3	33.1	33.0	1.7	5.2	8
	µg/l	V2M		0.00	6.74	15	6.74	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.00	2.20	10	2.20	2.23	2.23	0.06	2.6	12
	g/kg	KN4		0.65	32.8	15	34.4	32.3	32.8	1.8	5.5	7
	g/kg	KO4		0.59	33.7	15	35.2	33.2	33.7	2.4	7.1	10
	mg/l	TN3		-0.06	68.3	10	68.1	68.3	68.3	2.9	4.2	10
	mg/l	V2M		-0.43	32.9	10	32.2	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		-0.09	8.50	15	8.44	8.63	8.67	0.50	5.8	16
	mg/kg	KN4			0.89		0.89	0.89	1.10	0.36	32.8	5
	mg/kg	KO4		0.34	0.85	25	0.89	0.85	0.88	0.11	12.9	7
	µg/l	TN3		0.71	15.0	15	15.8	15.0	15.0	1.1	7.5	12
	µg/l	V2M		0.00	2.10	15	2.10	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		-0.54	55.5	10	54.0	56.0	56.4	2.7	4.9	15
	µg/l	TN3		0.40	30.3	15	31.2	30.5	30.3	2.4	7.9	11
	µg/l	V2M		-0.29	10.5	20	10.2	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-0.35	85.5	10	84.0	85.7	85.7	4.1	4.8	18
	mg/kg	KN4			31.4		36.4	31.4	33.1	3.1	9.2	5
	mg/kg	KO4		2.01	35.5	25	44.4	35.5	35.0	4.9	14.0	9
	µg/l	TN3		-0.17	77.1	15	76.1	77.9	76.9	4.0	5.2	13
	µg/l	V2M		-0.51	10.5	15	10.1	10.2	10.5	0.7	6.7	13

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Cu	µg/l	A1M		-0.41	68.0	10	66.6	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		0.58	330	20	349	345	330	26	7.8	7
	mg/kg	KO4		0.73	329	20	353	330	329	15	4.7	10
	µg/l	TN3		0.25	12.7	25	13.1	12.6	12.7	1.8	14.5	11
	µg/l	V2M		0.16	4.07	25	4.15	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		-0.26	925	10	913	932	936	38	4.0	20
	g/kg	KN4			125		72	125	103	32	30.6	7
	g/kg	KO4		0.62	130	20	138	130	130	6	4.5	9
	µg/l	TN3		-0.19	705	15	695	708	704	47	6.6	15
	µg/l	V2M		-0.17	119	20	117	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.07	0.45	20	0.45	0.44	0.45	0.04	9.8	13
	mg/kg	KN4			0.39		0.37	0.39	0.39	0.04	9.3	4
	mg/kg	KO4			0.31		0.45	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		0.11	1.82	20	1.84	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-0.39	2.84	20	2.73	2.83	2.84	0.17	6.1	11
K	mg/kg	KN4			9090		9090	9090	9297	301	3.2	5
	mg/kg	KO4		0.50	9115	15	9460	9050	9115	500	5.5	9
Mg	mg/l	A1M		0.50	1.20	10	1.23	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		0.03	4020	15	4030	4020	3995	220	5.5	6
	mg/kg	KO4		0.95	3985	15	4270	3980	3985	230	5.8	9
	mg/l	TN3		0.09	22.4	10	22.5	22.3	22.4	0.9	4.2	11
	mg/l	V2M		0.21	6.80	10	6.87	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.02	95.5	10	95.4	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		0.76	406	20	437	412	406	27	6.6	7
	mg/kg	KO4		1.01	405	20	446	404	405	34	8.3	10
	µg/l	TN3		-0.25	159	10	157	157	159	7	4.7	13
	µg/l	V2M		-0.29	83.5	15	81.7	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.19	73.5	10	74.2	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		4.83	5.32	5.11	0.92	18.1	6
	mg/kg	KO4		1.59	5.75	25	6.89	5.46	5.75	0.63	11.0	7
	µg/l	TN3		0.46	1688	10	1727	1689	1695	93	5.5	12
	µg/l	V2M		0.00	16.4	15	16.4	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-0.58	85.5	10	83.0	86.2	86.5	4.7	5.5	18
	mg/kg	KN4			30.4		31.2	30.4	30.4	3.5	11.4	5
	mg/kg	KO4		1.59	27.1	25	32.5	26.7	27.1	3.5	12.8	7
	µg/l	TN3		0.15	63.9	15	64.6	64.4	63.9	4.0	6.3	12
	µg/l	V2M		-0.64	4.35	15	4.14	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-0.08	73.6	10	73.3	73.0	72.6	4.0	5.5	15
	mg/kg	KN4			26.1		24.9	26.1	26.5	2.7	10.0	5
	mg/kg	KO4		1.19	22.7	20	25.4	23.0	22.7	2.2	9.5	9
	µg/l	TN3		-0.33	51.9	15	50.6	48.4	48.6	3.5	7.2	11
	µg/l	V2M		-0.05	5.17	15	5.15	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		0.00	32.4	15	32.4	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		-0.19	75.1	10	74.4	74.3	74.4	3.7	5.0	13
	µg/l	TN3		0.56	57.2	15	59.6	58.6	57.2	4.3	7.6	9
	µg/l	V2M		0.72	5.17	15	5.45	5.15	5.17	0.18	3.5	8

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Se	µg/l	A1M		0.00	35.5	10	35.5	36.3	36.5	3.0	8.3	13
	µg/l	TN3		0.46	23.3	15	24.1	23.0	23.3	1.5	6.3	9
	µg/l	V2M		0.00	5.11	15	5.11	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		0.09	22.5	10	22.6	23.1	23.1	1.0	4.3	10
	µg/l	TN3		0.57	24.5	20	25.9	24.5	24.6	1.9	7.8	6
	µg/l	V2M		0.23	3.55	15	3.61	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		0.25	89.5	10	90.6	90.7	90.6	3.2	3.6	12
	µg/l	TN3		-0.29	226	15	221	224	226	8	3.7	9
	µg/l	V2M		-0.44	91.0	10	89.0	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		-0.38	3.20	10	3.14	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		4730	7132	7174	3097	43.2	6
	mg/kg	KO4		3.44	10093	15	12700	10093	10114	609	6.0	8
	µg/l	TN3		-0.36	167000	10	164000	167000	169466	5335	3.1	9
	µg/l	V2M		-0.64	23973	10	23200	23973	24208	937	3.9	11
V	µg/l	A1M		-0.13	45.5	10	45.2	45.4	45.3	2.4	5.3	11
	mg/kg	KN4			31.6		31.8	31.6	31.5	0.4	1.3	4
	mg/kg	KO4		1.16	31.6	25	36.2	31.6	30.1	4.9	16.3	7
	µg/l	TN3		0.02	57.9	15	58.0	57.9	57.4	2.1	3.7	7
	µg/l	V2M		-0.19	10.4	20	10.2	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		-0.33	121	10	119	123	125	7	5.7	19
	mg/kg	KN4		0.50	614	15	637	614	603	36	5.9	7
	mg/kg	KO4		1.49	574	15	638	574	574	45	7.9	10
	µg/l	TN3		-0.30	134	15	131	137	134	11	7.8	15
	µg/l	V2M		-0.29	46.4	15	45.4	46.0	46.4	3.4	7.3	14

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		-2.61	850	10	739	869	873	28	3.2	15
	µg/l	TN3		-1.34	975	15	877	979	964	80	8.3	13
	µg/l	V2M		-0.91	261	20	237	260	264	27	10.0	13
As	µg/l	A1M		-1.44	35.0	10	32.5	35.0	34.7	1.5	4.2	16
	mg/kg	KN4			7.36		7.44	7.36	7.07	1.00	14.2	4
	µg/l	TN3		-0.59	100	15	96	101	101	5	5.2	12
	µg/l	V2M		-1.03	10.7	20	9.6	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-4.44	52.0	10	40.5	51.9	51.3	7.0	13.6	13
	µg/l	TN3		-1.36	246	20	213	246	246	23	9.5	9
	µg/l	V2M		-1.44	71.3	20	61.0	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		-0.91	77.0	10	73.5	78.0	77.7	5.8	7.4	12
	µg/l	TN3		-0.39	33.1	15	32.1	33.1	33.0	1.7	5.2	8
	µg/l	V2M		-0.28	6.74	15	6.60	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		3.11	2.20	10	2.54	2.23	2.23	0.06	2.6	12
	g/kg	KN4		-0.20	32.8	15	32.3	32.3	32.8	1.8	5.5	7
	mg/l	TN3		-0.88	68.3	10	65.3	68.3	68.3	2.9	4.2	10
	mg/l	V2M		-1.46	32.9	10	30.5	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		-0.35	8.50	15	8.28	8.63	8.67	0.50	5.8	16
	mg/kg	KN4			0.89		0.89	0.89	1.10	0.36	32.8	5
	µg/l	TN3		0.61	15.0	15	15.7	15.0	15.0	1.1	7.5	12
	µg/l	V2M		-0.13	2.10	15	2.08	2.10	2.09	0.14	6.7	12

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Co	µg/l	A1M		0.56	55.5	10	57.1	56.0	56.4	2.7	4.9	15
	µg/l	TN3		0.87	30.3	15	32.3	30.5	30.3	2.4	7.9	11
	µg/l	V2M		0.23	10.5	20	10.7	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-0.01	85.5	10	85.5	85.7	85.7	4.1	4.8	18
	mg/kg	KN4			31.4		36.4	31.4	33.1	3.1	9.2	5
	µg/l	TN3		0.52	77.1	15	80.1	77.9	76.9	4.0	5.2	13
	µg/l	V2M		0.51	10.5	15	10.9	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-0.10	68.0	10	67.7	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		0.45	330	20	345	345	330	26	7.8	7
	µg/l	TN3		-0.08	12.7	25	12.6	12.6	12.7	1.8	14.5	11
	µg/l	V2M		0.16	4.07	25	4.15	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		-0.27	925	10	913	932	936	38	4.0	20
	g/kg	KN4			125		133	125	103	32	30.6	7
	µg/l	TN3		0.61	705	15	737	708	704	47	6.6	15
	µg/l	V2M		0.05	119	20	120	119	119	10	8.0	15
Hg	µg/l	A1Hg		2.04	0.45	20	0.54	0.44	0.45	0.04	9.8	13
	mg/kg	KN4			0.39		0.41	0.39	0.39	0.04	9.3	4
	µg/l	T3Hg		0.87	1.82	20	1.98	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		0.62	2.84	20	3.02	2.83	2.84	0.17	6.1	11
K	mg/kg	KN4			9090		9065	9090	9297	301	3.2	5
Mg	mg/l	A1M		-0.17	1.20	10	1.19	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		-0.48	4020	15	3876	4020	3995	220	5.5	6
	mg/l	TN3		-0.37	22.4	10	22.0	22.3	22.4	0.9	4.2	11
	mg/l	V2M		0.13	6.80	10	6.84	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.09	95.5	10	95.1	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		0.21	406	20	415	412	406	27	6.6	7
	µg/l	TN3		0.37	159	10	162	157	159	7	4.7	13
	µg/l	V2M		0.06	83.5	15	83.9	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.06	73.5	10	73.7	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		5.84	5.32	5.11	0.92	18.1	6
	µg/l	TN3		-0.12	1688	10	1678	1689	1695	93	5.5	12
	µg/l	V2M		-0.33	16.4	15	16.0	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		0.18	85.5	10	86.3	86.2	86.5	4.7	5.5	18
	mg/kg	KN4			30.4		30.4	30.4	30.4	3.5	11.4	5
	µg/l	TN3		0.66	63.9	15	67.1	64.4	63.9	4.0	6.3	12
	µg/l	V2M		-0.61	4.35	15	4.15	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-1.50	73.6	10	68.1	73.0	72.6	4.0	5.5	15
	mg/kg	KN4			26.1		26.2	26.1	26.5	2.7	10.0	5
	µg/l	TN3		-0.89	51.9	15	48.4	48.4	48.6	3.5	7.2	11
	µg/l	V2M		-0.44	5.17	15	5.00	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KN4			32.4		31.8	32.4	32.4	0.7	2.0	3
Sb	µg/l	A1M		-0.81	75.1	10	72.1	74.3	74.4	3.7	5.0	13
	µg/l	TN3		-0.63	57.2	15	54.5	58.6	57.2	4.3	7.6	9
	µg/l	V2M		2.58	5.17	15	6.17	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		-0.80	35.5	10	34.1	36.3	36.5	3.0	8.3	13
	µg/l	TN3		-0.54	23.3	15	22.4	23.0	23.3	1.5	6.3	9
	µg/l	V2M		-0.23	5.11	15	5.02	5.11	5.09	0.13	2.6	5

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Sn	µg/l	A1M		-0.90	22.5	10	21.5	23.1	23.1	1.0	4.3	10
	µg/l	TN3		-0.38	24.5	20	23.6	24.5	24.6	1.9	7.8	6
	µg/l	V2M		-1.05	3.55	15	3.27	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		-0.63	89.5	10	86.7	90.7	90.6	3.2	3.6	12
	µg/l	TN3		-0.12	226	15	224	224	226	8	3.7	9
	µg/l	V2M		-0.92	91.0	10	86.8	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		-0.68	3.20	10	3.09	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		10663	7132	7174	3097	43.2	6
	µg/l	TN3		-0.20	167000	10	165357	167000	169466	5335	3.1	9
	µg/l	V2M		0.00	23973	10	23973	23973	24208	937	3.9	11
V	µg/l	A1M		-0.38	45.5	10	44.6	45.4	45.3	2.4	5.3	11
	mg/kg	KN4			31.6		31.9	31.6	31.5	0.4	1.3	4
	µg/l	TN3		-0.01	57.9	15	57.9	57.9	57.4	2.1	3.7	7
	µg/l	V2M		-0.88	10.4	20	9.5	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		-0.20	121	10	120	123	125	7	5.7	19
	mg/kg	KN4		-0.23	614	15	603	614	603	36	5.9	7
	µg/l	TN3		0.15	134	15	136	137	134	11	7.8	15
	µg/l	V2M		-0.38	46.4	15	45.1	46.0	46.4	3.4	7.3	14

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Hg	µg/l	A1Hg		-1.56	0.45	20	0.38	0.44	0.45	0.04	9.8	13
	µg/l	T3Hg		-1.21	1.82	20	1.60	1.88	1.86	0.14	7.6	12

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.96	850	10	891	869	873	28	3.2	15
	µg/l	TY3			1018		1290	1018	1020	36	3.5	4
	µg/l	V2M		0.84	261	20	283	260	264	27	10.0	13
As	µg/l	A1M		0.97	35.0	10	36.7	35.0	34.7	1.5	4.2	16
	mg/kg	KN4			7.36		7.93	7.36	7.07	1.00	14.2	4
	µg/l	TY3		1.60	106	20	123	106	106	11	10.6	6
	µg/l	V2M		1.12	10.7	20	11.9	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		2.46	52.0	10	58.4	51.9	51.3	7.0	13.6	13
	µg/l	TY3			280		304	280	275	38	13.9	5
	µg/l	V2M		1.64	71.3	20	83.0	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		1.45	77.0	10	82.6	78.0	77.7	5.8	7.4	12
	µg/l	TY3			33.9		39.3	33.9	34.7	2.7	7.8	5
	µg/l	V2M		1.33	6.74	15	7.41	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		4.73	2.20	10	2.72	2.23	2.23	0.06	2.6	12
	g/kg	KN4		-0.98	32.8	15	30.4	32.3	32.8	1.8	5.5	7
	mg/l	TY3			70.4		82.6	70.4	71.0	7.1	10.0	5
	mg/l	V2M		0.24	32.9	10	33.3	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		1.35	8.50	15	9.36	8.63	8.67	0.50	5.8	16
	mg/kg	KN4			0.89		1.17	0.89	1.10	0.36	32.8	5
	µg/l	TY3		1.35	15.5	20	17.6	15.0	15.5	1.3	8.2	6
	µg/l	V2M		1.21	2.10	15	2.29	2.10	2.09	0.14	6.7	12

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Co	µg/l	A1M		1.37	55.5	10	59.3	56.0	56.4	2.7	4.9	15
	µg/l	TY3			30.6		38.1	30.6	32.2	3.7	11.5	6
	µg/l	V2M		1.14	10.5	20	11.7	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		0.75	85.5	10	88.7	85.7	85.7	4.1	4.8	18
	mg/kg	KN4			31.4		30.2	31.4	33.1	3.1	9.2	5
	µg/l	TY3		1.67	83.6	20	97.6	80.7	83.6	9.1	10.9	7
	µg/l	V2M		1.14	10.5	15	11.4	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		2.12	68.0	10	75.2	67.4	68.1	3.9	5.8	17
	mg/kg	KN4		0.55	330	20	348	345	330	26	7.8	7
	µg/l	TY3			13.0		15.2	13.0	12.6	2.2	17.4	7
	µg/l	V2M		1.26	4.07	25	4.71	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		0.28	925	10	938	932	936	38	4.0	20
	g/kg	KN4			125		130	125	103	32	30.6	7
	µg/l	TY3		2.92	713	15	869	724	713	33	4.6	6
	µg/l	V2M		1.01	119	20	131	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.42	0.45	20	0.43	0.44	0.45	0.04	9.8	13
	mg/kg	KN4			0.39		0.43	0.39	0.39	0.04	9.3	4
	µg/l	T3Hg		1.21	1.82	20	2.04	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-0.25	2.84	20	2.77	2.83	2.84	0.17	6.1	11
K	mg/kg	KN4			9090		8	9090	9297	301	3.2	5
Mg	mg/l	A1M		0.33	1.20	10	1.22	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		-13.32	4020	15	3	4020	3995	220	5.5	6
	mg/l	TY3			21.4		26.3	21.4	22.4	2.3	10.1	6
	mg/l	V2M		0.62	6.80	10	7.01	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		0.63	95.5	10	98.5	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		-0.30	406	20	394	412	406	27	6.6	7
	µg/l	TY3			157		197	157	158	5	2.9	5
	µg/l	V2M		0.97	83.5	15	89.6	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.68	73.5	10	76.0	73.9	74.1	1.1	1.5	12
	mg/kg	KN4			5.32		5.95	5.32	5.11	0.92	18.1	6
	µg/l	TY3			1733		2040	1733	1766	172	9.7	6
	µg/l	V2M		0.41	16.4	15	16.9	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		0.91	85.5	10	89.4	86.2	86.5	4.7	5.5	18
	mg/kg	KN4			30.4		27.3	30.4	30.4	3.5	11.4	5
	µg/l	TY3		2.28	64.9	15	76.0	62.8	64.9	5.9	9.1	7
	µg/l	V2M		0.98	4.35	15	4.67	4.33	4.35	0.23	5.2	10
N_{tot}	mg/kg	KN4			24000		23100	24000	24000	1273	5.3	2
Pb	µg/l	A1M		0.57	73.6	10	75.7	73.0	72.6	4.0	5.5	15
	mg/kg	KN4			26.1		26.1	26.1	26.5	2.7	10.0	5
	µg/l	TY3		1.61	49.0	20	56.9	47.6	49.0	4.3	8.7	7
	µg/l	V2M		0.08	5.17	15	5.20	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KN4			32.4		39.4	32.4	32.4	0.7	2.0	3
Sb	µg/l	A1M		-0.05	75.1	10	74.9	74.3	74.4	3.7	5.0	13
	µg/l	TY3			57.1		55.5	57.1	57.2	2.7	4.7	5
	µg/l	V2M		-0.44	5.17	15	5.00	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		1.46	35.5	10	38.1	36.3	36.5	3.0	8.3	13
	µg/l	TY3			24.3		23.5	24.3	25.0	4.3	17.3	5
	µg/l	V2M		2.32	5.11	15	6.00	5.11	5.09	0.13	2.6	5

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Sn	µg/l	A1M		0.62	22.5	10	23.2	23.1	23.1	1.0	4.3	10
	µg/l	TY3			25.9		27.3	25.9	25.7	1.6	6.1	4
	µg/l	V2M		0.53	3.55	15	3.69	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		0.63	89.5	10	92.3	90.7	90.6	3.2	3.6	12
	µg/l	TY3			234		275	234	240	26	10.8	4
	µg/l	V2M		1.43	91.0	10	97.5	90.6	91.0	3.6	4.0	10
V	µg/l	A1M		0.92	45.5	10	47.6	45.4	45.3	2.4	5.3	11
	mg/kg	KN4			31.6		31.0	31.6	31.5	0.4	1.3	4
	µg/l	TY3			60.6		73.0	60.6	61.2	13.6	22.3	5
	µg/l	V2M		1.15	10.4	20	11.6	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		1.82	121	10	132	123	125	7	5.7	19
	mg/kg	KN4		0.04	614	15	616	614	603	36	5.9	7
	µg/l	TY3		1.72	134	20	157	134	136	14	10.5	7
	µg/l	V2M		1.32	46.4	15	51.0	46.0	46.4	3.4	7.3	14

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.59	850	10	875	869	873	28	3.2	15
	µg/l	TN3		-0.44	975	15	943	979	964	80	8.3	13
	µg/l	V2M		-0.16	261	20	257	260	264	27	10.0	13
As	µg/l	A1M		-0.86	35.0	10	33.5	35.0	34.7	1.5	4.2	16
	mg/kg	KO4		1.74	7.83	25	9.53	7.83	7.83	0.94	12.1	8
	µg/l	TN3		-0.56	100	15	96	101	101	5	5.2	12
	µg/l	V2M		0.17	10.7	20	10.9	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		0.46	52.0	10	53.2	51.9	51.3	7.0	13.6	13
	µg/l	TN3		0.45	246	20	257	246	246	23	9.5	9
	µg/l	V2M		0.72	71.3	20	76.4	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		0.08	77.0	10	77.3	78.0	77.7	5.8	7.4	12
	µg/l	TN3		0.20	33.1	15	33.6	33.1	33.0	1.7	5.2	8
	µg/l	V2M		0.32	6.74	15	6.90	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.64	2.20	10	2.27	2.23	2.23	0.06	2.6	12
	g/kg	KO4		-0.81	33.7	15	31.7	33.2	33.7	2.4	7.1	10
	mg/l	TN3		0.29	68.3	10	69.3	68.3	68.3	2.9	4.2	10
	mg/l	V2M		0.15	32.9	10	33.2	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		0.00	8.50	15	8.50	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		0.95	0.85	25	0.95	0.85	0.88	0.11	12.9	7
	µg/l	TN3		-0.62	15.0	15	14.3	15.0	15.0	1.1	7.5	12
	µg/l	V2M		-0.06	2.10	15	2.09	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		0.00	55.5	10	55.5	56.0	56.4	2.7	4.9	15
	µg/l	TN3		-1.41	30.3	15	27.1	30.5	30.3	2.4	7.9	11
	µg/l	V2M		-0.35	10.5	20	10.1	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		0.07	85.5	10	85.8	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		0.25	35.5	25	36.6	35.5	35.0	4.9	14.0	9
	µg/l	TN3		-0.59	77.1	15	73.7	77.9	76.9	4.0	5.2	13
	µg/l	V2M		-0.36	10.5	15	10.2	10.2	10.5	0.7	6.7	13

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Cu	µg/l	A1M		-0.18	68.0	10	67.4	67.4	68.1	3.9	5.8	17
	mg/kg	KO4		0.03	329	20	330	330	329	15	4.7	10
	µg/l	TN3		-0.69	12.7	25	11.6	12.6	12.7	1.8	14.5	11
	µg/l	V2M		-0.24	4.07	25	3.95	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		-0.17	925	10	917	932	936	38	4.0	20
	g/kg	KO4		-0.20	130	20	127	130	130	6	4.5	9
	µg/l	TN3		-0.79	705	15	663	708	704	47	6.6	15
	µg/l	V2M		-0.15	119	20	117	119	119	10	8.0	15
Hg	µg/l	A1Hg		-0.04	0.45	20	0.45	0.44	0.45	0.04	9.8	13
	mg/kg	KO4			0.31		0.38	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		0.00	1.82	20	1.82	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		0.14	2.84	20	2.88	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		0.55	9115	15	9494	9050	9115	500	5.5	9
Mg	mg/l	A1M		-0.03	1.20	10	1.20	1.22	1.23	0.05	3.7	16
	mg/kg	KO4		-0.09	3985	15	3957	3980	3985	230	5.8	9
	mg/l	TN3		-0.67	22.4	10	21.7	22.3	22.4	0.9	4.2	11
	mg/l	V2M		-0.53	6.80	10	6.62	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.25	95.5	10	94.3	95.3	96.8	4.6	4.7	17
	mg/kg	KO4		-0.15	405	20	399	404	405	34	8.3	10
	µg/l	TN3		-1.51	159	10	147	157	159	7	4.7	13
	µg/l	V2M		-0.15	83.5	15	82.6	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.27	73.5	10	74.5	73.9	74.1	1.1	1.5	12
	mg/kg	KO4		-0.49	5.75	25	5.40	5.46	5.75	0.63	11.0	7
	µg/l	TN3		-1.22	1688	10	1585	1689	1695	93	5.5	12
	µg/l	V2M		-0.08	16.4	15	16.3	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		0.05	85.5	10	85.7	86.2	86.5	4.7	5.5	18
	mg/kg	KO4		0.77	27.1	25	29.7	26.7	27.1	3.5	12.8	7
	µg/l	TN3		-1.21	63.9	15	58.1	64.4	63.9	4.0	6.3	12
	µg/l	V2M		-0.21	4.35	15	4.28	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-0.24	73.6	10	72.7	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		0.48	22.7	20	23.8	23.0	22.7	2.2	9.5	9
	µg/l	TN3		-0.64	51.9	15	49.4	48.4	48.6	3.5	7.2	11
	µg/l	V2M		-0.34	5.17	15	5.04	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		-0.40	32.4	15	31.4	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		0.03	75.1	10	75.2	74.3	74.4	3.7	5.0	13
	µg/l	TN3		-0.68	57.2	15	54.3	58.6	57.2	4.3	7.6	9
	µg/l	V2M		-0.67	5.17	15	4.91	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		0.11	35.5	10	35.7	36.3	36.5	3.0	8.3	13
	µg/l	TN3		-0.46	23.3	15	22.5	23.0	23.3	1.5	6.3	9
	µg/l	V2M		0.10	5.11	15	5.15	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		0.36	22.5	10	22.9	23.1	23.1	1.0	4.3	10
	µg/l	TN3		-0.98	24.5	20	22.1	24.5	24.6	1.9	7.8	6
	µg/l	V2M		0.11	3.55	15	3.58	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		0.27	89.5	10	90.7	90.7	90.6	3.2	3.6	12
	µg/l	TN3		0.00	226	15	226	224	226	8	3.7	9
	µg/l	V2M		0.09	91.0	10	91.4	90.6	91.0	3.6	4.0	10

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
S_{tot}	mg/l	A1M		-0.08	3.20	10	3.19	3.12	3.12	0.13	4.0	10
	mg/kg	KO4		0.05	10093	15	10130	10093	10114	609	6.0	8
	µg/l	TN3		1.21	167000	10	177100	167000	169466	5335	3.1	9
	µg/l	V2M		0.59	23973	10	24680	23973	24208	937	3.9	11
V	µg/l	A1M		0.48	45.5	10	46.6	45.4	45.3	2.4	5.3	11
	mg/kg	KO4		0.43	31.6	25	33.3	31.6	30.1	4.9	16.3	7
	µg/l	TN3		-0.71	57.9	15	54.8	57.9	57.4	2.1	3.7	7
	µg/l	V2M		-0.03	10.4	20	10.4	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		-0.17	121	10	120	123	125	7	5.7	19
	mg/kg	KO4		-0.70	574	15	544	574	574	45	7.9	10
	µg/l	TN3		-0.80	134	15	126	137	134	11	7.8	15
	µg/l	V2M		-0.88	46.4	15	43.3	46.0	46.4	3.4	7.3	14

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		1.34	850	10	907	869	873	28	3.2	15
	µg/l	TN3		3.60	975	15	1238	979	964	80	8.3	13
	µg/l	V2M		2.80	261	20	334	260	264	27	10.0	13
As	µg/l	A1M		1.03	35.0	10	36.8	35.0	34.7	1.5	4.2	16
	mg/kg	KO4		0.58	7.83	25	8.40	7.83	7.83	0.94	12.1	8
	µg/l	TY3		0.47	106	20	111	106	106	11	10.6	6
	µg/l	V2M		1.31	10.7	20	12.1	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		0.77	52.0	10	54.0	51.9	51.3	7.0	13.6	13
	µg/l	TY3			280		280	280	275	38	13.9	5
Ba	µg/l	A1M		0.16	77.0	10	77.6	78.0	77.7	5.8	7.4	12
	µg/l	TY3			33.9		33.2	33.9	34.7	2.7	7.8	5
	µg/l	V2M		-0.20	6.74	15	6.64	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.00	2.20	10	2.20	2.23	2.23	0.06	2.6	12
	g/kg	KO4		-0.67	33.7	15	32.0	33.2	33.7	2.4	7.1	10
	mg/l	TY3			70.4		64.0	70.4	71.0	7.1	10.0	5
	mg/l	V2M		-1.16	32.9	10	31.0	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		1.15	8.50	15	9.23	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		2.35	0.85	25	1.10	0.85	0.88	0.11	12.9	7
	µg/l	TY3		0.52	15.5	20	16.3	15.0	15.5	1.3	8.2	6
	µg/l	V2M		0.63	2.10	15	2.20	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		-0.11	55.5	10	55.2	56.0	56.4	2.7	4.9	15
	µg/l	TY3			30.6		35.4	30.6	32.2	3.7	11.5	6
	µg/l	V2M		0.86	10.5	20	11.4	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		0.00	85.5	10	85.5	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		-0.79	35.5	25	32.0	35.5	35.0	4.9	14.0	9
	µg/l	TY3		1.39	83.6	20	95.2	80.7	83.6	9.1	10.9	7
	µg/l	V2M		1.90	10.5	15	12.0	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-0.56	68.0	10	66.1	67.4	68.1	3.9	5.8	17
	mg/kg	KO4		-0.27	329	20	320	330	329	15	4.7	10
	µg/l	TY3			13.0		13.0	13.0	12.6	2.2	17.4	7
	µg/l	V2M		0.31	4.07	25	4.23	4.15	4.07	0.48	11.9	10

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Fe	µg/l	A1M		0.06	925	10	928	932	936	38	4.0	20
	g/kg	KO4		0.00	130	20	130	130	130	6	4.5	9
	µg/l	TY3		0.64	713	15	747	724	713	33	4.6	6
	µg/l	V2M		0.25	119	20	122	119	119	10	8.0	15
Hg	µg/l	A1Hg		0.67	0.45	20	0.48	0.44	0.45	0.04	9.8	13
	mg/kg	KO4			0.31		0.24	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		3.30	1.82	20	2.42	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		0.67	2.84	20	3.03	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		-1.19	9115	15	8300	9050	9115	500	5.5	9
Mg	mg/l	A1M		0.00	1.20	10	1.20	1.22	1.23	0.05	3.7	16
	mg/kg	KO4		-0.62	3985	15	3800	3980	3985	230	5.8	9
	mg/l	TY3			21.4		21.0	21.4	22.4	2.3	10.1	6
	mg/l	V2M		-0.88	6.80	10	6.50	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-1.11	95.5	10	90.2	95.3	96.8	4.6	4.7	17
	mg/kg	KO4		-0.37	405	20	390	404	405	34	8.3	10
	µg/l	TY3			157		158	157	158	5	2.9	5
	µg/l	V2M		-0.42	83.5	15	80.9	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		0.11	73.5	10	73.9	73.9	74.1	1.1	1.5	12
	mg/kg	KO4		-3.01	5.75	25	3.59	5.46	5.75	0.63	11.0	7
	µg/l	TY3			1733		1726	1733	1766	172	9.7	6
	µg/l	V2M		0.33	16.4	15	16.8	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-0.68	85.5	10	82.6	86.2	86.5	4.7	5.5	18
	mg/kg	KO4		-0.32	27.1	25	26.0	26.7	27.1	3.5	12.8	7
	µg/l	TY3		1.03	64.9	15	69.9	62.8	64.9	5.9	9.1	7
	µg/l	V2M		0.61	4.35	15	4.55	4.33	4.35	0.23	5.2	10
N_{tot}	mg/kg	KX4		0.06	23350	20	23500	23350	22936	1919	8.4	6
Pb	µg/l	A1M		0.84	73.6	10	76.7	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		0.13	22.7	20	23.0	23.0	22.7	2.2	9.5	9
	µg/l	TY3		-0.59	49.0	20	46.1	47.6	49.0	4.3	8.7	7
	µg/l	V2M		-2.53	5.17	15	4.19	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		-1.40	32.4	15	29.0	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		1.52	75.1	10	80.8	74.3	74.4	3.7	5.0	13
	µg/l	TY3			57.1		76.9	57.1	57.2	2.7	4.7	5
	µg/l	V2M		-0.23	5.17	15	5.08	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		2.76	35.5	10	40.4	36.3	36.5	3.0	8.3	13
	µg/l	TY3			24.3		28.6	24.3	25.0	4.3	17.3	5
	µg/l	V2M		3.18	5.11	15	6.33	5.11	5.09	0.13	2.6	5
Sn	µg/l	A1M		0.80	22.5	10	23.4	23.1	23.1	1.0	4.3	10
	µg/l	TY3			25.9		26.5	25.9	25.7	1.6	6.1	4
	µg/l	V2M		0.41	3.55	15	3.66	3.60	3.55	0.16	4.6	8
S_{tot}	mg/l	A1M		-0.63	3.20	10	3.10	3.12	3.12	0.13	4.0	10
	mg/kg	KO4		-1.31	10093	15	9100	10093	10114	609	6.0	8
	µg/l	TY3			170000		170000	170000	170667	4041	2.4	3
	µg/l	V2M		-0.81	23973	10	23000	23973	24208	937	3.9	11
V	µg/l	A1M		-0.04	45.5	10	45.4	45.4	45.3	2.4	5.3	11
	mg/kg	KO4		-0.91	31.6	25	28.0	31.6	30.1	4.9	16.3	7
	µg/l	TY3			60.6		73.8	60.6	61.2	13.6	22.3	5
	µg/l	V2M		1.73	10.4	20	12.2	10.4	10.5	1.0	9.2	9

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Zn	µg/l	A1M		2.64	121	10	137	123	125	7	5.7	19
	mg/kg	KO4		-1.02	574	15	530	574	574	45	7.9	10
	µg/l	TY3		1.34	134	20	152	134	136	14	10.5	7
	µg/l	V2M		1.81	46.4	15	52.7	46.0	46.4	3.4	7.3	14

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.25	850	10	861	869	873	28	3.2	15
	µg/l	TN3		0.21	975	15	991	979	964	80	8.3	13
	µg/l	TY3			1018		997	1018	1020	36	3.5	4
	µg/l	V2M		-0.02	261	20	260	260	264	27	10.0	13
As	µg/l	A1M		-0.67	35.0	10	33.8	35.0	34.7	1.5	4.2	16
	mg/kg	KO4		-1.43	7.83	25	6.43	7.83	7.83	0.94	12.1	8
	µg/l	TN3		-0.75	100	15	94	101	101	5	5.2	12
	µg/l	TY3		-1.32	106	20	92	106	106	11	10.6	6
	µg/l	V2M		-0.28	10.7	20	10.4	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		5.10	52.0	10	65.3	51.9	51.3	7.0	13.6	13
	µg/l	TN3		2.04	246	20	296	246	246	23	9.5	9
	µg/l	TY3			280		270	280	275	38	13.9	5
	µg/l	V2M		1.43	71.3	20	81.5	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		-0.21	77.0	10	76.2	78.0	77.7	5.8	7.4	12
	µg/l	TN3		0.28	33.1	15	33.8	33.1	33.0	1.7	5.2	8
	µg/l	TY3			33.9		32.4	33.9	34.7	2.7	7.8	5
	µg/l	V2M		0.14	6.74	15	6.81	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		6.55	2.20	10	2.92	2.23	2.23	0.06	2.6	12
	g/kg	KO4		1.98	33.7	15	38.7	33.2	33.7	2.4	7.1	10
	mg/l	TN3		-0.47	68.3	10	66.7	68.3	68.3	2.9	4.2	10
	mg/l	TY3			70.4		66.8	70.4	71.0	7.1	10.0	5
	mg/l	V2M		0.01	32.9	10	32.9	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		0.69	8.50	15	8.94	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		-5.84	0.85	25	0.23	0.85	0.88	0.11	12.9	7
	µg/l	TN3		0.41	15.0	15	15.5	15.0	15.0	1.1	7.5	12
	µg/l	TY3		-0.29	15.5	20	15.1	15.0	15.5	1.3	8.2	6
	µg/l	V2M		0.13	2.10	15	2.12	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		-0.68	55.5	10	53.6	56.0	56.4	2.7	4.9	15
	µg/l	TN3		-0.56	30.3	15	29.0	30.5	30.3	2.4	7.9	11
	µg/l	TY3			30.6		29.4	30.6	32.2	3.7	11.5	6
	µg/l	V2M		-0.43	10.5	20	10.1	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-0.51	85.5	10	83.3	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		-0.79	35.5	25	32.0	35.5	35.0	4.9	14.0	9
	µg/l	TN3		-0.23	77.1	15	75.8	77.9	76.9	4.0	5.2	13
	µg/l	TY3		-0.97	83.6	20	75.5	80.7	83.6	9.1	10.9	7
	µg/l	V2M		-0.34	10.5	15	10.2	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-0.73	68.0	10	65.5	67.4	68.1	3.9	5.8	17
	mg/kg	KO4		-0.33	329	20	318	330	329	15	4.7	10
	µg/l	TN3		-1.32	12.7	25	10.6	12.6	12.7	1.8	14.5	11
	µg/l	TY3			13.0		9.4	13.0	12.6	2.2	17.4	7
	µg/l	V2M		-1.67	4.07	25	3.22	4.15	4.07	0.48	11.9	10

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Fe	µg/l	A1M		-1.03	925	10	877	932	936	38	4.0	20
	g/kg	KO4		0.30	130	20	134	130	130	6	4.5	9
	µg/l	TN3		-0.16	705	15	697	708	704	47	6.6	15
	µg/l	TY3		-0.66	713	15	678	724	713	33	4.6	6
	µg/l	V2M		-0.83	119	20	109	119	119	10	8.0	15
Hg	µg/l	A1Hg		1.11	0.45	20	0.50	0.44	0.45	0.04	9.8	13
	mg/kg	KO4			0.31		0.24	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		0.60	1.82	20	1.93	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		0.60	2.84	20	3.01	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		0.83	9115	15	9685	9050	9115	500	5.5	9
Mg	mg/l	A1M		1.00	1.20	10	1.26	1.22	1.23	0.05	3.7	16
	mg/kg	KO4		-1.18	3985	15	3633	3980	3985	230	5.8	9
	mg/l	TN3		0.29	22.4	10	22.7	22.3	22.4	0.9	4.2	11
	mg/l	TY3			21.4		21.8	21.4	22.4	2.3	10.1	6
	mg/l	V2M		-0.26	6.80	10	6.71	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.53	95.5	10	93.0	95.3	96.8	4.6	4.7	17
	mg/kg	KO4		-1.60	405	20	340	404	405	34	8.3	10
	µg/l	TN3		-0.86	159	10	152	157	159	7	4.7	13
	µg/l	TY3			157		154	157	158	5	2.9	5
	µg/l	V2M		-0.41	83.5	15	80.9	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		-1.17	73.5	10	69.2	73.9	74.1	1.1	1.5	12
	mg/kg	KO4		-0.58	5.75	25	5.33	5.46	5.75	0.63	11.0	7
	µg/l	TN3		2.14	1688	10	1869	1689	1695	93	5.5	12
	µg/l	TY3			1733		1855	1733	1766	172	9.7	6
	µg/l	V2M		0.37	16.4	15	16.9	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-0.52	85.5	10	83.3	86.2	86.5	4.7	5.5	18
	mg/kg	KO4		-1.15	27.1	25	23.2	26.7	27.1	3.5	12.8	7
	µg/l	TN3		-0.93	63.9	15	59.5	64.4	63.9	4.0	6.3	12
	µg/l	TY3		-0.86	64.9	15	60.7	62.8	64.9	5.9	9.1	7
	µg/l	V2M		-0.80	4.35	15	4.09	4.33	4.35	0.23	5.2	10
N_{tot}	mg/kg	KX4		0.82	23350	20	25265	23350	22936	1919	8.4	6
Pb	µg/l	A1M		-0.05	73.6	10	73.4	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		-1.06	22.7	20	20.3	23.0	22.7	2.2	9.5	9
	µg/l	TN3		-1.21	51.9	15	47.2	48.4	48.6	3.5	7.2	11
	µg/l	TY3		-0.30	49.0	20	47.6	47.6	49.0	4.3	8.7	7
	µg/l	V2M		-0.88	5.17	15	4.83	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		0.62	32.4	15	33.9	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		-0.22	75.1	10	74.3	74.3	74.4	3.7	5.0	13
	µg/l	TN3		0.19	57.2	15	58.0	58.6	57.2	4.3	7.6	9
	µg/l	TY3			57.1		54.1	57.1	57.2	2.7	4.7	5
	µg/l	V2M		0.21	5.17	15	5.25	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		0.47	35.5	10	36.3	36.3	36.5	3.0	8.3	13
	µg/l	TN3		-0.47	23.3	15	22.5	23.0	23.3	1.5	6.3	9
	µg/l	TY3			24.3		18.9	24.3	25.0	4.3	17.3	5
	µg/l	V2M		0.42	5.11	15	5.27	5.11	5.09	0.13	2.6	5

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Sn	µg/l	A1M			22.5	10	< *50*	23.1	23.1	1.0	4.3	10
	µg/l	TN3			24.5	20	< *50*	24.5	24.6	1.9	7.8	6
	µg/l	TY3			25.9		< *50*	25.9	25.7	1.6	6.1	4
	µg/l	V2M			3.55	15	< *50*	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		0.27	89.5	10	90.7	90.7	90.6	3.2	3.6	12
	µg/l	TN3		-0.13	226	15	224	224	226	8	3.7	9
	µg/l	TY3			234		216	234	240	26	10.8	4
	µg/l	V2M		-0.07	91.0	10	90.7	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		1.63	3.20	10	3.46	3.12	3.12	0.13	4.0	10
	mg/kg	KO4		1.01	10093	15	10857	10093	10114	609	6.0	8
	µg/l	TN3		-19.98	167000	10	157	167000	169466	5335	3.1	9
	µg/l	TY3			170000		149	170000	170667	4041	2.4	3
	µg/l	V2M		0.78	23973	10	24913	23973	24208	937	3.9	11
V	µg/l	A1M		-0.91	45.5	10	43.4	45.4	45.3	2.4	5.3	11
	mg/kg	KO4		-2.56	31.6	25	21.5	31.6	30.1	4.9	16.3	7
	µg/l	TN3		-0.44	57.9	15	56.0	57.9	57.4	2.1	3.7	7
	µg/l	TY3			60.6		58.2	60.6	61.2	13.6	22.3	5
	µg/l	V2M		-0.51	10.4	20	9.9	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		-0.07	121	10	121	123	125	7	5.7	19
	mg/kg	KO4		-0.42	574	15	556	574	574	45	7.9	10
	µg/l	TN3		-1.97	134	15	114	137	134	11	7.8	15
	µg/l	TY3		-1.36	134	20	116	134	136	14	10.5	7
	µg/l	V2M		-0.78	46.4	15	43.7	46.0	46.4	3.4	7.3	14

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.19	850	10	858	869	873	28	3.2	15
	µg/l	TY3			1018		242	1018	1020	36	3.5	4
	µg/l	V2M		29.96	261	20	1043	260	264	27	10.0	13
As	µg/l	A1M		0.49	35.0	10	35.9	35.0	34.7	1.5	4.2	16
	mg/kg	KO4		0.38	7.83	25	8.20	7.83	7.83	0.94	12.1	8
	µg/l	TY3		-8.94	106	20	11	106	106	11	10.6	6
	µg/l	V2M		86.24	10.7	20	103.0	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-1.31	52.0	10	48.6	51.9	51.3	7.0	13.6	13
	µg/l	TY3			280		71	280	275	38	13.9	5
	µg/l	V2M		26.71	71.3	20	261.7	70.4	71.3	7.0	9.8	11
Ba	µg/l	A1M		-2.67	77.0	10	66.7	78.0	77.7	5.8	7.4	12
	µg/l	TY3			33.9		6.0	33.9	34.7	2.7	7.8	5
	µg/l	V2M		46.67	6.74	15	30.33	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.82	2.20	10	2.29	2.23	2.23	0.06	2.6	12
	g/kg	KO4		-0.61	33.7	15	32.2	33.2	33.7	2.4	7.1	10
	mg/l	TY3			70.4		33.0	70.4	71.0	7.1	10.0	5
	mg/l	V2M		21.13	32.9	10	67.7	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		0.21	8.50	15	8.63	8.63	8.67	0.50	5.8	16
	mg/kg	KO4		-0.92	0.85	25	0.75	0.85	0.88	0.11	12.9	7
	µg/l	TY3		-8.70	15.5	20	2.0	15.0	15.5	1.3	8.2	6
	µg/l	V2M		100.57	2.10	15	17.94	2.10	2.09	0.14	6.7	12

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Co	µg/l	A1M		-0.96	55.5	10	52.8	56.0	56.4	2.7	4.9	15
	µg/l	TY3			30.6		10.7	30.6	32.2	3.7	11.5	6
	µg/l	V2M		19.08	10.5	20	30.5	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-2.16	85.5	10	76.3	85.7	85.7	4.1	4.8	18
	mg/kg	KO4		-1.12	35.5	25	30.5	35.5	35.0	4.9	14.0	9
	µg/l	TY3		-8.89	83.6	20	9.3	80.7	83.6	9.1	10.9	7
	µg/l	V2M		75.89	10.5	15	70.3	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-1.91	68.0	10	61.5	67.4	68.1	3.9	5.8	17
	mg/kg	KO4		0.07	329	20	331	330	329	15	4.7	10
	µg/l	TY3			13.0		3.6	13.0	12.6	2.2	17.4	7
	µg/l	V2M		14.04	4.07	25	11.21	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		1.47	925	10	993	932	936	38	4.0	20
	g/kg	KO4		0.05	130	20	131	130	130	6	4.5	9
	µg/l	TY3		-11.06	713	15	122	724	713	33	4.6	6
	µg/l	V2M		53.84	119	20	760	119	119	10	8.0	15
Hg	µg/l	A1Hg		-4.09	0.45	20	0.27	0.44	0.45	0.04	9.8	13
	mg/kg	KO4			0.31		0.41	0.31	0.32	0.10	32.3	6
	µg/l	T3Hg		4.38	1.82	20	2.62	1.88	1.86	0.14	7.6	12
	µg/l	V2Hg		-3.42	2.84	20	1.87	2.83	2.84	0.17	6.1	11
K	mg/kg	KO4		-0.56	9115	15	8733	9050	9115	500	5.5	9
Mg	mg/l	A1M		1.73	1.20	10	1.30	1.22	1.23	0.05	3.7	16
	mg/kg	KO4		0.07	3985	15	4006	3980	3985	230	5.8	9
	mg/l	TY3			21.4		7.2	21.4	22.4	2.3	10.1	6
	mg/l	V2M		46.82	6.80	10	22.72	6.83	6.80	0.17	2.5	14
Mn	µg/l	A1M		-0.42	95.5	10	93.5	95.3	96.8	4.6	4.7	17
	mg/kg	KO4		0.81	405	20	438	404	405	34	8.3	10
	µg/l	TY3			157		77	157	158	5	2.9	5
	µg/l	V2M		12.74	83.5	15	163.3	83.0	83.5	4.4	5.2	14
Mo	µg/l	A1M		-2.63	73.5	10	63.9	73.9	74.1	1.1	1.5	12
	mg/kg	KO4		-0.41	5.75	25	5.46	5.46	5.75	0.63	11.0	7
	µg/l	TY3			1733		14	1733	1766	172	9.7	6
	µg/l	V2M		1393.79	16.4	15	1730.8	16.5	16.4	0.5	3.3	10
Ni	µg/l	A1M		-2.00	85.5	10	77.0	86.2	86.5	4.7	5.5	18
	mg/kg	KO4		-1.23	27.1	25	22.9	26.7	27.1	3.5	12.8	7
	µg/l	TY3		-12.52	64.9	15	4.0	62.8	64.9	5.9	9.1	7
	µg/l	V2M		167.92	4.35	15	59.13	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-2.20	73.6	10	65.5	73.0	72.6	4.0	5.5	15
	mg/kg	KO4		-0.59	22.7	20	21.4	23.0	22.7	2.2	9.5	9
	µg/l	TY3		-9.03	49.0	20	4.7	47.6	49.0	4.3	8.7	7
	µg/l	V2M		100.02	5.17	15	43.95	4.99	4.83	0.34	7.0	9
P_{tot}	g/kg	KO4		0.01	32.4	15	32.4	32.4	32.2	1.8	5.5	8
Sb	µg/l	A1M		-2.32	75.1	10	66.4	74.3	74.4	3.7	5.0	13
	µg/l	TY3			57.1		5.2	57.1	57.2	2.7	4.7	5
	µg/l	V2M		119.01	5.17	15	51.32	5.15	5.17	0.18	3.5	8
Se	µg/l	A1M		-3.42	35.5	10	29.4	36.3	36.5	3.0	8.3	13
	µg/l	TY3			24.3		4.5	24.3	25.0	4.3	17.3	5
	µg/l	V2M		36.98	5.11	15	19.28	5.11	5.09	0.13	2.6	5

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Sn	µg/l	A1M		-4.48	22.5	10	17.5	23.1	23.1	1.0	4.3	10
	µg/l	TY3			25.9		3.0	25.9	25.7	1.6	6.1	4
	µg/l	V2M		72.39	3.55	15	22.82	3.60	3.55	0.16	4.6	8
Sr	µg/l	A1M		0.39	89.5	10	91.3	90.7	90.6	3.2	3.6	12
	µg/l	TY3			234		90	234	240	26	10.8	4
	µg/l	V2M		28.89	91.0	10	222.5	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		19494	3.20	10	3122.16	3.12	3.12	0.13	4.0	10
	mg/kg	KO4		-0.05	10093	15	10057	10093	10114	609	6.0	8
	µg/l	TY3			170000		23937	170000	170667	4041	2.4	3
	µg/l	V2M		117.45	23973	10	164756	23973	24208	937	3.9	11
V	µg/l	A1M		-1.90	45.5	10	41.2	45.4	45.3	2.4	5.3	11
	mg/kg	KO4		-1.12	31.6	25	27.2	31.6	30.1	4.9	16.3	7
	µg/l	TY3			60.6		8.8	60.6	61.2	13.6	22.3	5
	µg/l	V2M		39.73	10.4	20	51.7	10.4	10.5	1.0	9.2	9
Zn	µg/l	A1M		0.31	121	10	123	123	125	7	5.7	19
	mg/kg	KO4		0.44	574	15	593	574	574	45	7.9	10
	µg/l	TY3		-6.83	134	20	42	134	136	14	10.5	7
	µg/l	V2M		26.34	46.4	15	138.1	46.0	46.4	3.4	7.3	14

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		1.25	850	10	903	869	873	28	3.2	15
	µg/l	TN3		0.05	975	15	979	979	964	80	8.3	13
As	µg/l	A1M		-0.86	35.0	10	33.5	35.0	34.7	1.5	4.2	16
	µg/l	TN3		-0.29	100	15	98	101	101	5	5.2	12
Ca	mg/l	A1M		-0.08	2.20	10	2.19	2.23	2.23	0.06	2.6	12
	mg/l	TN3		0.05	68.3	10	68.5	68.3	68.3	2.9	4.2	10
Cd	µg/l	A1M		0.63	8.50	15	8.90	8.63	8.67	0.50	5.8	16
	µg/l	TN3		0.09	15.0	15	15.1	15.0	15.0	1.1	7.5	12
Co	µg/l	A1M		1.37	55.5	10	59.3	56.0	56.4	2.7	4.9	15
	µg/l	TN3		0.66	30.3	15	31.8	30.5	30.3	2.4	7.9	11
Cr	µg/l	A1M		0.54	85.5	10	87.8	85.7	85.7	4.1	4.8	18
	µg/l	TN3		0.42	77.1	15	79.5	77.9	76.9	4.0	5.2	13
Cu	µg/l	A1M		1.24	68.0	10	72.2	67.4	68.1	3.9	5.8	17
	µg/l	TN3		0.69	12.7	25	13.8	12.6	12.7	1.8	14.5	11
Fe	µg/l	A1M		1.08	925	10	975	932	936	38	4.0	20
	µg/l	TN3		0.70	705	15	742	708	704	47	6.6	15
Hg	µg/l	A1Hg		-1.00	0.45	20	0.41	0.44	0.45	0.04	9.8	13
	µg/l	T3Hg		0.33	1.82	20	1.88	1.88	1.86	0.14	7.6	12
Mg	mg/l	A1M		0.77	1.20	10	1.25	1.22	1.23	0.05	3.7	16
	mg/l	TN3		-1.20	22.4	10	21.1	22.3	22.4	0.9	4.2	11
Mn	µg/l	A1M		-0.17	95.5	10	94.7	95.3	96.8	4.6	4.7	17
	µg/l	TN3		-0.75	159	10	153	157	159	7	4.7	13
Mo	µg/l	A1M		0.54	73.5	10	75.5	73.9	74.1	1.1	1.5	12
	µg/l	TN3		0.12	1688	10	1698	1689	1695	93	5.5	12
Ni	µg/l	A1M		1.10	85.5	10	90.2	86.2	86.5	4.7	5.5	18
	µg/l	TN3		0.92	63.9	15	68.3	64.4	63.9	4.0	6.3	12

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Pb	µg/l	A1M		1.25	73.6	10	78.2	73.0	72.6	4.0	5.5	15
	µg/l	TN3		-1.28	51.9	15	46.9	48.4	48.6	3.5	7.2	11
Sb	µg/l	A1M		-0.83	75.1	10	72.0	74.3	74.4	3.7	5.0	13
	µg/l	TN3		0.47	57.2	15	59.2	58.6	57.2	4.3	7.6	9
Se	µg/l	A1M		0.39	35.5	10	36.2	36.3	36.5	3.0	8.3	13
	µg/l	TN3		0.40	23.3	15	24.0	23.0	23.3	1.5	6.3	9
Sn	µg/l	A1M		-0.18	22.5	10	22.3	23.1	23.1	1.0	4.3	10
	µg/l	TN3		-0.49	24.5	20	23.3	24.5	24.6	1.9	7.8	6
Sr	µg/l	A1M		-0.09	89.5	10	89.1	90.7	90.6	3.2	3.6	12
	µg/l	TN3		-0.59	226	15	216	224	226	8	3.7	9
S_{tot}	mg/l	A1M		-1.91	3.20	10	2.90	3.12	3.12	0.13	4.0	10
	µg/l	TN3		-0.47	167000	10	163100	167000	169466	5335	3.1	9
Zn	µg/l	A1M		1.65	121	10	131	123	125	7	5.7	19
	µg/l	TN3		0.70	134	15	141	137	134	11	7.8	15

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		-0.61	850	10	824	869	873	28	3.2	15
	µg/l	TN3		0.05	975	15	979	979	964	80	8.3	13
	µg/l	V2M		-0.04	261	20	260	260	264	27	10.0	13
As	µg/l	A1M		-1.60	35.0	10	32.2	35.0	34.7	1.5	4.2	16
	µg/l	TN3		0.40	100	15	103	101	101	5	5.2	12
	µg/l	V2M		-3.60	10.7	20	6.9	10.6	10.7	0.8	7.3	11
B	µg/l	A1M		-0.04	52.0	10	51.9	51.9	51.3	7.0	13.6	13
	µg/l	TN3		-0.24	246	20	240	246	246	23	9.5	9
	µg/l	V2M		-0.13	71.3	20	70.4	70.4	71.3	7.0	9.8	11
Ca	mg/l	A1M		-0.75	2.20	10	2.12	2.23	2.23	0.06	2.6	12
	mg/l	TN3		-0.42	68.3	10	66.9	68.3	68.3	2.9	4.2	10
	mg/l	V2M		-1.18	32.9	10	31.0	32.9	32.6	1.3	4.0	13
Cd	µg/l	A1M		-1.18	8.50	15	7.75	8.63	8.67	0.50	5.8	16
	µg/l	TN3		-0.71	15.0	15	14.2	15.0	15.0	1.1	7.5	12
	µg/l	V2M		-3.17	2.10	15	1.60	2.10	2.09	0.14	6.7	12
Co	µg/l	A1M		-0.68	55.5	10	53.6	56.0	56.4	2.7	4.9	15
	µg/l	TN3		0.09	30.3	15	30.5	30.5	30.3	2.4	7.9	11
	µg/l	V2M		0.00	10.5	20	10.5	10.5	10.5	0.7	6.7	12
Cr	µg/l	A1M		-1.08	85.5	10	80.9	85.7	85.7	4.1	4.8	18
	µg/l	TN3		0.14	77.1	15	77.9	77.9	76.9	4.0	5.2	13
	µg/l	V2M		-0.51	10.5	15	10.1	10.2	10.5	0.7	6.7	13
Cu	µg/l	A1M		-1.03	68.0	10	64.5	67.4	68.1	3.9	5.8	17
	µg/l	TN3		-0.69	12.7	25	11.6	12.6	12.7	1.8	14.5	11
	µg/l	V2M		-0.33	4.07	25	3.90	4.15	4.07	0.48	11.9	10
Fe	µg/l	A1M		-1.19	925	10	870	932	936	38	4.0	20
	µg/l	TN3		0.09	705	15	710	708	704	47	6.6	15
	µg/l	V2M		-0.25	119	20	116	119	119	10	8.0	15
Mg	mg/l	A1M		-0.98	1.20	10	1.14	1.22	1.23	0.05	3.7	16
	mg/l	TN3		-0.89	22.4	10	21.4	22.3	22.4	0.9	4.2	11
	mg/l	V2M		-0.21	6.80	10	6.73	6.83	6.80	0.17	2.5	14

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Mn	µg/l	A1M		-0.86	95.5	10	91.4	95.3	96.8	4.6	4.7	17
	µg/l	TN3		-0.13	159	10	158	157	159	7	4.7	13
	µg/l	V2M		-0.22	83.5	15	82.1	83.0	83.5	4.4	5.2	14
Ni	µg/l	A1M		0.14	85.5	10	86.1	86.2	86.5	4.7	5.5	18
	µg/l	TN3		0.23	63.9	15	65.0	64.4	63.9	4.0	6.3	12
	µg/l	V2M		0.61	4.35	15	4.55	4.33	4.35	0.23	5.2	10
Pb	µg/l	A1M		-1.22	73.6	10	69.1	73.0	72.6	4.0	5.5	15
	µg/l	TN3		0.51	51.9	15	53.9	48.4	48.6	3.5	7.2	11
Sr	µg/l	A1M		-0.98	89.5	10	85.1	90.7	90.6	3.2	3.6	12
	µg/l	TN3		-0.41	226	15	219	224	226	8	3.7	9
	µg/l	V2M		-0.81	91.0	10	87.3	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		-0.13	3.20	10	3.18	3.12	3.12	0.13	4.0	10
	µg/l	TN3		0.60	167000	10	172037	167000	169466	5335	3.1	9
	µg/l	V2M		0.14	23973	10	24141	23973	24208	937	3.9	11
Zn	µg/l	A1M		-0.33	121	10	119	123	125	7	5.7	19
	µg/l	TN3		0.30	134	15	137	137	134	11	7.8	15
	µg/l	V2M		0.03	46.4	15	46.5	46.0	46.4	3.4	7.3	14

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Al	µg/l	A1M		0.09	850	10	854	869	873	28	3.2	15
	µg/l	TN3		0.75	975	15	1030	979	964	80	8.3	13
	µg/l	V2M		0.08	261	20	263	260	264	27	10.0	13
Ba	µg/l	A1M		0.47	77.0	10	78.8	78.0	77.7	5.8	7.4	12
	µg/l	TN3		-0.20	33.1	15	32.6	33.1	33.0	1.7	5.2	8
	µg/l	V2M		-0.28	6.74	15	6.60	6.69	6.74	0.36	5.4	10
Ca	mg/l	A1M		0.45	2.20	10	2.25	2.23	2.23	0.06	2.6	12
	g/kg	KN4		1.10	32.8	15	35.5	32.3	32.8	1.8	5.5	7
	g/kg	KO4		0.44	33.7	15	34.8	33.2	33.7	2.4	7.1	10
	mg/l	TN3		0.82	68.3	10	71.1	68.3	68.3	2.9	4.2	10
	mg/l	V2M		0.30	32.9	10	33.4	32.9	32.6	1.3	4.0	13
Cu	mg/kg	KN4		0.82	330	20	357	345	330	26	7.8	7
	mg/kg	KO4		0.61	329	20	349	330	329	15	4.7	10
Fe	µg/l	A1M		0.41	925	10	944	932	936	38	4.0	20
	g/kg	KN4			125		71	125	103	32	30.6	7
	g/kg	KO4		0.46	130	20	136	130	130	6	4.5	9
	µg/l	TN3		0.70	705	15	742	708	704	47	6.6	15
	µg/l	V2M		0.08	119	20	120	119	119	10	8.0	15
K	mg/kg	KN4			9090		9530	9090	9297	301	3.2	5
	mg/kg	KO4		0.86	9115	15	9700	9050	9115	500	5.5	9
Mg	mg/l	A1M		0.33	1.20	10	1.22	1.22	1.23	0.05	3.7	16
	mg/kg	KN4		0.66	4020	15	4220	4020	3995	220	5.5	6
	mg/kg	KO4		0.99	3985	15	4280	3980	3985	230	5.8	9
	mg/l	TN3		0.00	22.4	10	22.4	22.3	22.4	0.9	4.2	11
	mg/l	V2M		0.06	6.80	10	6.82	6.83	6.80	0.17	2.5	14

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Mn	µg/l	A1M		0.69	95.5	10	98.8	95.3	96.8	4.6	4.7	17
	mg/kg	KN4		0.71	406	20	435	412	406	27	6.6	7
	mg/kg	KO4		0.81	405	20	438	404	405	34	8.3	10
	µg/l	TN3		1.01	159	10	167	157	159	7	4.7	13
	µg/l	V2M		0.14	83.5	15	84.4	83.0	83.5	4.4	5.2	14
P_{tot}	g/kg	KO4		1.03	32.4	15	34.9	32.4	32.2	1.8	5.5	8
Sr	µg/l	A1M		0.63	89.5	10	92.3	90.7	90.6	3.2	3.6	12
	µg/l	TN3		0.12	226	15	228	224	226	8	3.7	9
	µg/l	V2M		-0.11	91.0	10	90.5	90.6	91.0	3.6	4.0	10
S_{tot}	mg/l	A1M		-0.38	3.20	10	3.14	3.12	3.12	0.13	4.0	10
	mg/kg	KN4			7132		4520	7132	7174	3097	43.2	6
	mg/kg	KO4		1.20	10093	15	11000	10093	10114	609	6.0	8
	µg/l	TN3		0.00	167000	10	167000	167000	169466	5335	3.1	9
	µg/l	V2M		-0.06	23973	10	23900	23973	24208	937	3.9	11
Zn	µg/l	A1M		-0.17	121	10	120	123	125	7	5.7	19
	mg/kg	KN4		0.59	614	15	641	614	603	36	5.9	7
	mg/kg	KO4		1.51	574	15	639	574	574	45	7.9	10
	µg/l	TN3		0.40	134	15	138	137	134	11	7.8	15
	µg/l	V2M		-0.14	46.4	15	45.9	46.0	46.4	3.4	7.3	14

APPENDIX 8: Summary of the z and E_n scores

z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	21	22	23	%
Al	A1M	S	S	S	.	q	.	S	S	S	S	.	S	q	.	S	S	S	S	S	S	S	S	88.9
	TN3	u	S	S	.	S	.	.	.	S	S	.	S	S	.	.	S	U	S	.	S	S	S	85.7
	V2M	S	S	S	.	q	.	.	S	.	S	.	S	S	.	S	S	Q	S	U	.	S	S	80.0
As	A1M	S	S	S	S	.	.	.	S	S	S	.	S	S	.	S	S	S	S	S	S	S	.	100
	KO4	.	.	.	.	.	S	.	S	.	S	.	S	.	.	.	S	S	S	S	.	.	.	100
	TN3	S	S	S	S	.	.	.	.	S	S	.	S	S	.	.	S	.	S	.	S	S	.	100
	TY3	.	u	.	S	.	.	.	S	.	S	.	.	.	.	S	.	S	S	u	.	.	.	75.0
	V2M	S	S	S	S	.	.	.	.	.	S	.	S	S	.	S	S	S	S	U	.	u	.	84.6
B	A1M	.	u	S	.	S	.	.	S	.	S	.	S	u	.	Q	S	S	U	S	.	S	.	69.2
	TN3	.	S	S	.	S	.	.	.	.	S	.	S	S	.	.	S	.	Q	.	.	S	.	88.9
	V2M	.	S	S	.	S	.	.	S	.	S	.	S	S	.	S	S	.	S	U	.	S	.	91.7
Ba	A1M	.	S	U	.	.	.	.	S	.	S	.	S	S	.	S	S	S	S	q	.	.	S	83.3
	TN3	.	S	S	.	.	.	.	.	.	S	.	S	S	.	.	S	.	S	.	.	.	S	100
	V2M	.	S	S	.	.	.	.	.	.	S	.	S	S	.	S	S	S	S	U	.	.	S	90.9
Ca	A1M	.	u	S	.	S	.	.	S	S	S	.	S	U	.	U	S	S	U	S	S	S	S	75.0
	KN4	.	.	S	.	S	.	.	.	.	S	.	S	S	.	S	.	.	.	.	.	.	S	100
	KO4	S	.	.	.	.	S	.	S	.	S	.	S	.	.	.	S	S	S	S	.	.	S	100
	TN3	.	u	S	.	S	.	.	.	.	S	.	S	S	.	.	S	.	S	.	S	S	S	90.9
	V2M	S	u	S	.	S	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	S	S	86.7
Cd	A1M	S	S	S	S	.	.	.	S	S	S	.	S	S	.	S	S	S	S	S	S	S	.	100
	KO4	S	.	.	.	.	.	.	S	.	S	.	S	.	.	.	S	Q	u	S	.	.	.	75.0
	TN3	S	S	S	S	.	.	.	.	S	S	.	S	S	.	.	S	.	S	.	S	S	.	100
	TY3	.	u	.	S	.	.	.	S	.	S	.	.	.	.	S	.	S	S	u	.	.	.	75.0
	V2M	S	S	S	S	.	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	u	.	85.7
Co	A1M	.	S	S	S	.	.	.	S	S	S	.	S	S	.	S	S	S	S	S	S	S	.	100
	TN3	.	S	S	S	.	.	.	.	S	S	.	S	S	.	.	S	.	S	.	S	S	.	100
	V2M	.	S	S	S	.	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	S	.	92.3
Cr	A1M	S	S	S	S	.	.	S	S	S	S	S	S	S	.	S	S	S	S	q	S	S	.	94.4
	KO4	S	.	.	.	.	S	.	S	.	S	.	Q	.	.	.	S	S	S	S	.	.	.	88.9
	TN3	S	S	S	S	.	.	.	.	S	S	S	S	S	.	.	S	.	S	.	S	S	.	100
	TY3	.	u	.	S	.	.	S	S	.	S	.	.	.	.	S	.	S	S	u	.	.	.	77.8
	V2M	S	S	S	S	.	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	S	.	92.9
Cu	A1M	.	S	S	S	S	.	S	S	S	S	.	S	S	.	Q	S	S	S	S	S	S	.	94.1
	KN4	.	.	S	.	S	.	.	.	.	S	.	S	S	.	S	.	.	.	.	.	.	S	100
	KO4	S	.	.	.	.	S	.	S	.	S	.	S	.	.	.	S	S	S	S	.	.	S	100
	TN3	U	S	S	S	.	.	.	.	Q	S	.	S	S	.	.	S	.	S	.	S	S	.	83.3
	V2M	U	S	S	.	.	.	.	.	.	S	.	S	S	.	S	S	S	S	U	.	S	.	83.3
Fe	A1M	S	S	S	S	S	.	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	100
	KO4	.	.	.	.	.	S	.	S	.	S	.	S	.	.	.	S	S	S	S	.	.	S	100
	TN3	S	S	S	S	S	.	.	.	S	S	S	S	S	.	.	S	.	S	.	S	S	S	100
	TY3	.	u	.	S	.	.	S	S	.	S	.	.	.	.	Q	.	S	S	u	.	.	.	66.7
	V2M	S	S	S	S	S	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	S	S	93.8

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	21	22	23	%
Hg	A1Hg	S	*u*	*S*	*S*	.	.	.	S	.	S	.	S	Q	S	S	S	S	S	u	S	.	.	80.0
	T3Hg	S	*u*	*S*	*S*	.	.	.	S	.	S	.	S	S	S	S	S	U	S	U	S	.	.	80.0
	V2Hg	S	*u*	*S*	*S*	.	.	.	S	.	S	.	S	S	.	S	S	S	S	u	.	.	.	84.6
K	KO4	*S*	.	.	.	.	S	.	*S*	.	u	.	*S*	.	.	.	*S*	*S*	*S*	S	.	.	S	90.0
Mg	A1M	.	*S*	*S*	.	S	.	.	S	*S*	S	.	*S*	S	.	S	S	S	S	S	*S*	*S*	S	100
	KN4	.	.	*S*	.	*S*	.	.	.	.	*S*	.	*S*	*S*	.	*u*	.	.	.	.	.	.	S	85.7
	KO4	.	.	.	.	.	S	.	S	.	*S*	.	*S*	.	.	.	*S*	*S*	*S*	S	.	.	S	100
	TN3	.	*S*	*S*	.	*S*	.	.	.	.	S	.	*S*	S	.	.	S	.	S	.	*S*	*S*	S	100
	V2M	*S*	*S*	*S*	.	*S*	.	.	S	.	S	.	*S*	S	.	S	S	*S*	S	U	.	*S*	S	93.3
Mn	A1M	.	*S*	*S*	.	Q	.	*S*	S	*S*	S	.	S	S	.	S	S	S	S	S	*S*	*S*	S	94.1
	KN4	.	.	*S*	.	*S*	.	.	.	.	*S*	.	*S*	*S*	.	*S*	.	.	.	.	.	.	S	100
	KO4	*S*	.	.	.	.	S	.	*S*	.	*S*	.	*S*	.	.	.	S	*S*	*S*	S	.	.	S	100
	TN3	*S*	*S*	*S*	.	*S*	.	.	.	*S*	S	.	S	S	.	.	S	.	S	.	*S*	*S*	S	100
	V2M	*S*	*S*	*S*	.	*S*	.	.	S	.	S	.	*S*	S	.	S	S	*S*	S	U	.	*S*	S	93.3
Mo	A1M	.	*S*	*S*	*S*	S	.	.	S	*S*	S	*S*	S	S	.	S	S	S	S	q	*S*	.	.	93.8
	KO4	.	.	.	.	.	S	.	S	.	S	.	*S*	.	.	.	S	*u*	S	S	.	.	.	87.5
	TN3	.	*Q*	*S*	*S*	*S*	.	.	.	*S*	S	*S*	S	S	.	.	S	.	*Q*	.	*S*	.	.	83.3
	V2M	.	*S*	*S*	*q*	.	.	.	S	.	S	.	S	S	.	S	S	S	*S*	U	.	.	.	83.3
Ni	A1M	S	*Q*	*S*	*S*	.	.	*S*	S	*S*	S	*S*	S	S	.	S	S	S	S	S	*S*	*S*	.	94.4
	KO4	.	.	.	.	.	.	.	S	.	S	.	*S*	.	.	.	S	S	S	S	.	.	.	100
	TN3	S	*S*	*S*	*q*	.	.	.	.	*S*	S	*S*	S	S	.	.	S	.	*S*	.	*S*	*S*	.	92.3
	TY3	.	*u*	.	*S*	.	.	*S*	S	.	S	.	.	.	.	Q	.	S	*S*	u	.	.	.	66.7
	V2M	.	*S*	*S*	.	.	.	.	.	.	S	.	S	S	.	S	S	S	*S*	U	.	*S*	.	90.9
N_{tot}	KX4	*S*	.	.	.	*S*	*S*	.	.	.	S	.	.	.	.	.	.	S	*S*	.	.	.	.	100
Pb	A1M	U	*S*	*S*	*S*	.	.	*S*	S	.	S	.	S	S	.	S	S	S	S	q	*S*	*S*	.	87.5
	KO4	*S*	.	.	.	.	S	.	S	.	S	.	*S*	.	.	.	S	S	S	*S*	.	.	.	100
	TN3	S	*S*	*S*	*q*	.	.	.	.	.	S	.	S	S	.	.	S	.	S	.	*S*	*S*	.	90.9
	TY3	.	*u*	.	*S*	.	.	*S*	S	.	S	.	.	.	.	S	.	S	S	u	.	.	.	77.8
	V2M	S	*S*	*U*	.	.	.	.	.	.	S	.	S	S	.	S	S	q	S	U	.	.	.	72.7
P_{tot}	KO4	.	.	.	.	.	S	.	*U*	.	S	.	*S*	.	.	.	*S*	*S*	*S*	S	.	.	*S*	88.9
Sb	A1M	.	*S*	*S*	*S*	.	.	.	S	.	S	.	S	S	.	S	S	S	S	q	*S*	.	.	92.3
	TN3	.	*S*	*S*	*q*	.	.	.	.	.	S	.	S	S	.	.	S	.	S	.	*S*	.	.	88.9
	V2M	.	*S*	*S*	.	.	.	.	.	.	S	.	S	Q	.	S	S	S	S	U	.	.	.	80.0
Se	A1M	.	*S*	*S*	*S*	.	.	.	U	.	S	.	S	S	.	S	S	Q	S	u	*S*	.	.	76.9
	TN3	.	*S*	*S*	*S*	.	.	.	.	.	S	.	S	S	.	.	S	.	S	.	*S*	.	.	100
	V2M	.	*u*	*Q*	.	.	.	.	.	.	S	.	S	S	.	Q	S	U	S	U	.	.	.	50.0
Sn	A1M	.	S	*Q*	.	.	.	.	S	.	S	.	S	S	.	*S*	*S*	*S*	.	u	*S*	.	.	81.8
	TN3	.	*S*	*U*	.	.	.	.	.	.	S	.	S	S	.	.	*S*	.	.	.	*S*	.	.	85.7
	TY3	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
	V2M	.	*S*	*S*	.	.	.	.	.	.	S	.	S	S	.	*S*	S	*S*	.	U	.	.	.	88.9
Sr	A1M	.	*S*	.	.	.	.	.	*S*	.	S	.	S	*S*	.	*S*	S	.	*S*	S	*S*	*S*	S	100
	TN3	.	*S*	.	.	.	.	.	.	.	S	.	*S*	*S*	.	.	S	.	*S*	.	*S*	*S*	S	100
	V2M	.	*S*	.	.	.	.	.	*S*	.	S	.	*S*	*S*	.	*S*	S	.	*S*	U	.	*S*	S	90.9
S_{tot}	A1M	.	.	*S*	.	S	.	.	*S*	.	S	.	*S*	*S*	.	.	S	*S*	*S*	U	*S*	*S*	S	92.3
	KO4	.	.	.	.	.	*S*	.	*S*	.	*S*	.	*U*	.	.	.	*S*	*S*	*S*	S	.	.	*S*	88.9
	TN3	.	.	*S*	.	*S*	.	.	.	.	S	.	*S*	*S*	.	.	S	.	*u*	.	*S*	*S*	*S*	90.0
	V2M	.	.	*S*	.	*S*	.	.	*S*	.	S	.	*S*	*S*	.	.	S	*S*	*S*	U	.	*S*	*S*	91.7

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	21	22	23	%
V	A1M	.	*S*	*S*	.	.	.	.	S	.	S	.	S	S	.	S	S	S	S	S	.	.	.	100
	KO4	.	.	.	.	.	.	.	S	.	S	.	*S*	.	.	.	S	S	q	S	.	.	.	85.7
	TN3	.	*S*	*S*	.	.	.	.	.	.	S	.	S	S	.	.	S	.	S	.	.	.	.	100
	V2M	.	*S*	*S*	.	.	.	.	.	.	S	.	S	S	.	S	S	S	*S*	U	.	.	.	90.0
Zn	A1M	.	*Q*	S	S	S	.	*S*	Q	*S*	S	*S*	S	S	.	S	S	Q	S	S	*S*	S	S	84.2
	KN4	.	.	*S*	.	*S*	.	.	.	.	S	.	*S*	S	.	*S*	.	.	.	.	.	.	S	100
	KO4	S	.	.	.	.	S	.	S	.	S	.	S	.	.	.	S	S	S	S	.	.	S	100
	TN3	S	*S*	S	S	*S*	.	.	.	*S*	S	*S*	S	S	.	.	S	.	S	.	*S*	S	S	100
	TY3	.	*u*	.	*S*	.	.	*S*	S	.	S	.	.	.	.	S	.	S	S	u	.	.	.	77.8
	V2M	S	*Q*	S	S	*S*	.	.	S	.	S	.	S	S	.	S	S	S	S	U	.	*S*	S	87.5
%		90	74	93	90	91	100	100	95	96	99	100	98	93	100	88	100	87	92	44	100	96	100	
accredited		26				11	11		53		92		59	66	2	49	80	56	59	70			22	

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, % - percentage of satisfactory results

Totally satisfactory, % in all: 90 % in accredited: 89 % in non-accredited: 92

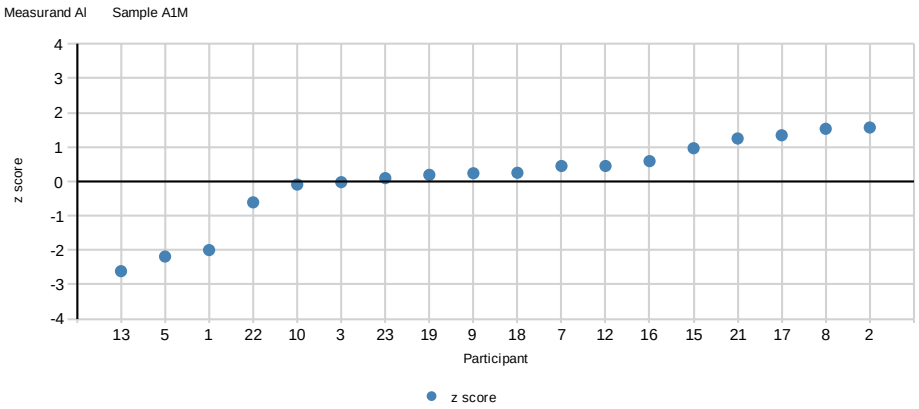
E_n scores

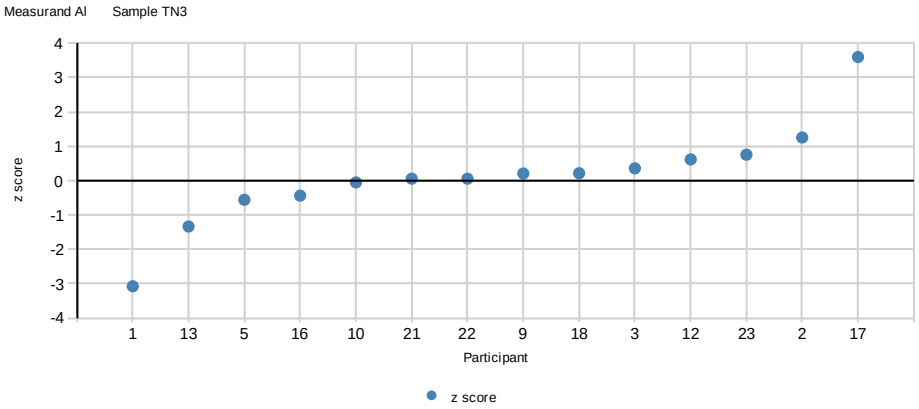
Measurand	Sample	2	5	7	8	10	12	13	15	16	17	18	19	23	%
Al	TY3	-28.5	.	0.1	0.2	-0.2	.	.	1.4	.	.	-0.2	-11.0	.	57.1
As	KN4	.	.	.	.	0.0	-1.1	0.0	0.3	.	.	.	.	.	75.0
B	TY3	-8.3	.	.	-1.1	0.4	.	.	0.3	.	0.0	.	-5.7	.	50.0
Ba	TY3	-14.3	.	.	0.0	0.0	.	.	0.8	.	-0.1	-0.4	-9.3	.	71.4
Ca	TY3	-11.2	.	.	0.0	0.0	.	.	0.9	.	-0.4	-0.5	-4.1	.	71.4
Cd	KN4	.	.	.	.	-0.1	0.0	0.0	0.8	.	.	.	.	.	100
Co	TY3	-10.6	.	.	0.0	0.0	.	.	1.2	.	0.7	-0.2	-5.6	.	57.1
Cr	KN4	.	.	.	.	0.0	0.5	0.5	-0.2	.	.	.	.	.	100
Cu	TY3	-7.6	.	-1.3	0.2	-0.4	.	.	0.8	.	0.0	-1.0	-5.1	.	50.0
Fe	KN4	.	-1.9	.	.	0.0	-1.7	0.2	0.1	.	.	.	.	-1.8	50.0
Hg	KN4	.	.	.	.	.	-0.2	0.2	0.4	.	.	.	.	.	100
	KO4	.	.	.	-1.0	.	1.2	.	.	0.7	-0.5	.	0.9	.	60.0
K	KN4	.	0.0	.	.	-34.5	0.0	0.0	-34.5	.	.	.	.	0.3	66.7
Mg	TY3	0.5	.	.	-0.1	-0.3	.	.	1.1	.	-0.1	0.1	-6.2	.	71.4
Mn	TY3	-39.9	.	0.0	0.4	-0.1	.	.	1.3	.	0.0	-0.1	-5.0	.	62.5
Mo	KN4	.	-1.6	.	.	0.3	-0.4	0.4	0.3	.	.	.	.	.	80.0
	TY3	-12.6	.	.	0.0	-0.1	.	.	0.9	.	0.0	0.5	-12.6	.	71.4
Ni	KN4	.	.	.	.	-0.4	0.1	0.0	-0.5	.	.	.	.	.	100
Pb	KN4	.	.	.	.	-0.3	-0.3	0.0	0.0	.	.	.	.	.	100
Sb	TY3	-23.8	.	.	0.0	0.4	.	.	-0.2	.	1.7	-0.2	-18.2	.	57.1
Se	TY3	-6.7	.	.	0.3	0.0	.	.	-0.1	.	0.7	-0.8	-5.1	.	71.4
Sn	TY3	-16.4	.	.	-0.2	-0.2	.	.	0.3	.	0.1	.	-12.6	.	66.7
Sr	TY3	-9.2	.	.	-0.2	0.2	.	.	0.8	.	.	.	-4.6	.	60.0
S_{tot}	KN4	.	-1.3	.	.	0.8	-0.9	1.0	.	.	.	.	.	-1.0	40.0
	TY3	.	.	.	0.1	-0.2	.	.	.	.	0.0	.	-22.0	.	75.0
V	KN4	.	.	.	.	0.0	0.0	0.0	-0.1	.	.	.	.	.	100
	TY3	-5.0	.	.	-0.9	0.0	.	.	0.8	.	0.7	-0.2	-4.2	.	71.4
%		7	25	67	88	96	75	100	79	100	93	91	6	67	

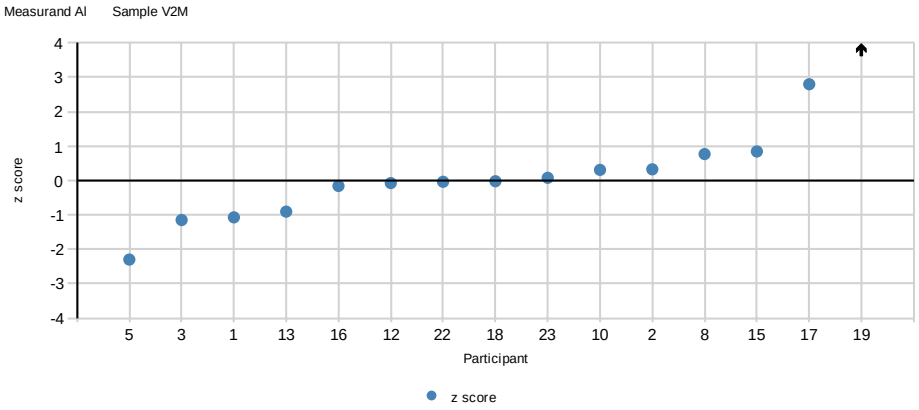
Scores of -1.0 < E_n < 1.0 indicate successful performance
Scores of E_n ≥ 1.0 or E_n ≤ -1.0 indicate a need to review the uncertainty estimated or to correct a measurement issue

Totally satisfactory, in all: 72 %

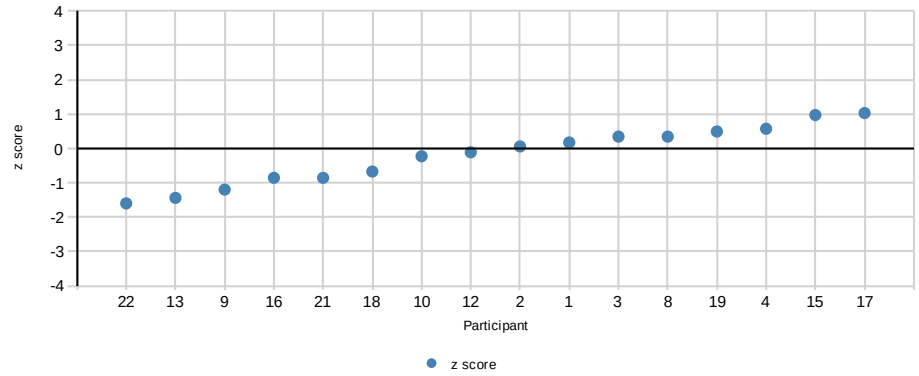
APPENDIX 9: z scores in ascending order



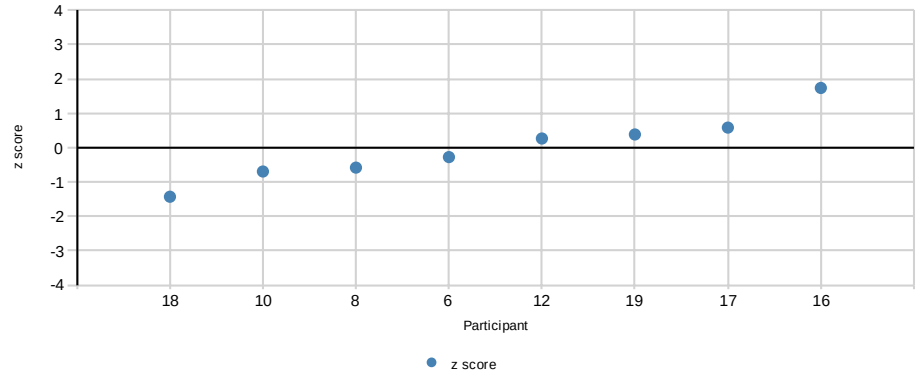




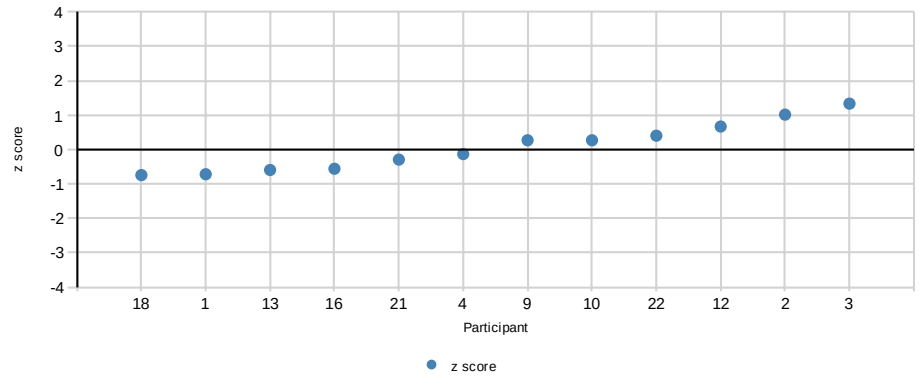
Measurand As Sample A1M

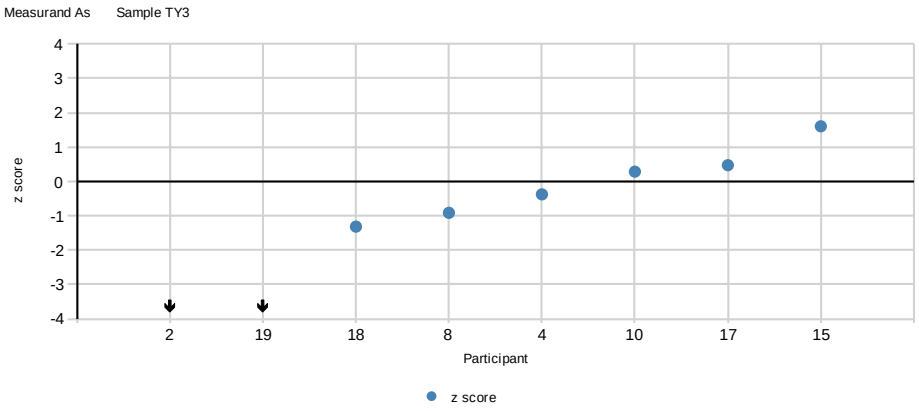


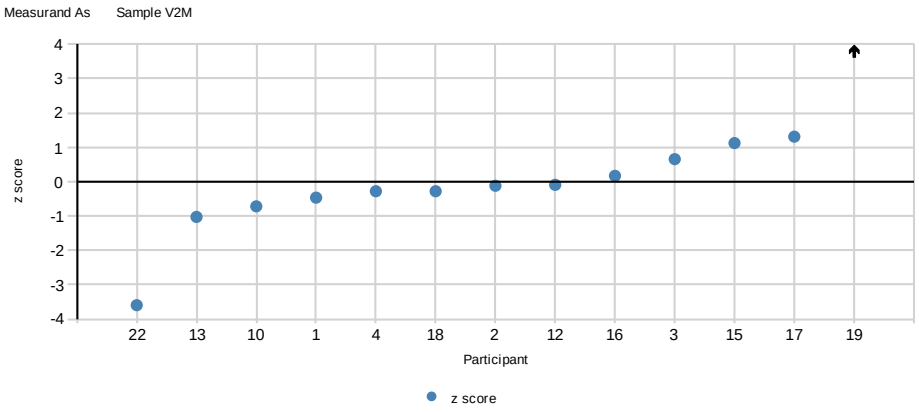
Measurand As Sample KO4

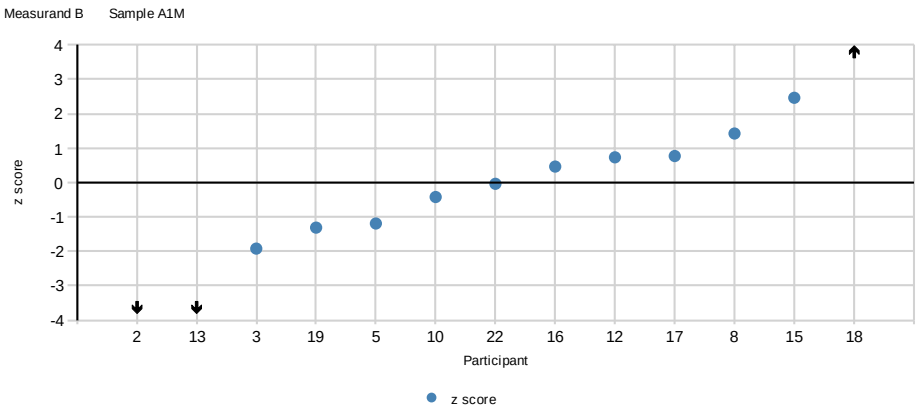


Measurand As Sample TN3

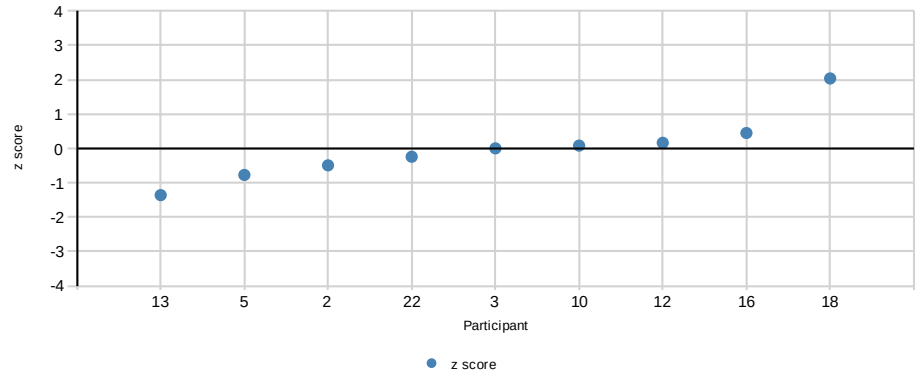



Measurand As Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
2
19
18
8
4
10
17
15
Participant
z score

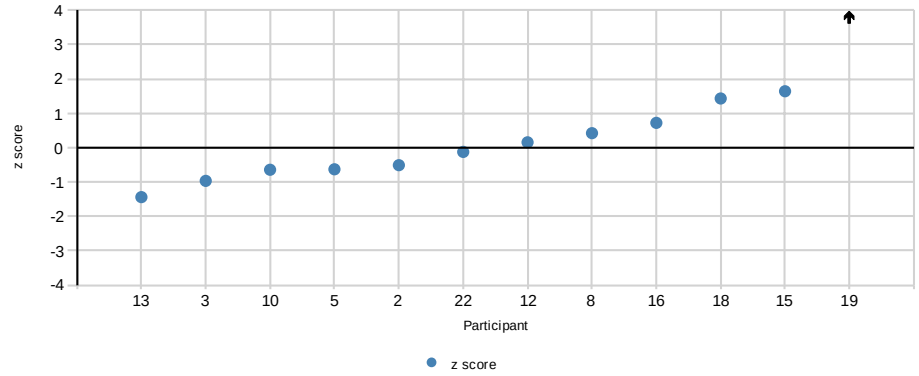

Measurand As Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
22
13
10
1
4
18
2
12
16
3
15
17
19
Participant
z score


Measurand B Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
2
13
3
19
5
10
22
16
12
17
8
15
18
Participant
z score

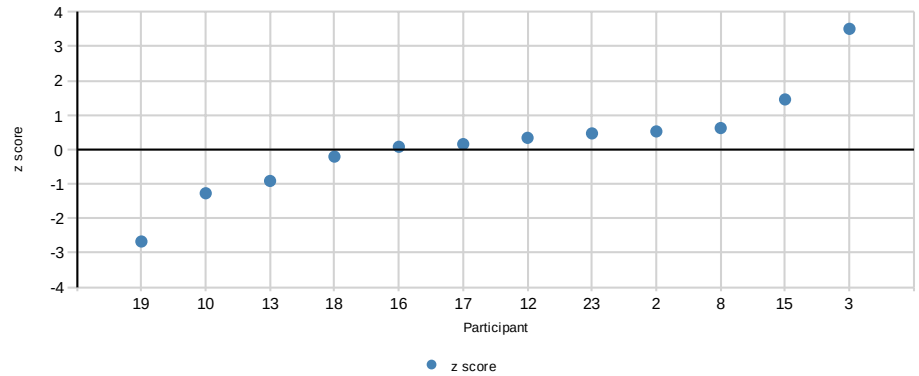
Measurand B Sample TN3

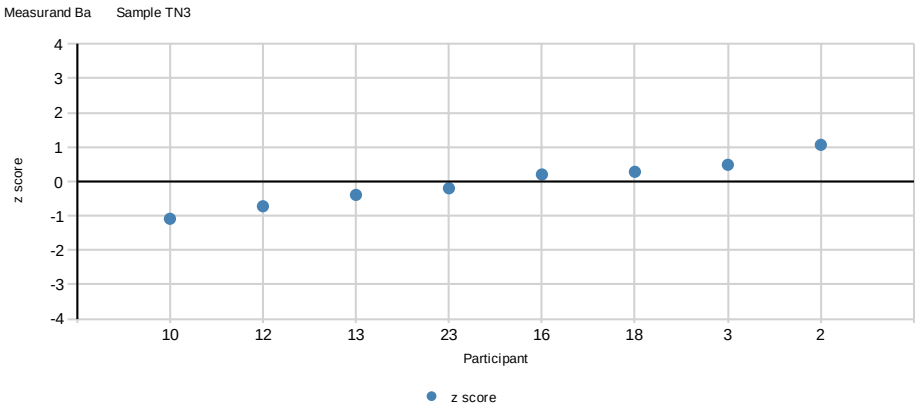


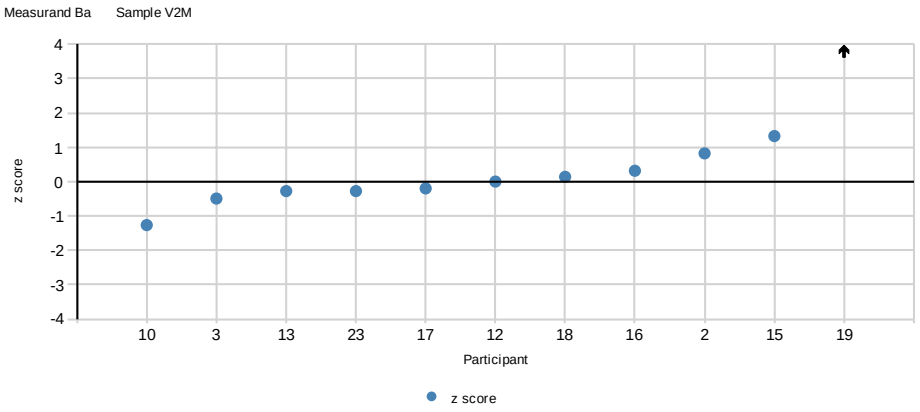
Measurand B Sample V2M

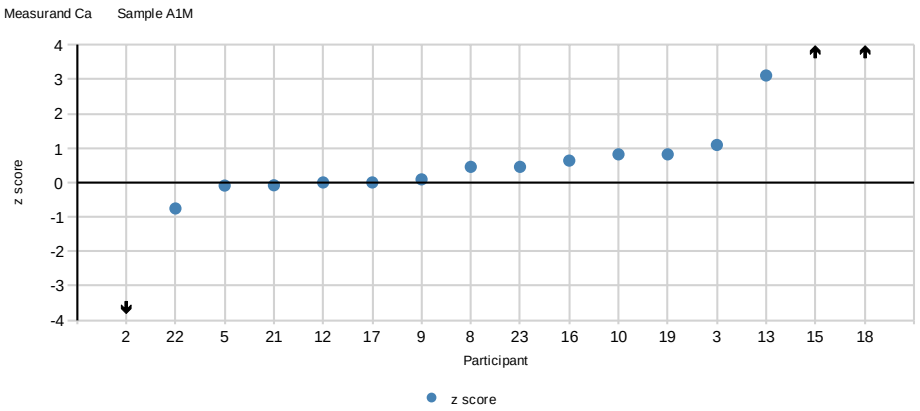


Measurand Ba Sample A1M

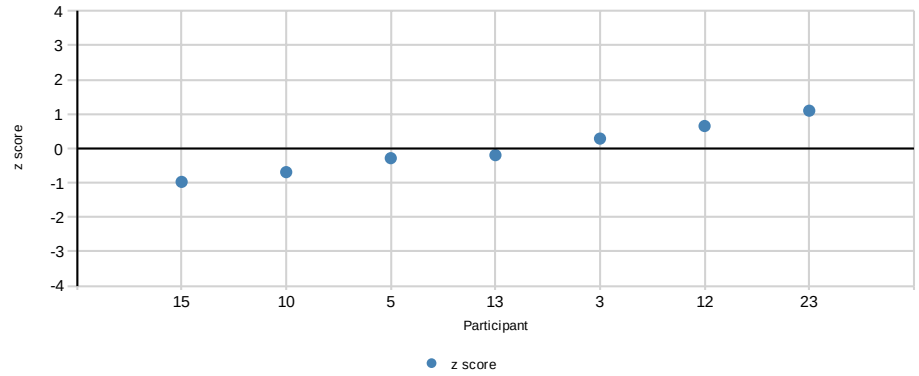



Measurand Ba Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
10 12 13 23 16 18 3 2
Participant
z score

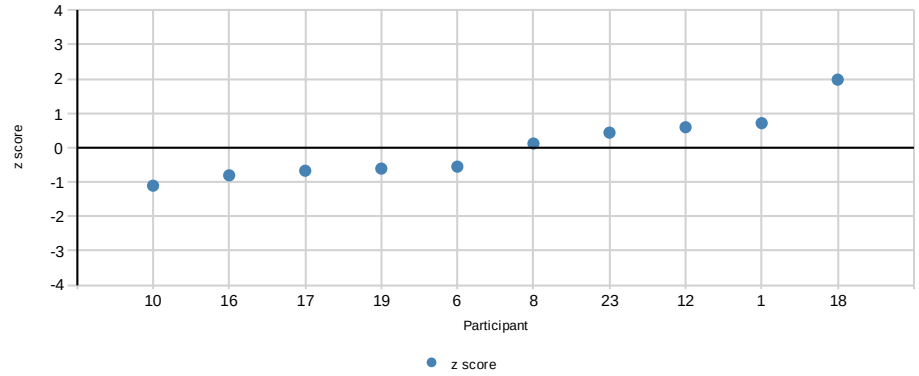

Measurand Ba Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
10 3 13 23 17 12 18 16 2 15 19
Participant
z score


Measurand Ca Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
2 22 5 21 12 17 9 8 23 16 10 19 3 13 15 18
Participant
z score

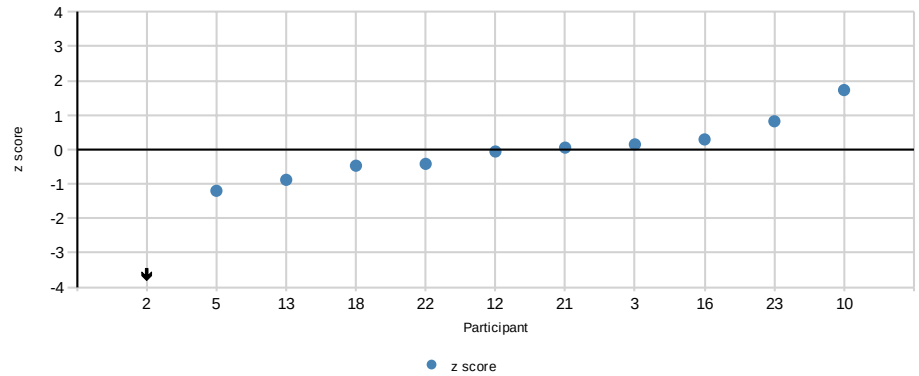
Measurand Ca Sample KN4

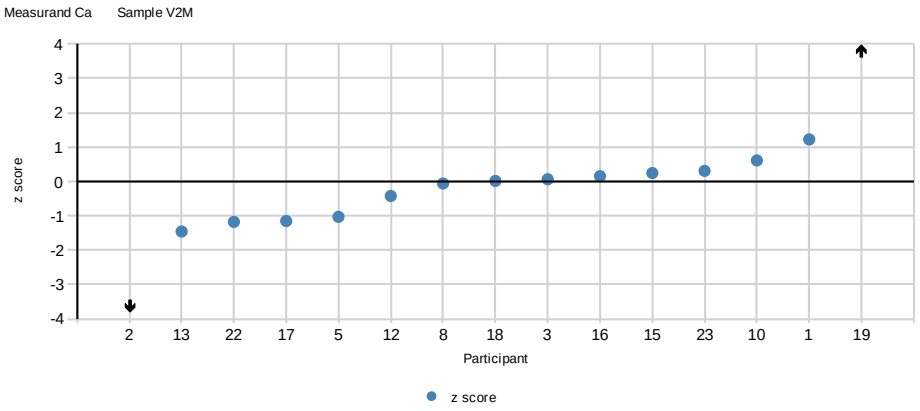


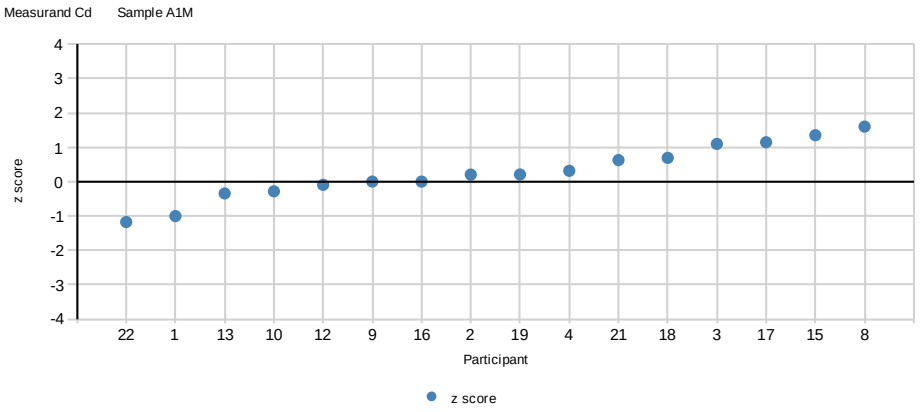
Measurand Ca Sample KO4

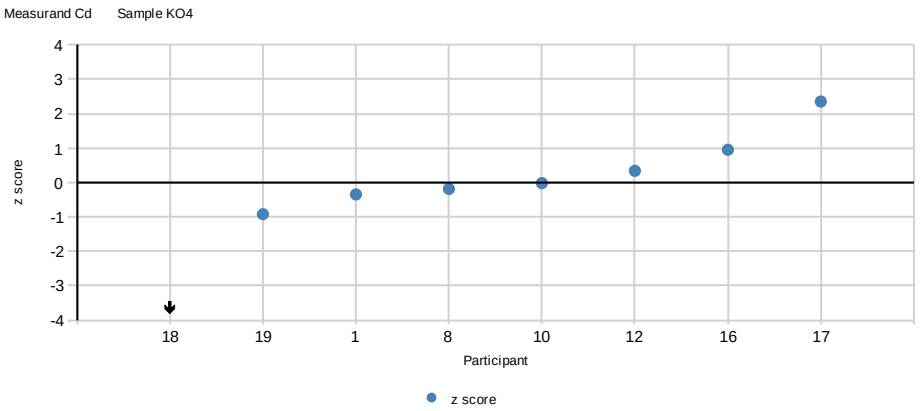


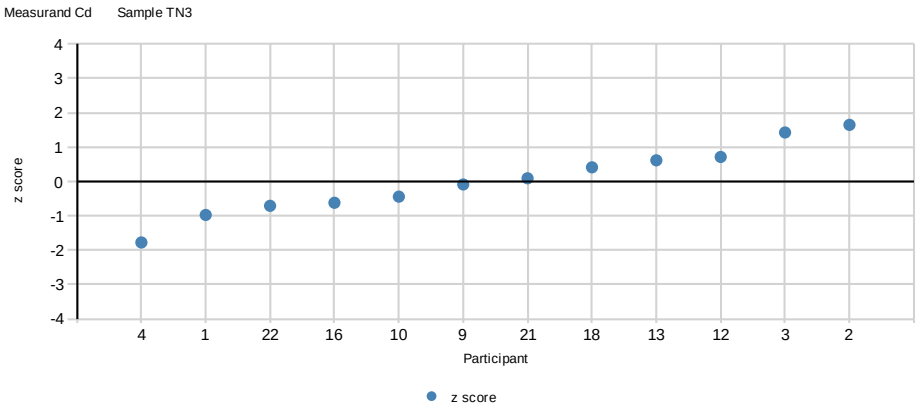
Measurand Ca Sample TN3

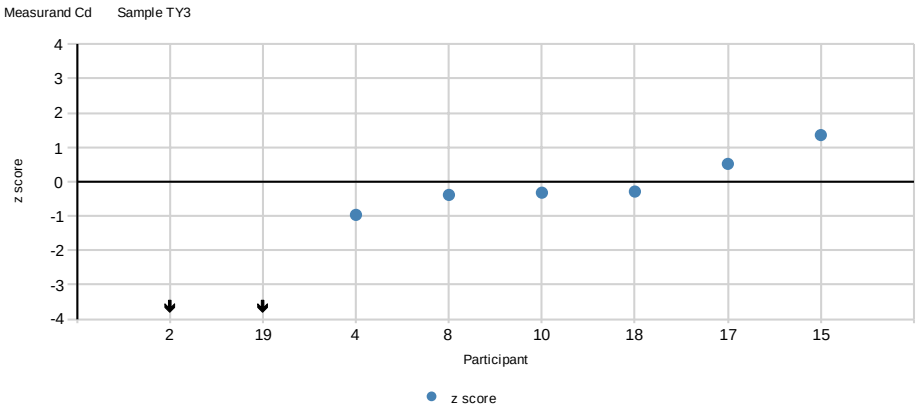


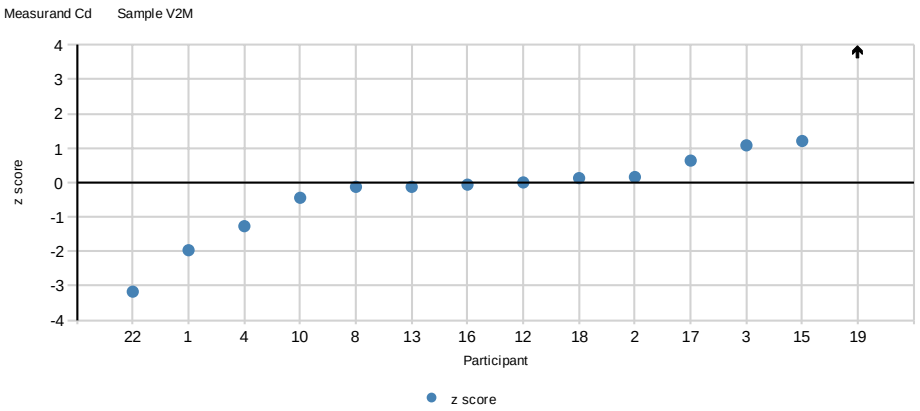

Measurand Ca Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
2 13 22 17 5 12 8 18 3 16 15 23 10 1 19
Participant
z score

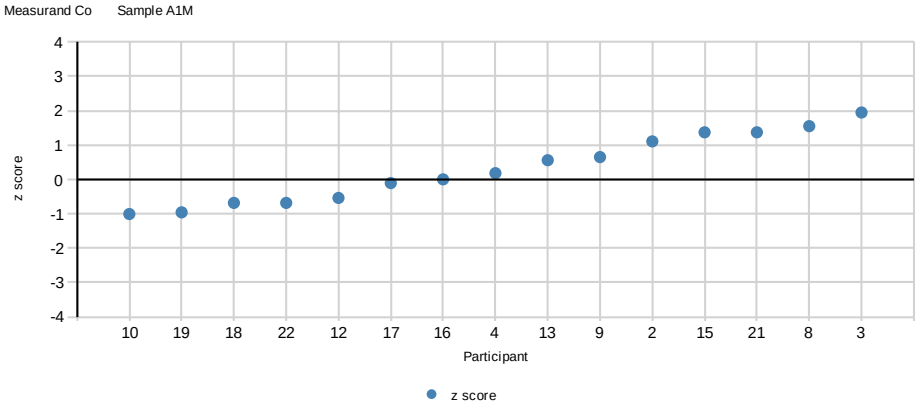

Measurand Cd Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
22 1 13 10 12 9 16 2 19 4 21 18 3 17 15 8
Participant
z score

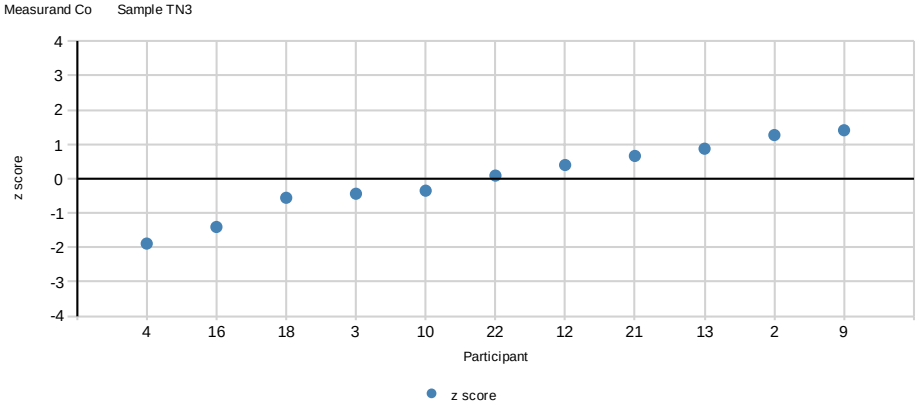

Measurand Cd Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
18 19 1 8 10 12 16 17
Participant
z score

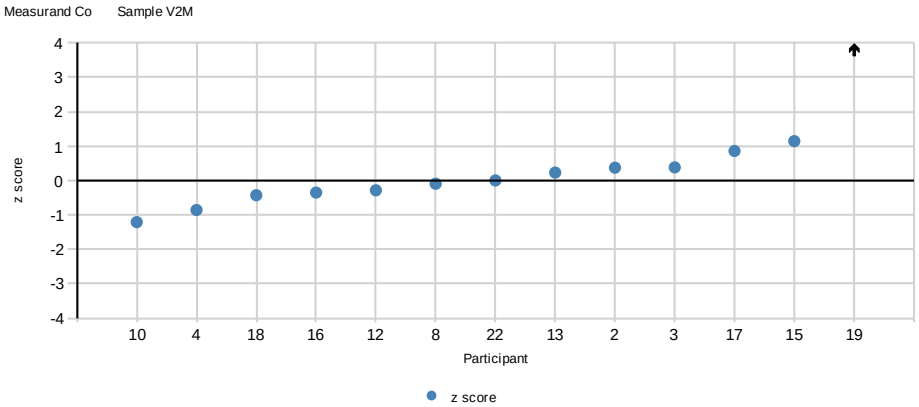

Measurand Cd
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4
1
22
16
10
9
21
18
13
12
3
2
Participant
z score


Measurand Cd
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
2
19
4
8
10
18
17
15
Participant
z score

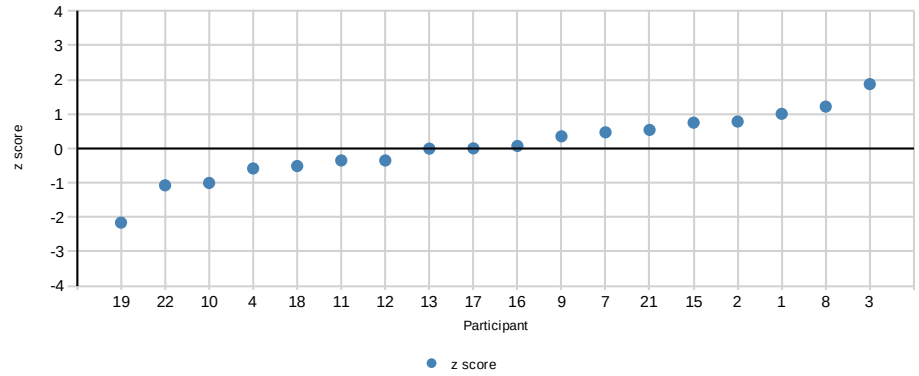

Measurand Cd
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
22
1
4
10
8
13
16
12
18
2
17
3
15
19
Participant
z score


Measurand Co
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
10 19 18 22 12 17 16 4 13 9 2 15 21 8 3
Participant
z score

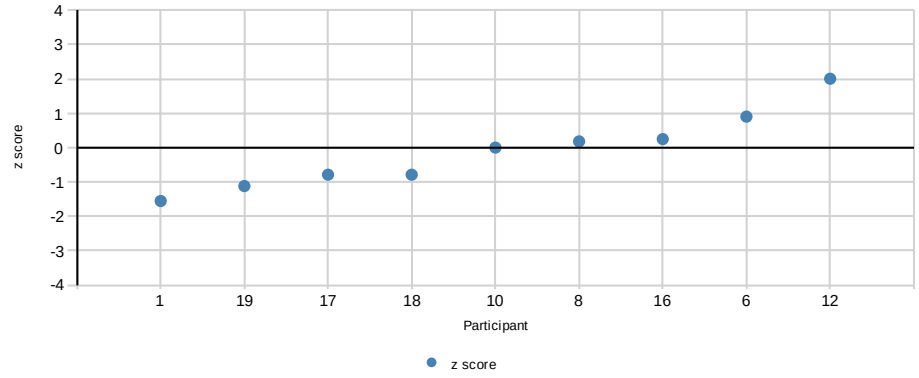

Measurand Co
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4 16 18 3 10 22 12 21 13 2 9
Participant
z score


Measurand Co
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
10 4 18 16 12 8 22 13 2 3 17 15 19
Participant
z score

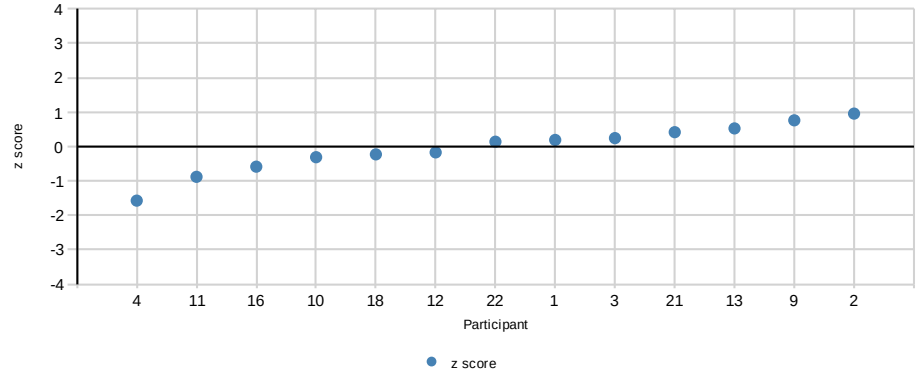
Measurand Cr Sample A1M

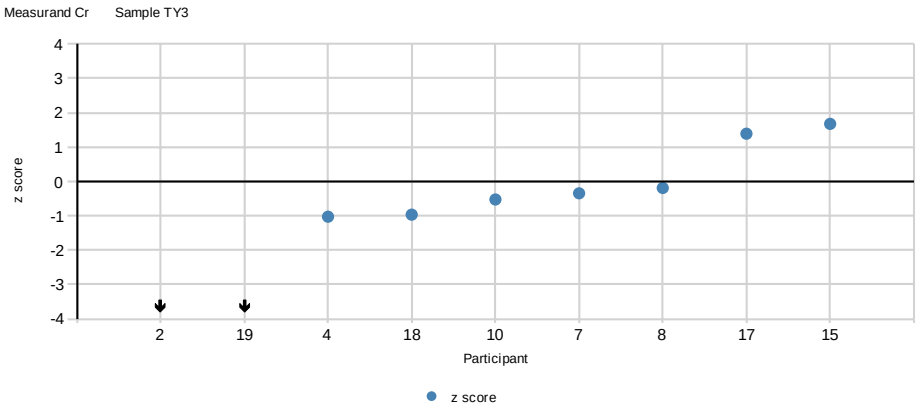


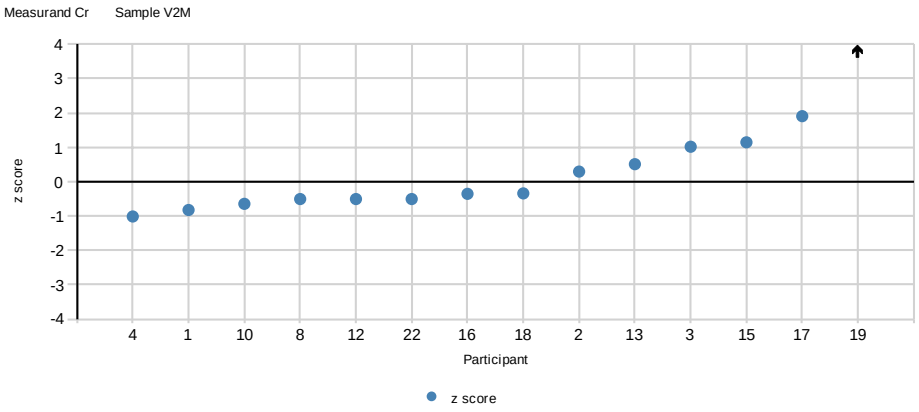
Measurand Cr Sample KO4

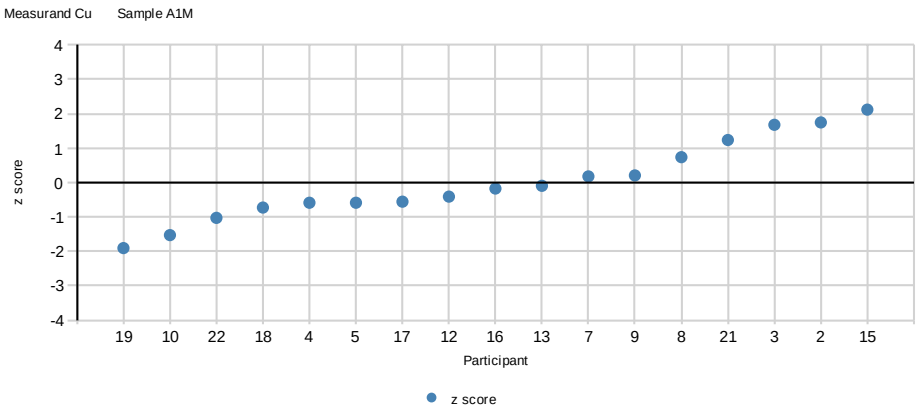


Measurand Cr Sample TN3

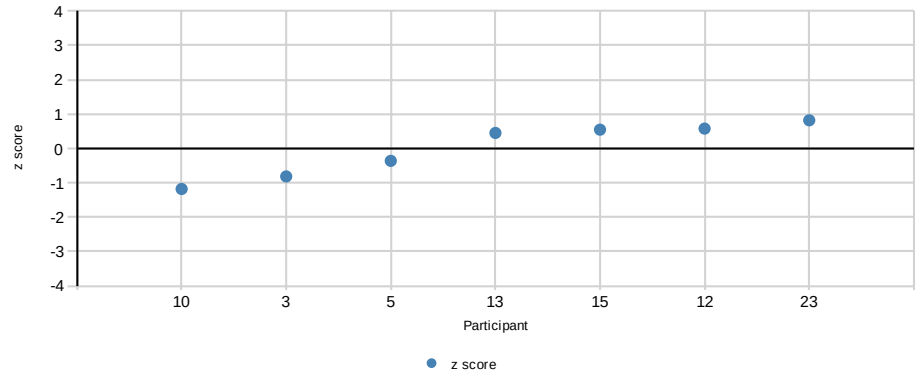



Measurand Cr Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
2 19 4 18 10 7 8 17 15
Participant
z score

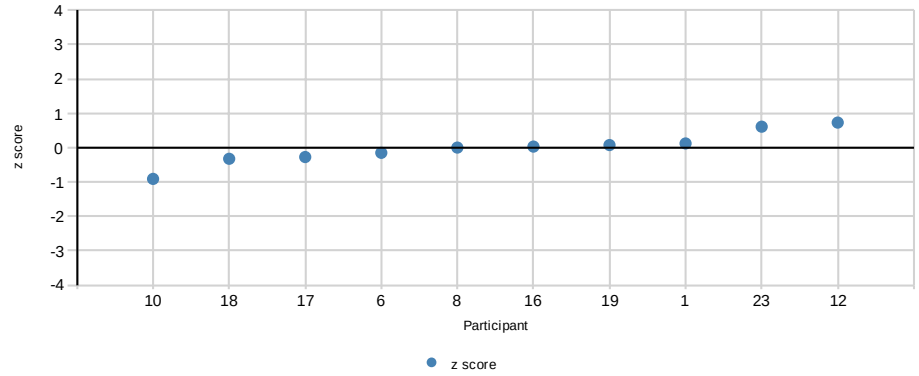

Measurand Cr Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
4 1 10 8 12 22 16 18 2 13 3 15 17 19
Participant
z score


Measurand Cu Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 10 22 18 4 5 17 12 16 13 7 9 8 21 3 2 15
Participant
z score

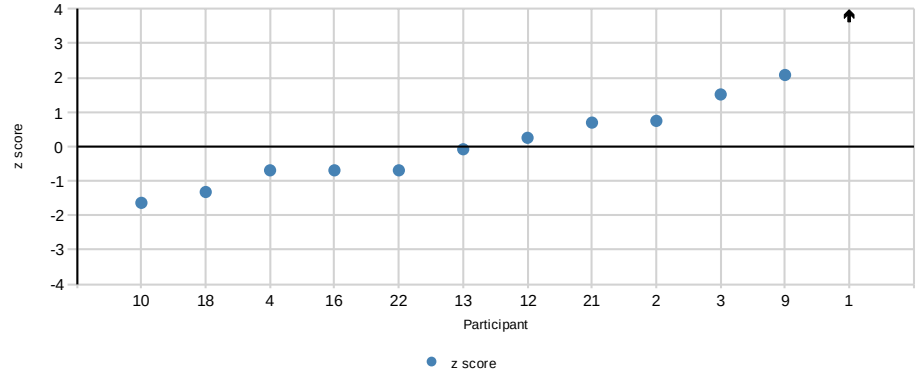
Measurand Cu Sample KN4

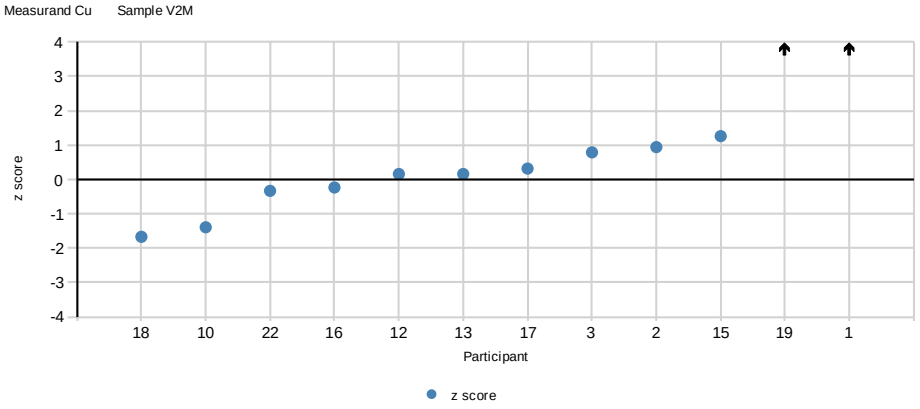


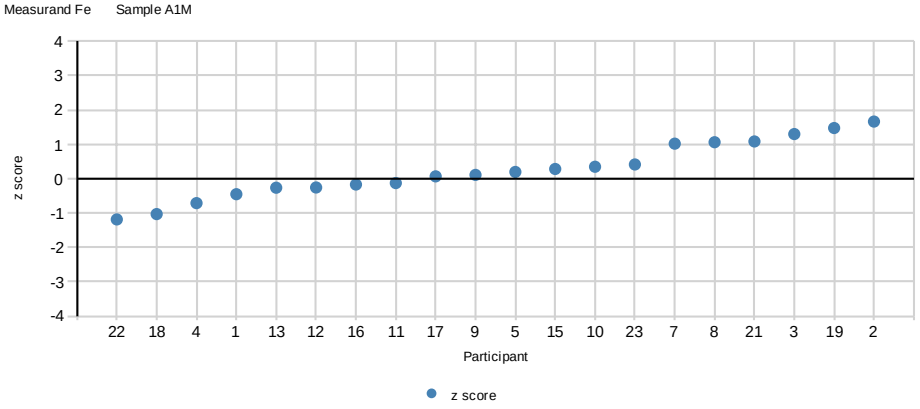
Measurand Cu Sample KO4

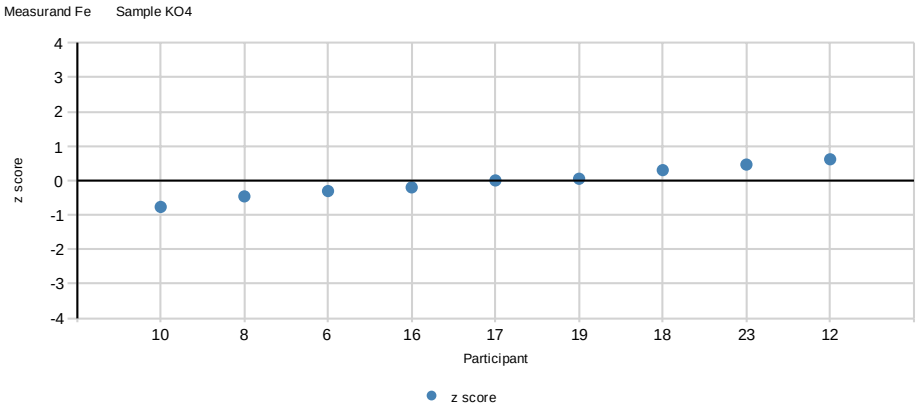


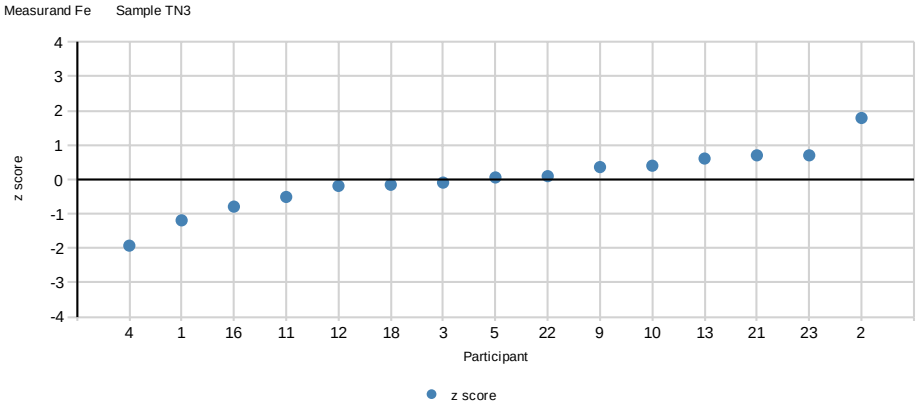
Measurand Cu Sample TN3

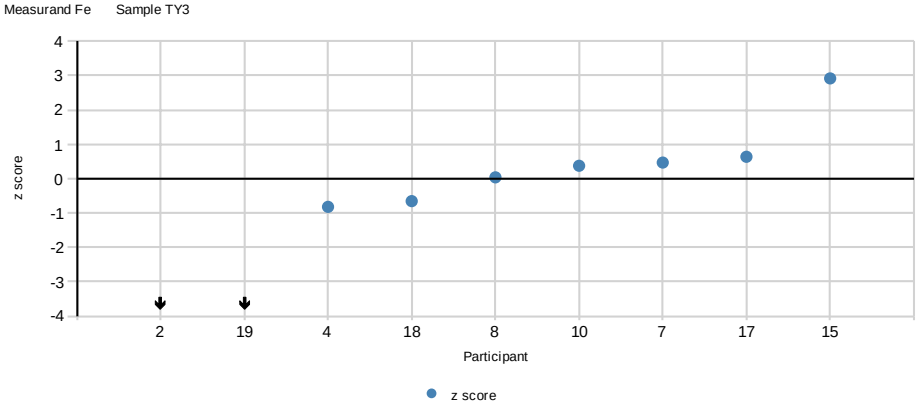


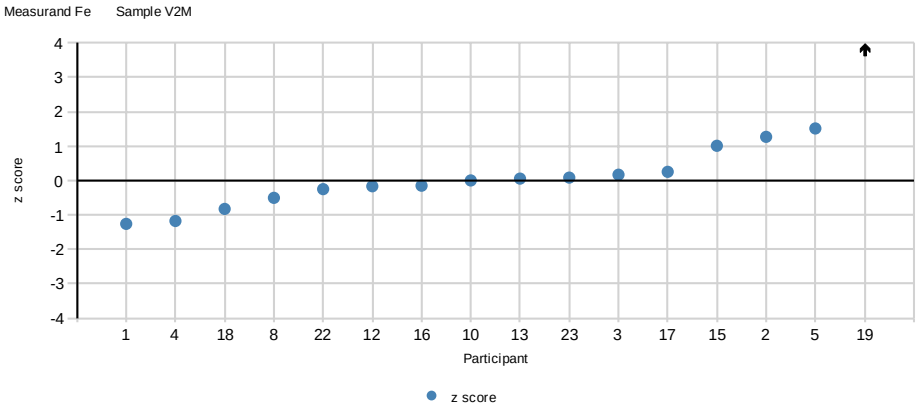

Measurand Cu Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
18 10 22 16 12 13 17 3 2 15 19 1
Participant
z score

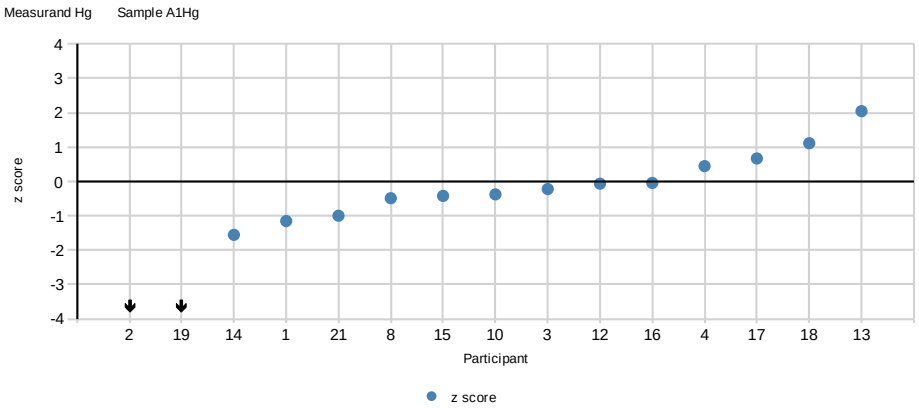

Measurand Fe Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
22 18 4 1 13 12 16 11 17 9 5 15 10 23 7 8 21 3 19 2
Participant
z score

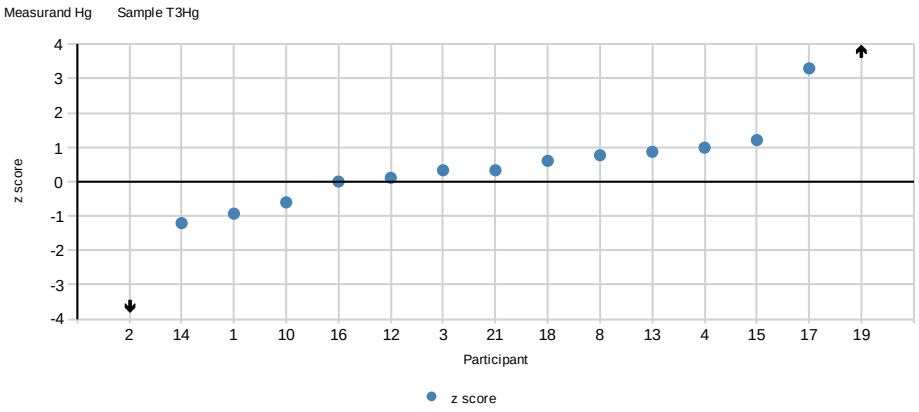

Measurand Fe Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
10 8 6 16 17 19 18 23 12
Participant
z score


Measurand Fe
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4 1 16 11 12 18 3 5 22 9 10 13 21 23 2
Participant
z score


Measurand Fe
Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
2 19 4 18 8 10 7 17 15
Participant
z score


Measurand Fe
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
1 4 18 8 22 12 16 10 13 23 3 17 15 2 5 19
Participant
z score


Measurand Hg Sample A1Hg
z score
4
3
2
1
0
-1
-2
-3
-4
2 19 14 1 21 8 15 10 3 12 16 4 17 18 13
Participant
z score


Measurand Hg Sample T3Hg
z score
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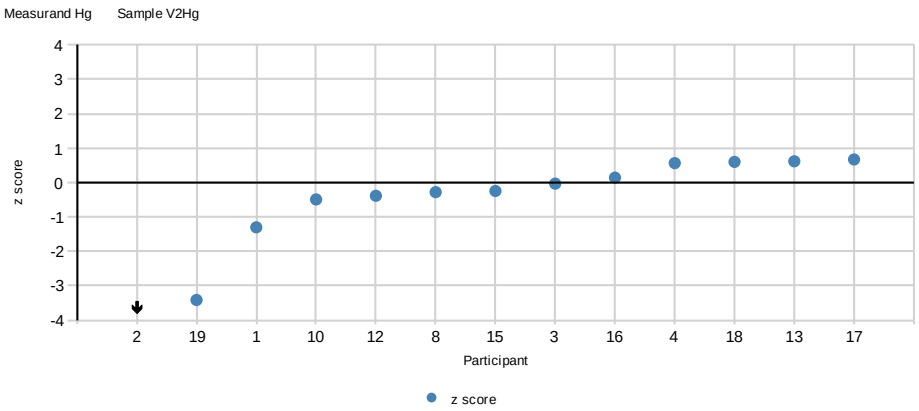
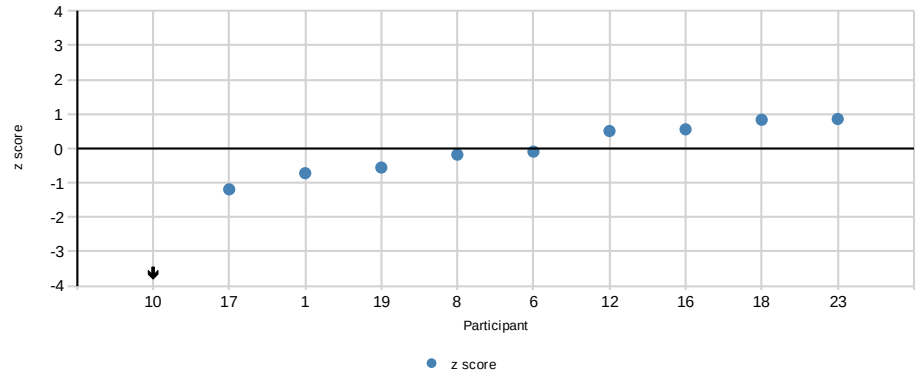
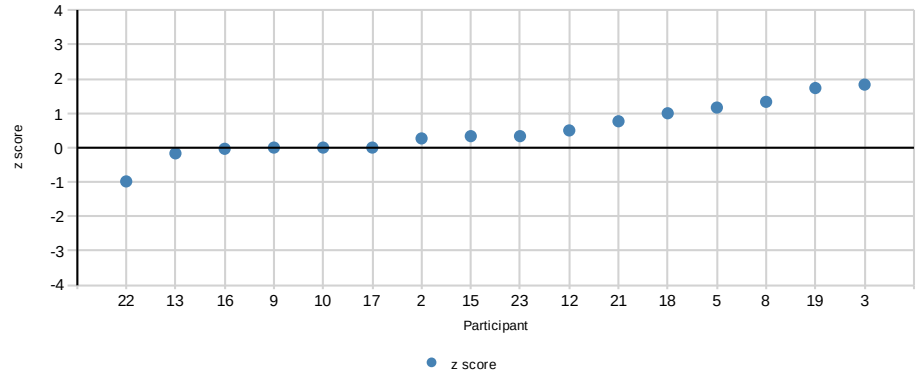
3
2
1
0
-1
-2
-3
-4
2 14 1 10 16 12 3 21 18 8 13 4 15 17 19
Participant
z score


Measurand Hg Sample V2Hg
z score
4
3
2
1
0
-1
-2
-3
-4
2 19 1 10 12 8 15 3 16 4 18 13 17
Participant
z score

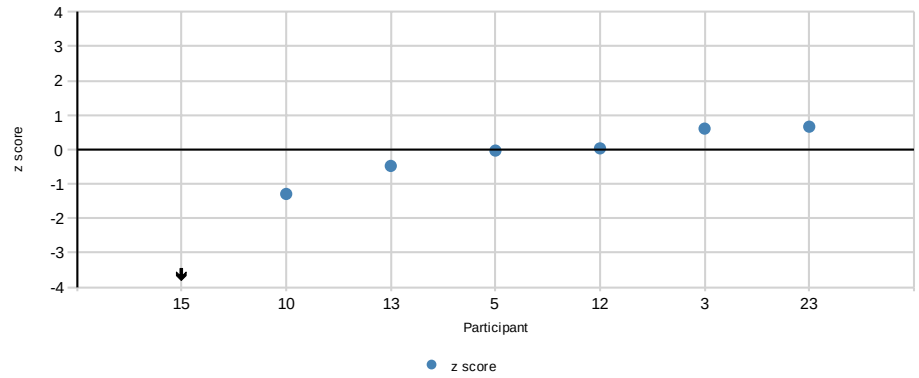
Measurand K Sample KO4

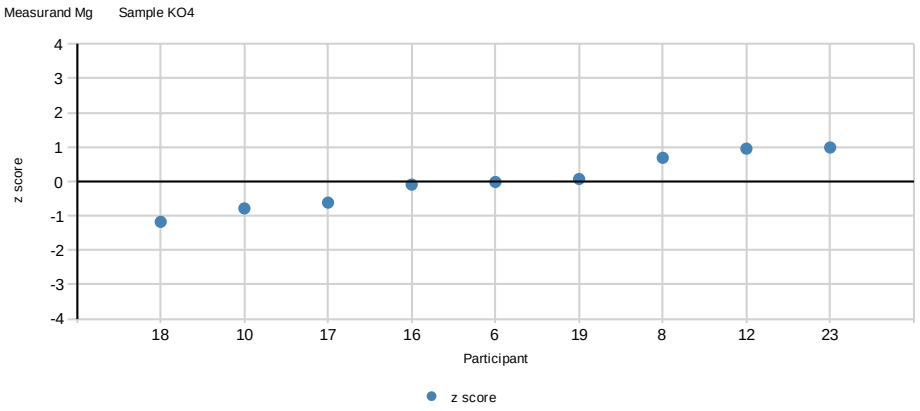


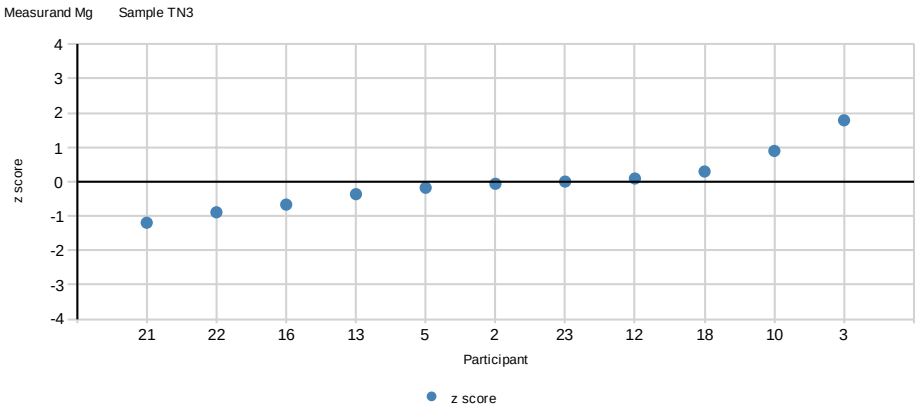
Measurand Mg Sample A1M

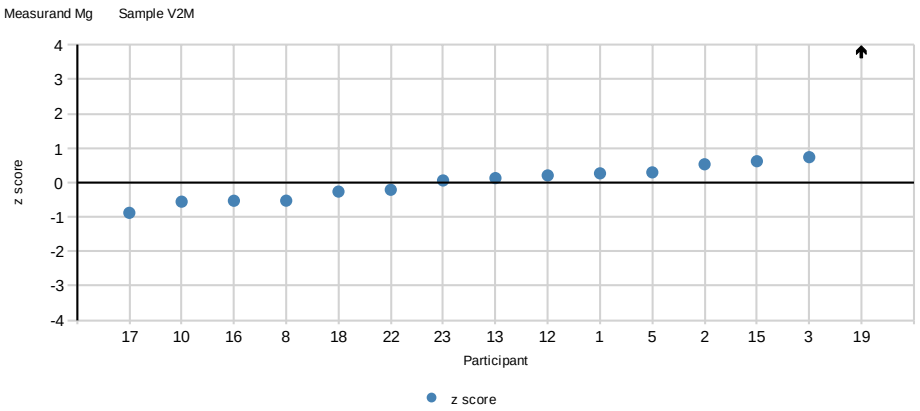


Measurand Mg Sample KN4

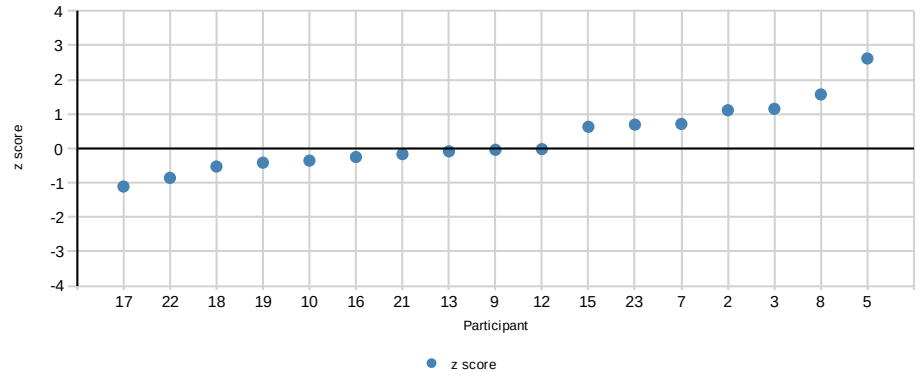



Measurand Mg Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
18 10 17 16 6 19 8 12 23
Participant
z score

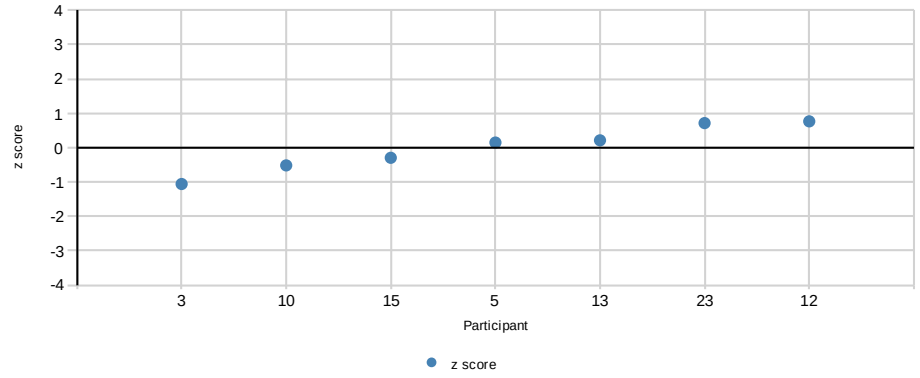

Measurand Mg Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
21 22 16 13 5 2 23 12 18 10 3
Participant
z score


Measurand Mg Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
17 10 16 8 18 22 23 13 12 1 5 2 15 3 19
Participant
z score

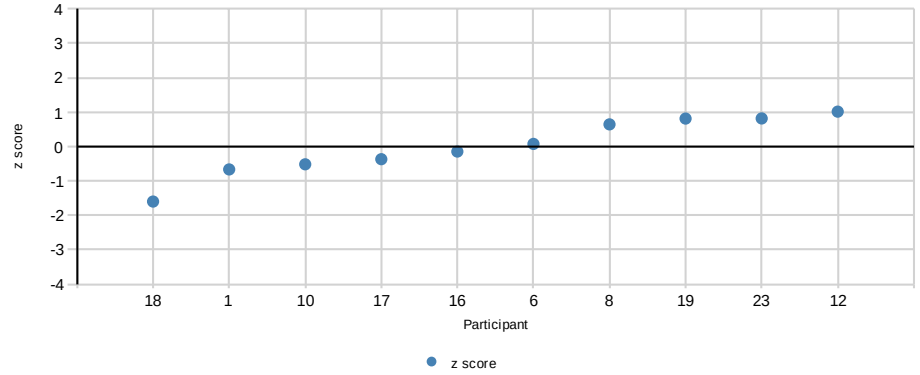
Measurand Mn Sample A1M

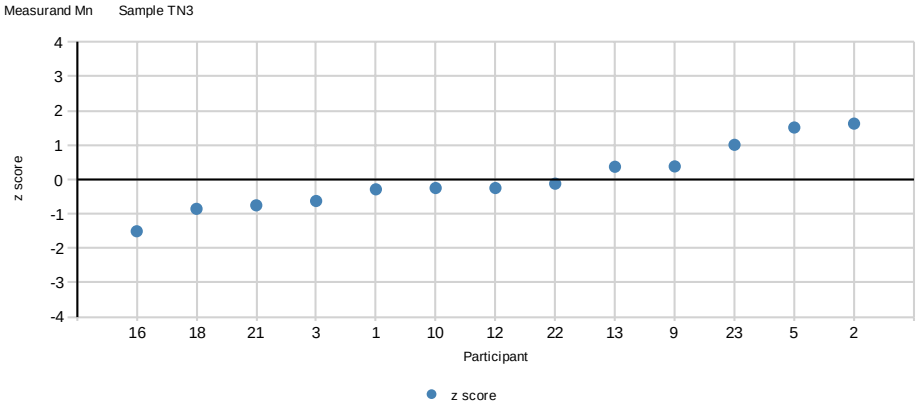


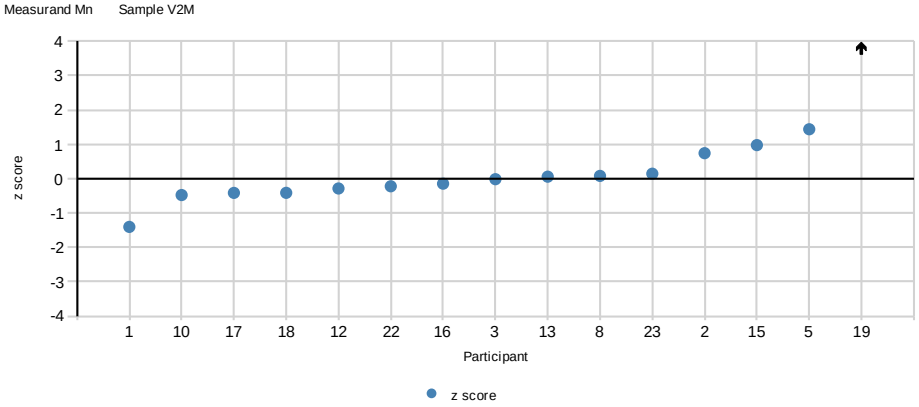
Measurand Mn Sample KN4

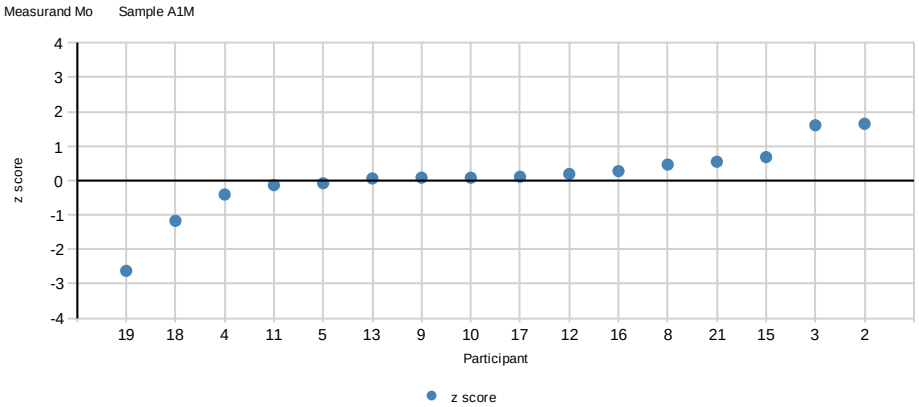


Measurand Mn Sample KO4

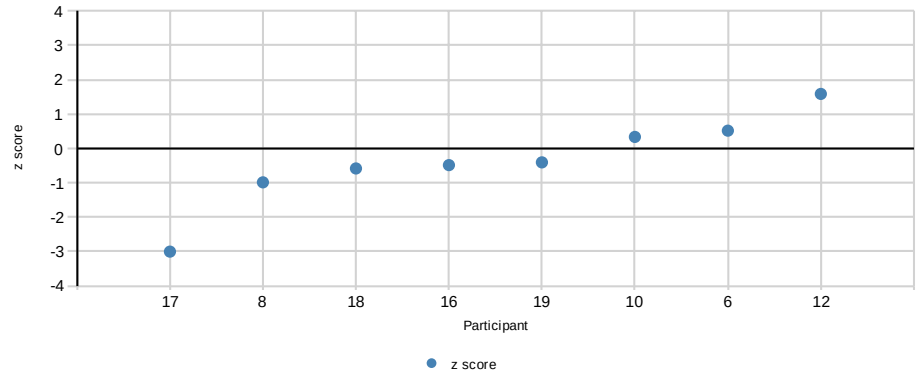



Measurand Mn Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
16 18 21 3 1 10 12 22 13 9 23 5 2
Participant
z score

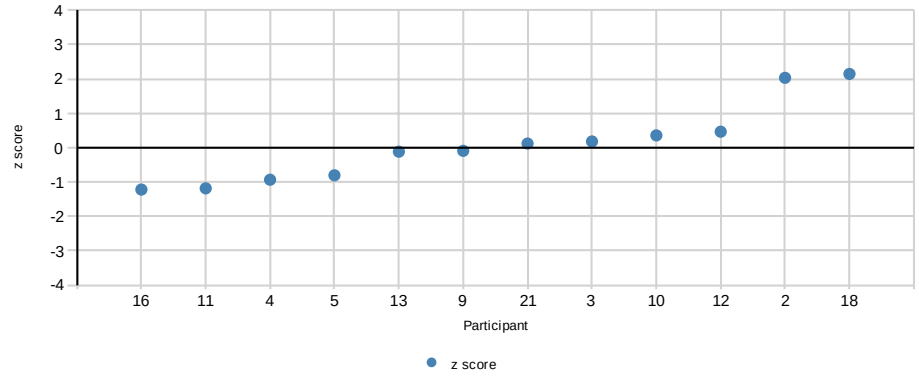

Measurand Mn Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
1 10 17 18 12 22 16 3 13 8 23 2 15 5 19
Participant
z score


Measurand Mo Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 18 4 11 5 13 9 10 17 12 16 8 21 15 3 2
Participant
z score

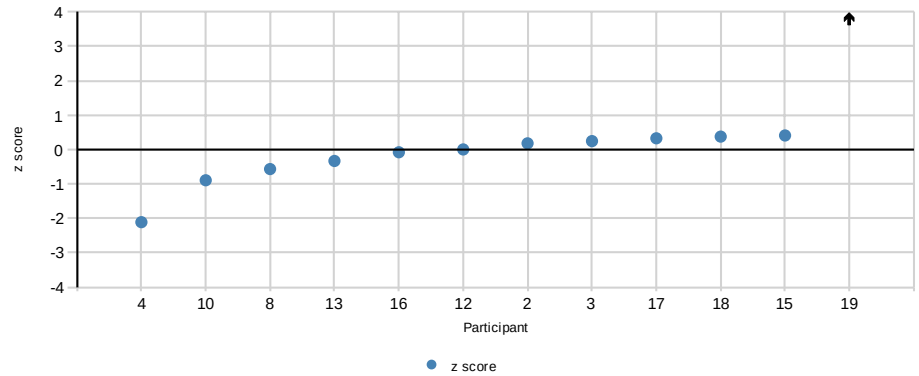
Measurand Mo Sample KO4

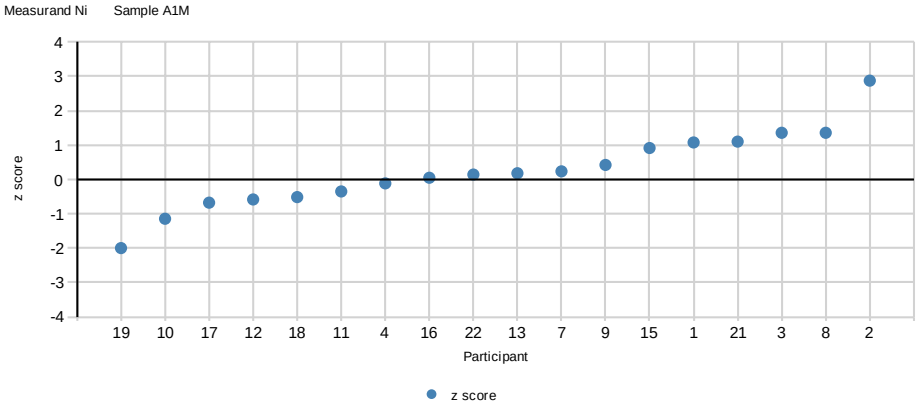


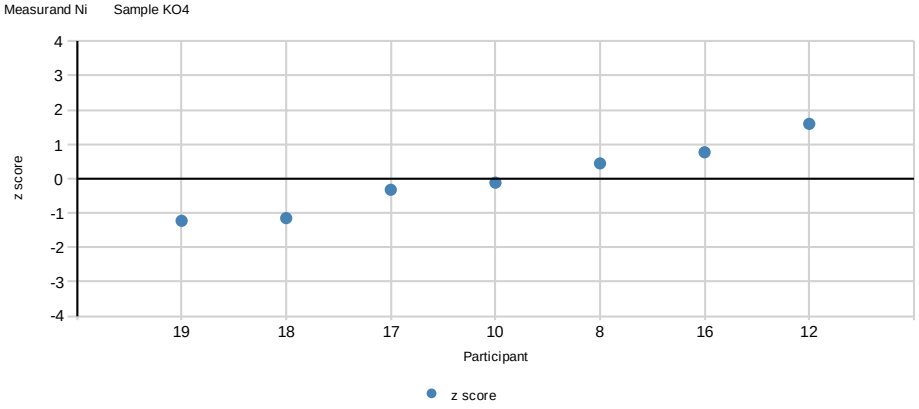
Measurand Mo Sample TN3

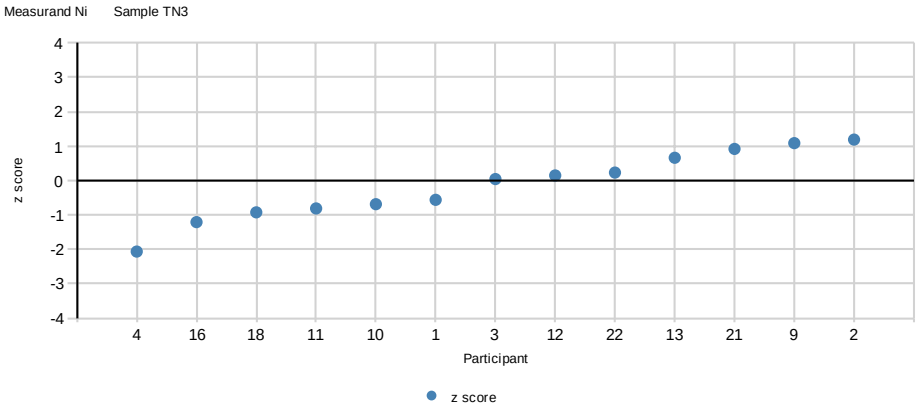


Measurand Mo Sample V2M

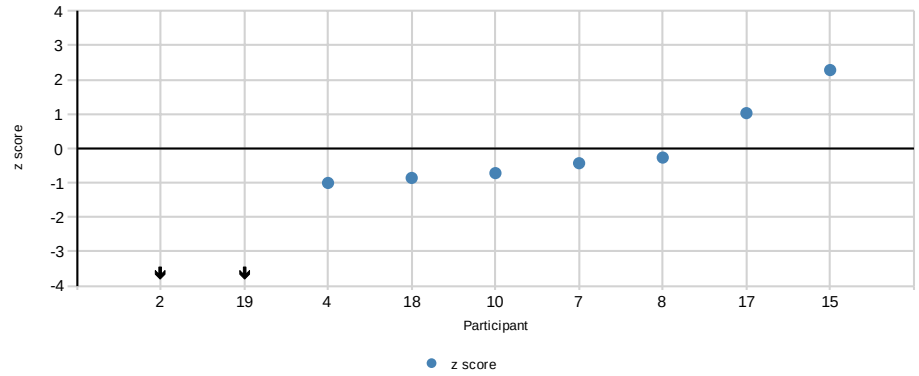



Measurand Ni Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 10 17 12 18 11 4 16 22 13 7 9 15 1 21 3 8 2
Participant
z score

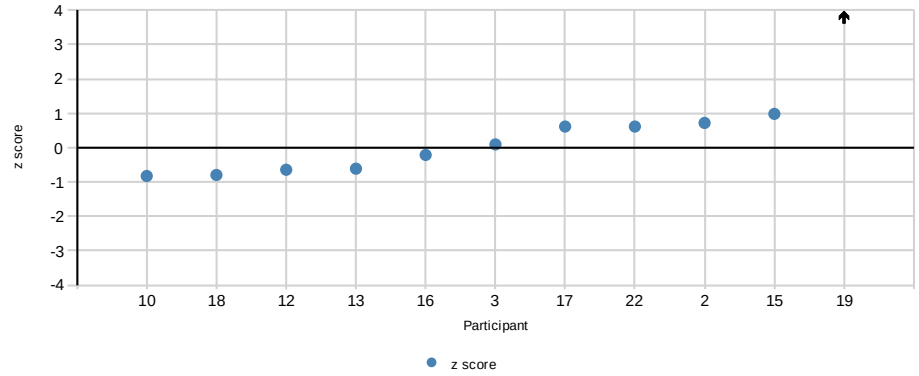

Measurand Ni Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
19 18 17 10 8 16 12
Participant
z score


Measurand Ni Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4 16 18 11 10 1 3 12 22 13 21 9 2
Participant
z score

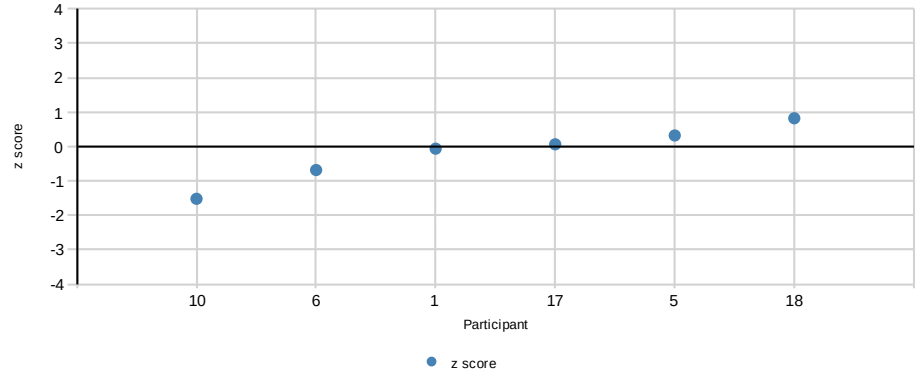
Measurand Ni Sample TY3

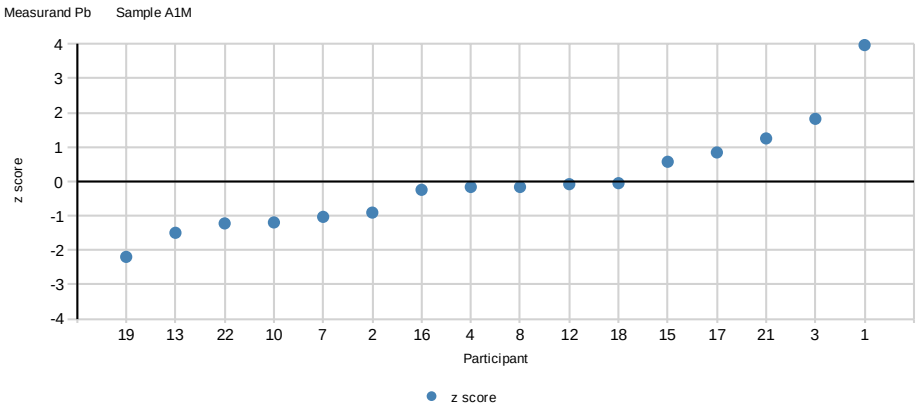


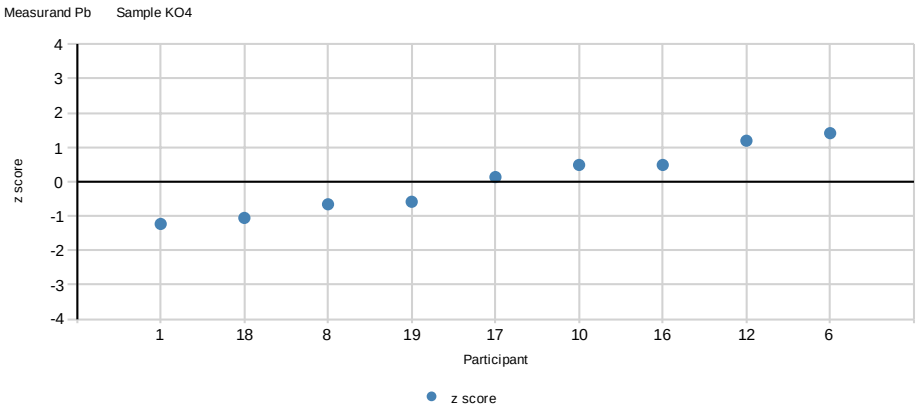
Measurand Ni Sample V2M

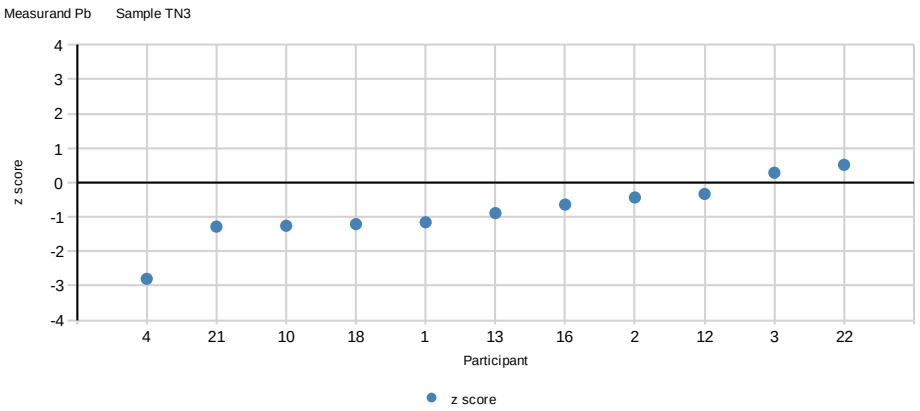


Measurand N_{tot} Sample KX4

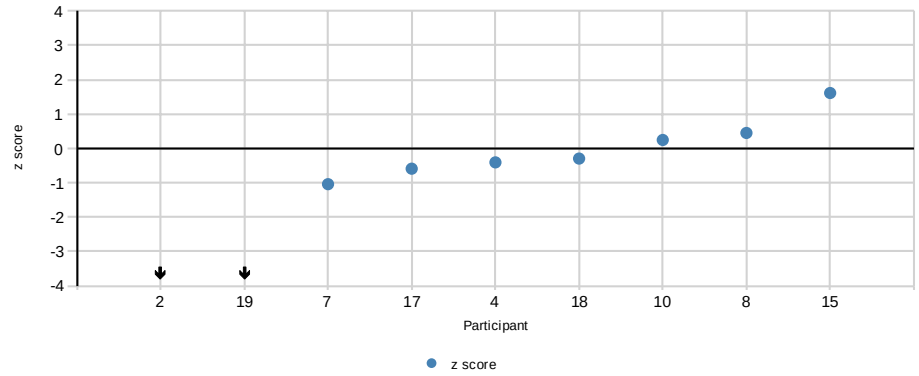



Measurand Pb Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 13 22 10 7 2 16 4 8 12 18 15 17 21 3 1
Participant
z score

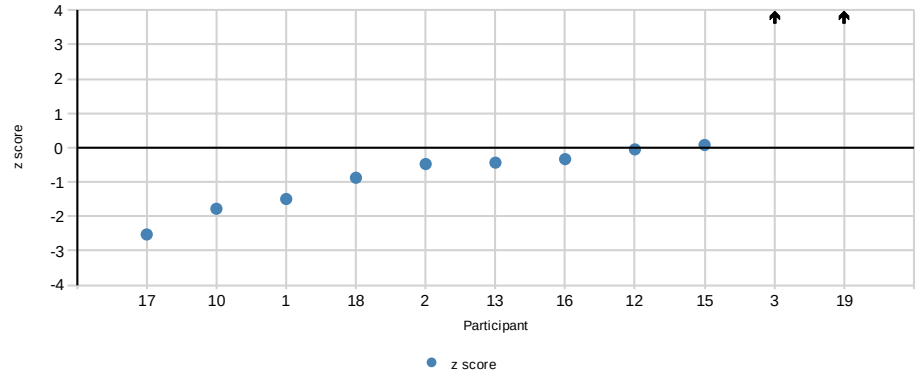

Measurand Pb Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
1 18 8 19 17 10 16 12 6
Participant
z score


Measurand Pb Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4 21 10 18 1 13 16 2 12 3 22
Participant
z score

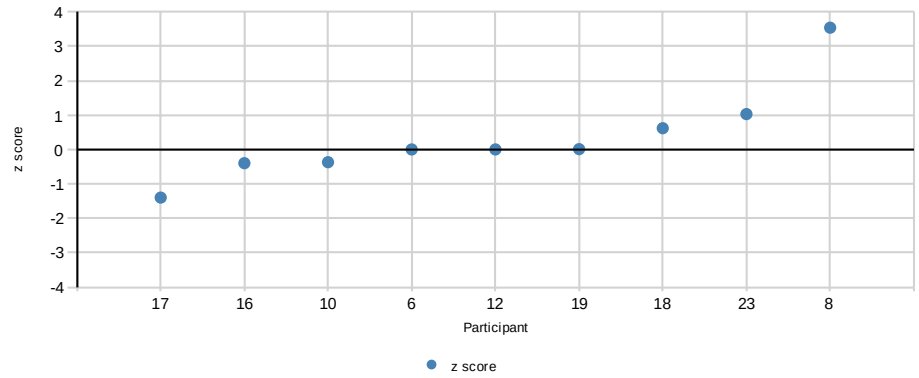
Measurand Pb Sample TY3

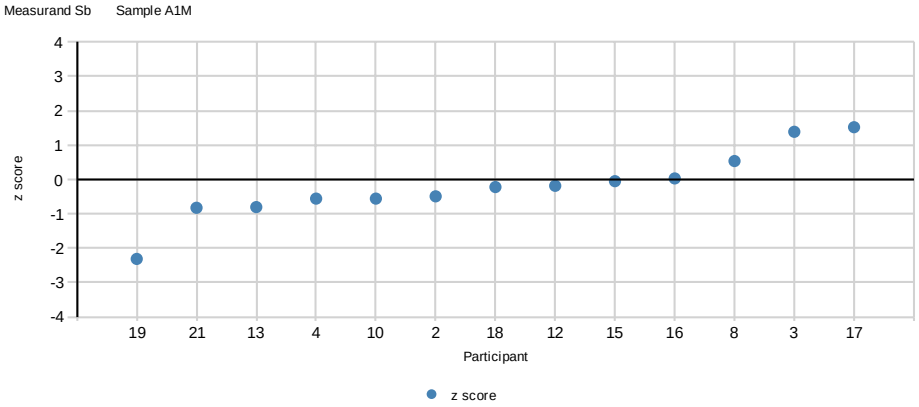


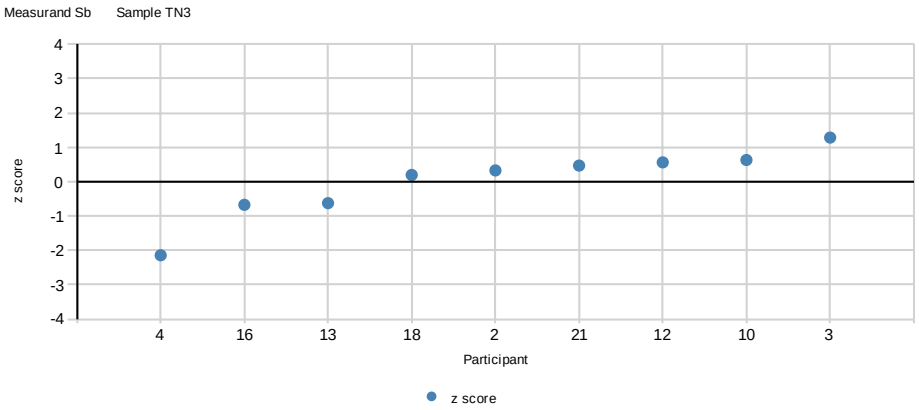
Measurand Pb Sample V2M

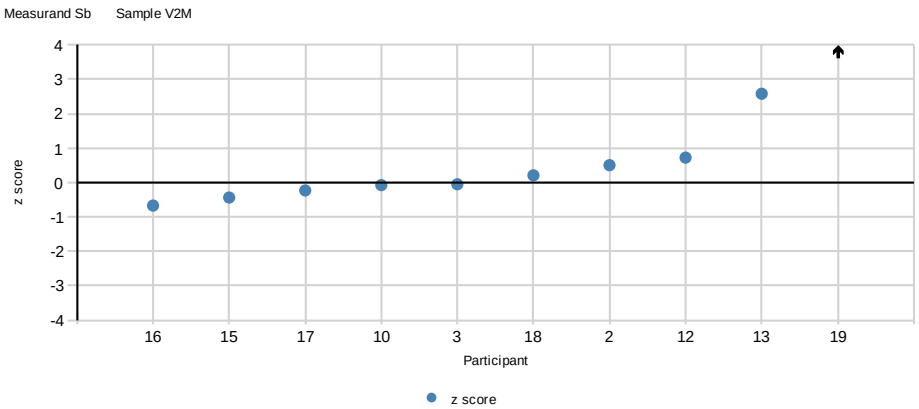


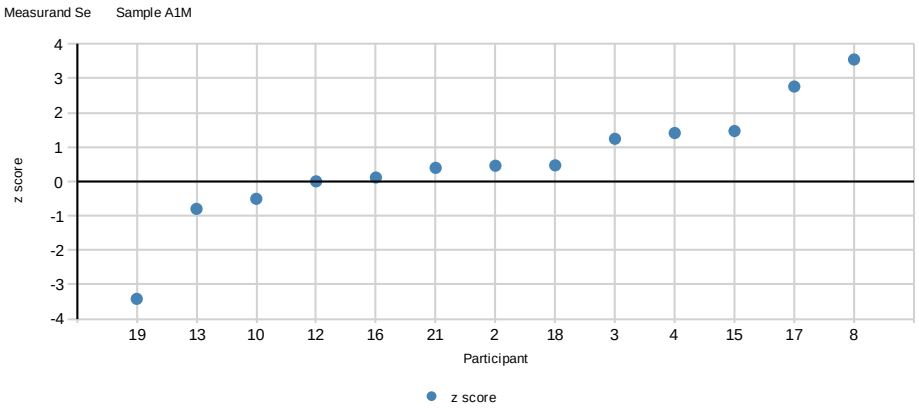
Measurand P_{tot} Sample KO4

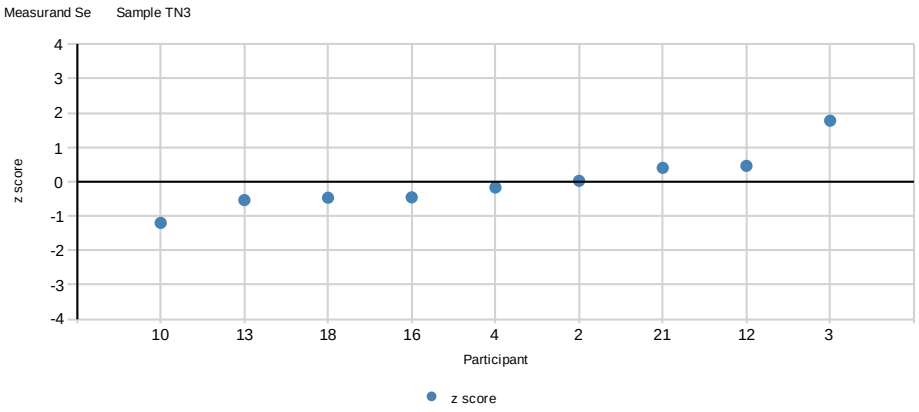


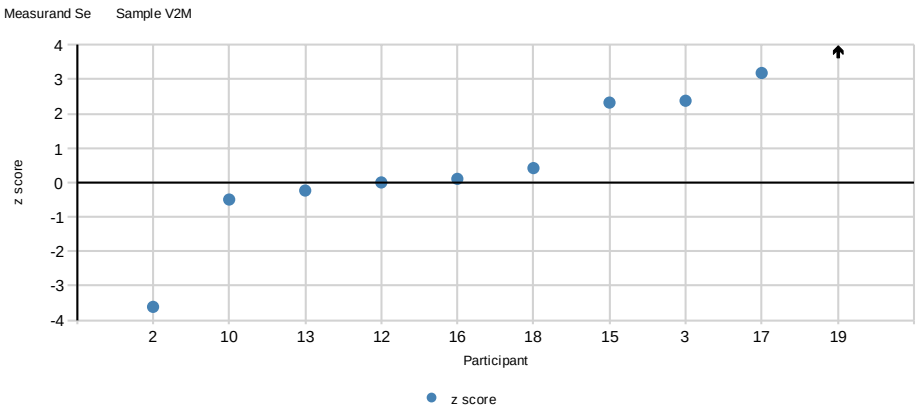

Measurand Sb Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 21 13 4 10 2 18 12 15 16 8 3 17
Participant
z score

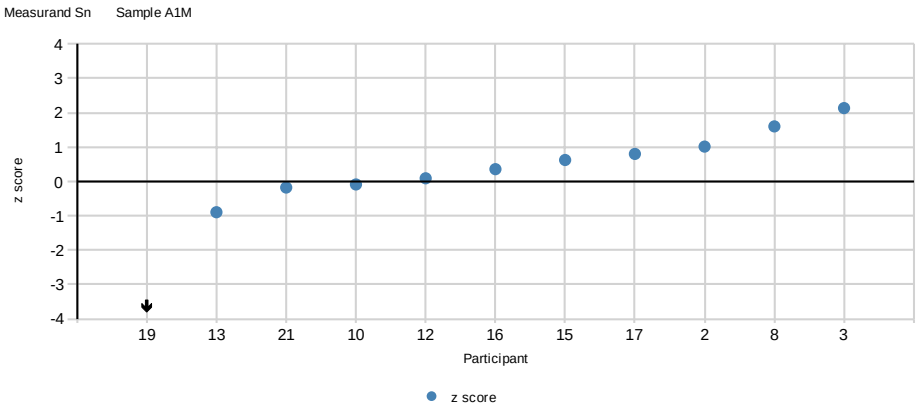

Measurand Sb Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
4 16 13 18 2 21 12 10 3
Participant
z score

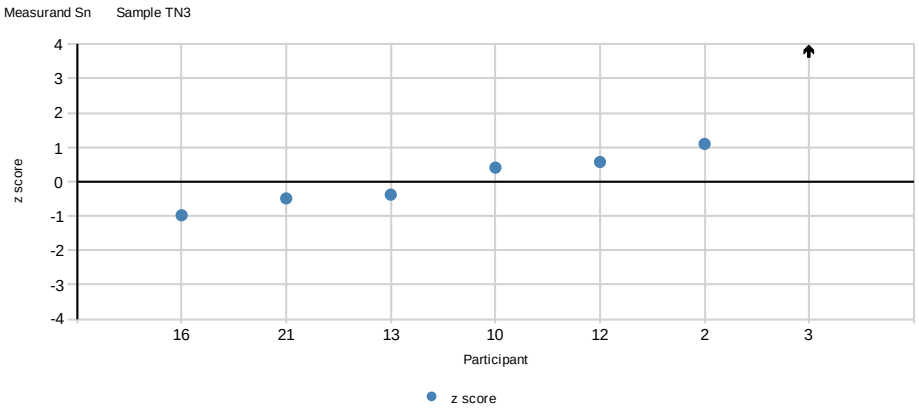

Measurand Sb Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
16 15 17 10 3 18 2 12 13 19
Participant
z score

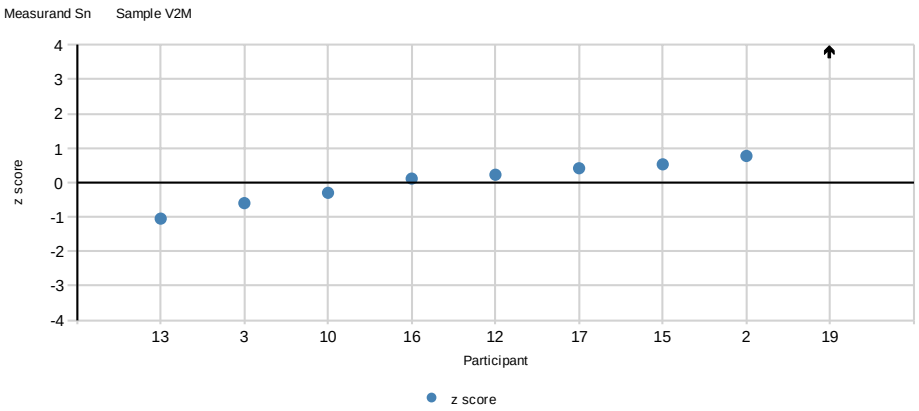

Measurand Se
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19
13
10
12
16
21
2
18
3
4
15
17
8
Participant
z score

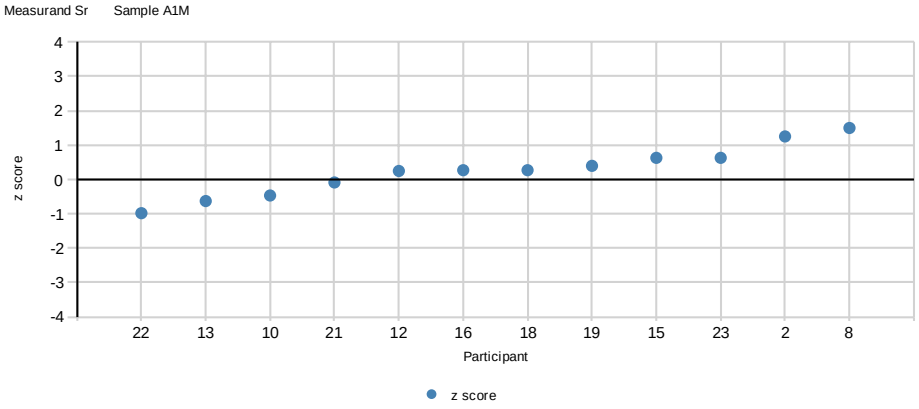

Measurand Se
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
10
13
18
16
4
2
21
12
3
Participant
z score

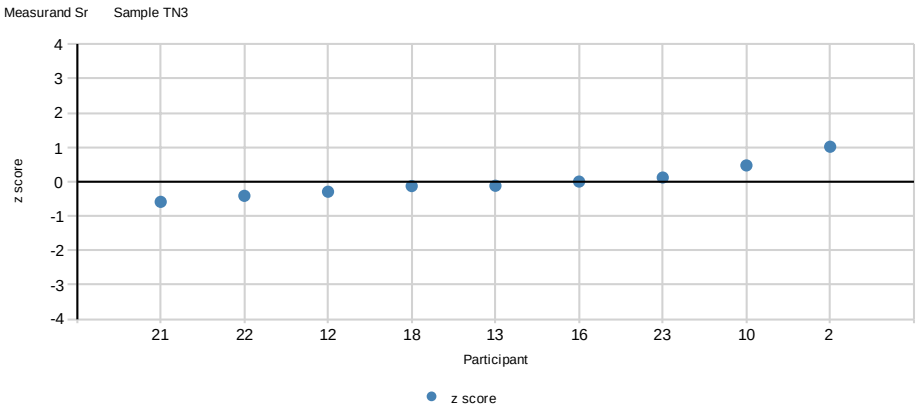

Measurand Se
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
2
10
13
12
16
18
15
3
17
19
Participant
z score

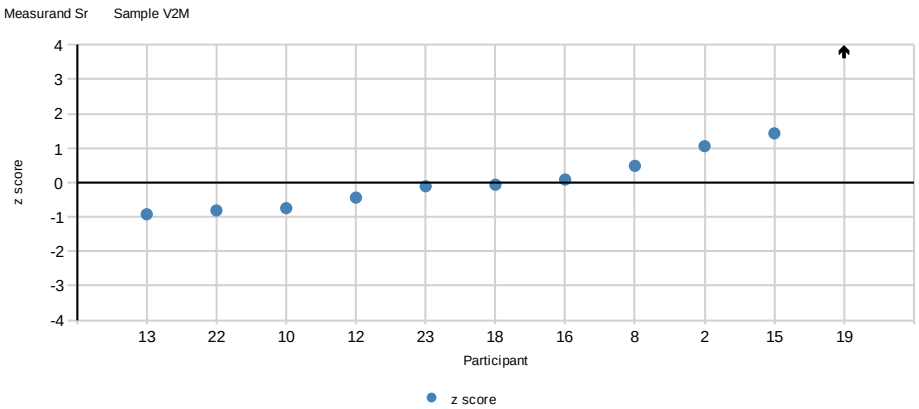

Measurand Sn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 13 21 10 12 16 15 17 2 8 3
Participant
z score

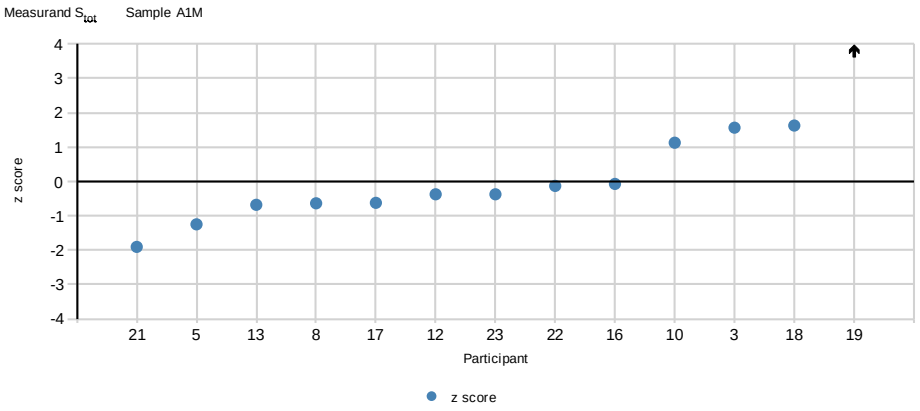

Measurand Sn Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
16 21 13 10 12 2 3
Participant
z score

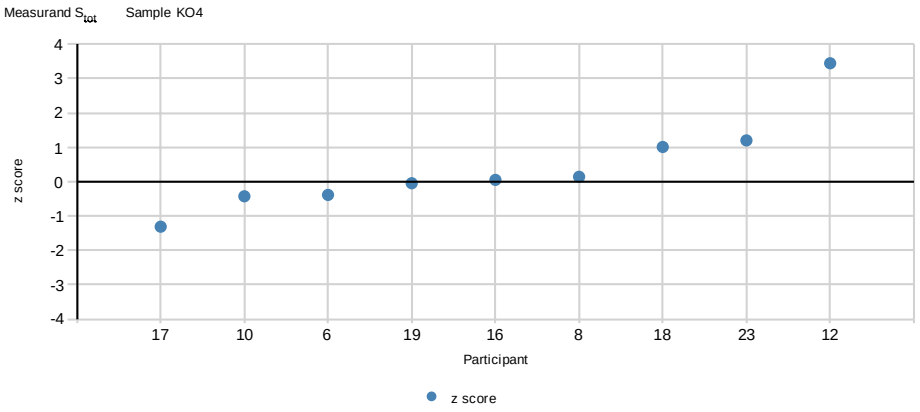

Measurand Sn Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
13 3 10 16 12 17 15 2 19
Participant
z score

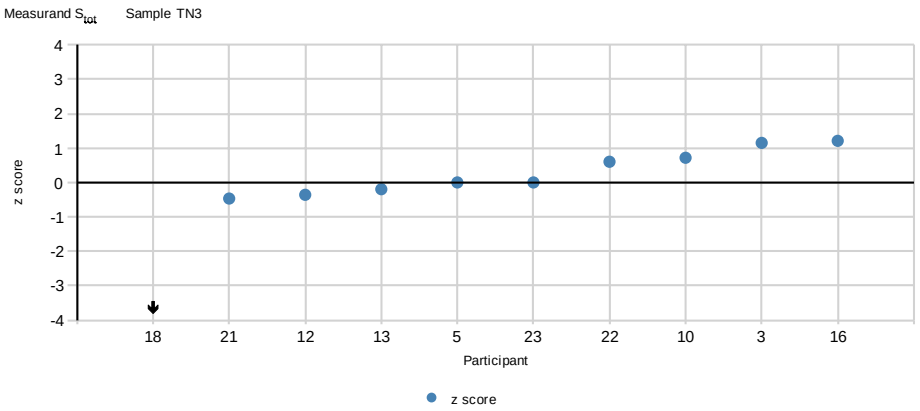

Measurand Sr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
22 13 10 21 12 16 18 19 15 23 2 8
Participant
z score

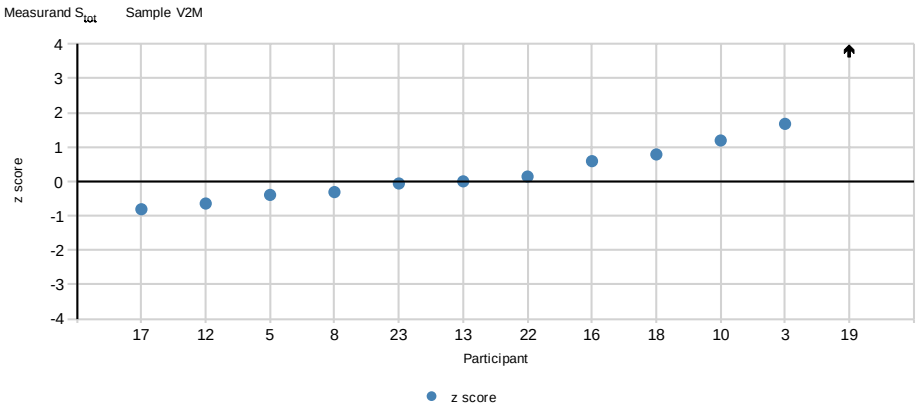

Measurand Sr Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
21 22 12 18 13 16 23 10 2
Participant
z score

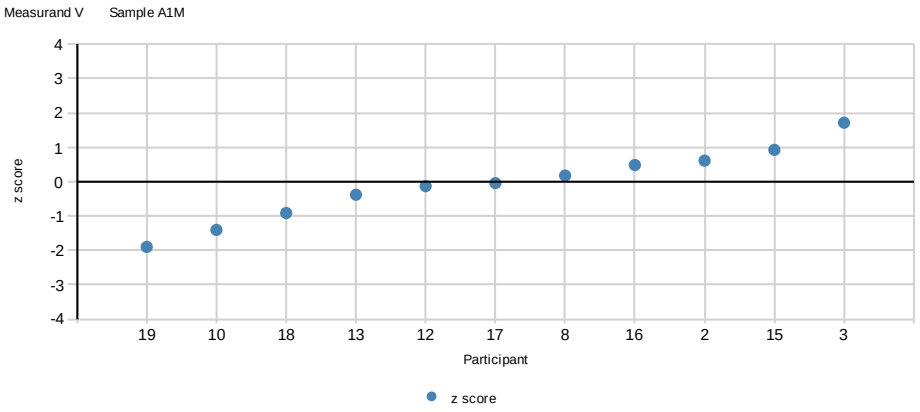

Measurand Sr Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
13 22 10 12 23 18 16 8 2 15 19
Participant
z score

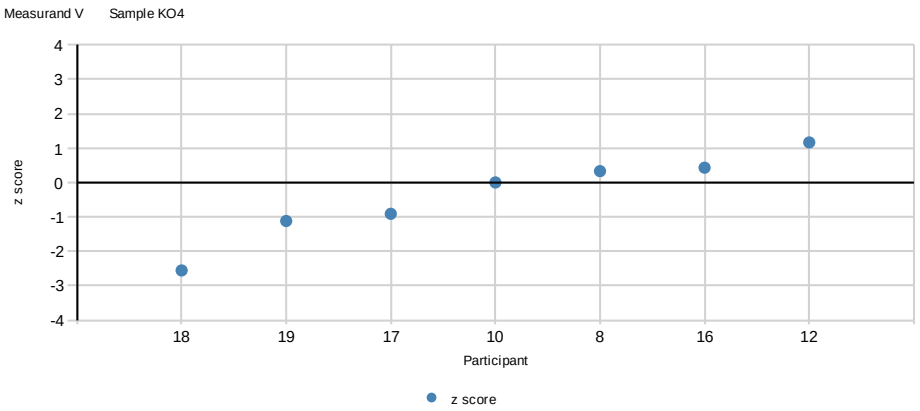

Measurand S_{tot} Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
21 5 13 8 17 12 23 22 16 10 3 18 19
Participant
z score

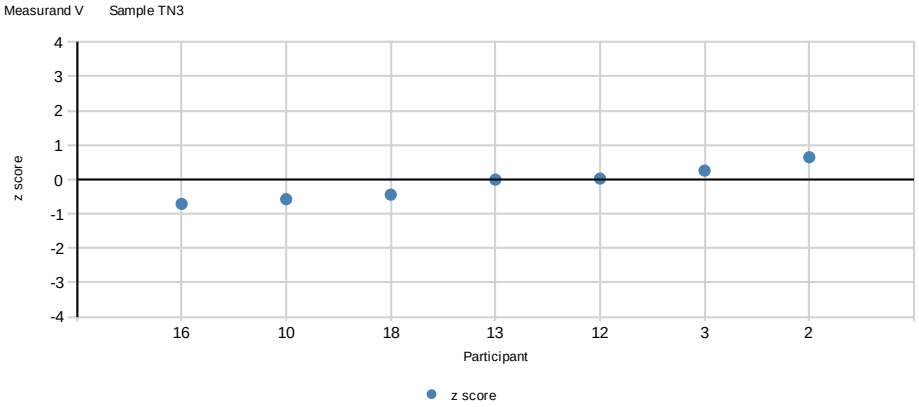

Measurand S_{tot} Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
17 10 6 19 16 8 18 23 12
Participant
z score

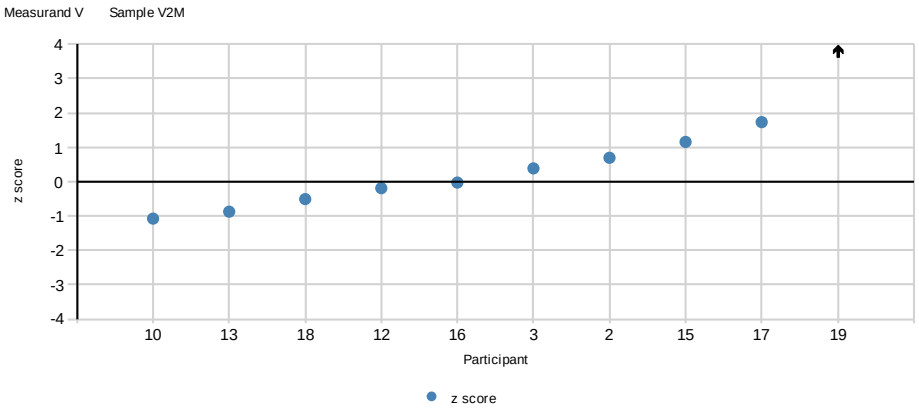

Measurand S_{tot} Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
18 21 12 13 5 23 22 10 3 16
Participant
z score

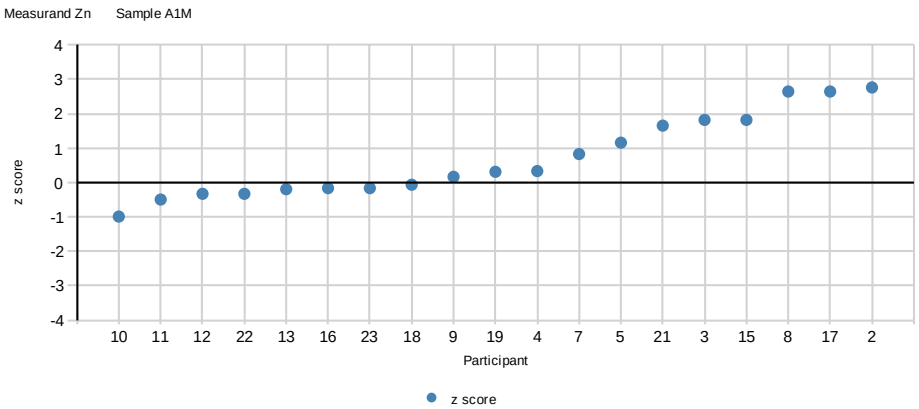

Measurand S_{tot} Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
17 12 5 8 23 13 22 16 18 10 3 19
Participant
z score


Measurand V Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 10 18 13 12 17 8 16 2 15 3
Participant
z score

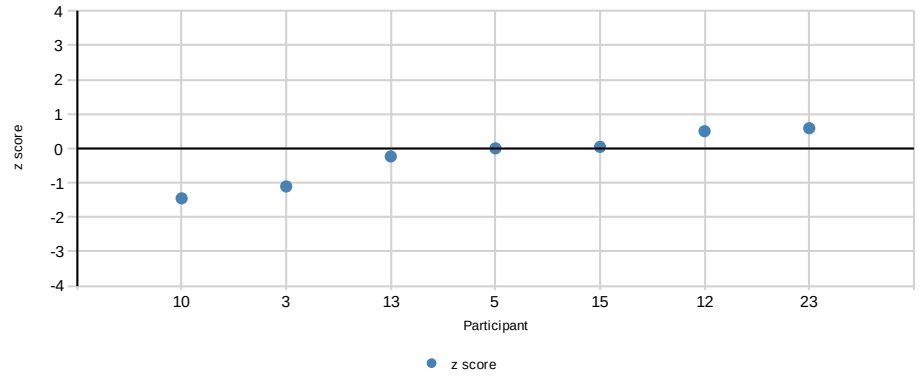

Measurand V Sample KO4
z score
4
3
2
1
0
-1
-2
-3
-4
18 19 17 10 8 16 12
Participant
z score


Measurand V
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
16
10
18
13
12
3
2
Participant
z score

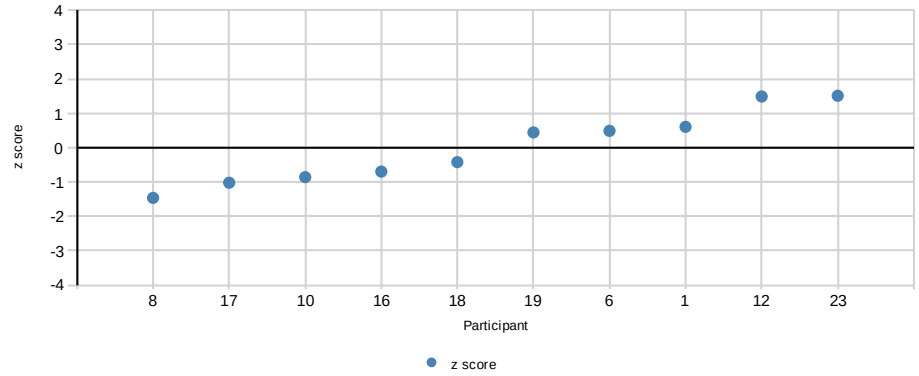

Measurand V
Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
10
13
18
12
16
3
2
15
17
19
Participant
z score


Measurand Zn
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
10
11
12
22
13
16
23
18
9
19
4
7
5
21
3
15
8
17
2
Participant
z score

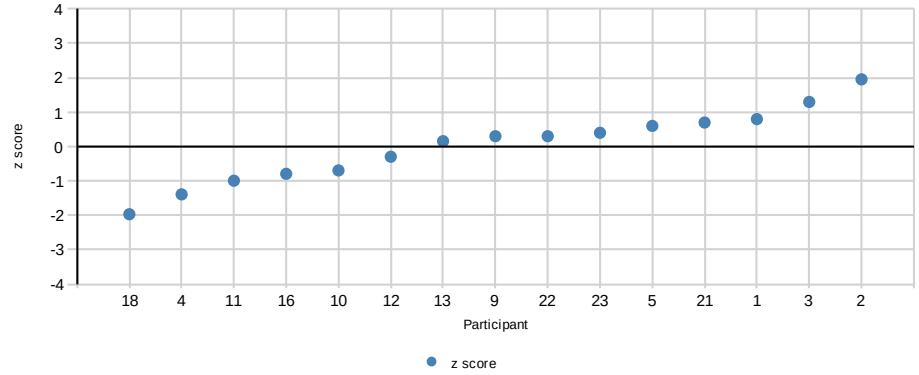
Measurand Zn Sample KN4

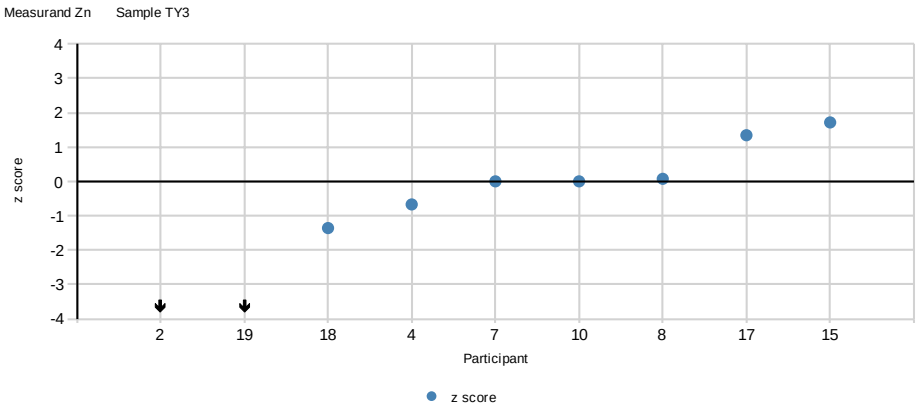


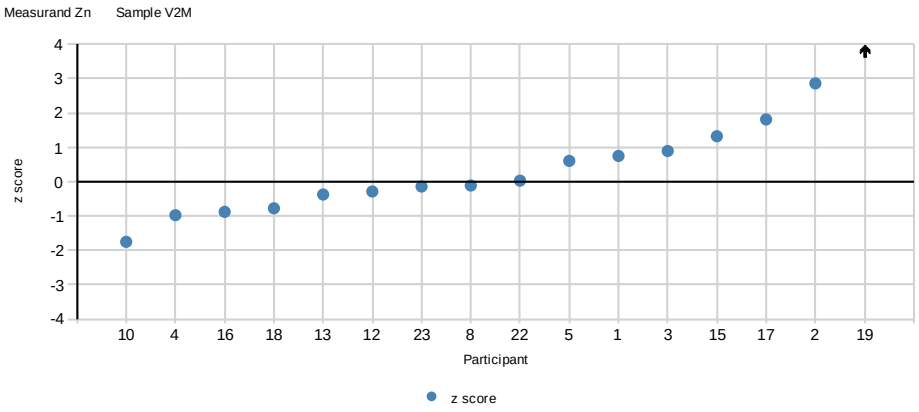
Measurand Zn Sample KO4



Measurand Zn Sample TN3




Measurand Zn Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
2
19
18
4
7
10
8
17
15
Participant
z score

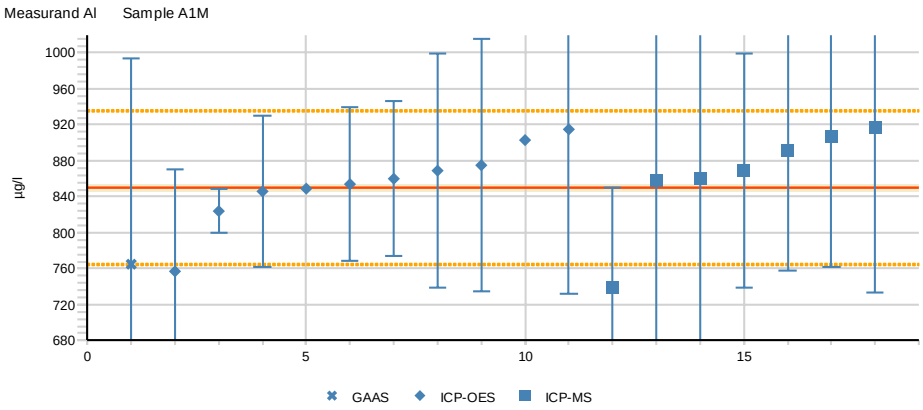

Measurand Zn Sample V2M
z score
4
3
2
1
0
-1
-2
-3
-4
10
4
16
18
13
12
23
8
22
5
1
3
15
17
2
19
Participant
z score

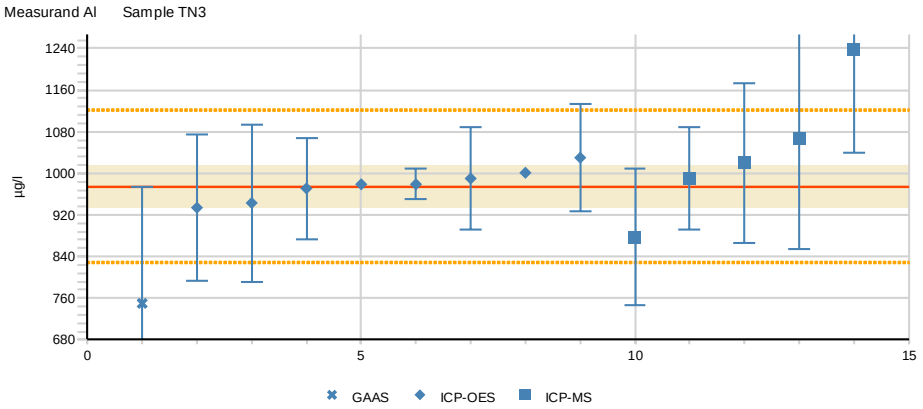
APPENDIX 10: Results grouped according to the methods

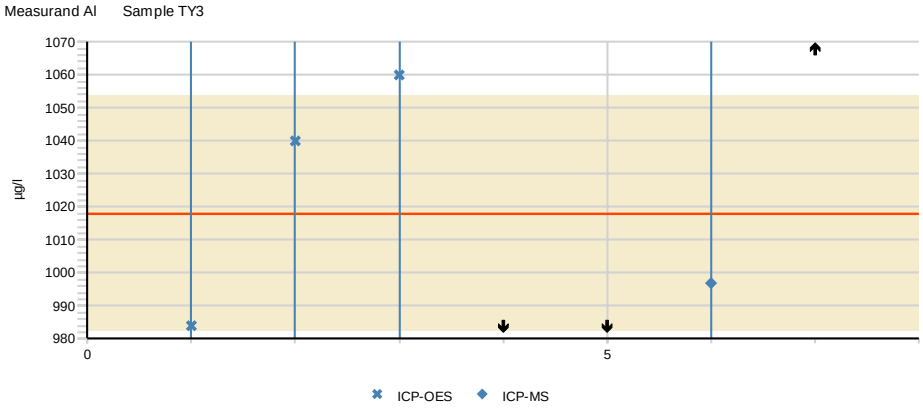
The results are shown in ascending order.

In figures:

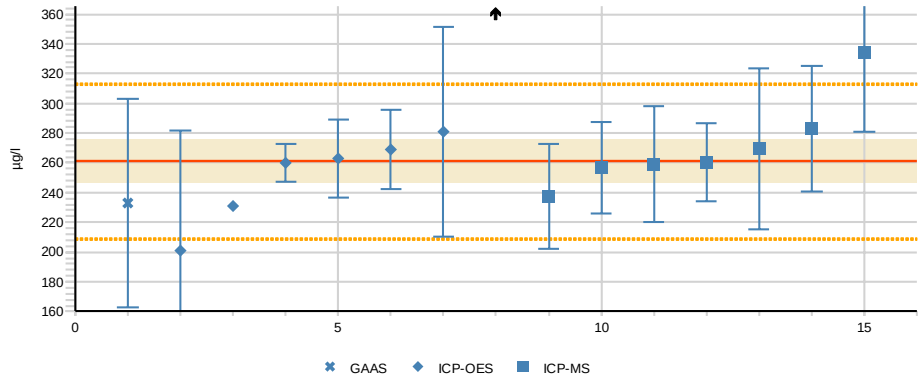
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



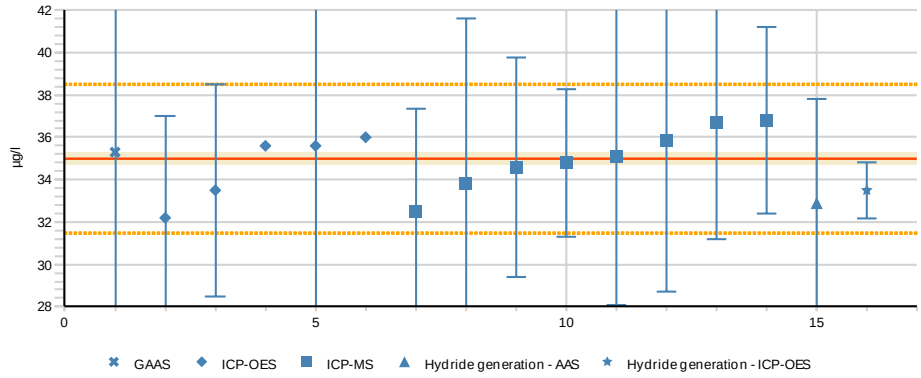




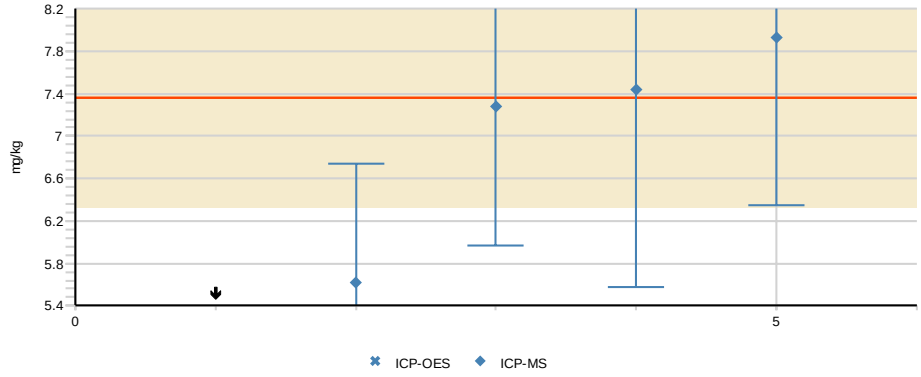
Measurand Al Sample V2M



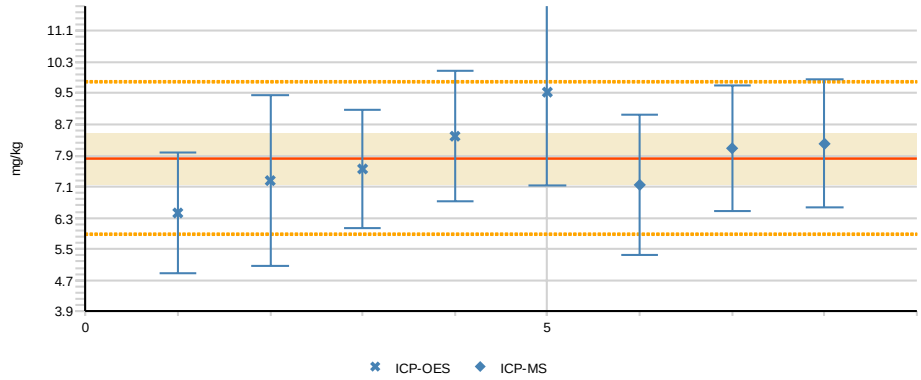
Measurand As Sample A1M



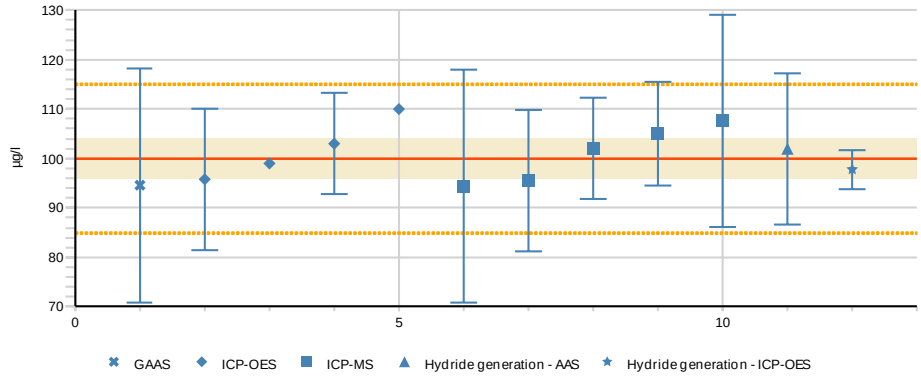
Measurand As Sample KN4



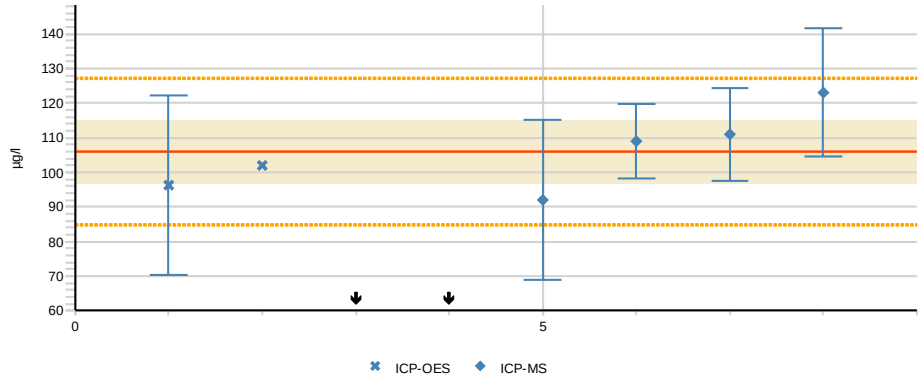
Measurand As Sample KO4



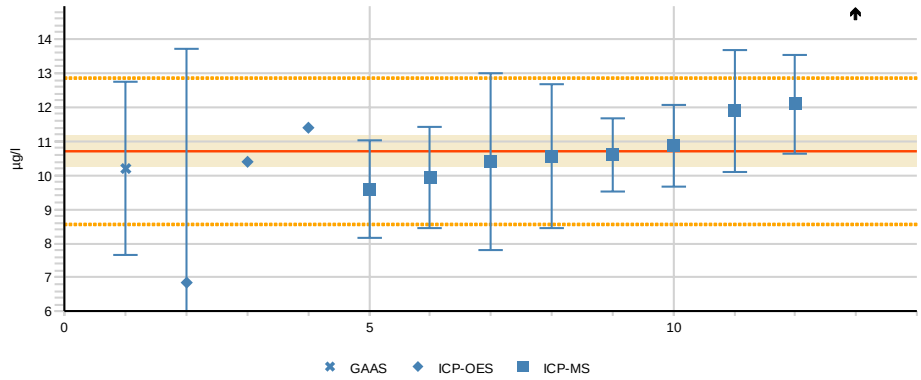
Measurand As Sample TN3



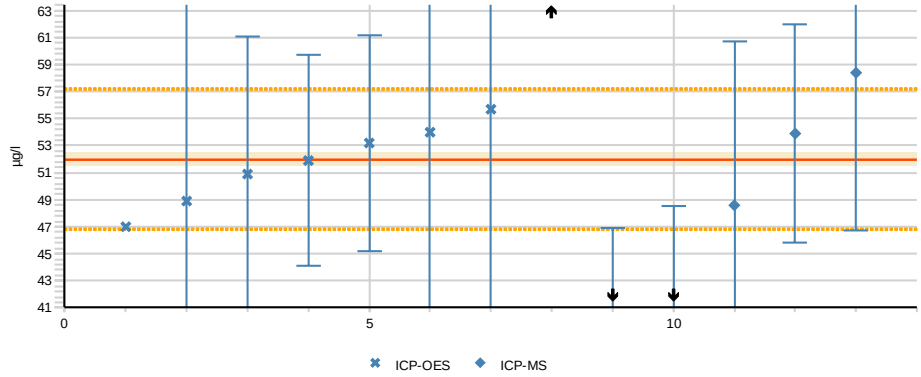
Measurand As Sample TY3



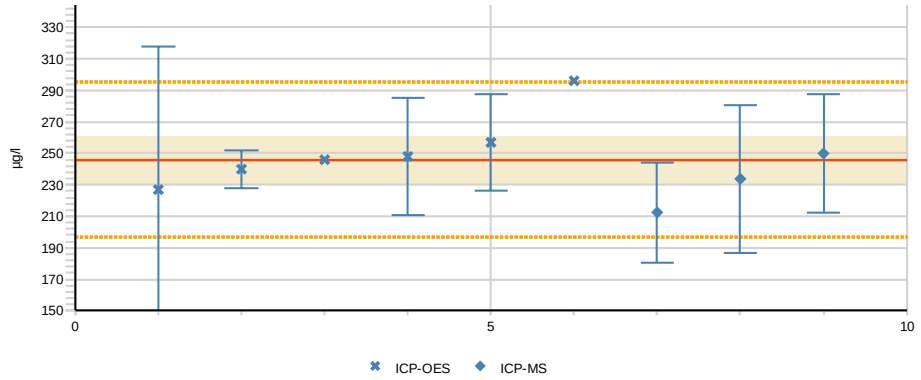
Measurand As Sample V2M



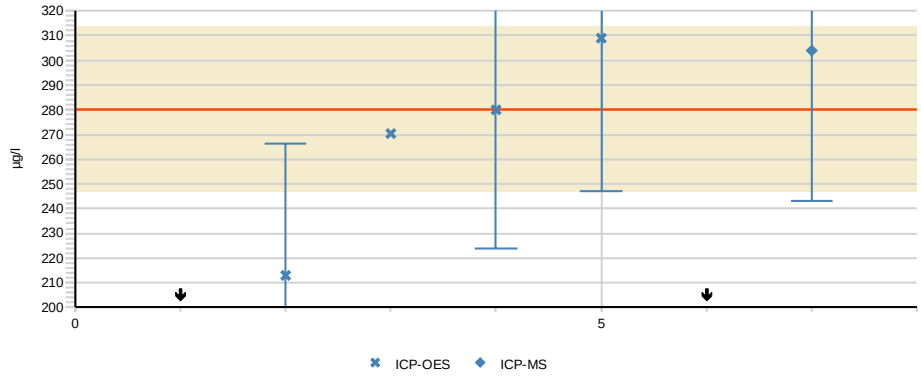
Measurand B Sample A1M



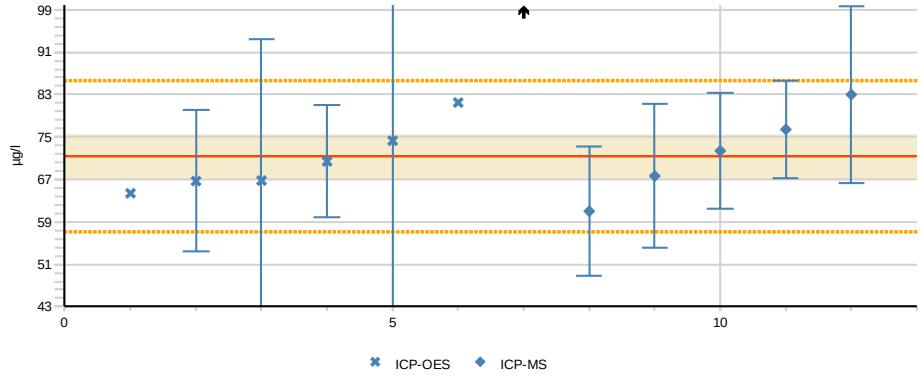
Measurand B Sample TN3



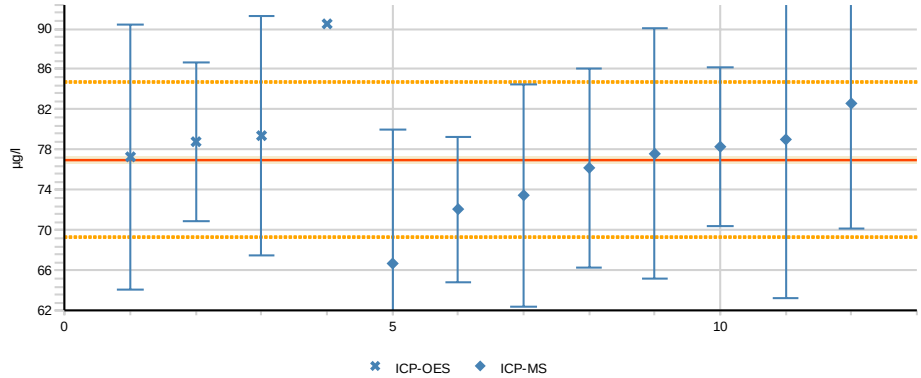
Measurand B Sample TY3



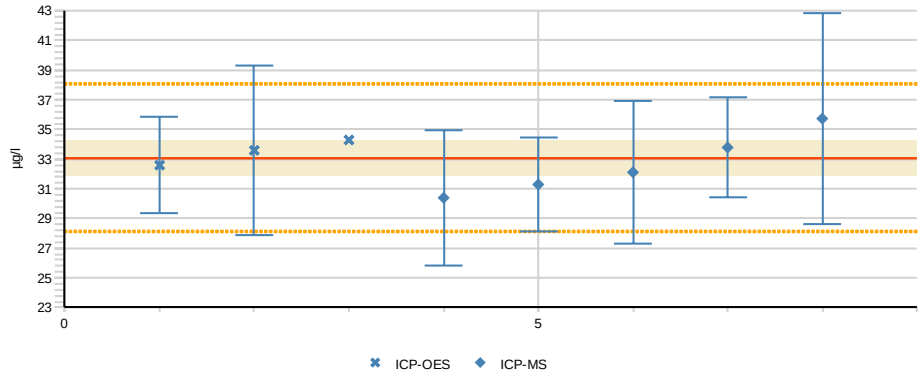
Measurand B Sample V2M



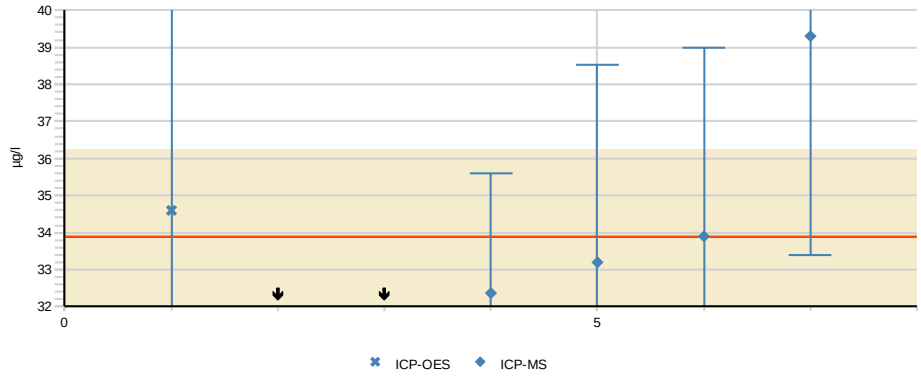
Measurand Ba Sample A1M



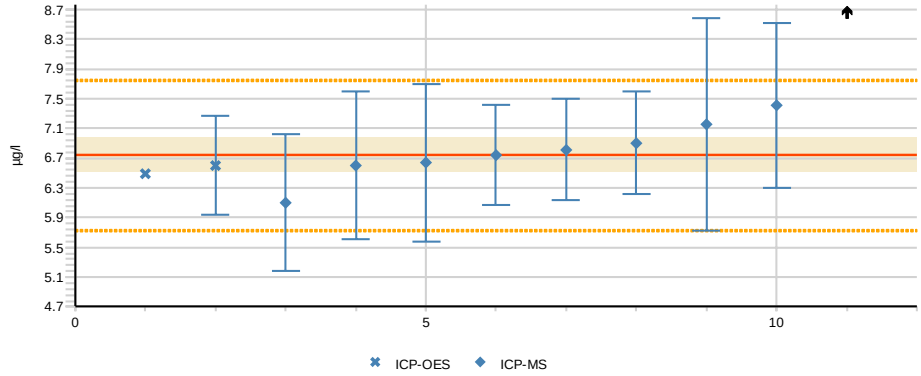
Measurand Ba Sample TN3



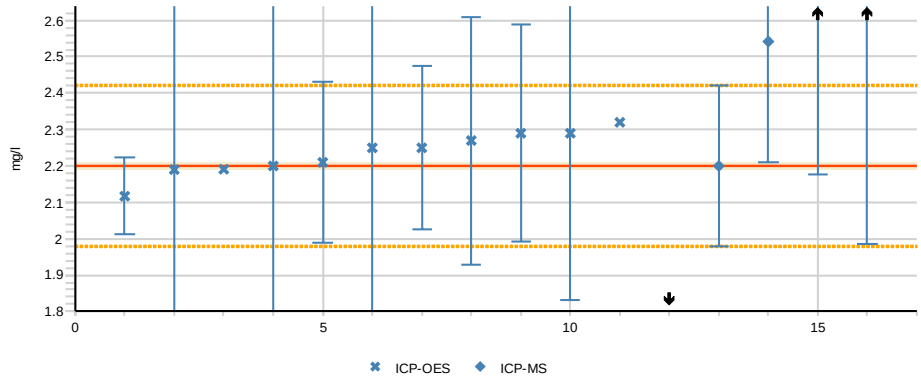
Measurand Ba Sample TY3



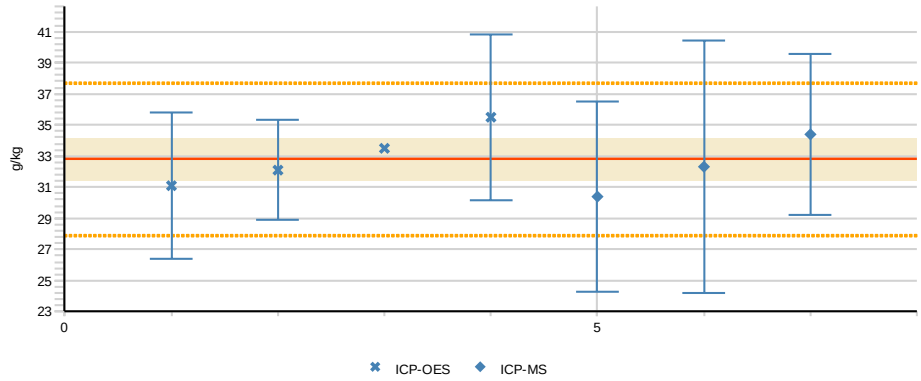
Measurand Ba Sample V2M



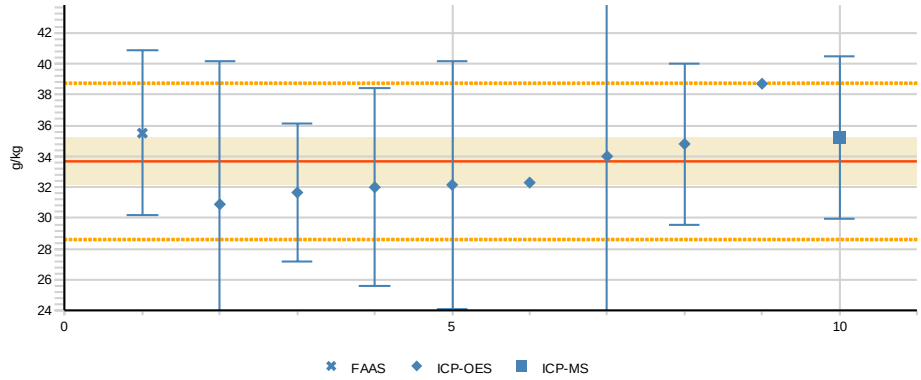
Measurand Ca Sample A1M

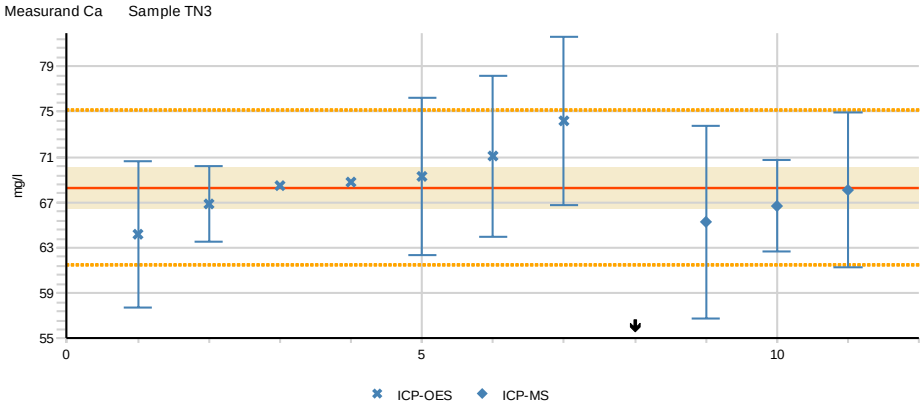


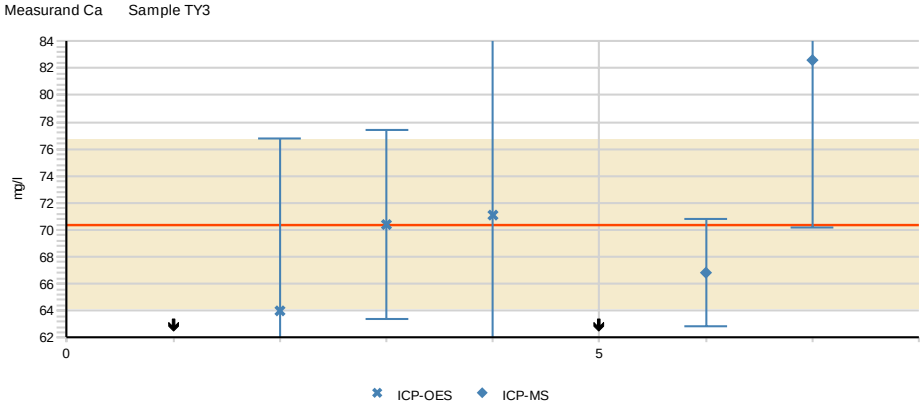
Measurand Ca Sample KN4

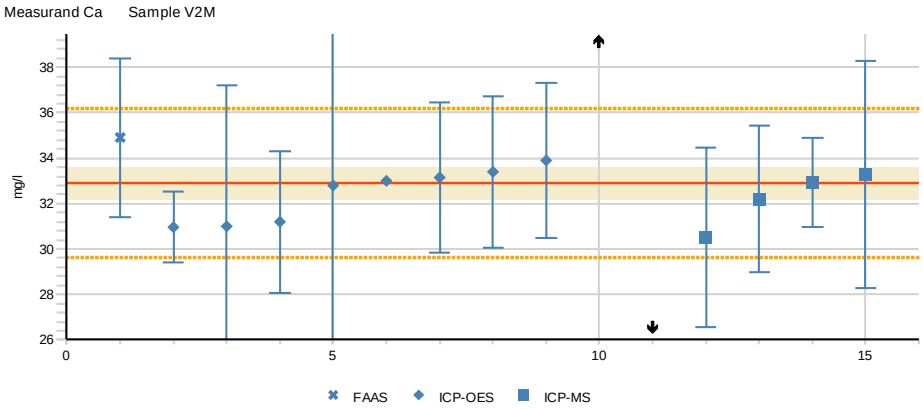


Measurand Ca Sample KO4

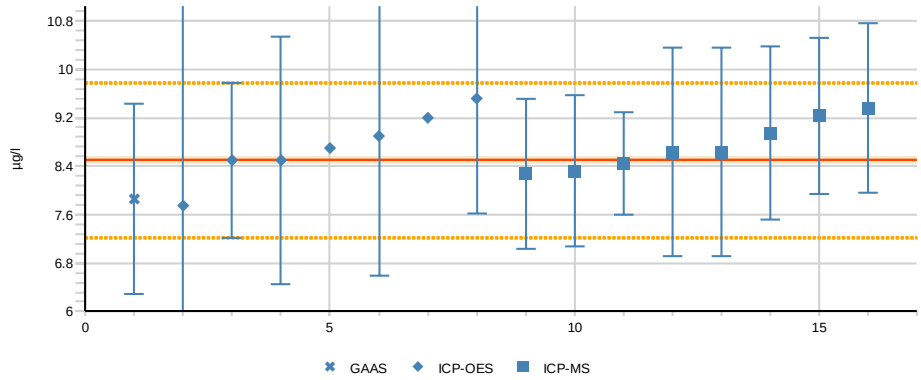



Measurand Ca
Sample TN3
mg/l
79
75
71
67
63
59
55
0
5
10
ICP-OES
ICP-MS

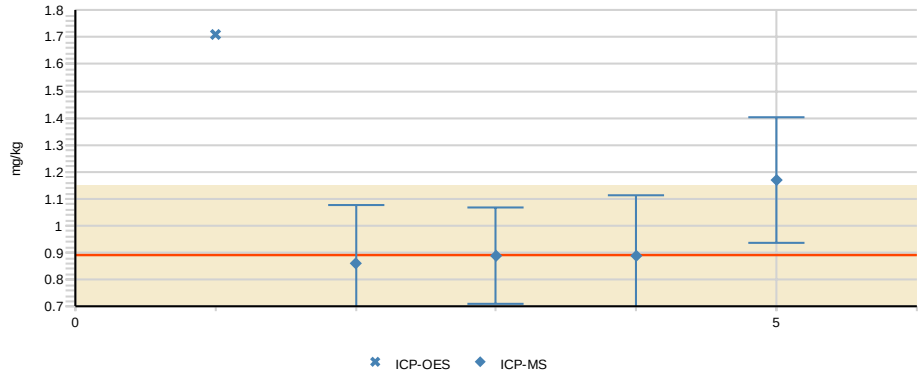

Measurand Ca
Sample TY3
mg/l
84
82
80
78
76
74
72
70
68
66
64
62
0
5
ICP-OES
ICP-MS


Measurand Ca
Sample V2M
mg/l
38
36
34
32
30
28
26
0
5
10
15
FAAS
ICP-OES
ICP-MS

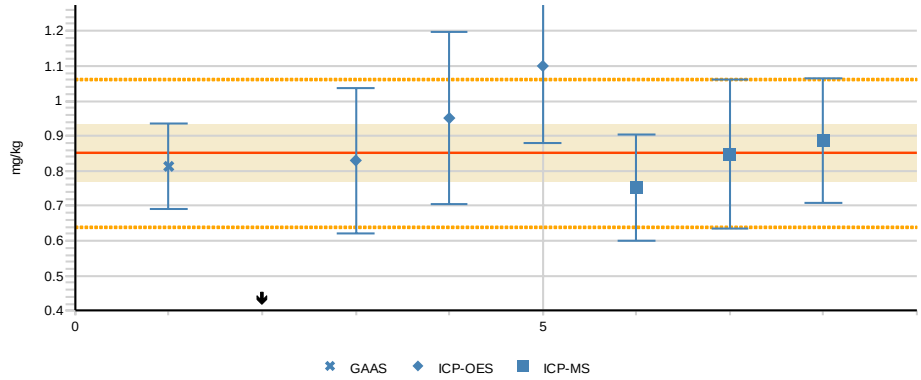
Measurand Cd Sample A1M

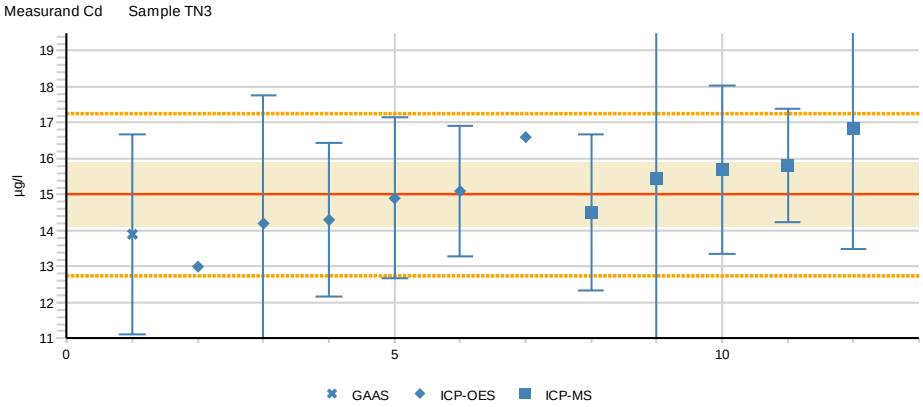


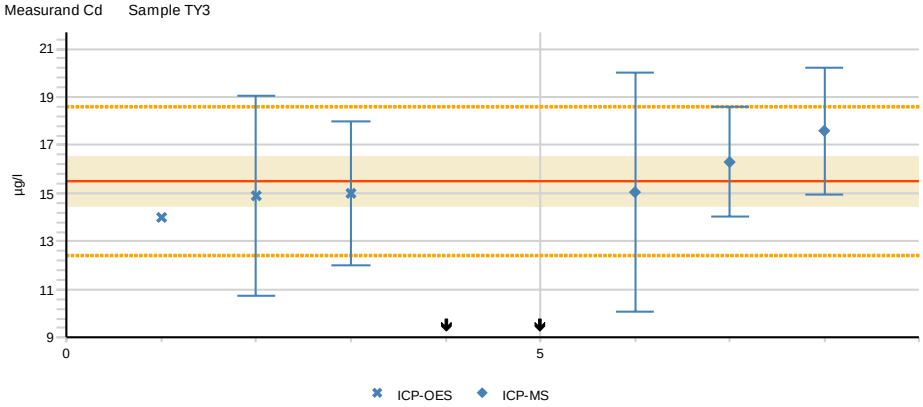
Measurand Cd Sample KN4

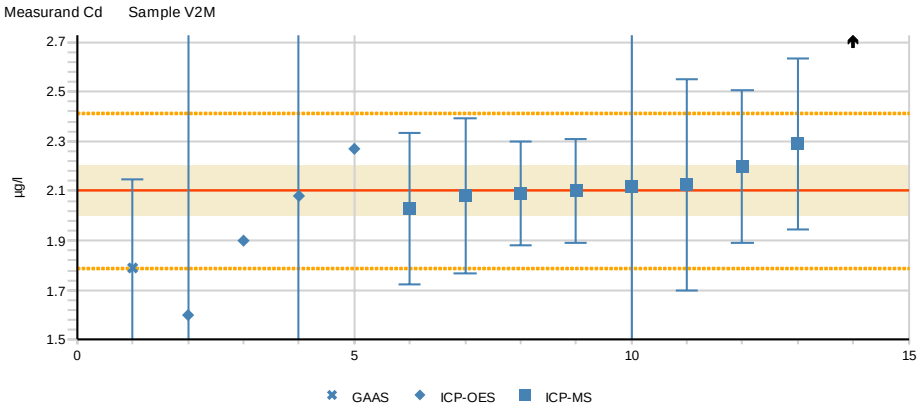


Measurand Cd Sample KO4

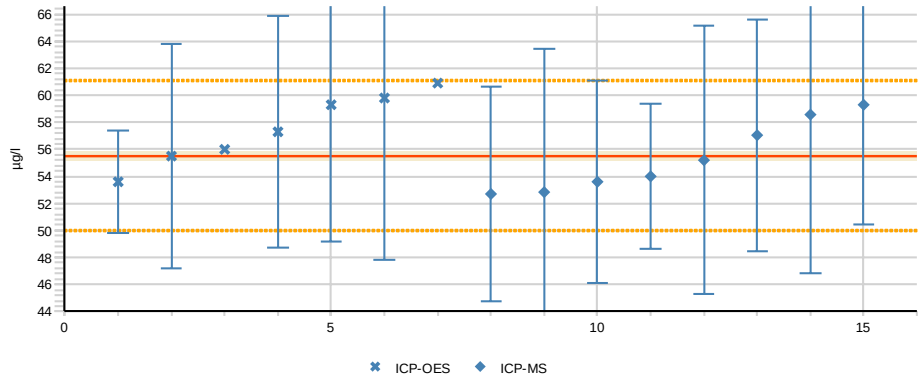



Measurand Cd Sample TN3
µg/l
19
18
17
16
15
14
13
12
11
0
5
10
GAAS
ICP-OES
ICP-MS

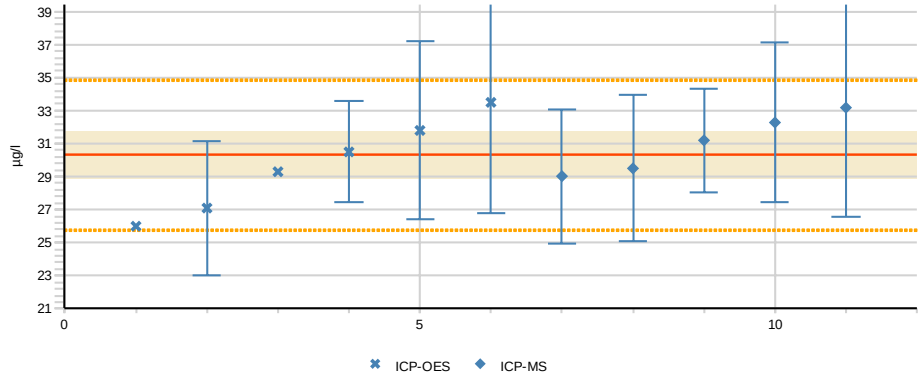

Measurand Cd Sample TY3
µg/l
21
19
17
15
13
11
9
0
5
ICP-OES
ICP-MS


Measurand Cd Sample V2M
µg/l
2.7
2.5
2.3
2.1
1.9
1.7
1.5
0
5
10
15
GAAS
ICP-OES
ICP-MS

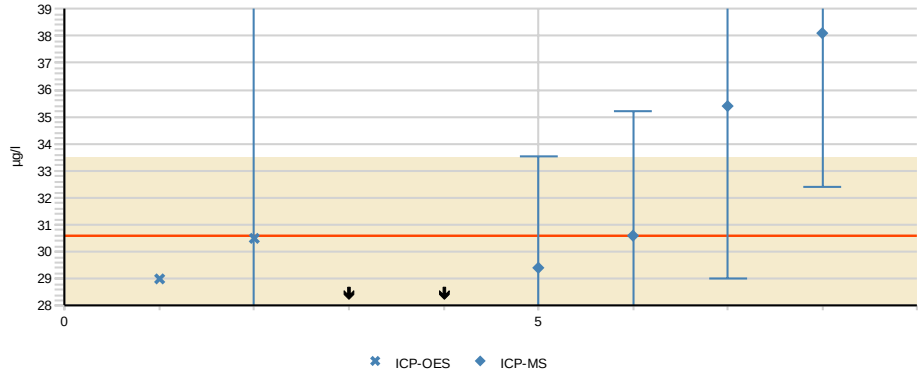
Measurand Co Sample A1M



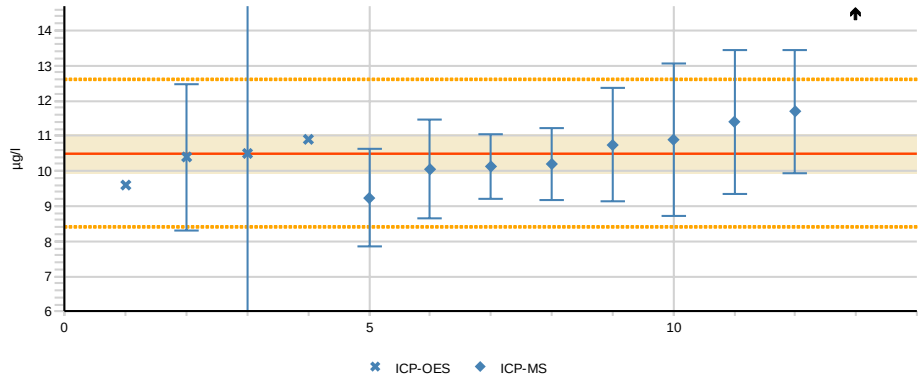
Measurand Co Sample TN3



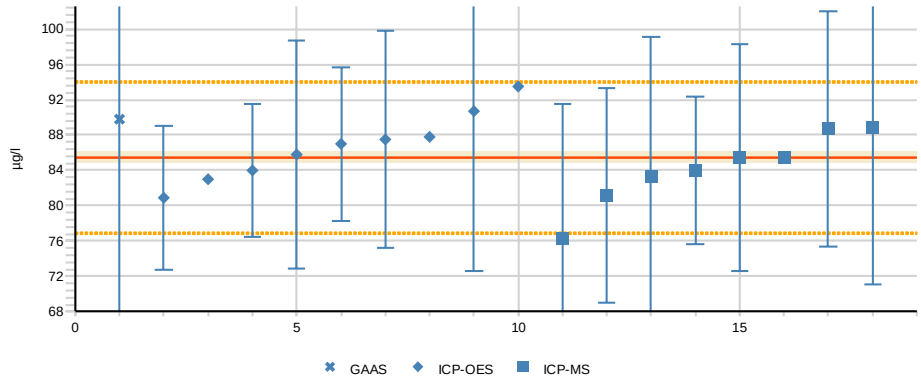
Measurand Co Sample TY3



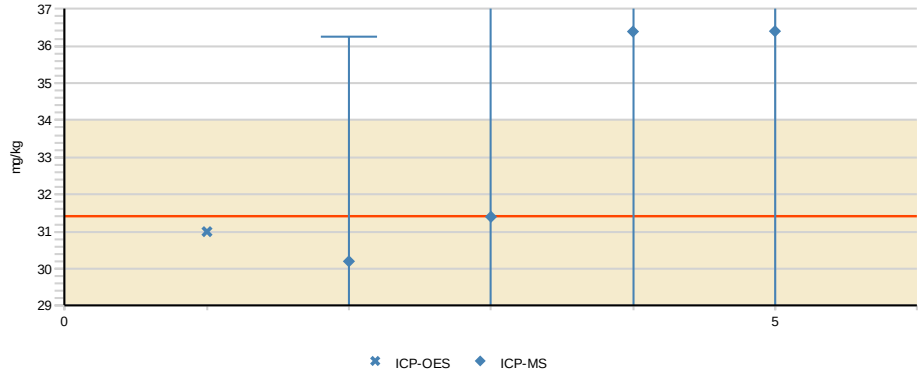
Measurand Co Sample V2M



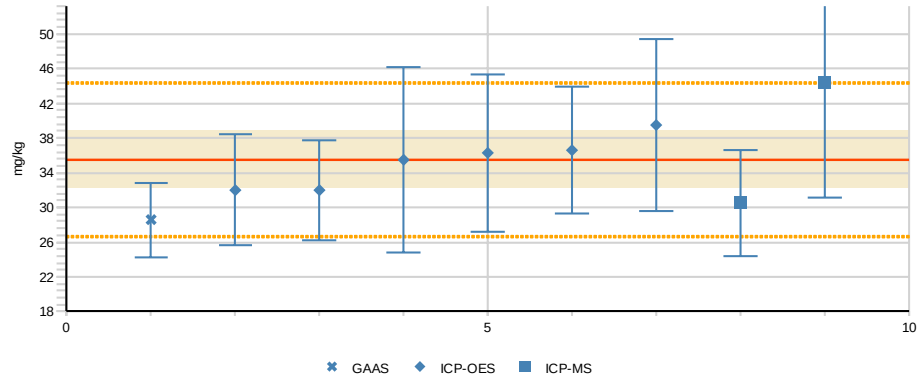
Measurand Cr Sample A1M



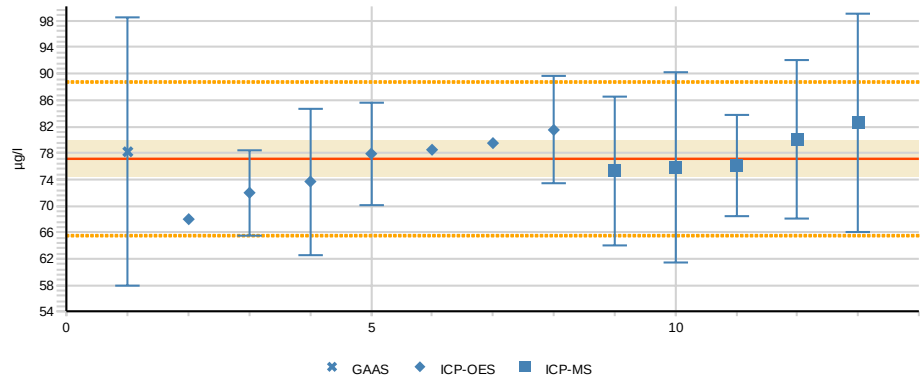
Measurand Cr Sample KN4



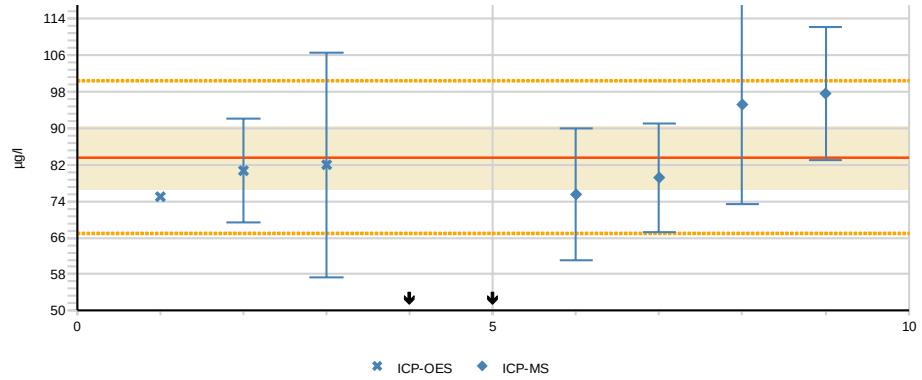
Measurand Cr Sample KO4

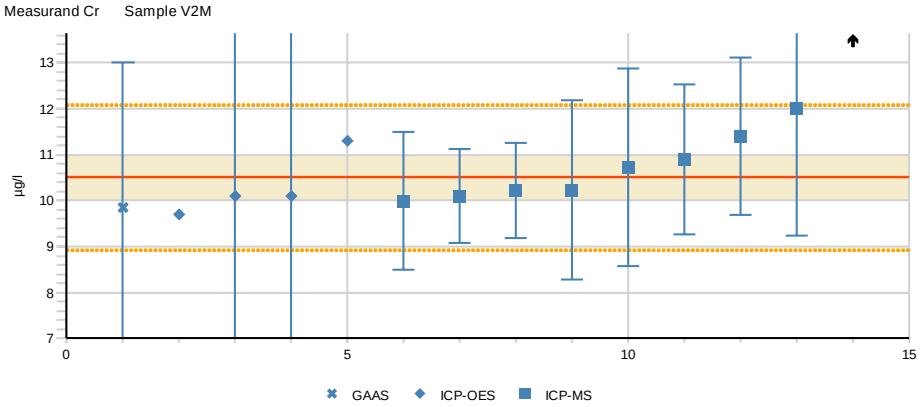


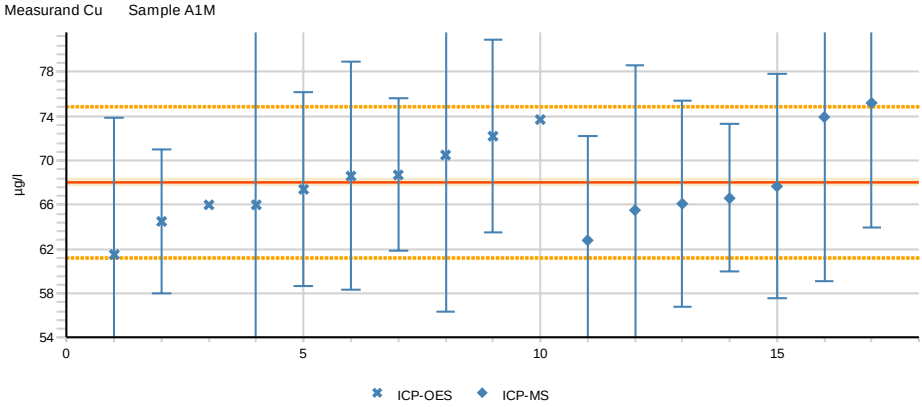
Measurand Cr Sample TN3

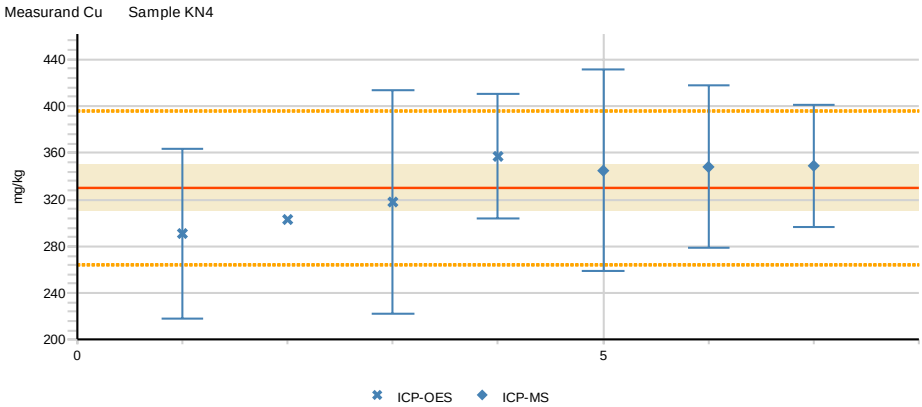


Measurand Cr Sample TY3

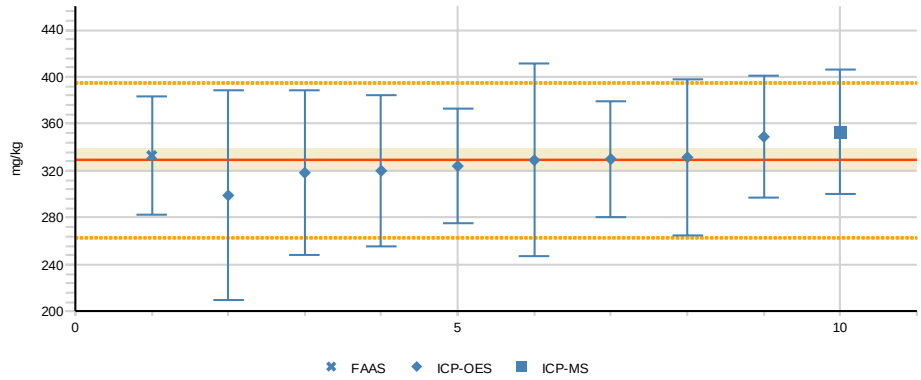



Measurand Cr Sample V2M
µg/l
13
12
11
10
9
8
7
0
5
10
15
GAAS
ICP-OES
ICP-MS

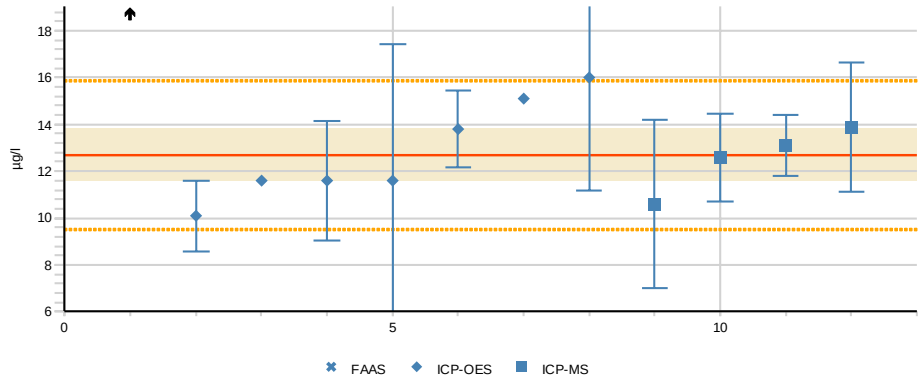

Measurand Cu Sample A1M
µg/l
78
74
70
66
62
58
54
0
5
10
15
ICP-OES
ICP-MS


Measurand Cu Sample KN4
mg/kg
440
400
360
320
280
240
200
0
5
ICP-OES
ICP-MS

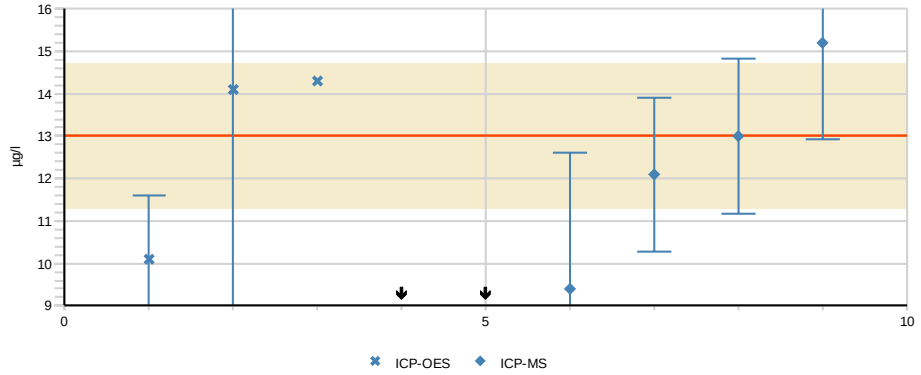
Measurand Cu Sample KO4

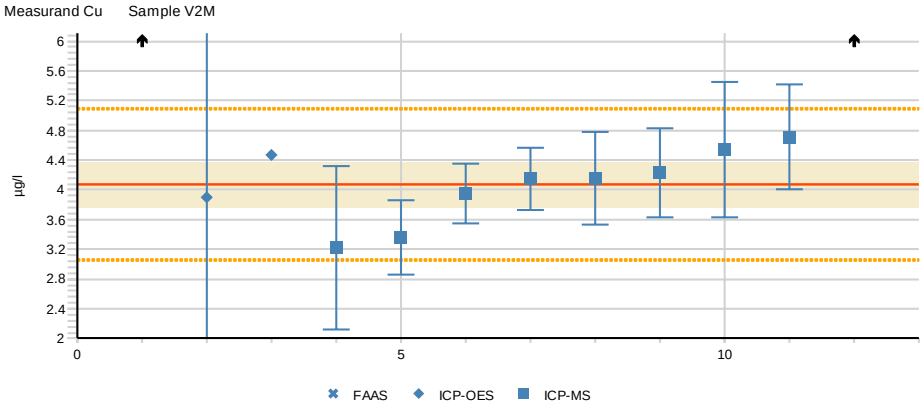


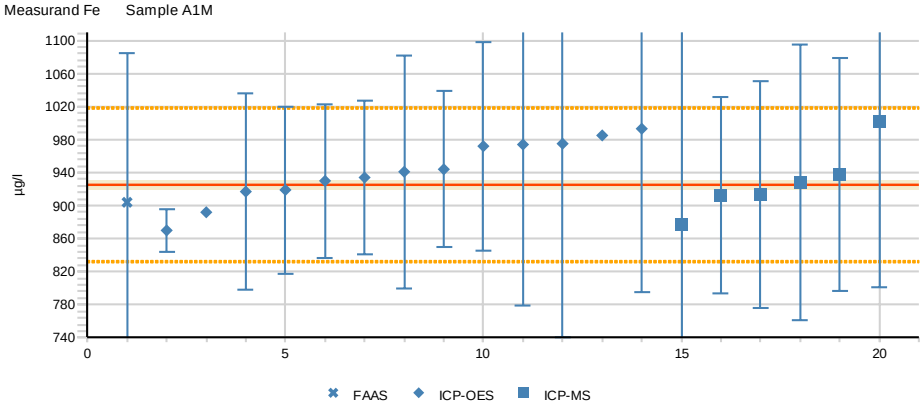
Measurand Cu Sample TN3

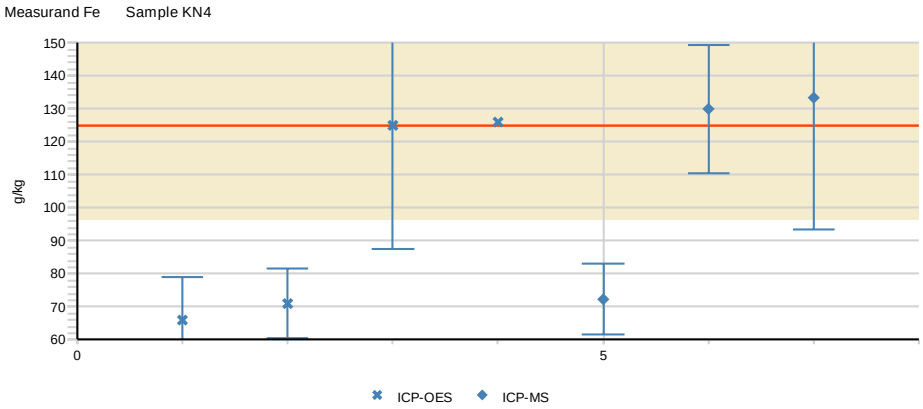


Measurand Cu Sample TY3

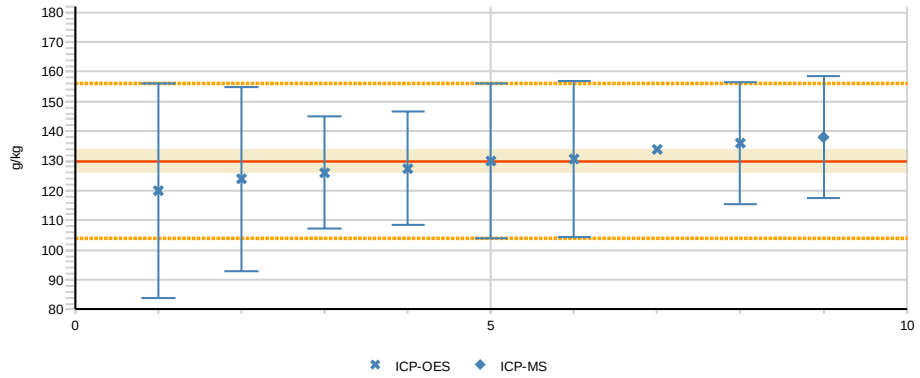



Measurand Cu
Sample V2M
µg/l
6
5.6
5.2
4.8
4.4
4
3.6
3.2
2.8
2.4
2
0
5
10
FAAS
ICP-OES
ICP-MS

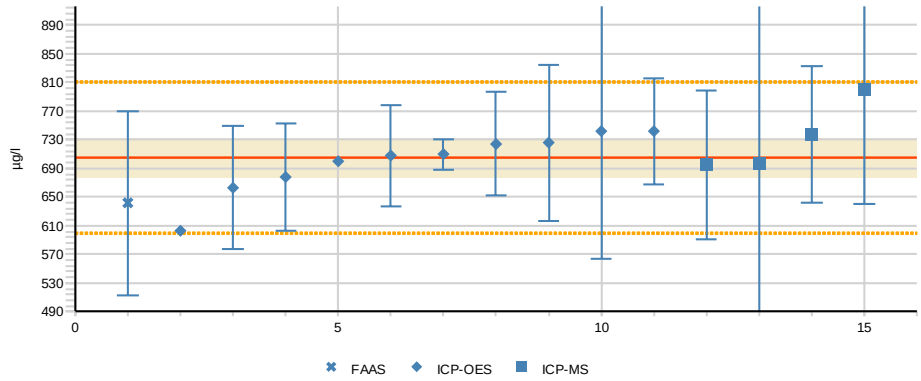

Measurand Fe
Sample A1M
µg/l
1100
1060
1020
980
940
900
860
820
780
740
0
5
10
15
20
FAAS
ICP-OES
ICP-MS


Measurand Fe
Sample KN4
g/kg
150
140
130
120
110
100
90
80
70
60
0
5
ICP-OES
ICP-MS

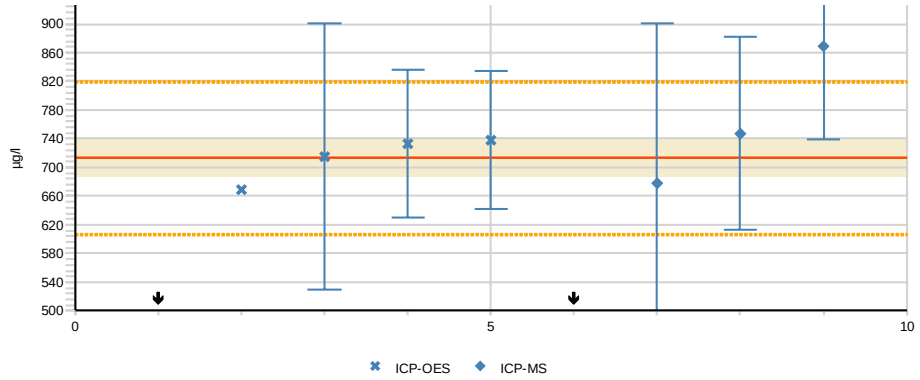
Measurand Fe Sample KO4



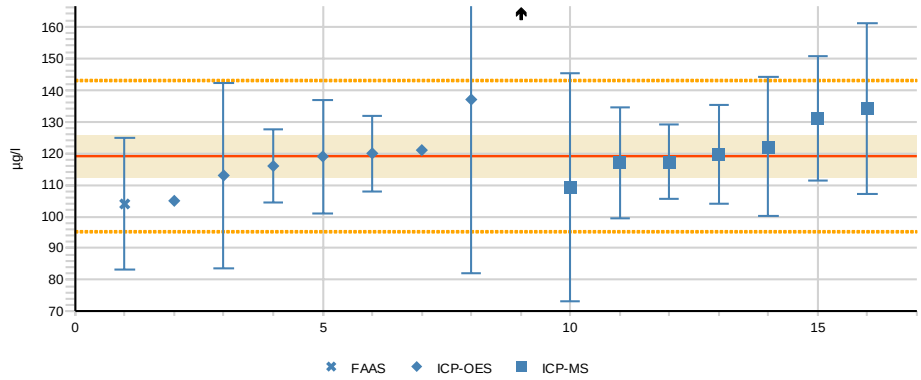
Measurand Fe Sample TN3



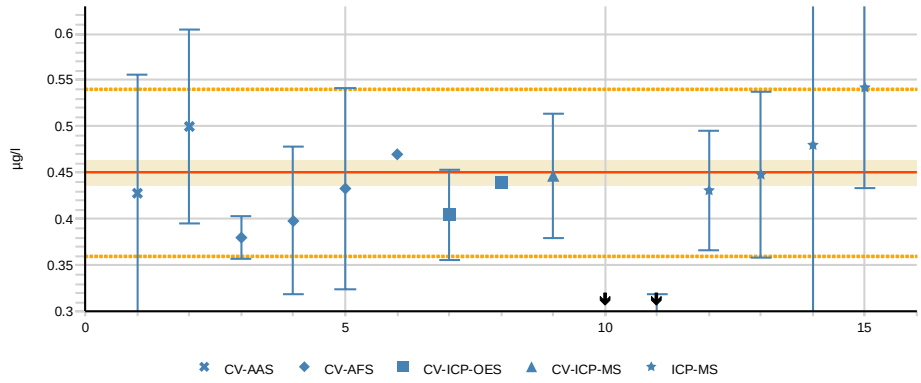
Measurand Fe Sample TY3



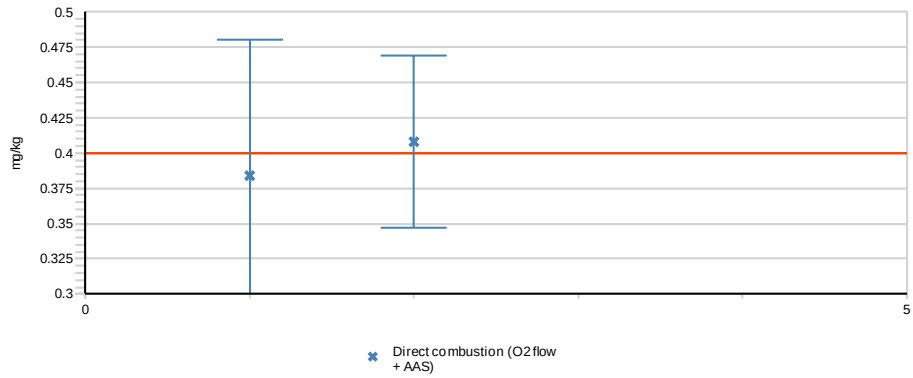
Measurand Fe Sample V2M



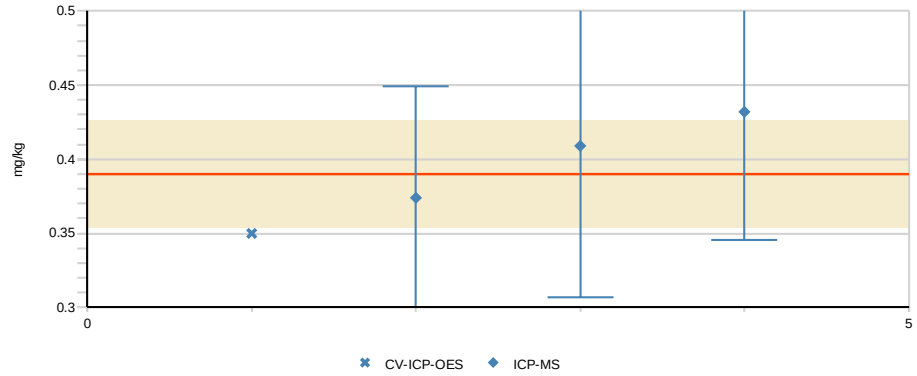
Measurand Hg Sample A1Hg



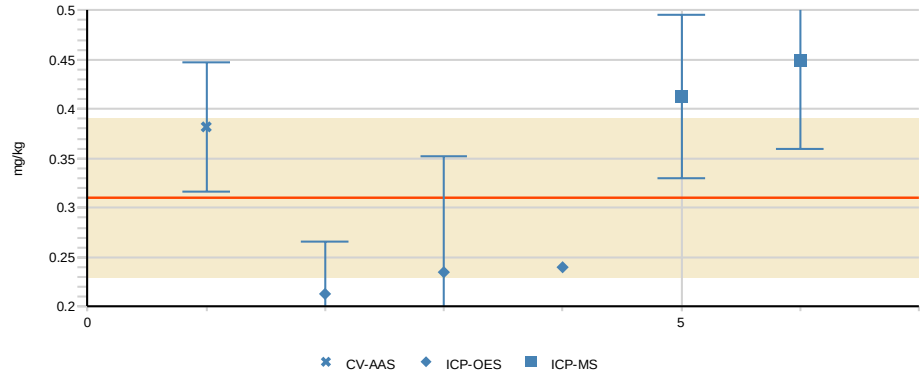
Measurand Hg Sample KC4



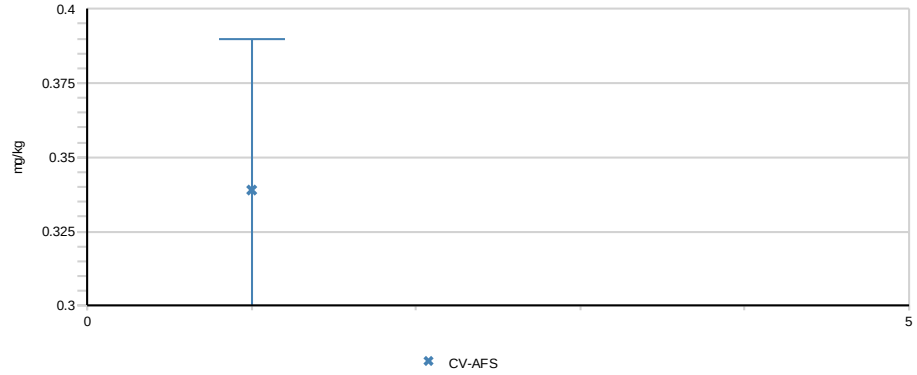
Measurand Hg Sample KN4

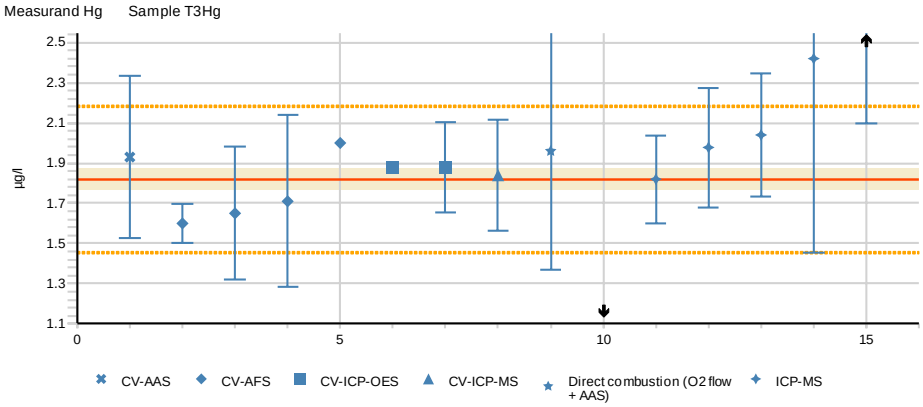


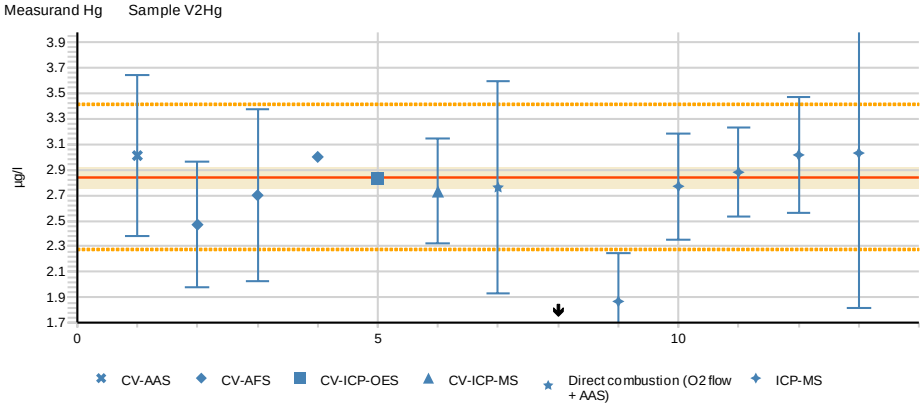
Measurand Hg Sample KO4

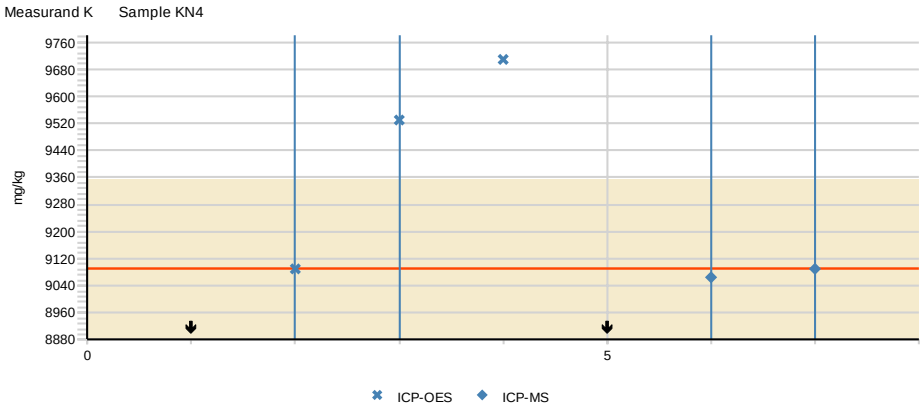


Measurand Hg Sample KX4

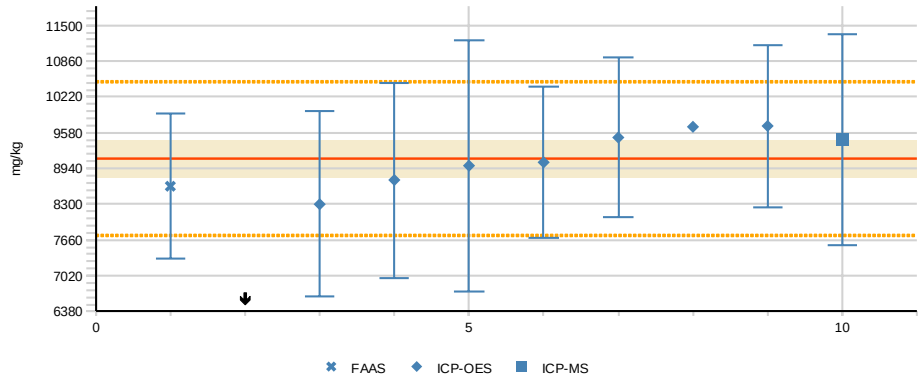



Measurand Hg Sample T3Hg
µg/l
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0
5
10
15
CV-AAS
CV-AFS
CV-ICP-OES
CV-ICP-MS
Direct combustion (O2 flow + AAS)
ICP-MS

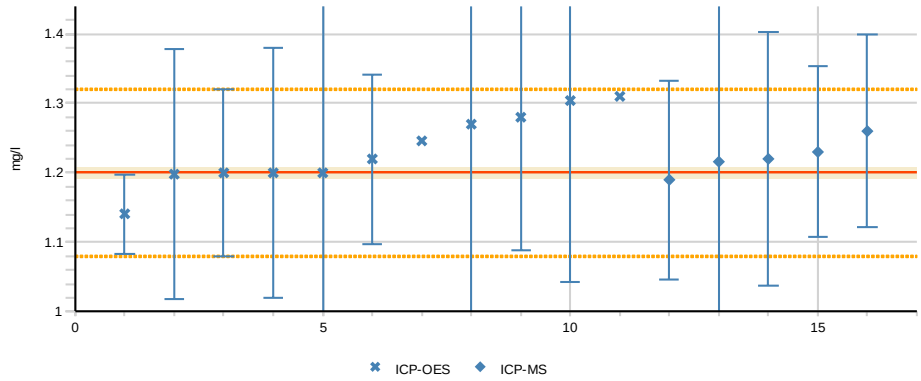

Measurand Hg Sample V2Hg
µg/l
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
0
5
10
CV-AAS
CV-AFS
CV-ICP-OES
CV-ICP-MS
Direct combustion (O2 flow + AAS)
ICP-MS


Measurand K Sample KN4
mg/kg
9760
9680
9600
9520
9440
9360
9280
9200
9120
9040
8960
8880
0
5
ICP-OES
ICP-MS

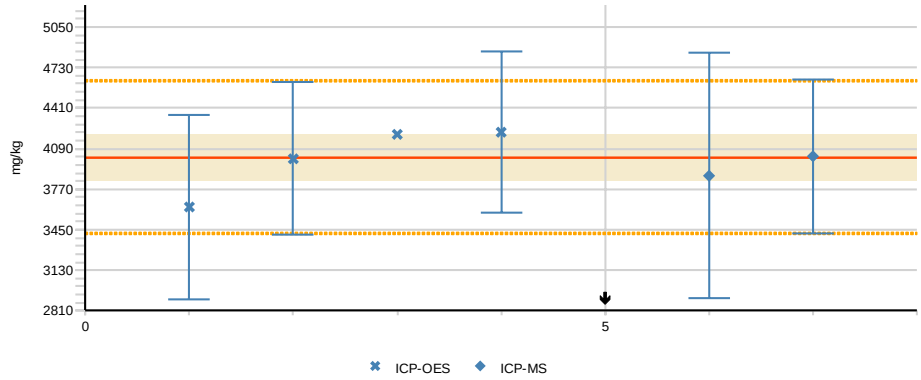
Measurand K Sample KO4

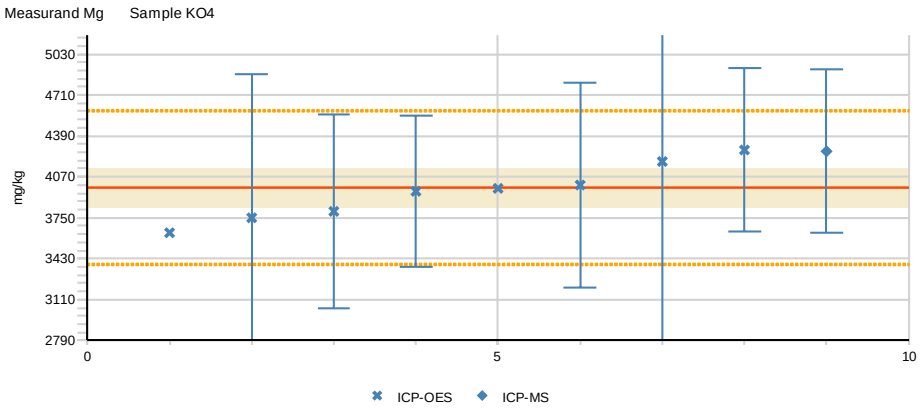


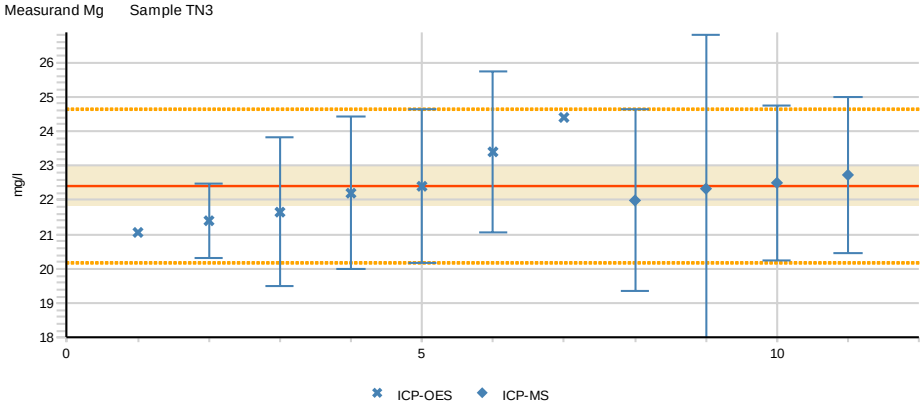
Measurand Mg Sample A1M

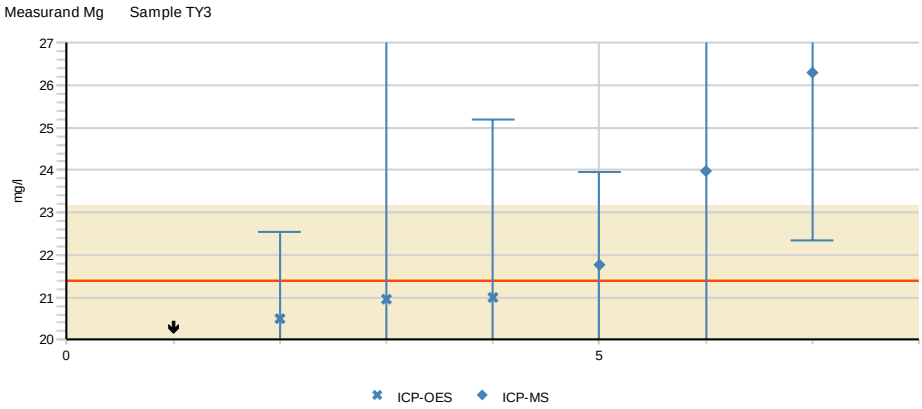


Measurand Mg Sample KN4

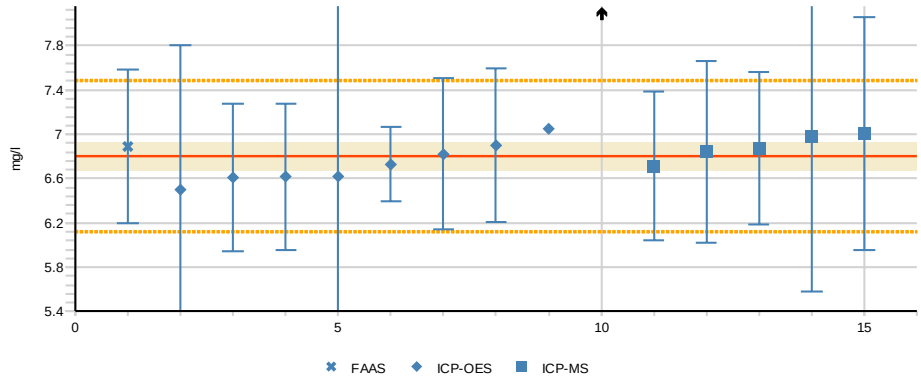



Measurand Mg
Sample KO4
mg/kg
5030
4710
4390
4070
3750
3430
3110
2790
0
5
10
ICP-OES
ICP-MS

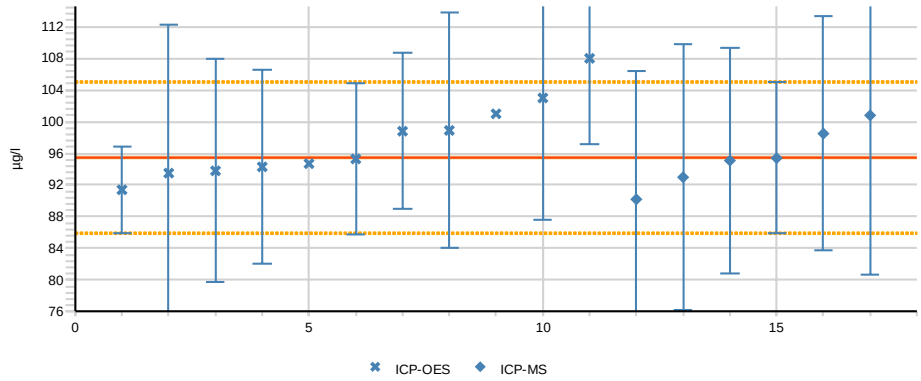

Measurand Mg
Sample TN3
mg/l
26
25
24
23
22
21
20
19
18
0
5
10
ICP-OES
ICP-MS


Measurand Mg
Sample TY3
mg/l
27
26
25
24
23
22
21
20
0
5
ICP-OES
ICP-MS

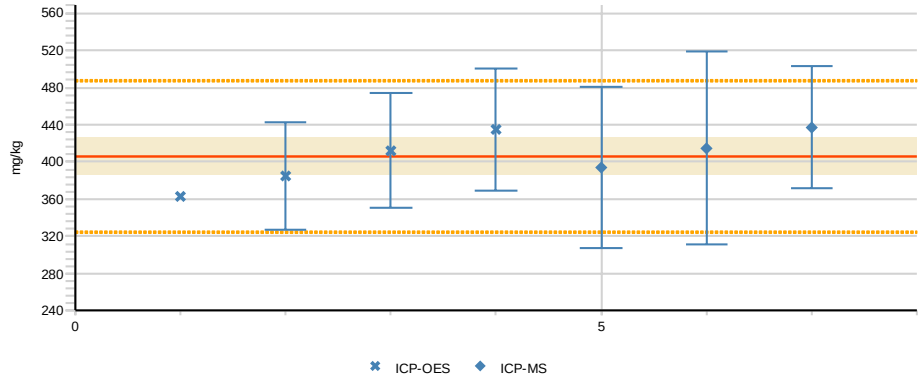
Measurand Mg Sample V2M

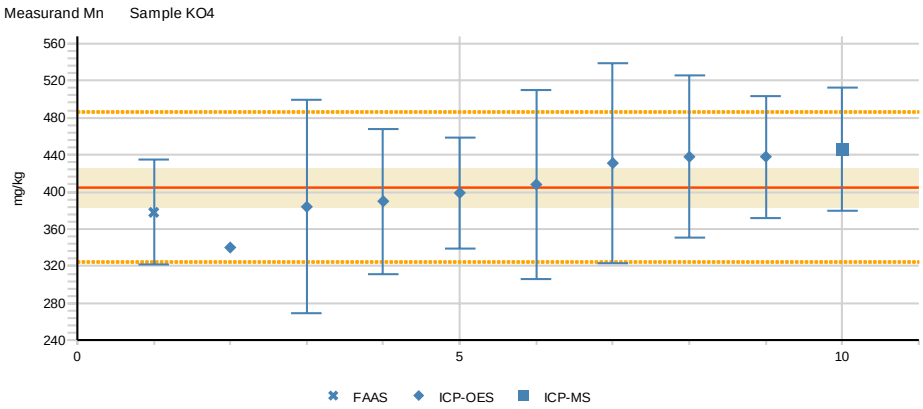


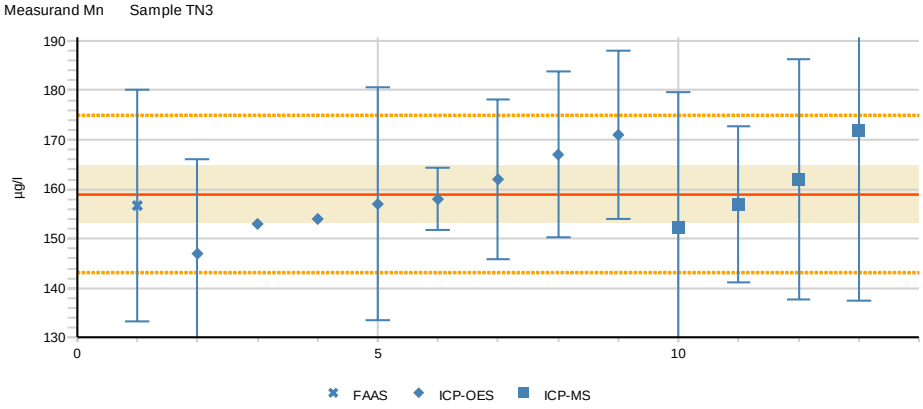
Measurand Mn Sample A1M

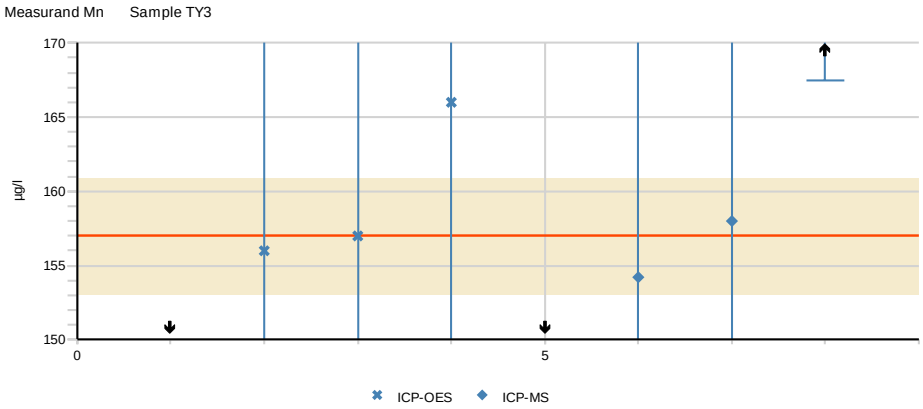


Measurand Mn Sample KN4

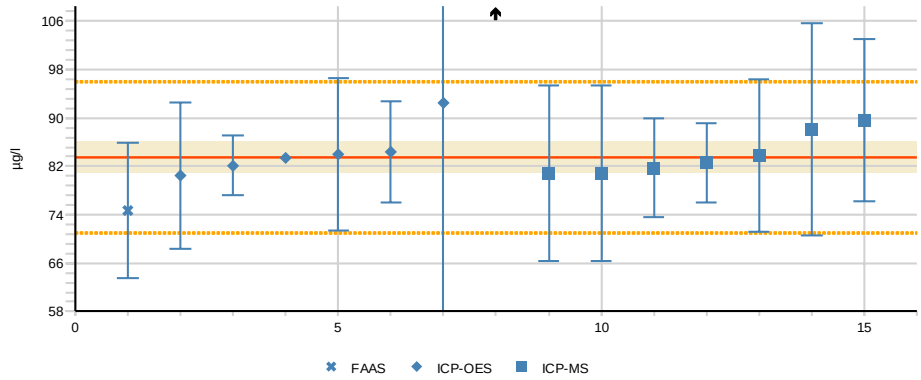



Measurand Mn
Sample KO4
mg/kg
560
520
480
440
400
360
320
280
240
0
5
10
FAAS
ICP-OES
ICP-MS

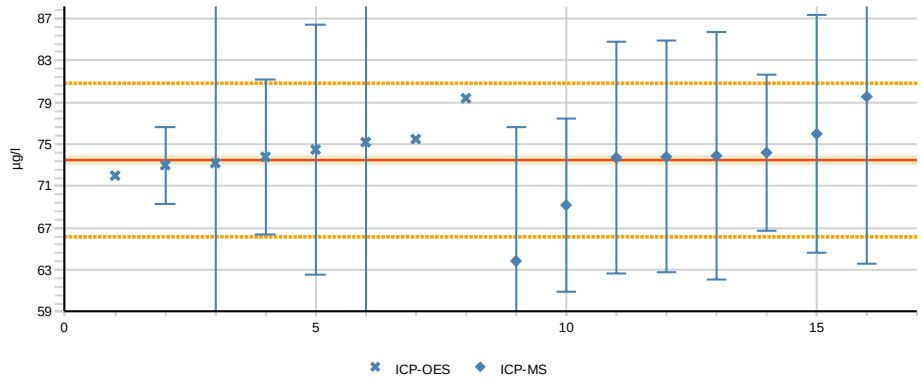

Measurand Mn
Sample TN3
µg/l
190
180
170
160
150
140
130
0
5
10
FAAS
ICP-OES
ICP-MS


Measurand Mn
Sample TY3
µg/l
170
165
160
155
150
0
5
ICP-OES
ICP-MS

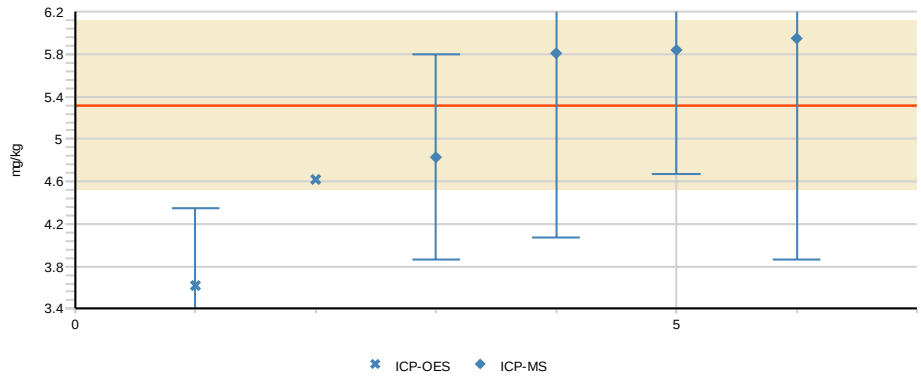
Measurand Mn Sample V2M

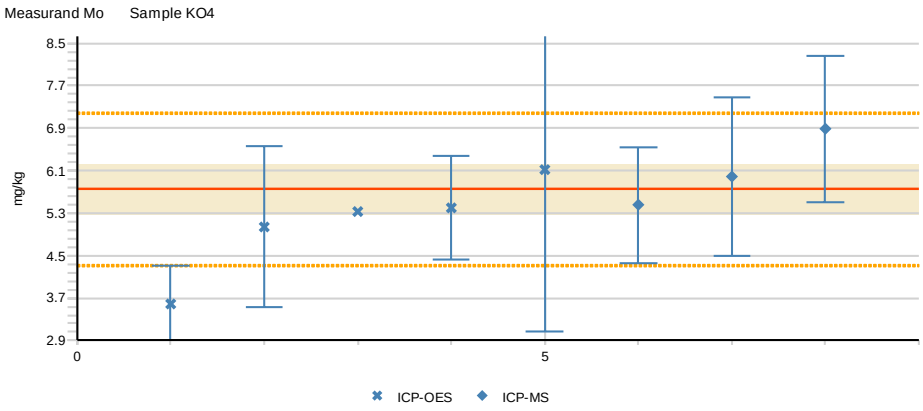


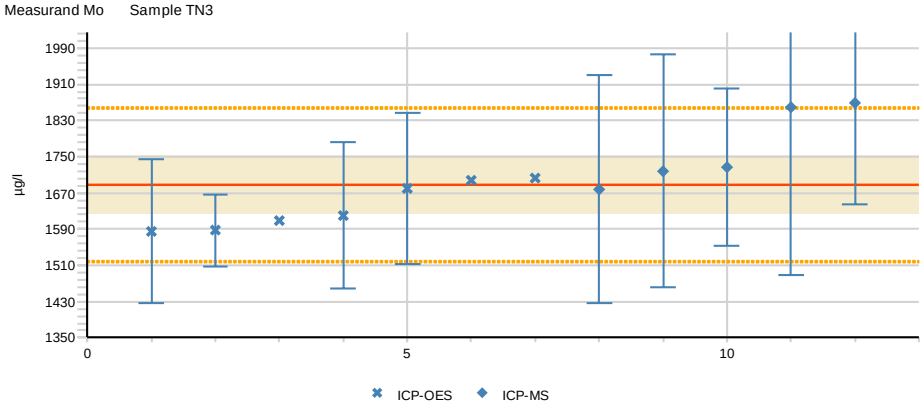
Measurand Mo Sample A1M

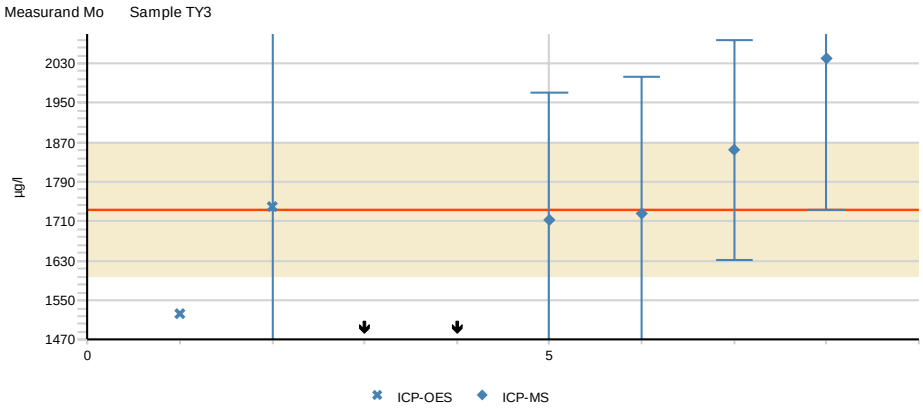


Measurand Mo Sample KN4

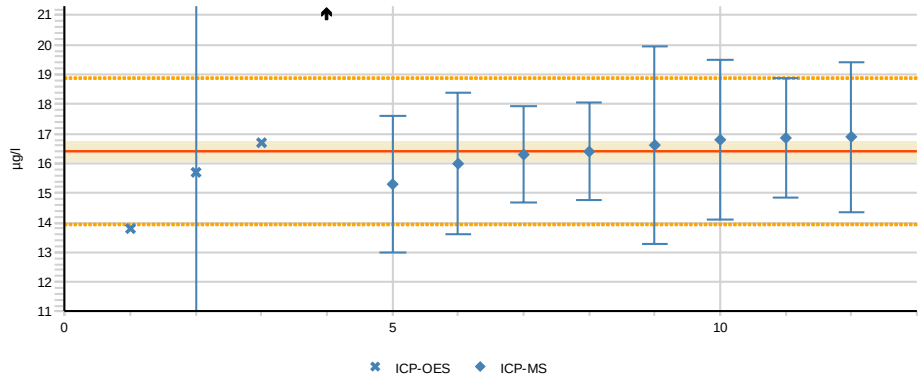



Measurand Mo
Sample KO4
mg/kg
8.5
7.7
6.9
6.1
5.3
4.5
3.7
2.9
0
5
ICP-OES
ICP-MS

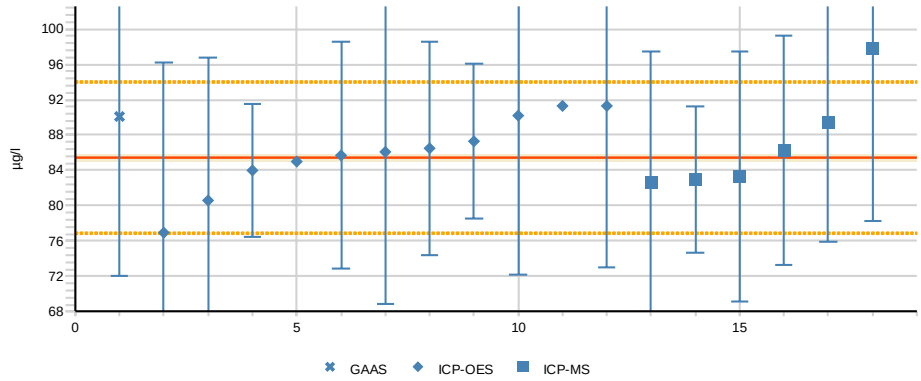

Measurand Mo
Sample TN3
µg/l
1990
1910
1830
1750
1670
1590
1510
1430
1350
0
5
10
ICP-OES
ICP-MS


Measurand Mo
Sample TY3
µg/l
2030
1950
1870
1790
1710
1630
1550
1470
0
5
ICP-OES
ICP-MS

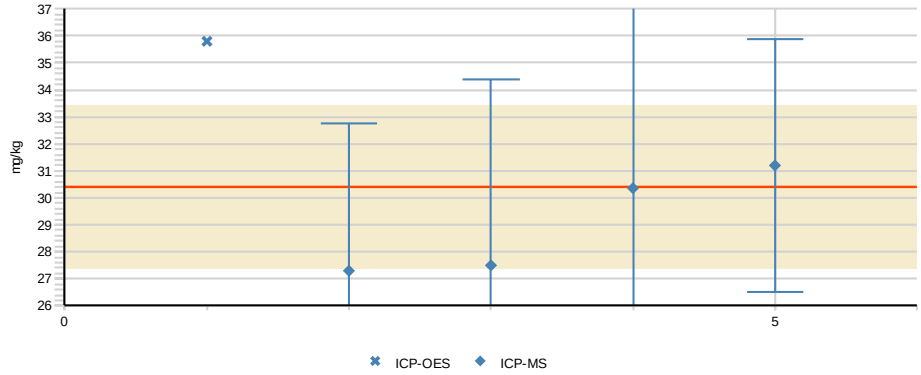
Measurand Mo Sample V2M

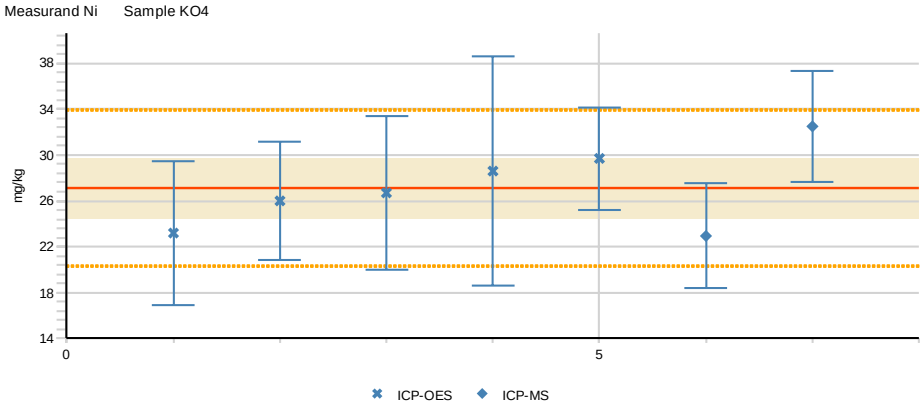


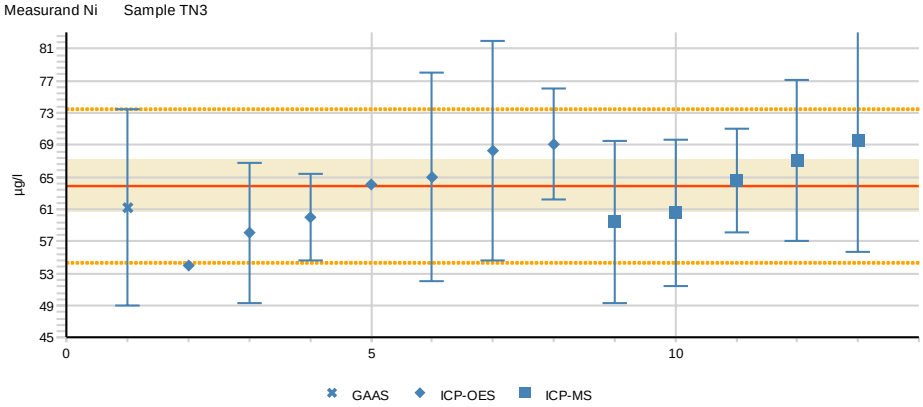
Measurand Ni Sample A1M

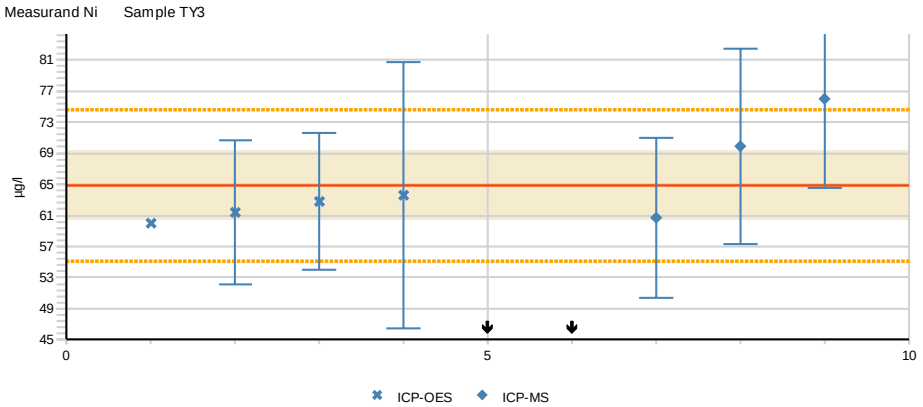


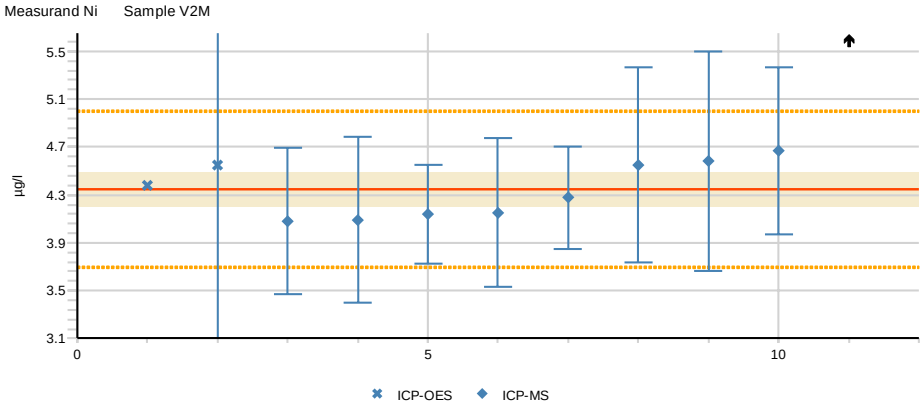
Measurand Ni Sample KN4

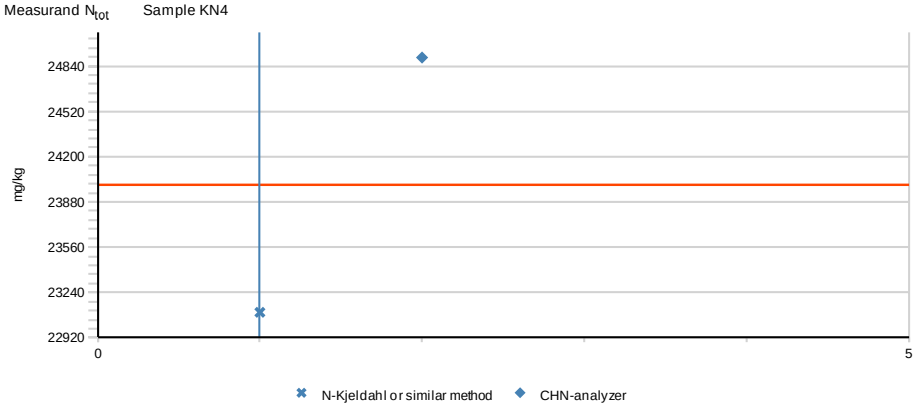


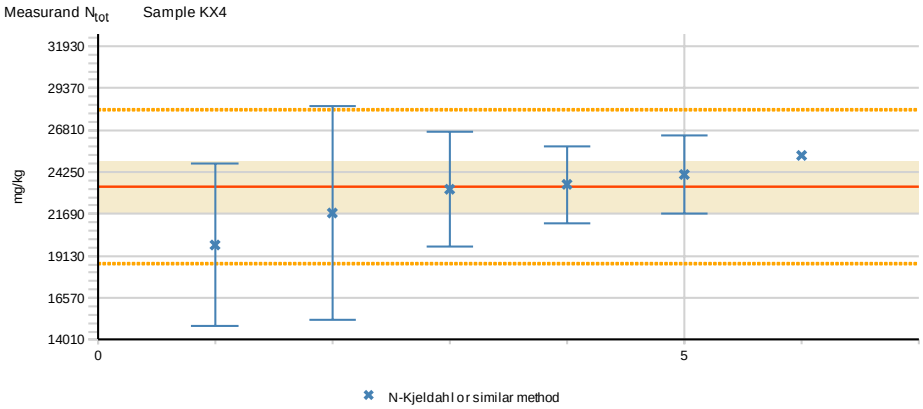

Measurand Ni Sample KO4
mg/kg
38
34
30
26
22
18
14
0
5
ICP-OES
ICP-MS

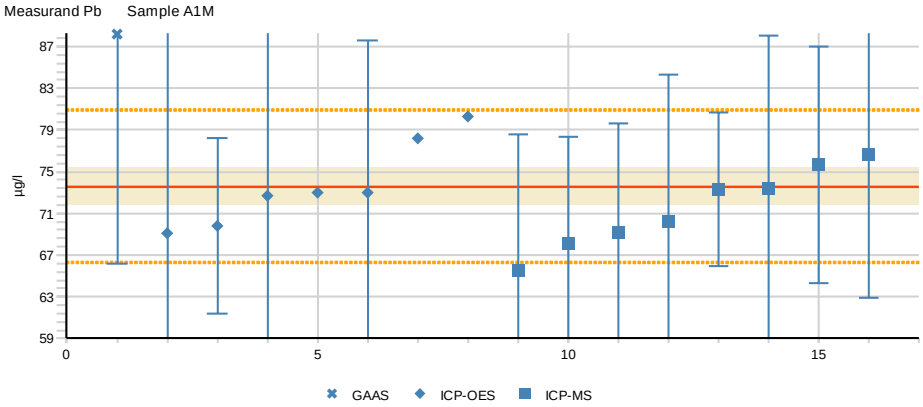

Measurand Ni Sample TN3
µg/l
81
77
73
69
65
61
57
53
49
45
0
5
10
GAAS
ICP-OES
ICP-MS

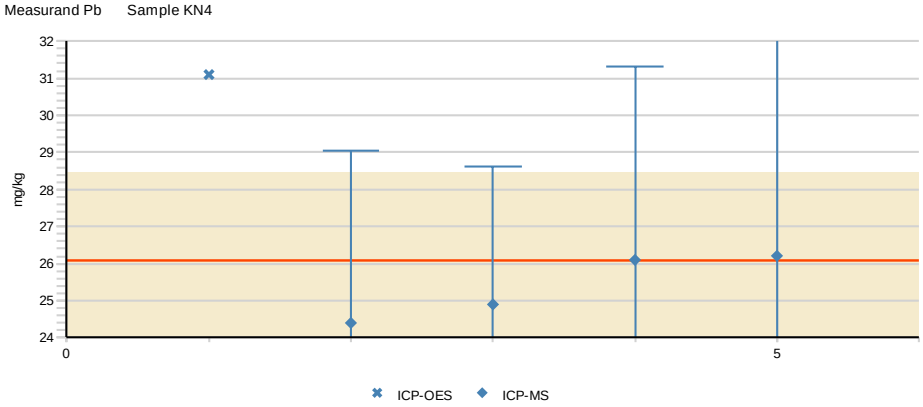

Measurand Ni Sample TY3
µg/l
81
77
73
69
65
61
57
53
49
45
0
5
10
ICP-OES
ICP-MS

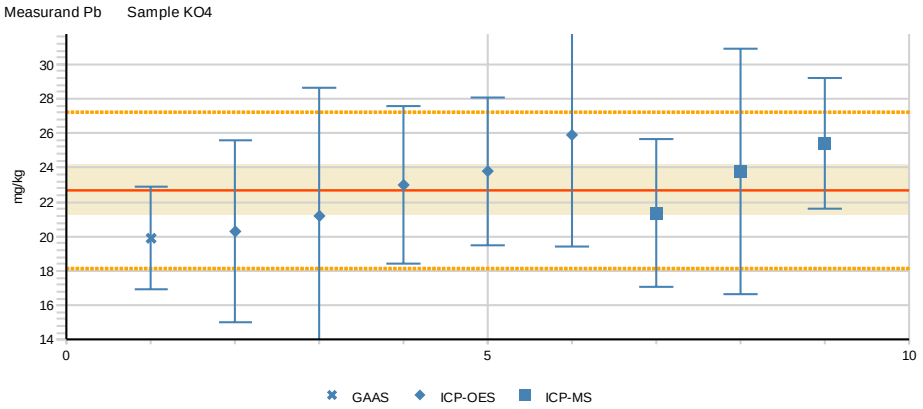

Measurand Ni
Sample V2M
µg/l
5.5
5.1
4.7
4.3
3.9
3.5
3.1
0
5
10
ICP-OES
ICP-MS


Measurand Ntot
Sample KN4
mg/kg
24840
24520
24200
23880
23560
23240
22920
0
5
N-Kjeldahl or similar method
CHN-analyzer

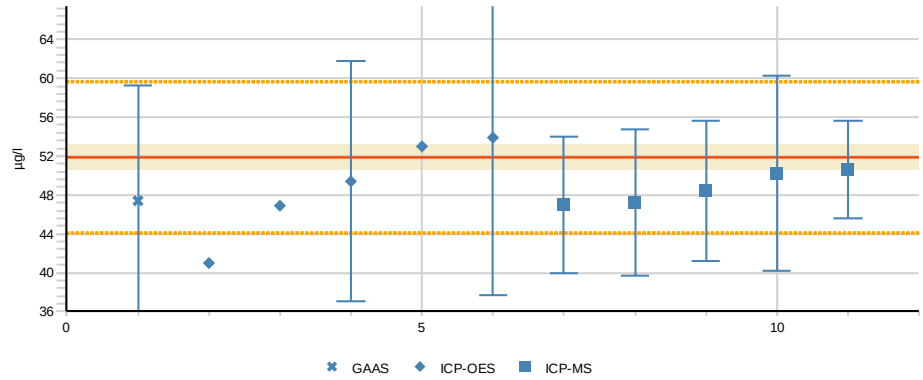

Measurand Ntot
Sample KX4
mg/kg
31930
29370
26810
24250
21690
19130
16570
14010
0
5
N-Kjeldahl or similar method


Measurand Pb Sample A1M
µg/l
87
83
79
75
71
67
63
59
0
5
10
15
GAAS
ICP-OES
ICP-MS

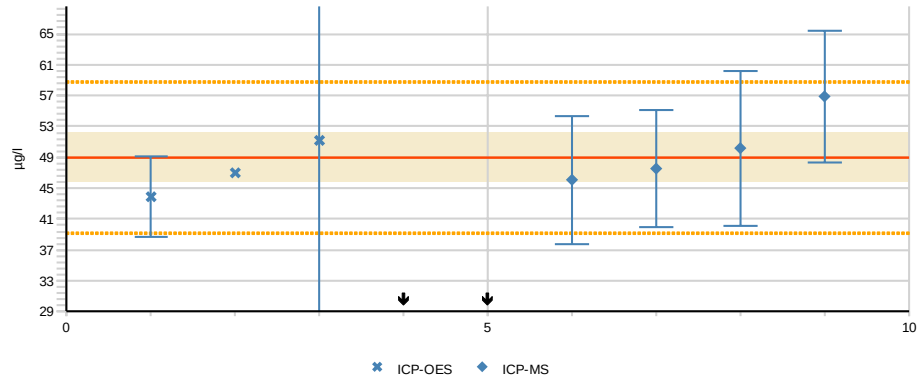

Measurand Pb Sample KN4
mg/kg
32
31
30
29
28
27
26
25
24
0
5
ICP-OES
ICP-MS


Measurand Pb Sample KO4
mg/kg
30
28
26
24
22
20
18
16
14
0
5
10
GAAS
ICP-OES
ICP-MS

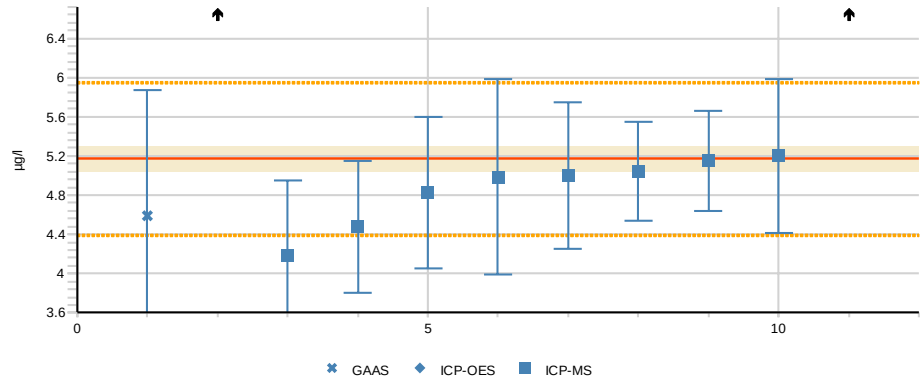
Measurand Pb Sample TN3

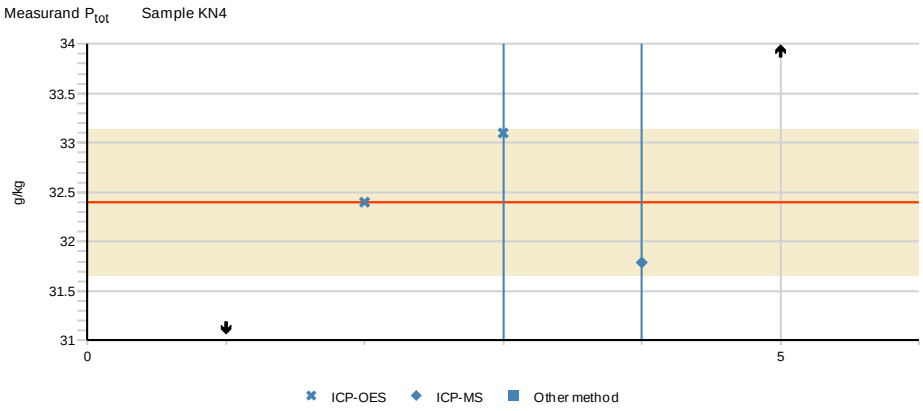


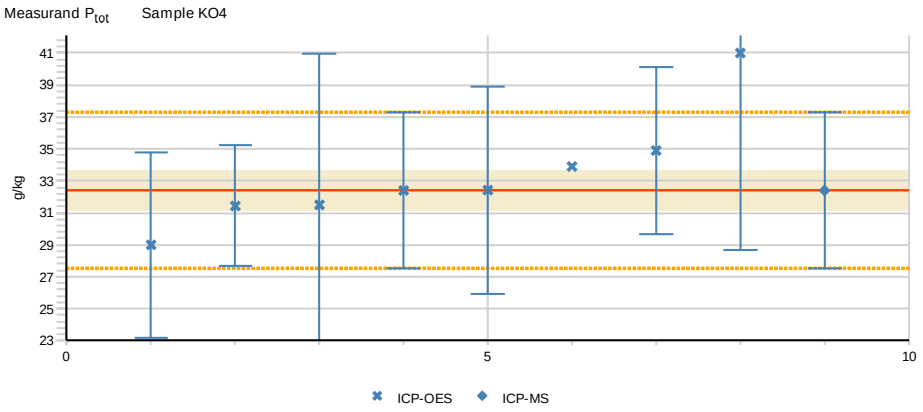
Measurand Pb Sample TY3

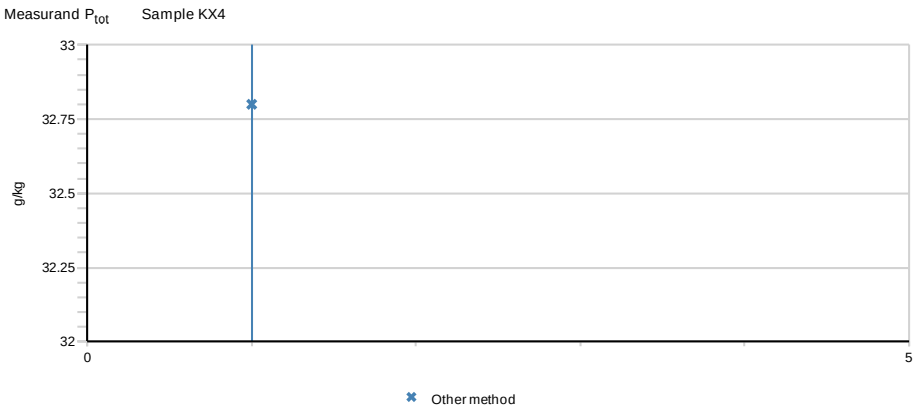


Measurand Pb Sample V2M

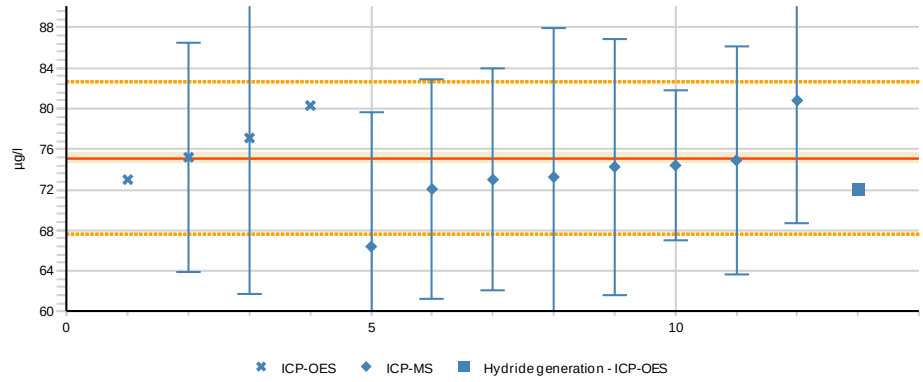



Measurand P_{tot} Sample KN4
34
33.5
33
32.5
32
31.5
31
mg/g
0
5
ICP-OES
ICP-MS
Other method

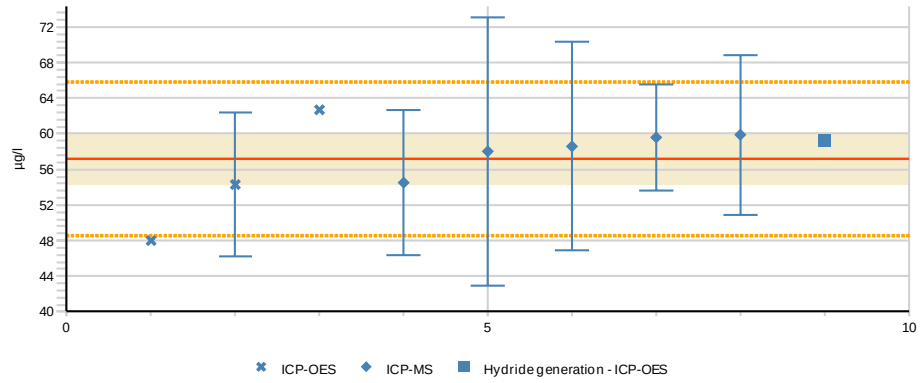

Measurand P_{tot} Sample KO4
41
39
37
35
33
31
29
27
25
23
mg/g
0
5
10
ICP-OES
ICP-MS


Measurand P_{tot} Sample KX4
33
32.75
32.5
32.25
32
mg/g
0
5
Other method

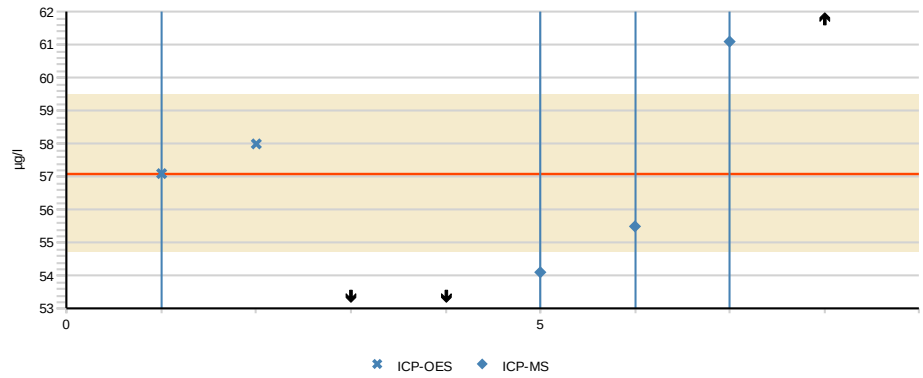
Measurand Sb Sample A1M



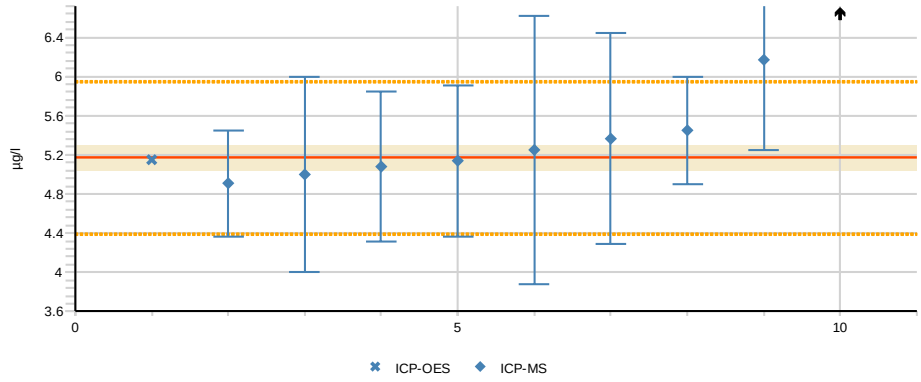
Measurand Sb Sample TN3



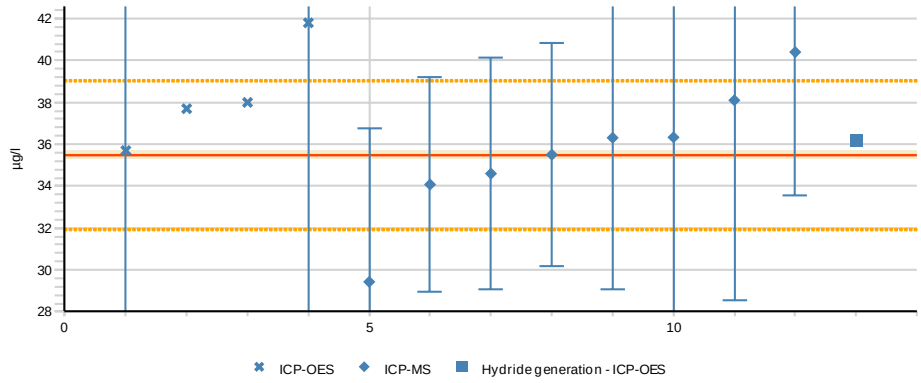
Measurand Sb Sample TY3



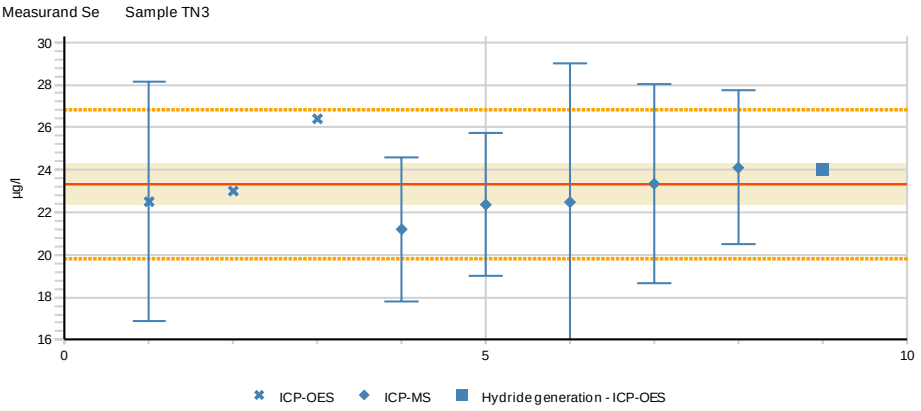
Measurand Sb Sample V2M



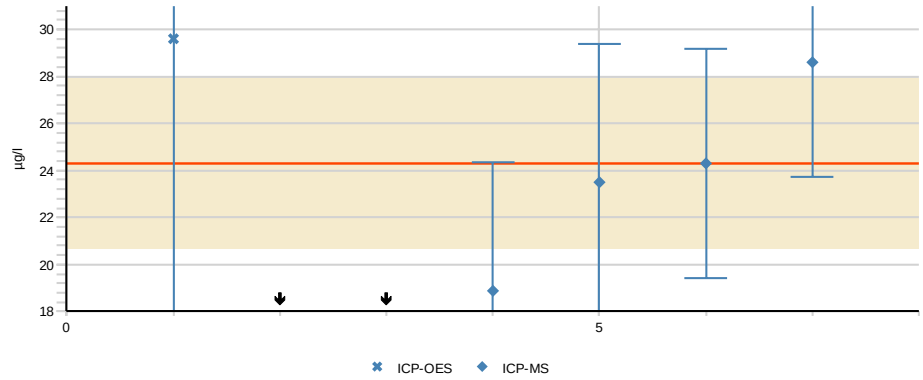
Measurand Se Sample A1M



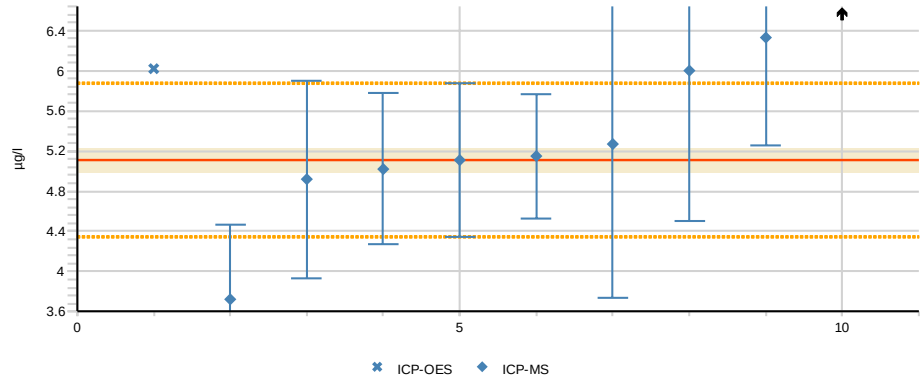
Measurand Se Sample TN3



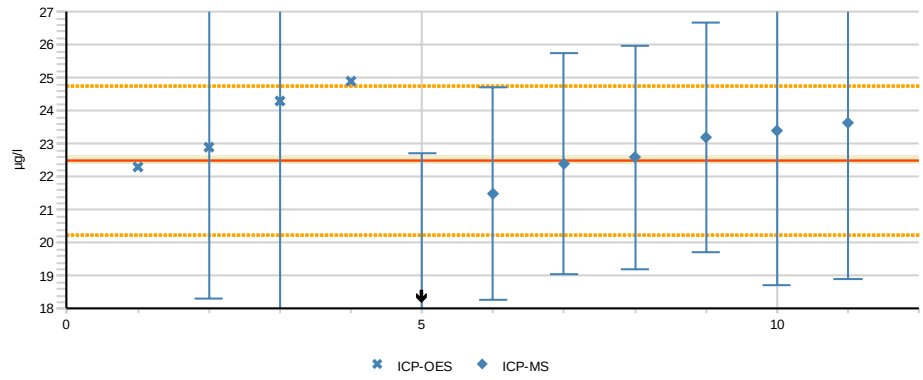
Measurand Se Sample TY3

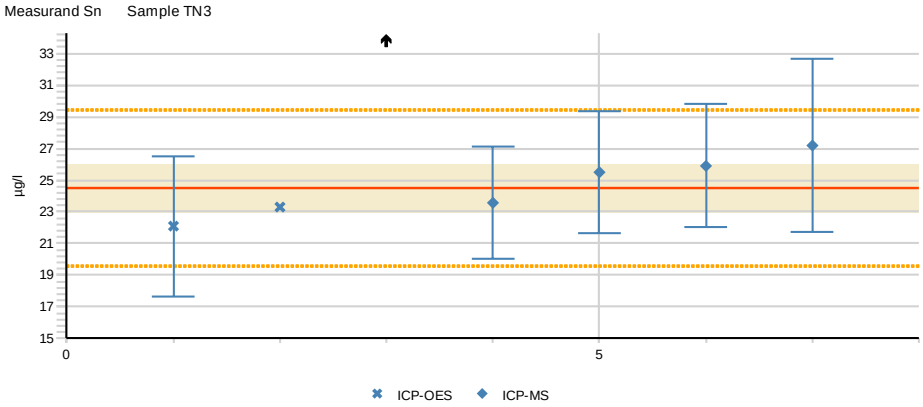


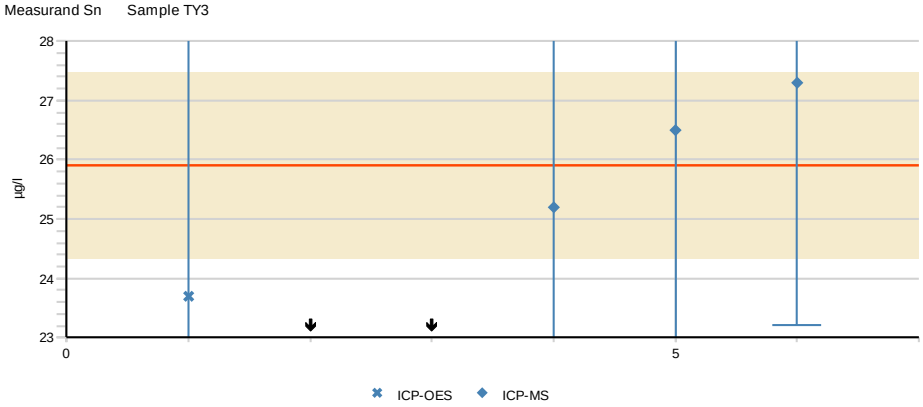
Measurand Se Sample V2M

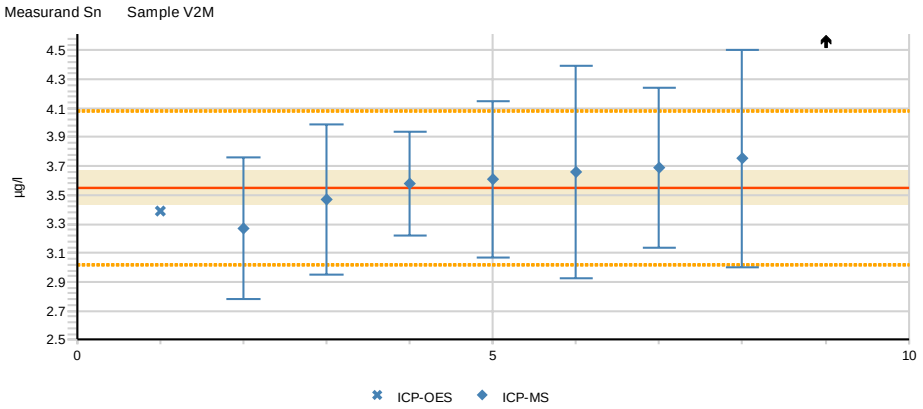


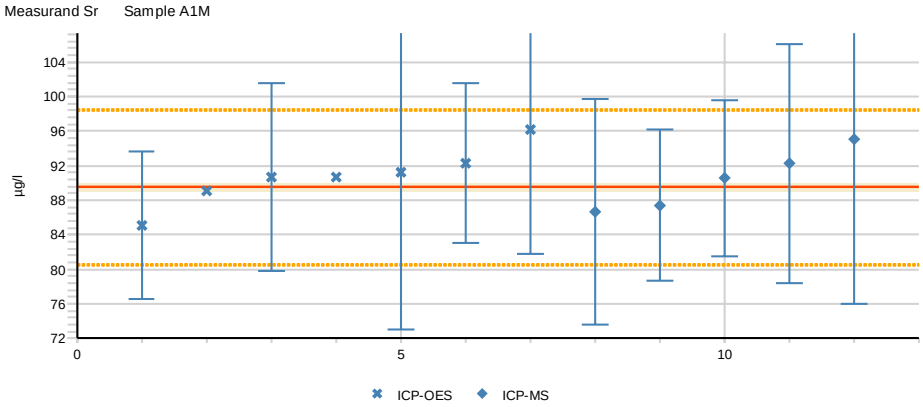
Measurand Sn Sample A1M

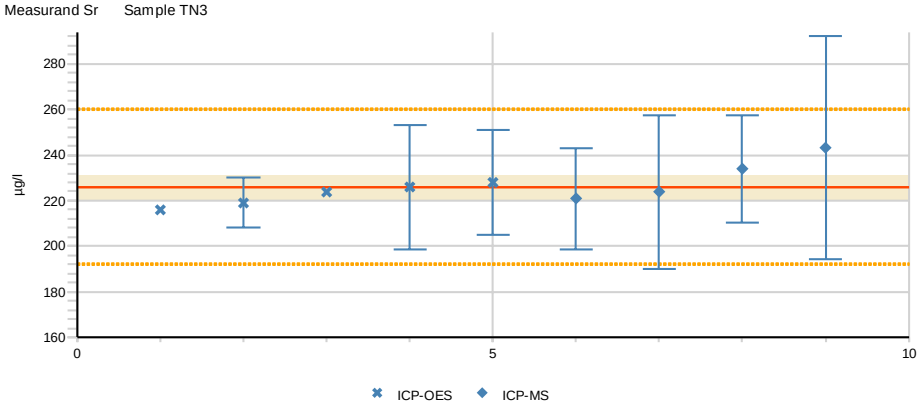


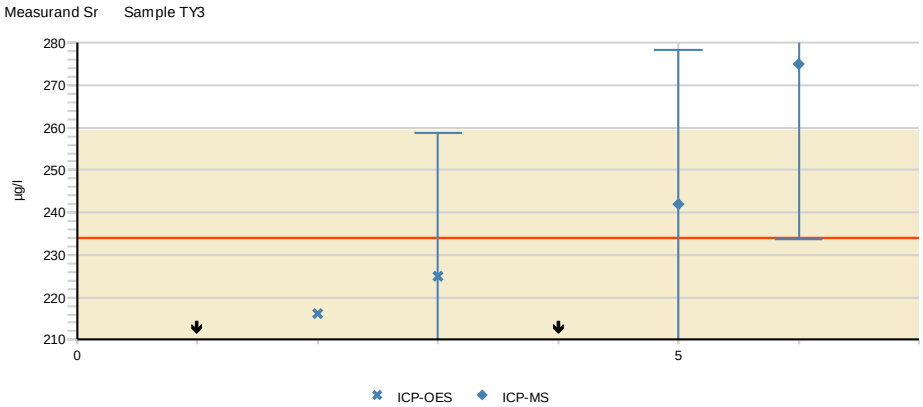

Measurand Sn Sample TN3
µg/l
33
31
29
27
25
23
21
19
17
15
0
5
ICP-OES
ICP-MS

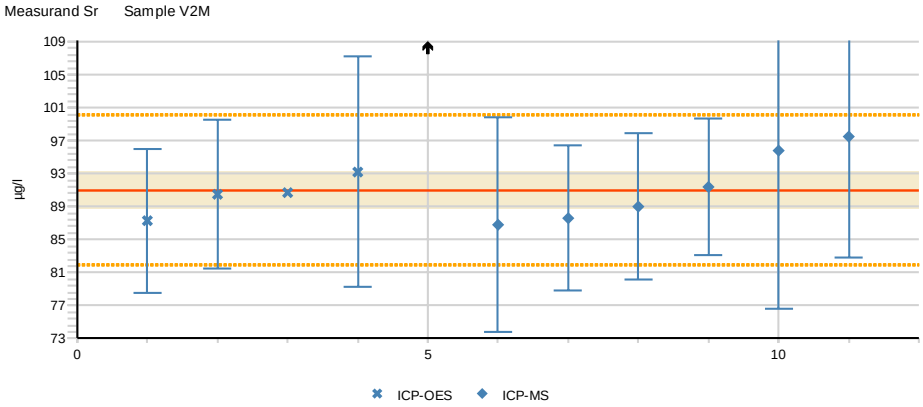

Measurand Sn Sample TY3
µg/l
28
27
26
25
24
23
0
5
ICP-OES
ICP-MS

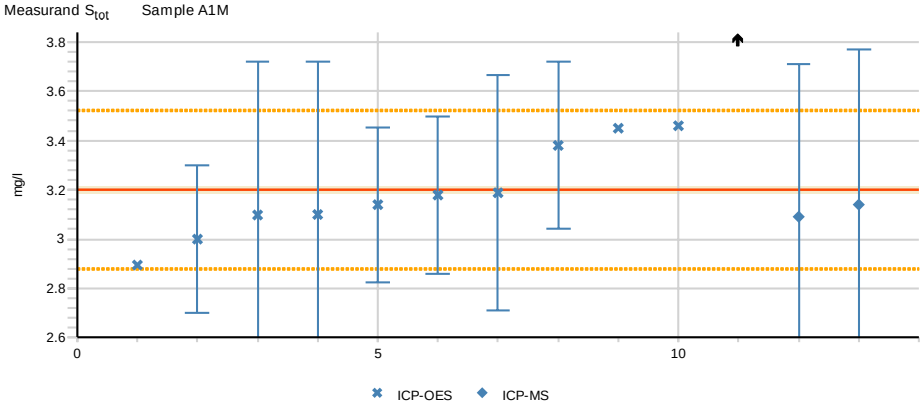

Measurand Sn Sample V2M
µg/l
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
0
5
10
ICP-OES
ICP-MS

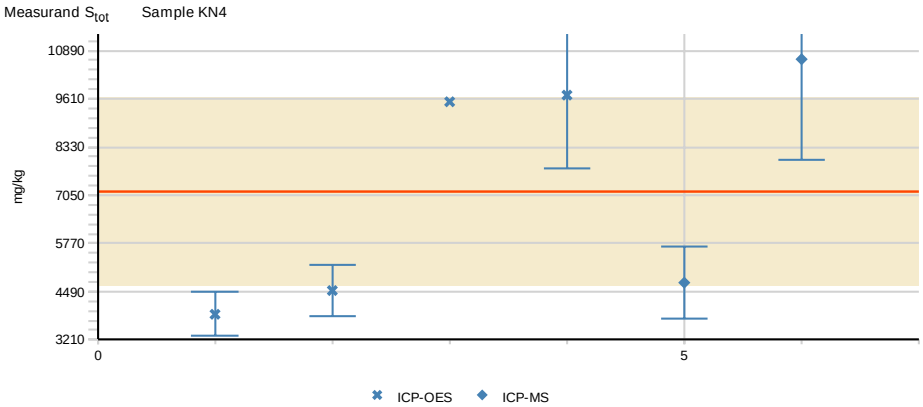

Measurand Sr Sample A1M
µg/l
104
100
96
92
88
84
80
76
72
0
5
10
ICP-OES
ICP-MS

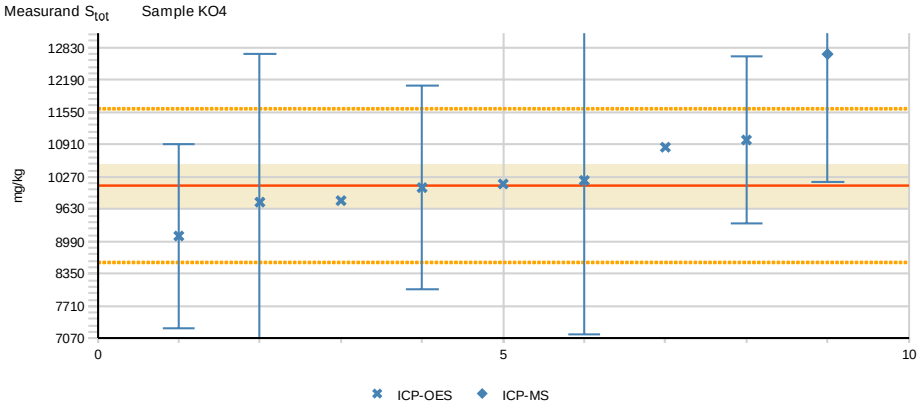

Measurand Sr Sample TN3
µg/l
280
260
240
220
200
180
160
0
5
10
ICP-OES
ICP-MS

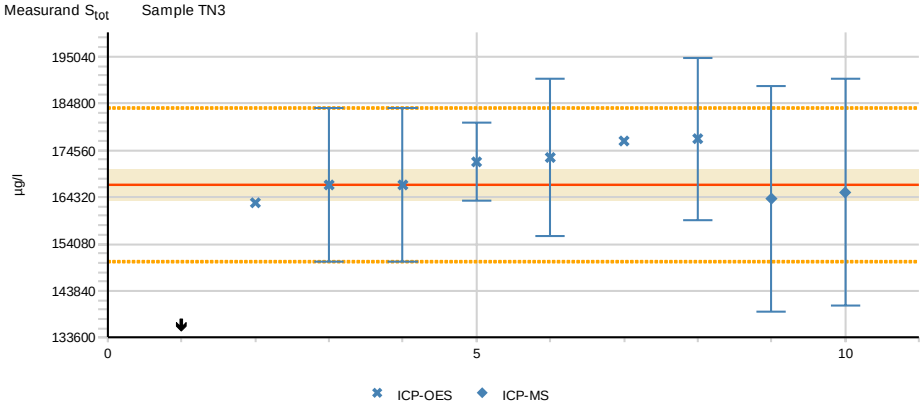

Measurand Sr Sample TY3
µg/l
280
270
260
250
240
230
220
210
0
5
ICP-OES
ICP-MS

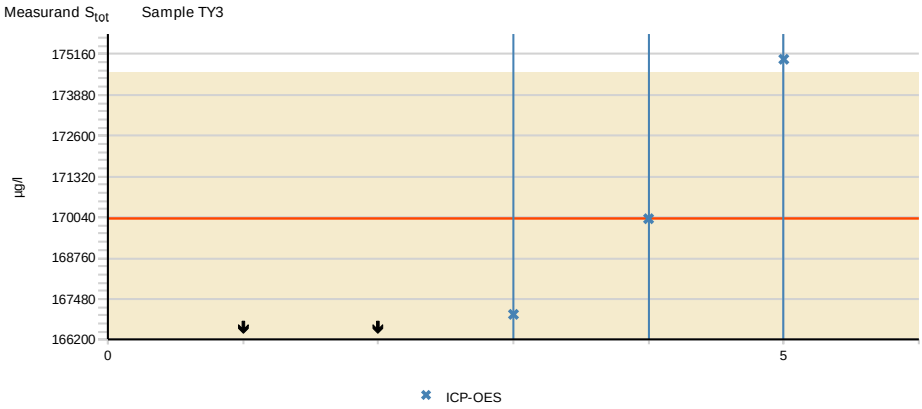

Measurand Sr
Sample V2M
µg/l
109
105
101
97
93
89
85
81
77
73
0
5
10
ICP-OES
ICP-MS

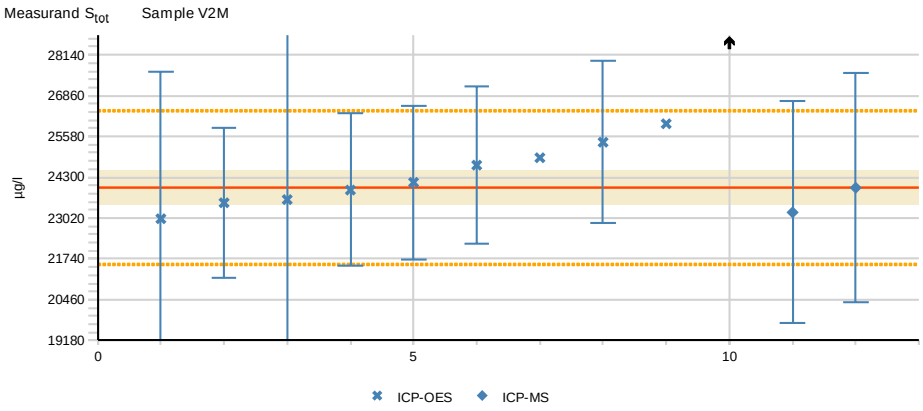

Measurand S_{tot}
Sample A1M
mg/l
3.8
3.6
3.4
3.2
3
2.8
2.6
0
5
10
ICP-OES
ICP-MS

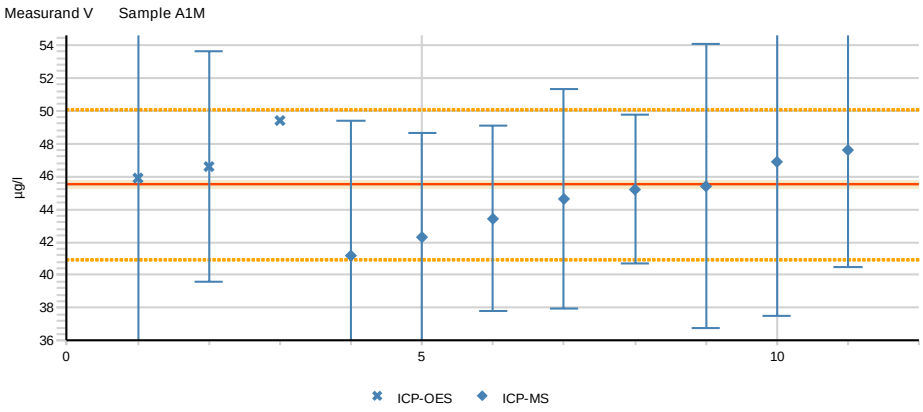

Measurand S_{tot}
Sample KN4
mg/kg
10890
9610
8330
7050
5770
4490
3210
0
5
ICP-OES
ICP-MS

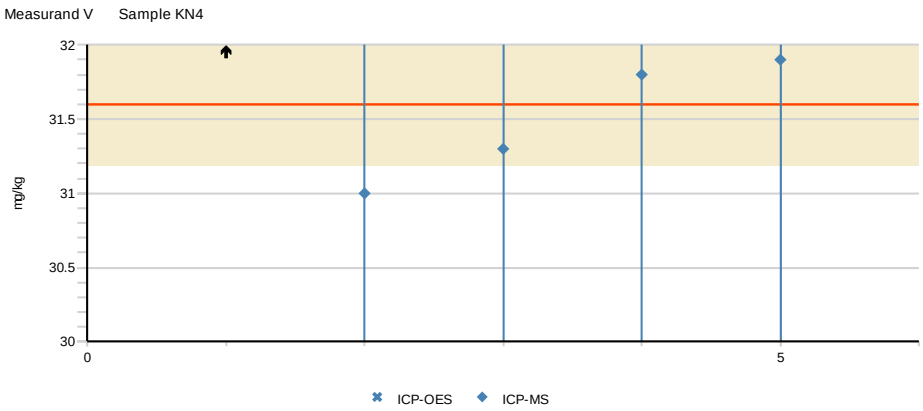

Measurand S_{tot}
Sample KO4
mg/kg
12830
12190
11550
10910
10270
9630
8990
8350
7710
7070
0
5
10
ICP-OES
ICP-MS


Measurand S_{tot}
Sample TN3
µg/l
195040
184800
174560
164320
154080
143840
133600
0
5
10
ICP-OES
ICP-MS

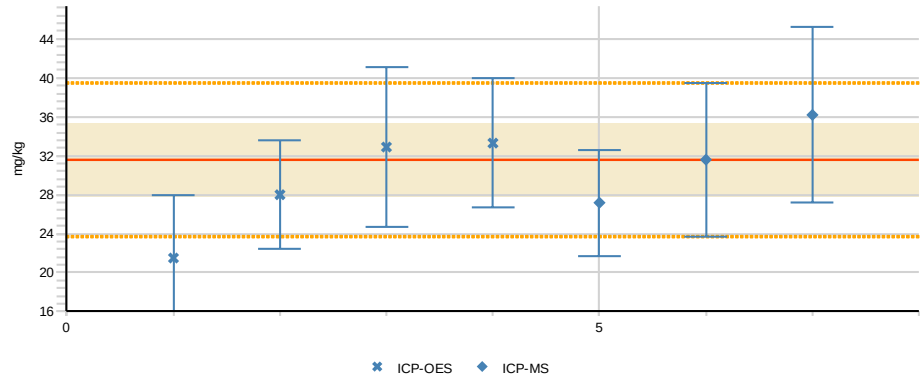

Measurand S_{tot}
Sample TY3
µg/l
175160
173880
172600
171320
170040
168760
167480
166200
0
5
ICP-OES


Measurand S_{tot} Sample V2M
µg/l
28140
26860
25580
24300
23020
21740
20460
19180
0
5
10
ICP-OES
ICP-MS

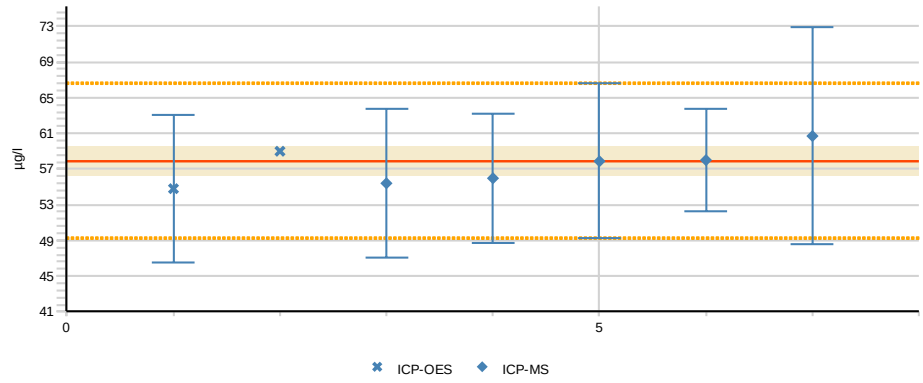

Measurand V Sample A1M
µg/l
54
52
50
48
46
44
42
40
38
36
0
5
10
ICP-OES
ICP-MS


Measurand V Sample KN4
mg/kg
32
31.5
31
30.5
30
0
5
ICP-OES
ICP-MS

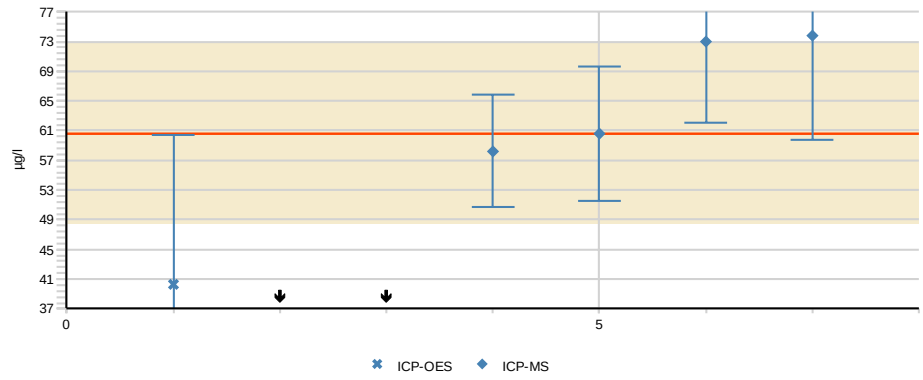
Measurand V Sample KO4

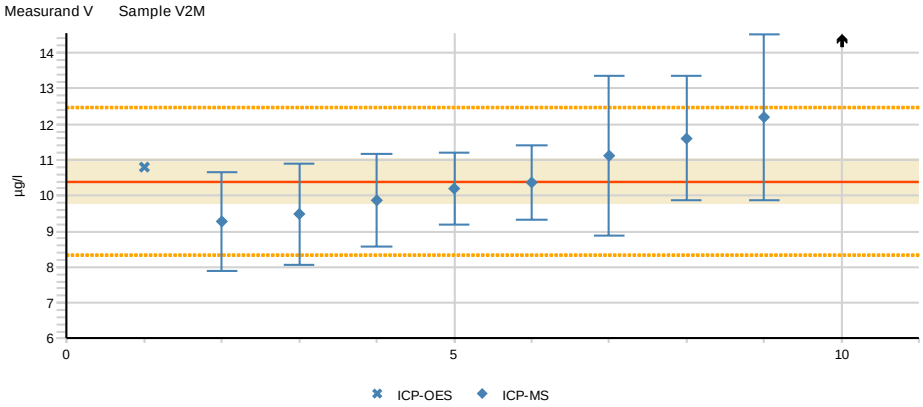


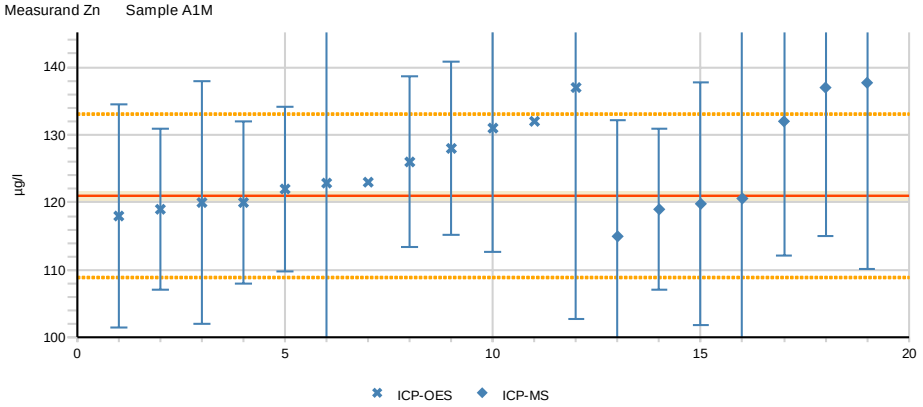
Measurand V Sample TN3

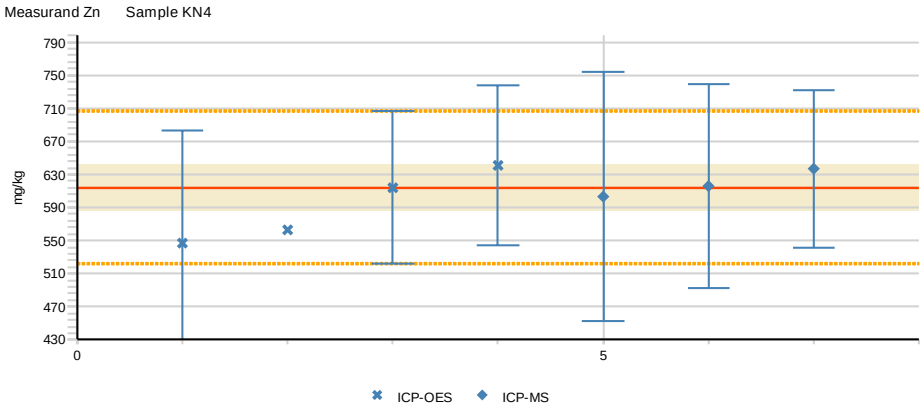


Measurand V Sample TY3

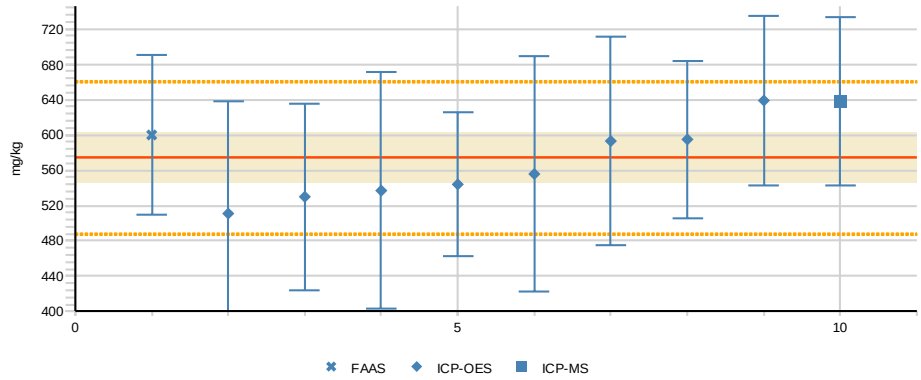



Measurand V Sample V2M
µg/l
14
13
12
11
10
9
8
7
6
0
5
10
ICP-OES
ICP-MS

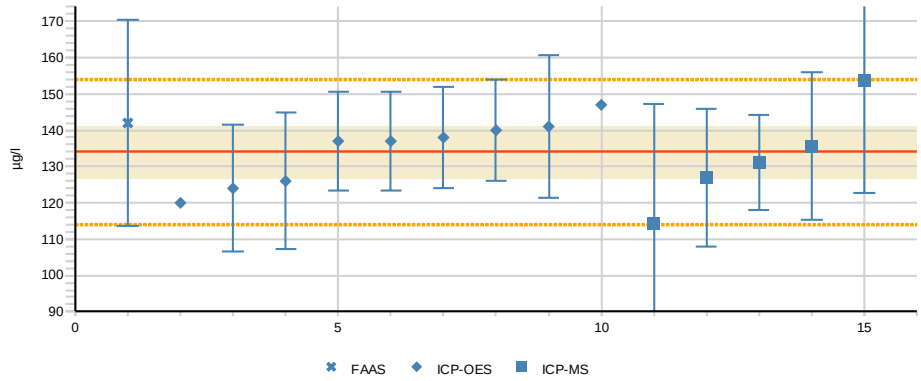

Measurand Zn Sample A1M
µg/l
140
130
120
110
100
0
5
10
15
20
ICP-OES
ICP-MS


Measurand Zn Sample KN4
mg/kg
790
750
710
670
630
590
550
510
470
430
0
5
ICP-OES
ICP-MS

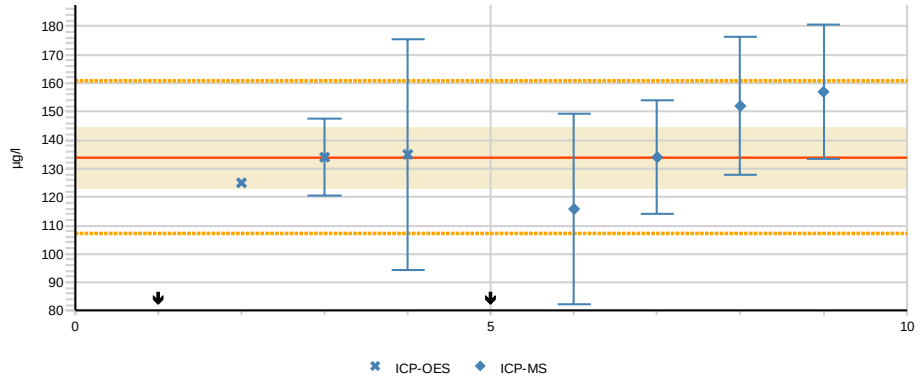
Measurand Zn Sample KO4

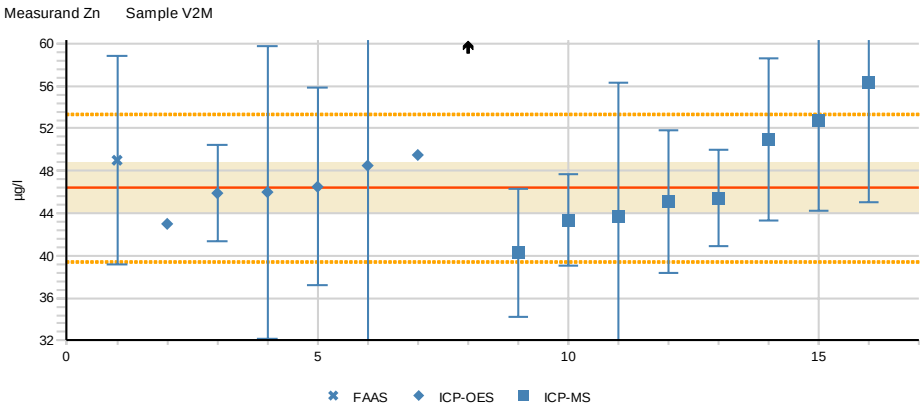


Measurand Zn Sample TN3



Measurand Zn Sample TY3

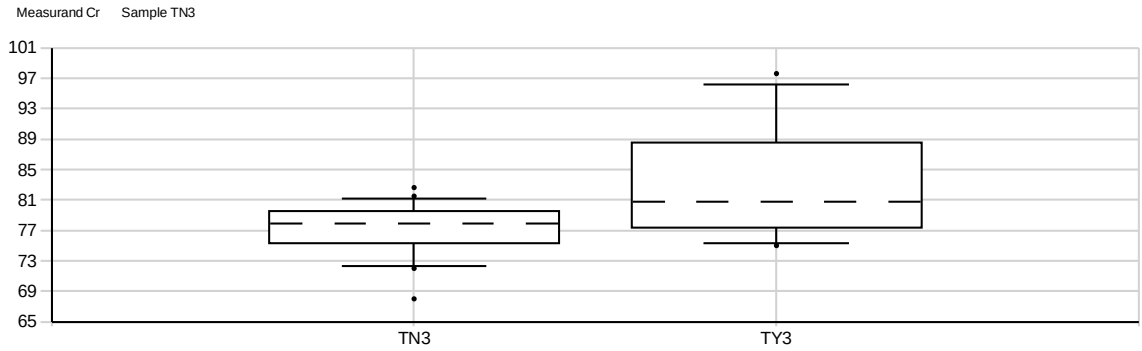



Measurand Zn
Sample V2M
µg/l
60
56
52
48
44
40
36
32
0
5
10
15
FAAS
ICP-OES
ICP-MS

APPENDIX 11: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit includes 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.

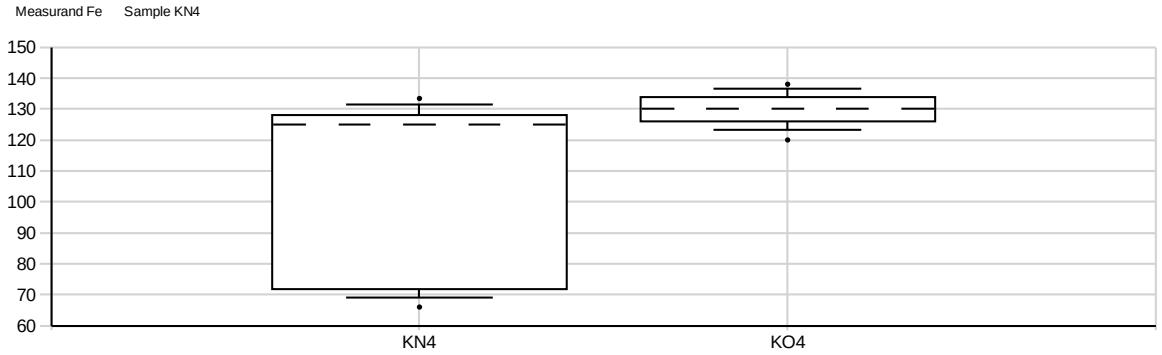
Statistically significant differences between pretreatment methods, waste water



Method	n	Mean (µg/l)	Median (µg/l)	s (µg/l)
TN3: no digestion	13	76.9	77.9	4.0
TY3: digestion with acid(s)	7	83.6	80.7	9.1

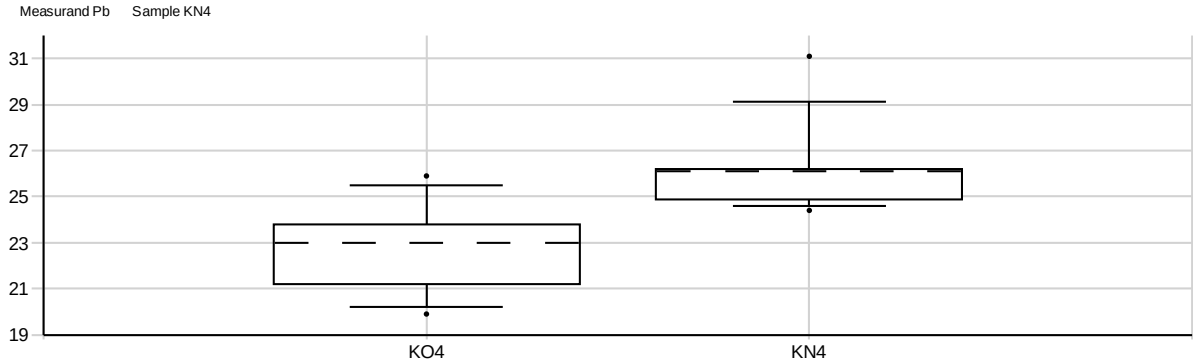
n=number of results; s=standard deviation

Statistically significant differences between pretreatment methods, compost sample



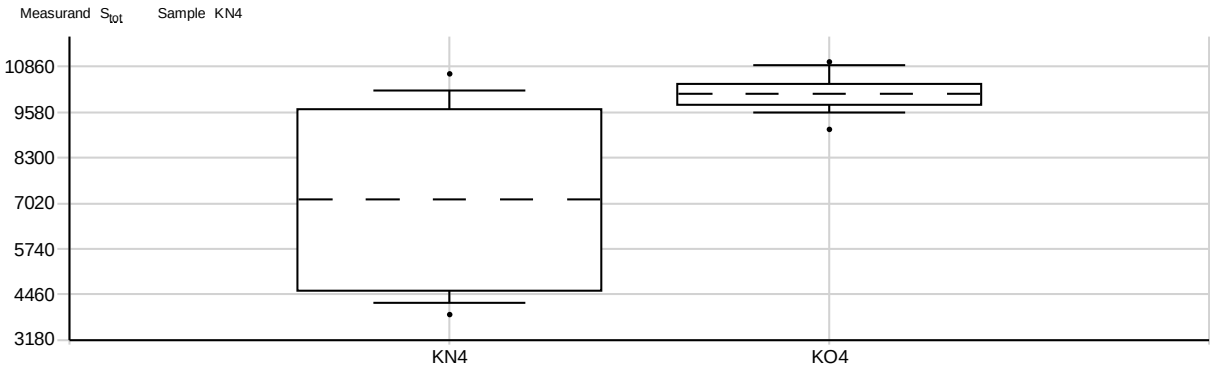
Method	s	Mean (g/kg)	Median (g/kg)	s (g/kg)
KN4: digestion with HNO_3	7	103	125	31.6
KO4: digestion with HNO_3+HCl	9	130	130	5.8

n=number of results; s=standard deviation



Method	**n**	**Mean (mg/kg)**	**Median (mg/kg)**	**s (mg/kg)**
KN4: digestion with HNO_3	5	26.5	26.1	2,7
KO4: digestion with HNO_3+HCl	9	22.7	23	2,2

n=number of results; s=standard deviation

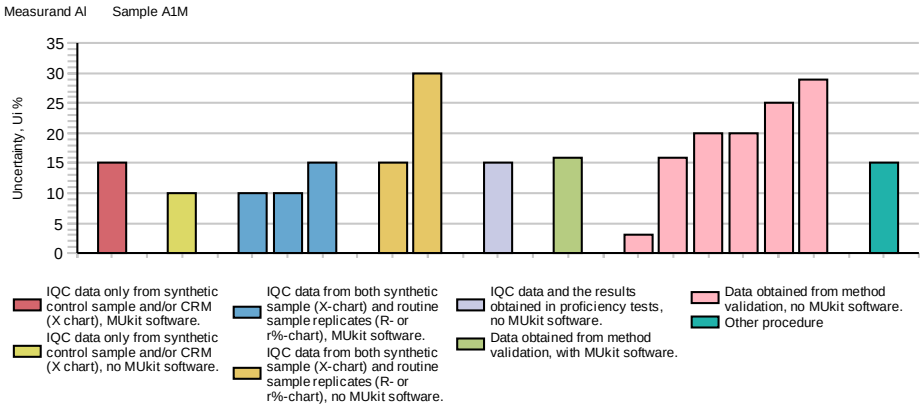


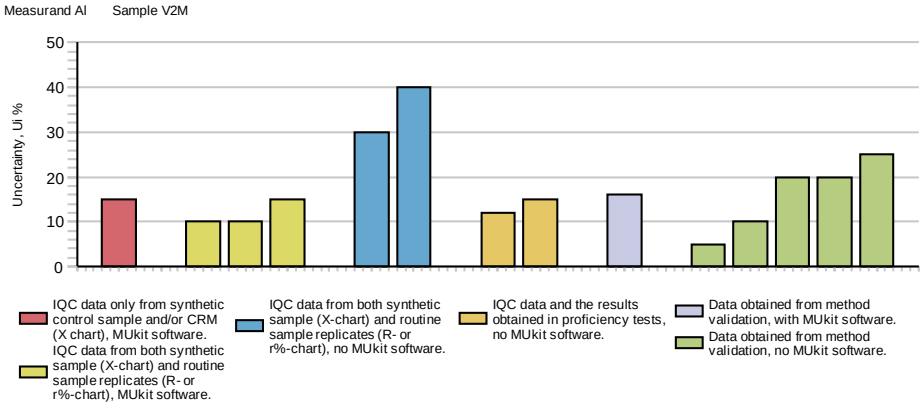
Method	n	Mean	Median	s
KN4: digestion with HNO_3	6	7174	7131	3097
KO4: digestion with HNO_3+HCl	8	10114	10093	609

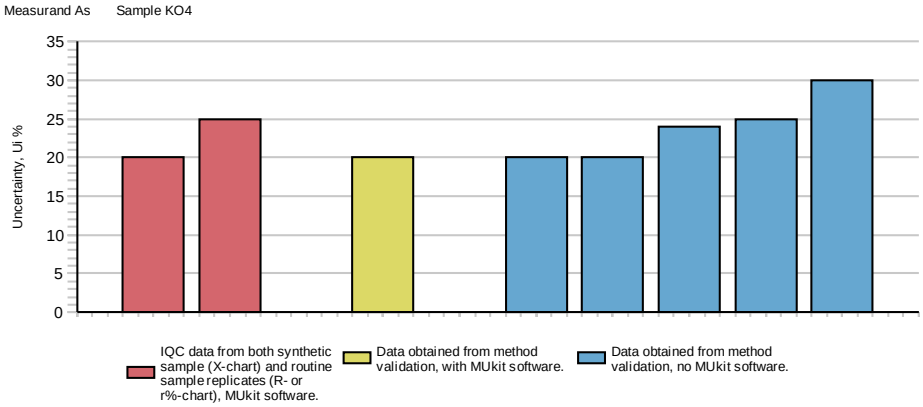
n=number of results; s=standard deviation

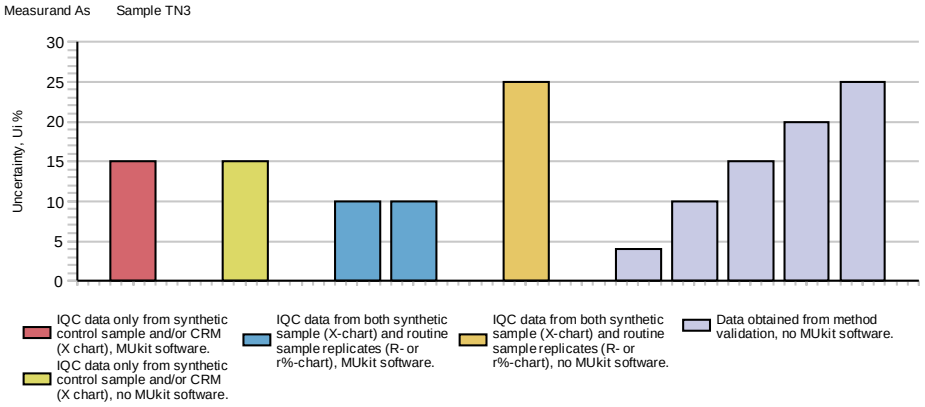
APPENDIX 12: Estimation of the measurement uncertainties reported by the participants

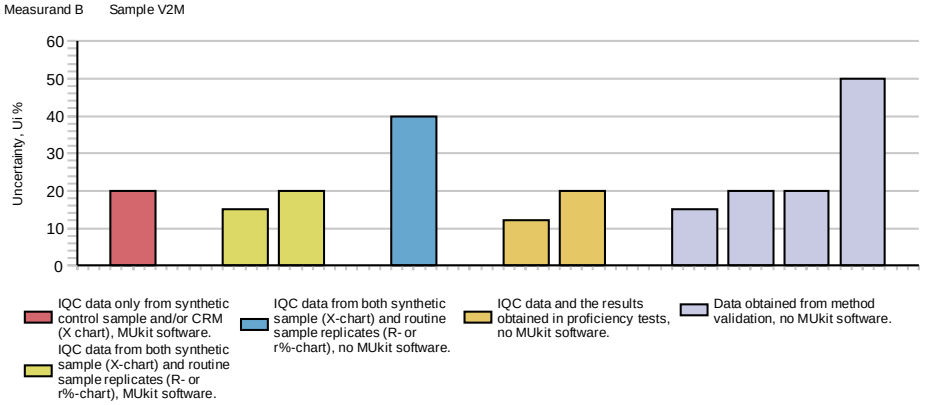
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g.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

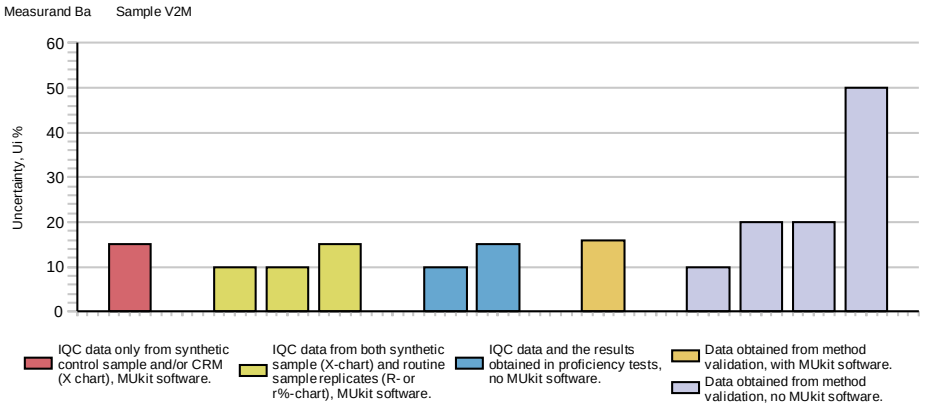




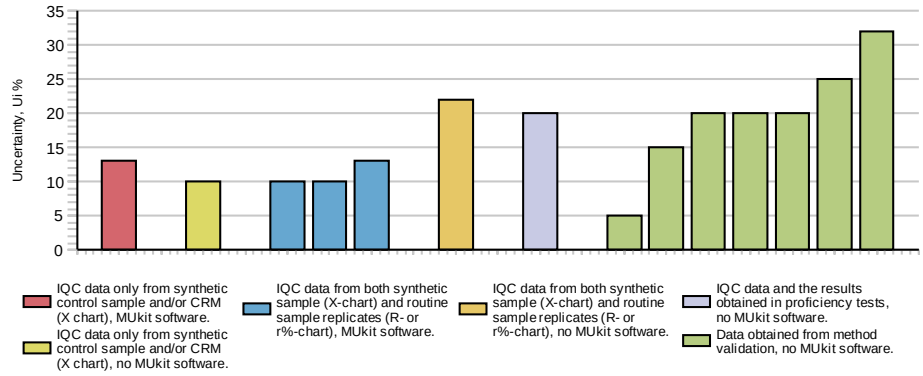



Measurand As Sample TN3
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and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

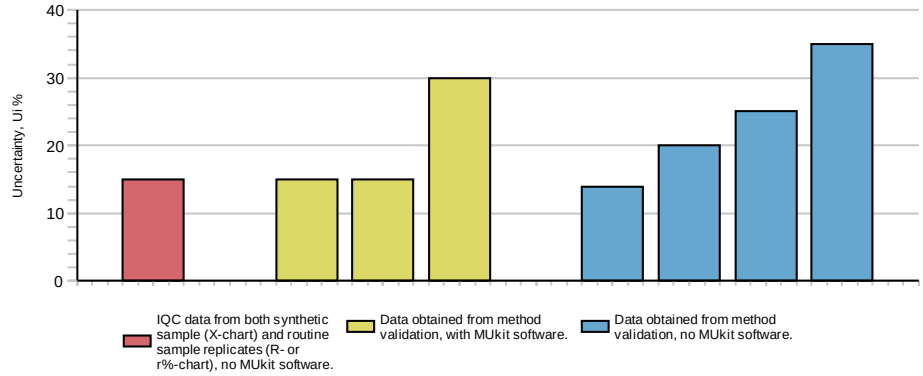

Measurand B Sample V2M
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand Ba Sample V2M
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
Data obtained from method validation, no MUkit software.

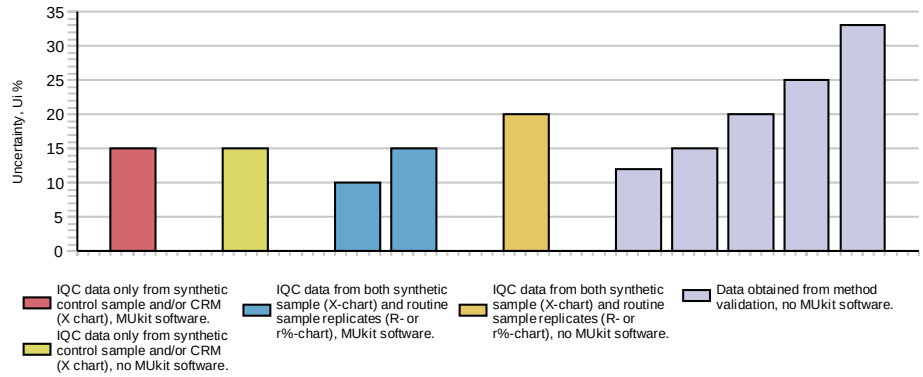
Measurand Ca Sample A1M

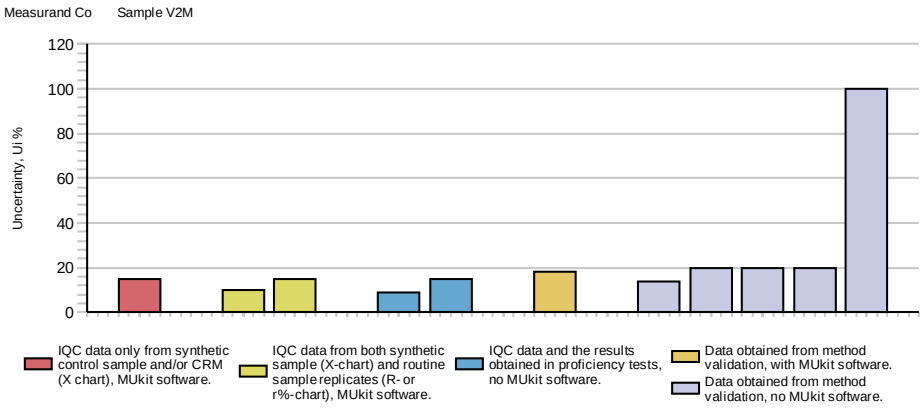


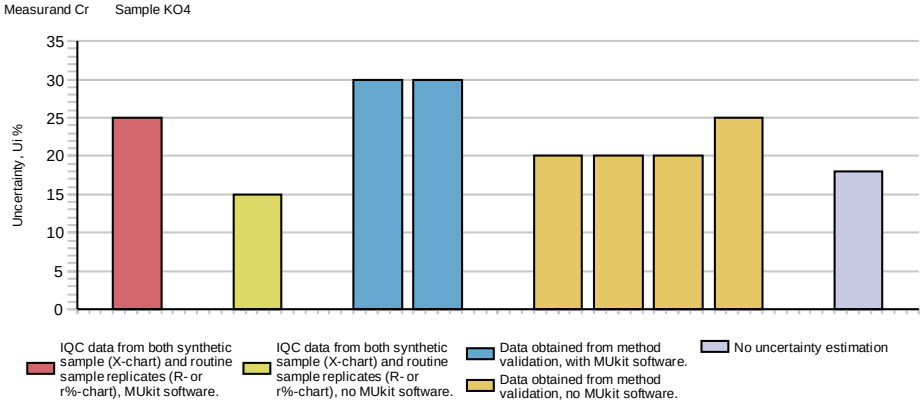
Measurand Ca Sample KO4

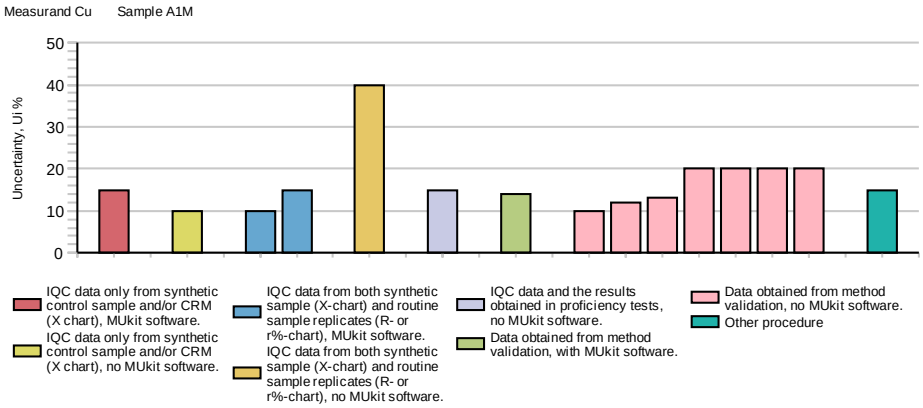


Measurand Cd Sample TN3

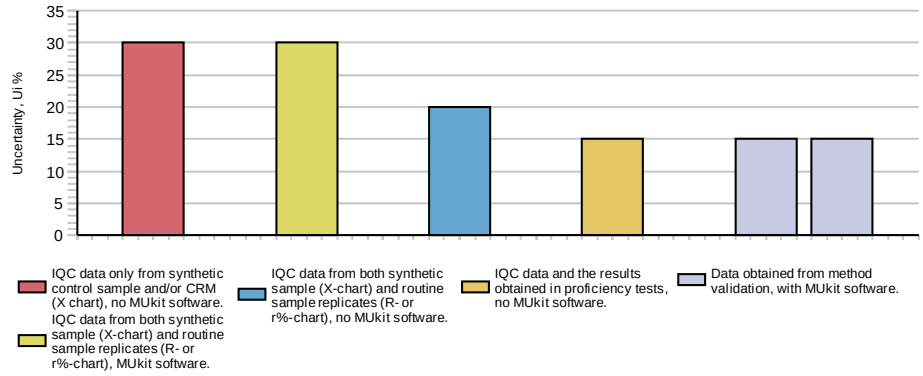



Measurand Co
Sample V2M
Uncertainty, Ui %
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

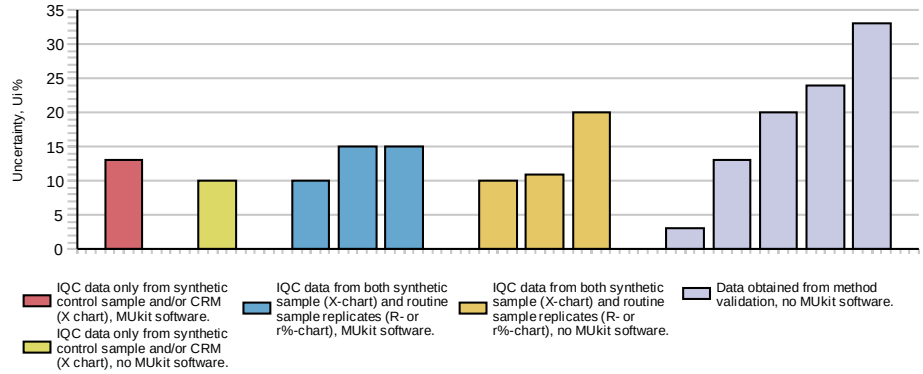

Measurand Cr
Sample KO4
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
No uncertainty estimation


Measurand Cu
Sample A1M
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
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.
Other procedure

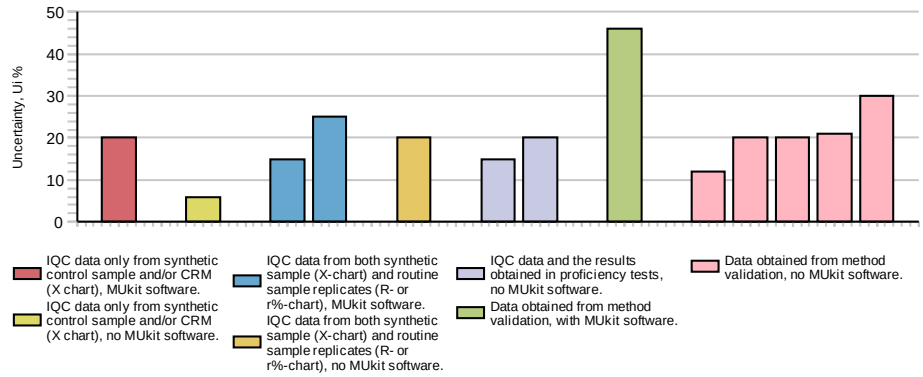
Measurand Fe Sample KN4

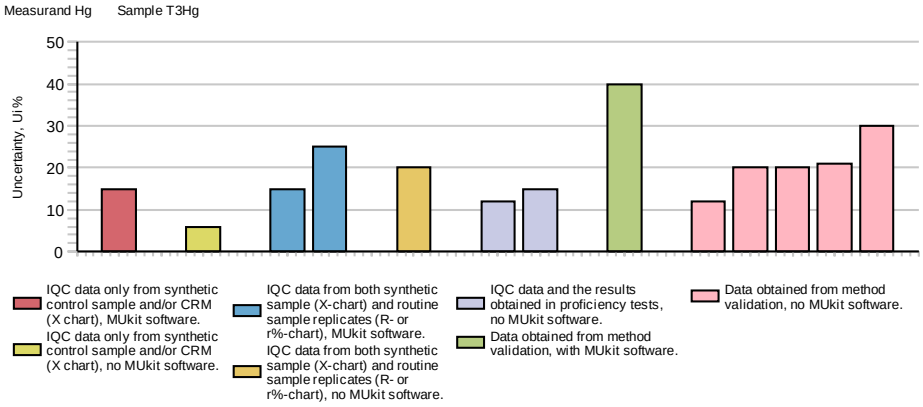


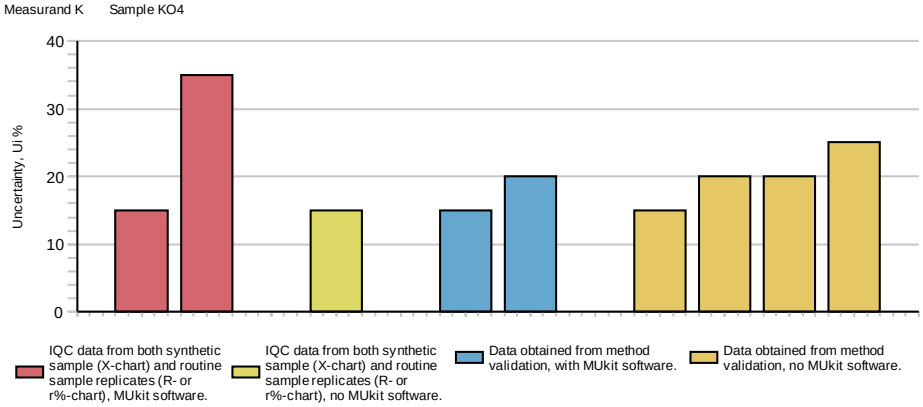
Measurand Fe Sample TN3

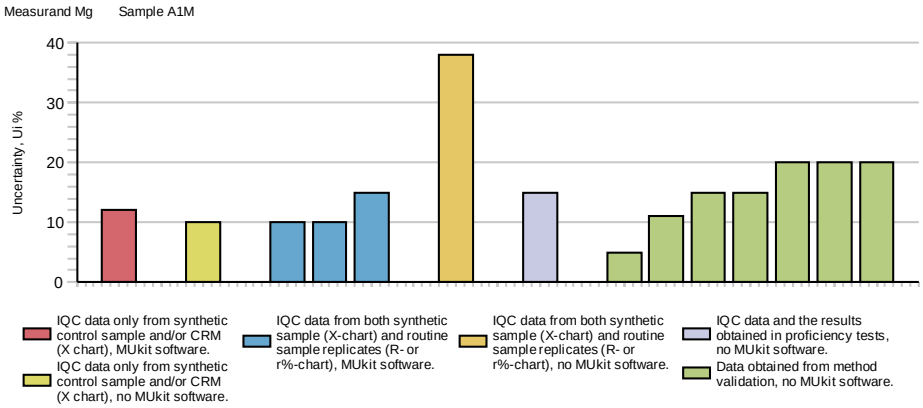


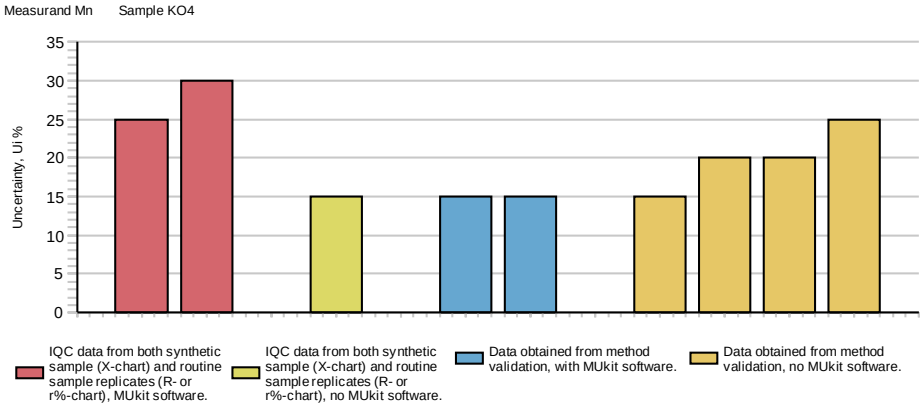
Measurand Hg Sample A1Hg

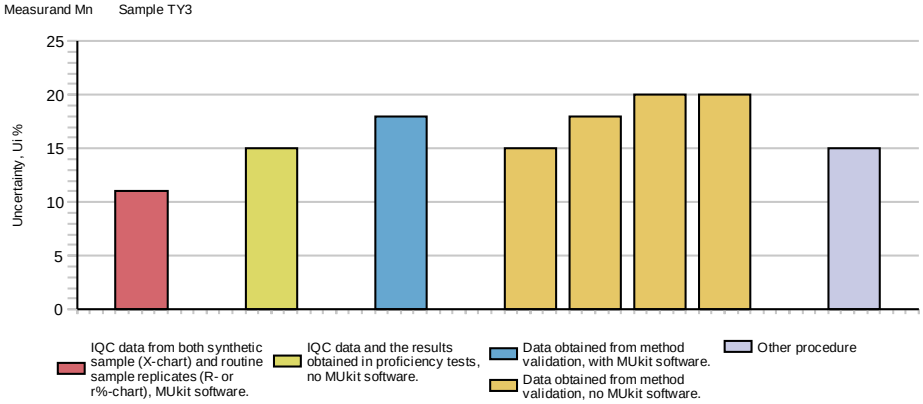


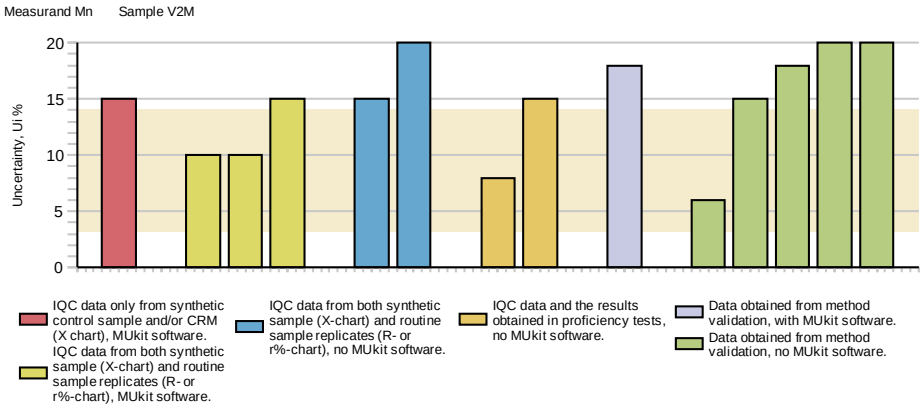

Measurand Hg Sample T3Hg
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (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.

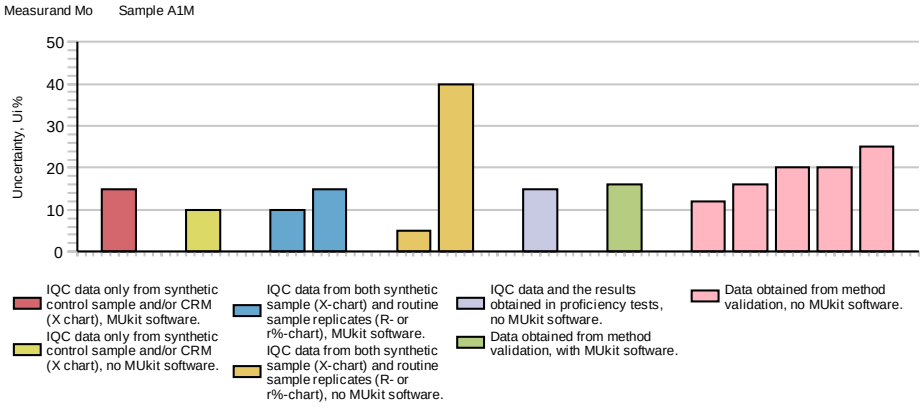

Measurand K Sample KO4
Uncertainty, Ui %
40
30
20
10
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

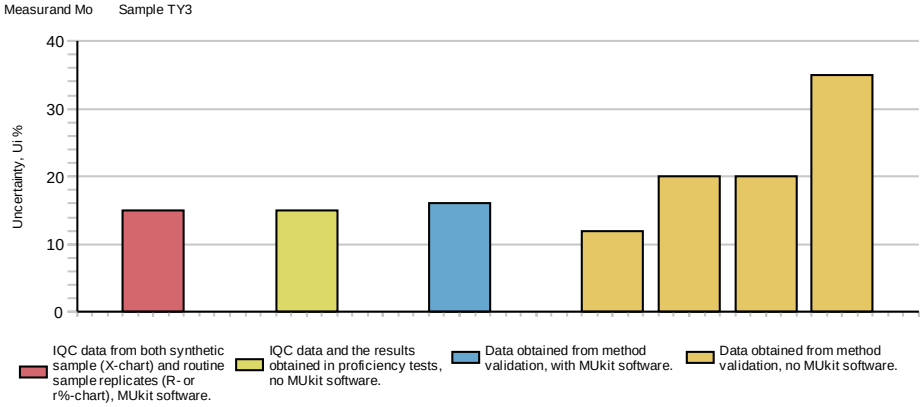

Measurand Mg Sample A1M
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- 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, no MUkit software.

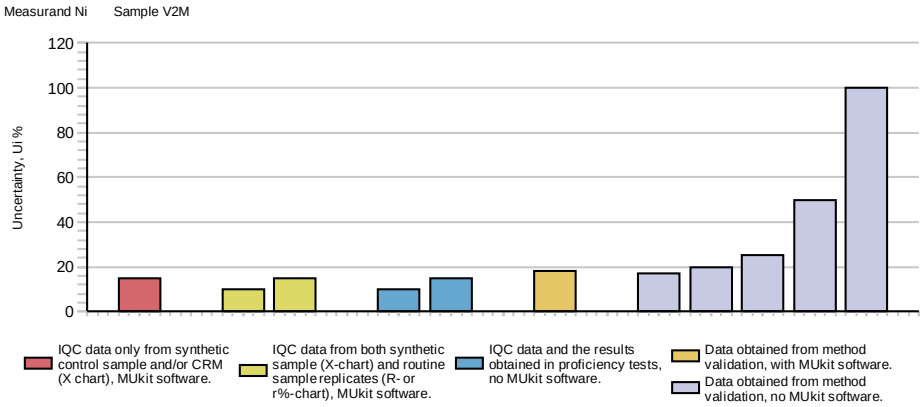

Measurand Mn
Sample KO4
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

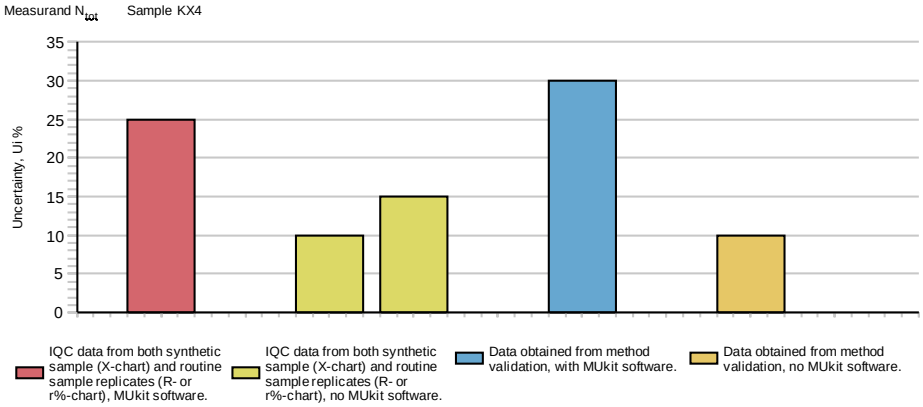

Measurand Mn
Sample TY3
Uncertainty, Ui %
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure

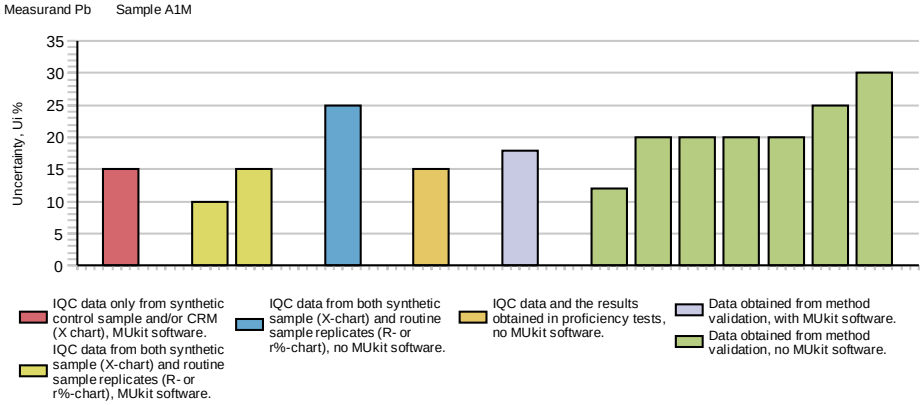

Measurand Mn
Sample V2M
Uncertainty, Ui %
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine 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.

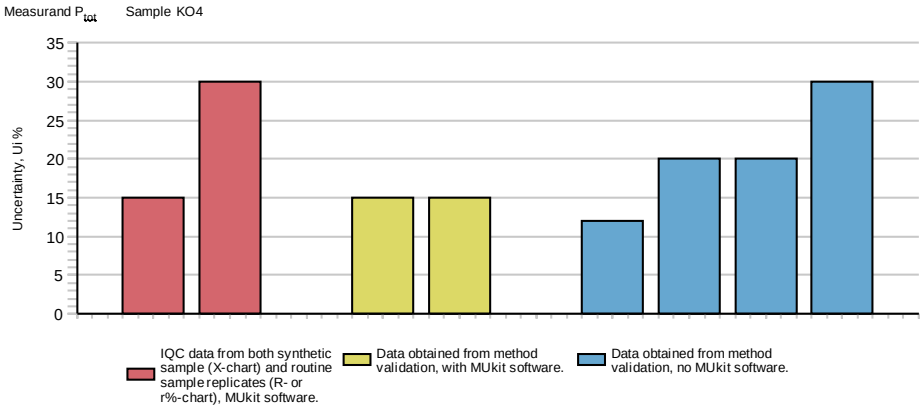

Measurand Mo
Sample A1M
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests,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

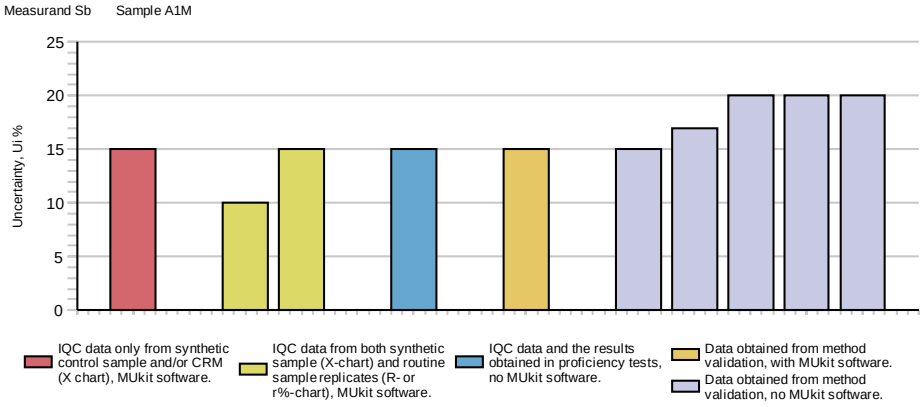

Measurand Mo
Sample TY3
Uncertainty, Ui %
40
30
20
10
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

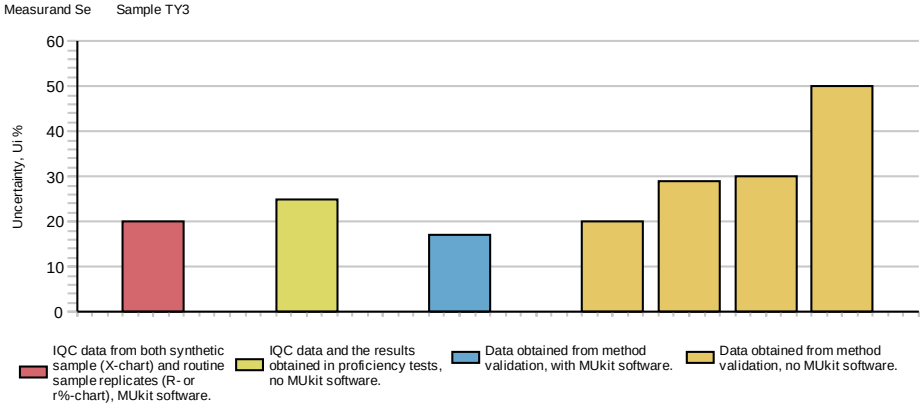

Measurand Ni
Sample V2M
Uncertainty, Ui %
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

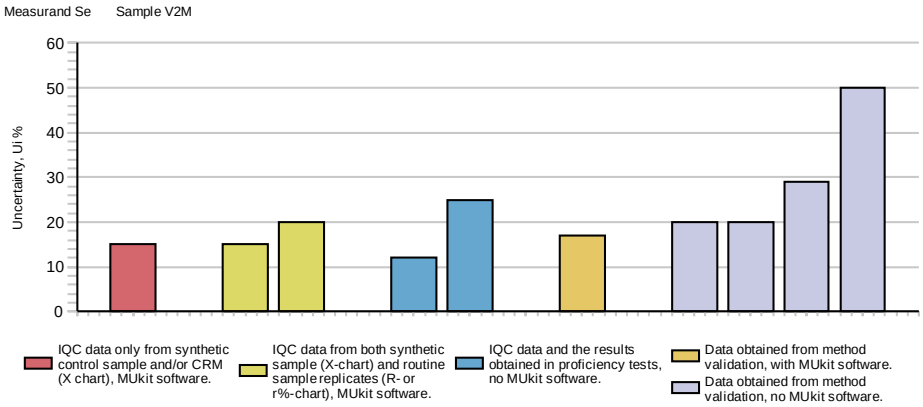

Measurand N_{tot} Sample KX4
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Pb Sample A1M
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.

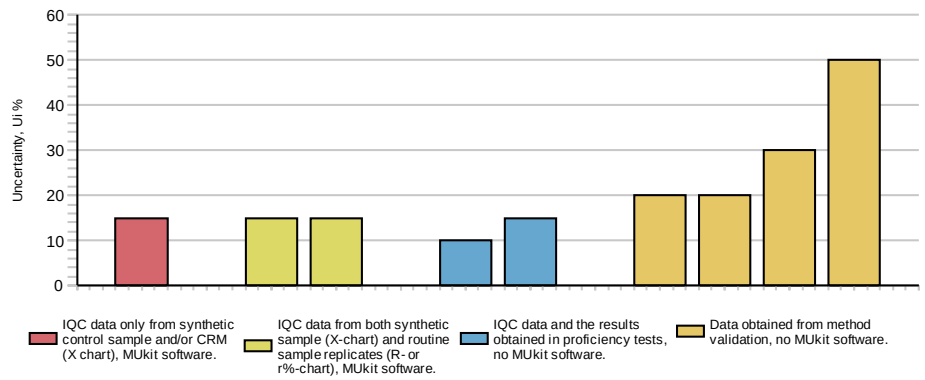

Measurand P_{tot} Sample KO4
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Sb
Sample A1M
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
Data obtained from method validation, no MUkit software.

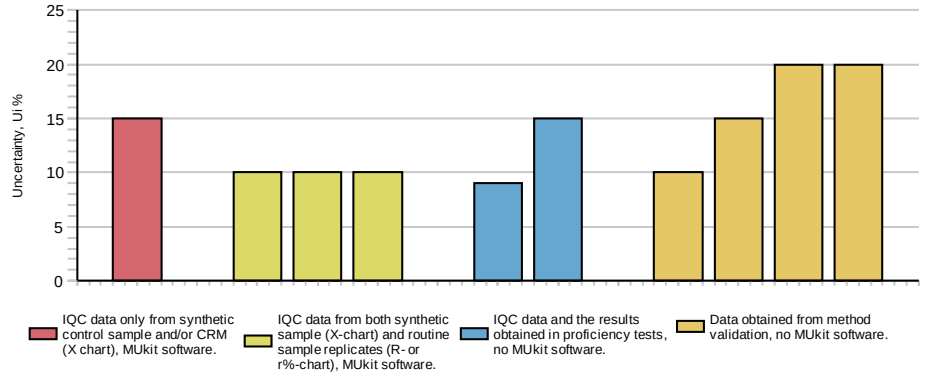

Measurand Se
Sample TY3
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Se
Sample V2M
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
Data obtained from method validation, no MUkit software.

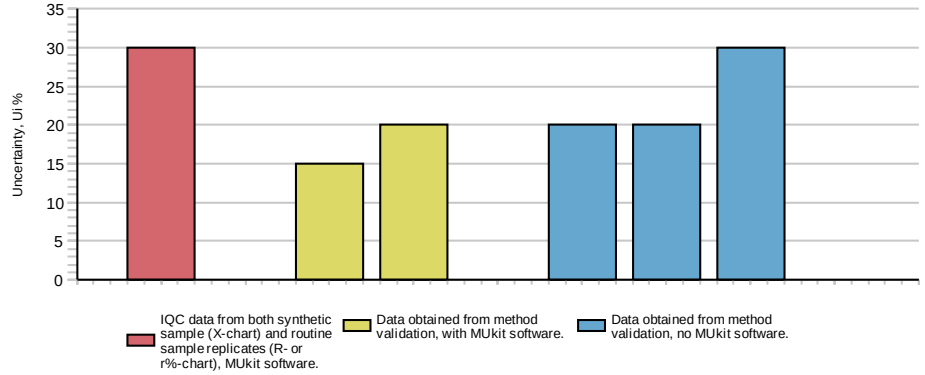
Measurand Sn Sample V2M

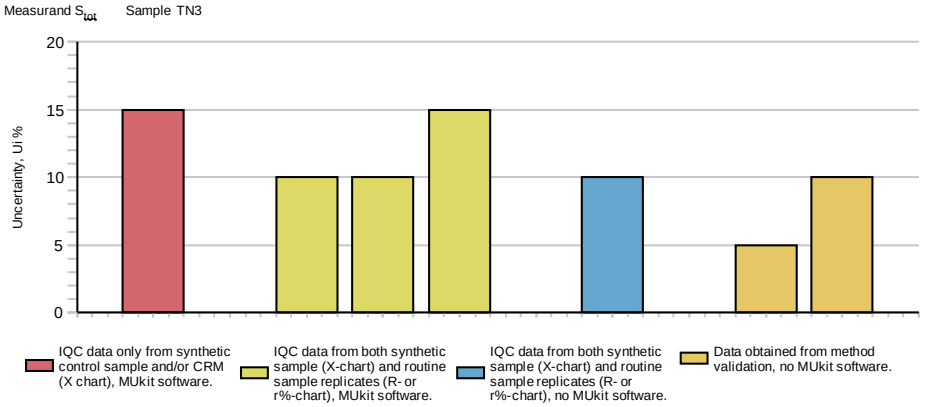


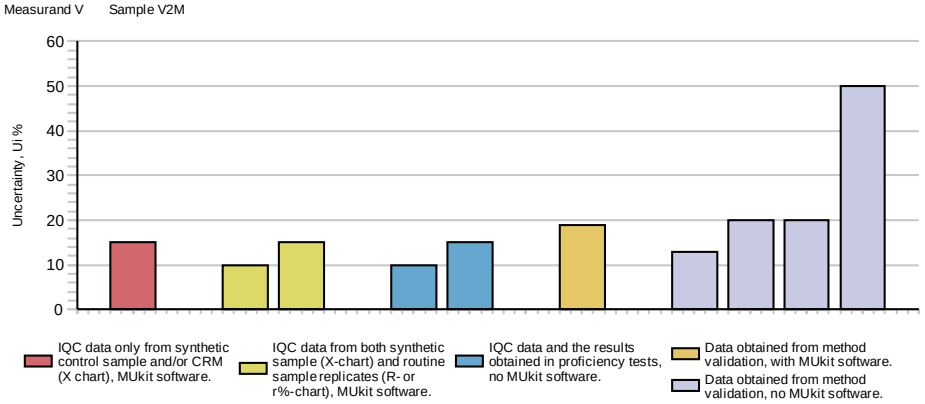
Measurand Sr Sample V2M

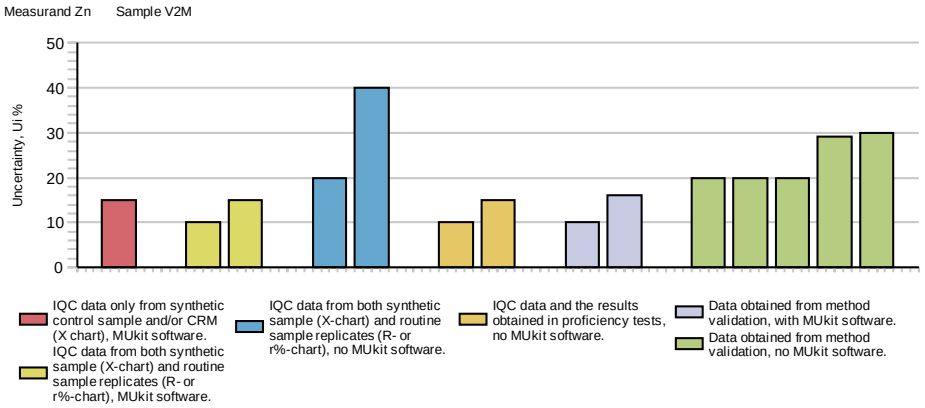


Measurand S_{tot} Sample KO4




Measurand S_{tot} Sample TN3
Uncertainty, Ui %
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
Data obtained from method validation, no MUkit software.


Measurand V Sample V2M
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
Data obtained from method validation, no MUkit software.


Measurand Zn Sample V2M
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), 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.
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