Federal Office of Consumer Protection and Food Safety

BfR
German Federal Institute for Risk Assessment

Science Report

14 March 2025

Method evaluation study on the determination of aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) in various simulants by ICP-MS and/or ICP-OES

NRL-FCM-DE-01/2024

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doi https://doi.org/10.17590/20250313-125326-0

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Method evaluation study on the determination of aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) in various simulants by ICP-MS and/or ICP-OES

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Joint report of the BfR and the BVL

This method evaluation study (MES) NRL-FCM-DE-01/2024 was organized by the German National Reference Laboratory for Food Contact Materials (NRL-FCM-DE), established within the Unit Product Analytics of the Department of Chemical and Product Safety at the German Federal Institute for Risk Assessment (BfR), in cooperation with the §64 UAG "Elemente in Bedarfsgegenständen" of the Federal Office of Consumer Protection and Food Safety (BVL). In this MES the concentrations of aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) in 3% acetic acid (*w*/*v*) (HAc), artificial tap water (ATW), 0.5% citric acid (CA) (*w*/*v*) as well as Ni in perspiration simulant had to be determined according to two drafts of methods for the official collection of samples and methods according to §64 of the German Food and Feed Code (LFGB) using either inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectroscopy (ICP-OES).

The participating laboratories received four solutions. Solution 1 contained the elements in 3% acetic acid (*w*/*v*), Solution 2 in artificial tap water, and Solution 3 in 0.5% citric acid (*w*/*v*). Solution 4 was a Ni-containing water solution to be used to prepare the perspiration simulant test solution. All test solutions were prepared in the labs of the German NRL-FCM and were acidified with HNO_3 to 2.6% (*v*/*v*).

In total, 29 laboratories registered for this MES and 28 laboratories submitted results, 24 for the ICP-MS method and 14 for the ICP-OES method. As the determination of Ni in the perspiration simulant was an optional task, only ten labs reported values for ICP-MS and eight for ICP-OES for Solution 4.

The results reported by the laboratories were evaluated quantitatively based on the reported concentrations for the elements in accordance with ISO 5725-2 [1] by

calculating the interlaboratory repeatability (s_r) and reproducibility (s_R) standard deviations and according to ISO 13528 [2] by calculating *z* scores.

The use of the provided ICP-MS method led to comparable and reproducible results. The calculated relative s_R values for Solutions 1–4 ranged from 4.2 to 7.8% except for As (11.5 to 16.6%) and Cd in HAc (12.6%). The relative s_r values ranged from 1.5 to 6.4% except for arsenic in HAc (10.5%) and in ATW (9.8%). Arsenic had the highest relative s_R and s_r values in all solutions.

For most elements, the ranges of relative s_R and s_r values obtained by the ICP-OES method were comparable to those obtained by the ICP-MS method. Relative s_R values ranged from 3.0 to 9.2% except for Pb (22.6%), Ni (15.4%) and Cd (13.1%) in HAc as well as Pb (17.9%) in CA. The relative s_r values ranged from 1.1 to 9.6% except for Ni in HAc (14.6%) and Pb in ATW (12.8%). Only two laboratories were able to quantify As by ICP-OES in HAc and CA and three laboratories have quantified As by ICP-OES in ATW, the concentrations determined were rather inaccurate. The number of As results for the ICP-OES method was insufficient for a statistical evaluation. The concentrations of As were reported to be below the laboratories' LOD/LOQ for nine laboratories in HAc and CA and for eight laboratories in ATW. According to these results the ICP-OES method is not suitable for the determination of As at such low concentrations. The determination of Pb and, to a lesser extent, Cd at low concentrations by ICP-OES was also challenging. Depending on the solution analyzed, only six to nine laboratories were able to quantify Pb. Four to seven laboratories reported that the concentration of Pb was below the laboratories' LOD/LOQ. Nine to ten laboratories were able to quantify Cd, and three to four laboratories reported that the concentration of Cd was below the laboratories' LOD/LOQ.

The majority of the ICP-MS results were acceptable in terms of *z* scores for all elements and solutions. Particularly good performance was demonstrated for the analysis of Co with *z* scores in the range from -2 to 2 for all laboratories and for all simulant solutions. The majority of the *z* scores for the ICP-OES results were in the same range for Al, Co, Cr, and Ni, for all simulant solutions while Cd was more difficult for the participants. Arsenic measured with ICP-OES was not evaluated due to the low number of quantified results.

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1 Introduction

The Method Evaluation Study (MES) NRL-FCM-DE-01/2024 was organized by the German National Reference Laboratory (NRL) for Food Contact Materials (FCM), established at the German Federal Institute for Risk Assessment (BfR), in cooperation with the §64 UAG "Elemente in Bedarfsgegenständen" of the Federal Office of Consumer Protection and Food Safety (BVL). According to §64 of the German Food and Feed Code (LFGB), the BVL publishes an official collection of methods for sampling and analysis (ASU) for the products listed in §2 section 1 LFGB, including consumer goods.

In this MES, the concentrations of aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) in 3% acetic acid (HAc) (w/v), artificial tap water (ATW), 0.5% citric acid (CA) (w/v), as well as Ni in perspiration simulant had to be determined according to two drafts of §64 methods using either inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectroscopy (ICP-OES).

This MES was open to National Reference Laboratories (NRL), Official Control Laboratories (OCL) and commercial laboratories (CL).

The results of the MES are summarized in this report.

2 Scope

The primary objective of the present MES was to evaluate the performance of two new methods for the ASU in terms of interlaboratory repeatability and reproducibility. To obtain further information from the submitted results a *z* score evaluation was performed.

This MES is identified as "NRL-FCM-DE-01/2024".

3 Set-up of the study

3.1 Time frame of the ILC

The invitation for the NRL-FCM-DE-01/2024 was sent on April 25, 2024 and registration was open until May 15, 2024. Samples were sent to the participants on May 28, 2024 and the deadline for reporting of results was set to June 30, 2024. This deadline was extended until July 5, 2024 for individual laboratories. The last results were received on July 5, 2024.

3.2 Quality assurance

The NRL-FCM-DE has a quality management system according to DIN EN ISO/IEC 17025 [3]. The reported results were evaluated following relevant administrative and logistic procedures.

3.3 Confidentiality

The procedures used to organize this MES guarantee that the identity of the participants and the information they provide is treated as confidential. Participants in this MES were given a unique laboratory code, which is used throughout this report.

3.4 Distribution

Each participant received 3 solutions (Solutions 1–3). The laboratories, which also participated in the investigation of Ni in perspiration solution, received a fourth solution (Solution 4):

- Solution 1: solution of elements in acetic acid 3% w/v for the analysis using ICP-MS (ca. 25 mL) and/or using ICP-OES (ca. 50 mL)
- Solution 2: solution of elements in artificial tap water for the analysis using ICP-MS (ca. 25 mL) and/or using ICP-OES (ca. 50 mL)
- Solution 3: solution of elements in citric acid 0.5% w/v for the analysis using ICP-MS (ca. 25 mL) and/or using ICP-OES (ca. 50 mL)
- Solution 4: Ni-containing water solution (ca. 20 mL) to be used to prepare the perspiration simulant test solution.

All test solutions were prepared in the labs of the German NRL-FCM and were acidified with HNO_3 to 2.6% v/v.

3.4.1 Instructions to participants

The drafts of the two methods for the ASU for the determination of Al, As, Cd, Co, Cr, Ni and Pb in various simulant solutions using either ICP-MS or ICP-OES were sent to the participants. Some further information to the participants were given in the instructions document (see 11.1).

The results and general information about the analytical procedure had to be submitted via a reporting website using a unique laboratory token.

4 Test items

4.1 Concentrations of elements in the test solutions

The concentrations of the elements in the test solutions (x_{pt}) were defined based on the SML/SRL of the elements in the food simulants and the recommended working ranges (RWR) for compliance testing selected according to the JRC guidelines for analytical methods in food control [4]. Here, a working range of at least 20 to 200% of the corresponding legal limit (SRL, SML) is recommended for enforcement. In general, all spiked values were in the range of 60 to 130% of the corresponding legal limits (LL), see Table 1 and Table 2.

4.1.1 Concentrations of elements in 3% acetic acid

3% acetic acid (food simulant B) is used among other food simulants for compliance testing of plastic materials and articles [5] as well as for testing the release of metal ions from enameled articles, which are intended to come into contact with food [6]. Thus, two – in part – different legal limits have to be considered. The recommended working ranges of the JRC guidelines can be adapted to the element-specific release limits of enameled articles. However, regarding the specific migration limits for plastic materials and articles as specified in regulation 10/2011, some elements are classified as "not detectable" (ND). For regulatory reasons, it is preferable that the LOQ of the method used should be at least equal to the corresponding limit value. Thus, the recommended working ranges for the elements were set as follows (Table 1):

- Al, Pb: SRL for enameled articles and SML for plastic articles are identical [SML for Pb is classified as ND, meaning SML = LOD (0.01 mg L^{-1})]; the recommended working range of 20 to 200% of SML/SRL is used
- As, Co, Ni: the lowest LL is not classified as ND; the recommended working range of 20 to 200% of the lowest SML/SRL is used
- Cd: SML for plasticware is classified as ND meaning that SML = LOD (0.002 mg L^{-1}) would be sufficient; however, as 20% of the SRL (0.005 mg L^{-1}) for enameled products is 0.001 mg L^{-1} and thus below the SML of the plastic regulation, the recommended working range starts at 20% of the SRL
- Cr: the SML for plasticware is classified as ND meaning that SML = LOD (0.01 mg L^{-1}) would be sufficient; thus, the SML is set as the lower limit of the recommended working range and the upper limit is set to 200% SML. It should be noted, that the SRL for enameled products is considerably higher than the SML for plastic; however, this MES focuses on the performance of the methods regarding quantification of low concentrations

Table 1: Concentrations of elements (x_{pt}) in 3% acetic acid (Solution 1), specific release limits (SRL; [6]), specific migration limits (SML; [5]) and the recommended working ranges (RWR; [4]) for testing according to the minimum value of SML and SRL (LL, legal limit). Due to the small density differences between predominantly aqueous simulants, 1 mg L^{-1} is assumed to be equal to 1 mg kg^{-1}, and all concentrations are given in mg L^{-1}.

Element	x_{pt}		SRL	SML	LL	RWR
	[mg L^{-1}]	[% of LL]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]
Al	0.9	90	1	1	1	0.2–2
As	0.0026	130	0.002	0.01#	0.002	0.0004–0.004
Cd	0.0016	80	0.005	0.002#	0.005	0.001–0.01
Co	0.035	70	0.1	0.05	0.05	0.01–0.1
Cr	0.01	100	0.25	0.01#	0.01	0.01–0.2
Ni	0.012	60	0.14	0.02	0.02	0.004–0.04
Pb	0.01	100	0.01	0.01#	0.01	0.002–0.02

Not detectable (ND), a limit of 0.01 mg L^{-1} is applicable unless specified differently for an individual substance (e.g. 0.002 mg L^{-1} for Cd).

4.1.2 Concentration of elements in artificial tap water and 0.5% citric acid

Artificial tap water and 0.5% citric acid are recommended for testing the release of elements from metals and alloys articles with the same specific release limits for the elements in both testing solutions [7]. The SRLs and the recommended working ranges [4] together with the x_{pt} values can be found in Table 2.

Table 2: Concentrations of elements (x_{pt}) in ATW (Solution 2) and in 0.5% citric acid (Solution 3), specific release limits (SRL; [7]), and the recommended working ranges for testing according to SRL (RWR; [4]). Due to the small density differences between predominantly aqueous simulants, 1 mg L^{-1} is assumed to be equal to 1 mg kg^{-1}, and all concentrations are given in mg L^{-1}.

Element	x_{pt} (Solution 2)		x_{pt} (Solution 3)		SRL	RWR
	[mg L^{-1}]	[% of SRL]	[mg L^{-1}]	[% of SRL]	[mg L^{-1}]	[mg L^{-1}]
Al	4	80	3.5	70	5	1–10
As	0.002	100	0.0016	80	0.002	0.0004–0.004
Cd	0.006	120	0.006	120	0.005	0.001–0.01
Co	0.018	90	0.02	100	0.02	0.004–0.04
Cr	0.2	80	0.225	90	0.25*	0.05–0.5
Ni	0.126	90	0.112	80	0.14	0.028–0.28
Pb	0.01	100	0.006	60	0.01	0.002–0.02

* The SRL value for Cr(III) of 1 mg L^{-1} was published in [8], after the analytical part of this MES

4.1.3 Concentration of Ni in perspiration simulant

In addition to the determination of elements in food simulant solutions, Ni could be analyzed in perspiration simulant as an optional task. Since the perspiration simulant is not stable over a longer period of time, the solution for the analysis of Ni in the perspiration simulant had to be prepared in the labs by dissolving 1 mL of Solution 4 in a freshly prepared perspiration simulant (according to DIN EN 1811 [9]) to a total volume of 50 mL. The concentration for the prepared test solution (x_{pt}) can be found in Table 3.

Table 3: Concentrations of Ni in the prepared perspiration simulant test solution (x_{pt}).

Element	x_{pt} [mg L^{-1}]
Ni	0.237

4.2 Preparation

4.2.1 Solutions

The solutions were prepared in the labs of the German NRL-FCM, acidified with HNO_3 to 2.6% v/v and stored at 4°C until shipment.

4.3 Stability

Stability study and statistical data evaluation were performed by the NRL-FCM-DE. Stability of Solutions 1–4 was tested over a period of 38 days, which is equal to the timeframe of this MES (see 3.1). The solutions were stable according to ISO 13528:2022 [2] (see 11.2).

5 Assigned values and standard deviations for proficiency assessment

The assigned values (x_{pt}) for the elements in Solutions 1–4 are shown in Table 4. The values for the standard deviations for proficiency assessment (σ_{pt}) were set to 15% of the corresponding assigned value for the analysis of elements in Solutions 1–4 by perception of experts.

Table 4: x_{pt} and σ_{pt} values for elements in Solution 1–4 for ICP-MS and ICP-OES.

Element	Solution 1 3% HAc		Solution 2 ATW		Solution 3 0.5% CA		Solution 4 perspiration simulant	
	x_{pt} [mg L^{-1}]	σ_{pt} [mg L^{-1}]	x_{pt} [mg L^{-1}]	σ_{pt} [mg L^{-1}]	x_{pt} [mg L^{-1}]	σ_{pt} [mg L^{-1}]	x_{pt} [mg L^{-1}]	σ_{pt} [mg L^{-1}]
Al	0.90	0.135	4.00	0.6	3.50	0.525	-	-
As	0.0026	0.0004	0.002	0.0003	0.0016	0.0002	-	-
Cd	0.0016	0.0002	0.006	0.001	0.006	0.0009	-	-
Co	0.035	0.005	0.018	0.003	0.020	0.003	-	-
Cr	0.01	0.002	0.20	0.03	0.225	0.034	-	-
Ni	0.012	0.002	0.126	0.019	0.112	0.017	0.237	0.036
Pb	0.01	0.002	0.01	0.002	0.006	0.001	-	-

6 Evaluation

6.1 Scores and evaluation criteria

The evaluation of a standard measurement method in terms of interlaboratory repeatability (s_r) and reproducibility (s_R) standard deviations was performed according to ISO 5725-2 [1]. The following equations were used for the calculations:

$$s_r = \sqrt{\frac{\sum_{i=1}^{p}(n_i - 1) \cdot s_i^2}{\sum_{i=1}^{p}(n_i - 1)}} \qquad \text{Equation 1}$$

where:

n_i	Number of individual results of the laboratory *i*
s_i	Standard deviation of the results of the laboratory *i*
p	Number of laboratories after elimination of outliers

$$s_R = \sqrt{s_r^2 + s_L^2} \qquad \text{Equation 2}$$

$$s_L^2 = \frac{s_d^2 - s_r^2}{\bar{n}} \qquad \text{Equation 3}$$

where:

$$s_d^2 = \frac{1}{p-1} \cdot \sum_{i=1}^{p} n_i \cdot (x_i - \bar{x})^2 \qquad \text{Equation 4}$$

$$\bar{n} = \frac{1}{p-1} \cdot \left(\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i} \right) \qquad \text{Equation 5}$$

and:

s_L^2	Variance between the laboratories
x_i	Mean value of the results of the laboratory *i*
$\bar{x}$	Overall mean value of the mean values of all the laboratories after the elimination of the outliers

In addition, the individual laboratory performance was expressed as *z* scores according to ISO 13528:2022 [2]. The *z* score describes the deviation between the participants' mean and the assigned value in terms of the standard deviation for proficiency assessment (σ_{pt}). The *z* scores for the proficiency test results x_i were calculated as follows:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}} \qquad \text{Equation 6}$$

The interpretation of the *z* performance scores is done according to ISO 13528:2022 [2]:

$\lvert z_i \rvert \leq 2.0$	acceptable performance	(green in Tables)
$2.0 < \lvert z_i \rvert < 3.0$	questionable performance	(orange in Tables)
$\lvert z_i \rvert \geq 3.0$	unacceptable performance	(red in Tables)

6.2 Technical equipment

Most laboratories used ICP-MS for the analysis of elements, while five applied tandem mass spectrometry (ICP-MS/MS). ICP-OES with dual view was the most used technique for optical emission spectroscopy (see Table 5).

Table 5: Analytical techniques used in this MES for the analysis of elements.

Technique	No. of labs	Technique	No. of labs
ICP-MS	19	ICP-OES axial	5
ICP-MS/MS	5	ICP-OES radial	2
		ICP-OES dual view	7
Total	**24**	**Total**	**14**

6.3 Evaluation of laboratories' results

In total, 29 laboratories were registered for the MES, but only 28 laboratories submitted results. 24 laboratories submitted results for the ICP-MS method and 14 laboratories submitted results for the ICP-OES method. Ten participants used both methods. Results for Solution 4 (Ni in perspiration simulant) were submitted by eleven participants for ICP-MS and by eight participants for ICP-OES.

The results for all elements were evaluated in terms of interlaboratory repeatability (s_r) and reproducibility (s_R), as well as *z* scores.

6.3.1 Statistical parameters for ICP-MS method

The evaluation of the MES results in terms of interlaboratory repeatability (s_r) and reproducibility (s_R) standard deviations for the ICP-MS method is summarized in Table 6 to Table 9. Relative s_r and s_R values between 1.5–10.5% and 4.2–16.6% were obtained. They were below 6.4% and 7.8% for most elements, except relative s_r values for arsenic in HAc (10.5%) and in ATW (9.8%) and relative s_R value for As (11.5 to 16.6%) and Cd in HAc (12.6%). These s_R values are lower than the corresponding predicted relative reproducibility standard deviations according to Horwitz/Thompson [$s_{R(Horwitz)}$] for all analyzed solutions and elements.

As, Cd, Co, Cr, Ni and Pb were quantified in Solution 1–3 by 24 laboratories, while Al was quantified in all three solutions by 22 participants. After the removal of outliers 20 to 24 results were available for evaluation. Eleven laboratories quantified Ni in Solution 4 and no outliers were found. However, one laboratory has reported that the Solution 4 was diluted in 2% nitric acid instead of perspiration simulant; therefore, the results from this laboratory for the analysis of Ni in Solution 4 were not included in the evaluation, reducing the number of results to ten.

Table 6: Statistical parameters for the determination of elements in 3% acetic acid (Solution 1) by ICP-MS.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	22	24	24	24	24	24	24
No. of labs without outliers	21	21	22	24	22	21	24
$\bar{x}$ [mg L^{-1}]	0.89	0.0028	0.0016	0.034	0.0099	0.012	0.010
s_r [mg L^{-1}]	0.030	0.00029	0.00010	0.00057	0.00029	0.00072	0.00032
Relative s_r [%]	3.4	10.5	6.2	1.7	3.0	6.2	3.2
s_R [mg L^{-1}]	0.065	0.00040	0.00021	0.0015	0.00051	0.00074	0.00054
Relative s_R [%]	7.2	14.4	12.6	4.3	5.1	6.4	5.4
$s_{R(Horwitz)}$ [%]	16.3	22.0	22.0	22.0	22.0	22.0	22.0

Table 7: Statistical parameters for the determination of elements in ATW (Solution 2) by ICP-MS.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	22	24	24	24	24	24	24
No. of labs without outliers	20	22	24	23	22	23	23
$\bar{x}$ [mg L^{-1}]	3.9	0.0019	0.0058	0.017	0.20	0.122	0.0096
s_r [mg L^{-1}]	0.106	0.00019	0.00028	0.00051	0.0049	0.0021	0.00034
Relative s_r [%]	2.7	9.8	4.8	3.0	2.5	1.7	3.5
s_R [mg L^{-1}]	0.28	0.00022	0.00046	0.00074	0.0095	0.0054	0.00058
Relative s_R [%]	7.2	11.5	7.8	4.2	4.8	4.4	6.1
$s_{R(Horwitz)}$ [%]	13.0	22.0	22.0	22.0	20.4	21.8	22.0

Table 8: Statistical parameters for the determination of elements in 0.5% citric acid (Solution 3) by ICP-MS.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	22	24	24	24	24	24	24
No. of labs without outliers	20	23	24	24	24	23	22
$\bar{x}$, mg/L	3.4	0.0015	0.0058	0.019	0.217	0.108	0.0056
s_r [mg/L]	0.094	0.000096	0.00019	0.00062	0.0058	0.0030	0.00012
Relative s_r [%]	2.8	6.4	3.2	3.2	2.7	2.8	2.1
s_R [mg/L]	0.24	0.00025	0.00041	0.00089	0.0098	0.0051	0.00035
Relative s_R [%]	7.0	16.6	7.1	4.6	4.5	4.8	6.3
$s_{R(Horwitz)}$ [%]	13.2	22.0	22.0	22.0	20.0	22.0	22.0

Table 9: Statistical parameters for the determination of Ni in perspiration simulant (prepared from Solution 4) by ICP-MS.

Parameter	Ni
No. of labs	10
No. of labs without outliers	10
$\bar{x}$ [mg L^{-1}]	0.236
s_r [mg L^{-1}]	0.0035
Relative s_r [%]	1.5
s_R [mg L^{-1}]	0.019
Relative s_R [%]	7.8
$s_{R(Horwitz)}$ [%]	19.9

6.3.2 Performance of the laboratories (*z* scores) for the ICP-MS method

3% acetic acid (Solution 1)

All laboratories obtained acceptable *z* scores for the analysis of Co and Pb (both 24 of 24) by ICP-MS in 3% acetic acid. Most laboratories received acceptable *z* scores for the analysis of Cd, Cr, Ni (all three 22 of 24), Al (21 of 22), and As (20 of 24). One laboratory obtained an unacceptable *z* score for Al and two laboratories achieved unacceptable *z* scores for Cr. For Cd and Ni one questionable and one unacceptable *z* score were obtained by the participating laboratories. One questionable and three unacceptable *z* scores were received by the laboratories for As. Two laboratories did not report results for Al (see Table 10).

Artificial tap water (ATW, Solution 2)

Acceptable *z* scores were received by all laboratories for the analysis of Cd, Co, Ni, and Pb (all four 24 of 24) by ICP-MS in ATW. Most laboratories achieved acceptable *z* scores for the analysis of Al (20 of 22), As (22 of 24) and Cr (23 of 24). One laboratory obtained an unacceptable *z* score for Cr and two laboratories obtained unacceptable *z* scores for each Al and As. Two laboratories did not report results for Al (see Table 11).

0.5 % citric acid (Solution 3)

All laboratories received acceptable *z* scores for the analysis of Cd, Co and Cr (all three 24 of 24) by ICP-MS in 0.5% citric acid. Most laboratories obtained acceptable *z* scores for the analysis of Al (20 of 22), As (21 of 24), Ni (23 of 24), and Pb (22 of 24). One laboratory achieved an unacceptable *z* score for Ni and two laboratories obtained unacceptable *z* scores for each Al and Pb. For As, two laboratories received questionable *z* scores and one laboratory received an unacceptable *z* score. Two laboratories did not report results for Al (see Table 12).

Perspiration simulant (prepared from Solution 4)

Acceptable *z* scores were obtained by all ten laboratories for the analysis of Ni by ICP-MS in perspiration simulant (see Table 13).

In general, the majority of the ICP-MS results were acceptable for all elements and solutions. Particularly good performance was demonstrated for the analysis of cobalt with acceptable *z* scores for all laboratories and for all simulant solutions. Questionable and unacceptable *z* scores were received mainly by Lab 1 for Al, Lab 23 for As, and Lab 27 for As and Al.

Although the results of some labs were removed as statistical outliers from the evaluation of this MES (see 6.3.1), these values obtained acceptable *z* scores. This applies to Lab 20 for Ni in 3% acetic acid and to Lab 27 for Co, Cr and Ni in artificial tap water.

Table 10: *z* scores for quantification of elements in 3% acetic acid (Solution 1) by ICP-MS. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		As		Cd		Co		Cr		Ni		Pb	
x_{pt} [mg L^{-1}]	0.90		0.0026		0.0016		0.035		0.010		0.012		0.010	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	0.21	-5.13	0.0028	0.45	0.0021	1.90	0.037	0.37	0.017	4.46	0.025	6.96	0.011	0.58
Lab 02	1.02	0.87	0.0030	1.03	0.0010	-2.50	0.033	-0.38	0.009	-0.67	0.011	-0.56	0.009	-0.67
Lab 03	0.83	-0.53	0.0028	0.50	0.0015	-0.40	0.034	-0.17	0.010	-0.12	0.011	-0.31	0.009	-0.38
Lab 04	0.87	-0.26	0.0026	0.00	0.0016	0.00	0.035	-0.10	0.010	0.00	0.012	0.00	0.010	0.00
Lab 06	0.90	0.01	0.0027	0.28	0.0016	0.19	0.036	0.18	0.010	-0.02	0.012	-0.06	0.009	-0.34
Lab 07	0.82	-0.59	0.0044	4.62	0.0020	1.67	0.033	-0.38	0.009	-0.47	0.012	-0.11	0.010	-0.23
Lab 08	0.96	0.43	0.0027	0.15	0.0016	-0.04	0.033	-0.40	0.010	0.10	0.011	-0.36	0.010	0.30
Lab 09	0.89	-0.09	0.0026	0.00	0.0016	-0.21	0.034	-0.15	0.010	-0.03	0.011	-0.39	0.010	-0.23
Lab 10	0.88	-0.13	0.0022	-0.95	0.0016	-0.19	0.033	-0.36	0.009	-0.57	0.011	-0.50	0.009	-0.40
Lab 11	0.90	-0.01	0.0032	1.54	0.0017	0.42	0.032	-0.53	0.010	0.20	0.012	-0.28	0.010	0.03
Lab 12	0.90	0.02	0.0028	0.51	0.0017	0.21	0.036	0.10	0.010	0.10	0.012	-0.08	0.010	0.00
Lab 14	0.89	-0.08	0.0026	-0.06	0.0016	-0.02	0.035	-0.07	0.009	-0.44	0.011	-0.39	0.010	0.23
Lab 16	0.88	-0.13	0.0030	1.06	0.0017	0.23	0.035	0.05	0.010	0.17	0.012	0.06	0.010	0.03
Lab 17	0.87	-0.20	0.0030	1.03	0.0020	1.67	0.035	-0.10	0.010	0.00	0.012	0.00	0.010	0.00
Lab 18	0.90	0.00	0.0033	1.79	0.0014	-0.83	0.035	0.00	0.010	0.00	0.011	-0.56	0.011	0.67
Lab 19	nv	-	0.0022	-0.94	0.0012	-1.52	0.034	-0.21	0.010	-0.14	0.011	-0.64	0.010	-0.09
Lab 20	0.76	-1.07	0.0033	1.79	0.0017	0.21	0.036	0.26	0.010	0.13	0.014	1.22	0.011	0.40
Lab 21	nv	-	0.0030	0.92	0.0016	-0.04	0.032	-0.60	0.010	0.07	0.011	-0.36	0.010	-0.29
Lab 23	0.79	-0.79	0.0497	121	0.0007	-3.65	0.033	-0.40	0.009	-0.35	0.011	-0.64	0.009	-0.51
Lab 24	0.92	0.16	0.0025	-0.38	0.0016	-0.21	0.034	-0.29	0.010	-0.27	0.012	-0.28	0.010	-0.23
Lab 25	0.91	0.07	0.0024	-0.51	0.0015	-0.42	0.035	-0.01	0.010	0.03	0.016	2.44	0.010	-0.17
Lab 26	0.90	0.01	0.0028	0.47	0.0016	0.06	0.035	0.01	0.011	0.40	0.012	-0.08	0.010	0.23
Lab 27	1.02	0.85	0.0095	18	0.0015	-0.42	0.032	-0.57	0.019	5.67	0.013	0.56	0.011	0.33
Lab 28	0.89	-0.07	0.0035	2.31	0.0018	0.83	0.035	-0.10	0.011	0.67	0.013	0.28	0.010	0.27

'nv' indicates that no value was submitted for this element
'-' indicates that no value could be calculated

Table 11: *z* scores for quantification of elements in ATW (Solution 2) by ICP-MS. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		As		Cd		Co		Cr		Ni		Pb	
x_{pt} [mg L^{-1}]	4.00		0.0020		0.0060		0.018		0.20		0.126		0.010	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	0.87	-5.21	0.0020	-0.12	0.0060	0.04	0.018	-0.04	0.19	-0.31	0.124	-0.13	0.011	0.38
Lab 02	4.08	0.13	0.0020	0.00	0.0060	0.00	0.017	-0.37	0.19	-0.23	0.123	-0.16	0.009	-0.67
Lab 03	3.79	-0.35	0.0019	-0.30	0.0058	-0.22	0.018	-0.19	0.19	-0.23	0.120	-0.34	0.009	-0.46
Lab 04	nv	-	0.0021	0.17	0.0059	-0.11	0.018	0.00	0.22	0.67	0.130	0.21	0.010	0.00
Lab 06	4.17	0.28	0.0021	0.30	0.0061	0.10	0.018	-0.02	0.20	0.07	0.126	0.02	0.009	-0.56
Lab 07	3.72	-0.47	0.0019	-0.27	0.0057	-0.33	0.017	-0.50	0.19	-0.35	0.120	-0.34	0.009	-0.43
Lab 08	4.03	0.05	0.0016	-1.30	0.0059	-0.07	0.017	-0.48	0.19	-0.42	0.111	-0.79	0.011	0.33
Lab 09	4.02	0.03	0.0021	0.23	0.0055	-0.61	0.018	-0.19	0.20	-0.05	0.123	-0.16	0.009	-0.77
Lab 10	3.95	-0.08	0.0016	-1.25	0.0058	-0.17	0.017	-0.47	0.19	-0.47	0.118	-0.41	0.009	-0.48
Lab 11	4.04	0.07	0.0019	-0.33	0.0058	-0.28	0.017	-0.46	0.20	0.07	0.122	-0.21	0.010	-0.27
Lab 12	3.98	-0.03	0.0021	0.33	0.0063	0.33	0.018	0.07	0.20	-0.15	0.122	-0.24	0.010	-0.10
Lab 14	4.02	0.03	0.0020	0.03	0.0061	0.06	0.017	-0.20	0.20	-0.07	0.125	-0.05	0.010	0.07
Lab 16	4.00	0.00	0.0019	-0.32	0.0058	-0.18	0.017	-0.22	0.20	-0.05	0.122	-0.24	0.009	-0.37
Lab 17	3.78	-0.37	0.0020	0.00	0.0060	0.00	0.018	-0.19	0.20	-0.07	0.122	-0.21	0.010	0.00
Lab 18	4.50	0.83	0.0019	-0.33	0.0057	-0.33	0.018	0.00	0.20	0.00	0.120	-0.32	0.010	0.00
Lab 19	3.34	-1.10	0.0016	-1.33	0.0050	-1.08	0.016	-0.78	0.19	-0.48	0.116	-0.54	0.009	-0.74
Lab 20	3.44	-0.93	0.0015	-1.83	0.0062	0.22	0.019	0.19	0.21	0.30	0.130	0.19	0.010	0.20
Lab 21	nv	-	0.0019	-0.20	0.0059	-0.11	0.017	-0.44	0.21	0.21	0.130	0.21	0.010	-0.06
Lab 23	3.44	-0.94	0.1750	577	0.0053	-0.77	0.018	-0.19	0.02	-6.04	0.120	-0.34	0.009	-0.66
Lab 24	4.31	0.51	0.0020	-0.17	0.0057	-0.39	0.017	-0.56	0.19	-0.42	0.115	-0.61	0.009	-0.60
Lab 25	4.12	0.20	0.0019	-0.33	0.0059	-0.11	0.018	-0.11	0.20	-0.15	0.122	-0.22	0.010	-0.23
Lab 26	3.95	-0.09	0.0021	0.18	0.0061	0.11	0.018	-0.15	0.21	0.27	0.125	-0.08	0.010	-0.19
Lab 27	1.94	-3.43	0.0010	-3.33	0.0050	-1.11	0.014	-1.48	0.16	-1.33	0.090	-1.90	0.007	-2.00
Lab 28	4.01	0.01	0.0020	0.00	0.0069	1.00	0.018	-0.19	0.20	-0.17	0.130	0.21	0.010	0.20

'nv' indicates that no value was submitted for this element
'-' indicates that no value could be calculated

Table 12: *z* scores for quantification of elements in 0.5% citric acid (Solution 3) by ICP-MS. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		As		Cd		Co		Cr		Ni		Pb	
x_{pt} [mg L^{-1}]	3.50		0.0016		0.006		0.020		0.225		0.112		0.006	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	0.68	-5.36	0.0014	-1.00	0.0060	0.03	0.020	0.00	0.220	-0.15	0.113	0.06	0.0108	5.38
Lab 02	3.55	0.10	0.0010	-2.50	0.0060	0.00	0.019	-0.33	0.207	-0.53	0.106	-0.36	0.0050	-1.11
Lab 03	3.29	-0.41	0.0016	-0.15	0.0057	-0.34	0.020	-0.17	0.212	-0.40	0.107	-0.33	0.0055	-0.61
Lab 04	nv	-	0.0016	-0.21	0.0060	0.00	0.020	-0.17	0.245	0.59	0.110	-0.12	0.0061	0.06
Lab 06	3.51	0.02	0.0016	0.17	0.0062	0.24	0.020	0.12	0.224	-0.03	0.114	0.12	0.0052	-0.84
Lab 07	3.28	-0.43	0.0017	0.42	0.0059	-0.17	0.019	-0.33	0.213	-0.36	0.110	-0.15	0.0057	-0.33
Lab 08	3.69	0.36	0.0012	-1.48	0.0057	-0.33	0.019	-0.50	0.208	-0.52	0.098	-0.82	0.0059	-0.11
Lab 09	3.46	-0.09	0.0015	-0.31	0.0053	-0.83	0.020	-0.12	0.217	-0.25	0.108	-0.24	0.0051	-1.00
Lab 10	3.48	-0.03	0.0014	-0.81	0.0057	-0.36	0.019	-0.32	0.212	-0.39	0.107	-0.29	0.0055	-0.54
Lab 11	3.43	-0.14	0.0016	0.00	0.0057	-0.33	0.019	-0.35	0.220	-0.16	0.108	-0.21	0.0056	-0.50
Lab 12	3.50	-0.01	0.0016	0.00	0.0061	0.06	0.020	0.08	0.223	-0.06	0.107	-0.31	0.0058	-0.22
Lab 14	3.48	-0.04	0.0016	-0.08	0.0059	-0.08	0.020	-0.15	0.219	-0.18	0.111	-0.06	0.0059	-0.10
Lab 16	3.42	-0.15	0.0020	1.50	0.0061	0.06	0.020	-0.03	0.219	-0.18	0.108	-0.27	0.0061	0.06
Lab 17	3.38	-0.22	0.0020	1.67	0.0060	0.00	0.020	-0.17	0.223	-0.06	0.111	-0.09	0.0060	0.00
Lab 18	3.60	0.19	0.0014	-0.83	0.0057	-0.33	0.020	0.00	0.220	-0.15	0.110	-0.12	0.0060	0.00
Lab 19	2.98	-0.98	0.0013	-1.46	0.0050	-1.07	0.017	-0.90	0.204	-0.64	0.106	-0.36	0.0054	-0.72
Lab 20	2.89	-1.17	0.0015	-0.63	0.0060	0.00	0.020	0.08	0.217	-0.24	0.113	0.03	0.0058	-0.22
Lab 21	nv	-	0.0015	-0.54	0.0059	-0.07	0.019	-0.28	0.221	-0.11	0.109	-0.21	0.0058	-0.21
Lab 23	2.97	-1.01	0.0969	397	0.0050	-1.16	0.018	-0.58	0.206	-0.58	0.548	26	0.0049	-1.27
Lab 24	3.67	0.32	0.0016	-0.21	0.0055	-0.56	0.019	-0.50	0.207	-0.53	0.103	-0.54	0.0055	-0.56
Lab 25	3.60	0.19	0.0015	-0.63	0.0061	0.06	0.020	-0.07	0.219	-0.16	0.111	-0.08	0.0059	-0.17
Lab 26	3.41	-0.18	0.0017	0.44	0.0061	0.13	0.019	-0.23	0.227	0.06	0.107	-0.30	0.0057	-0.31
Lab 27	1.91	-3.04	0.0010	-2.50	0.0050	-1.11	0.018	-0.67	0.215	-0.30	0.096	-0.98	0.0020	-4.44
Lab 28	3.32	-0.35	0.0016	-0.21	0.0062	0.22	0.020	-0.17	0.218	-0.21	0.115	0.18	0.0056	-0.50

'nv' indicates that no value was submitted for this element
'-' indicates that no value could be calculated

Table 13: *z* scores for quantification of Ni in perspiration simulant (prepared from Solution 4) by ICP-MS. The value of σ_{pt} was set to 15% of the x_{pt} value. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Ni	
x_{pt} [mg L^{-1}]	0.237	
	x_i [mg L^{-1}]	*z*
Lab 01	0.276	1.09
Lab 03	0.246	0.25
Lab 07	0.215	-0.62
Lab 09	0.254	0.46
Lab 21	0.234	-0.10
Lab 23	0.223	-0.40
Lab 24	0.237	0.00
Lab 26	0.226	-0.33
Lab 27	0.210	-0.76
Lab 28	0.245	0.22

6.3.3 Statistical parameters for ICP-OES method

The evaluation of the MES results in terms of interlaboratory repeatability (s_r) and reproducibility (s_R) standard deviations for the ICP-OES method are shown in Table 14 to Table 17. Relative s_r and s_R values between 1.1–14.6% and 3.0–17.9% were obtained. They were below 9.6% and 9.2% for most elements, except relative s_r values for Ni in HAc (14.6%) and Pb in ATW (12.8%) and relative s_R values for Pb (22.6%), Ni (15.4%) and Cd (13.1%) in HAc as well as Pb (17.9%) in CA. These s_R values are lower than the corresponding predicted relative reproducibility standard deviations according to Horwitz/Thompson [$s_{R(Horwitz)}$] for all elements and solutions except for Pb in 3% acetic acid (s_R=22.6% and $s_{R(Horwitz)}$=22%).

Only two to three laboratories were able to quantify As by ICP-OES in Solutions 1–3. The concentration of As was reported to be below the laboratories' LOD/LOQ for nine laboratories in HAc and CA and for eight laboratories in ATW. Because the number of results submitted for As is insufficient for a statistical evaluation, values for this element are not shown in Table 14 to Table 17.

Between nine and ten laboratories were able to quantify Cd and between six and nine laboratories were able to quantify Pb. Four to seven laboratories reported that the concentration of Pb was below their LOD/LOQ. The concentration of Cd was below the laboratories' LOD/LOQ for three to four laboratories. One laboratory was identified as an outlier for Cd and Pb in CA, and one laboratory was identified as an outlier for Pb in ATW.

Between 12 and 14 laboratories were able to quantify Al, Co, Cr and Ni. Only one result for the determination of Ni in 0.5% CA was identified as an outlier. Ni in perspiration simulant prepared from Solution 4 was quantified by eight laboratories and no outliers were found.

Table 14: Statistical parameters for the determination of elements in 3% acetic acid (Solution 1) by ICP-OES.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	13	2	9	12	12	13	9
No. of labs without outliers	13	-	8	12	12	13	8
$\bar{x}$ [mg L^{-1}]	0.88	-	0.0016	0.036	0.011	0.012	0.011
s_r [mg L^{-1}]	0.0094	-	0.00012	0.00061	0.00057	0.0018	0.0010
Relative s_r [%]	1.1	-	7.3	1.7	5.4	14.6	9.6
s_R [mg L^{-1}]	0.0806	-	0.00022	0.0022	0.00096	0.0019	0.0025
Relative s_R [%]	9.2	-	13.1	6.0	9.1	15.4	22.6
$s_{R(Horwitz)}$ [%]	16.3	22.0	22.0	22.0	22.0	22.0	22.0

Table 15: Statistical parameters for the determination of elements in ATW (Solution 2) by ICP-OES.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	14	3	10	12	13	13	8
No. of labs without outliers	14	-	10	12	13	13	7
$\bar{x}$ [mg L^{-1}]	3.9	-	0.0057	0.017	0.20	0.122	0.0089
s_r [mg L^{-1}]	0.0620	-	0.00033	0.00036	0.0077	0.0044	0.0011
Relative s_r [%]	1.6	-	5.8	2.1	3.9	3.6	12.8
s_R [mg L^{-1}]	0.26	-	0.00033	0.0011	0.013	0.0061	0.00071
Relative s_R [%]	6.6	-	5.8	6.2	6.7	5.0	8.0
$s_{R(Horwitz)}$ [%]	13.0	22.0	22.0	22.0	20.4	21.8	22.0

Table 16: Statistical parameters for the determination of elements in 0.5% citric acid (Solution 3) by ICP-OES.

Parameter	Al	As	Cd	Co	Cr	Ni	Pb
No. of labs	14	2	10	12	13	13	6
No. of labs without outliers	14	-	10	12	13	12	6
$\bar{x}$ [mg L^{-1}]	3.4	-	0.0057	0.020	0.223	0.109	0.0055
s_r [mg L^{-1}]	0.041	-	0.00016	0.00041	0.0033	0.0019	0.00053
Relative s_r [%]	1.2	-	2.9	2.1	1.5	1.7	9.6
s_R [mg L^{-1}]	0.27	-	0.00036	0.0011	0.0094	0.0032	0.0010
Relative s_R [%]	8.1	-	6.3	5.7	4.2	3.0	17.9
$s_{R(Horwitz)}$ [%]	13.2	22.0	22.0	22.0	20.0	22.0	22.0

Table 17: Statistical parameters for the determination of Ni in perspiration simulant (prepared from Solution 4) by ICP-OES.

Parameter	Ni
No. of labs	8
No. of labs without outliers	8
$\bar{x}$ [mg L^{-1}]	0.220
s_r [mg L^{-1}]	0.0036
Relative s_r [%]	1.6
s_R [mg L^{-1}]	0.017
Relative s_R [%]	7.5
$s_{R(Horwitz)}$ [%]	19.9

6.3.4 Performance of the laboratories (*z* scores) for the ICP-OES method

The majority of laboratories reported that the concentration of As in Solutions 1–3 was below their LOD/LOQ; therefore, *z* scores were not calculated for this element.

3% acetic acid (Solution 1)

All laboratories obtained acceptable *z* scores for the analysis of Al, Ni (both 13 of 13), Co, and Cr (both 12 of 12) by ICP-OES in 3% acetic acid. Most laboratories received acceptable *z* scores for the analysis of Cd (8 of 9) and Pb (6 of 9). One unacceptable *z* score was obtained for the analysis of Cd, while one unacceptable and two questionable *z* scores were obtained for the analysis of Pb. Several laboratories (four for Pb, four for Cd, one for Co, and one for Cr) reported that the concentrations of the elements were below their respective LOD/LOQ (see Table 18).

Artificial tap water (ATW, Solution 2)

Acceptable *z* scores were received by all laboratories for the analysis of Al (14 of 14), Cd (10 of 10), Co (12 of 12), Cr and Ni (both 13 of 13) by ICP-OES in ATW. All except one laboratory achieved acceptable *z* scores for the analysis of Pb (7 of 8), while one laboratory achieved a questionable *z* score. Several laboratories (five for Pb, three for Cd, and one for Co) reported that the concentrations of the elements were below their LOD/LOQ (see Table 19).

0.5% citric acid (Solution 3)

All laboratories received acceptable *z* scores for the analysis of Al (14 of 14), Cd (10 of 10), Co (12 of 12), Cr and Ni (both 13 of 13) by ICP-OES in 0.5% citric acid. All except one laboratory obtained acceptable *z* scores for the analysis of Pb (5 of 6), while one laboratory obtained a questionable *z* score. Several laboratories (seven for Pb, three for Cd, and one for Co) reported that the concentrations of the elements were below their respective LOD/LOQ (see Table 20).

Perspiration simulant (prepared from Solution 4)

Acceptable *z* scores were obtained by all eight laboratories for the analysis of Ni by ICP-OES in 0.5% citric acid (see Table 21).

In general, most of the quantified results were found to be acceptable in terms of *z* scores. However, the concentration of some elements was below the respective LOD/LOQ of the participating laboratories (e.g. for Pb, Cd and for one laboratory for Co). Especially for As, most laboratories reported that the concentration was below their respective LOD/LOQ.

Outliers were removed for the statistical evaluation of this MES (see 6.3.3). Nevertheless, in some cases, these outliers obtained acceptable *z* scores. This applies to the results of Lab 1 for Cd in 3% acetic acid and to the results of Lab 15 for Ni in 0.5% citric acid.

Table 18: *z* scores for quantification of elements in 3% acetic acid (Solution 1) by ICP-OES. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		**Cd**		**Co**		**Cr**		**Ni**		**Pb**	
x_{pt} [mg L^{-1}]	**0.90**		**0.0016**		**0.035**		**0.010**		**0.012**		**0.010**	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	0.94	0.27	0.0006	-4.21	0.035	0.00	0.009	-0.53	0.011	-0.56	0.009	-0.47
Lab 02	1.00	0.76	< 0.01	-	0.038	0.57	0.012	1.33	0.014	1.11	0.010	0.00
Lab 07	0.86	-0.28	0.0018	0.62	0.038	0.57	0.011	0.73	0.012	0.00	0.014	2.43
Lab 08	0.92	0.17	0.0016	-0.06	0.038	0.49	0.011	0.67	0.014	1.31	< LOQ	-
Lab 12	0.85	-0.38	< 0.05	-	0.036	0.10	0.012	1.00	0.012	0.00	< LOQ	-
Lab 13	0.74	-1.19	< LOD	-	< LOD	-	< LOQ	-	0.009	-1.67	< LOQ	-
Lab 15	0.94	0.30	0.0013	-1.25	0.037	0.38	0.011	0.40	0.013	0.72	0.001	-5.87
Lab 19	0.85	-0.34	0.0015	-0.52	0.035	0.03	0.010	-0.22	0.014	0.89	0.010	-0.20
Lab 21	0.77	-0.98	0.0017	0.42	0.036	0.12	0.010	0.27	0.012	0.03	0.012	1.00
Lab 22	0.91	0.05	0.0020	1.67	0.036	0.19	0.011	0.67	0.013	0.28	< LOD	-
Lab 26	0.90	0.01	0.0016	0.06	0.032	-0.55	0.010	-0.03	0.011	-0.36	0.010	-0.15
Lab 28	0.82	-0.59	0.0018	0.63	0.038	0.58	0.011	0.50	0.013	0.56	0.014	2.63
Lab 29	0.91	0.07	< LOQ	-	0.034	-0.19	0.009	-0.67	0.011	-0.56	0.009	-0.67

'-' indicates that no value could be calculated

Table 19: *z* scores for quantification of elements in ATW (Solution 2) by ICP-OES. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		**Cd**		**Co**		**Cr**		**Ni**		**Pb**	
x_{pt} [mg L^{-1}]	**4.00**		**0.0060**		**0.018**		**0.20**		**0.126**		**0.010**	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	4.06	0.11	0.0053	-0.78	0.017	-0.37	0.19	-0.33	0.120	-0.32	0.009	-0.73
Lab 02	4.05	0.09	< LOQ	-	0.018	0.00	0.20	-0.17	0.120	-0.32	< LOQ	-
Lab 04	3.39	-1.02	nv	-	nv	-	nv	-	nv	-	nv	-
Lab 07	3.90	-0.18	0.0058	-0.22	0.016	-0.59	0.19	-0.40	0.115	-0.58	0.009	-0.47
Lab 08	4.10	0.16	0.0059	-0.08	0.018	0.06	0.20	0.10	0.122	-0.21	< LOQ	-
Lab 12	3.90	-0.17	< LOQ	-	0.018	0.00	0.20	-0.15	0.125	-0.05	< LOQ	-
Lab 13	3.59	-0.69	< LOQ	-	< LOD	-	0.23	0.97	0.135	0.45	< LOQ	-
Lab 15	4.42	0.70	0.0062	0.22	0.017	-0.41	0.21	0.17	0.126	0.00	0.014	2.47
Lab 19	3.85	-0.25	0.0056	-0.43	0.018	-0.17	0.19	-0.23	0.121	-0.26	0.008	-1.13
Lab 21	3.91	-0.14	0.0055	-0.61	0.018	-0.17	0.20	-0.06	0.124	-0.12	0.009	-0.93
Lab 22	3.85	-0.25	0.0055	-0.56	0.018	-0.19	0.20	-0.12	0.122	-0.21	< LOD	-
Lab 26	4.03	0.05	0.0059	-0.16	0.015	-1.02	0.20	-0.17	0.119	-0.40	0.009	-0.77
Lab 28	3.80	-0.34	0.0057	-0.33	0.017	-0.50	0.19	-0.34	0.120	-0.32	0.009	-0.50
Lab 29	3.88	-0.20	0.0053	-0.78	0.016	-0.74	0.19	-0.27	0.117	-0.48	0.009	-0.80

'nv' indicates that no value was submitted for this element
'-' indicates that no value could be calculated

Table 20: *z* scores for quantification of elements in 0.5% citric acid (Solution 3) by ICP-OES. The value of σ_{pt} was set to 15% of the corresponding x_{pt} value for all elements. According to ISO 13528:2022 [2]: |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Al		**Cd**		**Co**		**Cr**		**Ni**		**Pb**	
x_{pt} [mg L^{-1}]	**3.50**		**0.006**		**0.020**		**0.225**		**0.112**		**0.006**	
	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*	x_i [mg L^{-1}]	*z*
Lab 01	3.71	0.40	0.0052	-0.89	0.020	0.00	0.230	0.15	0.110	-0.12	0.0062	0.22
Lab 02	3.58	0.15	< LOQ	-	0.020	0.00	0.225	0.00	0.105	-0.42	< LOQ	-
Lab 04	3.17	-0.63	nv	-	nv	-	nv	-	nv	-	nv	-
Lab 07	3.27	-0.45	0.0058	-0.22	0.019	-0.23	0.217	-0.24	0.109	-0.21	0.0062	0.17
Lab 08	3.64	0.26	0.0060	-0.04	0.021	0.30	0.235	0.30	0.112	0.00	< LOQ	-
Lab 12	3.34	-0.30	< LOQ	-	0.020	-0.17	0.219	-0.18	0.112	-0.03	< LOQ	-
Lab 13	2.95	-1.04	< LOQ	-	< LOD	-	0.219	-0.19	0.107	-0.33	< LOD	-
Lab 15	3.86	0.69	0.0061	0.11	0.019	-0.33	0.240	0.44	0.145	1.96	0.0050	-1.11
Lab 19	3.18	-0.61	0.0058	-0.23	0.019	-0.18	0.209	-0.47	0.105	-0.42	0.0041	-2.07
Lab 21	3.42	-0.16	0.0055	-0.61	0.020	0.08	0.227	0.07	0.113	0.06	0.0057	-0.39
Lab 22	3.50	0.00	0.0060	0.00	0.020	0.00	0.221	-0.13	0.110	-0.12	< LOD	-
Lab 26	3.57	0.12	0.0059	-0.12	0.017	-0.90	0.222	-0.09	0.111	-0.09	< LOQ	-
Lab 28	3.12	-0.73	0.0058	-0.28	0.020	-0.15	0.219	-0.17	0.110	-0.12	0.0058	-0.22
Lab 29	3.25	-0.48	0.0050	-1.11	0.019	-0.40	0.212	-0.39	0.105	-0.42	< LOQ	-

'nv' indicates that no value was submitted for this element
'-' indicates that no value could be calculated

Table 21: *z* scores for quantification of Ni in perspiration simulant (prepared from Solution 4) by ICP-OES. The value of σ_{pt} was set to 15% of the x_{pt} value. According to ISO 13528:2022 [2], |*z* score| ≤ 2.0 is considered acceptable (highlighted in green), 2.0 < |*z* score| < 3.0 is questionable (highlighted in orange), and |*z* score| ≥ 3.0 is unacceptable (highlighted in red).

	Ni	
x_{pt} **[mg L^{-1}]**	**0.237**	
	x_i **[mg L^{-1}]**	***z***
Lab 01	0.233	-0.11
Lab 07	0.195	-1.19
Lab 15	0.229	-0.22
Lab 21	0.197	-1.13
Lab 22	0.233	-0.12
Lab 23	0.226	-0.33
Lab 26	0.221	-0.47
Lab 28	0.225	-0.34

6.4 Additional information extracted from the questionnaire

6.4.1 Limits of detection and quantification for ICP-MS and ICP-OES methods

The limits of detection (LODs) and quantification (LOQs) for ICP-MS and ICP-OES methods submitted by the participants are shown in Table 22 to Table 25.

Table 22: LOD values submitted for ICP-MS.

Lab Code	Al [mg L^{-1}]	As [mg L^{-1}]	Cd [mg L^{-1}]	Cr [mg L^{-1}]	Co [mg L^{-1}]	Ni [mg L^{-1}]	Pb [mg L^{-1}]
Lab 01	0.0035	0.0001	0.0001	0.0001	0.0001	0.004	0.00004
Lab 02	0.01	0.00003	0.00003	0.0003	0.00003	0.0003	0.00003
Lab 03	7.93	0.15	0.03	0.18	0.05	0.05	0.14
Lab 04	0.0067	0.00003	0.000055	0.011	0.000006	0.00045	0.00015
Lab 06	0.0004	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
Lab 07	0.0002	0.00005	0.00001	0.0001	0.000003	0.00003	0.000017
Lab 08	0.0012	0.00003	0.00002	0.00009	0.00008	0.0023	0.00006
Lab 09	0.001	0.000025	0.000005	0.00002	0.000005	0.00003	0.00001
Lab 10	0.00008	0.00023	0.00001	0.00018	0.00001	0.00005	0.00003
Lab 12	0.001	0.0005	0.00025	0.0005	0.0005	0.0005	0.00025
Lab 14	0.0128	0.0000051	0.0000128	0.00064	0.000051	0.00036	0.0000256
Lab 16	0.002	0.00008	0.000006	0.0003	0.00002	0.00006	0.00005
Lab 17	0.000032	0.000007	0.00000028	0.000006	0.0000004	0.000006	0.0000004
Lab 18	nv	0.0005	0.00003	0.0013	nv	0.0009	0.0001
Lab 19	nv	0.000125	0.000125	nv	0.005	nv	0.00025
Lab 20	0.0005	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Lab 21	0.0167	0.000267	0.00033	0.00067	0.000167	0.00167	0.00067
Lab 23	0.00196	0.00048	0.000099	0.000069	0.000057	0.00078	0.00054
Lab 24	0.0007	0.0003	0.00007	0.0017	0.0003	0.0007	0.00007
Lab 25	0.003	0.00006	0.00006	0.00072	0.00015	0.00072	0.00015
Lab 26	0.0045	0.000033	0.000022	0.000084	0.00003	0.00015	0.000023
Lab 27	0.04	0.002	0.001	0.005	0.003	0.004	0.004

'nv' indicates that no value was submitted for this element

Table 23: LOQ values submitted for ICP-MS.

Lab Code	Al [mg L^{-1}]	As [mg L^{-1}]	Cd [mg L^{-1}]	Cr [mg L^{-1}]	Co [mg L^{-1}]	Ni [mg L^{-1}]	Pb [mg L^{-1}]
Lab 01	0.013	0.00032	0.00021	0.00023	0.00028	0.0141	0.00015
Lab 02	0.03	0.0001	0.0001	0.001	0.0001	0.001	0.0001
Lab 03	25.03	0.49	0.08	0.56	0.14	0.14	0.45
Lab 04	0.021	0.0001	0.00018	0.035	0.00002	0.0015	0.0005
Lab 06	0.0013	0.0007	0.0006	0.0008	0.0008	0.0006	0.0007
Lab 07	0.0008	0.0002	0.00004	0.0002	0.00001	0.00011	0.000057
Lab 08	0.0044	0.0001	0.00007	0.00034	0.00027	0.0081	0.00022
Lab 09	0.002	0.00005	0.00001	0.00004	0.00001	0.00006	0.00002
Lab 10	0.00026	0.00077	0.00002	0.00058	0.00004	0.00015	0.00011
Lab 11	0.005	0.00005	0.00005	0.0005	0.00005	0.0001	0.00005
Lab 12	0.010	0.001	0.0005	0.001	0.001	0.001	0.0005
Lab 14	0.0385	0.0000154	0.0000385	0.00192	0.000154	0.00108	0.0000769
Lab 16	0.010	0.0010	0.000020	0.0010	0.00005	0.0010	0.00015
Lab 17	0.000097	0.000021	0.00000083	0.000017	0.0000013	0.000021	0.0000013
Lab 18	nv	0.0015	0.0001	0.0034	nv	0.0023	0.0002
Lab 19	nv	0.00025	0.00025	nv	0.001	nv	0.0005
Lab 20	0.0015	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
Lab 21	0.05	0.0008	0.001	0.002	0.0005	0.005	0.002
Lab 23	0.00653	0.0016	0.00033	0.00023	0.00019	0.0026	0.0018
Lab 24	0.002	0.001	0.0002	0.005	0.001	0.002	0.0002
Lab 25	0.01	0.0002	0.0002	0.0024	0.0005	0.0024	0.0005
Lab 26	0.0150	0.000120	0.000080	0.000300	0.00010	0.00053	0.000080
Lab 27	0.13	0.01	0.004	0.02	0.01	0.01	0.01

'nv' indicates that no value was submitted for this element

Table 24: LOD values submitted for ICP-OES.

Lab Code	Al [mg L^{-1}]	As [mg L^{-1}]	Cd [mg L^{-1}]	Cr [mg L^{-1}]	Co [mg L^{-1}]	Ni [mg L^{-1}]	Pb [mg L^{-1}]
Lab 01	0.07	nv	0.015	0.019	0.01	0.009	0.012
Lab 02	0.166	0.003	0.003	0.003	0.003	0.003	0.003
Lab 04	0.017	nv	nv	nv	nv	nv	nv
Lab 07	0.001	0.003	0.0005	0.0004	0.006	0.001	0.0025
Lab 08	0.0035	0.0028	0.00016	0.0014	0.00031	0.00029	0.0035
Lab 12	0.01	0.01	0.005	0.005	0.005	0.005	0.01
Lab 13	0.003	0.003	0.003	0.006	0.002	0.002	0.009
Lab 15	0.000902	0.000599	0.000815	0.000441	0.001407	0.00129	0.005484
Lab 19	0.05	nv	nv	0.01	nv	0.005	nv
Lab 21	0.0167	0.00267	0.00067	0.001	0.001	0.00067	0.00167
Lab 22	0.1	0.5	0.005	0.005	0.005	0.02	0.2
Lab 23	0.00738	0.00465	0.000495	0.000249	0.00345	0.00525	0.00655
Lab 26	0.005	0.0031	0.0004	0.0011	0.0003	0.0007	0.0024

'nv' indicates that no value was submitted for this element

Table 25: LOQ values submitted for ICP-OES.

Lab Code	Al [mg L^{-1}]	As [mg L^{-1}]	Cd [mg L^{-1}]	Cr [mg L^{-1}]	Co [mg L^{-1}]	Ni [mg L^{-1}]	Pb [mg L^{-1}]
Lab 01	0.19	nv	0.046	0.055	0.031	0.028	0.035
Lab 02	0.5	0.01	0.01	0.01	0.01	0.01	0.01
Lab 04	0.055	nv	nv	nv	nv	nv	nv
Lab 07	0.004	0.011	0.002	0.0014	0.021	0.003	0.0085
Lab 08	0.0122	0.01	0.0006	0.0049	0.0011	0.00104	0.0125
Lab 12	0.10	0.5	0.050	0.01	0.01	0.01	0.5
Lab 13	0.01	0.01	0.01	0.02	0.005	0.007	0.03
Lab 15	0.003307	0.002229	0.003001	0.001655	0.005053	0.004652	0.021782
Lab 19	0.1	nv	nv	0.02	nv	0.01	nv
Lab 21	0.05	0.008	0.002	0.003	0.003	0.002	0.005
Lab 23	0.0246	0.0155	0.00165	0.00083	0.0115	0.0175	0.0131
Lab 26	0.015	0.0092	0.0013	0.004	0.0012	0.0024	0.0072

'nv' indicates that no value was submitted for this element

6.4.2 Measurement parameters used for ICP-MS and ICP-OES analyses

The measurement parameters of the ICP-MS and ICP-OES methods of the participated laboratories are listed in detail in Table 26 and Table 27.

Table 26: ISTDs and measured isotopes for ICP-MS. Note: Some laboratories have submitted incomplete data, e.g. an element without an atomic mass or an atomic mass without an assignment to an element.

	Al		As		Cd		Cr		Co		Ni		Pb	
Lab Code	**ISTD**	**Isotope**	**ISTD**	**Isotope**	**ISTD**	**Isotope**	**ISTD**	**Isotope**	**ISTD**	**Isotope**	**ISTD**	**Isotope**	**ISTD**	**Isotope**
Lab 01	^{45}Sc	^{27}Al	^{89}Y	^{75}As	^{103}Rh	^{114}Cd	^{45}Sc	^{52}Cr	^{45}Sc	^{59}Co	^{45}Sc	^{60}Ni	^{187}Re	^{206}Pb, ^{207}Pb, ^{208}Pb
Lab 02	Rh	^{27}Al	Rh	^{75}As	Rh	^{111}Cd	Rh	^{52}Cr	Rh	^{59}Co	Rh	^{60}Ni	Re	^{208}Pb
Lab 03	103	^{27}Al	103	^{75}As	103	^{111}Cd	103	^{52}Cr	103	^{59}Co	103	^{60}Ni	103	^{206}Pb+^{207}Pb+^{208}Pb in ^{208}Pb
Lab 04	Sc	^{27}Al	In	^{75}As	In	^{111}Cd	Sc	^{52}Cr	Sc	^{59}Co	Sc	^{60}Ni	In	^{208}Pb
Lab 06	Rh	^{27}Al	Ir	^{75}As	Ir	^{114}Cd	Rh	^{52}Cr	Rh	^{59}Co	Rh	^{60}Ni	Rh	^{208}Pb
Lab 07	Sc	^{27}Al	Ge	91	Rh	^{111}Cd	Sc	^{52}Cr	Sc	^{59}Co	Ge	^{60}Ni	Lu	^{208}Pb
Lab 08	Rh	^{27}Al	Rh	^{75}As	Rh	^{114}Cd	Rh	^{52}Cr	Rh	^{59}Co	Rh	^{60}Ni	Rh	^{206}Pb+^{207}Pb+^{208}Pb
Lab 09	^{71}Ga	^{27}Al	^{103}Rh	^{75}As	^{103}Rh	^{111}Cd	^{71}Ga	^{52}Cr	^{103}Rh	^{59}Co	^{103}Rh	^{60}Ni	^{175}Lu	^{208}Pb
Lab 10	Ge	^{27}Al	Ge	^{75}As	In	^{111}Cd	Ge	^{52}Cr	Ge	^{59}Co	Ge	^{60}Ni	Re	208
Lab 11	Rh	^{27}Al	Rh	^{75}As	Rh	^{111}Cd	Rh	^{53}Cr	Rh	^{59}Co	Rh	^{60}Ni	Re	^{206}Pb+^{207}Pb+^{208}Pb
Lab 12	^{103}Rh	nv	nv	nv	nv	nv	nv	nv	nv	nv	nv	nv	nv	nv
Lab 14	^{103}Rh	^{27}Al	^{103}Rh	^{75}As	^{103}Rh	^{111}Cd	^{103}Rh	^{52}Cr	^{103}Rh	^{59}Co	^{103}Rh	^{60}Ni	^{209}Bi	^{206}Pb+^{207}Pb+^{208}Pb
Lab 16	Rh	^{27}Al	Rh	^{75}As	Rh	^{111}Cd, ^{114}Cd	Rh	^{52}Cr, ^{53}Cr	Rh	^{59}Co	Rh	^{60}Ni, ^{62}Ni	Rh	^{206}Pb+^{207}Pb+^{208}Pb
Lab 17	^{89}Y	^{27}Al	^{89}Y	^{75}As	^{115}In	^{111}Cd	^{89}Y	^{52}Cr	^{89}Y	^{59}Co	^{89}Y	^{60}Ni	^{185}Re	^{208}Pb
Lab 18	^{89}Y	^{27}Al	^{89}Y	^{75}As	^{89}Y	^{111}Cd	^{89}Y	^{52}Cr	^{89}Y	^{59}Co	^{89}Y	^{60}Ni	^{89}Y	^{208}Pb
Lab 19	Rh	^{27}Al	Ir	91	Rh	^{114}Cd	Rh	^{52}Cr	Rh	^{59}Co	Sc	^{58}Ni	Re	^{208}Pb
Lab 20	103	^{27}Al	103	^{75}As	103	^{111}Cd	103	^{52}Cr	103	^{59}Co	103	^{60}Ni	103	^{208}Pb
Lab 21	^{103}Rh	^{27}Al	^{103}Rh	^{75}As	^{103}Rh	^{111}Cd	^{72}Ge	^{52}Cr	^{72}Ge	^{59}Co	^{72}Ge	^{60}Ni	^{185}Re	^{208}Pb
Lab 23	In	^{27}Al	In	^{75}As	In	^{111}Cd	In	^{52}Cr	In	^{59}Co	In	^{62}Ni	In	^{206}Pb
Lab 24	In	^{27}Al	In	^{75}As	In	^{111}Cd	In	^{52}Cr	In	^{59}Co	In	^{60}Ni	Re	^{208}Pb
Lab 25	Sc	^{27}Al	Ge	^{75}As	Rh	^{111}Cd	Sc	^{52}Cr	Rh	^{59}Co	Sc	^{60}Ni	Rh	^{206}Pb
Lab 26	Sc	^{27}Al	Rh	^{75}As	Lu	^{111}Cd	Lu	^{52}Cr	Rh	^{59}Co	Rh	^{60}Ni	Lu	^{208}Pb
Lab 27	^{45}Sc	^{27}Al	^{72}Ge	^{75}As	^{72}Ge	^{111}Cd	^{45}Sc	^{52}Cr	^{72}Ge	^{59}Co	^{72}Ge	^{60}Ni	^{159}Tb	^{208}Pb
Lab 28	^{103}Rh	^{27}Al	^{103}Rh	^{75}As	^{175}Lu	11	^{103}Rh	^{52}Cr	^{103}Rh	^{59}Co	^{103}Rh	^{60}Ni	^{175}Lu	^{208}Pb

'nv' indicates that no value was submitted for this element

Table 27: ISTDs, measured emission lines and plasma configurations for ICP-OES

Element	Parameter	Lab Code													
		Lab 01	**Lab 02**	**Lab 07**	**Lab 08**	**Lab 12**	**Lab 13**	**Lab 15**	**Lab 19**	**Lab 21**	**Lab 22**	**Lab 23**	**Lab 26**	**Lab 28**	**Lab 29**
Al	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	167.019	167.079	396.152	237	396	396.153	396.153	396.153	167.079	396.153	360.074	167.019	396.152	167
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	radial	axial	axial	axial	axial
As	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	188.98	189.042	188.98	189	188	193.696	228.812	188.979	189.042	188.979	360.074	188.980	-	189.042
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	-	axial
Cd	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	214.439	228.802	214.439	214	214	214.44	214.440	228.802	228.802	214.440	360.074	214.439	214.441	226.502
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	axial	axial
Cr	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	267.716	283.563	267.716	267	267	283.563	205.560	267.716	267.716	205.560	360.074	267.716	205.552	267.716
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	axial	axial
Co	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	228.615	228.616	238.892	228	228	238.892	228.616	228.616	228.616	228.616	360.074	228.615	228.615	230.786
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	axial	axial
Ni	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	231.604	221.647	216.555	216	231	221.648	221.648	231.604	221.647	231.604	360.074	231.604	221.648	221.647
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	axial	axial
Pb	ISTD	-	-	-	-	Sc	Y	Sc	-	-	Y	Y	Lu	-	Y
	Measured emission line [nm]	220.353	220.353	220.353	220	220	220.353	220.353	220.353	220.353	220.353	360.074	220.353	220.353	220.353
	Plasma conf. (axial/radial)	axial	radial	axial	axial	radial	axial	axial	axial	axial	axial	axial	axial	axial	axial

6.4.3 Sample preparation and analysis

The following information was extracted from the questionnaire.

Nine laboratories subtracted process blank values from their results, whereas 19 laboratories did not subtract process blank values.

Neither of the laboratories applied any special treatment to the provided solutions.

In 25 of 28 laboratories, samples were diluted prior to analysis using different dilution factors depending on the analytical technique, element and sample.

Eight laboratories reported problems with the analysis. Four of them described problems due to too low concentrations of the elements in the provided solutions.

Six laboratories added components such as hydrochloric acid or ethanol to the solutions to minimize matrix effects (HCl in four laboratories and ethanol in one laboratory). Citric and acetic acid were added by one laboratory and 2-propanol was added by two laboratories.

Two of 28 laboratories weighted their calibration lines with a factor of 1/x.

Seven laboratories gave further comments on deviations from the suggested method, for instance that the calibration range was enlarged, or information on the acidification of the solutions were given. One laboratory has reported that Solution 4 was diluted in 2% nitric acid instead of perspiration simulant. Therefore, the results from this laboratory were not included in the evaluation of Ni in Solution 4.

7 Summary and conclusions

The primary objective of this MES was to evaluate the performance of two new drafts of methods for the ASU for the determination of Al, As, Cd, Co, Cr, Ni and Pb in 3% acetic acid (*w*/*v*), artificial tab water, 0.5% citric acid (*w*/*v*) as well as Ni in perspiration simulant by ICP-MS and/or ICP-OES.

In total, 24 laboratories submitted results for the ICP-MS method and 14 for the ICP-OES method. After removal of statistical outliers, 20 to 24 results were available for evaluation of the ICP-MS method and 6 to 14 results were available for the ICP-OES method, depending on the element and solution. However, due to high precision of the data, values differing by only small amounts from the assigned value were sometimes defined as outliers although they still correspond to acceptable *z* scores.

The evaluation was performed in terms of relative interlaboratory repeatability (s_r) and reproducibility (s_R) standard deviations. The calculated s_R values for both methods and for all elements and solutions except for Pb in 3% acetic acid determined by ICP-OES were lower than the corresponding predicted relative reproducibility standard deviations according to Horwitz/Thompson. Relative s_r and s_R values for ICP-MS were below 10.5% and 16.6%, for most elements below 6.4% and 7.8%. Relative s_r and s_R values for ICP-OES were below 14.6% and 22.6%, for most elements below 9.6% and 9.2%.

For the ICP-MS method no laboratories reported that the concentrations of the elements were below their respective LODs or LOQs.

No laboratories reported that the concentrations of Al and Ni were below their respective LODs/LOQs for the ICP-OES method. However, the vast majority of laboratories reported that the concentrations of As in Solutions 1–3 analyzed by the ICP-OES method were below their LOD/LOQ. Therefore, it can be assumed that ICP-OES is an inappropriate analytical technique for the determination of As at concentrations close to the reference values that need to be measured to verify compliance with legislation. Some laboratories reported that the concentrations of Pb (31–54%), Cd (23–31%), Co (8%, one lab in all solutions), and Cr (0–8%, one lab in 3% HAc) were below the laboratories' LOD/LOQ. The majority of the ICP-MS results were acceptable in terms of *z* scores for all elements and solutions. Particularly good performance was demonstrated for the analysis of Co with acceptable *z* scores for all laboratories and for all of the simulant solutions. For the analysis of Al, Cd, Cr, Ni, and Pb, laboratories received two or fewer unacceptable or questionable results per solution (<10% of results). Two to four unacceptable or questionable results per solution (9–20%) were received for the analysis of As.

The majority of the *z* scores for the ICP-OES results were acceptable. The *z* scores for Al, Co, Cr, and Ni, were acceptable for all of the simulant solutions. All *z* scores for Cd were acceptable (89–100%) except for one unacceptable *z* score in 3% acetic acid. For analysis of Pb in ATW and in 0.5% citric acid, all *z* scores were acceptable (83–88%) except for one questionable *z* score per solution. For the analysis of Pb in 3% acetic acid, one *z* score was unacceptable and two were questionable (67% of acceptable results).

In general, the ICP-MS method demonstrated a high interlaboratory reproducibility and repeatability in all solutions for all examined elements and can therefore be recommended

for the determination of Al, As, Cd, Co, Cr, Ni and Pb in HAc, ATW, CA as well as for Ni in perspiration simulant.

For all the elements examined, except As, high reproducibility and repeatability values were achieved for all the solutions examined using the ICP-OES method. However, some laboratories reported that the concentrations of Pb, Cd, and, in a few cases, of Co and Cr were below the laboratories' LOD/LOQ.

8 Acknowledgments

The 28 laboratories listed here are kindly acknowledged for their participation in the MES. The laboratory codes were allocated randomly to the participants and do not correspond to the alphabetical order shown here.

Organization	Country
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit (OCL)	Germany
Bundesinstitut für Risikobewertung (NRL)	Germany
Bureau Veritas Consumer Products Services Germany GmbH (CL)	Germany
Chemisches und Veterinäruntersuchungsamt (CVUA) Münsterland-Emscher-Lippe (OCL)	Germany
Chemisches und Veterinäruntersuchungsamt (CVUA) Ostwestfalen-Lippe (OCL)	Germany
Chemisches und Veterinäruntersuchungsamt (CVUA) Stuttgart (OCL)	Germany
Croatian Institute of Public Health (NRL)	Croatia
Escola Superior de Biotecnologia da Universidade Católica Portuguesa (NRL)	Portugal
European Commission, Directorate-General Joint Research Centre (EURL)	Belgium
FAVV (OCL)	Belgium
Institut Kirchhoff Berlin GmbH (CL)	Germany
ISEGA Forschungs- und Untersuchungsgesellschaft mbH (CL)	Germany
Laboratoire SCL de BORDEAUX (NRL)	France
Landesamt für Gesundheit und Lebensmittelsicherheit Bayern (OCL)	Germany
Landesamt für Verbraucherschutz Saarland (OCL)	Germany
Landeslabor Schleswig-Holstein (OCL)	Germany
Landesuntersuchungsamt Rheinland-Pfalz (OCL)	Germany
Landesuntersuchungsanstalt für das Gesundheits- und Veterinärwesen Sachsen (OCL)	Germany
LMS/LSV/Gebrauchsgegenstände und Kosmetik (CL)	Germany
National Center of Food/Food Contact Materials Unit (NRL)	Spain
National Institute of Public Health (NRL)	Czech Republic
National Laboratory of Health, Environment and Food (NRL)	Slovenia
National Public Health Surveillance Laboratory (NRL)	Lithuania
Niedersächsisches Landesamt für Verbraucherschutz und Lebensmittelsicherheit (OCL)	Germany
Sciensano (NRL)	Belgium
Thüringer Landesamt für Verbraucherschutz (OCL)	Germany
TÜV Rheinland LGA Products GmbH (CL)	Germany
Zentrales Institut des Sanitätsdienstes der Bundeswehr (OCL)	Germany

9 References

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8. Metals and alloys used in food contact materials and articles: A technical guide for manufacturers and regulators, 2nd Edition, in TG CM/Res(2020)9. 2024.

9. Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin; German version EN 1811:2023. 2023.

10 List of Tables

11 Annex

11.1 Instructions

Instructions

Thank you for participating in the method evaluation study (MES) on the determination of Al, As, Cd, Cr, Co, Ni and Pb in simulation solutions (acetic acid 3% w/v, citric acid 0.5% w/v, artificial tap water (ATW)) and of Ni in a perspiration simulant using ICP-MS and/or ICP-OES.

Your parcel should contain the following items:

- solution 1 [3% AcOH]: solution of elements in acetic acid 3% w/v for the analysis using ICP-MS (ca. 25 mL) and/or using ICP-OES (ca. 50 mL)
- solution 2 [ATW]: solution of elements in artificial tap water (ca. 25 mL) for the analysis using ICP-MS and/or using ICP-OES (ca. 50 mL)
- solution 3 [0.5% CA]: solution of elements in citric acid 0.5% w/v (ca. 25 mL) for the analysis using ICP-MS and/or using ICP-OES (ca. 50 mL)

In addition, we send a Ni-containing water solution (2.6% HNO3), solution 4 [PS] (ca. 20 mL), which can be used to prepare a test solution in a perspiration simulant according to DIN EN 1811. To prepare the test solution, dissolve 1 mL of solution 4 in a freshly prepared perspiration simulant to a total volume of 50 mL.

All test solutions are already acidified with HNO3 to 2.6%!

Upon arrival of this parcel, please check whether the items are undamaged after the transport and promptly inform us if this is not the case. There is no need to send proof of delivery.

Items should be stored refrigerated before opening (start of the analyses).

Please determine the concentration of aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), nickel (Ni) and lead (Pb) in the provided solutions 1, 2, 3 and of Ni in perspiration simulant test solution with ICP-MS or/and ICP-OES according to the drafts of the § 64 LFBG working group. English and German versions of the method have been sent to you via e-mail.

Before starting the experiments, please read the Questionnaire carefully so that you can answer all questions.

Test results and the expanded uncertainty (U) should be expressed in mg/L of simulant solutions.

The deadline for submission of results is 30th of June 2024. For further information, please contact the MES coordinator (nrl-fcm@bfr.bund.de).

With kind regards,

NRL-FCM-DE Team

11.2 Stability

11.2.1 Stability assessment of Solution 1 – Elements in 3% acetic acid

Table 28: Results of the stability assessment of Solution 1. Stability was tested over a period of 38 days. The results were evaluated according to ISO 13528:2022 [2].

	Al	Cr	Co	Ni	As	Cd	Pb
$\|d_{38}\|$ [%]	0.9	0.1	0.2	1.2	0.0	1.3	0.5
σ_{pt} [%]	15	15	15	15	15	15	15
$0.3 \cdot \sigma_{pt}$ [%]	4.5	4.5	4.5	4.5	4.5	4.5	4.5
$\|d_{38}\| \leq 0.3 \cdot \sigma_{pt}$	passed	passed	passed	passed	passed	passed	passed
Assessment	stable	stable	stable	stable	stable	stable	stable

Where:

$|d_{38}|$ is the absolute percentage difference from the initial concentration at the end of the stability study

11.2.2 Stability assessment of Solution 2 – Elements in ATW

Table 29: Results of the stability assessment of Solution 2. Stability was tested over a period of 38 days. The results were evaluated according to ISO 13528:2022 [2].

	Al	Cr	Co	Ni	As	Cd	Pb
$\|d_{38}\|$ [%]	0.2	0.5	0.6	0.3	1.1	0.1	0.4
σ_{pt} [%]	15	15	15	15	15	15	15
$0.3 \cdot \sigma_{pt}$ [%]	4.5	4.5	4.5	4.5	4.5	4.5	4.5
$\|d_{38}\| \leq 0.3 \cdot \sigma_{pt}$	passed	passed	passed	passed	passed	passed	passed
Assessment	stable	stable	stable	stable	stable	stable	stable

Where:

$|d_{38}|$ is the absolute percentage difference from the initial concentration at the end of the stability study

σ_{pt} is the standard deviation for proficiency assessment

11.2.3 Stability assessment of Solution 3 – Elements in 0.5% citric acid

Table 30: Results of the stability assessment of Solution 3. Stability was tested over a period of 38 days. The results were evaluated according to ISO 13528:2022 [2].

	Al	Cr	Co	Ni	As	Cd	Pb
$\lvert d_{38} \rvert$ [%]	0.3	0.1	0.1	0.1	0.5	0.2	0.1
σ_{pt} [%]	15	15	15	15	15	15	15
$0.3 \cdot \sigma_{pt}$ [%]	4.5	4.5	4.5	4.5	4.5	4.5	4.5
$\lvert d_{38} \rvert \leq 0.3 \cdot \sigma_{pt}$	passed	passed	passed	passed	passed	passed	passed
Assessment	stable	stable	stable	stable	stable	stable	stable

Where:

$\lvert d_{38} \rvert$ is the absolute percentage difference from the initial concentration at the end of the stability study

σ_{pt} is the standard deviation for proficiency assessment

11.2.4 Stability assessment of Solution 4 – Ni containing water solution

Table 31: Results of the stability assessment of Solution 4. Stability was tested over a period of 38 days. The results were evaluated according to ISO 13528:2022 [2].

	Ni
$\lvert d_{38} \rvert$ [%]	0.1
σ_{pt} [%]	15
$0.3 \cdot \sigma_{pt}$ [%]	4.5
$\lvert d_{38} \rvert \leq 0.3 \cdot \sigma_{pt}$	passed
Assessment	stable

Where:

$\lvert d_{38} \rvert$ is the absolute percentage difference from the initial concentration at the end of the stability study

σ_{pt} is the standard deviation for proficiency assessment

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Weitere Autor/innen: Daniele Reimann
Anzahl Tabellen: 31
Anzahl Abbildungen: 0
Anzahl Seiten: 44

Institution under public law
Represented by the president Professor Dr Dr Dr h.c. Andreas Hensel
Supervisory Authority: Federal Ministry of Food and Agriculture
VAT ID No. DE 165 893 448
Responsible according to the German Press Law: Dr Suzan Fiack

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