



CCQM-K8 Key Comparison Monoelemental Calibration Solutions

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Note: In this report, the term „method“ is used according to the VIM and CCQM definitions. The units used for the results and the reference value are in agreement with T. Cvitas, Metrologia 1996, 33, 35-39.

1 Summary

Although different methods of measurement were applied, most of the participants achieved results within the required target range for the combined standard uncertainty of 0.5% relative for each element. The methods used were titrimetry, coulometry, gravimetry, isotope dilution mass spectrometry and inductive coupled plasma/emission spectrometry. As a conclusion, it can be stated that the CCQM-K8 key comparison reveals a high metrological quality of results.

2 Introduction

As aqueous monoelemental solutions are widely used as calibrants in element analysis by atomic spectrometry or other methods for element analysis, they are a decisive factor for the reliability of measurement results. For many of these solutions which are available from several private producers a very low uncertainty is declared on the label which in no way takes all uncertainty sources and possible changes of the declared value during storage into account. Market overviews carried out by LNE and EMPA have shown that not only the declared value is sometimes incorrect but the quoted uncertainty is far beyond reality in many cases. Regarding this fact, the inorganic working group of the CCQM initiated the CCQM-K8 key comparison on monoelemental solutions which was accepted by the CCQM at its 5th meeting in February 1999. EMPA and LNE were supposed to take the lead.

It was decided to choose four relevant elements and prepare solutions of a mass fraction of about 1 g/kg each. The methods of measurement were decided to be free of choice, however, a target value of 0.5 % combined standard uncertainty was required. Thus, this key comparison offers a possibility to prove whether a participating NMI is capable to measure elements in pure solutions with a sufficient accuracy. It also allows a comparison of different methods of measurement at a high level of accuracy.

3 Participants

Table 1 contains the names of all NMI having submitted valid results for at least three elements.

Table 1 Participants

Nr.	Institution	Country
1	BAM Bundesanstalt für Materialforschung und Prüfung	Germany
2	BNM-LNE Bureau National de Métrologie - Laboratoire National d'Essais	France
3	EMPA Federal Laboratories for Materials Testing and Research	Switzerland
4	KRISS Korean Research Institute of Standards and Science	Korea
5	LGC Laboratory of the Government Chemist	United Kingdom
6	NIMC National Institute of Materials and Chemical Research	Japan
7	NIST National Institute for Standards and Technology	USA
8	NPLI National Physical Laboratory of India	India
9	NRCCRM National Research Center for Certified Reference Materials	China
10	OMH National Office of Measures	Hungary
11	PTB Physikalisch-Technische Bundesanstalt	Germany
12	SMU Slovak Institute of Metrology	Slovakia
13	VNIIM D. I. Mendeleev Institute for Metrology	Russia

4 Samples

Monoelemental solutions were gravimetrically prepared from aluminium, copper, iron and magnesium. Aluminium was chosen as it represents an economically important monoisotopic element. Copper is a representative for a transition element with relevance in environmental analysis. Iron has some importance in clinical analysis. It is generally widely determined. Magnesium is a representative for the earth alkali elements.

4.1 Origin of the primary material (pure metal)

Aluminium and Magnesium were provided by NIST (Aluminium SRM 3101a, certificate from 22.04.1996 and Magnesium NP-Mg-1, certificate from 11.05.1999). Copper was provided by BAM (A-Primary-Cu 1, certificate from 30.07.1999). Iron was provided by LNE (B.N.M. 001, certificate from 01.11.1976). The metals were treated as recommended by the supplier before having been used.

4.2 Preparation and packing of the solutions

For each element a 10 l batch of a solution of a mass fraction of about 1 g/kg was gravimetrically prepared using a pure metal and both highly pure acid and water. The metal beads were weighed in a class E2 weighing room and transferred into a special FEP flask with prolonged neck using a teflon coated tweezer. The metal was treated in a laminar flow hood with diluted nitric acid whereby the acid concentration was increased during the dissolution process by adding amounts of concentrated nitric acid. In the case of Aluminium the dissolution reaction had to get started by adding concentrated hydrochloric acid. The reaction flask was covered with a FEP cap and cooled in an ice bath to avoid an uncontrolled violent reaction. After 6 hours the cooling bath was removed and the solution was allowed to stand for additional 12 hours at room temperature. No metal pieces were visible then. The clear solution was heated up to approximately 343 K for 1 hour to guarantee completion of the dissolution. Together with the diluting water the metal solution was then stored overnight in a class E2 weighing room to adapt the ambient temperature. After pouring the solution into a FEP coated mixing tank the flask was rinsed three times with water. The tank was positioned on a balance and the remaining amount of water was added very slowly to the solution using a thin teflon tube. As the weight was registered immediately before closing the mixing tank (teflon gasket) all evaporation effects were disregarded. The solution was shaken overhead for at least 24 hours and the samples were finally bottled by pumping the solution through a teflon pipe directly into the precleaned and dried HDPP-bottles with argon pressure (cleaning procedure see

technical protocol in Appendix A). Each bottle was immediately closed with a screw cap, wrapped with a PE foil, packed into a mylar foil, welded and labelled.

4.3 Homogeneity and stability

Homogeneity tests were carried out with randomly picked bottles using high precision ICP-OES and titrimetry. For each individual element the method that revealed the lowest repeatability was taken for the homogeneity assessment. In no case a significant inhomogeneity was observed. These data were also used for the approximation of inhomogeneity effects in the evaluation of type B uncertainty of the gravimetric reference value.

The stability of the packed samples in terms of evaporation was investigated by exposing the samples to air at a temperature of 295 K during 120 days. No significant evaporation was observed for the completely packed and sealed samples as described before. The observed evaporation of the closed PP bottles with and without a mylar bag is shown in Fig. 1. From these data it can be stated, that no significant evaporation has to be expected during the transport of the samples and during storing under original packaging. The weighing study revealed an average loss of weight of the unwrapped bottles of less than 0.007% per month. So even in the case of opening the bags a certain period of time before the analysis this effect should not be significant.

An additional analysis of an original sample was carried out one year after packing using titrimetry and high precision ICP-OES. The obtained values are shown in Fig. 2.

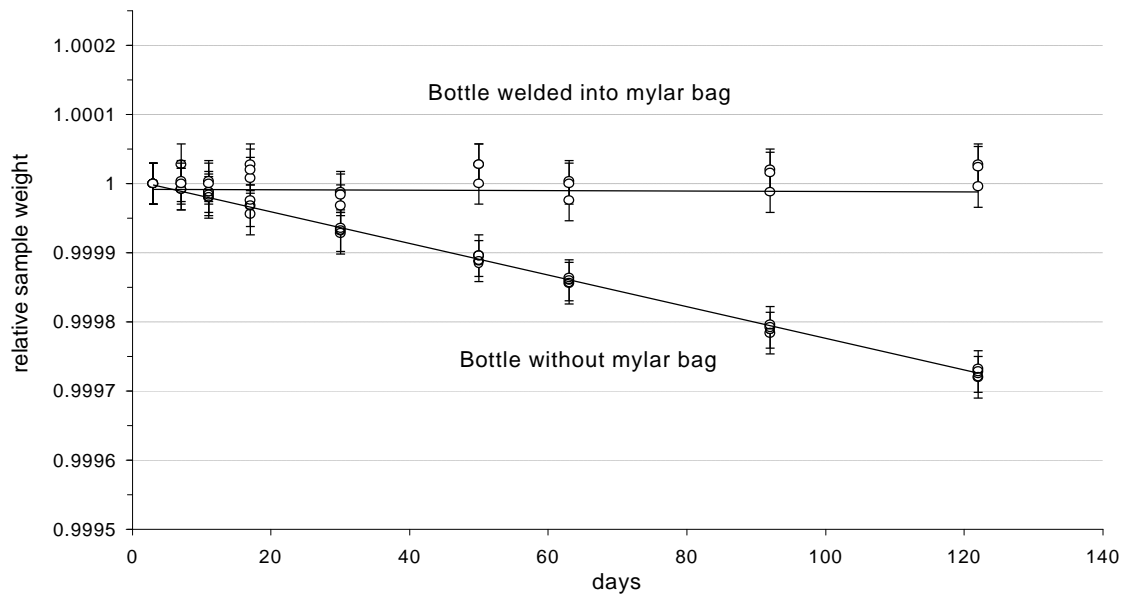


Fig. 1 Evaporation study of 250 ml HDPP bottles. Without mylar bag, a loss of weight of 0.007% per month was observed.

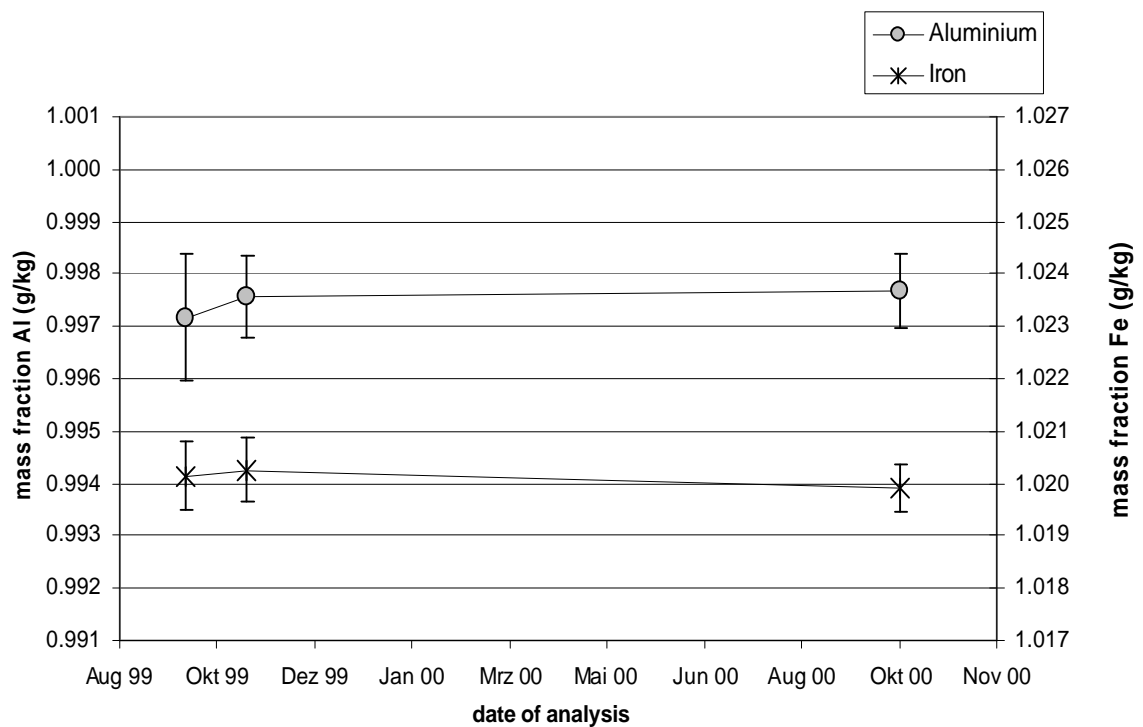


Fig. 2 Mean values from titrimetry and ICP/OES obtained from original Al and Fe samples within one year of storage at room temperature

4.4 Distribution of the samples

The samples were sent to the participants by DHL on October 1st in 1999. The following information was provided with each solution: type of element, type and approx. concentration of acid. All participants confirmed the reception of the samples originally sealed without any indication of damage. However a delay was caused by the customs of some countries.

Table 2 Confirmed reception date of the samples and responsible person

<i>Institution</i>	<i>Reception confirmed</i>	<i>Responsible person</i>
BAM	7.10.99	Ralf Matschat
BNM-LNE	7.10.99	Cédric Riviér
EMPA	5.10.99	Sergio Rezzonico
KRISS	4.10.99	Euijin Hwang
LGC	4.10.99	Chris Harrington
NIMC	5.10.99	Akiharu Hioki
NIST	4.10.99	Marc Salit
NPLI	27.10.99	A. K. Agrawal
NRCCRM	10.10.99	Ma Liandi
OMH	12.10.99	Éva Déak
PTB	4.10.99	Detlef Schiel
SMU	4.10.99	Michal Mariassy
VNIIM	12.11.99	L. A. Konopelko

5 Methods of measurement

The comparison neither was restricted to the use of primary methods of measurement nor to a special group of methods. However it was required that the results meet a target value for the combined standard uncertainty of smaller or equal 0.5% relative.

Those participants who applied more than one method and thus reported more than one result for some elements, clearly had to state which result shall be used for the calculation of the degree of equivalence. The methods of measurement which have been applied to obtain the final result are listed in Table 3 as reported by the participants. A more detailed description is given in the report of the CCQM study P30.

Table 3 *Methods of measurement as reported: ICP = inductively coupled plasma, ID = isotope dilution, OES = optical emission spectrometry, MS = mass spectrometry, TI = thermal ionization*

Institution	Methods of measurement			
	<i>Aluminium</i>	<i>Copper</i>	<i>Iron</i>	<i>Magnesium</i>
BAM	Titrimetry (EDTA)	ID-TI-MS and Electrogravimetry	Titrimetry (EDTA)	ID-ICP-MS and Titrimetry (EDTA)
BNM-LNE	Titrimetry (EDTA, back Zn)	Titrimetry (EDTA)	Titrimetry (EDTA)	Titrimetry (EDTA)
EMPA	Titrimetry (EDTA, back ZnSO ₄)	Titrimetry (EDTA)	Titrimetry (EDTA)	Titrimetry (EDTA)
KRISS	ICP-OES (internal standard)	ICP-OES (internal standard)	ICP-OES (internal standard)	ICP-OES (internal standard)
LGC	ICP-OES	ID-ICP-MS	ID-ICP-MS	ID-ICP-MS
NIMC	Titrimetry (CyDTA, back Pb(NO ₃) ₂)	Titrimetry (EDTA)	Titrimetry (EDTA, back Bi(NO ₃) ₃)	Titrimetry (EDTA)
NIST	ICP-OES (internal standard)	ICP-OES (internal standard)	ICP-OES (internal standard)	ICP-OES (internal standard)
NPLI	ICP-OES	ICP-OES	ICP-OES	ICP-OES
NRCCRM	Titrimetry (EDTA, back Pb)	Controlled potential Coulometry	Controlled potential Coulometry	Titrimetry (EDTA)
OMH	Gravimetry	Gravimetry		Gravimetry
PTB	ICP-MS	ID-ICP-MS	ID-ICP-MS	ID-ICP-MS
SMU	Titrimetry (EDTA, back Zn)	Titrimetry (EDTA, back Zn)	Titrimetry (EDTA)	Titrimetry (EDTA)
VNIIM	Titrimetry (EDTA, back Zn)	Titrimetry (EDTA, back Zn)	Titrimetry (EDTA)	Titrimetry (EDTA)

6 Instructions to participants

The participants were instructed concerning sample storing and handling, uncertainty calculation and reporting of the results. Details see technical protocol, appendix A.

7 Reference values

The reference values resulting from the gravimetric preparation is given in mass fraction (w , g/kg) and amount content (k , mol/kg) including a complete uncertainty statement for each value (Table 4). Details of the calculation of the reference values are described in Appendix B.

Aluminium: $w_{\text{Al}} = 0.99685$ g/kg $u_c(w_{\text{Al}}) = 0.00040$ g/kg
 $k_{\text{Al}} = 36.9460$ mmol/kg $u_c(k_{\text{Al}}) = 0.0148$ mmol/kg

Copper: $w_{\text{Cu}} = 0.98819$ g/kg $u_c(w_{\text{Cu}}) = 0.00003$ g/kg
 $k_{\text{Cu}} = 15.5507$ mmol/kg $u_c(k_{\text{Cu}}) = 0.0009$ mmol/kg

Iron: $w_{\text{Fe}} = 1.01966$ g/kg $u_c(w_{\text{Fe}}) = 0.00010$ g/kg
 $k_{\text{Fe}} = 18.2590$ mmol/kg $u_c(k_{\text{Fe}}) = 0.0018$ mmol/kg

Magnesium: $w_{\text{Mg}} = 1.00428$ g/kg $u_c(w_{\text{Mg}}) = 0.00009$ g/kg
 $k_{\text{Mg}} = 41.3190$ mmol/kg $u_c(k_{\text{Mg}}) = 0.0038$ mmol/kg

Table 4 Uncertainty budget (combined standard uncertainty, $k = 1$)

Uncertainty component		Aluminium	Copper	Iron	Magnesium
Metal weighing	$u_{\text{rel}}(W_M)$	$9.81 \cdot 10^{-6}$			
Metal weighing buoyancy correction	$u_{\text{rel}}(b_M)$	$1.23 \cdot 10^{-6}$	$< 10^{-7}$	$< 10^{-7}$	$2.25 \cdot 10^{-6}$
Solution weighing	$u_{\text{rel}}(W_{\text{Soln}})$	$1.18 \cdot 10^{-5}$			
Solution weighing buoyancy correction	$u_{\text{rel}}(b_{\text{Soln}})$	$4.33 \cdot 10^{-6}$			
Purity of metal	$u_{\text{rel}}(P_M)$	$3.97 \cdot 10^{-4}$	$5.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$
Homogeneity	$u_{\text{rel}}(H)$	$1.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$	$7.5 \cdot 10^{-5}$
Molar mass of metal	$u_{\text{rel}}(M_M)$	$7.4 \cdot 10^{-7}$	$4.7 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$
Comb. uncertainty of mass fraction	$u_{\text{c,rel}}(w_M)$	$4.10 \cdot 10^{-4}$	$3.35 \cdot 10^{-5}$	$9.35 \cdot 10^{-5}$	$8.84 \cdot 10^{-5}$
Comb. uncertainty of amount content	$u_{\text{c,rel}}(k_M)$	$4.10 \cdot 10^{-4}$	$5.77 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$9.19 \cdot 10^{-5}$

8 Results

Each participant was expected to report at least valid results for three elements.

Table 5 Results for Aluminium, Copper, Iron and Magnesium

<i>Institution</i>	<i>Results obtained</i>	<i>Reported value and comb. standard uncertainty (g/kg)</i>							
		<i>Aluminium</i>		<i>Copper</i>		<i>Iron</i>		<i>Magnesium</i>	
BAM	3.2.2000	0.9878	0.0023	0.9901	0.0048	1.0122	0.0018	1.0026	0.0067
BNM-LNE	24.1.2000	0.9961	0.0011	0.9878	0.00077	1.0219	0.00064	1.0071	0.0015
EMPA	11.2.2000	0.99795	0.00052	0.98860	0.00022	1.01998	0.00025	1.00466	0.00025
KRISS	2.2.2000	0.9973	0.0011	0.9898	0.0011	1.0196	0.0013	1.0089	0.0018
LGC	9.2.2000	0.9957	0.0023	0.9868	0.0024	1.0205	0.0042	1.0082	0.0011
NIMC	31.1.2000	0.9976	0.00041	0.9885	0.00025	1.0196	0.00031	1.0050	0.00080
NIST	11.2.2000	0.9974	0.00073	0.9881	0.00122	1.0201	0.00041	1.0046	0.00069
NPLI	14.3.2000	0.9875	0.0059	0.9739	0.00519	1.0455	0.0054	1.1896	0.0072
NRCCRM	10.1.2000	0.9974	0.0037	0.9888	0.0017	1.0162	0.0019	1.0073	0.0031
OMH	19.2.2000	1.0030	0.0019	0.9899	0.0043	not measured		1.0006	0.00187
PTB	1.2.2000	0.9985	0.0008	0.9890	0.0015	1.0175	0.0014	1.0015	0.0014
SMU	31.1.2000	0.99731	0.00028	0.98815	0.00034	1.01817	0.00041	1.00509	0.00031
VNIIM	9.3.2000	0.9963	0.0014	0.9872	0.0013	1.015	0.0018	1.009	0.0012

The results for individual elements are shown in the Figures 3 to 6 in an alphabetical order of the NMI. Each table also contains the reference range (value and combined standard uncertainty; $k=1$).

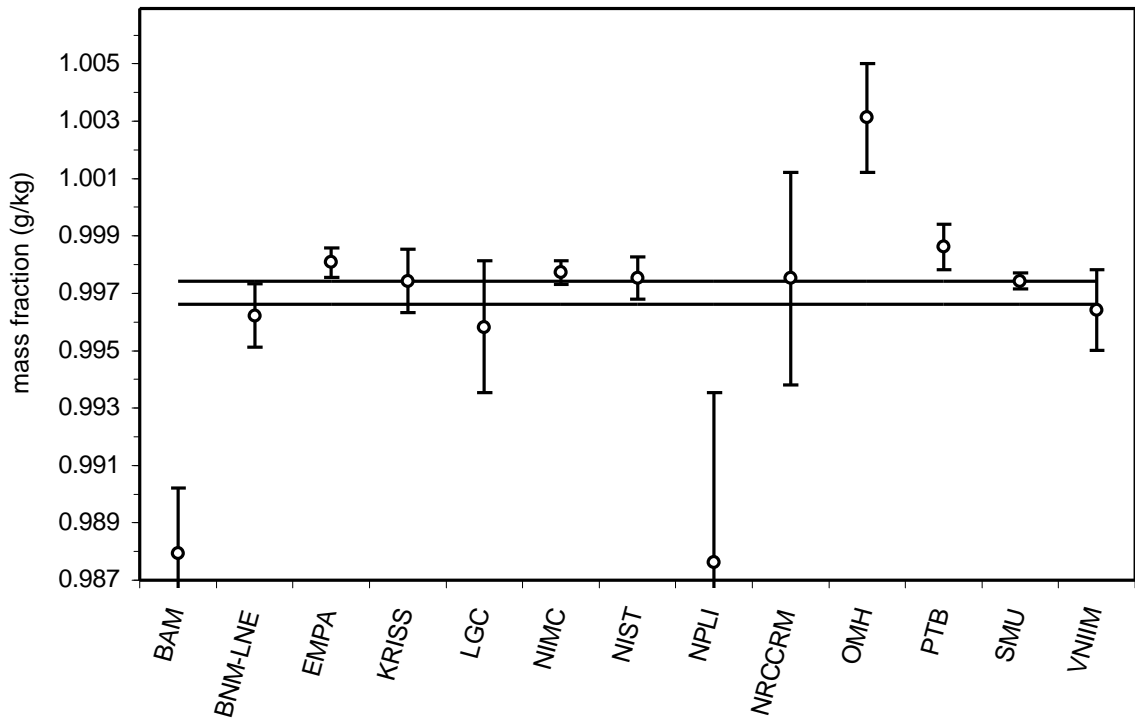


Fig. 3 Results of aluminium comparison

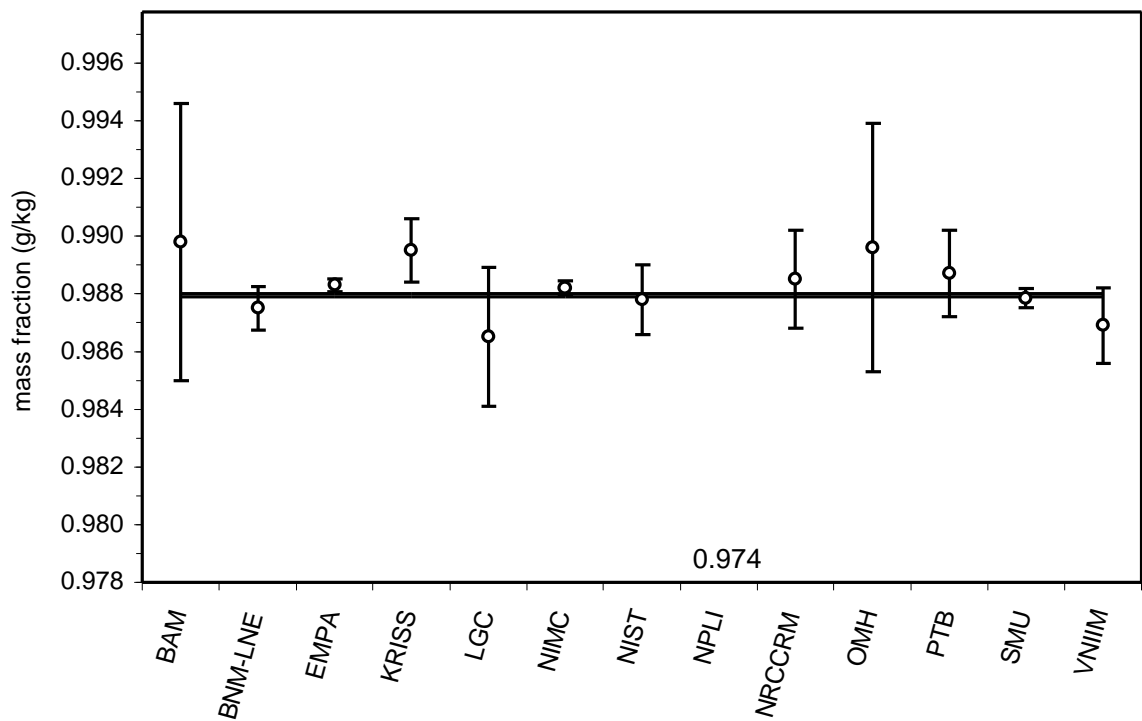


Fig. 4 Results of copper comparison

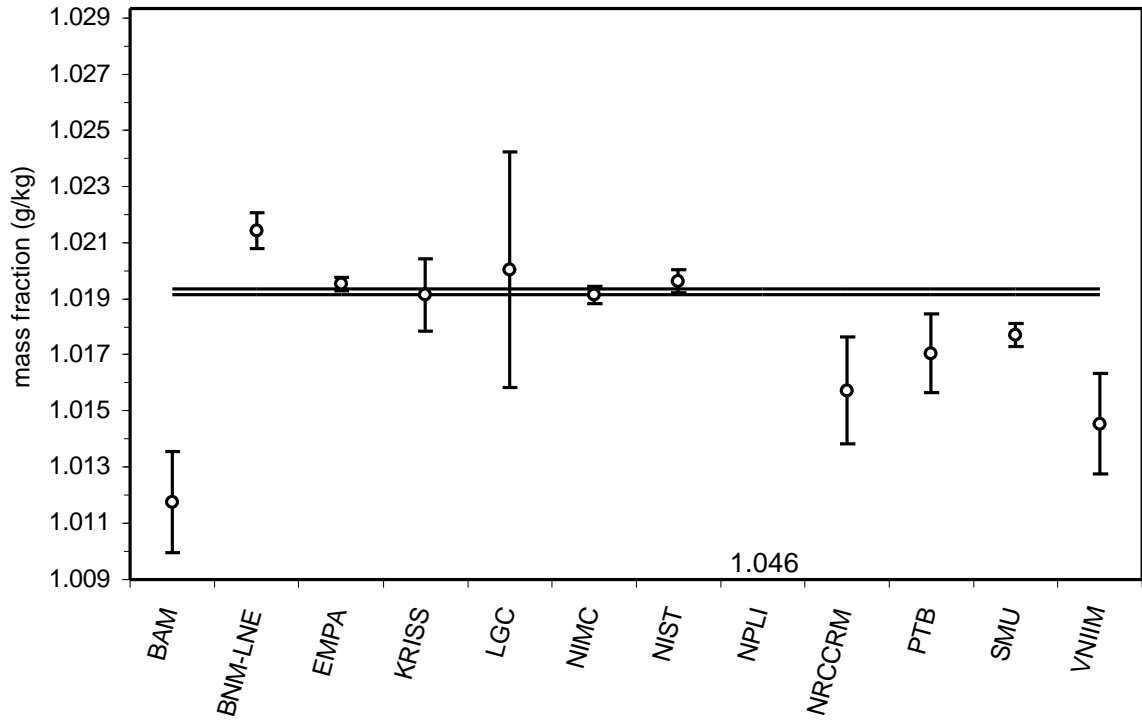


Fig. 5 Results of iron comparison

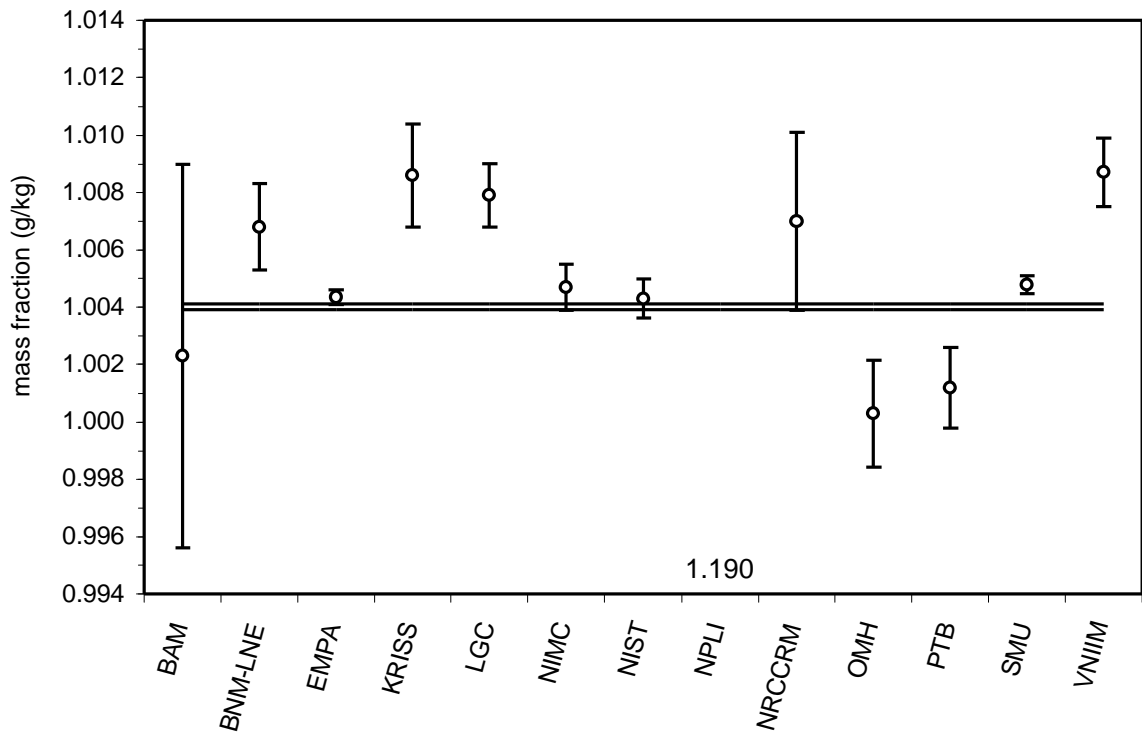


Fig. 6 Results of magnesium comparison

9 Discussion and conclusions

Most of the results meet the required target value of 0.5 % relative combined standard uncertainty. This is a promising fact regarding the variety of methods that have been applied. The methods range from the primary methods titrimetry, IDMS, gravimetry and coulometry to the non-primary method ICP-OES. Among a certain method, especially titrimetry which was mainly used, all sorts of procedures have been realised. Regarding the design of an experiment, also completely different concepts have been applied.

Significant differences can still be observed regarding the uncertainty evaluations. Some participants did not clearly distinguish between type A and type B evaluation of uncertainties. There is still no consensus on the treatment of uncertainty sources which may be composed of a type A and a type B component. The large differences in the reported uncertainties are also due to the experimental design and the number of replicates which allows a statistical reduction of the uncertainty to a different extent.

As a conclusion, the results demonstrate a high metrological quality not only of the primary methods, but also of other methods when applied properly.

10 Acknowledgement

Our special gratitude is addressed to those scientists who have contributed to the enforcement of this key comparison:

- A. Marschal and C. Riviér from LNE acted as co-pilot in the organization of the key comparison and the preparation of the technical protocol. LNE also provided the primary material for the Iron solutions. The costs for the dispatch of the samples by DHL were shared by LNE and EMPA.
- M. Sargent and co-workers from LGC gave valuable comments for preparing the technical protocol.
- M. Salit from NIST contributed importantly to the design of the key comparison (technical protocol and sample preparation). NIST also provided the primary materials for the Magnesium and Aluminium solutions. M. Salit also contributed to the homogeneity tests of the solutions which were carried out at EMPA both using ICP/OES and titrimetry.
- R. Matschat from BAM provided the primary material for the Copper solutions.
- D. Schiel from PTB gave valuable comments during the preparation of the technical protocol.

Appendix A

Technical Protocol

Introduction

Aqueous solutions of single or multiple elements are widely used as calibrants in atomic spectrometry. Therefore they are a decisive factor for the reliability of measurement results. In many commercial single element solutions the concentration of the analyte is declared as 1.000 g/l with an uncertainty of 0.002 – 0.005 g/l.

Several market survey studies carried out by LNE and EMPA have shown that in many cases the declared content as well as the declared uncertainty is not correct. Deviations up to several percent of the declared content were found. The CCQM inorganic working group proposed the analysis of monoelemental calibration solutions as a key comparison based on the above mentioned fact and the importance of these solutions. The key comparison was accepted by the CCQM and is carried out by EMPA and LNE as pilot laboratories.

1. Samples

- *Elements*: The following elements were chosen: Al, Cu, Fe, Mg. Aluminium represents an element with relevance in environmental analysis. Iron has some importance in clinical analysis and is generally widely applied. Magnesium is a representative for the earth alkali elements. Deviations were often found especially in Mg solutions.
- *Solutions A (key comparison)*: For each element a gravimetric solution of a mass fraction of about 1 g/kg is prepared by EMPA using a pure element or compound, highly pure acid and water. About 250 ml of each solution are provided. The analysis of solutions A is mandatory.
- *Solutions B (optional study)*: Additionally for each element a commercially available single element solution is provided by LNE. These solutions might contain more impurities than solutions A. Probably the concentration of the analyte is slightly changed by LNE. The origin of the solutions B is being kept anonymous. About 250 ml of each solution are provided. The analysis of solutions B is optional.
- *Packaging and labelling*: 250 ml polypropylen bottles are precleaned with water, acetone and ethanol, then rinsed with water, leached with 10% nitric acid, rinsed again with pure water and dried in a clean atmosphere. After filling in the solutions the bottles are closed with a screw cap and sealed. To avoid a relevant transpiration of the dilutant during transport the bottles are put in a sealed plastic foil and then in a sealed mylar foil. The following informations will be provided on the label of solutions A: type of element, type and approx. concentration of the acid. The origin and purity of the primary material used for the preparation of solutions A will be provided in the report. No further information than the type of the element is provided on the label of solutions B.
- *Distribution*: Eight bottles in total (solution A and B of each element) are dispatched to the participants by DHL. The participants will be informed by the pilot laboratory about the date of dispatching the samples. Participants are required to confirm the receipt of the sealed samples. In case of any damage of the samples the pilot laboratory has to be informed immediately.
- *Handling and storing instructions*: To avoid transpiration the samples shall be kept sealed until they are used. After receipt they shall be shaken rigorously and kept in an upright position. They have to be opened carefully and not kept open longer than needed for taking the required sample aliquot. Participants shall be aware that an accelerated evaporation of the solvent may occur when the solution is exposed to air, especially when drops are formed on the inner surface of the screw cap. As for the rest participants are

expected to handle the samples in a way that any contamination by air, the dilutant or the used equipment is avoided (work in clean environment, check of dilutant, reagents and all labware used). All dilutions or calibration solutions must be prepared gravimetrically taking into account all uncertainty sources.

2. Methods of measurement

The comparison is not restricted to the use of primary methods of measurement. The laboratory has to decide itself which methods are chosen. However the target value for the combined standard uncertainty is smaller or equal 0.5% relative. It is strictly required that only methods of measurement are used for which their rigorous estimate of the combined standard uncertainty is commensurate with the target value.

3. Reporting

All results shall be given in g/kg with a complete uncertainty statement according to the GUM (Guide to the Expression of Uncertainty in Measurement, ISO 1993). The uncertainty has to be evaluated at a level of one standard uncertainty including information on the number of effective degrees of freedom.

For solutions A participants are expected to contribute results for at least 3 elements. If more than one method is applied for a certain element, participants must clearly indicate whether they require their equivalence to the reference value to be evaluated on the basis of the mean or one specified method.

In order to allow a sufficient evaluation of the comparison, the report must include

- the complete calculation of the result including corrections e.g. of blanks and interferences. If the final result has been calculated from more than one method, the individual results from the contributing methods must also clearly be reported.
- the calculation of the uncertainty expressed as combined standard uncertainty. This must include the complete specification of the measurand, especially
 - the identification and quantification of all uncertainty sources (list or table)
 - the calculation of the combined standard uncertainty u_c (complete formula) and information on the number of effective degrees of freedom
 - a detailed description of the applied method of measurement. If more than one method is applied, a detailed description must be given for each method.
 - a description of the used equipment (e.g. type, technical specifications)
 - a description of the software used for data collecting and processing
 - informations about sample preparation (e.g. dilution, including type, origin and quality of the used dilutant)
 - informations about the reference material used for calibration (origin, purity, isotopic ratio if necessary) or any other material used during the analytical procedure
 - information on how the uncertainty of the used reference material has been evaluated

4. Reference value

The reference value of solutions A resulting from the gravimetric preparation will be given in g/kg including a complete uncertainty statement.

A reference value of solutions B will be calculated from the applied primary methods of measurement. However as this still is a subject of discussion the working group might agree on another procedure.

5. Proposed time schedule

The samples are distributed to participants in September. The results should be returned to EMPA by mid of January 2000. Draft A of the report will be sent to participants end of February for comments. Comments shall be returned to EMPA by end of March. It is intended to have a Draft B ready for discussion during the working group meeting in April.

6. Participants

Participation is open to all interested CCQM members and official observers who have sufficient experience in this type of measurement. If the CCQM member or observer does not participate itself another competent institute may be nominated.

7. Evaluation of equivalence (according to Appendix B of the MRA)

The equivalence of an NMI is evaluated on the basis of one result per element which has to be clearly indicated by the NMI. It is for individual pairs of NMI's to agree whether their results within the target range for the combined standard uncertainty demonstrate adequate bilateral equivalence for their specific need.

8. Finances

Each participant is responsible for its own costs of the measurements. The costs for the organisation of the key comparison as well as sample preparation and distribution is taken over by the pilot institutes. The primary material used for sample preparation is provided by different institutes.

9. Adress for correspondence

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Appendix B

Uncertainty budget for the gravimetric content value

The steps for preparation of the solutions A are shown in the flow diagram (Fig. 1) with the assigned uncertainty components. On the assumption that using the described procedures for dissolving and diluting the metals a quantitative dissolution of each metal is achieved. The uncertainty contributions of these steps are regarded as neglectable.

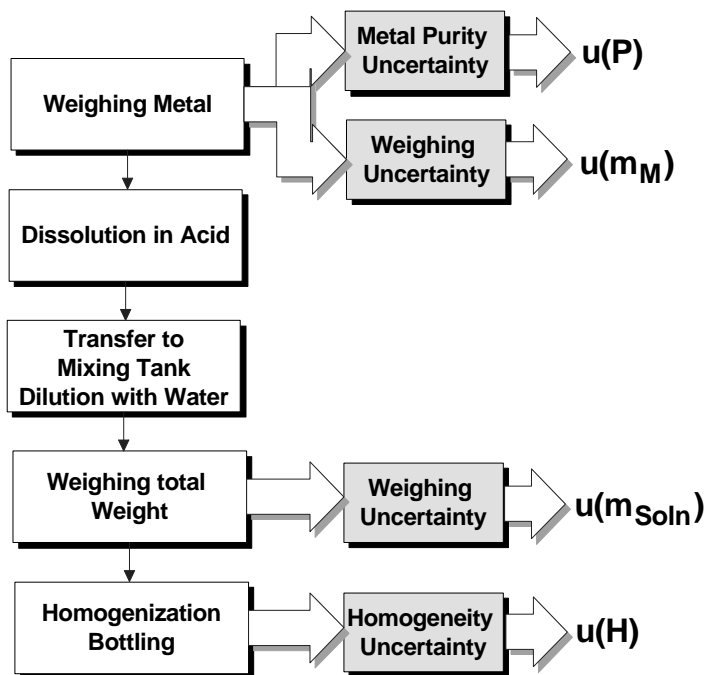


Fig. 1: Preparation of a mono-elemental solution and uncertainty components

The composition of the solutions is given as mass fraction w_M (metal mass m_M divided by total solution mass m_{Soln}) and as amount content k_M (number of moles metal n_M divided by the total solution mass m_{Soln}). The mass fraction w and the amount content k are defined by the following equations (where M is standing for “metal” and Soln is an abbreviation for “solution”)

$$w_M = \frac{m_M}{m_{\text{Soln}}} \quad (1)$$

$$k_M = \frac{w_M}{M_M} \quad (2)$$

Thus, the amount content k_M arises from the mass fraction w_i by division with the molar mass of the metal M_M . Therefore the uncertainty budget of the amount content includes the uncertainty of the molar mass of the metals. Further calculations were made for the mass fraction only.

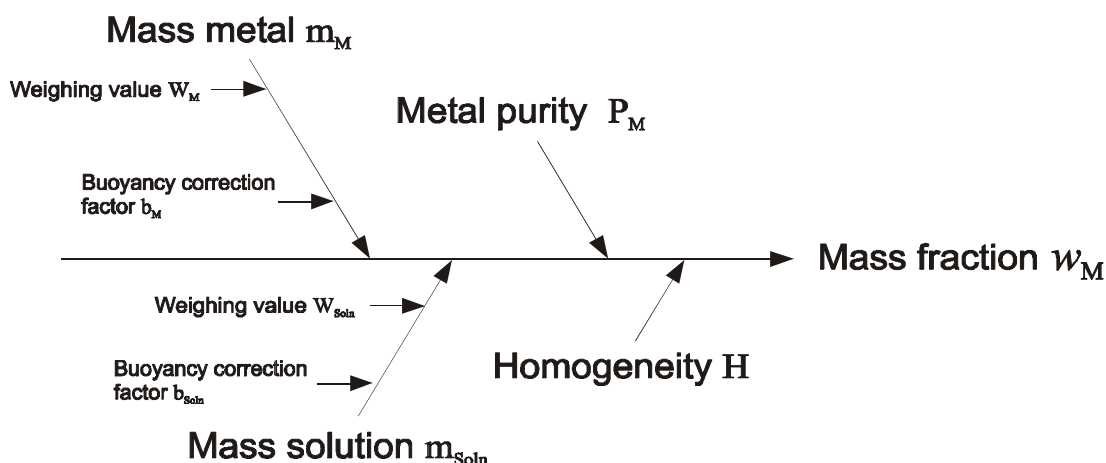
Using the symbol W for the weighing value (balance display) and b for the buoyancy correction factor the mass fraction is given by

$$w_M = \frac{m_M}{m_{\text{Soln}}} = \frac{W_M \cdot b_M}{W_{\text{Soln}} \cdot b_{\text{Soln}}} \quad (3)$$

Because the metal purity, inhomogeneity effects and evaporation during storage have to be considered too we can expand the equation with the three factors P_M for the Purity, H for the inhomogeneity effects and V for the evaporation contribution. The inhomogeneity factor H is expected to be exactly 1 whereas its uncertainty is different from zero. V is estimated to 1.00005 and its uncertainty is calculated. This leads to the expanded expression for the mass fraction

$$k_M = \frac{m_M}{m_{\text{Soln}} \cdot M_M} = \frac{W_M \cdot b_M \cdot P_M \cdot H \cdot V}{W_{\text{Soln}} \cdot b_{\text{Soln}} \cdot M_M} \quad (4)$$

and the following cause and effect diagram



These four major contributions are described individually. For the amount content the uncertainty of the molar mass of the metals has to be included as a fifth major contribution.

All uncertainties are calculated using the “law of propagation of uncertainty” [1,2,3]. When the result y of a measurand Y is determined from N quantities X_i with input estimates x_i the uncertainty $u(y)$ of y is estimated by the equation

$$u(y)^2 = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u(x_i)^2 \quad \text{where } y = f(x_1, x_2, \dots, x_N) \quad (5)$$

The partial derivative is often called sensitivity coefficient because it describes how the measurement result varies with changes in the values of the input estimates.

¹ ISO (1995) Guide to the expression of uncertainty in measurement, 1st edition

² EURACHEM (1995) Quantifying uncertainty in analytical measurement, 1st edn. EURACHEM

³ Miller JC, Miller JN (1993) Statistics for analytical chemistry, 3rd edn. Ellis Horwood, New York

It has to be noted that this equation is an approximation that is valid only if all the quantities are independant (not correlated). The equation can be simplified if all the quantities X_i are related to Y by multiplication or division only. In this case the uncertainty of the measurand estimate $u(y)$ can easily be determined by connecting the relative uncertainties of the input quantities by the “RSS“ method (square root of the sum-of-the-squares) [4].

$$\left(\frac{u(y)}{y}\right)^2 = \left(\frac{u(x_1)}{x_1}\right)^2 + \left(\frac{u(x_2)}{x_2}\right)^2 + \dots + \left(\frac{u(x_N)}{x_N}\right)^2 \tag{6}$$

with sensitivity coefficients given by

$$\frac{\partial f}{\partial x_i} = \frac{y}{x_i} \tag{7}$$

If all the input estimates x_i are related to y only by additions or subtractions the equation becomes

$$u(y)^2 = u(x_1)^2 + u(x_2)^2 + \dots + u(x_N)^2 \tag{8}$$

with all the sensitivity coefficients equal to 1.

Uncertainty of metal purity $u(P_M)$

The uncertainty contributions of the metal purity are given by the providing NMI and directly used for further calculations. In most cases the purity of a reference material is determined by the “100%-sum of impurities“ method whereby the uncertainties of the impurities are estimated values. Therefore the uncertainty of the metal purity $u(P)$ is also an estimation and so it is a sole type B uncertainty.

The following contents and uncertainties given by the providing NMI (in parentheses) are used

Analyte	Purity (P_M)	Uncertainty $u(P_M)$	NMI	Material Code
Aluminium	0.999295	0.000397	NIST	SRM 3101a
Copper	0.999968	0.000005	BAM	A-Primary-Cu 1
Iron	0.99995	0.00004	BNM / LNE	B.N.M. 001
Magnesium	0.999770	0.000044	NIST	NIST-NP-Mg-1

⁴ NIST Technical Note 1297 (1994) Guidelines for evaluating and expressing the uncertainty of NIST measurement results, 1st edn. NIST Gaithersburg

Uncertainty contribution for inhomogeneity effects $u(H)$

In cooperation with M. Salit (NIST) measurements were performed at EMPA to estimate the inhomogeneity for solutions A. The tests were carried out with eight bottles using ICP/OES and titrimetry. For each individual element the method that revealed the lowest repeatability was taken for the homogeneity assessment. This is certainly a conservative approximation because the repeatability of a method is not only influenced by inhomogeneity of the sample. However, the individual random fluctuations of the measurement method can not easily be quantified separately. Nevertheless this is not a reason for neglecting any sample inhomogeneities. Hence we decided to take the lowest revealed repeatability minus the uncertainty of the weighing as the uncertainty $u(H)$ of solution inhomogeneity. The uncertainty of the weighing was estimated to 10^{-5} .

$$u(H) = \sqrt{[\text{Repeatability}]^2 - [u(\text{Weighing})]^2} = \sqrt{[\text{Repeatability}]^2 - [10^{-5}]^2} \quad (9)$$

Analyte	Repeatability titrimetry	Repeatability ICP-OES	$u_{\text{rel}}(H)$
Aluminium	0.000101	0.000127	0.000100
Copper	0.000031	0.000119	0.000029
Iron	0.000155	0.000084	0.000083
Magnesium	0.000076	0.000123	0.000075

Uncertainty of the molar mass of the metals M_M

The data were taken from IUPAC Technical report „Atomic weights of the elements 1995“. It has to be noted that an atomic weight of an element $A_r(E)$ is not the same as its molecular mass M_E . The latter arises from the atomic weight by multiplication with the atomic mass unit (u) and the Avogadro constant (N_A). However, the uncertainties of N_A and u are not significant for the uncertainty budget and therefore the atomic weights are used.

Analyte	Molar mass M_M (g/mol)	Uncertainty $u(M_M)$ (g/mol)	Relative uncertainty $u_{\text{rel}}(M_M)$
Aluminium	26.981538	0.000002	7.4 E-7
Copper	63.546	0.003	4.7 E-5
Iron	55.845	0.002	3.6 E-5
Magnesium	24.3050	0.0006	2.5 E-5

Uncertainty of mass determination of metal and solution $u(m_i)$

The uncertainty of mass determination has to be split up into several contributions. As described above each mass m_i of a sample i arises from a weighing value W_i (balance display) corrected for its buoyancy using the buoyancy correction factor b_i

$$m_i = W_i \cdot b_i \quad (10)$$

The uncertainty of a weighing value is affected by several contributions which can not all be taken into account. We considered the following contributions: repeatability, nonlinearity, temperature coefficient and calibration weight effects. Further effects with a smaller uncertainty than 10^{-7} were neglected e.g. sample shape and height, eccentric loading effects etc..

An equation can therefore be written for the weighing value W_i

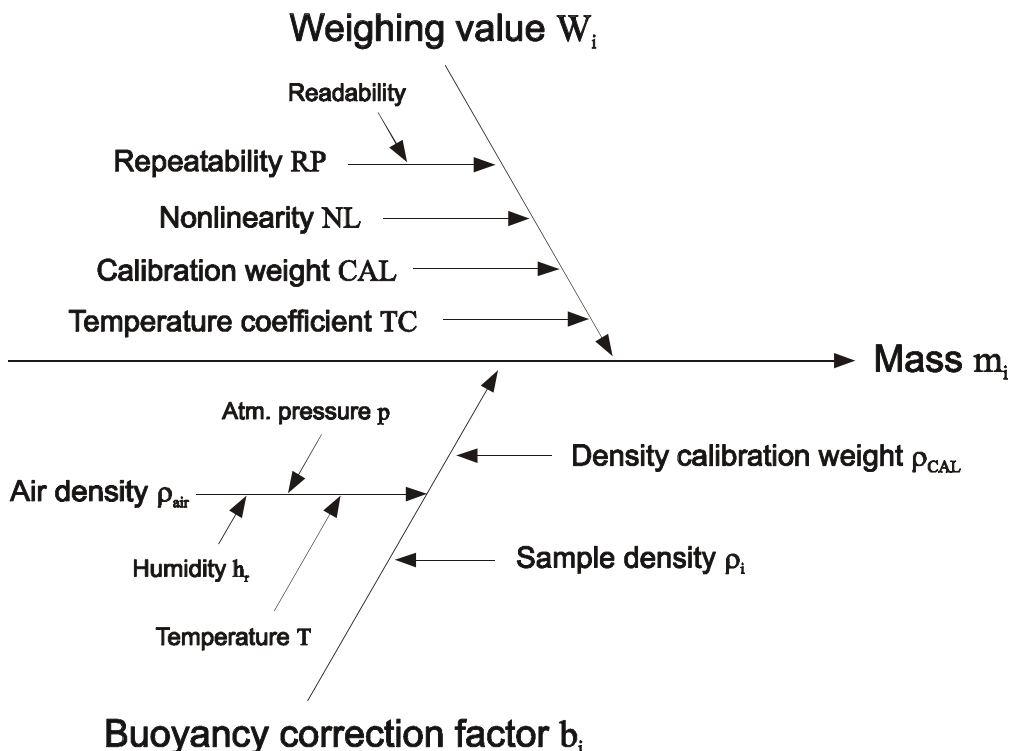
$$W_i = W_i' + \delta_{\text{Repeatability}} + \delta_{\text{Nonlinearity}} + \delta_{\text{Temperature coefficient}} + \delta_{\text{Calibration weight}} \quad (11)$$

where all quantities δ_i are connected additively and the input estimates of these quantities are expected to be zero. This is certainly not true for the corresponding uncertainties of these quantities. Therefore a more simple denotation for the above mentioned contributions characterised by the symbols RP, NL, TC and CAL was used.

Contribution	Symbol	Uncertainty for metal weighing value W_M on a Mettler AT 201	Uncertainty for solution weighing value W_{Soln} on a Mettler KA 32S	Type
Repeatability	$u_{\text{abs}}(\text{RP})$	0.006 mg	0.05 g	A
Nonlinearity	$u_{\text{abs}}(\text{NL})$	0.12 mg	0.20 g	B
Temperature coefficient	$u_{\text{rel}}(\text{TC})$	$1.5 \cdot 10^{-6} / \text{K}^{-1}$	$1.5 \cdot 10^{-6} / \text{K}^{-1}$	B
Uncertainty of calibration weights	$u_{\text{rel}}(\text{CAL})$	$1.5 \cdot 10^{-6}$	$3.7 \cdot 10^{-6}$	B

The repeatability was determined with a calibration weight having about the same mass as the sample and therefore the readability is included into this value. All other data are given by the manufacturer of the balances. The weighing room where the weighings were performed is fulfilling the OIML Class E2 conditions. The maximum temperature fluctuation ΔT in the weighing room is ± 0.3 K. Measurement uncertainty for pressure is less than 1 mbar and the uncertainty of relative air humidity measurement is less than 1%. A rectangular distribution is applied to approximate a normal distribution for all Type B components.

The major contributions by which the uncertainty of a mass is influenced can be represented as a cause and effect diagram



Uncertainty calculation of a weighing value $u(W_i)$

The type A uncertainty of a weighing value is given by

$$u^{TypeA}(W_i) = u_{abs}(RP) \tag{12}$$

The type B uncertainty of a weighing value is given by

$$u^{TypeB}(W_i) = \sqrt{2 \cdot \left(\frac{u_{abs}(NL)}{\sqrt{3}}\right)^2 + \left(\frac{u_{abs}(CAL)}{\sqrt{3}}\right)^2 + \left(\frac{u_{abs}(TC)}{\sqrt{3}}\right)^2} \tag{13}$$

$$= \sqrt{\frac{2}{3} u_{abs}(NL)^2 + \frac{m_i^2}{3} \left[u_{rel}(CAL)^2 + \left(u_{rel}(TC) \cdot \frac{T}{\sqrt{3}} \right)^2 \right]}$$

The combined uncertainty for a weighing value is expressed by

$$u_c(W_i) = \sqrt{u^{TypeA}(W_i)^2 + u^{TypeB}(W_i)^2} \tag{14}$$

Using a mass of 10 g and the specifications for a Mettler type balance AT 201 leads to

$$u^{\text{TypeA}}(W_M) = 6 \cdot 10^{-9} \text{ kg} \quad (15)$$

$$\begin{aligned} u^{\text{TypeB}}(W_M) &= \sqrt{\frac{2}{3}(0.12 \cdot 10^{-6})^2 + \frac{0.01^2}{3} \left[(1.5 \cdot 10^{-6})^2 + \left(1.5 \cdot 10^{-6} \cdot \frac{0.3}{\sqrt{3}} \right)^2 \right]} \\ &= \sqrt{9.6 \cdot 10^{-15} + 7.5 \cdot 10^{-17} + 2.25 \cdot 10^{-18}} \\ &= 9.8 \cdot 10^{-8} \text{ kg} \end{aligned} \quad (16)$$

$$u_c(W_M) = \sqrt{(6 \cdot 10^{-9} \text{ kg})^2 + (9.8 \cdot 10^{-8} \text{ kg})^2} = 9.8 \cdot 10^{-8} \text{ kg} \quad (17)$$

$$\frac{u_c(W_M)}{W_M} = \frac{9.81 \cdot 10^{-8} \text{ kg}}{0.010 \text{ kg}} = 9.8 \cdot 10^{-6} \quad (18)$$

Using a mass of 15 kg (solution incl. mixing tank) and the specifications for a Mettler type balance KA 32S leads to

$$u^{\text{TypeA}}(W_{\text{Soln}}) = 5 \cdot 10^{-5} \text{ kg} \quad (19)$$

$$\begin{aligned} u^{\text{TypeB}}(W_{\text{Soln}}) &= \sqrt{\frac{2}{3}(0.2 \cdot 10^{-3})^2 + \frac{15^2}{3} \left[(3.7 \cdot 10^{-6})^2 + \left(1.5 \cdot 10^{-6} \cdot \frac{0.3}{\sqrt{3}} \right)^2 \right]} \\ &= \sqrt{2.7 \cdot 10^{-8} + 1.0 \cdot 10^{-9} + 5.0 \cdot 10^{-12}} \\ &= 1.7 \cdot 10^{-4} \text{ kg} \end{aligned} \quad (20)$$

$$u_c(W_{\text{Soln}}) = \sqrt{(5 \cdot 10^{-5} \text{ kg})^2 + (1.7 \cdot 10^{-4} \text{ kg})^2} = 1.8 \cdot 10^{-4} \text{ kg} \quad (21)$$

$$\frac{u_c(W_{\text{Soln}})}{W_{\text{Soln}}} = \frac{1.77 \cdot 10^{-4} \text{ kg}}{15 \text{ kg}} = 1.2 \cdot 10^{-5} \quad (22)$$

Uncertainty of buoyancy correction factor $u(b)$

The buoyancy correction factor denoted as b_i for a sample i is given by the equation

$$b_i = \frac{\left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{CAL}}}\right)}{\left(1 - \frac{\rho_{\text{air}}}{\rho_i}\right)} \quad (23)$$

For the uncertainty calculation the partial derivatives are needed (sensitivity coefficients)

$$\left(\frac{\partial b_i}{\partial \rho_{\text{air}}}\right) = \frac{\rho_i}{\rho_{\text{CAL}}} \cdot \frac{(\rho_{\text{CAL}} - \rho_i)}{(\rho_i - \rho_{\text{air}})^2} \quad (24)$$

$$\left(\frac{\partial b_i}{\partial \rho_{\text{CAL}}}\right) = \frac{\rho_i}{(\rho_i - \rho_{\text{air}})} \cdot \frac{\rho_{\text{air}}}{\rho_{\text{CAL}}^2} \quad (25)$$

$$\left(\frac{\partial b_i}{\partial \rho_i}\right) = \frac{(\rho_{\text{CAL}} - \rho_{\text{air}})}{\rho_{\text{CAL}}} \cdot \frac{(-\rho_{\text{air}})}{(\rho_i - \rho_{\text{air}})^2} \quad (26)$$

Only the term with the coefficient of the air density uncertainty (24) has to be taken into account. The other two sensitivity coefficients expressed in equations (25) and (26) are much smaller and therefore these two contributions can be neglected. This is even true when the uncertainties of the calibration weight and the sample is higher than the uncertainty of the air density. The uncertainty for the buoyancy correction factor can therefore be approximated by using the air density contribution only:

$$u(b_i) = \sqrt{\left(\frac{\partial b_i}{\partial \rho_{\text{air}}}\right)^2 \cdot u(\rho_{\text{air}})^2} = \sqrt{\left(\frac{\rho_i}{\rho_{\text{CAL}}} \cdot \frac{(\rho_{\text{CAL}} - \rho_i)}{(\rho_i - \rho_{\text{air}})^2}\right)^2 \cdot u(\rho_{\text{air}})^2} \quad (27)$$

Referred to [5] the air density was approximated as follows

$$\rho_{\text{air}} = \frac{0.34848 \cdot p - 0.009024 \cdot h_r \cdot \exp(0.0612 \cdot (T - 273.15))}{T} \quad (28)$$

⁵ Kochsiek M, Gläser M (2000) Comprehensive mass metrology, Wiley VCH, Berlin

Using an estimated relative uncertainty for the air density of 0.005 (rather conservative) leads to the following uncertainties for the buoyancy correction factors for different materials

Sample i	Density ρ_i (kg/m ³)	$u(b_i)/b_i$
Aluminium	2700	$1.23 \cdot 10^{-6}$
Copper	8960	$6.70 \cdot 10^{-8}$
Iron	7860	$1.11 \cdot 10^{-8}$
Magnesium	1740	$2.25 \cdot 10^{-6}$
Solution	1010	$4.33 \cdot 10^{-6}$

Calculation of the combined uncertainties $u_c(w_M)$ and $u_c(k_M)$

As described before the mass fraction is given by the equation

$$w_M = \frac{W_M \cdot b_M \cdot P_M \cdot H}{W_{So\ In} \cdot b_{So\ In}} \quad (4)$$

where all the quantities are connected by multiplication or division only. Therefore the relative uncertainties of the input estimates can be combined directly to give the relative combined uncertainty of the measurand estimate

(29)

$$\frac{u(k_M)}{k_M} = \sqrt{\left(\frac{u(W_M)}{W_M}\right)^2 + \left(\frac{u(b_M)}{b_M}\right)^2 + \left(\frac{u(P_M)}{P_M}\right)^2 + \left(\frac{u(H)}{H}\right)^2 + \left(\frac{u(W_{So\ In})}{W_{So\ In}}\right)^2 + \left(\frac{u(b_{So\ In})}{b_{So\ In}}\right)^2 + \left(\frac{u(V)}{V}\right)^2 + \left(\frac{u(M_M)}{M_M}\right)^2}$$

For calculating the uncertainty of the amount content k_M the uncertainty of the molar mass of metal $u(M_M)/M_M$ must be considered as additional contribution. This can simply be done by adding the squared relative uncertainty into equation (29).

This leads finally to the relative uncertainties for the solution content given in mass fraction and amount of substance

Uncertainty component		Aluminium	Copper	Iron	Magnesium
Metal weighing	$u_{\text{rel}}(W_M)$	$9.81 \cdot 10^{-6}$			
Metal weighing buoyancy correction	$u_{\text{rel}}(b_M)$	$1.2 \cdot 10^{-6}$	$< 10^{-7}$	$< 10^{-7}$	$2.2 \cdot 10^{-6}$
Solution weighing	$u_{\text{rel}}(W_{\text{Soln}})$	$1.18 \cdot 10^{-5}$			
Solution weighing buoyancy correction	$u_{\text{rel}}(b_{\text{Soln}})$	$4.33 \cdot 10^{-6}$			
Purity of metal	$u_{\text{rel}}(P_M)$	$3.97 \cdot 10^{-4}$	$5.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$
Homogeneity	$u_{\text{rel}}(H)$	$1.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$	$7.5 \cdot 10^{-5}$
Molar mass of metal	$u_{\text{rel}}(M_M)$	$7.4 \cdot 10^{-7}$	$4.7 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$
Evaporation Correction	$u_{\text{rel}}(V)$	$5 \cdot 10^{-5}$			
Comb. uncertainty of mass fraction	$u_{\text{c,rel}}(w_M)$	$4.1 \cdot 10^{-4}$	$6.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$
Comb. uncertainty of amount content	$u_{\text{c,rel}}(k_M)$	$4.1 \cdot 10^{-4}$	$7.6 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$

And the following results with absolute uncertainties

Aluminium: $w_{\text{Al}} = 0.99690 \text{ g/kg}$ $u_{\text{c}}(w_{\text{Al}}) = 0.00041 \text{ g/kg}$
 $k_{\text{Al}} = 36.9478 \text{ mmol/kg}$ $u_{\text{c}}(k_{\text{Al}}) = 0.0153 \text{ mmol/kg}$

Copper: $w_{\text{Cu}} = 0.98824 \text{ g/kg}$ $u_{\text{c}}(w_{\text{Cu}}) = 0.00006 \text{ g/kg}$
 $k_{\text{Cu}} = 15.5515 \text{ mmol/kg}$ $u_{\text{c}}(k_{\text{Cu}}) = 0.0012 \text{ mmol/kg}$

Iron: $w_{\text{Fe}} = 1.01971 \text{ g/kg}$ $u_{\text{c}}(w_{\text{Fe}}) = 0.00011 \text{ g/kg}$
 $k_{\text{Fe}} = 18.2599 \text{ mmol/kg}$ $u_{\text{c}}(k_{\text{Fe}}) = 0.0020 \text{ mmol/kg}$

Magnesium: $w_{\text{Mg}} = 1.00433 \text{ g/kg}$ $u_{\text{c}}(w_{\text{Mg}}) = 0.00010 \text{ g/kg}$
 $k_{\text{Mg}} = 41.3211 \text{ mmol/kg}$ $u_{\text{c}}(k_{\text{Mg}}) = 0.0043 \text{ mmol/kg}$

Data sheets for the weighingsData sheet for the preparation of CCQM-K8 aluminium solution A

Data of metal weighing

Date	10-09-1999
Balance type	Mettler AT 201
Temperature (T)	294.9 K
Atm. Pressure (p)	946 hPa
Rel. air humidity (h_r)	53.2 %
Air density (ρ_{air})	1.111154 kgm ⁻³
Metal density (ρ_M)	2700 kgm ⁻³
Molar mass (M_M)	26.981538 gmol ⁻¹
Weighing value metal (W_M)	12.03339 g
Buoyancy correction factor (b)	1.000273
Mass metal (m_M)	12.03667 g
Metal purity (P_{Al})	0.999295

Data of solution weighing

Date	11-09-1999
Balance type	Mettler KA 32S
Temperature (T)	295.0 K
Atm. Pressure (p)	947 hPa
Rel. air humidity (h_r)	52.2 %
Air density (ρ_{air})	1.112273 kgm ⁻³
Solution density (ρ_{Soln})	1010 kgm ⁻³
Weighing value solution (W_{Soln})	12054.63 g
Buoyancy correction factor (b)	1.000963
Mass solution (m_{Soln})	12066.24 g
Mass of conc. nitric acid (W_{HNO_3})	244 g
Mass of conc. hydrochloric acid (W_{HCl})	481 g

Calculated content of CCQM-K8 aluminium solution A

mass fraction	$w_{\text{Al}} = m_{\text{Al}}/m_{\text{Soln}} P_{\text{Al}}$	=	0.99685 g/kg
amount content	$k_{\text{Al}} = w_{\text{Al}} \cdot M_{\text{Al}}^{-1}$	=	36.946 mmol/kg

Data sheet for the preparation of CCQM-K8 copper solution A

Data of metal weighing

Date	24-08-1999
Balance type	Mettler AT 201
Temperature (T)	295.3 K
Atm. Pressure (p)	945 hPa
Rel. air humidity (h _r)	50.3 %
Air density (ρ _{air})	1.109427 kgm ⁻³
Metal density (ρ _M)	8960 kgm ⁻³
Molar mass (M _M)	63.546 gmol ⁻¹
Weighing value metal (W _M)	12.19535 g
Buoyancy correction factor (b)	0.999985
Mass metal (m _M)	12.19517 g
Metal purity (P _{Cu})	0.999968

Data of solution weighing

Date	26-08-1999
Balance type	Mettler KA 32S
Temperature (T)	295.1 K
Atm. Pressure (p)	944 hPa
Rel. air humidity (h _r)	59.8 %
Air density (ρ _{air})	1.107960 kgm ⁻³
Solution density (ρ _{Soln})	1010 kgm ⁻³
Weighing value solution (W _{Soln})	12328.75 g
Buoyancy correction factor (b)	1.000959
Mass solution (m _{Soln})	12340.58 g
Mass of conc. nitric acid (W _{HNO₃})	410 g

Calculated content of CCQM-K8 copper solution A

mass fraction	$w_{\text{Cu}} = m_{\text{Cu}}/m_{\text{Soln}} \cdot P_{\text{Cu}}$	=	0.98819 g/kg
amount content	$k_{\text{Cu}} = w_{\text{Cu}} \cdot M_{\text{Cu}}^{-1}$	=	15.5507 mmol/kg

Data sheet for the preparation of CCQM-K8 iron solution A

Data of metal weighing

Date	30-08-1999
Balance type	Mettler AT 201
Temperature (T)	295.0 K
Atm. Pressure (p)	944 hPa
Rel. air humidity (h_r)	52.8 %
Air density (ρ_{air})	1.109192 kgm ⁻³
Metal density (ρ_M)	7860 kgm ⁻³
Molar mass (M_M)	55.845 gmol ⁻¹
Weighing value metal (W_M)	11.93363 g
Buoyancy correction factor (b)	1.000002
Mass metal (m_M)	11.93366g
Metal purity (P_{Fe})	0.99995

Data of solution weighing

Date	01-09-1999
Balance type	Mettler KA 32S
Temperature (T)	295.0 K
Atm. Pressure (p)	943 hPa
Rel. air humidity (h_r)	50.4 %
Air density (ρ_{air})	1.108289 kgm ⁻³
Solution density (ρ_{Soln})	1010 kgm ⁻³
Weighing value solution (W_{Soln})	11691.62 g
Buoyancy correction factor (b)	1.000960
Mass solution (m_{Soln})	11702.84 g
Mass of conc. nitric acid (W_{HNO_3})	422 g

Calculated content of CCQM-K8 iron solution A

mass fraction	$w_{\text{Fe}} = m_{\text{Fe}}/m_{\text{Soln}} P_{\text{Fe}}$	=	1.01966 g/kg
amount content	$k_{\text{Fe}} = w_{\text{Fe}} \cdot M_{\text{Fe}}^{-1}$	=	18.2590 mmol/kg

Data sheet for the preparation of CCQM-K8 magnesium solution A

Data of metal weighing

Date	18-09-1999
Balance type	Mettler AT 201
Temperature (T)	295.4 K
Atm. Pressure (p)	934 hPa
Rel. air humidity (h _r)	49.9 %
Air density (ρ _{air})	1.096083 kgm ⁻³
Metal density (ρ _M)	1740 kgm ⁻³
Molar mass (M _M)	24.3050 g mol ⁻¹
Weighing value metal (W _M)	12.68743 g
Buoyancy correction factor (b)	1.000493
Mass metal (m _M)	12.69369 g
Metal purity (P _{Mg})	0.99977

Data of solution weighing

Date	19-09-1999
Balance type	Mettler KA 32S
Temperature (T)	295.3 K
Atm. Pressure (p)	942 hPa
Rel. air humidity (h _r)	49.8 %
Air density (ρ _{air})	1.096083 kgm ⁻³
Solution density (ρ _{Soln})	1010 kgm ⁻³
Weighing value solution (W _{Soln})	12624.70 g
Buoyancy correction factor (b)	1.000949
Mass solution (m _{Soln})	12636.68 g
Mass of conc. nitric acid (W _{HNO₃})	408 g

Calculated content of CCQM-K8 magnesium solution A

mass fraction	$w_{Mg} = m_{Mg}/m_{Soln} P_{Mg}$	=	1.00428 g/kg
amount content	$k_{Mg} = w_{Mg} \cdot M_{Mg}^{-1}$	=	41.319 mmol/kg

Appendix C

Degrees of equivalence

Overview

Monoelemental standard solutions of aluminium, copper, iron and magnesium with a nominal value of 1 g/kg were gravimetrically prepared. Each participant had to provide a valid result for at least three elements. The methods of measurement were free of choice, however a uncertainty target of 0.5% relative combined standard uncertainty was required.

In this appendix the following abbreviations are used:

- D_i degree of equivalence of laboratory i with respect to the reference value
 U_i combined standard uncertainty of D_i
 x_i result of measurement carried out by laboratory i
 u_i combined standard uncertainty of x_i
 x_{grav} gravimetric reference value of the mass fraction
 u_{grav} combined standard uncertainty of x_{grav}

Results

Laboratory i	Results obtained	Aluminium		Copper		Iron		Magnesium	
		x_i	u_i	x_i	u_i	x_i	u_i	x_i	u_i
BAM	3.2.2000	0.9878	0.0023	0.9901	0.0048	1.0122	0.0018	1.0026	0.0067
BNM-LNE	24.1.2000	0.9961	0.0011	0.9878	0.00077	1.0219	0.00064	1.0071	0.0015
EMPA	11.2.2000	0.99795	0.00052	0.98860	0.00022	1.01998	0.00025	1.00466	0.00025
KRISS	2.2.2000	0.9973	0.0011	0.9898	0.0011	1.0196	0.0013	1.0089	0.0018
LGC	9.2.2000	0.9957	0.0023	0.9868	0.0024	1.0205	0.0042	1.0082	0.0011
NIMC	31.1.2000	0.9976	0.00041	0.9885	0.00025	1.0196	0.00031	1.0050	0.00080
NIST	11.2.2000	0.9974	0.00073	0.9881	0.00122	1.0201	0.00041	1.0046	0.00069
NPLI	14.3.2000	0.9875	0.0059	0.9739	0.00519	1.0455	0.0054	1.1896	0.0072
NRCCRM	10.1.2000	0.9974	0.0037	0.9888	0.0017	1.0162	0.0019	1.0073	0.0031
OMH	19.2.2000	1.0030	0.0019	0.9899	0.0043	not measured		1.0006	0.00187
PTB	1.2.2000	0.9985	0.0008	0.9890	0.0015	1.0175	0.0014	1.0015	0.0014
SMU	31.1.2000	0.99731	0.00028	0.98815	0.00034	1.01817	0.00041	1.00509	0.00031
VNIIM	9.3.2000	0.9963	0.0014	0.9872	0.0013	1.015	0.0018	1.009	0.0012
Grav. reference value		0.99685	0.00040	0.98819	0.00003	1.01966	0.00010	1.00428	0.00009

Degree of equivalence

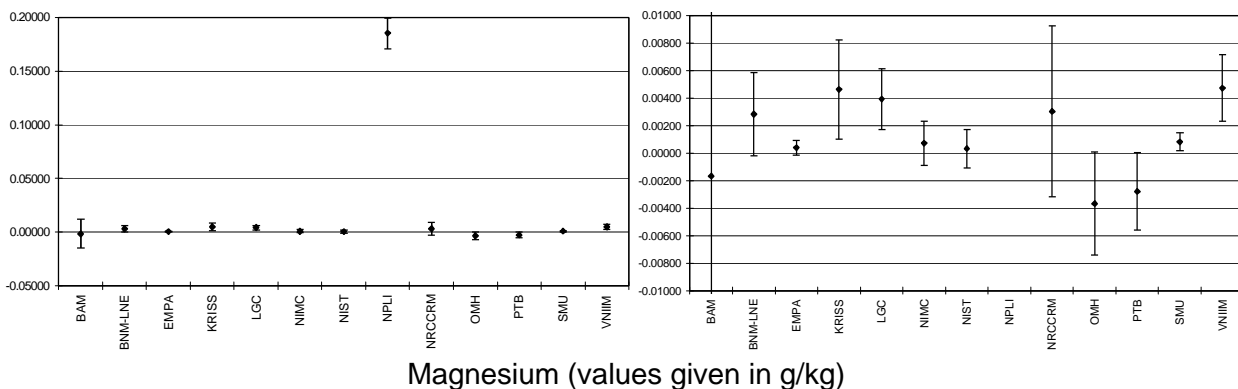
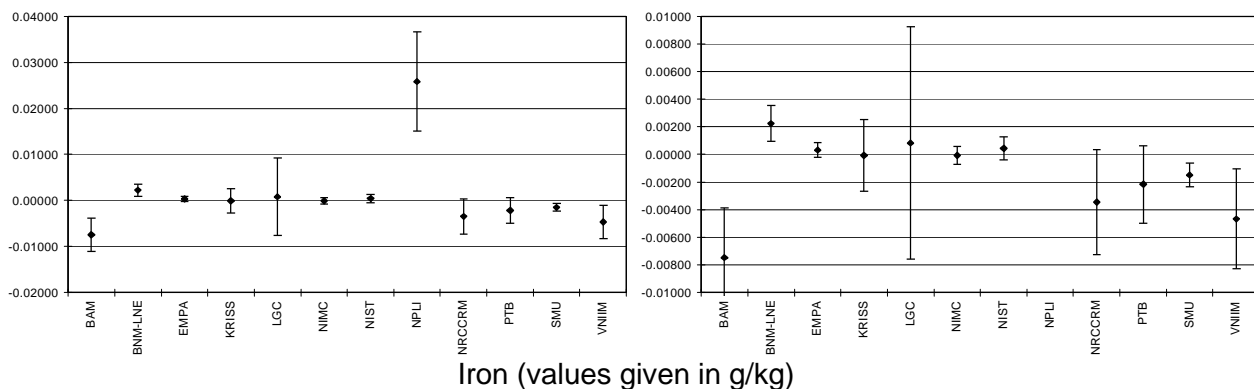
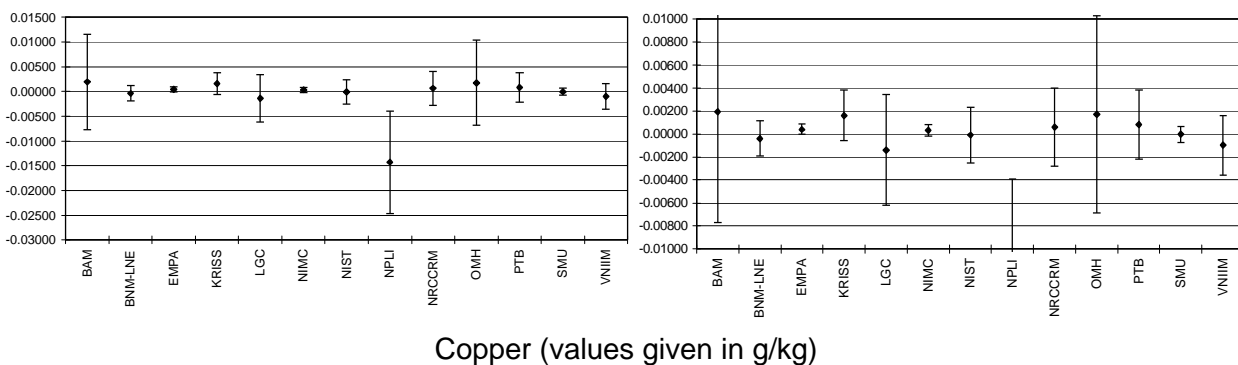
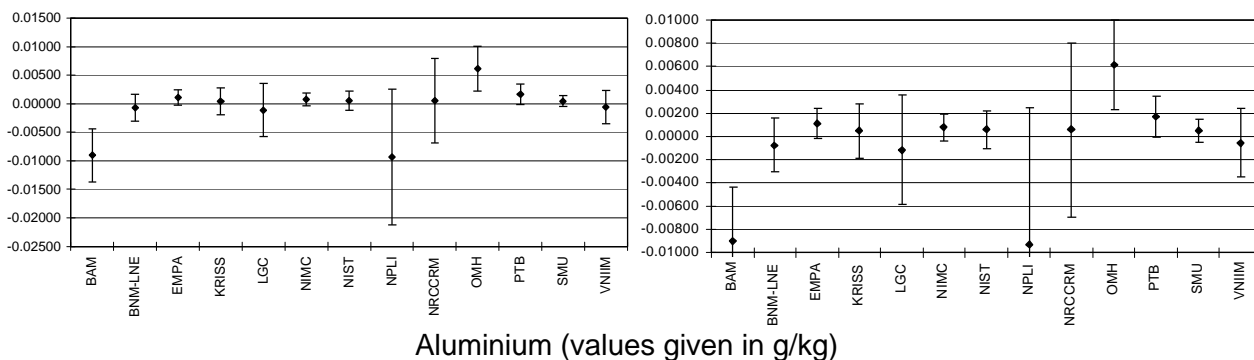
The degree of equivalence of each laboratory with respect to the reference value D_i and its combined standard uncertainty ($k = 2$) U_i , both expressed in g/kg, are given by the equations:

$$D_i = (x_i - x_{\text{grav}}) \quad \text{and} \quad U_i^2 = 2^2(u_i^2 + u_{\text{grav}}^2)$$

The degree of equivalence between two laboratories and its combined standard uncertainty ($k = 2$), both expressed in g/kg, are given by the equations:

$$D_{ij} = D_i - D_j = x_i - x_j \quad \text{and} \quad U_{ij}^2 = 2^2(u_i^2 + u_j^2)$$

Graphs



Tables

Table with degrees of equivalence for aluminium results

Lab *j* \longrightarrow

Lab *i* \downarrow

	BAM		BNM-LNE		EMPA		KRISS			
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}		
	g/kg		g/kg		g/kg		g/kg			
BAM	-0.0091	0.0047			-0.0083	0.0051	-0.0102	0.0047	-0.0095	0.0051
BNM-LNE	-0.0008	0.0023	0.0083	0.0051			-0.0019	0.0024	-0.0012	0.0031
EMPA	0.0011	0.0013	0.0102	0.0047	0.0019	0.0024			0.0007	0.0024
KRISS	0.0004	0.0023	0.0095	0.0051	0.0012	0.0031	-0.0007	0.0024		
LGC	-0.0011	0.0047	0.0079	0.0065	-0.0004	0.0051	-0.0022	0.0047	-0.0016	0.0051
NIMC	0.0008	0.0011	0.0098	0.0047	0.0015	0.0023	-0.0003	0.0013	0.0003	0.0023
NIST	0.0005	0.0017	0.0096	0.0048	0.0013	0.0026	-0.0006	0.0018	0.0001	0.0026
NPLI	-0.0093	0.0118	-0.0003	0.0127	-0.0086	0.0120	-0.0105	0.0118	-0.0098	0.0120
NRCCRM	0.0005	0.0074	0.0096	0.0087	0.0013	0.0077	-0.0006	0.0075	0.0001	0.0077
OMH	0.0061	0.0039	0.0152	0.0060	0.0069	0.0044	0.0050	0.0039	0.0057	0.0044
PTB	0.0017	0.0018	0.0107	0.0049	0.0024	0.0027	0.0006	0.0019	0.0012	0.0027
SMU	0.0005	0.0010	0.0095	0.0046	0.0012	0.0023	-0.0006	0.0012	0.0000	0.0023
VNIIM	-0.0006	0.0029	0.0085	0.0054	0.0002	0.0036	-0.0017	0.0030	-0.0010	0.0036

	LGC		NIMC		NIST		NPLI		NRCCRM	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	-0.0079	0.0065	-0.0098	0.0047	-0.0096	0.0048	0.0003	0.0127	-0.0096	0.0087
BNM-LNE	0.0004	0.0051	-0.0015	0.0023	-0.0013	0.0026	0.0086	0.0120	-0.0013	0.0077
EMPA	0.0022	0.0047	0.0003	0.0013	0.0006	0.0018	0.0105	0.0118	0.0006	0.0075
KRISS	0.0016	0.0051	-0.0003	0.0023	-0.0001	0.0026	0.0098	0.0120	-0.0001	0.0077
LGC			-0.0019	0.0047	-0.0017	0.0048	0.0082	0.0127	-0.0017	0.0087
NIMC	0.0019	0.0047			0.0002	0.0017	0.0101	0.0118	0.0002	0.0074
NIST	0.0017	0.0048	-0.0002	0.0017			0.0099	0.0119	0.0000	0.0075
NPLI	-0.0082	0.0127	-0.0101	0.0118	-0.0099	0.0119			-0.0099	0.0139
NRCCRM	0.0017	0.0087	-0.0002	0.0074	0.0000	0.0075	0.0099	0.0139		
OMH	0.0073	0.0060	0.0054	0.0039	0.0056	0.0041	0.0155	0.0124	0.0056	0.0083
PTB	0.0028	0.0049	0.0009	0.0018	0.0011	0.0022	0.0110	0.0119	0.0011	0.0076
SMU	0.0016	0.0046	-0.0003	0.0010	-0.0001	0.0016	0.0098	0.0118	-0.0001	0.0074
VNIIM	0.0006	0.0054	-0.0013	0.0029	-0.0011	0.0032	0.0088	0.0121	-0.0011	0.0079

	OMH		PTB		SMU		VNIIM	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	g/kg		g/kg		g/kg		g/kg	
BAM	-0.0152	0.0060	-0.0107	0.0049	-0.0095	0.0046	-0.0085	0.0054
BNM-LNE	-0.0069	0.0044	-0.0024	0.0027	-0.0012	0.0023	-0.0002	0.0036
EMPA	-0.0050	0.0039	-0.0006	0.0019	0.0006	0.0012	0.0017	0.0030
KRISS	-0.0057	0.0044	-0.0012	0.0027	0.0000	0.0023	0.0010	0.0036
LGC	-0.0073	0.0060	-0.0028	0.0049	-0.0016	0.0046	-0.0006	0.0054
NIMC	-0.0054	0.0039	-0.0009	0.0018	0.0003	0.0010	0.0013	0.0029
NIST	-0.0056	0.0041	-0.0011	0.0022	0.0001	0.0016	0.0011	0.0032
NPLI	-0.0155	0.0124	-0.0110	0.0119	-0.0098	0.0118	-0.0088	0.0121
NRCCRM	-0.0056	0.0083	-0.0011	0.0076	0.0001	0.0074	0.0011	0.0079
OMH			0.0045	0.0041	0.0057	0.0038	0.0067	0.0047
PTB	-0.0045	0.0041			0.0012	0.0017	0.0022	0.0032
SMU	-0.0057	0.0038	-0.0012	0.0017			0.0010	0.0029
VNIIM	-0.0067	0.0047	-0.0022	0.0032	-0.0010	0.0029		

Table with degrees of equivalence for copper results

Lab *j* →Lab *i* ↓

	<i>D_i</i> <i>U_i</i>		BAM		BNM-LNE		EMPA		KRISS	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	0.0019	0.0096			0.0023	0.0097	0.0015	0.0096	0.0003	0.0098
BNM-LNE	-0.0004	0.0015	-0.0023	0.0097			-0.0008	0.0016	-0.0020	0.0027
EMPA	0.0004	0.0004	-0.0015	0.0096	0.0008	0.0016			-0.0012	0.0022
KRISS	0.0016	0.0022	-0.0003	0.0098	0.0020	0.0027	0.0012	0.0022		
LGC	-0.0014	0.0048	-0.0033	0.0107	-0.0010	0.0050	-0.0018	0.0048	-0.0030	0.0053
NIMC	0.0003	0.0005	-0.0016	0.0096	0.0007	0.0016	-0.0001	0.0007	-0.0013	0.0023
NIST	-0.0001	0.0024	-0.0020	0.0099	0.0003	0.0029	-0.0005	0.0025	-0.0017	0.0033
NPLI	-0.0143	0.0104	-0.0162	0.0141	-0.0139	0.0105	-0.0147	0.0104	-0.0159	0.0106
NRCCRM	0.0006	0.0034	-0.0013	0.0102	0.0010	0.0037	0.0002	0.0034	-0.0010	0.0040
OMH	0.0017	0.0086	-0.0002	0.0129	0.0021	0.0087	0.0013	0.0086	0.0001	0.0089
PTB	0.0008	0.0030	-0.0011	0.0101	0.0012	0.0034	0.0004	0.0030	-0.0008	0.0037
SMU	0.0000	0.0007	-0.0020	0.0096	0.0003	0.0017	-0.0005	0.0008	-0.0017	0.0023
VNIIM	-0.0010	0.0026	-0.0029	0.0099	-0.0006	0.0030	-0.0014	0.0026	-0.0026	0.0034

	LGC		NIMC		NIST		NPLI		NRCCRM	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	0.0033	0.0107	0.0016	0.0096	0.0020	0.0099	0.0162	0.0141	0.0013	0.0102
BNM-LNE	0.0010	0.0050	-0.0007	0.0016	-0.0003	0.0029	0.0139	0.0105	-0.0010	0.0037
EMPA	0.0018	0.0048	0.0001	0.0007	0.0005	0.0025	0.0147	0.0104	-0.0002	0.0034
KRISS	0.0030	0.0053	0.0013	0.0023	0.0017	0.0033	0.0159	0.0106	0.0010	0.0040
LGC			-0.0017	0.0048	-0.0013	0.0054	0.0129	0.0114	-0.0020	0.0059
NIMC	0.0017	0.0048			0.0004	0.0025	0.0146	0.0104	-0.0003	0.0034
NIST	0.0013	0.0054	-0.0004	0.0025			0.0142	0.0107	-0.0007	0.0042
NPLI	-0.0129	0.0114	-0.0146	0.0104	-0.0142	0.0107			-0.0149	0.0109
NRCCRM	0.0020	0.0059	0.0003	0.0034	0.0007	0.0042	0.0149	0.0109		
OMH	0.0031	0.0098	0.0014	0.0086	0.0018	0.0089	0.0160	0.0135	0.0011	0.0092
PTB	0.0022	0.0057	0.0005	0.0030	0.0009	0.0039	0.0151	0.0108	0.0002	0.0045
SMU	0.0013	0.0048	-0.0004	0.0008	0.0000	0.0025	0.0143	0.0104	-0.0007	0.0035
VNIIM	0.0004	0.0055	-0.0013	0.0026	-0.0009	0.0036	0.0133	0.0107	-0.0016	0.0043

	OMH		PTB		SMU		VNIIM	
	g/kg		g/kg		g/kg		g/kg	
BAM	0.0002	0.0129	0.0011	0.0101	0.0020	0.0096	0.0029	0.0099
BNM-LNE	-0.0021	0.0087	-0.0012	0.0034	-0.0003	0.0017	0.0006	0.0030
EMPA	-0.0013	0.0086	-0.0004	0.0030	0.0005	0.0008	0.0014	0.0026
KRISS	-0.0001	0.0089	0.0008	0.0037	0.0017	0.0023	0.0026	0.0034
LGC	-0.0031	0.0098	-0.0022	0.0057	-0.0013	0.0048	-0.0004	0.0055
NIMC	-0.0014	0.0086	-0.0005	0.0030	0.0004	0.0008	0.0013	0.0026
NIST	-0.0018	0.0089	-0.0009	0.0039	0.0000	0.0025	0.0009	0.0036
NPLI	-0.0160	0.0135	-0.0151	0.0108	-0.0143	0.0104	-0.0133	0.0107
NRCCRM	-0.0011	0.0092	-0.0002	0.0045	0.0007	0.0035	0.0016	0.0043
OMH			0.0009	0.0091	0.0018	0.0086	0.0027	0.0090
PTB	-0.0009	0.0091			0.0009	0.0031	0.0018	0.0040
SMU	-0.0018	0.0086	-0.0009	0.0031			0.0010	0.0027
VNIIM	-0.0027	0.0090	-0.0018	0.0040	-0.0010	0.0027		

Table with degrees of equivalence for iron results

Lab *j* →Lab *i* ↓

	D_i U_i		BAM		BNM-LNE		EMPA		KRISS	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	-0.0075	0.0036			-0.0097	0.0038	-0.0078	0.0036	-0.0074	0.0044
BNM-LNE	0.0022	0.0013	0.0097	0.0038			0.0019	0.0014	0.0023	0.0029
EMPA	0.0003	0.0005	0.0078	0.0036	-0.0019	0.0014			0.0004	0.0026
KRISS	-0.0001	0.0026	0.0074	0.0044	-0.0023	0.0029	-0.0004	0.0026		
LGC	0.0008	0.0084	0.0083	0.0091	-0.0014	0.0085	0.0005	0.0084	0.0009	0.0088
NIMC	-0.0001	0.0007	0.0074	0.0037	-0.0023	0.0014	-0.0004	0.0008	0.0000	0.0027
NIST	0.0004	0.0008	0.0079	0.0037	-0.0018	0.0015	0.0001	0.0010	0.0005	0.0027
NPLI	0.0258	0.0108	0.0333	0.0114	0.0236	0.0109	0.0255	0.0108	0.0259	0.0111
NRCCRM	-0.0035	0.0038	0.0040	0.0052	-0.0057	0.0040	-0.0038	0.0038	-0.0034	0.0046
PTB	-0.0022	0.0028	0.0053	0.0046	-0.0044	0.0031	-0.0025	0.0028	-0.0021	0.0038
SMU	-0.0015	0.0008	0.0060	0.0037	-0.0037	0.0015	-0.0018	0.0010	-0.0014	0.0027
VNIIM	-0.0047	0.0036	0.0028	0.0051	-0.0069	0.0038	-0.0050	0.0036	-0.0046	0.0044

	LGC		NIMC		NIST		NPLI		NRCCRM	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	-0.0083	0.0091	-0.0074	0.0037	-0.0079	0.0037	-0.0333	0.0114	-0.0040	0.0052
BNM-LNE	0.0014	0.0085	0.0023	0.0014	0.0018	0.0015	-0.0236	0.0109	0.0057	0.0040
EMPA	-0.0005	0.0084	0.0004	0.0008	-0.0001	0.0010	-0.0255	0.0108	0.0038	0.0038
KRISS	-0.0009	0.0088	0.0000	0.0027	-0.0005	0.0027	-0.0259	0.0111	0.0034	0.0046
LGC			0.0009	0.0084	0.0004	0.0084	-0.0250	0.0137	0.0043	0.0092
NIMC	-0.0009	0.0084			-0.0005	0.0010	-0.0259	0.0108	0.0034	0.0039
NIST	-0.0004	0.0084	0.0005	0.0010			-0.0254	0.0108	0.0039	0.0039
NPLI	0.0250	0.0137	0.0259	0.0108	0.0254	0.0108			0.0293	0.0114
NRCCRM	-0.0043	0.0092	-0.0034	0.0039	-0.0039	0.0039	-0.0293	0.0114		
PTB	-0.0030	0.0089	-0.0021	0.0029	-0.0026	0.0029	-0.0280	0.0112	0.0013	0.0047
SMU	-0.0023	0.0084	-0.0014	0.0010	-0.0019	0.0012	-0.0273	0.0108	0.0020	0.0039
VNIIM	-0.0055	0.0091	-0.0046	0.0037	-0.0051	0.0037	-0.0305	0.0114	-0.0012	0.0052

	PTB		SMU		VNIIM	
	g/kg		g/kg		g/kg	
BAM	-0.0053	0.0046	-0.0060	0.0037	-0.0028	0.0051
BNM-LNE	0.0044	0.0031	0.0037	0.0015	0.0069	0.0038
EMPA	0.0025	0.0028	0.0018	0.0010	0.0050	0.0036
KRISS	0.0021	0.0038	0.0014	0.0027	0.0046	0.0044
LGC	0.0030	0.0089	0.0023	0.0084	0.0055	0.0091
NIMC	0.0021	0.0029	0.0014	0.0010	0.0046	0.0037
NIST	0.0026	0.0029	0.0019	0.0012	0.0051	0.0037
NPLI	0.0280	0.0112	0.0273	0.0108	0.0305	0.0114
NRCCRM	-0.0013	0.0047	-0.0020	0.0039	0.0012	0.0052
PTB			-0.0007	0.0029	0.0025	0.0046
SMU	0.0007	0.0029			0.0032	0.0037
VNIIM	-0.0025	0.0046	-0.0032	0.0037		

Table with degrees of equivalence for magnesium results

Lab *j* \longrightarrow

Lab *i* \downarrow

	D_i U_i		BAM		BNM-LNE		EMPA		KRISS	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	-0.0017	0.0134			-0.0045	0.0137	-0.0021	0.0134	-0.0063	0.0139
BNM-LNE	0.0028	0.0030	0.0045	0.0137			0.0024	0.0030	-0.0018	0.0047
EMPA	0.0004	0.0005	0.0021	0.0134	-0.0024	0.0030			-0.0042	0.0036
KRISS	0.0046	0.0036	0.0063	0.0139	0.0018	0.0047	0.0042	0.0036		
LGC	0.0039	0.0022	0.0056	0.0136	0.0011	0.0037	0.0035	0.0023	-0.0007	0.0042
NIMC	0.0007	0.0016	0.0024	0.0135	-0.0021	0.0034	0.0003	0.0017	-0.0039	0.0039
NIST	0.0003	0.0014	0.0020	0.0135	-0.0025	0.0033	-0.0001	0.0015	-0.0043	0.0039
NPLI	0.1853	0.0144	0.1870	0.0197	0.1825	0.0147	0.1849	0.0144	0.1807	0.0148
NRCCRM	0.0030	0.0062	0.0047	0.0148	0.0002	0.0069	0.0026	0.0062	-0.0016	0.0072
OMH	-0.0037	0.0037	-0.0020	0.0139	-0.0065	0.0048	-0.0041	0.0038	-0.0083	0.0052
PTB	-0.0028	0.0028	-0.0011	0.0137	-0.0056	0.0041	-0.0032	0.0028	-0.0074	0.0046
SMU	0.0008	0.0006	0.0025	0.0134	-0.0020	0.0031	0.0004	0.0008	-0.0038	0.0037
VNIIM	0.0047	0.0024	0.0064	0.0136	0.0019	0.0038	0.0043	0.0025	0.0001	0.0043

	LGC		NIMC		NIST		NPLI		NRCCRM	
	g/kg		g/kg		g/kg		g/kg		g/kg	
BAM	-0.0056	0.0136	-0.0024	0.0135	-0.0020	0.0135	-0.1870	0.0197	-0.0047	0.0148
BNM-LNE	-0.0011	0.0037	0.0021	0.0034	0.0025	0.0033	-0.1825	0.0147	-0.0002	0.0069
EMPA	-0.0035	0.0023	-0.0003	0.0017	0.0001	0.0015	-0.1849	0.0144	-0.0026	0.0062
KRISS	0.0007	0.0042	0.0039	0.0039	0.0043	0.0039	-0.1807	0.0148	0.0016	0.0072
LGC			0.0032	0.0027	0.0036	0.0026	-0.1814	0.0146	0.0009	0.0066
NIMC	-0.0032	0.0027			0.0004	0.0021	-0.1846	0.0145	-0.0023	0.0064
NIST	-0.0036	0.0026	-0.0004	0.0021			-0.1850	0.0145	-0.0027	0.0064
NPLI	0.1814	0.0146	0.1846	0.0145	0.1850	0.0145			0.1823	0.0157
NRCCRM	-0.0009	0.0066	0.0023	0.0064	0.0027	0.0064	-0.1823	0.0157		
OMH	-0.0076	0.0043	-0.0044	0.0041	-0.0040	0.0040	-0.1890	0.0149	-0.0067	0.0072
PTB	-0.0067	0.0036	-0.0035	0.0032	-0.0031	0.0031	-0.1881	0.0147	-0.0058	0.0068
SMU	-0.0031	0.0023	0.0001	0.0017	0.0005	0.0015	-0.1845	0.0144	-0.0022	0.0062
VNIIM	0.0008	0.0033	0.0040	0.0029	0.0044	0.0028	-0.1806	0.0146	0.0017	0.0066

	OMH		PTB		SMU		VNIIM	
	g/kg		g/kg		g/kg		g/kg	
BAM	0.0020	0.0139	0.0011	0.0137	-0.0025	0.0134	-0.0064	0.0136
BNM-LNE	0.0065	0.0048	0.0056	0.0041	0.0020	0.0031	-0.0019	0.0038
EMPA	0.0041	0.0038	0.0032	0.0028	-0.0004	0.0008	-0.0043	0.0025
KRISS	0.0083	0.0052	0.0074	0.0046	0.0038	0.0037	-0.0001	0.0043
LGC	0.0076	0.0043	0.0067	0.0036	0.0031	0.0023	-0.0008	0.0033
NIMC	0.0044	0.0041	0.0035	0.0032	-0.0001	0.0017	-0.0040	0.0029
NIST	0.0040	0.0040	0.0031	0.0031	-0.0005	0.0015	-0.0044	0.0028
NPLI	0.1890	0.0149	0.1881	0.0147	0.1845	0.0144	0.1806	0.0146
NRCCRM	0.0067	0.0072	0.0058	0.0068	0.0022	0.0062	-0.0017	0.0066
OMH			-0.0009	0.0047	-0.0045	0.0038	-0.0084	0.0044
PTB	0.0009	0.0047			-0.0036	0.0029	-0.0075	0.0037
SMU	0.0045	0.0038	0.0036	0.0029			-0.0039	0.0025
VNIIM	0.0084	0.0044	0.0075	0.0037	0.0039	0.0025		