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Final report of the key comparison CCQM-K72: purity of zinc with respect to six defined metallic analytes

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CCQM-K72
Purity of Zinc with respect to six defined metallic analytes

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1.   Motivation

High purity elements can serve as a realisation of the SI unit *amount of substance* for the specific element. Solutions prepared from high purity metals by applying gravimetric preparation and the concept of molar mass are used as 'calibration' solutions in many fields of analytical chemistry and provide the metrological basis in elemental analysis. Since ideal purity does not exist for real materials, the actual purity of the high purity material must be known with a specified uncertainty. Such purity data, however, are only accessible via measurements, which are limited by their measurement uncertainty. Aiming at uncertainties around 10^{-4} relative on the purity statement in almost all cases a direct measurement of the element in itself is not applicable, because the available methods are not sufficiently selective and/or accurate. Therefore the indirect approach is followed in order to achieve uncertainties at this level. In the indirect approach the mass fractions of all impurities, in other words all elements excepting the matrix element, are measured and their sum is subtracted from the value for ideal purity, which is 1 kg/kg. Uncertainties at the 10^{-4} level are aimed at because high purity metals are not only destined for being used as convenient primary realisations of the SI unit, but also as primary assays or so-called back-spikes in double isotope dilution mass spectrometry (IDMS). With double IDMS combined uncertainties down to $5 \cdot 10^{-4}$ can be achieved and therefore the uncertainty on the purity statement for these materials should be at or even lower than 10^{-4} relative in order not to compromise the IDMS results.

As a first step, only six metallic impurities are considered in previous studies and also in this comparison, in order to limit the effort within this study. Other metallic and non-metallic impurities might be subject to future CCQM studies. Zinc was chosen as matrix, due to its ease of handling and its high technical and economical relevance. A similar study design has been applied in CCQM-P107, the predecessor of the current key comparison K72. CCQM-P107 (Purity of Zn with respect to six metallic analytes) was carried out in 2007/2008, because its preceding study CCQM-P62 showed results differing by a factor of 8 (reported mass fraction w= 3.1 mg/kg – 25.4 mg/kg), which did not allow a follow-up as key comparison [1]. The results obtained within CCQM-P107 improved significantly and showed a spread between individual results of less than 30 % (reported mass fraction w= 8.1 mg/kg – 10.7 mg/kg) [2]. On this basis the IAWG decided to start the key comparison K72 with a parallel pilot study P107.1.

Preferred, of course, is the full characterization of such a material, which admittedly is considerably more work than the quantification of only six analytes. A recent example for a complete characterization of a high purity Ag material is given in ref. [3]. The importance of completely characterized high purity metals which serve as realization of the SI has been recognized by the European Commission. This is clearly expressed by funding the project "Primary standards for challenging elements" (EMRP-SIB09 [4]) through the European Metrology Research Programme. Also CCQM is aware of the difference between a characterization based on only six analytes and a complete characterization. Therefore, the pilot study CCQM-P149 has been initiated and already started, which focuses on the fit-for-purpose approaches for the purity determination of metals (here: zinc) to be used as primary standards in elemental analysis.

Note: The topic of this comparison is the measurement of the purity of zinc based on the determination of six analytes. The topic is not trace analysis of specific analytes in zinc. This subtle distinction defines different measurands.

2. Framework & predefinitions of the comparison

2.1 Measurand and reporting

Mandatory measurand
The sum of the Ag, Bi, Cd, Cr, Ni and Tl mass fractions in the bulk zinc material provided as sample: $w(Ag)+w(Al)+w(Cd)+w(Cr)+w(Ni)+w(Tl)$

Mandatory interim results
The individual mass fractions of Ag, Bi, Cd, Cr, Ni and Tl in the bulk zinc material provided as sample: $w(Ag)$; $w(Al)$; $w(Cd)$; $w(Cr)$; $w(Ni)$; $w(Tl)$

As already stated above, the aim of CCQM-K72 was to measure the sum of all requested impurities with sufficiently small uncertainty. Therefore it was useless to measure only five of the six requested impurities with very small uncertainty, but not the sixth analyte.

Each participant was asked to report one result for the sum of the six requested impurities and the individual results for the six impurities. The results had to be reported in mass fractions, accompanied by a full uncertainty statement including a combined standard uncertainty and an expanded uncertainty with a coverage factor applied. In addition the report had to include technical details on the measurement procedure, traceability links and uncertainty contributions.

2.2 Methods of measurement

Each participant was free to use any suitable method(s) for the measurement of the individual impurities. In case several methods were used for one specific impurity, only one (composite) result had to be reported.

Methods with highest metrological quality, such as IDMS, were in principle not excluded. It should be considered, that in contrast to the artificially reduced impurity analysis in CCQM-K72 real impurity analysis requires the quantification of all impurities. The whole range of elements including also mono-isotopic elements is impracticable for IDMS. However, IDMS may be used to determine single impurities where lower uncertainties become necessary due to higher concentration levels.

More suitable for purity determination are multi-element techniques enabling quantification at trace levels such as IDMS or GDMS. Important in this context is the ability of providing traceable measurement results. Preferred are procedures, which provide traceability in the shortest possible way e.g. by calibration against sufficiently pure materials. However, procedures requiring matrix reference materials for calibration (e.g. solid sampling techniques) are not excluded provided the matrix reference material used is stated, a proper uncertainty estimation was carried out and traceability is enabled.

2.3   Guidance values and target uncertainty

The material was selected in a way that the individual mass fractions of the six requested analytes range was between 0.1 mg/kg and 5.0 mg/kg.

Since this type of purity analysis most commonly is applied to high purity materials, even a rather large relative target uncertainty of 30 % (k=1) on the individual impurities was considered to be fit for purpose.

2.4   Key comparison reference value (KCRV)

Reference values based on IDMS were provided for w(Ag), w(Cd), w(Cr), w(Ni) and w(Tl). As Al is mono-isotopic, IDMS cannot be used in this case. Therefore, the reference value for Al is based on the median of all accepted results. The KCRV for the sum of the six metallic impurities consequently is calculated from the IDMS results for w(Ag), w(Cd), w(Cr), w(Ni) and w(Tl) and the median of all accepted results for w(Al).

This procedure has been proved successful for the reference values in CCQM-P62 and P107 and has been decided beforehand for CCQM-K72.

2.5   Time schedule of the comparison

The key comparison was agreed upon by IAWG in 2009. Due to time and logistical requirements at IAWG, BAM and the participating institutes the start was delayed until end of 2011. The preliminary time scale of CCQM-K72 listed in the technical protocol required updating. The final version of this time scale is given in Table 1. After updating, all deadlines have been met.

Table 1:   Final time scale of CCQM-K72.

Action	Deadline
Call for participants	End of March 2012
Registration of participants	30th of June 2012
Latest arrival of samples at participants	End of September 2012
Results reporting	31st of March 2013
Report A:	End of September 2013
Report B:	End of December 2013

3.   Participants

In total 9 NMIs or designated institutes participated in CCQM-K72 and provided in total nine independent data sets as listed in Table 2. BAM and PTB provided two additional reference data sets (see section results). All measurement results and details were reported by the participants in time. One institute (BAM) provided more than one result, which was bound for CCQM-P107.1 and which is listed together with the results of UNIIM in the CCQM-P107.1 report.

Table 2:   Participants in CCQM-K72.

Lab. No.	Responsible/Contact	Abbrev.	Institute	Country
1	Tsutomu Miura	NMIJ	National Metrology Institute of Japan	JP
2	Zhou Tao	NIM	National Metrology Institute P.R. China	CN
3	Nilgün Tokman	UME	TÜBÍTAK UME National Metrology Institute	TR
4	Judith Velina Lara Manzano	CENAM	Centro Nacional de Metrología	MX
5	Rodrigo Caciano de Sena	INMETRO	National Institute of Metrology, Standardization and Industrial Quality	BR
6	Heinrich Kipphardt	BAM	Federal Institute for Materials Research and Testing	DE
7	Gregory C. Turk	NIST	National Institute of Standards and Technology	US
8	Ralph Sturgeon	NRCC	National Research Council of Canada Measurement Science and Standards	CD
9	Yong-Hyeon Yim	KRISS	Korea Research Institute of Standards and Science	KR

4.   Samples

4.1   Sample material and instructions for use

The starting material were five zinc ingots purchased from Alfa Aesar Johnson Matthey, Karlsruhe/DE with a nominal metal based purity of 99.99 % (Lot No. F26S010). Preliminary measurements demonstrated that two of the five ingots were different regarding their impurity levels. The remaining three ingots were cut in pieces of cubic geometry (4 mm^3) and pin geometry (about 3.5 mm $\times$ 3.5 mm $\times$ 20 mm) for GDMS measurements by water jet cutting. The samples in cubic geometry were packed in PE-bottles each containing about four pieces and 1.8 g zinc in total and send to the participants. Pin geometry samples were sent to NIM and NRCC on their request. In order to remove surface impurities participants were asked to etch the samples before use.

4.2   Homogeneity of the sample material

Based on theoretical considerations and confirmed by own previous investigations the impurities were expected to be distributed sufficiently homogeneously within the volumes relevant for analysis. Possible problems with contaminations were not detected in earlier investigations on this type of material. The randomised sampling for the individual bottles distributed, was supposed to make potential contaminations visible as within bottle variations. The material is sufficiently homogenous, when the variation of the specific mass fractions is significantly better than < 30 % (target uncertainty of individual mass fractions), expressed as standard deviation of repeated measurements.

The material was tested for homogeneity at BAM by J. Pfeifer using GDMS. Measurements within piece and between pieces were performed under repeatability conditions. For the nine individual pieces, five repeated measurements were performed. Cylindrical samples (OD x H = 8 mm x 20 mm) were cut from the

beginning the middle and the end of each ingot. These samples were pressed to flat disks (OD x H = 2 mm x 25 mm). Subsequently, the pressed samples were cleaned with ethanol, etched with nitric acid/water (1+5), repeatedly rinsed with water and ethanol and at last dried under a clean bench. Before measurements were recorded the samples were pre-sputtered for 2 minutes in the GDMS. The GDMS measurements were calibrated by Standard RSF, because for homogeneity tests only the reproducibility is of interest but not the trueness of the single results.

The results for the six analytes of interest for this key comparison are summarised in Table 3, where each sample value represents the mean of five repeated measurements. Looking at the standard deviation of the single mean values and the standard deviation of the mean of means, it is obvious that there is a visible between unit inhomogeneity for all elements excepting Ag. When performing a one way ANOVA (F-test) the results are significantly larger than the tabulated F-value for a nested design, F(0.01,8,36)=3.052. Only for Ag the F-test result is close to the tabulated value. This demonstrates a significant inhomogeneity of the material for GDMS measurements. From the data in Table 4 in principle an uncertainty contribution for inhomogeneity can be calculated, following common approaches (eqn. 1,[5]). The uncertainty contributions u_{bb} resulting from eqn. 1 are listed in Table 3 for each analyte.

$$u_{bb} = \sqrt{\left(\frac{MS_{among} - MS_{within}}{n} + \frac{MS_{within}}{n} \cdot e^{-\frac{MS_{among}}{MS_{within}}} \right)} \qquad \text{eqn. 1}$$

Table 3a: Homogeneity investigation of the Zn material by GDMS. Expressed by the mass fractions of Al, Ag and Cd on nine individual samples as described in the text. Each sample value represents the mean of five repeated measurements. For explanation of F-value, u_{bb} and u_{inhom} see text.

	Ag			Al			Cd		
	w / mg/kg	s / mg/kg	s_{rel} / %	w / mg/kg	s / mg/kg	s_{rel} / %	w / mg/kg	s / mg/kg	s_{rel} / %
Sample 1	0.646	0.012	2	0.257	0.024	9	0.422	0.013	3
Sample 2	0.606	0.027	4	0.181	0.007	4	0.375	0.015	4
Sample 3	0.639	0.037	6	0.286	0.008	3	0.419	0.022	5
Sample 4	0.691	0.044	6	0.319	0.017	5	0.490	0.015	3
Sample 5	0.606	0.056	9	0.197	0.008	4	0.442	0.014	3
Sample 6	0.683	0.048	7	0.286	0.013	5	0.507	0.030	6
Sample 7	0.642	0.029	5	0.254	0.011	4	0.549	0.019	4
Sample 8	0.629	0.040	6	0.263	0.012	5	0.477	0.022	5
Sample 9	0.671	0.025	4	0.199	0.016	8	0.484	0.023	5
Mean	0.680	0.031	5	0.249	0.047	19	0.463	0.053	11
F-value	3.36			57.6			35.4		
u_{bb}		0.026	3.8		0.047	19		0.052	11
u_{inhom}		0.012	1.8		0.018	7.3		0.020	4.4

Table 3b: Homogeneity investigation of the Zn material by GDMS. Expressed by the mass fractions of Cr, Ni and Tl on nine individual samples as described in the text. Each sample value represents the mean of five repeated measurements. For explanation of F-value, u_{bb} and u_{inhom} see text.

	Cr			Ni			Tl		
	w / mg/kg	s / mg/kg	s_{rel} / %	w / mg/kg	s / mg/kg	s_{rel} / %	w / mg/kg	s / mg/kg	s_{rel} / %
Sample 1	2.055	0.194	9	2.363	0.081	3	0.322	0.012	4
Sample 2	2.098	0.207	10	2.594	0.044	2	0.252	0.009	4
Sample 3	2.438	0.223	9	2.601	0.054	2	0.277	0.006	2
Sample 4	1.984	0.078	4	2.860	0.147	5	0.345	0.007	2
Sample 5	1.450	0.032	2	2.253	0.048	2	0.287	0.008	3
Sample 6	1.751	0.022	1	2.489	0.149	6	0.319	0.012	4
Sample 7	1.576	0.056	4	2.195	0.093	4	0.372	0.015	4
Sample 8	1.511	0.023	1	2.402	0.121	5	0.272	0.012	5
Sample 9	1.587	0.028	2	2.163	0.102	5	0.353	0.012	3
Mean	1.828	0.334	18	2.435	0.226	9	0.311	0.041	13
F-value	35.3			25.1			74.0		
u_{bb}		0.33	18		0.22	9.0		0.041	13
u_{inhom}		0.13	7.0		0.087	3.6		0.016	5.1

The accordingly calculated u_{bb} values are not significantly smaller than the standard deviation of the mean of means, which is reasonable as according to the F-test significant inhomogeneity is detected by GDMS. However, these results have to be put into perspective of this key comparison on two reasons. First, the detected inhomogeneity is acceptable, because it is significantly lower than the target uncertainty (30%) for each analyte. And in terms of this target uncertainty the material is sufficiently homogenous. Second, the basic data have been obtained by GDMS, which uses a sample mass in the low mg range[1], whereas the majority of the applied methods (e.g. ICP-MS, AAS) used sample masses above 100 mg for wet chemical sample preparation. It is known from reference material certifications, that the smaller the sample mass the more important inhomogeneity issues will get. This is supported by the IDMS reference measurements, where maximum standard deviations (n > 4) significantly below 4 % have been observed for sample masses above 600 mg (Table 4). Additionally, the GDMS results provided by NRCC offer significantly lower standard deviations, although smaller sample masses have been used than for the BAM GDMS data.

Therefore a different and very pragmatic approach is used to estimate the uncertainty contribution due to inhomogeneity: the standard uncertainty of the mean is used as defined in eqn. 2 [6,7]:

$$u_{inhom} = u_{Mean} = \sqrt{\frac{(n-1)}{(n-3)}} \cdot \frac{s}{\sqrt{n}}$$

eqn. 2

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[1] Crater depth for one measurement 10.6 µm, diameter 0.75 cm, density of Zn ~ 7.14 g/cm^3 gives ~ 3.3 mg Zn

The so calculated uncertainty contributions for inhomogeneity are displayed in Table 3a and 3b and are used for the calculation of the uncertainties for the reference values and the KCRV.

As this approach is new and has not been used before it is decided to verify it by means of experimental data. For this purpose the experimental reproducibility of all participants, the homogeneity test and the reference measurements are listed in Table 3c. From this data the Median was calculated for each element, which should reflect an independent and realistic estimate for inhomogeneities in the Zn samples. When comparing this Median with u_{inhom} from Table 3a and 3b the agreement is reasonably good demonstrating the above described approach as valid.

Table 3c: Experimental reproducibility as reported by the participants, expressed as relative standard deviation for independently processed samples. The Median reflects the average contribution by inhomogeneity issues.

Institute	Experimental reproducibility in %					
	Ag	Al	Cd	Cr	Ni	Tl
NMIJ	3.71	39.5	1.85	2.12	5.40	2.80
NIM	4.3	3.3	6.2	3.3	2.3	2.3
UME	3.14	10.7	3.51	4.32	7.45	0.96
CENAM	3.36	16.3	0.71	1.77	3.22	2.13
INMETRO	0.2	11.1	1.7	4.9	5.7	0.5
BAM	1.38	8.8	4.92	3.80	7.83	1.40
NIST	1.2	26	5.5	8.9	8.0	0.58
NRCC	1.98	3.80	1.95	3.58	5.40	2.74
KRISS	1.4	26.7	2.6	7.2	17.8	2.6
GDMS BAM	5	19	11	18	9	13
IDMS BAM	0.36	-	3.71	-	-	0.09
IDMS PTB	-	-	-	0.83	3.42	-
MEDIAN	**2.0**	**13.7**	**3.5**	**3.8**	**5.7**	**2.1**
u_{inhom}	**1.8**	**7.3**	**4.4**	**7.0**	**3.6**	**5.1**

5.   Results and discussion

5.1   Reference measurements and reference values for KCRV

As described in chapter 2.4 (KCRV) it was decided to use results obtained by IDMS as reference values for w(Ag), w(Cd), w(Cr), w(Ni) and w(Tl). Due to its methodology and proven records in elemental analysis IDMS is widely accepted as reference method. When applied properly IDMS has the potential to be a primary method of measurement enabling SI-traceable values with smallest uncertainties, which has been demonstrated in numerous CCQM pilot studies and key comparison. Of course IDMS is not infallible by definition, but when applied properly this is no issue.

Table 4:   Reference values for the mass fractions of Ag, Al Cd, Cr, Ni and Tl in the CCQM-K72 sample.($U=k \cdot u_c$; with $k=2$)

Element	Type of Reference	Source	Mass fraction in mg/kg	u_c in mg/kg	U in mg/kg	s_{exp} in %
Ag	IDMS	BAM	1.4311	0.0029	0.0058	0.36
Al	Median	All	0.708	0.014	0.027	n.a.
Cd	IDMS	BAM	1.290	0.022	0.044	3.7
Cr	IDMS	PTB	3.669	0.036	0.072	0.83
Ni	IDMS	PTB	2.92	0.11	0.22	3.4
Tl	IDMS	BAM	0.8610	0.0013	0.0026	0.09

IDMS analysis for w(Ag), w(Cd), and w(Tl) in CCQM-K72 were carried out by D. Becker, M. Koenig and J. Vogl at BAM and for w(Cr) and w(Ni) in CCQM-K72 by R. Jährling and O. Rienitz at PTB. At BAM double IDMS in combination with thermal ionization mass spectrometry (TIMS) was applied. Prior to measurement the analytes Ag, Cd and Tl were separated from the matrix by ion exchange chromatographic procedures. At PTB exact matching double IDMS was applied in combination with SF-ICP-MS to Cr and Ni without separation. The results reported by BAM and PTB using IDMS are summarised in Table 4.

For Cd and Ni a spread unusually high for IDMS was observed in parallel measurements. This spread is reflected in the relative uncertainties for Cd and Ni, which are untypically large for double IDMS analysis. The only meaningful reasons for the spread observed are inhomogeneity issues. The same has been observed in CCQM-P107 for the Cr and Ni mass fractions in the zinc material. For more details on homogeneity/inhomogeneity see section 4.2. However, the spread observed by IDMS was so small compared with the uncertainties of the applied methods that it did not affect the assessment of the key comparison.

The results provided by IDMS were well consistent with the individual results reported by the participants. Taking inhomogeneity issues of the material into account the agreement between the IDMS values and the mean or median of all reported results is reasonably good. For Al, which basically is not accessible by IDMS due to its mono-isotopic nature, the median of the reported results was used as predefined (see section 2.4 KCRV). The median agrees well with the arithmetic mean within their standard uncertainties. Standard uncertainties for mean and

median are calculated as shown in eqn. 2 & 3. The median, however, is the better choice, because the distribution of the reported results is asymmetric. Due to observable inhomogeneities (see section 4.2), an uncertainty contribution for inhomogeneity is added to the final reference values and hence to the KCRV (eqn. 4). The reference values and the KCRV with their final uncertainties are displayed in Table 5.

Several participants reported that outlier values occurred presumably due to inhomogeneity. Those outliers have been included in the final result, but no measure for the inhomogeneity has been reported by the participants.

Standard uncertainty of the Median [6]:

$$u_{\text{Median}}^2 = \frac{\pi}{2n} \cdot \hat{\sigma}^2 \qquad \text{with} \qquad \hat{\sigma} = MAD_{\text{E}} = 1.483 \cdot MAD \qquad \text{eqn. 3}$$

Final combined uncertainty of reference values:

$$u_c^2 = u_{\text{Ref}}^2 + u_{\text{inhom}}^2 \qquad\qquad \text{eqn. 4}$$

Table 5: Reference values for the mass fractions of Ag, Al, Cd, Cr, Ni and Tl in the CCQM-K72 sample and KCRV for the sum of the six metallic impurities together with their combined uncertainties u_c and their expanded uncertainties U ($U = k \cdot u_c$; with $k=2$)

Element	Type of Reference	Mass fraction in mg/kg	u_c in mg/kg	U in mg/kg
Ag	Reference	1.431	0.026	0.052
Al	Reference	0.708	0.053	0.11
Cd	Reference	1.290	0.061	0.12
Cr	Reference	3.67	0.26	0.52
Ni	Reference	2.92	0.15	0.30
Tl	Reference	0.861	0.044	0.088
Σ_{Imp}	**KRCV**	**10.88**	**0.32**	**0.63**

5.2 Results as reported from the participants

For the summary as given in Table 6 the following applies:

❯ Results and combined standard uncertainties were taken from the reports
❯ If the results show one digit less than the combined standard uncertainty, a zero is appended to the result.
❯ Combined standard uncertainties with only one significant digit were left untouched
❯ Combined standard uncertainties were given in brackets and do apply to the last one or two digits of the value

Table 6: Summary of results for CCQM-K72 obtained from the reported data as described.

Institute	Mass fraction in mg·kg^{-1}						
	$w(\Sigma Imp)$	$w(Ag)$	$w(Al)$	$w(Cd)$	$w(Cr)$	$w(Ni)$	$w(Tl)$
1 NMIJ	10.93(17)	1.530(34)	0.49(11)	1.320(16)	3.670(44)	3.00(11)	0.920(16)
2 NIM	10.82(23)	1.32(8)	0.73(8)	1.20(9)	3.73(13)	3.08(8)	0.76(8)
3 UME	10.53(29)	1.304(45)	0.704(77)	1.167(45)	3.70(17)	2.82(22)	0.836(14)
4 CENAM	9.22(59)	1.13(16)	0.565(56)	1.06(10)	2.83(55)	2.789(91)	0.835(14)
5 INMETRO	10.4(2)	1.31(6)	0.73(8)	1.24(6)	3.54(12)	2.69(10)	0.89(2)
6 BAM	10.68(30)	1.37(10)	0.72(6)	1.30(7)	3.69(15)	2.75(22)	0.86(4)
7 NIST	11.14(21)	1.5216(83)	0.708(83)	1.259(31)	3.84(15)	2.93(10)	0.8820(25)
8 NRC	10.6(1.6)	1.472(96)	0.664(13)	1.209(65)	3.2(1.5)	3.21(15)	0.883(20)
9 KRISS	10.46(39)	1.258(49)	0.71(11)	0.983(42)	3.58(15)	3.19(33)	0.733(42)

with

$w(\Sigma Imp)$	Sum of the mass fractions of Ag, Al, Cd, Cr, Ni and Tl in the bulk of the zinc material
$w(Ag)$	Mass fraction of Ag in the bulk of the zinc material
$w(Al)$	Mass fraction of Al in the bulk of the zinc material
$w(Cd)$	Mass fraction of Cd in the bulk of the zinc material
$w(Cr)$	Mass fraction of Cr in the bulk of the zinc material
$w(Ni)$	Mass fraction of Ni in the bulk of the zinc material
$w(Tl)$	Mass fraction of Tl in the bulk of the zinc material

5.3 Summary of reported measurement details

The total of the reported measurement details gives such a huge amount of information that several pages for each analyte would be required. Therefore the amount of displayed details here is restricted to the measurement technique, the calibration approach and the source of traceability (Table 7). Please note, that within methods or even within laboratories different measurement procedures and calibration strategies were applied, as reflected in the different size of the reported measurement uncertainties. Three institutes (CENAM, NIM, NMIJ) applied more than one technique for some of the analytes, but reported composite results.

Table 7a: Overview on the applied analytical techniques, the calibration approaches used and the sources of traceability (abbreviations are explained below).

Institute	Ag			Al		
	Method	Calibration	Traceability	Method	Calibration	Traceability
NMIJ	ICP-SFMS	MM, IS	NMIJ CRM 3640	ICP-SFMS	MM, IS	NMIJ CRM 3605
NIM	ICP-SFMS	SA, CRM	GWB08610	ICP-SFMS GF-AAS	SA SA	GBW(E)080219
UME	ICPMS	SA, IS	NIST SRM 3151	ICPMS	SA, IS	NIST SRM 3101a
CENAM	ICP-SFMS GF-AAS	SA, IS EC, SA	NIST SRM 3151	ICP-SFMS	SA, IS	NIST SRM 3101
INMETRO	ICPMS	IS	NIST SRM 3151	ICPMS	IS	NIST SRM 3101a
BAM	ICP-SFMS	SA, IS	BAM *	ICP-SFMS	SA, IS	BAM *
NIST	ICP-QMS	SA, IS	NIST SRM 3151	ICP-QMS	SA, IS	NIST SRM 3101a
NRC	GDMS	MM, Ratio	NIST SRM-683	GDMS	MM, Ratio	BCR-354
KRISS	ICP-SFMS	EC	KRISS Ag	ICP-SFMS	EC	KRISS Al

* by means of commercial traceable standards, crosschecked in-house by BAM

Table 7b: Overview on the applied analytical techniques, the calibration approaches used and the sources of traceability (abbreviations are explained below).

Institute	Cd			Cr		
	Method	Calibration	Traceability	Method	Calibration	Traceability
NMIJ	ICP-SFMS	MM, IS	NMIJ CRM 3609	ICP-SFMS	MM, IS	NMIJ CRM 3617
NIM	ICP-SFMS, GF-AAS	SA, CRM	GBW08612	ICP-SFMS, GF-AAS	SA	GBW08614
UME	ICPMS	SA, IS	NIST SRM 3108	ICP-SFMS	SA, IS	NIST SRM 3112a
CENAM	ICP-SFMS GF-AAS	SA, IS EC, SA	DMR-461 DMR-461	ICP-SFMS GF-AAS	SA, IS EC, SA	DMR-440 DMR-440
INMETRO	ICPMS	IS	NIST SRM 3108	ICPMS	MM	NIST SRM 3112a
BAM	ICP-SFMS	SA, IS	BAM *	ICP-SFMS	SA, IS	BAM *
NIST	ICP-QMS	SA, IS	NIST SRM 3108	ICP-QMS	SA, IS	NIST SRM 3112a
NRC	GDMS	MM, Ratio	BCR-354	GDMS	RSF	CRMs
KRISS	ICP-SFMS	EC	KRISS Cd	ICP-SFMS	EC	KRISS Cr

* by means of commercial traceable standards, crosschecked in-house by BAM

Table 7c: Overview on the applied analytical techniques, the calibration approaches used and the sources of traceability (abbreviations are explained below).

Institute	Ni			Tl		
	Method	Calibration	Traceability	Method	Calibration	Traceability
NMIJ	ICP-SFMS	MM, IS	NMIJ CRM 3612	ICP-SFMS	MM, IS	NMIJ CRM 3625
NIM	ICP-SFMS GF-AAS	SA, CRM	GBW08618	ICP-SFMS	SA, CRM	NIST SRM 728
UME	ICP-SFMS	SA, IS	NIST SRM 3136	ICPMS	SA, IS	NIST SRM 3158
CENAM	ICP-SFMS GF-AAS	SA, IS EC, SA	DMR-465 DMR-465	ICP-SFMS	SA, IS	NIST SRM 3158
INMETRO	ICPMS	MM	NIST SRM 3136	ICPMS	IS	NIST SRM 3158
BAM	ICP-SFMS	SA, IS	BAM *	ICP-SFMS	SA, IS	BAM *
NIST	ICP-QMS	SA, IS	NIST SRM 3136	ICP-QMS	SA, IS	NIST SRM 3158
NRC	GDMS	MM, Ratio	BCR-354	GDMS	MM, Ratio	BCR-354
KRISS	ICP-SFMS	EC	KRISS Ni	ICP-SFMS	EC	NIST SRM 3158

* by means of commercial traceable standards, crosschecked in-house by BAM

AAS:	Atomic Absorption Spectrometry
GF-AAS:	Graphite Furnace Atomic Absorption Spectrometry
GDMS	Glow Discharge Mass Spectrometry
ICPMS:	Inductively Coupled Plasma Mass Spectrometry
ICP-QMS:	Inductively Coupled Plasma Quadrupole Mass Spectrometry
ICP-SFMS:	Inductively Coupled Plasma Sector Field Mass Spectrometry
MM:	Matrix Matched calibration
IS:	Internal Standardization
SA:	Standard Addition technique
CRM:	Matrix CRM used for validation
RSF:	Relative Sensitivity Factors
EC:	External Calibration

5.4 Comparison by measurand

5.4.1 Explanation

The individual results of the nine data sets reported by the participants are grouped in ascending order. The mean value, the median and the reference values/KCRV for each measurand are added to the tables. These data are displayed for each measurand separately in Figs. 1-7 and Table 8-14. The displayed uncertainties are combined standard uncertainties as reported by the participants or as calculated for the mean, the median and the reference value/KCRV as described in section 5.1. In Figs. 1-7 additionally the target uncertainty (30%) is displayed as dotted line referring to the reference values or the KCRV.

Each result reported by the participants for the six analytes was additionally tested with respect to the reference values and also with respect to the target uncertainty. The results are given in Tables 9-15 in the last three columns.

Most important is the compatibility of the measurement results with the corresponding reference value. According to VIM3 [7] measurement results are compatible, when the difference, Δ_{ab}, between both is smaller than a chosen multiple

of the standard uncertainty of this difference (eqn. 5a & b). In this context a multiple (coverage factor) k=2 is chosen and the result is expressed as "+" or "-" in the columns marked "C" of the Tables 9-15. When taking the uncertainties of the reported values and those of the reference values, the uncertainty contribution for inhomogeneity is at least partially double-counted. This double-counting cannot be corrected for in a practicable way. As the uncertainty of the difference can only be enlarged by this, it is considered as conservative approach for the compatibility. This of course corresponds with the concept of the "Degree of Equivalence" (DoE). However, since the mass fractions of the single analyte are not the measurand no Key Comparison Reference Value (KCRV) was calculated and thus no DoE. Therefore this concept on compatibility was used.

$$|\Delta_{\text{ab}}| < k \cdot u_{\Delta_{\text{ab}}}$$
eqn. 5a

for uncorrelated results and for k=2 follows

$$|(w_{\text{i}} - w_{\text{Ref}})| / \left(2 \cdot \sqrt{u_{\text{i}}^2 + u_{\text{Ref}}^2} \right) \overset{?}{<} 1$$
eqn. 5b

Consistency of a measurement result with the reference value within the target standard uncertainty of 30 % is calculated according to eqn. 6, irrespectively of the reported uncertainties. The result expressed as "+" or "-" is displayed in the columns marked "T" of the Tables 9-15.

$$|(w_{\text{i}} - w_{\text{Ref}})| / (0.3 \cdot w_{\text{Ref}}) \overset{?}{<} 1$$
eqn. 6

The column marked with "U" indicates, whether the reported measurement uncertainty is below the target uncertainty of 30 % or not.

5.4.2 Mass fraction of silver in pure zinc

Table 8: Results for silver in zinc. (for columns C, T, U see section 5.4.1).

Institute	Mass fraction in mg·kg^{-1}		u_{rel}	C	T	U
	w(Ag)	$u(w$(Ag))				
CENAM	1.13	0.16	14 %	+	+	+
KRISS	1.258	0.049	3.9 %	-	+	+
UME	1.304	0.045	3.5 %	-	+	+
INMETRO	1.31	0.06	4.6 %	+	+	+
NIM	1.32	0.08	6.1 %	+	+	+
BAM	1.4	0.1	7.3%	+	+	+
NRC	1.472	0.096	6.5%	+	+	+
NIST	1.5216	0.0083	0.5 %	-	+	+
NMIJ	1.530	0.034	2.2 %	-	+	+
Mean	1.357	0.051	3.7 %			
Median	1.320	0.038	2.9 %			
Reference	1.4311	0.026	1.8 %			

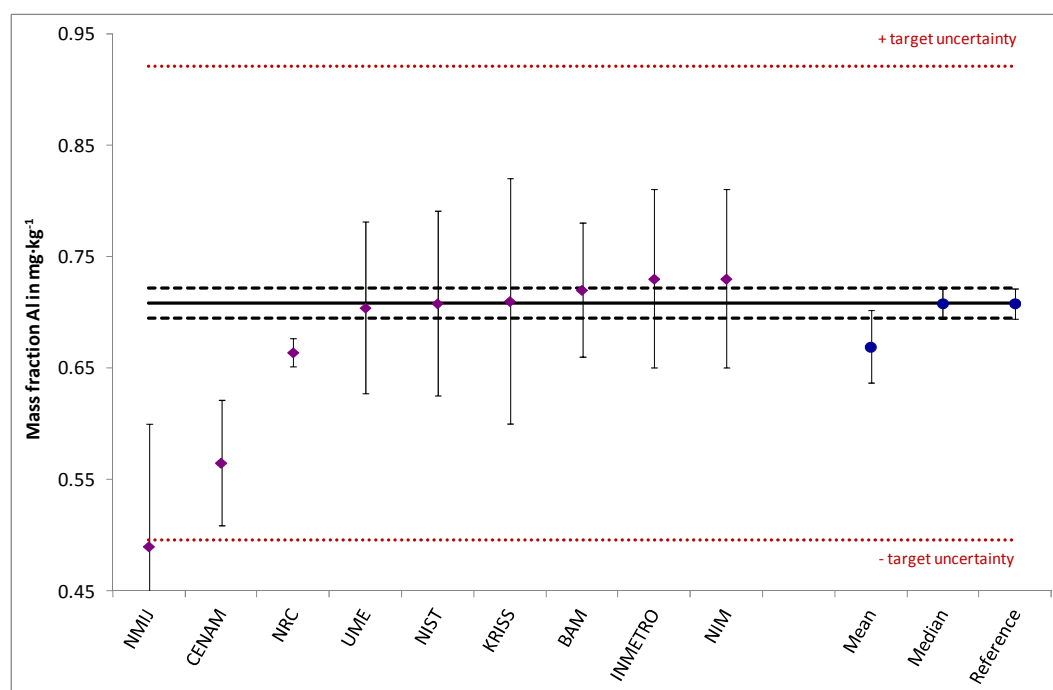

Fig. 1: Results for silver in zinc (k=1).

The reported mass fractions of silver show a standard deviation of < 10 %, demonstrating a good agreement of all reported results. The mean from all participants is compatible with the reference value, the median marginal not according to eqn. 5b. Five reported results (CENAM, INMETRO, NIM, BAM, NRC) are compatible with the reference value, four reported results (KRISS, UME, NIST, NMIJ) are not compatible with the reference, interestingly those with the smallest reported measurement uncertainty. However, all reported results agree with the reference value within the target uncertainty. The overall result for silver is even slightly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for silver as an analyte is possible within the target uncertainty of 30 %.

5.4.2 Mass fraction of aluminium in pure zinc

Table 9: Results for aluminium in zinc. (for columns C, T, U see section 5.4.1).

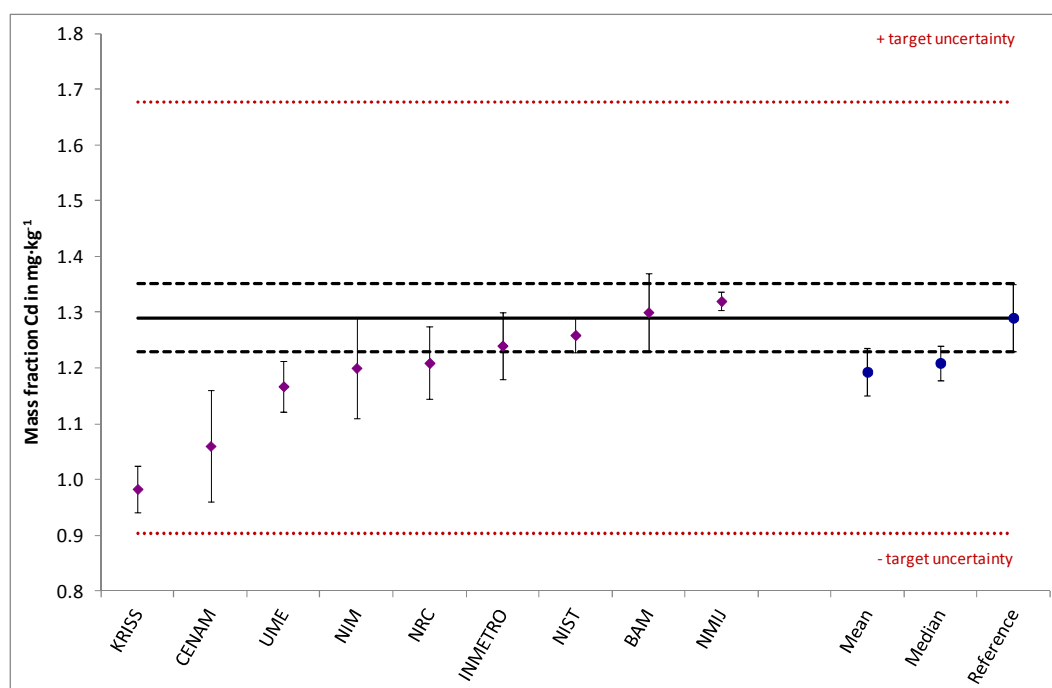| Institute	Mass fraction in mg·kg^{-1}		u_{rel}	C	T	U
	w(Al)	$u(w$(Al))				
NMIJ	0.49	0.11	22 %	+	-	+
CENAM	0.565	0.056	9.9 %	-	+	+
NRC	0.664	0.013	2.0 %	-	+	+
UME	0.704	0.077	11 %	+	+	+
NIST	0.708	0.083	12 %	+	+	+
KRISS	0.71	0.11	15%	+	+	+
BAM	0.72	0.06	8.3%	+	+	+
INMETRO	0.73	0.08	11 %	+	+	+
NIM	0.73	0.08	11 %	+	+	+
Mean	0.669	0.033	3.7 %			
Median	0.708	0.014	2.9 %			
Reference	0.708	0.014	1.8 %			

Fig. 2: Results for aluminium in zinc (k=1).

The reported mass fractions of aluminium show a standard deviation of < 13 %, demonstrating a good agreement of all reported results. A reference value by IDMS is not possible, because Al is mono-isotopic. The mean and the median from all participants are compatible with each other. As the distribution of the reported values is asymmetric the median is the better choice and additionally it was decided beforehand to use the median as reference in absence of IDMS values.

Only two results (CENAM, NRC) are not compatible with the reference value (here median) and one result (NMIJ) is slightly outside the target uncertainty, but is compatible with the reference value, whereas all reported results show combined standard uncertainties below the target uncertainty. The overall result for aluminium

is significantly better than the result for Bi (also mono-isotopic) obtained in CCQM-P107. Here it has to be considered that on one hand the mass fraction of aluminium are one order of magnitude higher than for bismuth in CCQM-P107, but on the other hand aluminium is more difficult to determine than bismuth.

For the purpose of impurity analysis in zinc, comparability of measurement results for aluminium as an analyte is possible within the target uncertainty of 30 %.

5.4.3 Mass fraction of cadmium in pure zinc

Table 10: Results for cadmium in zinc. (for columns C, T, U see section 5.4.1).

Institute	Mass fraction in mg·kg⁻¹		u_{rel}	C	T	U
	w(Cd)	$u(w$(Cd))				
KRISS	0.983	0.042	4.3 %	-	+	+
CENAM	1.06	0.10	9.4 %	+	+	+
UME	1.167	0.045	3.9 %	+	+	+
NIM	1.20	0.09	7.5%	+	+	+
NRC	1.209	0.065	5.4 %	+	+	+
INMETRO	1.24	0.06	4.8%	+	+	+
NIST	1.259	0.031	2.5 %	+	+	+
BAM	1.30	0.07	5.4 %	+	+	+
NMIJ	1.32	0.016	1.2 %	+	+	+
Mean	1.193	0.042	3.6 %			
Median	1.209	0.031	2.6 %			
Reference	1.290	0.061	4.7 %			

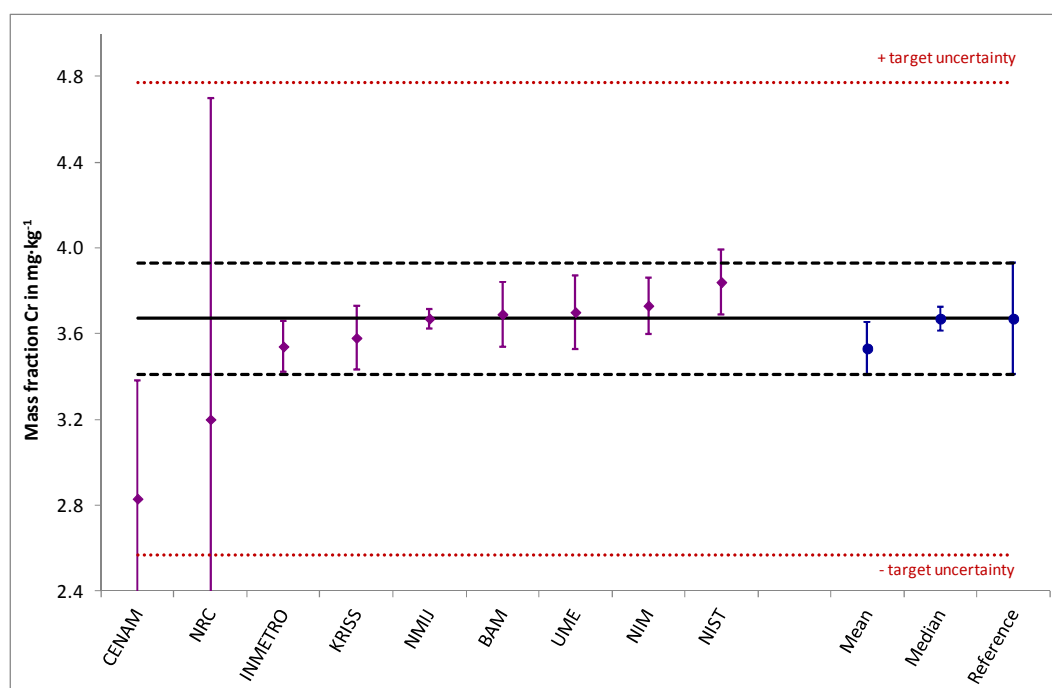Fig. 3   Results for cadmium in zinc (k=1).

The reported mass fractions of cadmium show a standard deviation of 9 %, demonstrating a good agreement of all reported results. The mean and the median from all participants are compatible with the reference value. Only one reported result (KRISS) is not compatible with the reference value. However, all reported results are compatible with the reference value within the target uncertainty and all reported results underrun the target uncertainty. The overall result for cadmium is significantly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for cadmium as an analyte is possible within the target uncertainty of 30 %.

5.4.4 Mass fraction of chromium in pure zinc

Table 11: Results for chromium in zinc. (for columns C, T, U see section 5.4.1).

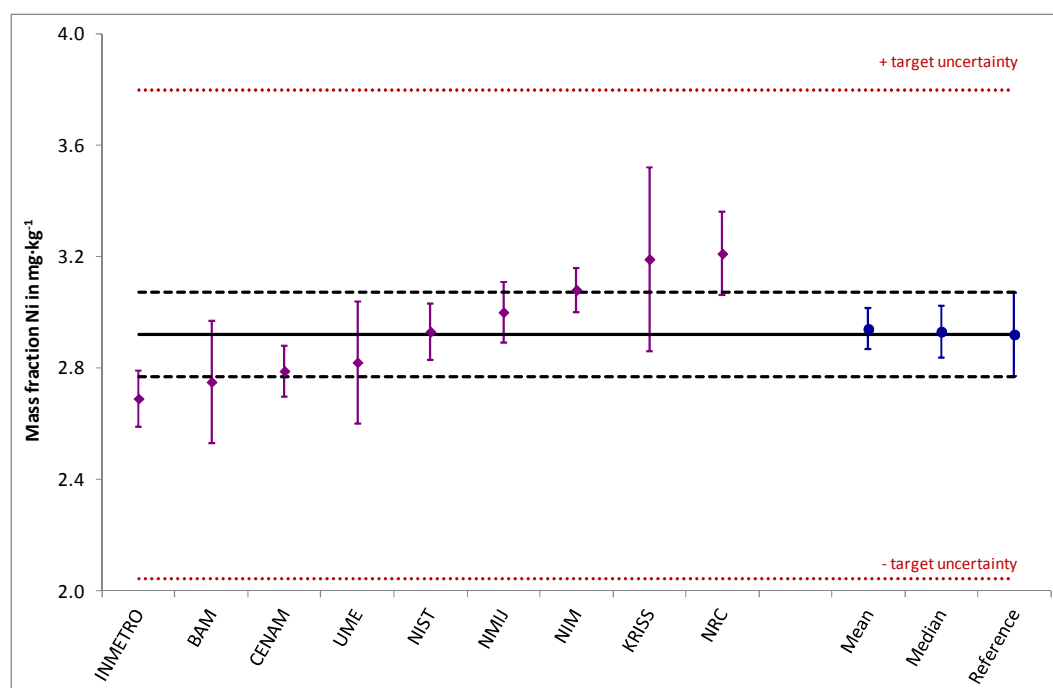| Institute	Mass fraction in mg·kg⁻¹		u_{rel}	C	T	U
	$w(Cr)$	$u(w(Cr))$				
CENAM	2.83	0.55	19 %	+	+	+
NRC	3.2	1.5	47 %	+	+	-
INMETRO	3.54	0.12	3.4 %	+	+	+
KRISS	3.58	0.15	4.2 %	+	+	+
NMIJ	3.670	0.044	1.2 %	+	+	+
BAM	3.69	0.15	4.1 %	+	+	+
UME	3.70	0.17	4.6 %	+	+	+
NIM	3.73	0.13	3.5 %	+	+	+
NIST	3.84	0.15	3.9 %	+	+	+
Mean	3.53	0.12	3.5 %			
Median	3.67	0.06	1.5 %			
Reference	3.67	0.26	7.1 %			

Fig. 4:   Results for chromium in zinc (k=1).

The reported mass fractions of chromium show a standard deviation of 9 %, demonstrating a good agreement of all reported results. The mean and the median from all participants are compatible with the reference value and so do all reported results. Additionally all reported results are compatible with the reference value within the target uncertainty and underrun the target uncertainty, excepting those of NRC. This, however, is due to the calibration by using Relative Sensitivity Factors (RSF), which generally creates significantly larger uncertainties. The overall result for chromium is significantly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for chromium as an analyte is possible within the target uncertainty of 30 %.

5.4.5 Mass fraction of nickel in pure zinc

Table 12: Results for nickel in zinc. (for columns C, T, U see section 5.4.1).

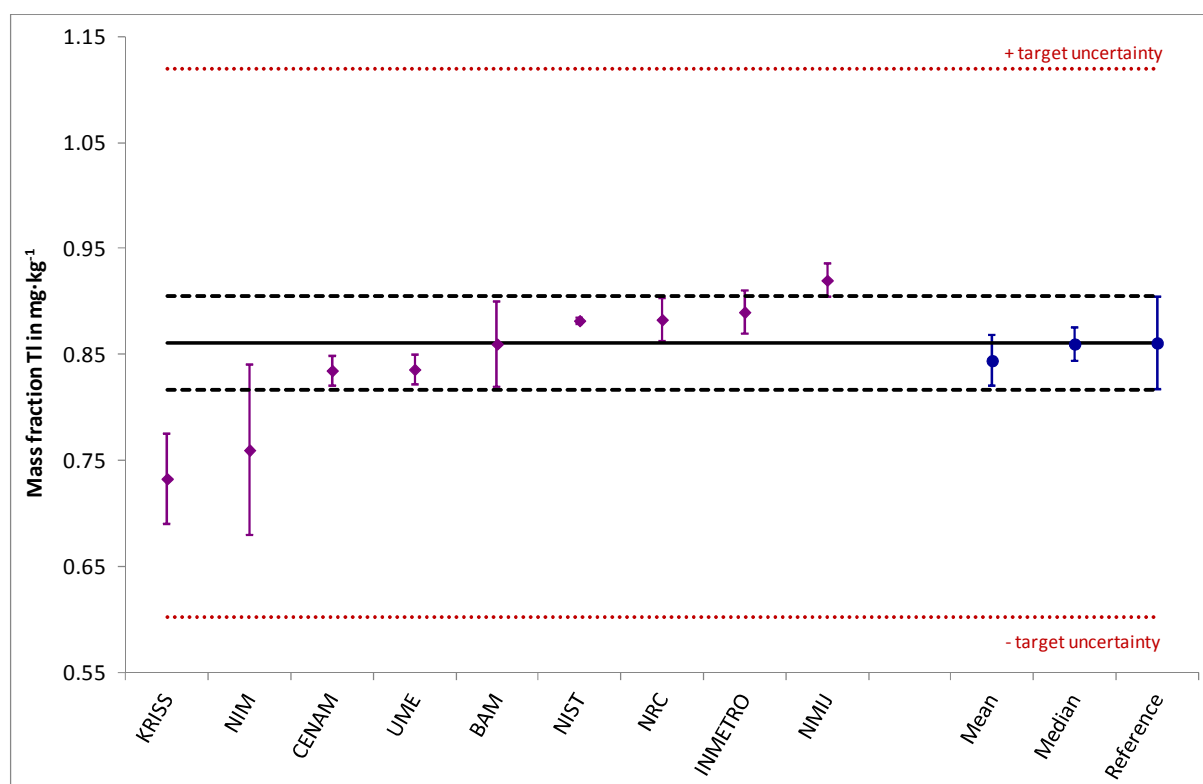| Institute	Mass fraction in mg·kg^{-1}		u_{rel}	C	T	U
	w(Ni)	$u(w$(Ni))				
INMETRO	2.69	0.10	3.7 %	+	+	+
BAM	2.75	0.22	8.0 %	+	+	+
CENAM	2.789	0.091	3.3 %	+	+	+
UME	2.82	0.22	7.8 %	+	+	+
NIST	2.93	0.10	3.4 %	+	+	+
NMIJ	3.00	0.11	3.7 %	+	+	+
NIM	3.08	0.08	2.6 %	+	+	+
KRISS	3.19	0.33	10 %	+	+	+
NRC	3.21	0.15	4.7 %	+	+	+
Mean	2.940	0.074	2.5 %			
Median	2.930	0.093	3.2 %			
Reference	2.92	0.15	5.1 %			

Fig. 5:   Results for nickel in zinc (k=1).

The reported mass fractions of nickel show a standard deviation of < 7 %, demonstrating a good agreement of all reported results. The mean and the median from all participants are compatible with the reference value. All reported results are compatible with the reference value. Additionally all reported results are compatible with the reference value within the target uncertainty and underrun the target uncertainty. The overall result for nickel is significantly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for nickel as an analyte is possible within the target uncertainty of 30 %.

5.4.6 Mass fraction of thallium in pure zinc

Table 13: Results for thallium in zinc. (for columns C, T, U see section 5.4.1).

Institute	Mass fraction in mg·kg^{-1}		u_{rel}	C	T	U
	w(Tl)	$u(w$(Tl))				
KRISS	0.733	0.042	5.7 %	-	+	+
NIM	0.76	0.08	11 %	+	+	+
CENAM	0.835	0.014	1.7 %	+	+	+
UME	0.836	0.014	1.7 %	+	+	+
BAM	0.86	0.04	4.7 %	+	+	+
NIST	0.8820	0.0025	0.3 %	+	+	+
NRC	0.883	0.02	2.3 %	+	+	+
INMETRO	0.89	0.02	2.2 %	+	+	+
NMIJ	0.920	0.016	1.7 %	+	+	+
Mean	0.844	0.024	2.8 %			
Median	0.860	0.015	1.8 %			
Reference	0.861	0.044	5.1 %			

Fig. 6:   Results for thallium in zinc (k=1).

The reported mass fractions of thallium show a standard deviation of 7 %, demonstrating a good agreement of all reported results. The mean and the median from all participants are compatible with the reference value. Only one reported result (KRISS) is not compatible with the reference value. However, all reported results are compatible with the reference value within the target uncertainty and underrun the

target uncertainty. The overall result for thallium is significantly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for thallium as an analyte is possible within the target uncertainty of 30 %.

5.4.7 Total impurity of zinc expressed as the sum of the mass fractions of six defined analytes (Ag, Al, Cd, Cr, Ni, Tl)

Table 14: Results for total impurity expressed as the sum of the mass fractions of six defined analytes Ag, Al, Cd, Cr, Ni, Tl. (for columns C, T, U see 5.4.1).

Institute	Mass fraction in mg·kg^{-1}		u_{rel}	C	T	U
	$w(\Sigma)$	$u(w(\Sigma))$				
CENAM	9.22	0.59	6.4 %	-	+	+
INMETRO	10.4	0.2	1.9 %	+	+	+
KRISS	10.46	0.39	3.7 %	+	+	+
UME	10.53	0.29	2.8 %	+	+	+
NRC	10.6	1.6	15 %	+	+	+
BAM	10.68	0.3	2.8 %	+	+	+
NIM	10.82	0.23	2.1 %	+	+	+
NMIJ	10.93	0.17	1.6 %	+	+	+
NIST	11.14	0.21	1.9 %	+	+	+
Mean	10.53	0.21	2.0 %			
Median	10.60	0.12	1.2 %			
Reference	10.88	0.32	2.9 %			

Fig. 7: Results for total impurity expressed as the sum of the mass fractions of six defined analytes Ag, Al, Cd, Cr, Ni, Tl. (k=1).

The reported mass fractions for the sum of six impurities (Ag, Al, Cd, Cr, Ni, Tl) show a standard deviation of 5 %, demonstrating an excellent agreement of all reported results. The mean and the median are compatible with the reference value. Only one reported result (CENAM) is not compatible with the reference value. However, all reported results are compatible with the reference value within the target uncertainty and all reported results underrun the target uncertainty. The overall result for the sum of six impurities is significantly better than those obtained in CCQM-P107.

For the purpose of impurity analysis in zinc, comparability of measurement results for the sum of six impurities as an analyte is possible within the target uncertainty of 30 %.

Aspects regarding reference values

Both, median and arithmetic mean have their advantages and disadvantages for the evaluation of the interlaboratory comparison. For ideal (or close to ideal) data sets as in the case of the data set for Ni there is hardly a difference. In presence of asymmetric distributions as in the data set of Al the median is more robust and the corresponding uncertainty is smaller than the uncertainty of the mean. Generally, the median is more robust towards inconsistent measurement results (i.e. values with small claimed uncertainty but large difference to the reference value) or asymmetric distributions than the arithmetic mean. Therefore, the median seems to be more appropriate for the evaluation of the interlaboratory comparison.

The best case is to have independent reference values in place such as the IDMS results for Ag, Cd, Cr, Ni or Tl as has been demonstrated in previous studies (CCQM-P62, CCQM-P107 & CCQM-K64). For impurity determination, however, this approach is limited, because mono-isotopic elements such as Na, Al, P, Co and Bi are not accessible. Therefore, a combined reference value using IDMS results and the median of all results for mono-isotopic elements is the best approach for studies like this.

Methodical Aspects

Within this study several measurement techniques were applied namely AAS, ICP-QMS, ICP-SFMS, GDMS and IDMS in combination with ICPMS and with TIMS. The quality of the measurement result more depends on the actual measurement procedure applied than on the measurement technique. Just by definition no method is superior to another. AAS can deliver very good measurement results for single analytes. However, for impurity analysis the suitability of AAS is rather limited, because it is a mono-elemental technique with a limited dynamic range. Nevertheless, AAS is an important supplementary technique in purity analysis for specific single analytes. ICP-MS overcomes the limitations of AAS with its multi-element capability and the wide dynamic range. However ICP-MS suffers from isobaric and molecular interferences, which need to be considered. Compared to ICP-SFMS, ICP-QMS is inexpensive and requires less effort, but in some cases interferences occur, which are difficult to deal with. Such interferences can be reduced to an insignificant level in ICP-QMS by the use of collision cells, but using this technique the multi-element capability is partly lost. ICP-SFMS is usually even more sensitive than ICP-QMS and many spectral interferences can be resolved by higher mass resolution, unfortunately, however, at the expense of sensitivity (drop by a factor of 10-20). Disadvantages of ICP-SFMS are rather high purchase and running costs and the complexity of the instrument.

IDMS in combination with analyte–matrix separation either applied to TIMS or ICP-MS is an established calibration strategy for performing reference measurements. The use of the perfect internal standard, the element itself in an isotope enriched form, enables smallest measurement uncertainties. However, IDMS is a mono- or oligo-element method and therefore is not suitable for performing a complete impurity analysis, because on one side the effort would be too high and on the other side a substantial number of elements is not accessible due to its mono-isotopic nature.

Solid sampling techniques such as GDMS have big advantages, because sample preparation is minimized and so is the risk of contamination and analyte losses. GDMS is sensitive and multi-element capable, even for analytes such as the non-metals, which are not accessible via ICP-MS. Additionally GDMS is fast in the entire analytical procedure compared to ICP-MS. The largest disadvantage of solid sampling methods is the calibration. For GDMS different ways exist. One is the concept of standard relative sensitivity factors (standard-RSF), which does not involve a measurement standard at all, but increases the uncertainties e.g. for metallic analytes by a factor of two. Another, straightforward approach would be the use of Certified Reference Materials (CRMs) offering the same or similar matrix composition as the sample. This approach can result in much smaller uncertainties, which is shown in this study. Drawbacks are that the traceability of the measurement result is not established in the shortest possible way or sometimes even missing and that only a limited number of suitable CRMs is available. A third calibration approach is based on the use of matrix matched synthetic standards prepared from a high purity metal powder, which is doped with liquid standards of known concentration. The major advantage is, that these standards may provide traceability to the SI in the shortest possible way provided the applied materials offer traceable values. A drawback of this approach is, that the preparation of such standards is laborious and requires specific know-how, because there are difficulties concerning losses, homogeneity and contamination. The feasibility of all approaches for a complete characterization might be demonstrated in CCQM-P149.

5.4.8 Degrees of equivalence

The degree of equivalence (DoE), d_i, between an individual NMI result, $w_i(\Sigma)$, and the key comparison reference value, $w_{KCRV}(\Sigma)$, and the associated uncertainty $u(d_i)$ is calculated following eqns. 7 and 8 [8]. The so calculated DoEs are listed together with their associated uncertainties in Table 15 and are graphically displayed in Fig. 8.

$$d_i = w_i(\Sigma) - w_{KCRV}(\Sigma) \qquad\qquad \text{eqn. 7}$$

$$u^2(d_i) = u^2\big(w_i(\Sigma)\big) + u^2\big(w_{KCRV}(\Sigma)\big) - 2 \cdot cov\big(w_i(\Sigma), w_{KCRV}(\Sigma)\big) \qquad \text{eqn. 8}$$

The KCRV is calculated as described in section 5.1. Therefore, only in the case of the Al mass fraction correlations between reference value and individual NMI results may occur, because the median was chosen as reference value. For all other analytes (Ag, Cd, Cr, Ni and Tl) independently obtained IDMS values were used as reference values. On this reason correlations in the case of the KCRV were estimated to be negligible and the covariance in eqn. 8 was set to zero.

In case participants did not report expanded uncertainties a coverage factor k=2 was assumed and the expanded uncertainty was calculated from the combined standard uncertainty.

Table 15: Mass fractions $w_i(\Sigma)$ and their associated combined and expanded uncertainties $u_c(w_i)$ and $U(w_i)$, respectively, together with the coverage factor k_i as reported by the participants in the order of increasing mass fraction values. Degrees of equivalence d_i and their associated combined and expanded uncertainties $u(d_i)$ and $U(d_i)$, respectively, are displayed according to eqns. 7 & 8 with $U(d_i)=k \cdot u(d_i)$ using a coverage factor of $k=2$.

	$w_i(\Sigma)$	$u_c(w_i)$	k_i	$U(w_i)$	d_i	$u(d_i)$	$U(d_i)$
CENAM	9.22	0.59	2	1.2	- 1.66	0.67	1.3
INMETRO	10.4	0.2	2	0.4	- 0.48	0.38	0.75
KRISS	10.46	0.39	3.18	1.24	- 0.42	0.50	1.0
UME	10.53	0.29	2	0.58	- 0.35	0.43	0.86
NRC	10.6	1.6	2	3.2	- 0.28	1.63	3.3
BAM	10.68	0.30	2	0.60	- 0.20	0.44	0.88
NIM	10.82	0.23	2	0.46	- 0.06	0.39	0.79
NMIJ	10.93	0.17	2	0.34	0.05	0.36	0.72
NIST	11.14	0.21	2.26	0.47	0.26	0.38	0.77

Fig. 8: Graphical representation of the equivalence statements related to the KCRV – DoE plot of the data reported by the participants. The black diamonds show the degree of equivalence (DoE), d_i, while the error bars denote the expanded uncertainty associated with the degree of equivalence $U(d_i)$ according to eqn. 8 and with $U(d_i)=k \cdot u(d_i)$ using a coverage factor of $k=2$. Results enclosing zero within their uncertainty interval are considered to be consistent with the KCRV.

5.4.9 Applicability of this key comparison to CMC claims

The analytical challenge is the quantification of metallic impurities in a pure (metallic) element. The impurities range in low mg·kg^{-1} range or below and the quantification is hindered by high matrix load, which may cause numerous interferences. The mass fractions of the impurities are summed up and used to gain a purity statement of the pure element.
A successful participation in this key comparison can support CMC claims for the quantification of metal impurities in pure (metallic) elements, which do not have intrinsic difficulties with the dissolution process. However, such claims shall be restricted to applications for purity determination.

6. Conclusion and Outlook

- The observed spread for the measurement results reported by the NMIs and designated institutes expressed as standard deviation for Ag, Al, Cd, Cr, Ni, Tl and the sum of these impurities were 10 %, 13 %, 9 %, 9 %, 7 %, 7 % and 5 % respectively.
- The observed spreads were significantly lower than those of a similar study CCQM-P107 (12 %, 41 %, 29 %, 20 %, 11 %, 15 % and 10 %)
- The observed spreads were well below the target uncertainty of 30 % relative.
- As a consequence, comparability within the group of NMIs and designated laboratories participating is demonstrated to be established.
- The individual measurement results, mean values and medians derived were in all cases very consistent with the reference values obtained by IDMS.
- As a consequence, accuracy of the measurement results for the group of NMIs and designated laboratories participating is demonstrated to be established.
- Especially with the results of CCQM-P62 and CCQM-P107 in mind, the outcome of CCQM-K72 can be considered as a big step forward in the community.
- Concerning the importance of high purity materials used as realisation of the SI unit for chemical measurements, the number of NMIs/DIs increased, but still can be improved.
- A possible follow-up as a pilot study on total purity assessment has already been started (CCQM-P149).
- A follow-up in form of a pilot study on non-metal impurities is mandatory, because non-metal impurities such as oxygen, nitrogen and sulphur often make up the largest contributions.

7. References

[1] H. Kipphardt and R. Matschat, Purity assessment for providing primary standards for element determination - a snap shot of international comparability, Mikrochim. Acta 162 (2008) 269-276
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[7] R. Kacker, B. Toman and D. Huang, Comparison of ISO-GUM, draft GUM Supplement 1 and Bayesian statistics using simple linear calibration, Metrologia 43 (2006) 167-177

[8] CCQM/13-22: CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 2013-04-12

[9] International Vocabulary of Metrology – Basic and General Concepts and Associated Terms VIM, 3rd edition, JCGM 200:2008, http://www.bipm.org/en/publications/guides/vim.html also ISO Guide 99-12:2007

Appendix I: Invitation

To CCQM members, official observers and other interested parties

Invitation to the key comparison / pilot study CCQM-K72 / CCQM-P107.1 on the measurement of the purity of zinc with respect to six metallic impurities and the pilot study CCQM-P107.2 on the evaluation of all impurities present in zinc.

Dear colleagues,

We invite you to participate in the CCQM-K72 key comparison and CCQM-P107.1 pilot study "Purity analysis of zinc with respect to six metallic analytes". During discussion of the comparison at the CCQM IAWG meeting in April 2012 it was agreed that it was important to investigate all detectable impurities in this type of calibration material. Accordingly, an additional pilot study (which may use a different zinc sample, depending on number of participants) will be organized for this purpose. The objective of this study is to evaluate the fit-for-purpose impurity checks which many NMIs use with commercially available high purity metals. Hence semi-quantitative multi-elemental analysis may be appropriate for metallic impurities present at very low concentrations. It is felt, that all labs with inorganic CMCs claiming SI traceability to in-house standards should register for CCQM-P107.2 regardless of their participation in CCQM-K72 / CCQM-P107.1. In the attached files, you can find the registration form and the technical protocol.

Bottles with zinc samples each containing about 1.8 g of the material in 4 pieces of about cubic geometry $(4 \text{ mm})^3$ have been prepared. Additionally few samples in pin geometry for GD-MS measurements (about 3.5 mm × 3.5 mm × 20 mm) are available. We plan to distribute the samples by end of September 2012. Pilot laboratory will be BAM (Germany).

If you want to participate in CCQM-K72 / CCQM-P107.1/ CCQM-P107.2, please send us a confirmation of participation by e-mail or fax by **31. July 2012** using the attached registration form. We have already some verbal expression of interest in participation; however, we ask all interested participants to register officially by e-mail or fax.

The results of the study will be presented in the form of a report to the CCQM, available to participants and members of the IAWG. The report will identify the results with the names of the participating institutes. Preliminary and final drafts of the report will be circulated to participants for comment and correction. A scientific paper describing the study may be published separately in an appropriate journal provided participants agree to this.

Organisations which are a national metrological institute (NMI), or an appropriate designated laboratory in accordance with the CIPM MRA, are eligible to participate in the key comparison. Other expert institutes, from countries that are members of the Metre Convention, may also participate in the corresponding pilot study provided that their contribution has added scientific value or where they may qualify later as a designated institute in the field under study. The process of nomination of expert laboratories for participation in a CCQM pilot study should preferably be nationally co-ordinated. Expert laboratories which respond to this invitation are requested to inform their national metrological institute of their participation in the pilot study and to advise the co-ordinating laboratory of the appropriate contact at their NMI. In accordance with the requirements of the CCQM President, the IAWG Chairman will be asked to formally notify each relevant NMI of the participation by an expert institute from their country.

If you have further questions or remarks, please do not hesitate to contact us.

Best regards,
Heinrich Kipphardt

<u>Pilot laboratory:</u>   BAM Federal Institute for Materials Research and Testing - Division 1.4
Richard-Willstätterstr. 11
12489 Berlin
GERMANY

<u>contact persons:</u>

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Fax.: +49 30 8104 1117

Appendix II: Registration Form

<div align="center">

REGISTRATION FORM
CCQM-K72 / CCQM-P107.1
Measurement of the purity of zinc with respect to six metallic impurities
CCQM-P107.2
Evaluation of detectable impurities in zinc

</div>

Name (contact person): _____

Institute: _____

Shipping address: _____

_____

Telephone: _____

Fax: _____

E-mail: _____

Participation CCQM-K72   ☐ **Yes**   ☐ **No**

Participation CCQM-P107.1   ☐ **Yes**   ☐ **No**

Participation CCQM-P107.2   ☐ **Yes**   ☐ **No**

Preferred Special sample geometry: ☐ **cubic**

And/or

☐ **pins (for GD-MS only)**

Signature: _____

Date: _____

<u>Please return this sheet by e-mail or fax no later than 31. July 2012 to:</u>

Heinrich Kipphardt
BAM Federal Institute for Materials Research and Testing
Division 1.4
Richard-Willstaetterstr. 11
12489 Berlin
GERMANY
Tel.: +49 30 8104 1116 Fax.: +49 30 8104 1117
e-mail: heinrich.kipphardt@bam.de

Appendix III: Technical Protocol

CCQM-K72 / CCQM-P107.1 - Measurement of the purity of zinc with respect to six metallic impurities

Technical protocol

1. Introduction
In a previous study CCQM-P62 (Ni Purity with respect to six metallic analytes) discrepancies of a factor of not less than eight between the seven participants were observed (reported massfraction w= 3,1 mg/kg – 25,4 mg/kg) [1]. After discussion in IAWG a further pilot study CCQM-P107 on zinc matrix was conducted with much better consistency (reported massfraction w= 8,1 mg/kg – 10,7 mg/kg) [2]. After further discussion in IAWG it was decided to drive this further to a key comparison with a parallel pilot study.

During discussion of the comparison at the CCQM IAWG meeting in April 2012 it was agreed that it was important to investigate all detectable impurities in this type of calibration material. Accordingly, an additional pilot study CCQM-P149 (formerly named CCQM-P107.2 on "Evaluation of detectable impurities in zinc") now described in a separate technical protocol will be organized for this purpose.

High purity metals can serve as a realisation of the SI unit amount of substance for a specific substance. In Analytical Chemistry, solutions prepared from high purity metals using gravimetric preparation and the concept of molar mass are used as 'calibration' solutions in many fields of application. Since ideal purity does not exist for real materials, the actual purity of the high purity material must be known. The purity data are only accessible via measurements. Aiming at small uncertainties (i.e. 10^{-4} relative on the purity statement) in almost all cases a direct measurement of the matrix element in a high purity metal is not applicable, because the methods available are not sufficiently selective and/or accurate. In order to achieve a low level of uncertainty, usually the indirect approach is followed. In this approach, the mass fractions of all impurities are measured and their sum is subtracted from the value for ideal purity (i.e. 1 kg/kg). In principle all impurities (i.e. all elements not being the matrix element), metals and non-metals, must be considered.

As a first step, only six metallic impurities are considered in this study. (Some other metallic impurities and non-metallic impurities might be subject to future CCQM studies). Zinc was chosen as matrix, because it is considered to be easy to decompose and of high relevance. The deliberate limitation to six analytes was made in order to restrict the measurement effort for this study.
Note, the topic of this study is the measurement of the purity of the zinc (matrix) with respect to six analytes and not trace analysis of analytes in zinc. This distinction seems to be small, but defines different measurands.

There are many CMCs based on the use of commercial high purity metals for which labs undertake their own assessment of impurities using GDMS, "semi-quant" ICP-MS or ICP-OES, etc. It would be useful that these labs register for the pilot and use their techniques to look for as many impurities as possible.

2. Measurand and reporting

- Mandatory measurand (for CCQM-K72 / CCQM-P107.1)

$w(Ag)+w(Al)+w(Cd)+w(Cr)+w(Ni)+w(Tl)$: value for the sum of the mass fractions of Ag, Al, Cd, Cr, Ni and Tl in the bulk of the zinc material

- mandatory interim results (for CCQM-K72 / CCQM-P107.1)

$w(Ag)$; $w(Al)$; $w(Cd)$; $w(Cr)$; $w(Ni)$; $w(Tl)$: list of individual values for the mass fraction of Ag, Al, Cd, Cr, Ni and Tl in the bulk of the zinc material

The aim of CCQM-K72 / CCQM-P107.1 is to measure the sum of all requested impurities with sufficiently small uncertainty. With this in mind, it is useless to measure only five of the six requested impurities with very small uncertainty, and not to report a value at all for the sixth analyte.

Each participant shall only report one result for the value of the sum of the six requested impurities (and the individual values for each element). The results should be reported in mass fractions, accompanied by a full uncertainty statement (including a combined standard uncertainty and an expanded uncertainty with a coverage factor applied). In addition the report should include technical details on the measurement procedure, traceability links and uncertainty contributions.

- Optional measurands

Those laboratories participating in CCQM-K72 or CCQM-P107.1 that use methods of measurements providing multi element results (e.g. GDMS, ICP-MS, ICP OES etc.) are encouraged to provide additionally a list of individual values for the mass fractions of other metallic and non-metallic impurities. This additional data is of high benefit and will be put into the pilot study report.

3. Guidance values and target uncertainty

The material is selected in a way that the individual mass fractions of the six requested analytes are about between 0.1 mg/kg and 5.0 mg/kg.

Since for this type of purity analysis materials of very high purity are considered, even a rather large relative target uncertainty of 30 % on the individual impurities, seems to be fit for purpose.

4. KCRVs

Reference values based on IDMS will be provided as KCRVs for $w(Ag)$, $w(Cd)$, $w(Cr)$, $w(Ni)$ and $w(Tl)$. As Al is mono isotopic, IDMS can not be used to establish the reference value. Hence the KCRV for Al will be based on the median of all accepted datasets for Al in CCQM-K72.

5. Methods of measurement

Each participant may use any suitable method(s) for the measurement of the individual impurities. Any participant that chooses to use multiple methods for the measurement of an individual impurity must report only one composite result (e.g. an average value from different methods) for each impurity.

For individual elements, mono-element techniques such as IDMS, which require huge effort but potentially give smallest combined uncertainty, are certainly not excluded, however, one should keep in mind, that it is only due to the (deliberately taken) limitation to six analytes in this study that this effort might be affordable at all. Moreover, one should keep in mind, that in the state of the practice even at the NMIs, these techniques are typically not used, when the purity of a high purity material for calibration purposes is measured.

More realistic for this type of measurements seems to be the application of procedures/methods, which are more easily capable of multi element analysis (e.g. ICP-MS) at trace level. Preferred are procedures/methods, which provide traceability of the

measurement result in the shortest way (e.g. via calibration against sufficiently pure materials), however, procedures requiring matrix reference materials for calibration (e.g. special types of GDMS measurements) are not excluded, if the matrix reference material used is stated and of sufficient metrological quality and if the uncertainties of the values of the matrix reference material are taken into account.

6. Planned time schedule

call for participants:	by end of March 2012
latest registration of participant:	by end of July 2012 (updated)
latest arrival of samples at participants:	by end of September 2012
latest report of results:	by end of February 2013
report A:	by end of May 2013
report B:	by end of July 2013

7. Samples

A bottle is planed to contain about 1.8 g of the material in four pieces of about cubic geometry $(4 \text{ mm})^3$. Additionally few samples in pin geometry for GD-MS measurements (about 3.5 mm × 3.5 mm × 20 mm) are available. Please specify which geometry you prefer. In order to prepare a clean surface, etching is recommended before use.

8. Pilot laboratory

BAM Federal Institute for Materials Research and Testing
Division 1.4

Richard-Willstaetterstr. 11
12489 Berlin
GERMANY

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and
Dr. Silke Richter
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Fax.: +49 30 8104 1117

9. References

1.   H. Kipphardt and R. Matschat: ‚Purity assessment for providing primary standards for element determination - a snap shot of international comparability', Mikrochim. Acta 162 (2008), 269-276, DOI: 10.1007/s00604-007-0937-2.

2.   H. Kipphardt, R. Matschat, J. Vogl, T. Gusarova, M. Czerwensky, H.-J. Heinrich, A. Hioki, L.A. Konopelko, B. Methven, T. Miura, O. Petersen, G. Riebe, R. Sturgeon, G. Turk and L. Yu: 'Purity determination as needed for the realisation of primary standards for elemental determination - status of international comparability', Accred. Qual. Assur. 15 (2010), 29-37, DOI : 10.1007/s00769-009-0557-0.

Appendix IV: Reporting Form

CCQM-K72 / CCQM-P107.1 - Measurement of the purity of zinc with respect to six metallic impurities

Form for reporting results

Name of Institute
Number of bag

☐ Participation CCQM-K72   ☐ Participation CCQM-P107.1

Mandatory result and mandatory interim results	Value	(combined) standard uncertainty	Unit
sum of the mass fractions of Ag, Al, Cd, Cr, Ni and Tl in the bulk of the zinc material: $w(\text{Imp})=w(\text{Ag})+w(\text{Al})+w(\text{Cd})+w(\text{Cr})+w(\text{Ni})+w(\text{Tl})$:	±		mg/kg
Mass fraction of Ag in the bulk of the zinc material: $w(\text{Ag})$	±		mg/kg
Mass fraction of Al in the bulk of the zinc material: $w(\text{Al})$	±		mg/kg
Mass fraction of Cd in the bulk of the zinc material: $w(\text{Cd})$	±		mg/kg
Mass fraction of Cr in the bulk of the zinc material: $w(\text{Cr})$	±		mg/kg
Mass fraction of Ni in the bulk of the zinc material: $w(\text{Ni})$	±		mg/kg
Mass fraction of Tl in the bulk of the zinc material: $w(\text{Tl})$	±		mg/kg

Additional comments

Name of responsible person:
Date:
Signature:

Measurement procedure used for **Ag**:
Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:
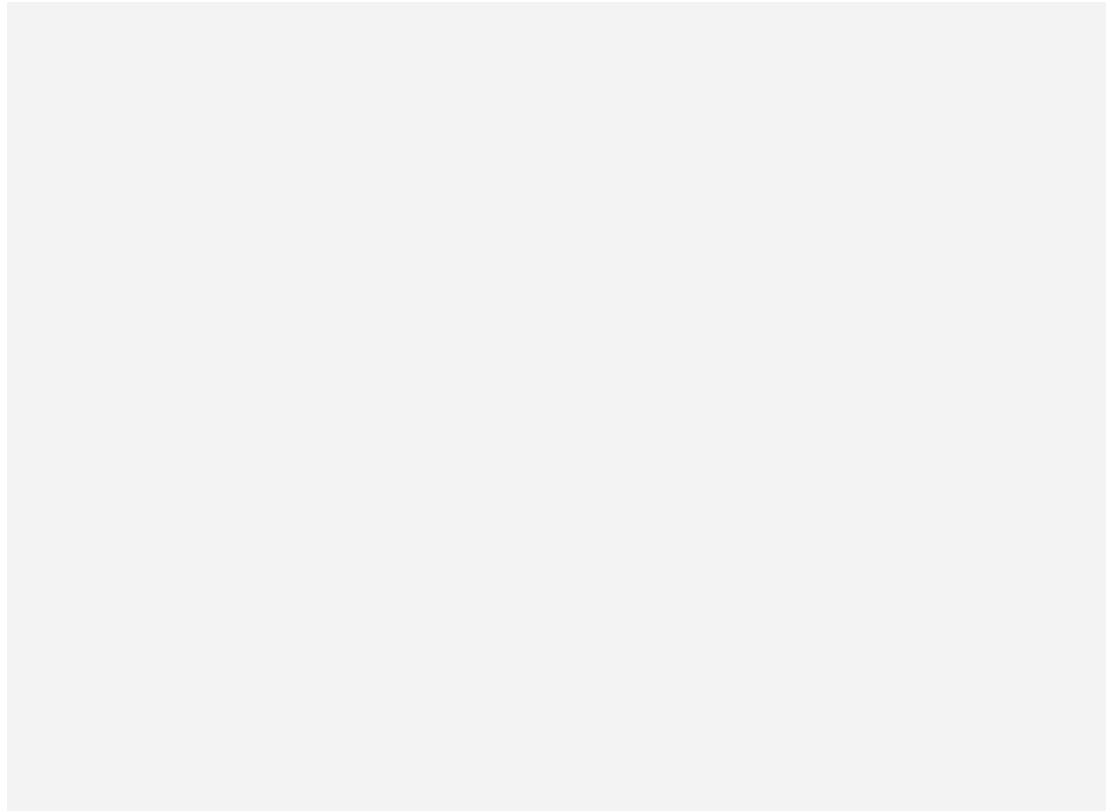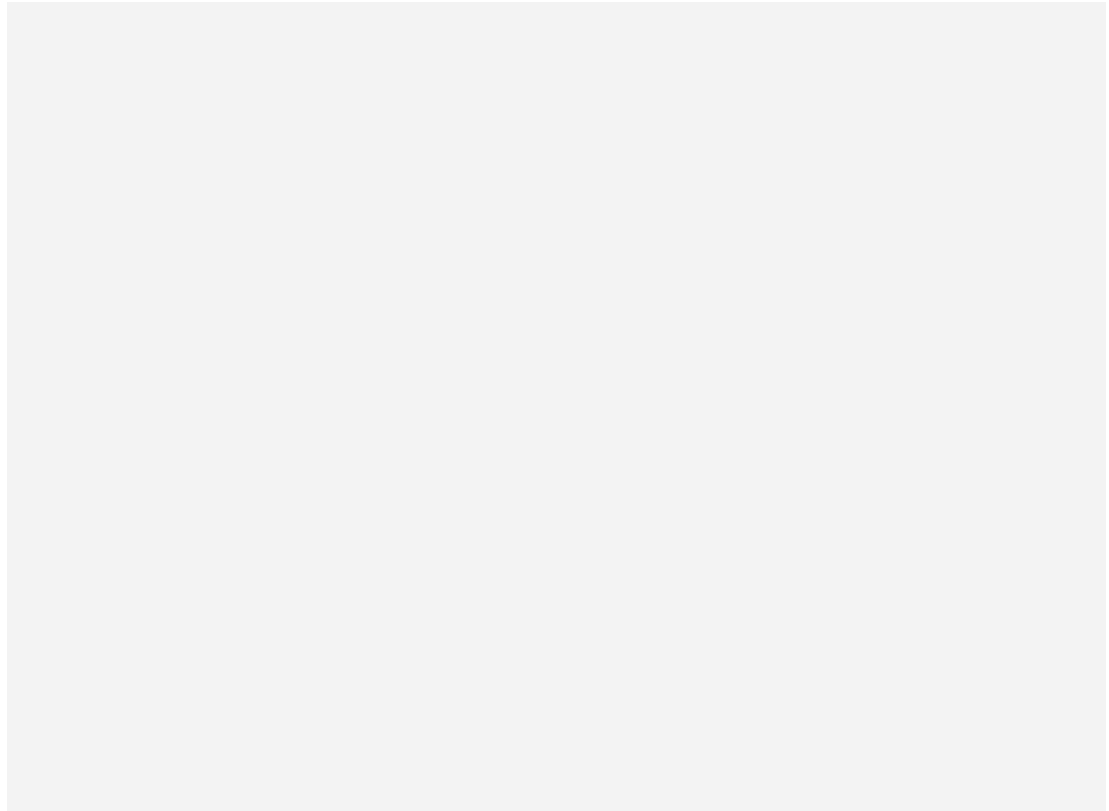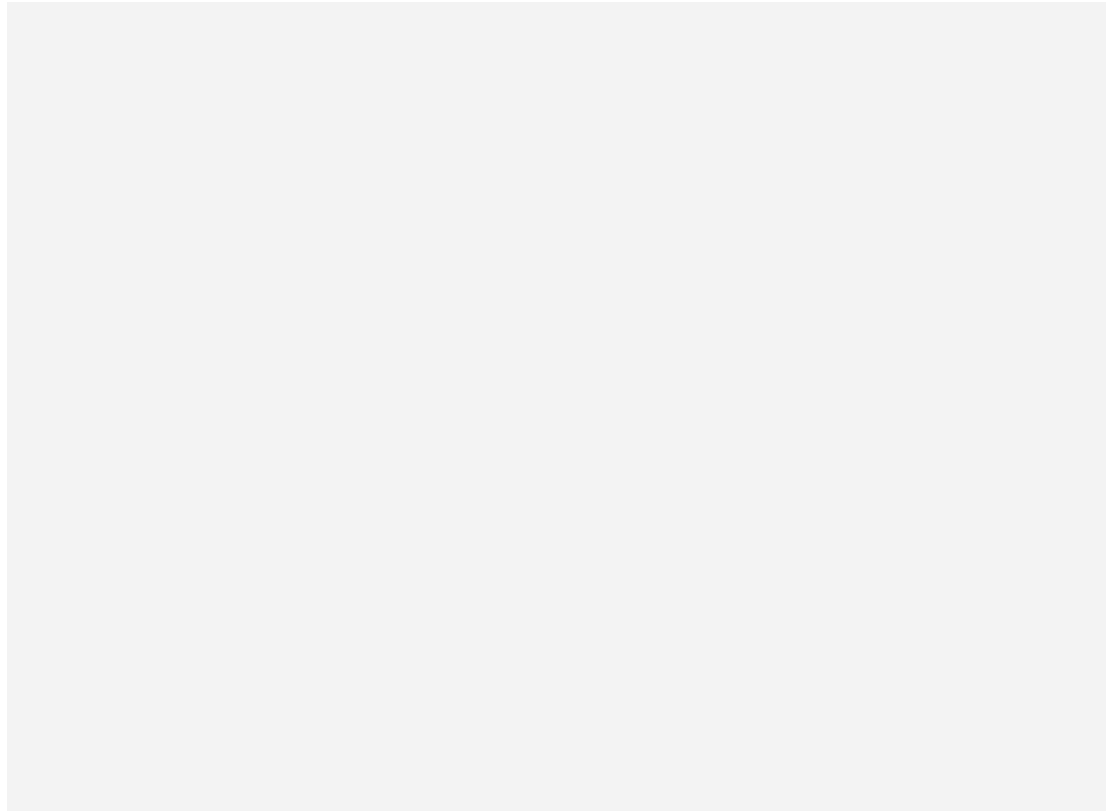
Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.

Measurement procedure used for **Al**

Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:

Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.

Measurement procedure used for **Cd**

Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:
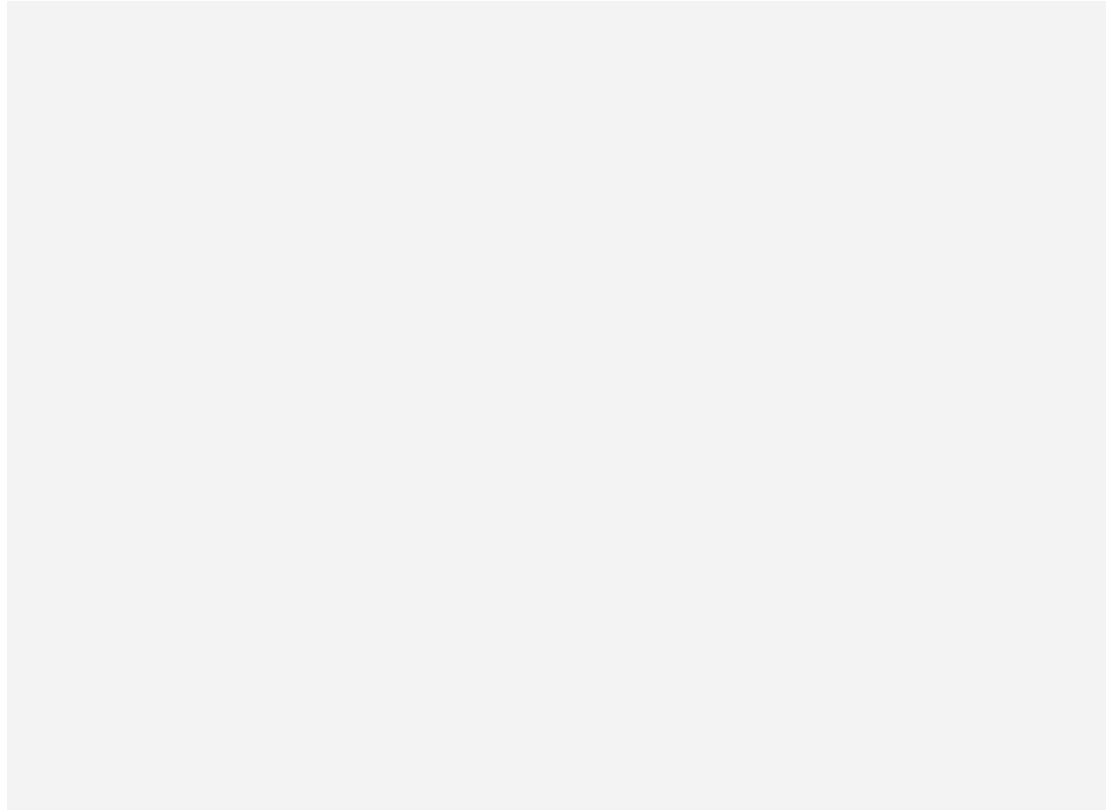
Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.

Measurement procedure used for **Cr**

Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:
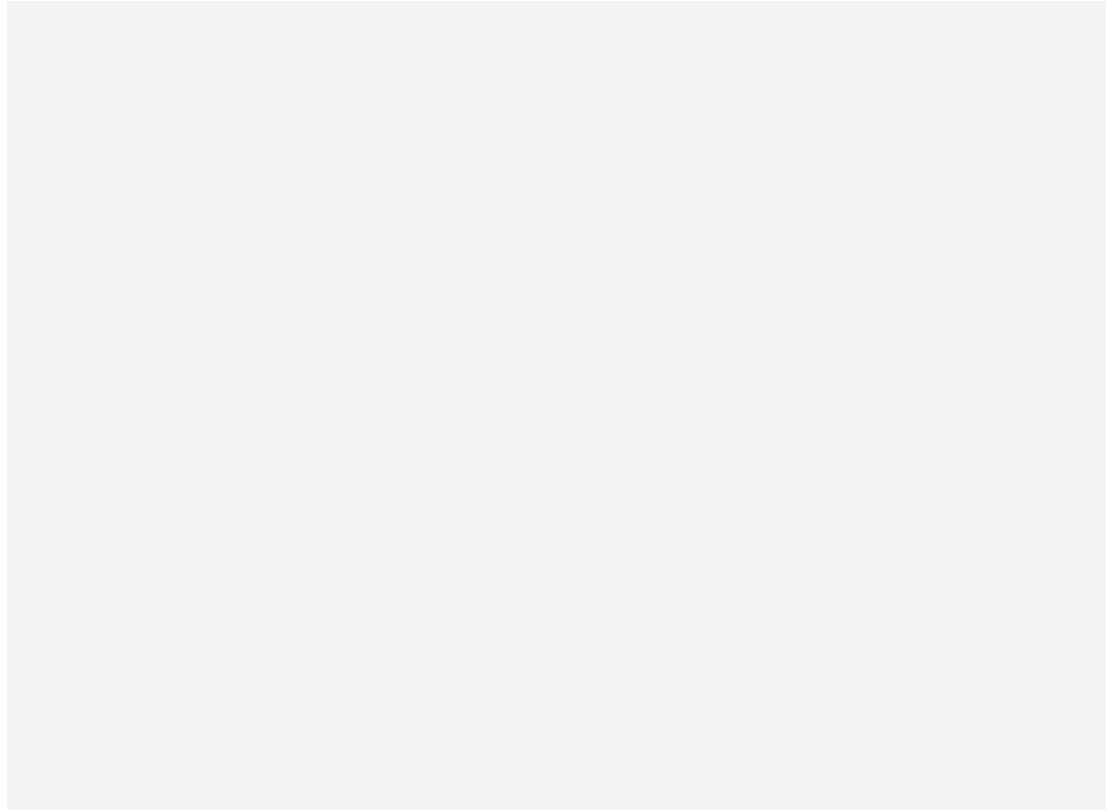
Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.

Measurement procedure used for **Ni**

Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:

Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.

Measurement procedure used for **Tl**
Sample pre-treatment:

Sample mass analysed:

Sample decomposition:

Treatment of decomposed material (dilution, separation, ect.):

Method used in determination step:
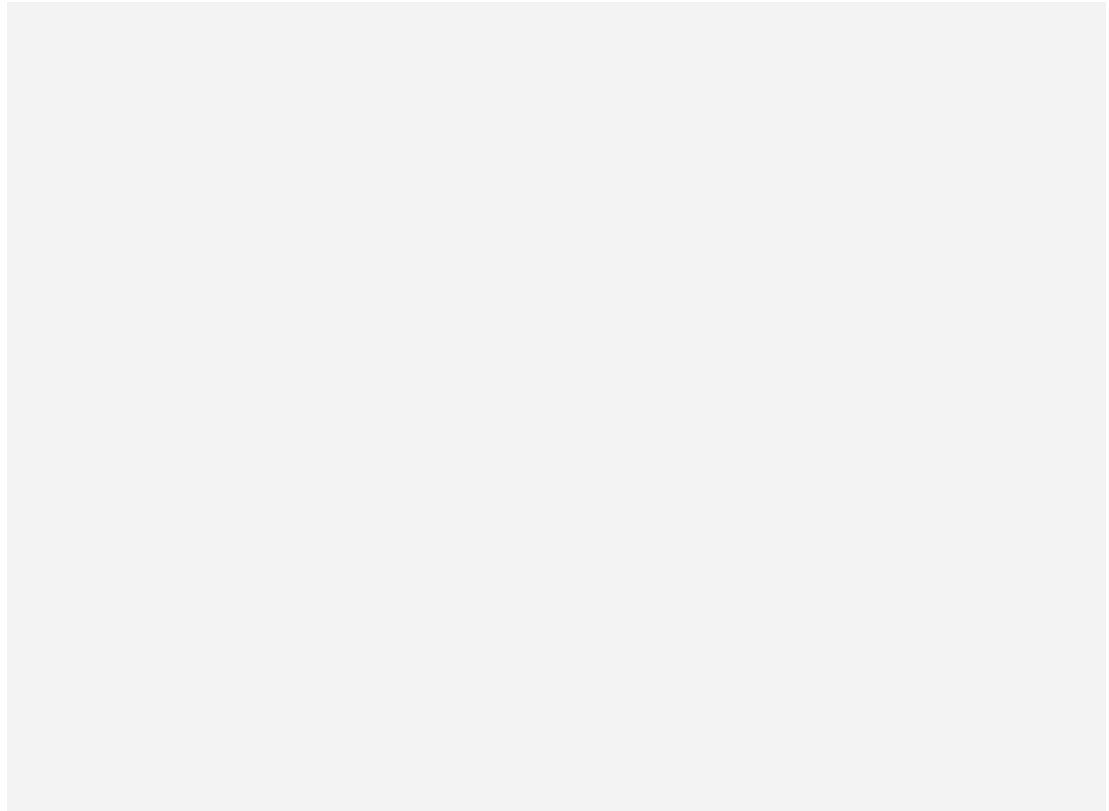
Calibration approach:

Calibration material:

Traceability of values used for calibration:

Calculation of measurement result:

Calculation of (combined) standard uncertainty:

Additional remarks:

Use extra sheet if required.