# Certification Report

## Certified Reference Materials

## BAM-M382a

## Pure Copper

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## Summary

This report describes preparation, analysis, and certification of the copper reference material BAM-M382a.
The certified reference material (CRM) is available in the form of discs (40 mm diameter and 30 mm height). It is intended for establishing and checking the calibration of spark optical emission spectrometers for the analysis of samples of similar materials. It is also suitable for wet chemical analysis.

The following mass fractions and uncertainties have been certified:

| Element | Mass fraction [1)] in mg/kg | Uncertainty [2)] in mg/kg |
|---|---|---|
| Ag | 2.9 | 0.2 |
| Al | < 2.0 | |
| As | 0.73 | 0.12 |
| Bi | 0.75 | 0.11 |
| Cd | 0.50 | 0.05 |
| Co | 0.92 | 0.08 |
| Cr | 0.24 | 0.07 |
| Fe | 10.3 | 0.7 |
| Mg | 1.9 | 0.3 |
| Mn | 2.5 | 0.2 |
| Ni | 2.7 | 0.3 |
| Pb | 2.2 | 0.5 |
| S | 6.7 | 1.0 |
| Sb | 0.87 | 0.14 |
| Se | 0.77 | 0.07 |
| Sn | 4.7 | 0.4 |
| Te | 0.72 | 0.08 |
| Ti | 0.57 | 0.06 |
| Zn | 7.6 | 0.6 |

1) Unweighted mean value of the means of accepted sets of data (consisting of at least 4 but usually 6 single results), each set being obtained by a different laboratory and/or a different method of measurement.

2) Estimated expanded uncertainty *U* with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

The certified values are based on the results of 11 laboratories which participated in the certification interlaboratory comparison. The mass fraction of P is given for information.

## Content

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**List of abbreviations**
(if not explained elsewhere)

| | |
|---|---|
| CRM | certified reference material |
| ETAAS | electrothermal atomic absorption spectrometry |
| ICP-OES | inductively coupled plasma optical emission spectrometry |
| ICP-MS | inductively coupled plasma mass spectrometry |
| GD-MS | glow discharge mass spectrometry |
| SOES | spark optical emission spectrometry |
| $M$ | mean value |
| $n$ | number of accepted data sets |
| $s$ | standard deviation of an individual data set |
| $s_M$ | standard deviation of laboratory means |
| $s_{rel}$ | relative standard deviation |
| $\bar{s}_i$ | square root of mean of variances of data sets under repeatability conditions |
| $M_i$ | single result |
| I | ICP-OES (Tables 2 – 21) |
| IMS | ICP-MS (Tables 2 – 21) |
| EA | ETAAS (Tables 2 – 21) |
| V | Combustion/infrared absorption (Tables 2 – 21) |
| GD | GD-MS (Tables 2 – 21) |

## 1. Introduction

In the metal-producing and metal-processing industry mainly spark optical emission spectrometry (SOES) and X-ray fluorescence spectrometry (XRF) are used for reception inspection of raw materials, e.g. scrap, for quality control of end products and production control. These time-saving analytical techniques require suitable reference materials for calibration and recalibration.

The certified reference material BAM-M382a is based on pure copper. It replaces the out of stock CRM BAM-M382. Certification of BAM-M382a was carried out in cooperation with the working group „Copper" of the Committee of Chemists within the Society of Metallurgists und Miners (GDMB). The needs were defined by this working group, since the members are potential users of the prepared CRM. Participating laboratories were recruited from this group. Since all of them are highly experienced with copper analysis and had participated in earlier inter-laboratory comparisons, there was no preceding round for qualification necessary.

Certification of reference material BAM-M382a was carried out on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

## 2. Companies/laboratories involved

<u>Manufacturing of the material</u>

- Wieland-Werke AG, Vöhringen, Germany

<u>Test for homogeneity</u>

- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
- Participating laboratories

<u>Participants in the certification inter-laboratory comparison</u>

- Alfred H Knight International, Prescot, Knowsley, United Kingdom
- Aurubis AG, Hamburg, Germany
- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
- Diehl Metall Stiftung & Co KG, Röthenbach, Germany
- Forschungsinstitut Edelmetalle + Metallchemie, Schwäbisch Gmünd, Germany
- Heimerle + Meule GmbH, Pforzheim, Germany
- Inspectorate International Limited, Witham, United Kingdom
- Institut Glörfeld, Willich, Germany
- KM Europa Metal AG, Osnabrück, Germany
- KME Mansfeld GmbH, Hettstedt, Germany
- Montanwerke Brixlegg, Brixlegg, Austria

<u>Statistical evaluation of the data</u>

- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

## 3. Candidate material

The candidate material foreseen for CRM BAM-M382a was cast by Wieland-Werke AG, Vöhringen starting with pure copper (Aurubis AG, Hamburg) which was doped with the desired impurities. Starting from the melt a total of 4 billets were cast. These were examined for homogeneity using FOES. Subsequently, the billets were pressed into 4 bars. Each extrusion bar was then drawn into two rods, each with a length of 3 m and a diameter of 40 mm. These rods were delivered to BAM and then cut into 24 segments of approx. 960 mm length, see Figure 1. Discs taken between these 1 m rods were taken for analysis.

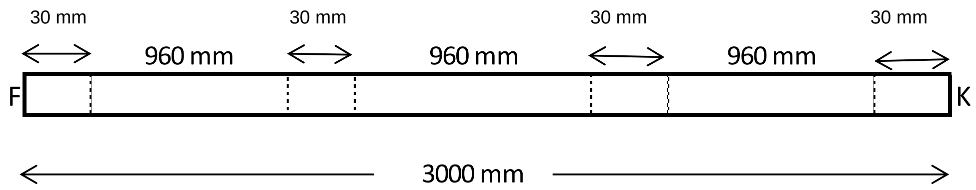



Figure 1: Cutting plan of pure copper reference material BAM-M382a

About 750 discs of BAM-M382a with a diameter of approx. 40 mm and 30 mm height were obtained from the total batch.

## 4. Homogeneity testing

BAM-M382a was produced together with BAM-M386a, BAM-M383d and BAM-M384c. The contents of the impurities in BAM-M382a are quite low. In case of the spark emission spectrometer of BAM, the contents for some elements were too low to be determined. Therefore, a detailed homogeneity test was not performed. Data from the homogeneity test of BAM-M386a was used instead. This procedure was already performed when BAM-M382 was certified in 2006. Inhomogeneity contributions related to axial inhomogeneity were estimated between 1 and 4 % rel. Inhomogeneity contributions related to radial inhomogeneity were estimated to 2 % rel. (see Figure 2). For some elements with higher content (Ag, Fe, Mg, Mn, Ni, Pb, S, Sn, and Zn) data from the accompanying spark emission round robin test was used to calculate the inhomogeneity contribution to the total uncertainty. the number of sparks in this round robin was nine (outer circle: 4 sparks, inner circle: 4 sparks; centre: 1 spark). To calculate the necessary data an unbalanced ANOVA was carried out considering that the number of single measurements is different for the centre, the inner and the outer circle. For technical reasons, at r_0 (centre) only one measurement is possible. An ANOVA requires a minimum of two measurements per factor value. Thus, the value for r_0 should be replaced by a dummy. This dummy is defined as follows:

The two values replacing the one measured have a mean equal to the value measured, and a standard deviation equal to the average within-variation. This resembles the situation where one could take two independent measurements at the same place, with values deviating by the average standard deviation (non-destructive testing method). A first guess for the average standard deviation may be calculated from the data for r_in (inner circle) and r_out (outer circle). As results from these calculations an inhomogeneity component for the radius of the disc is obtained. From these values, a combined inhomogeneity component is calculated. This component is compared with the within standard deviation calculated from the ANOVA. The higher component is used for the uncertainty calculation.

Annex 1 shows the results of the calculations for Ag, Fe, Mg, Mn, Ni, Pb, S, Sn, and Zn.

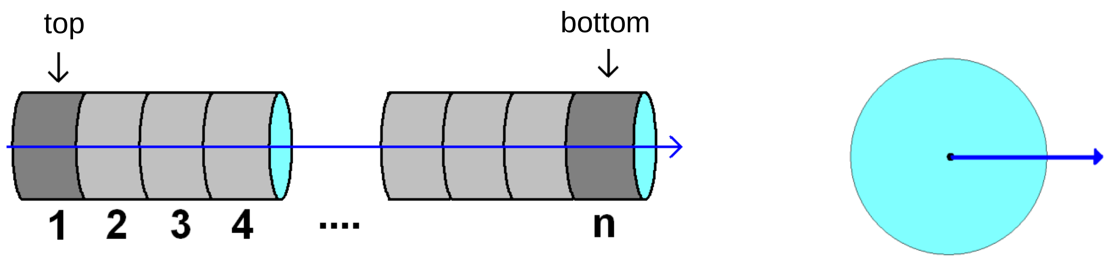



Fig. 2: Axial and radial composition gradient

## 5. Characterisation study

### 5.1 Analytical procedures

Eleven laboratories participated in the certification inter-laboratory comparison. For some elements part of the laboratories used more than one analytical method reporting more than one data set.
The laboratories were asked to analyse six subsamples. They were free to choose any suitable analytical method for their determinations. Table 1 shows the analytical methods used by the participating laboratories.
For all analytical procedures where a calibration was necessary this was performed using liquid standard solutions. All participating laboratories were asked to use only standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

Table 1: Analytical procedures used by the participating laboratories

| Lab-No. | Element. | Sample mass | Sample pretreatment | Analytical method |
|---|---|---|---|---|
| 1* | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Ti, Zn | 10 mg | Dissolution with $HNO_3$ | ICP-MS calibration with commercial solutions |
| 2 | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Zn | 1 g | Dissolution with $HCl/HNO_3$ (1 + 1) | ICP-MS, calibration with commercial solution (Spex Certi Prep, traceable to NIST) |
| | P | 1 g | Dissolution with $HCl/HNO_3$ (1 + 1) | ICP-OES, matrix matched calibration with commercial solutions (Spex Certi Prep, traceable to NIST) |
| 3* | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn | 2 g | Dissolution with $HCl/HNO_3/H_2O$ (2:1:1) | ICP-OES, matrix matched calibration with commercial solutions (Roth) |
| 4 | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, Zn | 1 g | Dissolution with $HNO_3/HCl$ | ICP-OES, calibration with commercial standard solutions (Bernd Kraft) |
| 5* | Al, As, P, Si | 1 g | Dissolution with $HNO_3$ | ICP-OES, matrix matched calibration with commercial standard solutions |
| | Ag, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Zn | 1 g | Dissolution with $HNO_3$ | ICP-MS, matrix matched calibration with commercial solutions |
| 6 | Ag, As, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, S, Sb, Sn, Ti, Zn | 1 g | Dissolution with $HNO_3$ | ICP-OES, matrix matched calibration with commercial standard solutions (Alfa Aesar) |

*Laboratory accredited acc. to ISO/IEC 17025

Table 1 (cont.): Analytical procedures used by the participating laboratories

| Lab-No. | Element. | Sample mass | Sample pretreatment | Analytical method |
|---|---|---|---|---|
| 7 | Fe, Zn | 1 g | Dissolution with $HNO_3$/HCl | ICP-OES, matrix matched calibration with standard solutions prepared from pure metals |
| | Al, As, Bi, Cd, Co, Cr, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te | 1 g | Dissolution with $HNO_3$/HCl | ETAAS, matrix matched calibration with standard solutions prepared from pure metals |
| | Ag | | Dissolution with $HNO_3$ | ICP-OES, matrix matched calibration with standard solution prepared from pure silver |
| | S | 2 g | | Combustion/iodometric titration, calibration with $Na_2S_2O_3$ |
| 8 | Ag, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, Sb, Se, Sn, Te, Ti, Zn | 0.5 g | Dissolution with $HNO_3$/HCl | ICP-MS, matrix matched calibration with commercial solutions (Bernd Kraft) |
| | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, Zn | | | GDMS, calibration with doped pressed powder pellets |
| 9* | As, Bi, Co, Cr | 1 g | Dissolution with $HNO_3$ | ETAAS (according to DIN 14935), matrix matched calibration with commercial standard solutions (Merck) |
| 9* | S | 1 g | | Combustion/IR, Calibration with $K_2SO_4$ |
| 9 | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn | | | GDMS, calibration with ERM-EB383, ERM-EB384, BAM-M384b, BAM-M385a, ERM-EB386, ERM-EB074a and ERM-EB075a |
| 10 | As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Sn, Ti | 1 g | Dissolution with $HNO_3$/HF/$H_3BO_3$ | ICP-OES, matrix matched calibration with commercial mono-element solution (Merck Certipur) |
| 11 | Ag, Al, As, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Se, Sn, Ti, Zn | 1 g | Dissolution with $HNO_3$ | ICP-OES, matrix matched calibration with commercial mono-element solution (Roth) |
| 12 | Ag, Al, As, Bi, Cd, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Sb, Se, Si, Sn, Te, Ti, Zn | 0.5 g | Dissolution with $HNO_3$/HF | ICP-MS, matrix matched calibration with commercial mono-element solutions (Merck) |

*Laboratory accredited acc. to ISO/IEC 17025

## 5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 2 to 21. These tables show the single results ($M_i$) of each laboratory, the respective laboratories' mean values (M), absolute and relative intra-laboratory standard deviation ($s$ and $s_{rel}$, respectively), the standard deviation of laboratory means ($s_M$), and in addition the square root of mean of variances of data sets under repeatability conditions ($\overline{s_i}$), where $n$ is the number of accepted data sets. The continuous line marks the certified value (mean of the laboratories' means), the broken lines mark the standard deviation, calculated from the laboratories' means.
In the related figures for each laboratory its mean value and single standard deviation is given. Outliers which have been excluded after discussion with the respective laboratories are highlighted in yellow.

Table 2: Results for Ag in BAM-M382a

| Lab./Meth. | 6/I | 4/I | 3/I | 5/IMS | 8/GD | 12/IMS | 1/IMS | 11/I | 2/IMS | 9/GD | 8/IMS | 7/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 2.67 | 2.8 | 3.04 | 2.9 | 2.8 | 3.10 | 2.97 | 2.91 | 3.09 | 3.35 | 4.3 | 4.41 | | *n* |
| | 2.58 | 2.6 | 2.94 | 3.0 | 2.9 | 3.00 | 2.98 | 3.17 | 3.05 | 3.38 | 4.4 | 4.38 | | 10 |
| | 2.31 | 2.7 | 2.92 | 2.9 | 2.9 | 2.99 | 2.98 | 3.07 | 3.12 | 3.36 | 4.0 | 4.50 | | |
| | 2.54 | 2.8 | 2.90 | 3.0 | 3.1 | 3.02 | 3.00 | 2.98 | 3.05 | 3.39 | 4.0 | 4.28 | | |
| | 2.10 | | 2.90 | 3.0 | 3.1 | 2.98 | 3.09 | 3.08 | 3.25 | 3.23 | 4.0 | 4.21 | | |
| | 1.96 | | 2.86 | 3.0 | 3.2 | 2.96 | 3.05 | 3.00 | 3.10 | 3.31 | | 4.46 | | |
| | | | | | | | | | | 3.24 | | | | |
| | | | | | | | | | | 3.30 | | | | |
| **$M$ [mg/kg]** | **2.36** | **2.73** | **2.93** | **2.98** | **3.00** | **3.01** | **3.01** | **3.04** | **3.11** | **3.32** | **4.13** | **4.37** | | **2.95** |
| $s$ [mg/kg] | 0.29 | 0.10 | 0.06 | 0.04 | 0.16 | 0.05 | 0.05 | 0.09 | 0.07 | 0.06 | 0.21 | 0.11 | $s_M$ [mg/kg] | 0.25 |
| | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.12 |
| $s_{rel}$ | 0.1209 | 0.0351 | 0.0210 | 0.0126 | 0.0537 | 0.0160 | 0.0159 | 0.0300 | 0.0240 | 0.0181 | 0.0515 | 0.0251 | | 0.0861 |

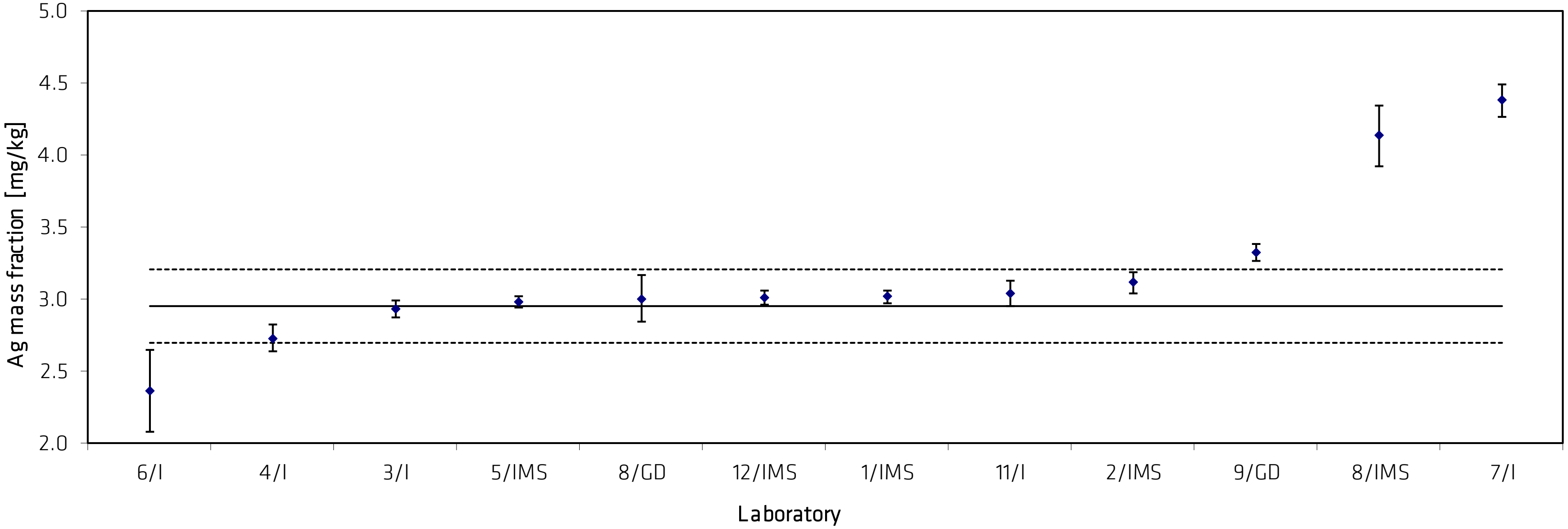
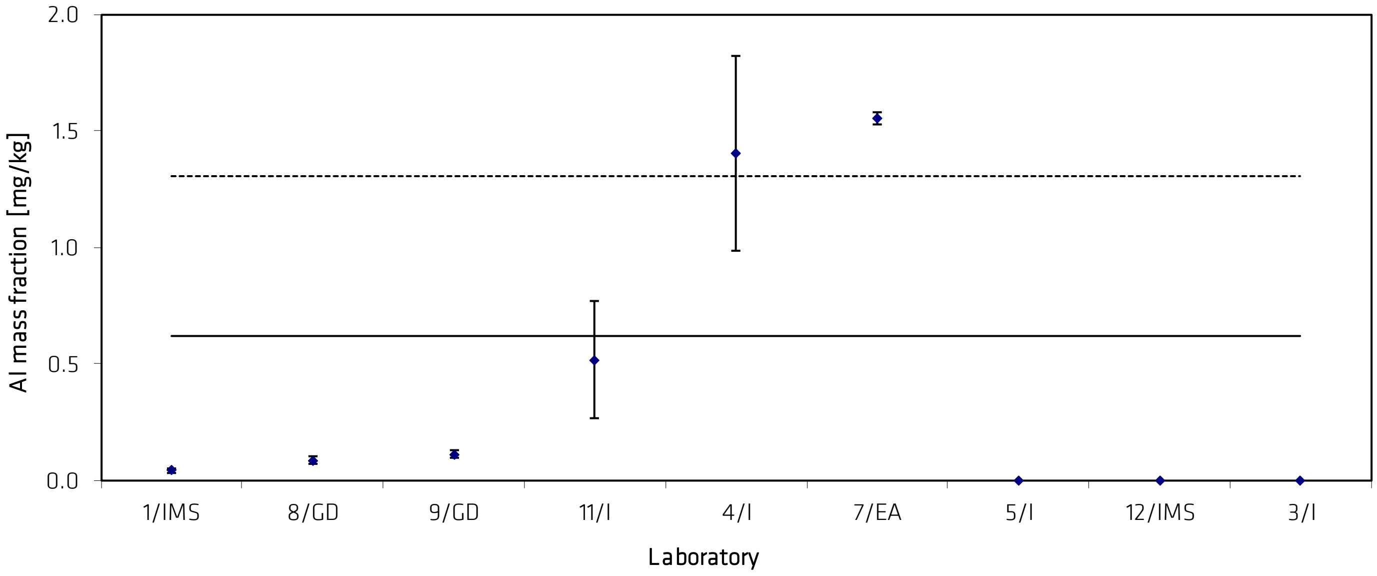


Table 3: Results for Al in BAM-M382a

| Lab./Meth. | 1/IMS | 8/GD | 9/GD | 11/I | 4/I | 7/EA | 5/I | 12/IMS | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.04 | 0.11 | 0.11 | 0.76 | 1.9 | 1.52 | <0.5 | <0.9 | <1 | | *n* |
| | 0.03 | 0.10 | 0.10 | 0.70 | 1.8 | 1.52 | <0.5 | <0.9 | <1 | | 6 |
| | 0.03 | 0.09 | 0.12 | 0.70 | 1.0 | 1.56 | <0.5 | <0.9 | <1 | | |
| | 0.05 | 0.08 | 0.11 | 0.51 | 1.1 | 1.57 | <0.5 | <0.9 | <1 | | |
| | 0.05 | 0.07 | 0.11 | 0.25 | 1.2 | 1.57 | <0.5 | <0.9 | <1 | | |
| | 0.05 | 0.06 | 0.15 | 0.18 | | 1.58 | <0.5 | <0.9 | <1 | | |
| | | | 0.09 | | | | | | | | |
| | | | 0.11 | | | | | | | | |
| **$M$ [mg/kg]** | **0.04** | **0.09** | **0.11** | **0.52** | **1.40** | **1.55** | **<0.5** | **<0.9** | **<1** | | **0.62** |
| $s$ [mg/kg] | 0.01 | 0.02 | 0.02 | 0.25 | 0.42 | 0.03 | | | | $s_M$ [mg/kg] | 0.69 |
| | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.16 |
| $s_{rel}$ | 0.2360 | 0.2201 | 0.1441 | 0.4827 | 0.2988 | 0.0171 | | | | | 1.1139 |



## Table 4: Results for As in BAM-M382a

| Lab./Meth. | 10/I | 7/EA | 11/I | 8/GD | 8/IMS | 12/IMS | 2/IMS | 1/IMS | 9/GD | 6/I | 9/EA | 4/I | 3/I | 5/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.40 | 0.46 | 0.89 | 0.69 | 0.90 | 0.77 | 0.89 | 0.85 | 0.88 | 0.98 | 3.04 | <1 | <1 | <1 | | *n* |
| | 0.41 | 0.42 | 0.64 | 0.72 | 0.87 | 0.78 | 0.69 | 0.85 | 0.88 | 0.90 | 3.27 | <1 | <1 | <1 | | 10 |
| | 0.42 | 0.45 | 0.65 | 0.76 | 0.82 | 0.78 | 0.82 | 0.84 | 0.86 | 0.60 | 2.94 | <1 | <1 | 1.1 | | |
| | 0.46 | 0.41 | 0.72 | 0.67 | 0.62 | 0.77 | 0.77 | 0.86 | 0.85 | 0.85 | 3.17 | <1 | <1 | <1 | | |
| | 0.23 | 0.47 | 0.68 | 0.71 | 0.66 | 0.80 | 0.89 | 0.86 | 0.88 | 0.96 | 3.42 | <1 | <1 | 1.3 | | |
| | 0.46 | 0.49 | 0.37 | 0.70 | | 0.77 | 0.83 | 0.86 | 0.86 | 1.43 | 2.98 | <1 | <1 | 1.3 | | |
| | | | | | | | | | 0.86 | | | | | | | |
| | | | | | | | | | 0.87 | | | | | | | |
| **$M$ [mg/kg]** | **0.40** | **0.45** | **0.66** | **0.71** | **0.77** | **0.78** | **0.82** | **0.85** | **0.87** | **0.95** | **3.14** | **<1** | **<1** | **< 1.4** | | **0.73** |
| $s$ [mg/kg] | 0.09 | 0.03 | 0.17 | 0.03 | 0.13 | 0.01 | 0.08 | 0.01 | 0.01 | 0.27 | 0.19 | | | | $s_M$ [mg/kg] | 0.18 |
| | | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.12 |
| $s_{rel}$ | 0.2155 | 0.0674 | 0.2555 | 0.0432 | 0.1633 | 0.0131 | 0.0934 | 0.0096 | 0.0128 | 0.2839 | 0.0591 | | | | | 0.2476 |

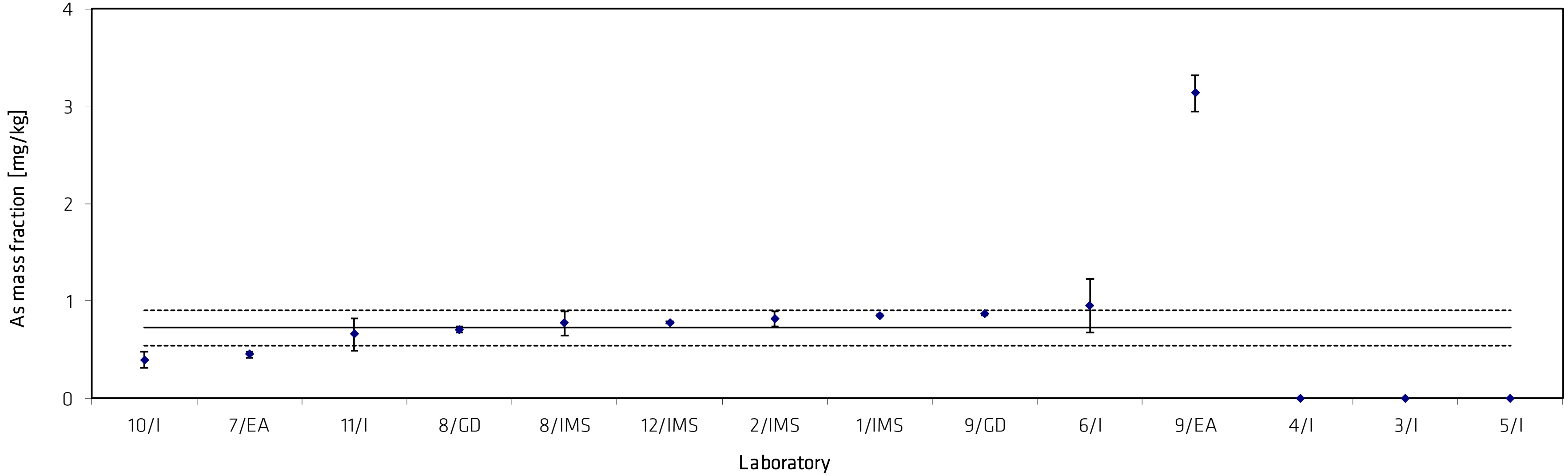


Table 5: Results for Bi in BAM-M382a

| Lab./Meth. | 8/GD | 12/IMS | 1/IMS | 2/IMS | 8/IMS | 9/GD | 10/I | 9/EA | 7/EA | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.51 | 0.65 | 0.69 | 0.70 | 0.68 | 0.76 | 0.78 | 0.99 | 1.70 | <1 | | *n* |
| | 0.49 | 0.66 | 0.68 | 0.70 | 0.72 | 0.76 | 0.80 | 0.98 | 1.76 | <1 | | 8 |
| | 0.49 | 0.66 | 0.69 | 0.73 | 0.68 | 0.79 | 1.12 | 0.87 | 1.69 | <1 | | |
| | 0.69 | 0.65 | 0.70 | 0.67 | 0.86 | 0.79 | 0.80 | 0.97 | 1.74 | <1 | | |
| | 0.64 | 0.66 | 0.70 | 0.74 | 0.71 | 0.69 | 0.94 | | 1.77 | <1 | | |
| | 0.63 | 0.64 | 0.70 | 0.68 | 0.68 | 0.74 | 1.22 | | 1.65 | <1 | | |
| | | | | | | 0.72 | | | | | | |
| | | | | | | 0.76 | | | | | | |
| **$M$ [mg/kg]** | **0.58** | **0.65** | **0.69** | **0.70** | **0.72** | **0.75** | **0.94** | **0.95** | **1.72** | **<1** | | **0.75** |
| $s$ [mg/kg] | 0.09 | 0.01 | 0.01 | 0.03 | 0.07 | 0.04 | 0.19 | 0.06 | 0.05 | | $s_M$ [mg/kg] | 0.13 |
| | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.08 |
| $s_{rel}$ | 0.1539 | 0.0108 | 0.0118 | 0.0385 | 0.0970 | 0.0466 | 0.1986 | 0.0584 | 0.0269 | | | 0.1780 |

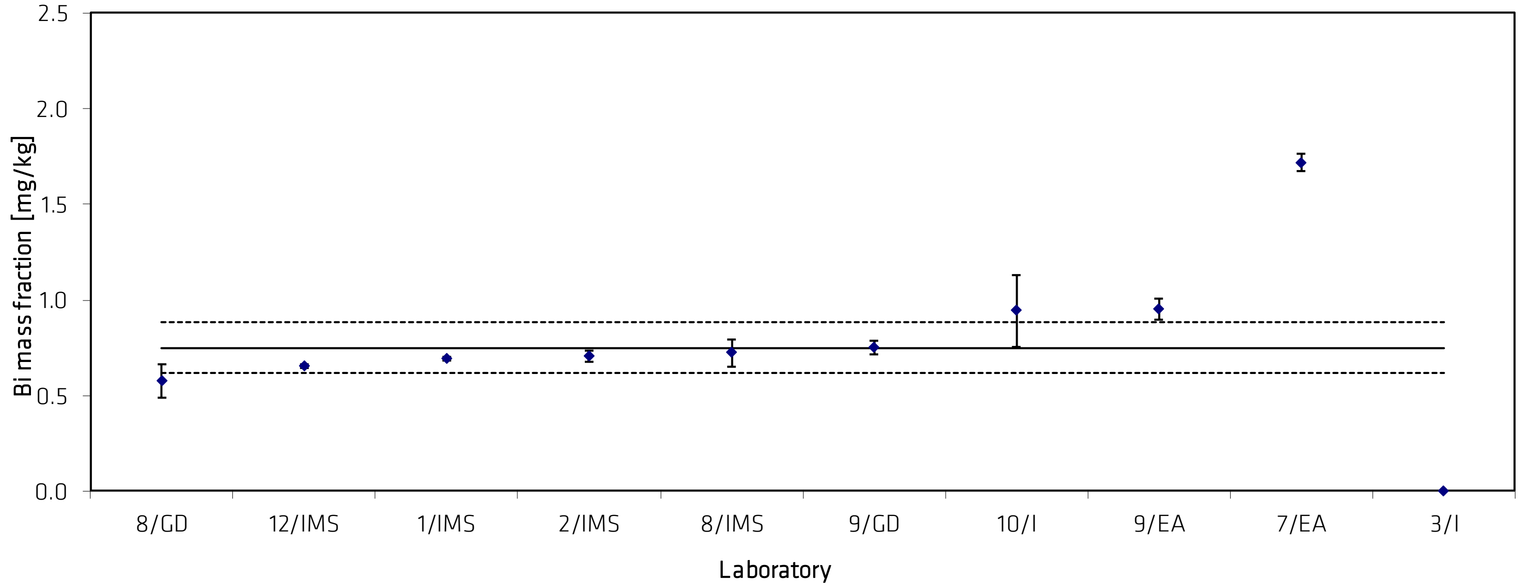
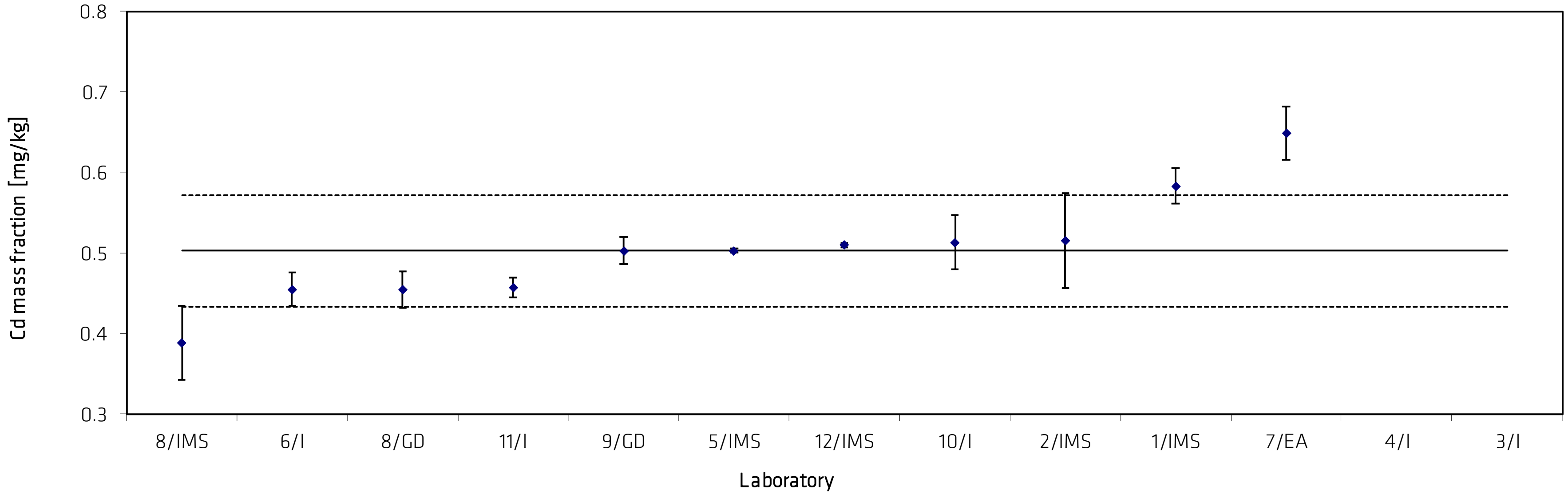


Table 6: Results for Cd in BAM-M382a

| Lab./Meth. | 8/IMS | 6/I | 8/GD | 11/I | 9/GD | 5/IMS | 12/IMS | 10/I | 2/IMS | 1/IMS | 7/EA | 4/I | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.43 | 0.43 | 0.43 | 0.46 | 0.51 | 0.50 | 0.51 | 0.54 | 0.52 | 0.59 | 0.60 | <0.5 | <1 | | *n* |
| | 0.33 | 0.44 | 0.46 | 0.45 | 0.52 | 0.50 | 0.51 | 0.51 | 0.47 | 0.60 | 0.65 | <0.5 | <1 | | 11 |
| | 0.33 | 0.47 | 0.47 | 0.45 | 0.52 | 0.50 | 0.51 | 0.55 | 0.55 | 0.56 | 0.63 | <0.5 | <1 | | |
| | 0.42 | 0.44 | 0.49 | 0.45 | 0.52 | 0.50 | 0.51 | 0.53 | 0.49 | 0.55 | 0.66 | <0.5 | <1 | | |
| | 0.42 | 0.47 | 0.44 | 0.48 | 0.48 | 0.51 | 0.51 | 0.49 | 0.62 | 0.60 | 0.65 | <0.5 | <1 | | |
| | 0.40 | 0.48 | 0.44 | 0.45 | 0.50 | 0.50 | 0.51 | 0.46 | 0.46 | 0.60 | 0.70 | <0.5 | <1 | | |
| | | | | | 0.48 | | | | | | | | | | |
| | | | | | 0.50 | | | | | | | | | | |
| ***M* [mg/kg]** | **0.39** | **0.46** | **0.46** | **0.46** | **0.50** | **0.50** | **0.51** | **0.51** | **0.52** | **0.58** | **0.65** | **<0.5** | **<1** | | **0.50** |
| *s* [mg/kg] | 0.05 | 0.02 | 0.02 | 0.01 | 0.02 | 0.00 | 0.00 | 0.03 | 0.06 | 0.02 | 0.03 | | | $s_M$ [mg/kg] | 0.07 |
| | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.03 |
| $s_{rel}$ | 0.1190 | 0.0456 | 0.0496 | 0.0265 | 0.0338 | 0.0049 | 0.0052 | 0.0660 | 0.1136 | 0.0386 | 0.0511 | | | | 0.1375 |



## Table 7: Results for Co in BAM-M382a

| Lab./Meth. | 6/I | 4/I | 11/I | 5/IMS | 2/IMS | 9/EA | 1/IMS | 8/IMS | 12/IMS | 9/GD | 8/GD | 10/I | 7/EA | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.90 | 0.6 | 0.8 | 0.86 | 0.84 | 0.91 | 0.93 | 0.94 | 0.95 | 0.98 | 1.05 | 1.19 | 2.21 | <1 | | *n* |
| | 0.69 | 0.7 | 0.7 | 0.86 | 0.83 | 0.88 | 0.94 | 0.97 | 1.02 | 0.98 | 1.01 | 0.97 | 2.05 | <1 | | 12 |
| | 0.75 | 0.7 | 0.8 | 0.86 | 0.86 | 0.92 | 0.96 | 0.97 | 0.94 | 0.93 | 1.02 | 1.30 | 2.11 | <1 | | |
| | 0.98 | 0.6 | 0.8 | 0.88 | 0.94 | 0.93 | 0.90 | 0.92 | 0.94 | 0.91 | 1.00 | 1.24 | 2.03 | <1 | | |
| | 0.66 | 1.2 | 0.8 | 0.86 | 0.90 | 0.92 | 0.95 | 0.99 | 0.96 | 1.03 | 0.91 | 1.29 | 2.25 | <1 | | |
| | 0.70 | 1.0 | 0.9 | 0.86 | 0.92 | 0.91 | 0.95 | 0.94 | 0.95 | 0.98 | 1.01 | 1.21 | 2.17 | <1 | | |
| | | | | | | | | | | 1.00 | | | | | | |
| | | | | | | | | | | 1.00 | | | | | | |
| **$M$ [mg/kg]** | **0.78** | **0.80** | **0.81** | **0.86** | **0.88** | **0.91** | **0.94** | **0.96** | **0.96** | **0.98** | **1.00** | **1.20** | **2.14** | **<1** | | **0.92** |
| $s$ [mg/kg] | 0.13 | 0.24 | 0.05 | 0.01 | 0.04 | 0.02 | 0.02 | 0.03 | 0.03 | 0.04 | 0.05 | 0.12 | 0.09 | | $s_M$ [mg/kg] | 0.11 |
| | | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.09 |
| $s_{rel}$ | 0.1664 | 0.3062 | 0.0664 | 0.0102 | 0.0509 | 0.0189 | 0.0228 | 0.0271 | 0.0347 | 0.0388 | 0.0473 | 0.1006 | 0.0413 | | | 0.1235 |

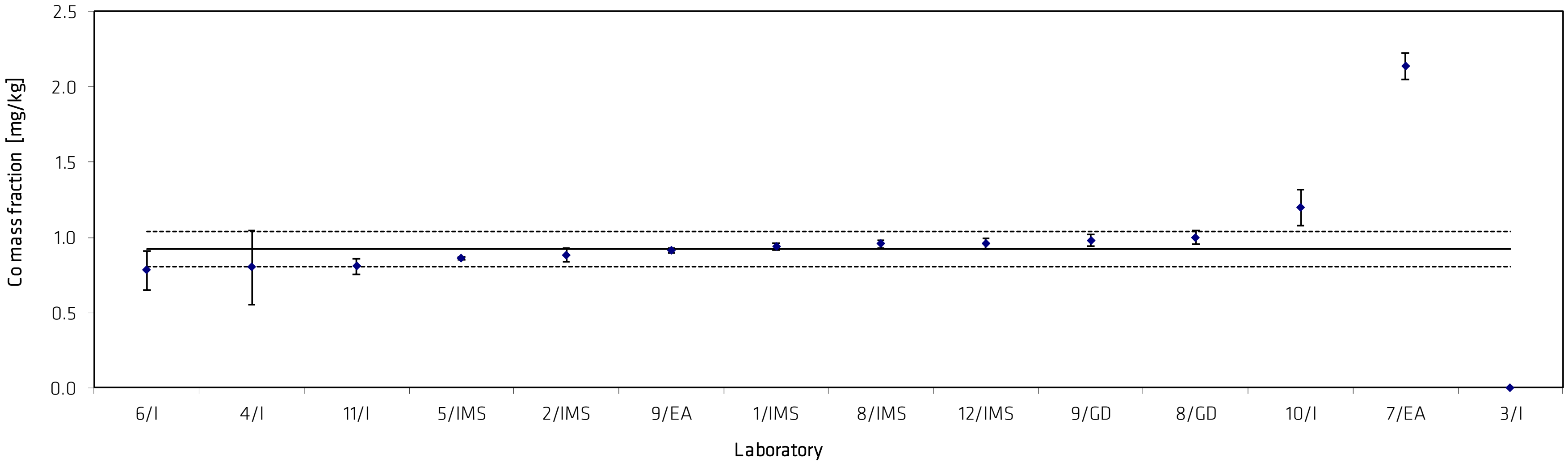
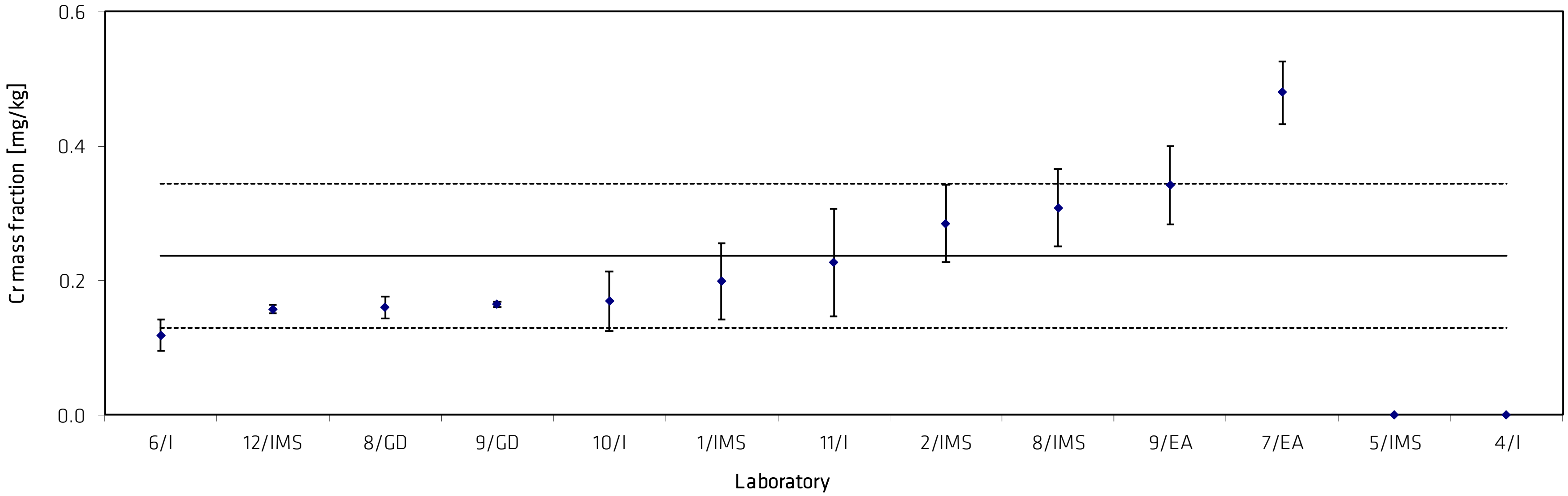


Table 8: Results for Cr in BAM-M382a

| Lab./Meth. | 6/I | 12/IMS | 8/GD | 9/GD | 10/I | 1/IMS | 11/I | 2/IMS | 8/IMS | 9/EA | 7/EA | 5/IMS | 4/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.11 | 0.16 | 0.17 | 0.16 | 0.21 | 0.15 | 0.19 | 0.21 | 0.26 | 0.42 | 0.55 | <0.3 | <0.5 | | $n$ |
| | 0.12 | 0.16 | 0.17 | 0.17 | 0.15 | 0.14 | 0.20 | 0.27 | 0.26 | 0.27 | 0.45 | <0.3 | <0.5 | | 11 |
| | 0.14 | 0.16 | 0.18 | 0.17 | 0.23 | 0.15 | 0.38 | 0.26 | 0.31 | 0.37 | 0.49 | <0.3 | <0.5 | | |
| | 0.10 | 0.16 | 0.14 | 0.16 | 0.12 | 0.25 | 0.25 | 0.36 | 0.31 | 0.29 | 0.46 | <0.3 | <0.5 | | |
| | 0.15 | 0.15 | 0.14 | 0.16 | 0.18 | 0.25 | 0.17 | 0.34 | 0.40 | 0.38 | 0.51 | <0.3 | <0.5 | | |
| | 0.09 | 0.15 | 0.16 | 0.17 | 0.13 | 0.25 | 0.17 | 0.27 | | 0.32 | 0.42 | <0.3 | <0.5 | | |
| | | | | 0.16 | | | | | | | | | | | |
| | | | | 0.16 | | | | | | | | | | | |
| **$M$ [mg/kg]** | **0.12** | **0.16** | **0.16** | **0.16** | **0.17** | **0.20** | **0.23** | **0.28** | **0.31** | **0.34** | **0.48** | **<0.3** | **<0.5** | | **0.24** |
| $s$ [mg/kg] | 0.02 | 0.01 | 0.02 | 0.00 | 0.04 | 0.06 | 0.08 | 0.06 | 0.06 | 0.06 | 0.05 | | | $s_M$ [mg/kg] | 0.11 |
| | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.05 |
| $s_{rel}$ | 0.1958 | 0.0394 | 0.1046 | 0.0235 | 0.2604 | 0.2860 | 0.3559 | 0.2025 | 0.1857 | 0.1691 | 0.0968 | | | | 0.4526 |



## Table 9: Results for Fe in BAM-M382a

| Lab./Meth. | 5/IMS | 10/I | 7/I | 12/IMS | 6/I | 3/I | 11/I | 4/I | 8/GD | 9/GD | 8/IMS | 2/IMS | 1/IMS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 8.1 | 8.88 | 9.79 | 9.88 | 10.0 | 10.3 | 9.8 | 10 | 11.5 | 11.0 | 11.3 | 11.3 | 11.1 | | *n* |
| | 7.7 | 8.67 | 9.91 | 10.09 | 10.0 | 10.0 | 10.5 | 12 | 11.1 | 10.9 | 11.1 | 11.1 | 11.5 | | 13 |
| | 8.1 | 8.47 | 9.92 | 9.98 | 9.9 | 10.3 | 11.3 | 11 | 11.1 | 10.6 | 10.3 | 10.8 | 11.0 | | |
| | 8.0 | 8.79 | 9.98 | 9.88 | 10.0 | 10.0 | 9.9 | 10 | 10.7 | 10.8 | 11.2 | 11.6 | 12.9 | | |
| | 7.9 | 8.77 | 9.79 | 10.06 | 10.2 | 9.9 | 9.8 | 10 | 10.2 | 11.1 | 11.8 | 11.7 | 13.4 | | |
| | 7.9 | 8.57 | 9.88 | 9.90 | 9.9 | 9.9 | 10.5 | 10 | 10.5 | 10.7 | | 10.6 | 13.0 | | |
| | | | | | | | | | | 10.8 | | | | | |
| | | | | | | | | | | 11.1 | | | | | |
| **$M$ [mg/kg]** | **8.0** | **8.7** | **9.9** | **10.0** | **10.0** | **10.1** | **10.3** | **10.5** | **10.9** | **10.9** | **11.1** | **11.2** | **12.1** | | **10.3** |
| $s$ [mg/kg] | 0.13 | 0.15 | 0.08 | 0.09 | 0.10 | 0.20 | 0.60 | 0.84 | 0.47 | 0.19 | 0.54 | 0.46 | 1.07 | $s_M$ [mg/kg] | 1.08 |
| | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.50 |
| $s_{rel}$ | 0.0162 | 0.0175 | 0.0077 | 0.0093 | 0.0097 | 0.0202 | 0.0583 | 0.0797 | 0.0435 | 0.0177 | 0.0486 | 0.0409 | 0.0878 | | 0.1053 |

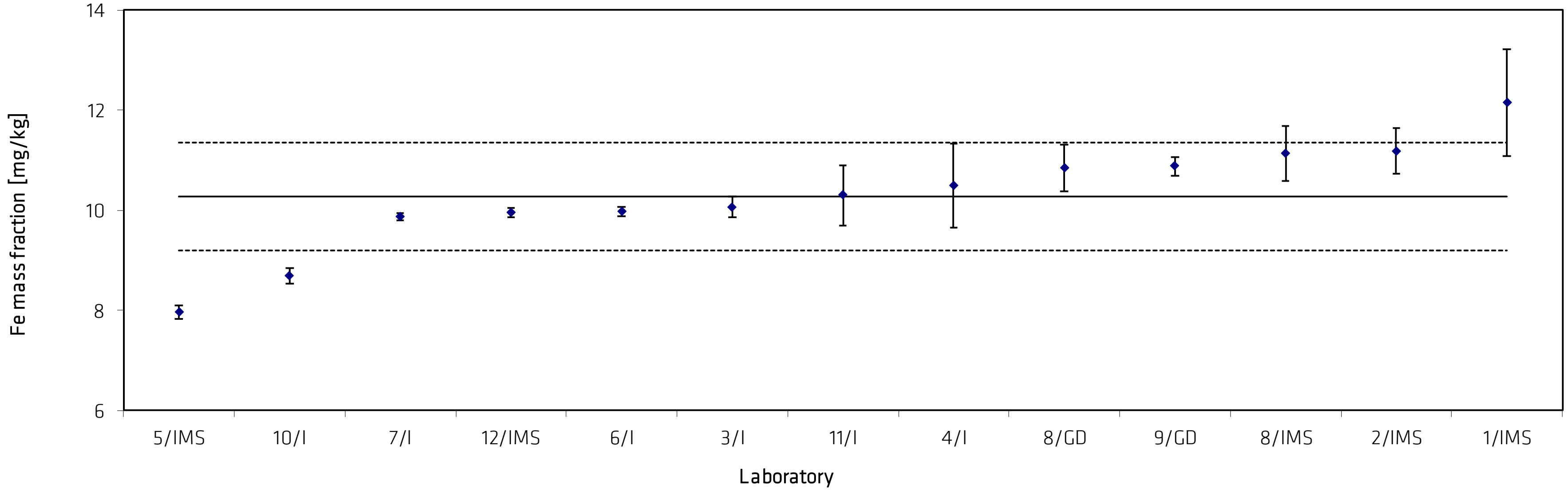


Table 10: Results for Mg in BAM-M382a

| Lab./Meth. | 10/I | 8/GD | 5/IMS | 11/I | 8/IMS | 6/I | 3/I | 12/IMS | 7/EA | 4/I | 9/GD | 1/IMS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 1.01 | 1.93 | 1.66 | 1.90 | 1.89 | 2.00 | 2.01 | 2.02 | 2.15 | 1.8 | 2.3 | 4.83 | | *n* |
| | 1.21 | 1.92 | 1.77 | 1.80 | 1.97 | 1.93 | 1.98 | 2.14 | 2.24 | 2.3 | 2.3 | 4.76 | | 11 |
| | 1.27 | 1.97 | 1.76 | 1.92 | 2.02 | 1.90 | 2.03 | 2.02 | 2.06 | 2.4 | 2.3 | 4.48 | | |
| | 1.45 | 1.24 | 1.76 | 1.84 | 2.07 | 2.01 | 1.97 | 2.08 | 2.17 | 2.2 | 2.3 | 4.84 | | |
| | 0.90 | 1.33 | 1.69 | 1.90 | 1.89 | 2.04 | 1.93 | 2.03 | 2.21 | 2.2 | 2.6 | 4.53 | | |
| | 0.88 | 1.42 | 1.69 | 2.22 | | 1.95 | 1.91 | 2.03 | 2.09 | 2.2 | 2.7 | 4.86 | | |
| | | | | | | | | | | | 2.4 | | | |
| | | | | | | | | | | | 2.4 | | | |
| **$M$ [mg/kg]** | **1.12** | **1.64** | **1.72** | **1.93** | **1.97** | **1.97** | **1.97** | **2.05** | **2.15** | **2.18** | **2.40** | **4.72** | | **1.92** |
| $s$ [mg/kg] | 0.23 | 0.34 | 0.05 | 0.15 | 0.08 | 0.05 | 0.05 | 0.05 | 0.07 | 0.20 | 0.14 | 0.17 | $s_M$ [mg/kg] | 0.34 |
| | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.16 |
| $s_{rel}$ | 0.2027 | 0.2075 | 0.0273 | 0.0772 | 0.0404 | 0.0271 | 0.0232 | 0.0235 | 0.0320 | 0.0935 | 0.0567 | 0.0356 | | 0.1760 |

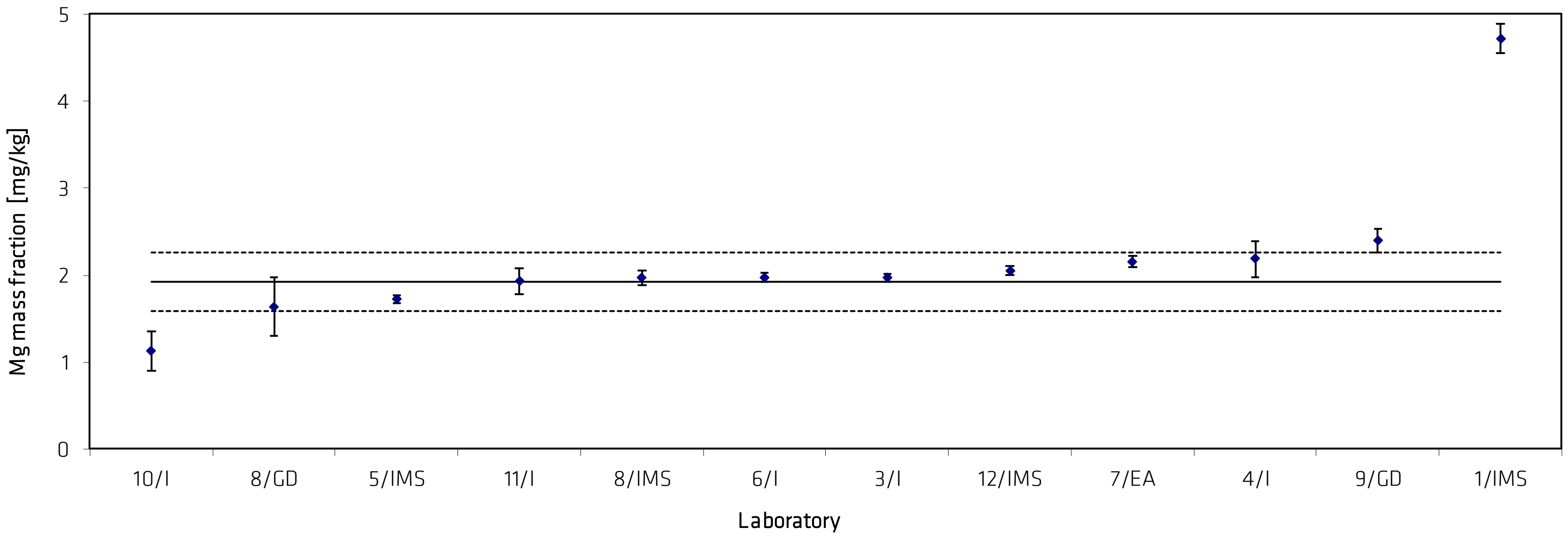


Table 11: Results for Mn in BAM-M382a

| Lab./Meth. | 7/EA | 4/I | 3/I | 5/IMS | 2/IMS | 8/IMS | 11/I | 1/IMS | 12/IMS | 10/I | 6/I | 8/GD | 9/GD | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 2.01 | 2.0 | 2.45 | 2.46 | 2.39 | 2.4 | 2.5 | 2.51 | 2.5 | 2.5 | 2.58 | 2.7 | 2.63 | | *n* |
| | 2.02 | 2.2 | 2.44 | 2.44 | 2.39 | 2.5 | 2.5 | 2.52 | 2.5 | 2.6 | 2.55 | 2.7 | 2.65 | | 11 |
| | 2.04 | 2.2 | 2.41 | 2.44 | 2.46 | 2.6 | 2.5 | 2.50 | 2.6 | 2.5 | 2.54 | 2.7 | 2.60 | | |
| | 2.05 | 2.1 | 2.41 | 2.45 | 2.43 | 2.5 | 2.5 | 2.55 | 2.4 | 2.6 | 2.56 | 2.5 | 2.65 | | |
| | 2.01 | 2.1 | 2.41 | 2.50 | 2.70 | 2.5 | 2.5 | 2.54 | 2.5 | 2.5 | 2.55 | 2.4 | 2.61 | | |
| | 2.01 | 2.1 | 2.37 | 2.47 | 2.45 | | 2.6 | 2.54 | 2.5 | 2.6 | 2.53 | 2.5 | 2.62 | | |
| | | | | | | | | | | | | | 2.62 | | |
| | | | | | | | | | | | | | 2.60 | | |
| **$M$ [mg/kg]** | **2.02** | **2.12** | **2.42** | **2.46** | **2.47** | **2.49** | **2.52** | **2.53** | **2.53** | **2.55** | **2.55** | **2.58** | **2.62** | | **2.52** |
| $s$ [mg/kg] | 0.02 | 0.08 | 0.03 | 0.02 | 0.12 | 0.07 | 0.05 | 0.02 | 0.06 | 0.05 | 0.02 | 0.13 | 0.02 | $s_M$ [mg/kg] | 0.06 |
| | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.07 |
| $s_{rel}$ | 0.0087 | 0.0356 | 0.0116 | 0.0087 | 0.0468 | 0.0299 | 0.0212 | 0.0078 | 0.0220 | 0.0185 | 0.0068 | 0.0512 | 0.0076 | | 0.0230 |

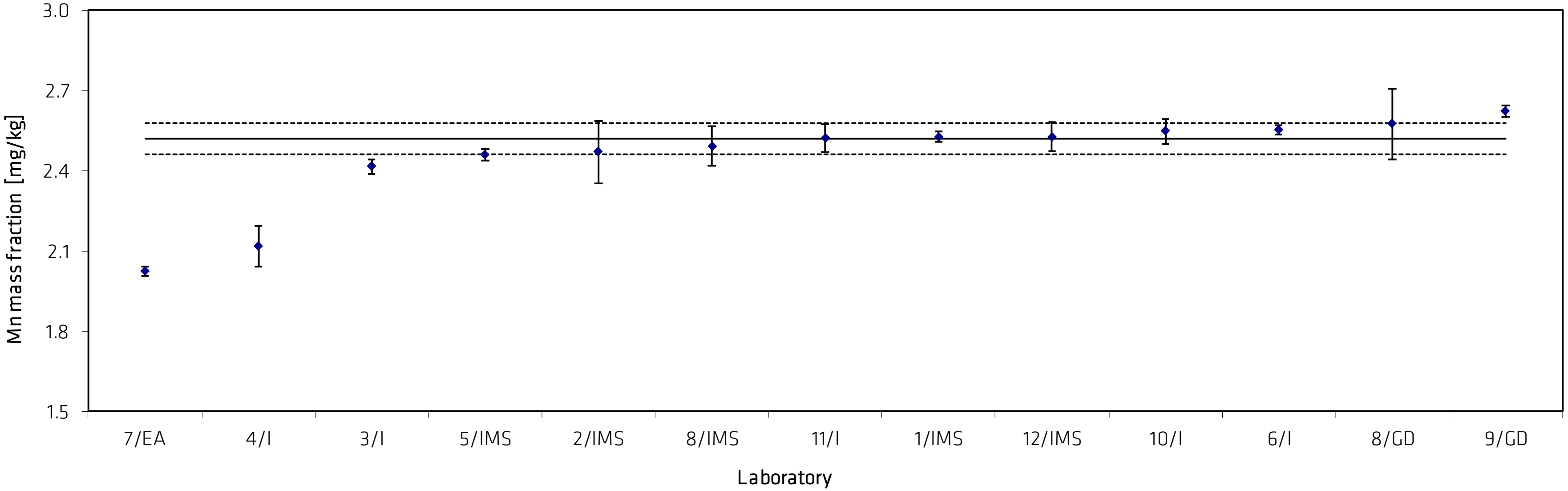


Table 12: Results for Ni in BAM-M382a

| Lab./Meth. | 7/EA | 5/IMS | 10/I | 3/I | 6/I | 12/IMS | 8/IMS | 11/I | 9/GD | 2/IMS | 8/GD | 1/IMS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.99 | 1.96 | 2.44 | 2.50 | 2.69 | 2.66 | 2.62 | 2.55 | 2.94 | 3.01 | 2.87 | 2.97 | | *n* |
| | 1.06 | 1.95 | 2.36 | 2.48 | 2.56 | 2.80 | 2.91 | 2.49 | 2.93 | 2.96 | 2.90 | 2.86 | | 10 |
| | 1.03 | 2.08 | 2.38 | 2.47 | 2.77 | 2.73 | 2.97 | 3.05 | 2.73 | 2.71 | 2.95 | 2.81 | | |
| | 1.10 | 2.02 | 2.47 | 2.46 | 2.31 | 2.60 | 2.54 | 2.84 | 2.74 | 2.69 | 2.92 | 2.80 | | |
| | 1.07 | 1.95 | 2.40 | 2.45 | 2.21 | 2.70 | 2.89 | 2.58 | 2.87 | 2.89 | 2.87 | 3.00 | | |
| | 1.10 | 1.90 | 2.36 | 2.41 | 2.55 | 2.63 | | 3.21 | 2.71 | 2.78 | 2.64 | 2.81 | | |
| | | | | | | | | | 2.77 | | | | | |
| | | | | | | | | | 2.73 | | | | | |
| *M* [mg/kg] | **1.06** | **1.98** | **2.40** | **2.46** | **2.52** | **2.69** | **2.79** | **2.79** | **2.80** | **2.84** | **2.86** | **2.88** | | **2.70** |
| *s* [mg/kg] | 0.04 | 0.06 | 0.04 | 0.03 | 0.22 | 0.08 | 0.19 | 0.30 | 0.10 | 0.13 | 0.11 | 0.09 | $s_M$ [mg/kg] | 0.18 |
| | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.15 |
| $s_{rel}$ | 0.0403 | 0.0315 | 0.0187 | 0.0124 | 0.0860 | 0.0283 | 0.0691 | 0.1062 | 0.0340 | 0.0467 | 0.0389 | 0.0307 | | 0.0653 |

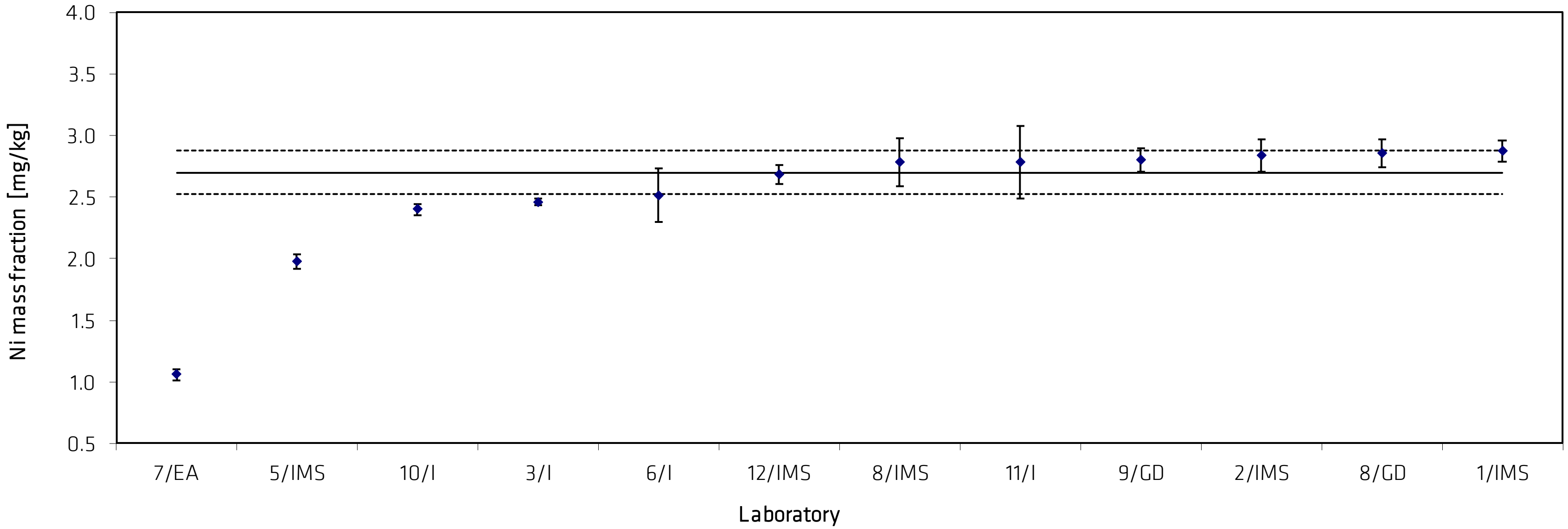


Table 13: Results for P in BAM-M382a

| Lab./Meth. | 8/GD | 9/GD | 10/I | 11/I | 3/I | 5/I | 4/I | 2/I | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.24 | 0.38 | 0.51 | 1.42 | <1 | <1 | <5 | <5 | | *n* |
| | 0.22 | 0.40 | 0.83 | 1.54 | <1 | <1 | <5 | <5 | | 4 |
| | 0.25 | 0.35 | 0.58 | 1.24 | <1 | <1 | <5 | <5 | | |
| | 0.14 | 0.34 | 0.74 | 1.68 | <1 | <1 | <5 | <5 | | |
| | 0.16 | 0.40 | 0.54 | 2.79 | <1 | <1 | <5 | <5 | | |
| | 0.19 | 0.38 | 0.77 | 1.73 | <1 | <1 | <5 | <5 | | |
| | | 0.37 | | | | | | | | |
| | | 0.40 | | | | | | | | |
| **$M$ [mg/kg]** | **0.20** | **0.38** | **0.66** | **1.73** | **<1** | **<1** | **<5** | **<5** | | **0.74** |
| $s$ [mg/kg] | 0.04 | 0.02 | 0.13 | 0.55 | | | | | $s_M$ [mg/kg] | 0.69 |
| | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.20 |
| $s_{rel}$ | 0.2214 | 0.0620 | 0.2035 | 0.3158 | | | | | | 0.9245 |

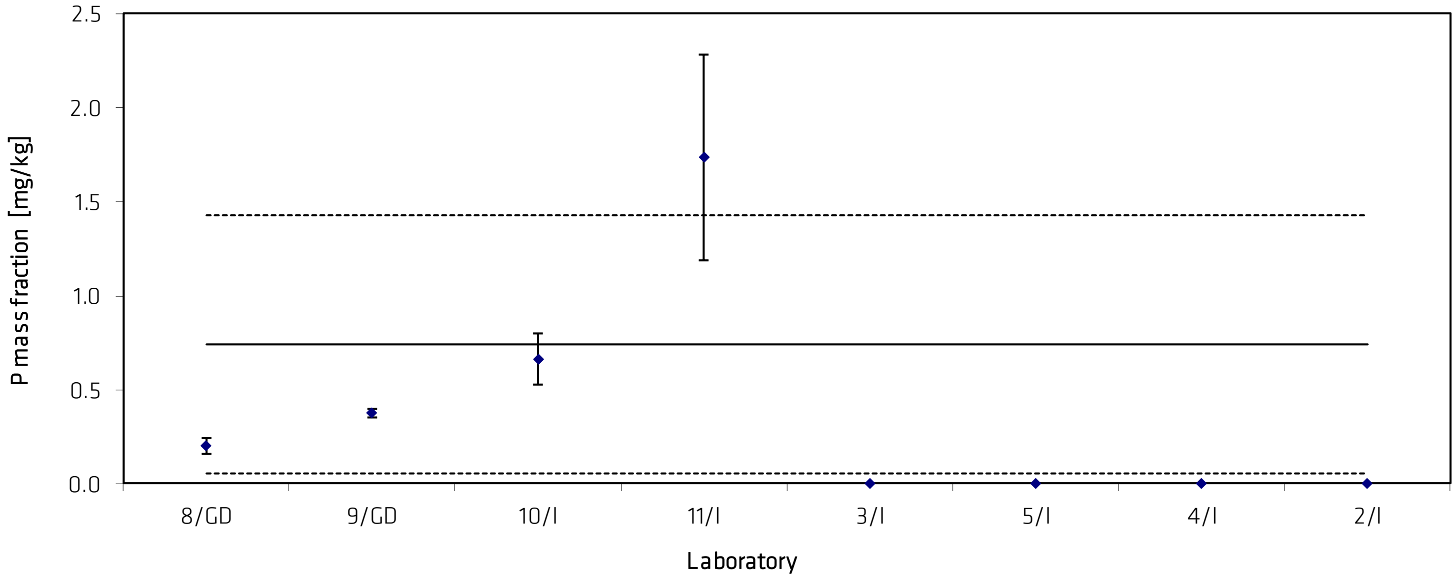


Table 14: Results for Pb in BAM-M382a

| Lab./Meth. | 6/I | 3/I | 8/GD | 9/GD | 5/IMS | 12/IMS | 2/IMS | 1/IMS | 7/EA | 8/IMS | 4/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 1.29 | 1.44 | 1.55 | 2.34 | 2.23 | 2.32 | 2.39 | 2.20 | 2.91 | 3.21 | <2 | | *n* |
| | 1.23 | 1.85 | 1.58 | 2.35 | 2.26 | 2.38 | 2.31 | 2.25 | 2.85 | 3.89 | <2 | | 10 |
| | 1.29 | 2.17 | 1.52 | 2.37 | 2.16 | 2.45 | 2.43 | 2.21 | 2.78 | 3.10 | <2 | | |
| | 1.14 | 1.38 | 2.04 | 2.37 | 2.20 | 2.23 | 2.28 | 2.55 | 2.75 | 2.71 | <2 | | |
| | 1.00 | 1.50 | 1.97 | 1.38 | 2.26 | 2.23 | 2.35 | 2.45 | 2.94 | 2.52 | <2 | | |
| | 1.10 | 1.26 | 2.05 | 1.49 | 2.23 | 2.18 | 2.22 | 2.50 | 2.83 | | <2 | | |
| | | | | 1.45 | | | | | | | | | |
| | | | | 1.53 | | | | | | | | | |
| **$M$ [mg/kg]** | **1.18** | **1.60** | **1.79** | **1.91** | **2.22** | **2.30** | **2.33** | **2.36** | **2.84** | **3.09** | **<2** | | **2.16** |
| $s$ [mg/kg] | 0.12 | 0.34 | 0.26 | 0.48 | 0.04 | 0.10 | 0.08 | 0.16 | 0.07 | 0.53 | | $s_M$ [mg/kg] | 0.57 |
| | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.26 |
| $s_{rel}$ | 0.0985 | 0.2141 | 0.1454 | 0.2514 | 0.0160 | 0.0453 | 0.0325 | 0.0667 | 0.0257 | 0.1718 | | | 0.2629 |

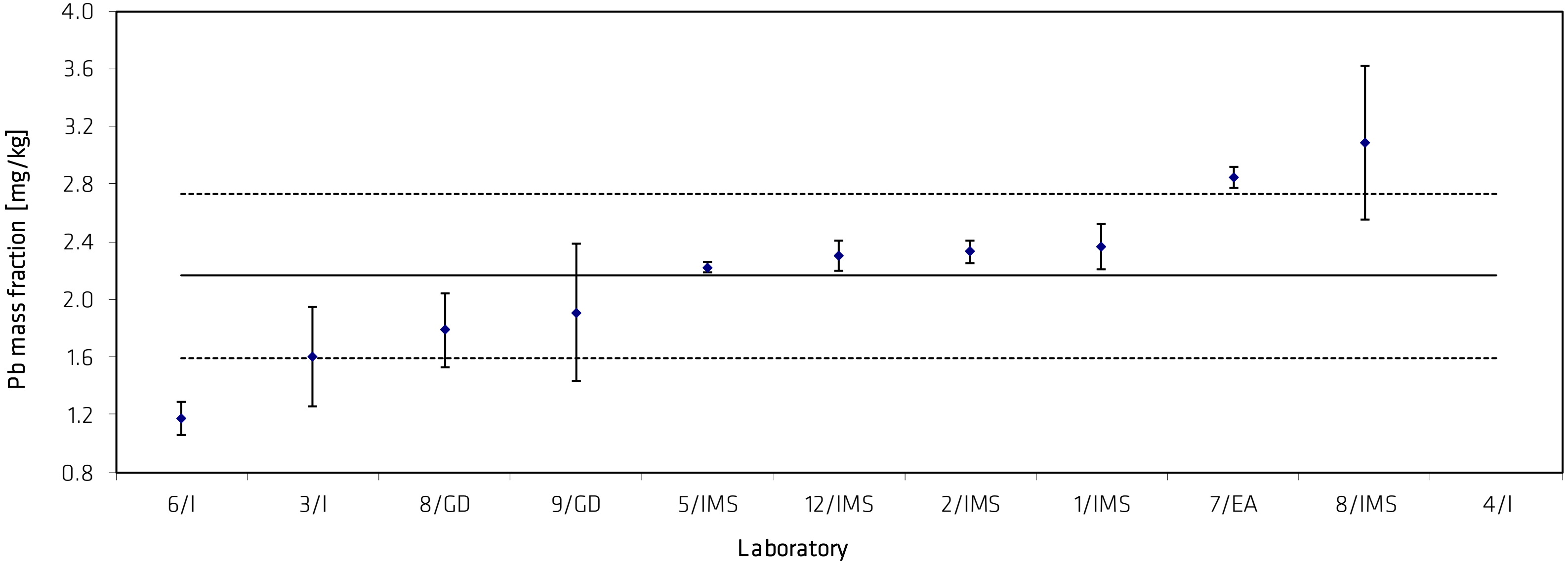


Table 15: Results for S in BAM-M382a

| Lab./Meth. | 6/I | 3/I | 8/GD | 9/GD | 9/V | 7/V | | |
|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 1.76 | 5.81 | 6.36 | 7.03 | 7.30 | 7.60 | | *n* |
| | 2.64 | 5.70 | 6.23 | 7.07 | 7.50 | 7.60 | | 5 |
| | 2.37 | 5.45 | 6.46 | 6.69 | 6.80 | 7.60 | | |
| | 1.76 | 5.56 | 4.96 | 6.80 | 7.40 | 7.60 | | |
| | 2.14 | 5.66 | 5.19 | 7.09 | 7.70 | 7.60 | | |
| | 2.24 | 5.52 | 4.79 | 6.55 | 7.60 | 8.00 | | |
| | | | | 6.70 | 8.10 | | | |
| | | | | 7.37 | | | | |
| **$M$ [mg/kg]** | **2.15** | **5.62** | **5.67** | **6.91** | **7.49** | **7.67** | | **6.67** |
| $s$ [mg/kg] | 0.35 | 0.13 | 0.76 | 0.27 | 0.40 | 0.16 | $s_M$ [mg/kg] | 0.98 |
| | | | | | | | $\bar{s}_i$ [mg/kg] | 0.40 |
| $s_{rel}$ | 0.1611 | 0.0234 | 0.1350 | 0.0394 | 0.0531 | 0.0213 | | 0.1469 |

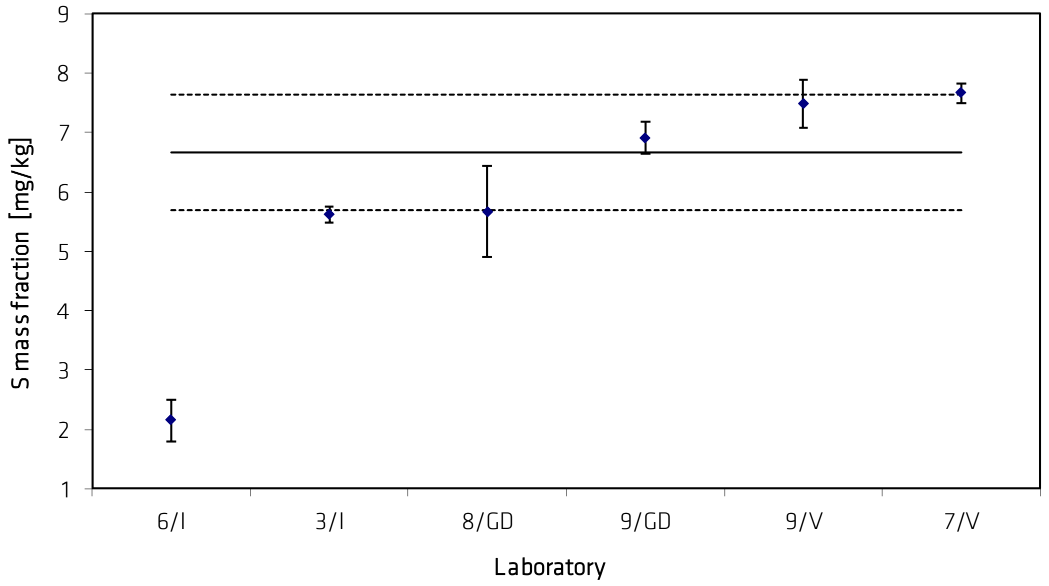


Table 16: Results for Sb in BAM-M382a

| Lab./Meth. | 7/EA | 8/GD | 8/IMS | 1/IMS | 9/GD | 12/IMS | 5/IMS | 6/I | 2/IMS | 3/I | 4/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.70 | 0.65 | 0.95 | 0.82 | 0.85 | 0.86 | 0.96 | 0.97 | <0.5 | <1 | 1.1 | | *n* |
| | 0.61 | 0.69 | 0.77 | 0.79 | 0.85 | 0.81 | 1.14 | 1.13 | <0.5 | <1 | <1 | | 8 |
| | 0.58 | 0.69 | 0.75 | 0.81 | 0.88 | 0.86 | 1.17 | 1.16 | <0.5 | <1 | 1.0 | | |
| | 0.74 | 0.76 | 0.83 | 0.71 | 0.88 | 0.84 | 1.14 | 1.39 | <0.5 | <1 | <1 | | |
| | 0.65 | 0.76 | 0.62 | 0.85 | 0.78 | 0.96 | 1.18 | 1.42 | <0.5 | <1 | <1 | | |
| | 0.72 | 0.79 | | 0.75 | 0.82 | 1.04 | 0.99 | 0.95 | <0.5 | <1 | <1 | | |
| | | | | | 0.80 | | | | | | | | |
| | | | | | 0.84 | | | | | | | | |
| **$M$ [mg/kg]** | **0.67** | **0.72** | **0.78** | **0.79** | **0.84** | **0.90** | **1.10** | **1.17** | **<0.5** | **<1** | **<1.2** | | **0.87** |
| $s$ [mg/kg] | 0.06 | 0.05 | 0.12 | 0.05 | 0.04 | 0.09 | 0.10 | 0.20 | | | | $s_M$ [mg/kg] | 0.18 |
| | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.09 |
| $s_{rel}$ | 0.0957 | 0.0750 | 0.1535 | 0.0644 | 0.0420 | 0.0987 | 0.0885 | 0.1714 | | | | | 0.2036 |

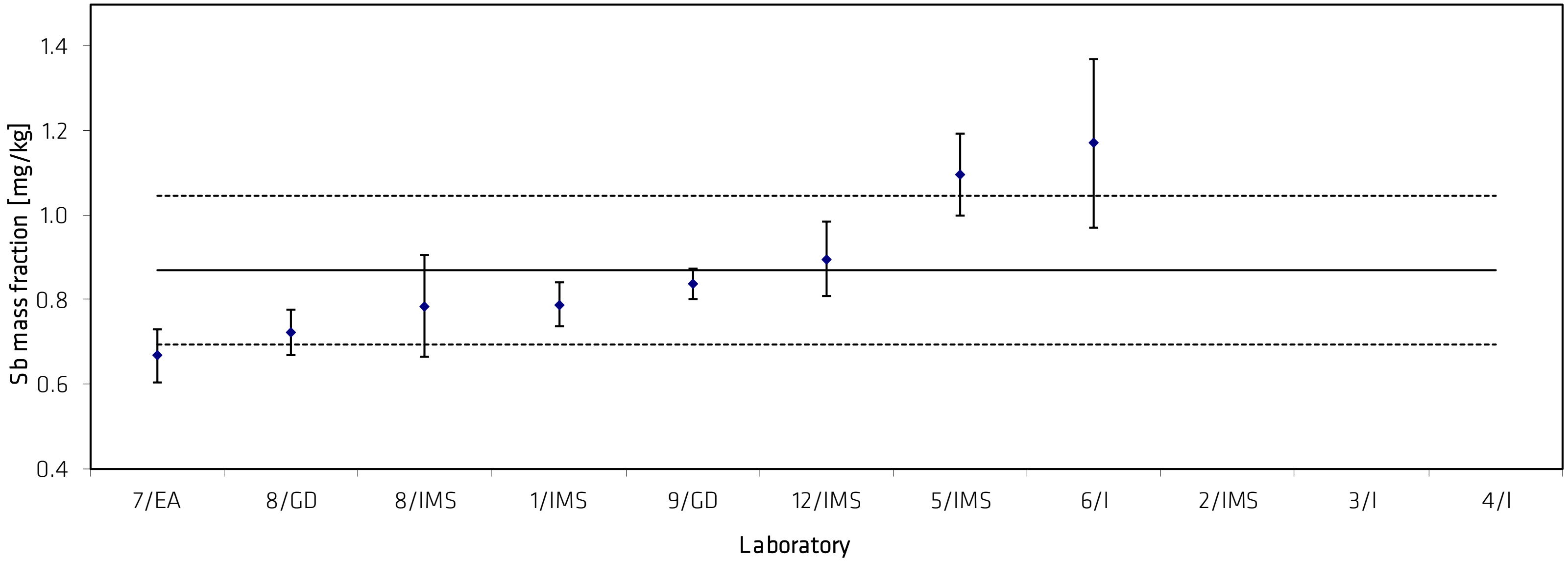


Table 17: Results for Se in BAM-M382a

| Lab./Meth. | 8/GD | 9/GD | 1/IMS | 12/IMS | 7/EA | 2/IMS | 11/I | 5/IMS | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.61 | 0.77 | 0.68 | 0.81 | 0.79 | 0.87 | 0.90 | <0.3 | <1 | | *n* |
| | 0.55 | 0.78 | 0.66 | 0.81 | 0.89 | 0.75 | 1.04 | <0.3 | <1 | | 6 |
| | 0.69 | 0.75 | 0.64 | 0.86 | 0.83 | 0.76 | 1.08 | <0.3 | <1 | | |
| | 0.79 | 0.76 | 0.92 | 0.78 | 0.74 | 0.68 | 0.74 | <0.3 | <1 | | |
| | 0.86 | 0.71 | 0.87 | 0.80 | 0.75 | 0.91 | 1.12 | <0.3 | <1 | | |
| | 0.70 | 0.72 | 0.77 | 0.78 | 0.86 | 0.92 | 1.28 | <0.3 | <1 | | |
| | | 0.71 | | | | | | | | | |
| | | 0.72 | | | | | | | | | |
| **$M$ [mg/kg]** | **0.70** | **0.74** | **0.76** | **0.81** | **0.81** | **0.82** | **1.03** | **<0.3** | <1 | | **0.77** |
| $s$ [mg/kg] | 0.11 | 0.03 | 0.12 | 0.03 | 0.06 | 0.10 | 0.19 | | | $s_M$ [mg/kg] | 0.05 |
| | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.08 |
| $s_{rel}$ | 0.1621 | 0.0372 | 0.1547 | 0.0355 | 0.0745 | 0.1228 | 0.1818 | | | | 0.0608 |

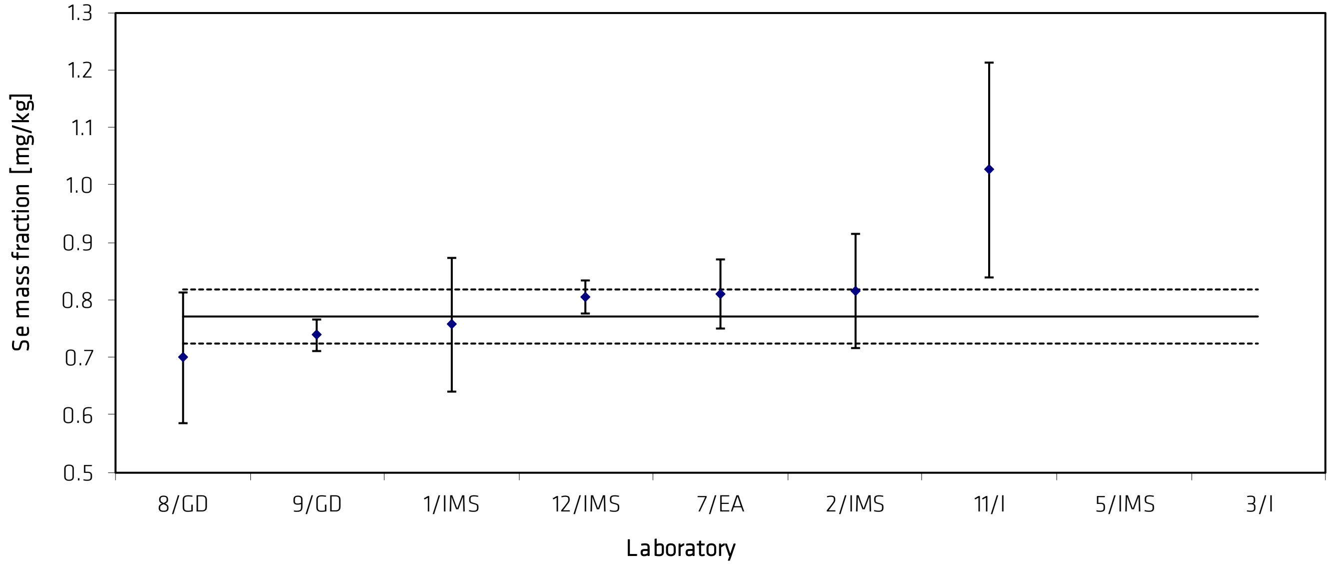


Table 18: Results for Sn in BAM-M382a

| Lab./Meth. | 8/GD | 6/I | 7/EA | 10/I | 3/I | 8/IMS | 1/IMS | 5/IMS | 12/IMS | 2/IMS | 9/GD | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 3.84 | 3.35 | 4.35 | 4.58 | 4.81 | 4.76 | 4.95 | 4.91 | 5.03 | 5.06 | 5.16 | | *n* |
| | 3.72 | 3.98 | 4.34 | 4.70 | 4.78 | 4.83 | 4.87 | 4.94 | 4.99 | 4.92 | 5.16 | | 11 |
| | 3.76 | 4.15 | 4.38 | 4.76 | 4.73 | 4.68 | 4.87 | 4.93 | 5.04 | 5.14 | 5.32 | | |
| | 4.37 | 4.06 | 4.22 | 4.51 | 4.76 | 4.95 | 4.87 | 4.92 | 4.95 | 5.04 | 5.37 | | |
| | 4.38 | 4.54 | 4.20 | 4.88 | 4.79 | 4.98 | 4.86 | 4.97 | 5.06 | 5.23 | 4.70 | | |
| | 4.19 | 4.29 | 4.31 | 4.89 | 4.74 | | 4.96 | 4.92 | 4.98 | 4.89 | 4.96 | | |
| | | | | | | | | | | | 4.86 | | |
| | | | | | | | | | | | 5.03 | | |
| **$M$ [mg/kg]** | **4.04** | **4.06** | **4.30** | **4.72** | **4.77** | **4.84** | **4.90** | **4.93** | **5.01** | **5.05** | **5.07** | | **4.70** |
| $s$ [mg/kg] | 0.31 | 0.40 | 0.07 | 0.16 | 0.03 | 0.13 | 0.05 | 0.02 | 0.04 | 0.13 | 0.23 | $s_M$ [mg/kg] | 0.38 |
| | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.18 |
| $s_{rel}$ | 0.0756 | 0.0986 | 0.0171 | 0.0328 | 0.0064 | 0.0261 | 0.0093 | 0.0044 | 0.0085 | 0.0252 | 0.0454 | | 0.0815 |

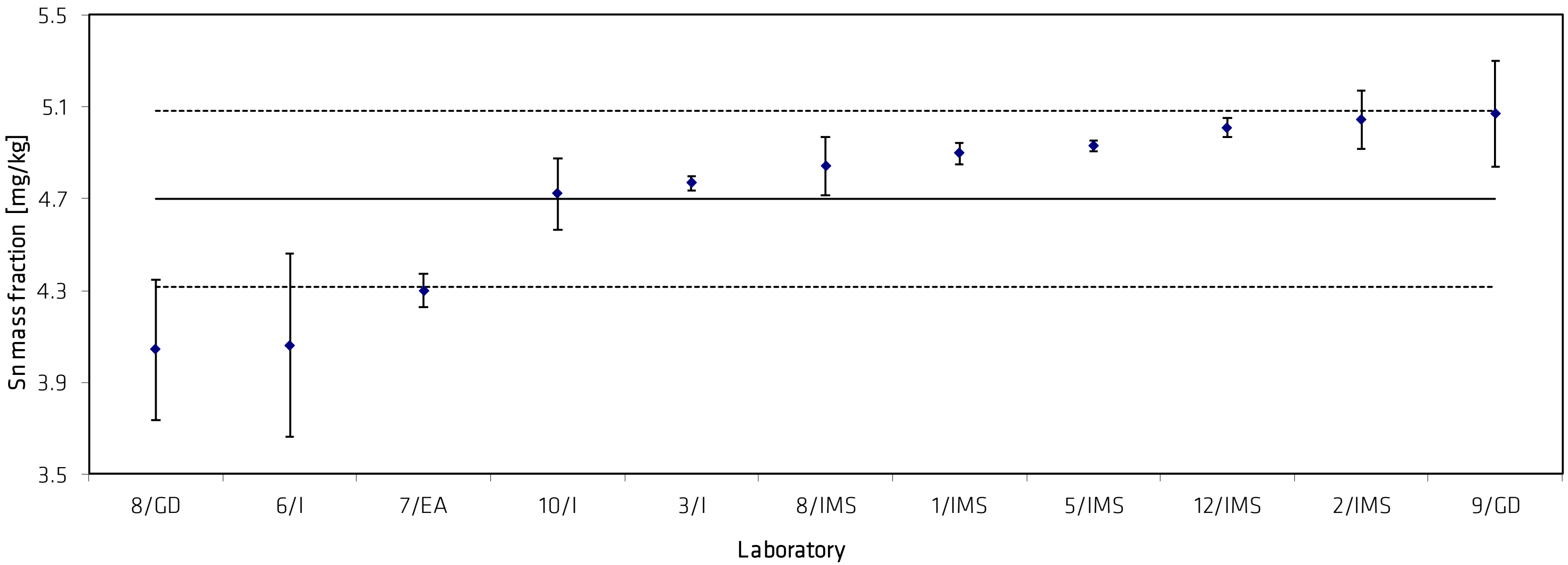


Table 19: Results for Te in BAM-M382a

| Lab./Meth. | 7/EA | 8/GD | 1/IMS | 9/GD | 2/IMS | 12/IMS | 8/IMS | 5/IMS | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.66 | 0.59 | 0.77 | 0.74 | 0.79 | 0.79 | 0.84 | 1.18 | <1 | | *n* |
| | 0.60 | 0.56 | 0.66 | 0.75 | 0.72 | 0.84 | 0.85 | 1.24 | <1 | | 7 |
| | 0.54 | 0.65 | 0.68 | 0.74 | 0.80 | 0.83 | 0.81 | 1.27 | <1 | | |
| | 0.51 | 0.65 | 0.75 | 0.76 | 0.69 | 0.82 | 0.82 | 1.18 | | | |
| | 0.63 | 0.69 | 0.70 | 0.69 | 0.79 | 0.82 | 0.85 | 1.32 | <1 | | |
| | 0.69 | 0.63 | 0.70 | 0.71 | 0.73 | 0.82 | 0.77 | 1.31 | <1 | | |
| | | | | 0.69 | | | | | | | |
| | | | | 0.72 | | | | | | | |
| **$M$ [mg/kg]** | **0.61** | **0.63** | **0.71** | **0.73** | **0.76** | **0.82** | **0.82** | **1.25** | **<1** | | **0.72** |
| $s$ [mg/kg] | 0.07 | 0.05 | 0.04 | 0.03 | 0.04 | 0.02 | 0.03 | 0.06 | | $s_M$ [mg/kg] | 0.09 |
| | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.04 |
| $s_{rel}$ | 0.1149 | 0.0743 | 0.0591 | 0.0356 | 0.0593 | 0.0210 | 0.0374 | 0.0505 | | | 0.1179 |

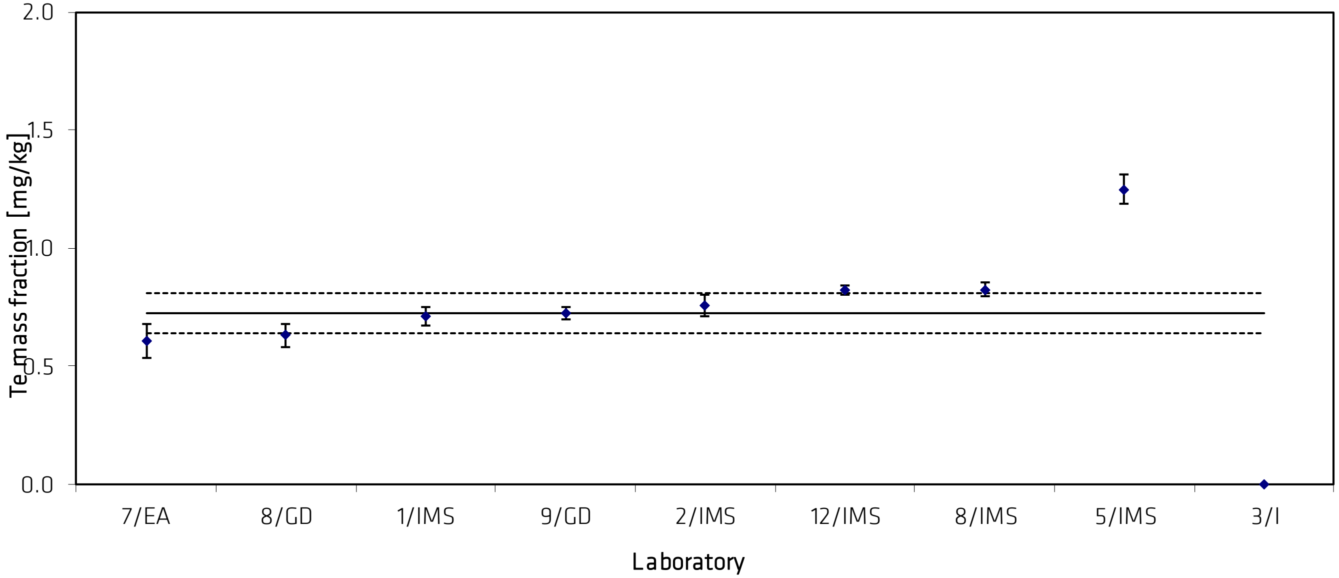


Table 20: Results for Ti in BAM-M382a

| Lab./Meth. | 8/GD | 1/IMS | 12/IMS | 9/GD | 10/I | 8/IMS | 11/I | 6/I | 3/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 0.45 | 0.52 | 0.54 | 0.55 | 0.48 | 0.72 | 0.67 | 0.68 | <1 | | *n* |
| | 0.45 | 0.50 | 0.53 | 0.54 | 0.51 | 0.79 | 0.66 | 0.67 | <1 | | 8 |
| | 0.48 | 0.50 | 0.53 | 0.57 | 0.48 | 0.63 | 0.68 | 0.63 | <1 | | |
| | 0.43 | 0.55 | 0.53 | 0.59 | 0.63 | 0.49 | 0.71 | 0.62 | <1 | | |
| | 0.41 | 0.55 | 0.54 | 0.50 | 0.66 | 0.48 | 0.62 | 0.66 | <1 | | |
| | 0.42 | 0.55 | 0.53 | 0.58 | 0.70 | | 0.56 | 0.67 | <1 | | |
| | | | | 0.50 | | | | | | | |
| | | | | 0.55 | | | | | | | |
| **$M$ [mg/kg]** | **0.44** | **0.53** | **0.53** | **0.55** | **0.58** | **0.62** | **0.65** | **0.66** | **<1** | | **0.57** |
| $s$ [mg/kg] | 0.03 | 0.02 | 0.01 | 0.03 | 0.10 | 0.14 | 0.05 | 0.02 | | $s_M$ [mg/kg] | 0.07 |
| | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.07 |
| $s_{rel}$ | 0.0575 | 0.0470 | 0.0131 | 0.0602 | 0.1701 | 0.2208 | 0.0814 | 0.0371 | | | 0.1272 |

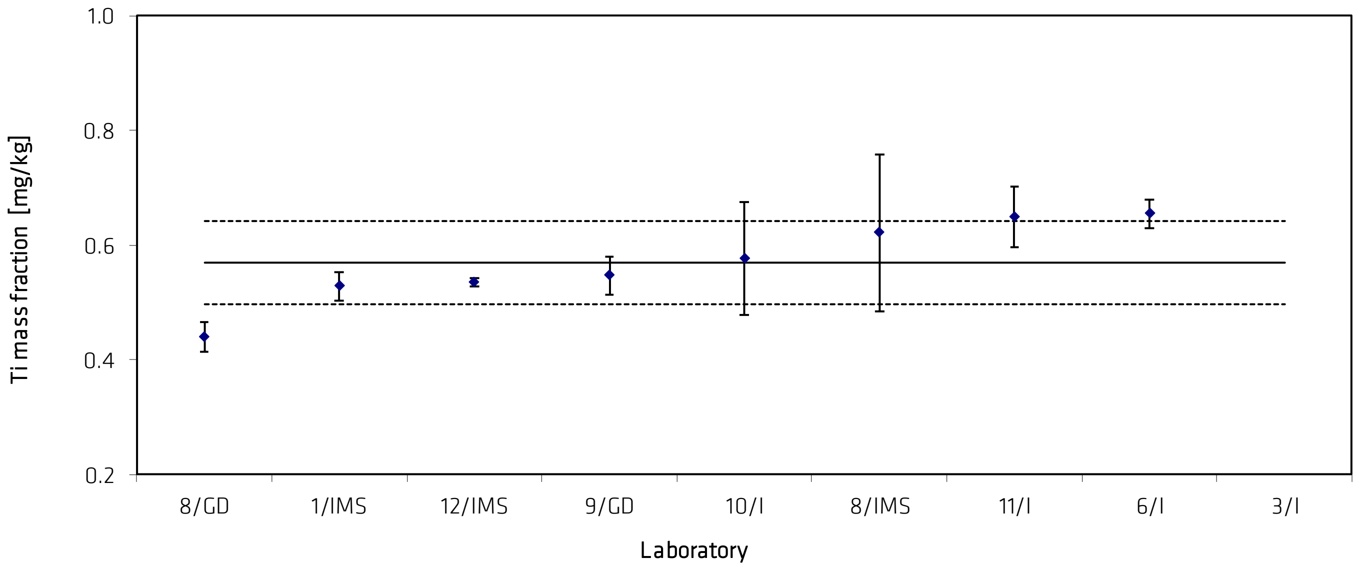
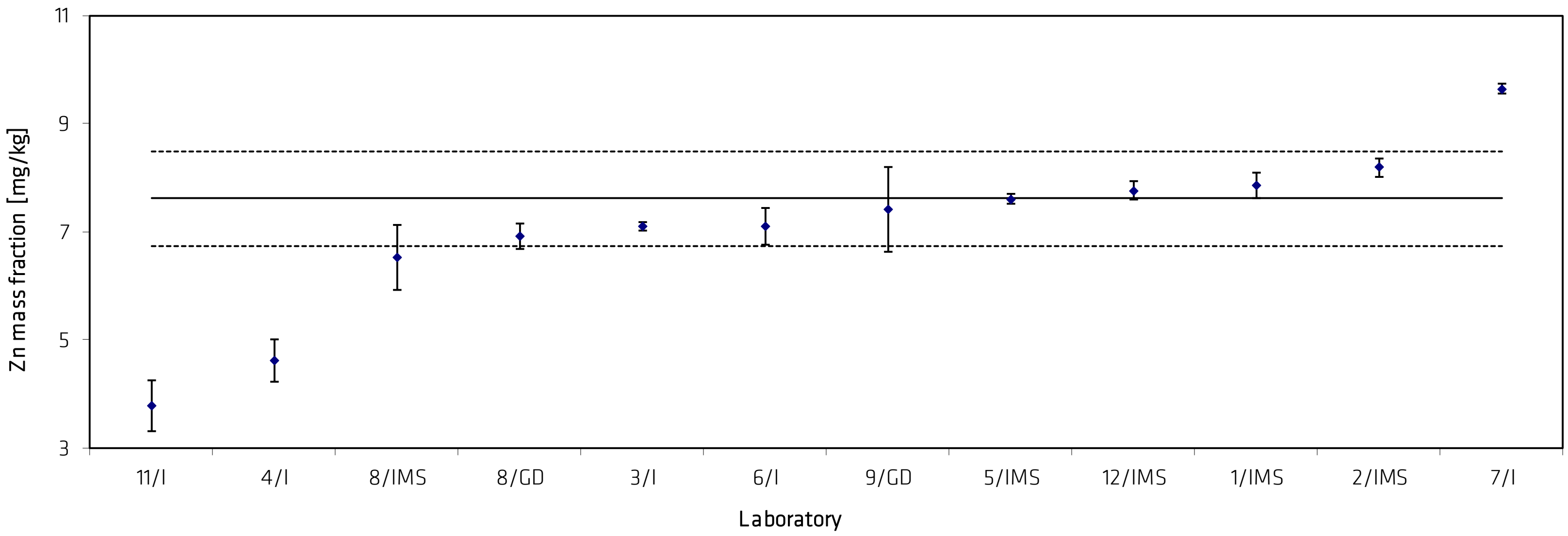


Table 21: Results for Zn in BAM-M382a

| Lab./Meth. | 11/I | 4/I | 8/IMS | 8/GD | 3/I | 6/I | 9/GD | 5/IMS | 12/IMS | 1/IMS | 2/IMS | 7/I | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 4.04 | 4.0 | 6.29 | 7.00 | 7.20 | 6.92 | 8.4 | 7.55 | 7.69 | 8.03 | 8.43 | 9.66 | | *n* |
| | 4.02 | 5.0 | 5.96 | 6.97 | 7.14 | 6.85 | 8.1 | 7.76 | 7.93 | 7.93 | 7.96 | 9.52 | | 10 |
| | 3.30 | 5.0 | 6.44 | 7.27 | 7.06 | 6.95 | 8.0 | 7.55 | 8.01 | 8.19 | 8.31 | 9.60 | | |
| | 3.70 | 4.4 | 7.36 | 6.72 | 7.09 | 7.74 | 8.1 | 7.54 | 7.65 | 7.66 | 8.23 | 9.57 | | |
| | 3.21 | 4.8 | | 6.60 | 7.08 | 7.21 | 6.8 | 7.56 | 7.71 | 7.74 | 8.09 | 9.71 | | |
| | 4.42 | 4.5 | | 6.95 | 6.99 | 6.90 | 6.6 | 7.64 | 7.54 | 7.54 | 8.09 | 9.75 | | |
| | | | | | | | 6.7 | | | | | | | |
| | | | | | | | 6.6 | | | | | | | |
| *M* [mg/kg] | **3.78** | **4.62** | **6.51** | **6.92** | **7.09** | **7.10** | **7.40** | **7.60** | **7.76** | **7.85** | **8.18** | **9.64** | | **7.60** |
| *s* [mg/kg] | 0.47 | 0.39 | 0.60 | 0.23 | 0.07 | 0.34 | 0.79 | 0.09 | 0.18 | 0.24 | 0.17 | 0.09 | $s_M$ [mg/kg] | 0.87 |
| | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 0.36 |
| $s_{rel}$ | 0.1238 | 0.0849 | 0.0921 | 0.0339 | 0.0101 | 0.0480 | 0.1065 | 0.0114 | 0.0228 | 0.0311 | 0.0209 | 0.0091 | | 0.1140 |



The data was statistically evaluated to detect outlying values (Grubbs, Nalimov, Dixon, Cochran). The Cochran-test was performed only once. The following results were obtained:

Tab. 22: Outcome of statistical tests on the results obtained for Ag

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 12 | 10 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 7 | Lab. 6 |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 7 | Lab. 6 |
| Nalimov ($\alpha$ = 0.01) | --- | Lab. 6 |
| Grubbs ($\alpha$ = 0.05) | --- | Lab. 6 |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | Labs. 7 and 8/IMS | Labs. 6 and 4 |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran ($\alpha$ = 0.01) | Lab. 6 | Lab. 6 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers (Labs. 7 and 8/IMS, 1st run) were removed, the outliers (Labs. 6 and 4, 2nd run) were not removed.

Tab. 23: Outcome of statistical tests on the results obtained for Al and Cd ("<-values" were not considered)

| | Al | Cd |
|---|---|---|
| Number of data sets | 6 | 11 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | --- | Lab. 7 |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | --- | Lab. 7 |
| Nalimov ($\alpha$ = 0.01) | --- | Lab. 7 |
| Grubbs ($\alpha$ = 0.05) | --- | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 4 | Lab. 2 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers were not removed.

Tab. 24: Outcome of statistical tests on the results obtained for As ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 11 | 10 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Labs. 9/EA and 10 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 9/EA | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 9/EA | Lab. 10 |
| Nalimov ($\alpha$ = 0.01) | Lab. 9/EA | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 9/EA | --- |
| Grubbs ($\alpha$ = 0.01) | Lab. 9/EA | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | Labs. 10 and 7 |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 6 | Lab. 6 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 9/EA, 1st run) was removed, the outliers (Labs. 10 and 7, 2nd run, Lab. 6) were not removed.

Tab. 25: Outcome of statistical tests on the results obtained for Bi ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 9 | 8 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 7 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 10 | Lab. 10 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 7, 1st run) was removed, the Cochran outlier was not removed.

Tab. 26: Outcome of statistical tests on the results obtained for Co ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 13 | 11 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 7 | Lab. 10 |
| Dixon ($\alpha$ = 0.01) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 7 | Lab. 10 |
| Nalimov ($\alpha$ = 0.01) | Lab. 7 | Lab. 10 |
| Grubbs ($\alpha$ = 0.05) | Lab. 7 | Lab. 10 |
| Grubbs ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 4 | Lab. 4 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 7, 1st run) was removed, the outliers (Lab. 10, 2nd run, Lab. 4) were not removed.

Tab. 27: Outcome of statistical tests on the results obtained for Cr and Pb ("<-values" were not considered)

| | Cr | Pb |
|---|---|---|
| Number of data sets | 11 | 10 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | --- | --- |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | --- | --- |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier was not removed.

Tab. 28: Outcome of statistical tests on the results obtained for Fe

| | 1st run |
|---|---|
| Number of data sets | 13 |
| Scheffe's test (data compatible?) | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed |
| Dixon (α = 0.05) | Lab. 5 |
| Dixon (α = 0.01) | --- |
| Nalimov (α = 0.05) | Lab. 5 |
| Nalimov (α = 0.01) | --- |
| Grubbs (α = 0.05) | --- |
| Grubbs (α = 0.01) | --- |
| Grubbs Pair (α = 0.05) | Labs. 5 and 10 |
| Grubbs Pair (α = 0.01) | --- |
| Cochran | Lab. 1 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal |

The outliers were not removed.

Tab. 29: Outcome of statistical tests on the results obtained for Mg

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 12 | 11 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon (α = 0.05) | Lab. 1 | --- |
| Dixon (α = 0.01) | Lab. 1 | --- |
| Nalimov (α = 0.05) | Lab. 1 | Lab. 10 |
| Nalimov (α = 0.01) | Lab. 1 | --- |
| Grubbs (α = 0.05) | Lab. 1 | Lab. 10 |
| Grubbs (α = 0.01) | Lab. 1 | --- |
| Grubbs Pair (α = 0.05) | --- | Labs. 10 and 8/GD |
| Grubbs Pair (α = 0.01) | --- | --- |
| Cochran | Lab. 8/GD | Lab. 8/GD |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 1, 1st run) was removed, the other outliers were not removed.

Tab. 30: Outcome of statistical tests on the results obtained for Mn

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 13 | 11 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 7 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.05) | Labs. 7 and 4 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | Labs. 7 and 4 | --- |
| Grubbs Pair ($\alpha$ = 0.01) | Labs. 7 and 4 | --- |
| Cochran | Lab. 8/GD | Lab. 8/GD |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers (Labs. 7 and 4, 1st run) were removed, the Cochran outlier was not removed.

Tab. 31: Outcome of statistical tests on the results obtained for Ni ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 12 | 10 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 7 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 7 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 7 | --- |
| Grubbs ($\alpha$ = 0.01) | Lab. 7 | --- |
| Grubbs Pair ($\alpha$ = 0.05) | Labs. 7 and 5 | --- |
| Grubbs Pair ($\alpha$ = 0.01) | Labs. 7 and 5 | --- |
| Cochran | Lab. 11 | Lab. 11 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers (Labs. 7 and 5, 1st run) were removed, the Cochran outlier was not removed.

Tab. 32: Outcome of statistical tests on the results obtained for S ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 6 | 5 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 6 | --- |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 6 | --- |
| Nalimov ($\alpha$ = 0.01) | --- | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 6 | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | Labs. 9 and 7 |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 8/GD | Lab. 8/GD |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 6, 1st run) was removed, the other outliers were not removed.

Tab. 33: Outcome of statistical tests on the results obtained for Se ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 7 | 6 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 11 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 11 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 11 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 11 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 11 | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | --- | --- |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers (Lab. 11, 1st run) was removed.

Tab. 34: Outcome of statistical tests on the results obtained for Sn ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 12 | 11 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 11 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 11 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 11 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 11 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 11 | --- |
| Grubbs ($\alpha$ = 0.01) | Lab. 11 | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 11 | Lab. 6 |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 11, 1st run) was removed, the Cochran outlier was not removed.

Tab. 35: Outcome of statistical tests on the results obtained for Sb and Ti ("<-values" were not considered)

| | Sb | Ti |
|---|---|---|
| Number of data sets | 8 | 8 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | --- | --- |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | --- | Lab. 8/GD |
| Nalimov ($\alpha$ = 0.01) | --- | --- |
| Grubbs ($\alpha$ = 0.05) | --- | --- |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | Labs. 5 and 6 | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 6 | Lab. 8/IMS |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers were not removed.

Tab. 36: Outcome of statistical tests on the results obtained for Te ("<-values" were not considered)

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 8 | 7 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 5 | --- |
| Dixon ($\alpha$ = 0.01) | Lab. 5 | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 5 | --- |
| Nalimov ($\alpha$ = 0.01) | Lab. 5 | --- |
| Grubbs ($\alpha$ = 0.05) | Lab. 5 | --- |
| Grubbs ($\alpha$ = 0.01) | Lab. 5 | --- |
| Grubbs Pair ($\alpha$ = 0.05) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | --- | --- |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outlier (Lab. 5, 1st run) was removed.

Tab. 37: Outcome of statistical tests on the results obtained for Zn

| | 1st run | 2nd run |
|---|---|---|
| Number of data sets | 12 | 10 |
| Scheffe's test (data compatible?) | yes | yes |
| Snedecor-F-Test and Bartlett-Test | Pooling not allowed | Pooling not allowed |
| Dixon ($\alpha$ = 0.05) | Lab. 11 | Lab. 7 |
| Dixon ($\alpha$ = 0.01) | --- | --- |
| Nalimov ($\alpha$ = 0.05) | Lab. 11 | Lab. 7 |
| Nalimov ($\alpha$ = 0.01) | --- | Lab. 7 |
| Grubbs ($\alpha$ = 0.05) | --- | Lab. 7 |
| Grubbs ($\alpha$ = 0.01) | --- | --- |
| Grubbs Pair ($\alpha$ = 0.05) | Labs. 11 and 4 | --- |
| Grubbs Pair ($\alpha$ = 0.01) | --- | --- |
| Cochran | Lab. 9/GD | Lab. 9/GD |
| Kolmogorov-Smirnov-Lilliefors Test | Distribution: normal | Distribution: normal |

The outliers (Labs. 11 and 4, 1st run) were removed, the other outliers were not removed.

The resp. combined uncertainties were calculated from the spread resulting from the certification inter-laboratory comparison ($u_{\mathrm{ilc}}$) and the uncertainty contributions from possible inhomogeneity of the material using Equation 1.

$$u_{\mathrm{combined}} = \sqrt{u_{ilc}^2 + u_{bb}^2(1) + u_{bb}^2(2)} \qquad (1)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$ : uncertainty contribution resulting from inter-laboratory comparison

$n$ : number of data sets used for calculating the certified mass fraction of each element

Table 38: Uncertainty calculation (uncertainty contribution from possible inhomogeneities $u_{bb}$_(rel) estimated from the data of BAM-M386a for most of the elements)

| | | | uncertainty contribution from | | | | | | | $u_{bb\_}$(rel) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | M | n | $s_M$ | $u_{ilc}$ | $u_{bb}$ (1) Length | $u_{bb}$ (2) Area | u(comb) | U | | Length | Area | |
| | mg/kg | | mg/kg | mg/kg | mg/kg | mg/kg | | | | | | |
| Ag | 2.95 | 10 | 0.2537 | 0.0802 | 0.0295 | 0.0191 | 0.0876 | 0.1752 | | 1.0000 | 0.6480 | * |
| Al | 0.62 | 6 | 0.6884 | 0.2810 | 0.0248 | 0.0124 | 0.2824 | 0.5648 | | 4.0000 | 2.0000 | |
| As | 0.73 | 10 | 0.1797 | 0.0568 | 0.0073 | 0.0146 | 0.0591 | 0.1182 | | 1.0000 | 2.0000 | |
| Bi | 0.75 | 8 | 0.1334 | 0.0472 | 0.0075 | 0.0150 | 0.0500 | 0.1001 | | 1.0000 | 2.0000 | |
| Cd | 0.50 | 11 | 0.0691 | 0.0208 | 0.0050 | 0.0100 | 0.0237 | 0.0473 | | 1.0000 | 2.0000 | |
| Co | 0.92 | 12 | 0.1140 | 0.0329 | 0.0092 | 0.0184 | 0.0388 | 0.0776 | | 1.0000 | 2.0000 | |
| Cr | 0.24 | 11 | 0.1073 | 0.0324 | 0.0096 | 0.0048 | 0.0341 | 0.0682 | | 4.0000 | 2.0000 | |
| Fe | 10.30 | 13 | 1.0822 | 0.3001 | 0.1030 | 0.0879 | 0.3293 | 0.6586 | | 1.0000 | 0.8538 | * |
| Mg | 1.92 | 11 | 0.3377 | 0.1018 | 0.0192 | 0.0495 | 0.1149 | 0.2297 | | 1.0000 | 2.5802 | * |
| Mn | 2.52 | 11 | 0.0580 | 0.0175 | 0.0504 | 0.0426 | 0.0683 | 0.1366 | | 2.0000 | 1.6918 | * |
| Ni | 2.70 | 10 | 0.1764 | 0.0558 | 0.0810 | 0.0482 | 0.1095 | 0.2190 | | 3.0000 | 1.7837 | * |
| P | 0.74 | 4 | 0.6870 | 0.3435 | 0.0148 | 0.0148 | 0.3441 | 0.6883 | | 2.0000 | 2.0000 | |
| Pb | 2.16 | 10 | 0.5680 | 0.1796 | 0.0432 | 0.1380 | 0.2306 | 0.4612 | | 2.0000 | 6.3876 | * |
| S | 6.67 | 5 | 0.9795 | 0.4380 | 0.0667 | 0.1544 | 0.4692 | 0.9384 | | 1.0000 | 2.3147 | * |
| Sb | 0.87 | 8 | 0.1771 | 0.0626 | 0.0087 | 0.0174 | 0.0656 | 0.1312 | | 1.0000 | 2.0000 | |
| Se | 0.77 | 6 | 0.0469 | 0.0191 | 0.0231 | 0.0154 | 0.0337 | 0.0674 | | 3.0000 | 2.0000 | |
| Sn | 4.70 | 11 | 0.3830 | 0.1155 | 0.0940 | 0.1131 | 0.1870 | 0.3740 | | 2.0000 | 2.4064 | * |
| Te | 0.72 | 7 | 0.0854 | 0.0323 | 0.0072 | 0.0144 | 0.0361 | 0.0721 | | 1.0000 | 2.0000 | |
| Ti | 0.57 | 8 | 0.0724 | 0.0256 | 0.0057 | 0.0114 | 0.0286 | 0.0572 | | 1.0000 | 2.0000 | |
| Zn | 7.60 | 10 | 0.8671 | 0.2742 | 0.0760 | 0.0897 | 0.2983 | 0.5967 | | 1.0000 | 1.1803 | * |
| | | | | | | | | | | *ext. Laboratory | | |

The expanded uncertainties $U$ are calculated by multiplication of $u_{combined}$ with a coverage factor of $k$ = 2 using Equation 2.

$$U = k \cdot u_{\text{combined}} \tag{2}$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 3 of this report. Rounding was done according to DIN 1333 [4].

In addition to the wet chemical characterization some of the laboratories analysed the material with spark emission to check if there is agreement between SOES and wet chemistry. Tab. 39 shows the mean values of wet chemical and spark emission results as well as their standard deviations. The agreement between wet chemistry and SOES is acceptable for all elements except for Pb and Te, considering that for some elements there are only two datasets obtained with SOES.

Tab. 39: Comparison wet chemistry vs. SOES

| Element | Wet chemical analysis | | | Spark emission | | |
|---|---|---|---|---|---|---|
| | **Mass fraction** in mg/kg | **Std.-dev.** in mg/kg | ***n*** | **Mass fraction** in mg/kg | **Std.-dev.** in mg/kg | ***n*** |
| Ag | ..2.95 | 0.26 | 10 | 3.3 | 1.1 | 4 |
| Al | 0.62 | 0.69 | 6 | 1.13 | 0.7 | 3 |
| As | 0.76 | 0.15 | 9 | 0.76 | 0.03 | 2 |
| Bi | 0.72 | 0.12 | 7 | 0.72 | 0.14 | 3 |
| Cd | 0.50 | 0.08 | 10 | 0.73 | 0.18 | 2 |
| Co | 0.90 | 0.08 | 11 | 0.90 | 0.15 | 4 |
| Cr | 0.24 | 0.12 | 10 | 0.42 | 0.12 | 2 |
| Fe | 10.6 | 0.7 | 11 | 9.8 | 0.5 | 4 |
| Mg | 2.00 | 0.23 | 10 | 2.13 | 0.44 | 4 |
| Mn | 2.52 | 0.07 | 10 | 2.67 | 0.50 | 4 |
| Ni | 2.73 | 0.16 | 9 | 2.91 | 0.94 | 4 |
| P | --- | --- | - | 0.6 | 0.1 | 2 |
| Pb | 2.16 | 0.57 | 10 | 1.46 | 0.58 | 2 |
| S | 6.7 | 1.0 | 5 | 6.9 | 0.4 | 4 |
| Sb | 0.87 | 0.18 | 8 | 1.0 | --- | 2 |
| Se | 0.77 | 0.05 | 6 | 0.93 | 0.60 | 2 |
| Sn | 4.7 | 0.5 | 10 | 4.8 | 1.0 | 4 |
| Te | 0.72 | 0.09 | 7 | 1.38 | 0.54 | 2 |
| Ti | 0.57 | 0.08 | 7 | 1.31 | 1.1 | 4 |
| Zn | 7.6 | 0.9 | 10 | 7.3 | 1.6 | 3 |

## 6. Instructions for users and stability statement

The certified reference material BAM-M382a is intended for the calibration and quality control of spark emission spectrometry used for the analysis of similar materials. It can also be used for wet chemical analysis.
Before analysis the surface of the material should be cleaned by turning or milling. The preparation of the surface has to be done slowly to avoid heating of the disc.
If chips prepared from the compact material are used for wet chemical analysis, a minimum sample intake of 0.2 g should be used.
The material will remain stable if it is not subjected to excessive heat (e.g., during preparation of the working surface).

## 7. Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

## 8. References

[1] DIN EN ISO 17034, General requirements for the competence of reference material producers, 2017

[2] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[3] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[4] DIN 1333:1992-02 Zahlenangaben

## 9. Information on and purchase of the CRM

Certified reference material BAM-M382a is supplied by
**Bundesanstalt für Materialforschung und -prüfung (BAM)**
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

Each disc will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.

## **Annex 1:** Calculation of uncertainty contribution of potential inhomogeneity (area)

Ag in BAM-M382a:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| r_0 | 4.41 | 4.59 | | | | | |
| r_in | 4.50 | 4.50 | 4.40 | 4.40 | | | |
| r_out | 4.50 | 4.40 | 4.50 | 4.40 | | | |
| | | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* | |
| Between groups | 0.004 | 2 | 0.002 | 0.4 | 0.684718451 | 4.737414128 | |
| Within groups | 0.035 | 7 | 0.005 | | | | |
| | | | | | | | |
| Total | 0.039 | 9 | | | | | |
| | | | | | | | |
| within-sd | 0.070710678 | | | | | | |
| | | | | | | | |
| effective n | 3.20 | | | | | | |
| *s_bb* | 0 | | | | | | |
| *s_bb_min* | 0.028899678 | | | | | | |
| *u_bb* | 0.028899678 | | | 4.46 | | | |
| | | | | | | | |
| *u_bb(rel.)* | 0.64797484 | | | | | | |

Fe in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 10.24 | 10.76 | | | | |
| r_in | 10.55 | 10.18 | 10.49 | 10.52 | | |
| r_out | 10.38 | 10.45 | 10.47 | 10.81 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.017675 | 2 | 0.0088375 | 0.184194529 | 0.83567848 | 4.737414128 |
| Within groups | 0.335854167 | 7 | 0.047979167 | | | |
| | | | | | | |
| Total | 0.353529167 | 9 | | | | |
| | | | | | | |
| within-sd | 0.219041472 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0 | | | | | |
| s_bb_min | 0.089522943 | | | | | |
| u_bb | 0.089522943 | | | | | |
| | | | | | | |
| u_bb(rel.) | 0.853819197 | | | | | |

Mg in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 1.63 | 1.78 | | | | |
| r_in | 1.80 | 1.90 | 1.80 | 1.80 | | |
| r_out | 1.70 | 1.80 | 1.80 | 1.80 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.021 | 2 | 0.0105 | 2.8 | 0.127804525 | 4.737414128 |
| Within groups | 0.02625 | 7 | 0.00375 | | | |
| | | | | | | |
| Total | 0.04725 | 9 | | | | |
| | | | | | | |
| within-sd | 0.061237244 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| *s_bb* | 0.045927933 | | | | | |
| *s_bb_min* | 0.025027855 | | | | | |
| *u_bb* | 0.045927933 | | | | | |
| | | | | | | |
| *u_bb(rel.)* | 2.580220937 | | | | | |

Mn in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 2.36 | 2.40 | | | | |
| r_in | 2.43 | 2.41 | 2.41 | 2.43 | | |
| r_out | 2.43 | 2.48 | 2.47 | 2.51 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.01230215 | 2 | 0.006151075 | 8.438653253 | 0.013642516 | 4.737414128 |
| Within groups | 0.005102417 | 7 | 0.000728917 | | | |
| | | | | | | |
| Total | 0.017404567 | 9 | | | | |
| | | | | | | |
| within-sd | 0.026998457 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0.041163388 | | | | | |
| s_bb_min | 0.011034355 | | | | | |
| u_bb | 0.041163388 | | | | | |
| | | | | | | |
| u_bb(rel.) | 1.691808294 | | | | | |

Ni in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 2.43 | 2.65 | | | | |
| r_in | 2.54 | 2.48 | 2.56 | 2.64 | | |
| r_out | 2.67 | 2.58 | 2.81 | 2.61 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.03306815 | 2 | 0.016534075 | 1.71128457 | 0.248274087 | 4.737414128 |
| Within groups | 0.067632542 | 7 | 0.009661792 | | | |
| | | | | | | |
| Total | 0.100700692 | 9 | | | | |
| | | | | | | |
| within-sd | 0.098294413 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0.046342082 | | | | | |
| s_bb_min | 0.040173238 | | | | | |
| u_bb | 0.046342082 | | | | | |
| | | | | | | |
| u_bb(rel.) | 1.783691227 | | | | | |

Pb in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 1.58 | 2.37 | | | | |
| r_in | 2.26 | 1.73 | 1.66 | 2.01 | | |
| r_out | 1.63 | 1.77 | 1.98 | 1.81 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.04961575 | 2 | 0.024807875 | 0.28720159 | 0.758793628 | 4.737414128 |
| Within groups | 0.604645417 | 7 | 0.086377917 | | | |
| | | | | | | |
| Total | 0.654261167 | 9 | | | | |
| | | | | | | |
| within-sd | 0.293901202 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0 | | | | | |
| s_bb_min | 0.120118351 | | | | | |
| u_bb | 0.120118351 | | | | | |
| | | | | | | |
| u_bb(rel.) | 6.387575178 | | | | | |

S in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 6.46 | 6.74 | | | | |
| r_in | 7.00 | 6.90 | 6.80 | 7.00 | | |
| r_out | 6.90 | 7.00 | 7.00 | 6.90 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.1835 | 2 | 0.09175 | 8.469230769 | 0.013520922 | 4.737414128 |
| Within groups | 0.075833333 | 7 | 0.010833333 | | | |
| | | | | | | |
| Total | 0.259333333 | 9 | | | | |
| | | | | | | |
| within-sd | 0.1040833 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0.159017164 | | | | | |
| s_bb_min | 0.042539174 | | | | | |
| u_bb | 0.159017164 | | | | | |
| | | | | | | |
| u_bb(rel.) | 2.314660315 | | | | | |

Sn in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 3.66 | 3.94 | | | | |
| r_in | 3.90 | 4.00 | 4.10 | 4.00 | | |
| r_out | 4.10 | 4.30 | 3.90 | 4.00 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.1015 | 2 | 0.05075 | 2.388235294 | 0.161916128 | 4.737414128 |
| Within groups | 0.14875 | 7 | 0.02125 | | | |
| | | | | | | |
| Total | 0.25025 | 9 | | | | |
| | | | | | | |
| within-sd | 0.145773797 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| s_bb | 0.096014322 | | | | | |
| s_bb_min | 0.059578212 | | | | | |
| u_bb | 0.096014322 | | | | | |
| | | | | | | |
| u_bb(rel.) | 2.406373981 | | | | | |

Zn in BAM-M382a:

| | | | | | | |
|---|---|---|---|---|---|---|
| r_0 | 8.38 | 9.02 | | | | |
| r_in | 8.40 | 8.90 | 8.50 | 8.60 | | |
| r_out | 8.30 | 8.40 | 8.50 | 8.70 | | |
| | | | | | | |
| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
| Between groups | 0.0735 | 2 | 0.03675 | 0.6 | 0.574770747 | 4.737414128 |
| Within groups | 0.42875 | 7 | 0.06125 | | | |
| | | | | | | |
| Total | 0.50225 | 9 | | | | |
| | | | | | | |
| within-sd | 0.247487373 | | | | | |
| | | | | | | |
| effective n | 3.20 | | | | | |
| *s_bb* | 0 | | | | | |
| *s_bb_min* | 0.101148873 | | | | | |
| *u_bb* | 0.101148873 | | | | | |
| | | | | | | |
| *u_bb(rel.)* | 1.180266891 | | | | | |