Report of the study CCQM-K64

Analysis of a Copper Alloy

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With participation of:

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CONTENT

1. SUMMARY

The CCQM-K64 study was performed to demonstrate and document the measurement capabilities of national metrology institutes in the determination of main and minor elements in copper alloys. The key comparison was co-ordinated by BAM Federal Institute for Materials Research and Testing, Berlin, Germany as an activity of the Inorganic Analysis Working Group of CCQM. Elements to be determined were Cu, Pb, Sn, Fe and Ni in a lead containing brass.
Five national metrology institutes registered to participate in CCQM-K64. Three of them analysed all five elements requested, two of them did not perform analyses for tin. The participants used different analytical methods, all of them seem to be suitable, especially for Cu-determination.
The BAM reference material AKP 220/2 Special Brass (unknown to the participants) was used as test sample in this study.

CCQM-K64 demonstrates the abilities of metrological institutes to measure the mass fractions of main, minor and trace components of a copper alloy for copper (main element, > 50 % mass fraction), lead (minor element, 1 – 5 % mass fraction) and iron, nickel and with reservations tin (as trace components, 0,01 – 0,5 % mass fraction). Only three of five participants determined tin.
The analytical methods used were electrogravimetry (for copper and lead), flame-AAS, and ICP-MS.
The scope of the key comparison extends to other copper alloys comprising the same or similar constituents and other elements in the same mass fraction range when analysed using the technique(s) applied in CCQM-64. It extends also to other non ferrous metal alloys if the sample preparation is similar.

2. INTRODUCTION

Metal and metal alloy industries are huge, and the economic impact of chemical measurement is very large. The range of commercial metal and alloy materials is also very wide. Thus, it has been a challenge in the frame of CCQM to identify the appropriate measurement capability in this area. Therefore BAM suggested an international key comparison “Analysis of a Copper Alloy” following the previos pilot study CCQM-P76. This was agreed within the Inorganic Analysis Working Group.
Elements to be determined were Cu, Pb, Sn, Fe and Ni in a leaded brass. The concentrations levels (as mass fractions) of the main elements were about 58 % for Cu and 1.4 % for Pb and between 0.03 % and 0.16 % for the other elements. In July 2007, the pilot lab BAM asked for participation. Five NMIs (including the pilot lab) expressed their participation. After studies on steel (CCQM-K33) and aluminium (CCQM-K42) this was the third key comparison within CCQM in the field of metal-and metal-alloy analysis.

3. LIST OF PARTICIPANTS

Table 1 contains all participants of CCQM-K64.

Table 1: CCQM-K64 participants

Participant	Analytes	Country	Contact
BAM Federal Institute for Materials Research and Testing	Cu, Pb, Fe, Ni, Sn	Germany	Dr. Sebastian Recknagel
CENAM National Center of Metrology	Cu, Pb, Fe, Ni, Sn	Mexico	Ma. Genoveva Moreno-Ramirez
INM Romania National Institute of Metrology	Cu, Pb, Fe, Ni	Romania	Dr. Mirella Buzoianu
INMETRO Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Cu, Pb, Fe, Ni, Sn	Brazil	Dr. T. Oliveira Araujo
INTI Instituto Nacional de Tecnologia Industrial – Centro de QUIMICA	Cu, Pb, Fe, Ni	Argentina	Licenciada Mónica Borinsky

INTI reported an additional set of results for lead for information using a different analytical method.

The samples were distributed to the participants by mail on December 04, 2007. All samples reached their destination safely. Results were asked to be sent until March 31, 2008.

4. SAMPLES

The material taken for CCQM-K64 was a special brass BAM reference material AKP 220/2. Approx. 200 g of finely divided chips were distributed into 6 bottles. The composition of the material was:
57.78 % of copper
1.36 % of lead
0.03 % of tin
0.16 % of iron
0.94 % of manganese
0.002 % of bismuth
0.06 % of nickel
Rest: zinc

A homogeneity test was carried out using all 6 bottles foreseen for distribution to the participating laboratories. 4 x 0.5 g were taken from each bottle and dissolved in HCl/HNO_3. Determination of Cu, Sn, Pb, Ni and Fe was done using ICP OES. Table 2 shows the results of the homogeneity test. Especially in case of copper it can be seen that the method used for the homogeneity test (ICP OES) is not the ideal one because of the high spread. Electrogravimetry which was used for certification analysis is much more suitable for Cu-determination but it was not used for homogeneity testing because of its high sample consumption.
The variance between-bottle was calculated using Equation 1, the variance within bottle using Equation 2:

$$s^2_{between} = \frac{\sum_{L=1}^{Z} (\bar{x}_L - \bar{\bar{x}})^2}{Z-1} \qquad (1)$$

$Z = \text{number of samples} (= 6)$

$\bar{x}_L = \text{mean within bottle} (n = 4)$

$\bar{\bar{x}} = \text{mean of all determinations} (n = 24)$

$$s_{within}^2 = \frac{\sum_{L=1}^{Z} (s_L)^2}{Z} \qquad (2)$$

$$Z = \text{number of samples} (= 6)$$

s_L = standard deviation of single results in bottle L (n = 4)

The inhomogeneity contribution s is calculated according to Equation 3:

$$s = \sqrt{s_{between}^2 + s_{within}^2} \qquad (3)$$

The results given in Table 2 indicate that the inhomogeneity contribution is less than 0.8% (relative) for Cu, Fe, and Ni, less than 0.5% (relative) for Pb and about 1.7% (relative) for Sn. This inhomogeneity estimation can be understood as a "worst-case" estimation because the spread of results coming from the method used for the homogeneity test (ICP OES), which pretends inhomogeneities, is included in the spread of the results.

Table 2: Results from homogeneity testing

	Cu	**Pb**	**Sn**	**Fe**	**Ni**
Inhomogeneity contribution (rel.)	0.77 %	0.45 %	1.7 %	0.73 %	0.71 %

5. TECHNICAL PROTOCOL

The technical protocol attached as appendix A instructed participants concerning test sample, methods of measurement, reporting, and time schedule.

6. METHODS OF MEASUREMENT

Any suitable method(s) of measurement were allowed to be used. Four measurements for each element were required to be carried out by each participant. An overview of the measurement and sample preparation methods used by each participant is given in Appendix B.

7. KEY COMPARISON REFERENCE VALUE

Depending on the element different approaches to establish the key comparison reference value (KCRV) were used. For copper four of five participants performed their determinations using electrogravimetry. Since this method is accepted as primary method of analysis, the mean of the laboratories' means was taken as KCRV. The expanded uncertainty (k = 2) of the KCRV for Cu was calculated from the combined uncertainty values including the standard deviation calculated from the laboratories' means and those coming from the homogeneity testing. In case of the other elements Pb, Fe, Ni and Sn isotope dilution mass spectrometry (IDMS) as primary method of analysis was used to establish the KCRVs. For the element Sn an ICP-MS instrument and for the elements Pb, Fe and Ni a thermion mass spectrometer (TIMS) was used. In all cases the matrix was separated using ion exchange after dissolution of the test sample with HCl and H_2O_2. For each element five test portions were dissolved for analysis.

The expanded uncertainties (k = 2) of the KCRVs were calculated from the combined uncertainty values including the uncertainties of the ID-MS measurements and those coming from the homogeneity testing following Equations 4 (Cu) and 5 (Pb, Fe, Sn, Ni):

$$U(KCRV) = 2 \cdot \sqrt{\frac{s_{KC}^2}{n} + s_{homo}^2} \quad (4)$$

$$U(KCRV) = 2 \cdot \sqrt{u_{IDMS}^2 + s_{homo}^2} \quad (5)$$

with s_{KC} : std-dev. of laboratory means
n : number of participants (datasets used for calculation)
s_{homo} : uncertainty contribution coming from homogeneity testing
u_{IDMS} : uncertainty of IDMS-measurement.

The KCRVs for all elements together with their uncertainties are given in Tab. 8.

8. RESULTS

The results for all elements, their standard deviation of the single values and the expanded uncertainties (rounded according to DIN 1333) reported by each participant are given in Tables 3 - 7 including information on the measurement methods and calibration used by the participating laboratories. The labotratories used pure metals or chemicals or certified reference materials (NIST, CENAM, Merck) for calibration. (Laboratory INMETRO did not report any uncertainty, therefore the standard deviations of the single results multiplied with a coverage factor of 2 were used as a measure for the uncertainty of this laboratory). All results including the KCRV are illustrated in Figures 1 - 5. The bars of each data in the figures indicate the uncertainties reported by each laboratory.
Table 8 summerizes the results of the key comparison and shows mean of means, median and range of laboratory means.

Table 3: Results for Copper

Participant	Method	Materials used for calibration	Matrix matching	Reported value / mass fraction (%)	Std-dev. (%) of single results	Combined standard uncertainty / mass fraction (%)	
BAM	Electro-gravimetry	Cu-metal^{+} (> 99.99%)	------	57.89	0.086	0.18 (k = 2)	*1
CENAM	Electro-gravimetry	DMR-17f^{+}	------	57.62	0,042	0.60 (k = 2)	*1 *2
INM Romania	Electro-gravimetry	------	------	57.71	0.073	0.46 (k = 2)	*1
INMETRO	FAAS	SRM 3114 (NIST)	------	57.83	0.36		
INTI	Electro-gravimetry	std soln.$^{+}$ (Merck Certipur)	------	57.96	0.032	0.035 (k = 2)	

*1 Determination of residual copper with FAAS
*2 mean of 6 single results
$^{+}$ Calibration for FAAS-determination of residual copper in the test portion solution after electrolysis

Table 4: Results for Lead

Participant	Method	Materials used for calibration	Matrix matching	Reported value / mass fraction (%)	Std-dev. (%) of single results	Combined standard uncertainty / mass fraction (%)	
BAM	FAAS	Pb-metal (> 99.99%)	Cu	1.361	0.015	0.03 (k = 2)	
CENAM	FAAS	DMR-63d	------	1.363	0.008	0.046 (k = 2)	*1
INM Romania	FAAS	Certipur (Merck)	yes	1.323	0.048	0.10 (k = 2)	
INMETRO	FAAS	SRM 3128 (NIST)	------	1.292	0.006	------	
INTI-1	Electro-gravimetry	------	------	1.419	0.031	0.03 (k = 2)	
INTI-2	*FAAS*	*Certipur (Merck)*	------	*1.412*	*0.022*	*0.04 (k = 2)*	*2

*1 mean of 6 single results
*2 additional result for information

Table 5: Results for Tin

Participant	Method	Materials used for calibration	Matrix matching	Reported value / mass fraction (%)	Std-dev. (%) of single results	Combined standard uncertainty / mass fraction (%)	
BAM	FAAS after extraction	Sn-metal (> 99.9%)	------	0.0283	0.0011	0.0022 (k = 2)	
CENAM	ICP-MS	SRM 3161a (NIST)	------	0.0301	0.0001	0.0008 (k = 2)	*1
INM Romania	------	------	------	------	------	------	
INMETRO	FAAS	SRM 3161a (NIST)	------	0.0359	0.0001		
INTI	------	------	------	------	------	------	

*1 mean of 6 single results

Table 6: Results for Iron

Participant	Method	Materials used for calibration	Matrix matching	Reported value / mass fraction (%)	Std-dev. (%) of single results	Combined standard uncertainty / mass fraction (%)	
BAM	FAAS	Fe-metal (> 99.9%)	------	0.175	0.0029	0.006 (k = 2)	*2
CENAM	FAAS	SRM 3126 (NIST)	------	0.171	0.0006	0.004 (k = 2)	*1
INM Romania	FAAS	Certipur (Merck)	yes	0.172	0.0051	0.006 (k = 2)	
INMETRO	FAAS	SRM 3126a (NIST)	------	0.159	0.0072	------	
INTI	FAAS	Certipur (Merck)	------	0.171	0.0025	0.0033 (k = 2)	

*1 mean of 6 single results
*2 analysis carried out in the solution after electrolytic separation of Cu

Table 7: Results for Nickel

Participant	Method	Materials used for calibration	Matrix matching	Reported value / mass fraction (%)	Std-dev. (%) of single results	Combined standard uncertainty / mass fraction (%)	
BAM	FAAS	Ni-metal BAM RS4	------	0.0649	0.0009	0.0018 (k = 2)	*2
CENAM	FAAS	DMR-40d	------	0.0666	0.0003	0.0049 (k = 2)	*1
INM Romania	FAAS	Certipur (Merck)	yes	0.0667	0.0017	0.0060 (k = 2)	
INMETRO	FAAS	SRM 3136 (NIST)	------	0.0658	0.0002	------	
INTI	FAAS	Certipur (Merck)	------	0.0631	0.0025	0.0010 (k = 2)	

*1 mean of 6 single results
*2 analysis carried out in the solution after electrolytic separation of Cu

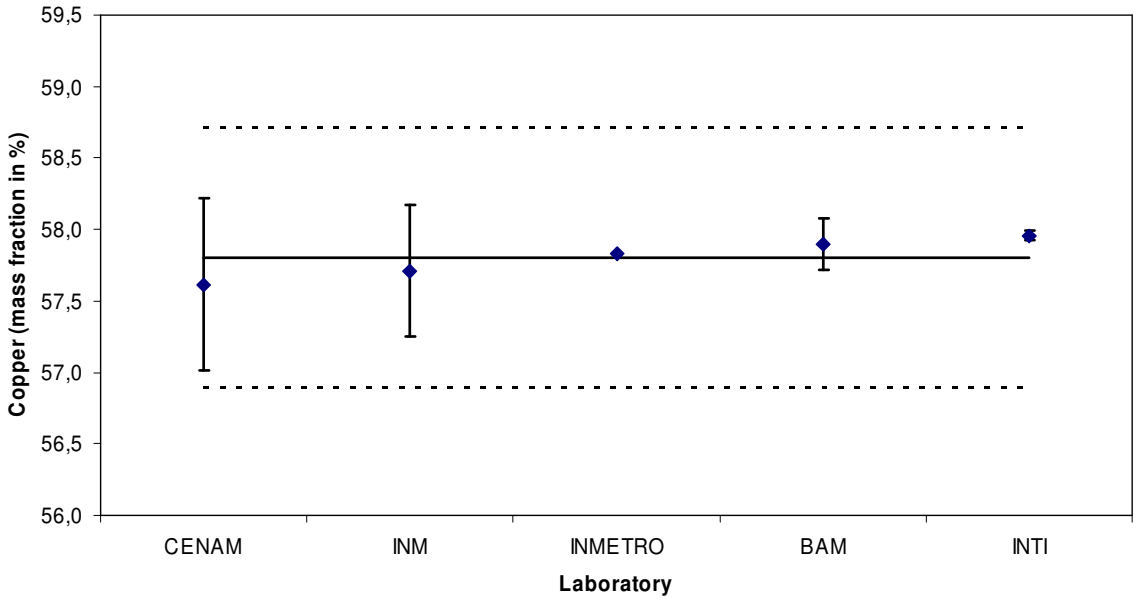

Fig. 1: Results for the element Cu (continuous line: KCRV; dotted line: U(KCRV), k = 2, note: INMETRO did not report any uncertainty)

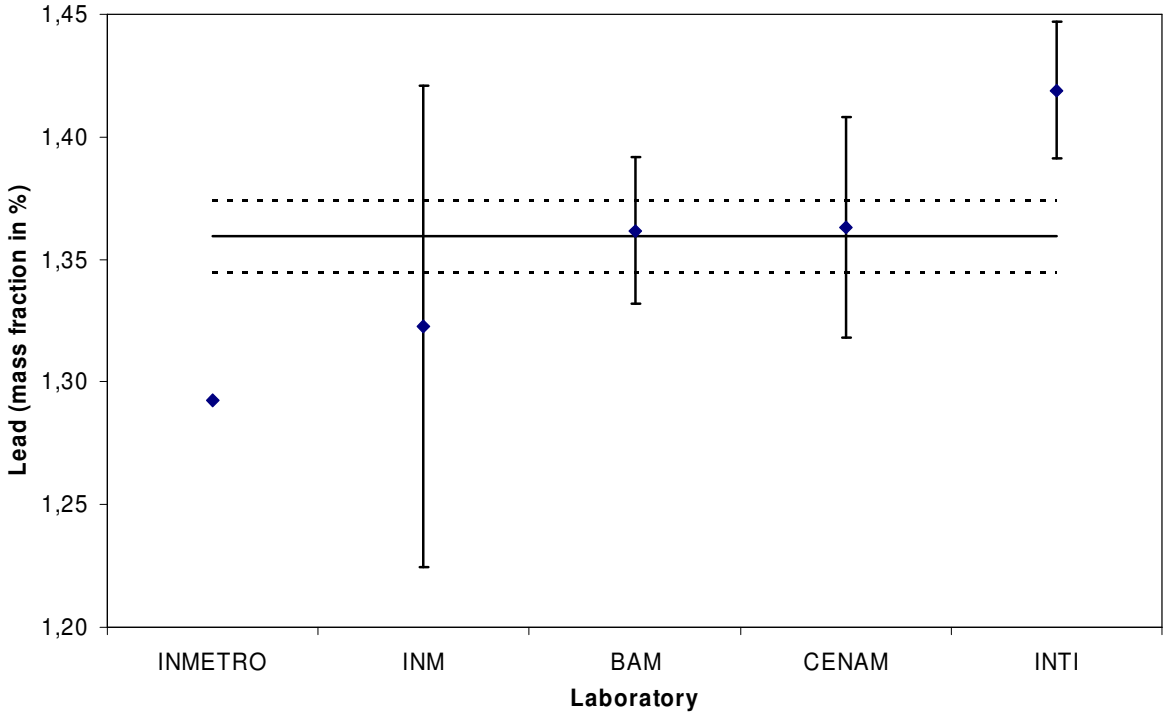

Fig. 2: Results for the element Pb (continuous line: KCRV; dotted line: *U*(KCRV), *k* = 2; note: INMETRO did not report any uncertainty)

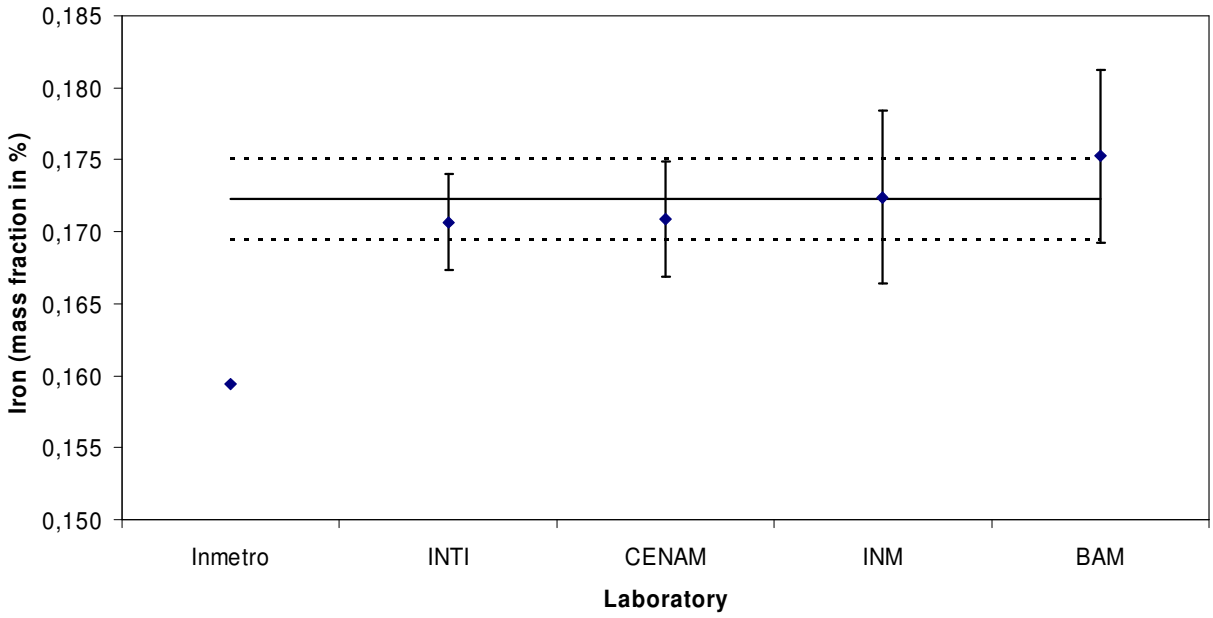

Fig. 3: Results for the element Fe (continuous line: KCRV; dotted line: *U*(KCRV), *k* = 2; note: INMETRO did not report any uncertainty)

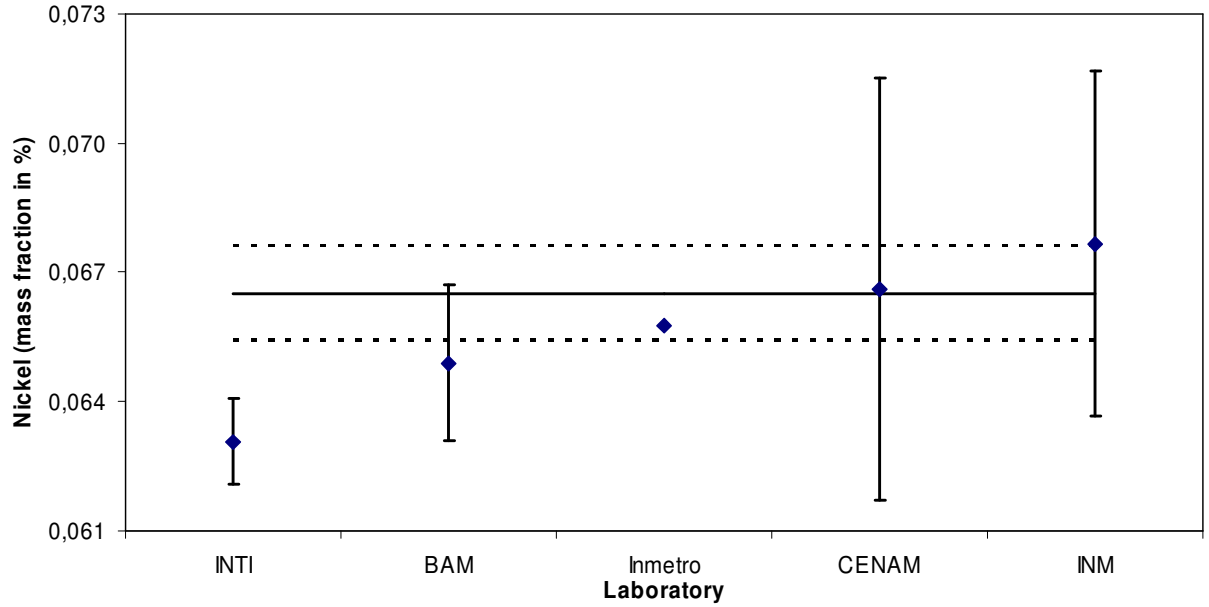

Fig. 4: Results for the element Ni (continuous line: KCRV; dotted line: U(KCRV), k = 2; note: INMETRO did not report any uncertainty)

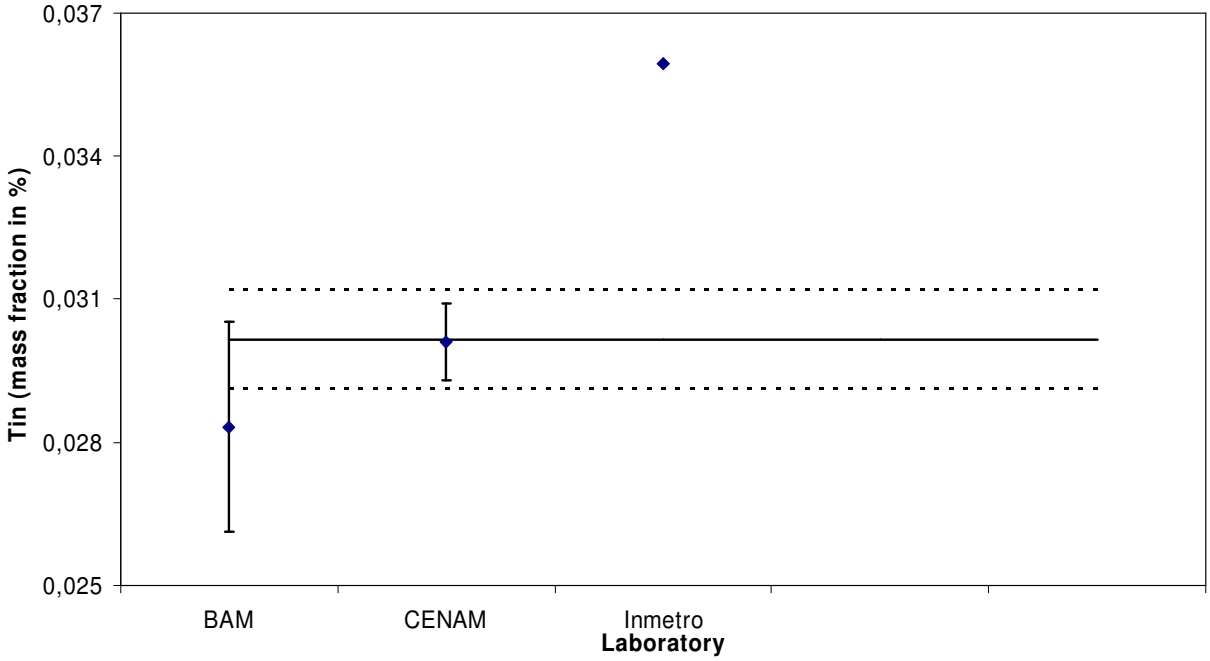

Fig. 5: Results for the element Sn (continuous line: KCRV; dotted line: U(KCRV), k = 2; note: INMETRO did not report any uncertainty)

Table 8: Results of CCQM-K64 (given as mass fraction in %)

	Cu	Pb	Sn	Fe	Ni
KCRV	57.80	1.359	0.03017	0.1723	0.0665
U(KCRV), *k* = 2	0.91	0.015	0.0011	0.0029	0.0011
Mean	57.80	1.36	0.031	0.170	0.066
Std.-dev.	0.139	0.049	0.0044	0.0061	0.0017
Median	57.83	1.36	0.030	0.171	0.066
MAD	0.12	0.040	0.0018	0.0016	0.0009
Min	57.62	1.29	0.027	0.159	0.063
Max	57.96	1.42	0.036	0.175	0.068
Number of data reported	5	5*	3	5	5

* 1 participant reported a second dataset for Pb for information

9. DEGREE OF EQUIVALENCE

For the benchmarking of participant mean values *w*(x) of the determined analyte x the degree of equivalence D_i for the participant i is calculated as the absolute difference between *w*(x) of participant i and the key comparison reference value KCRV(x).

$$D_i = w_i(x) - KCRV(x)$$

$$D_i rel = \frac{D_i}{KCRV}$$

The combined uncertainty $u[D_i]$ of the degree of equivalence can be calculated by

$$u_x[D_i] = \sqrt{u^2[w_i(x)] + u^2[KCRV(x)]}$$

$$u_x[D_i]_{rel\%} = 100 \cdot \frac{\sqrt{u^2[w_i(x)] + u^2[KCRV(x)]}}{KCRV}$$

with

$u_i[w(x)]$: Standard uncertainty of the mean value *w*(x) of participant i

u[KCRV(x)]: Standard uncertainty of the key comparison reference value

The expanded uncertainty of the degree of equivalence is then calculated by

$$U_x[D_i] = k \cdot u_x[D_i] = 2 \cdot u_x[D_i]$$

using a coverage factor *k* = 2.

Tab. 9 – 13 show the calculated *D*-values and its uncertainties, Fig. 6 – 10 show the relative degrees of equivalence $D_i$rel for the participating laboratories with the KCRVs for the determined elements.

Tab. 9: Degree of equivalence for the element Cu

KCRV(Cu)	**57,7950**
***u*[KCRV(Cu)]**	**0,4550**
n	**4**

CCQM-K64 copper alloy
Degree of equivalence Analyte x: **Cu**

1	2	3	4	5	6
No.	Participant	$D = w(Cu) - KCRV(Cu)$ [% abs.]	$U_{Cu}(D)$ [% abs.]	$U_{Cu}(D)_{rel.\%}$ [% rel.]	D_{rel} [% rel.]
1	**BAM**	0,100	0,93	1,6	0,17
2	**CENAM**	-0,18	1,09	1,9	-0,31
3	**INM**	-0,086	1,02	1,8	-0,15
4	**INMETRO**				
5	**INTI**	0,16	0,91	1,6	0,28

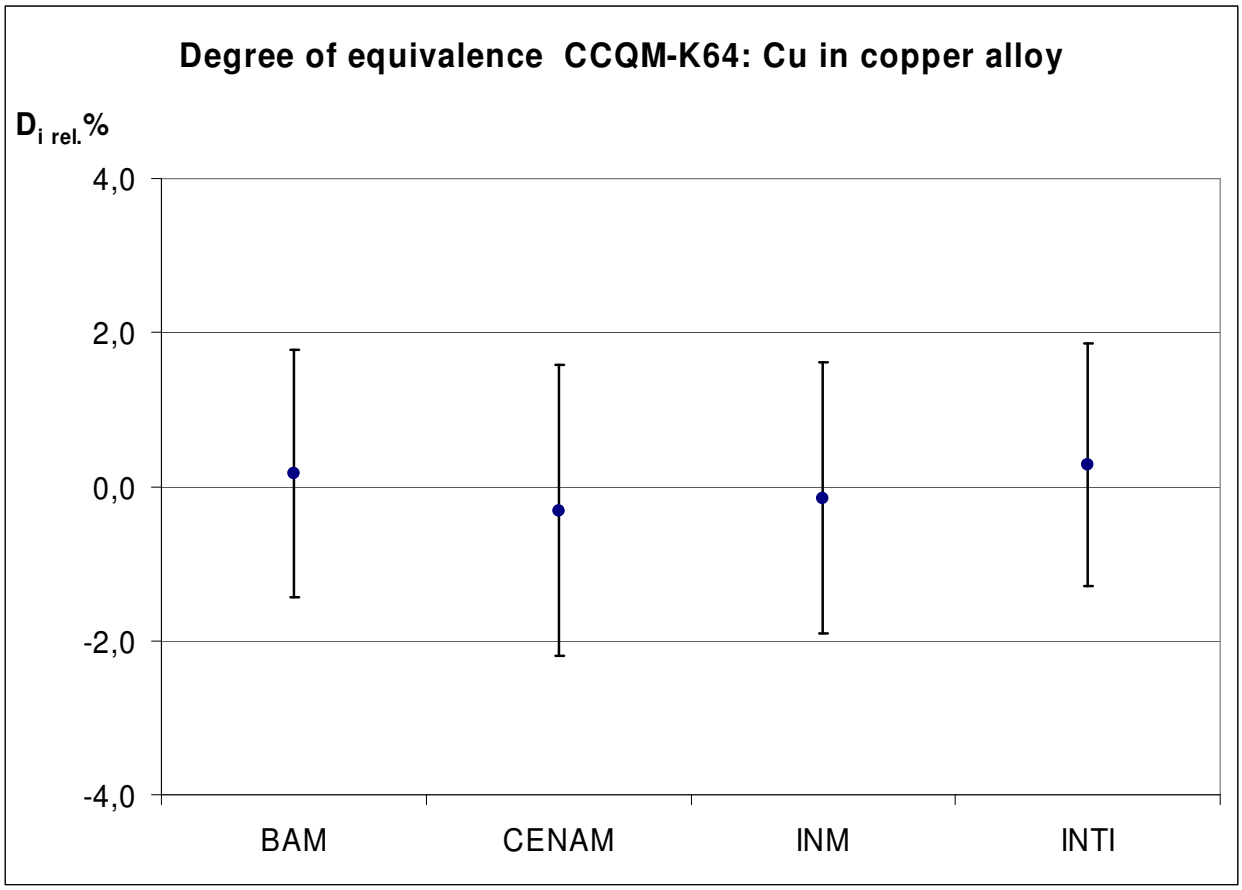

Fig. 6: Relative degree of equivalence of the participating laboratories for the element Cu

Tab. 10: Degree of equivalence for the element Pb

KCRV(Pb)	**1,3593**
***u*[KCRV(Pb)]**	**0,0072**

CCQM-K64 copper alloy
Degree of equivalence Analyte x: **Pb**

1	2	3	4	5	6
No.	Participant	$D = w$(Pb) - KCRV(Pb) [% abs.]	U_{Pb}(D) [% abs.]	$U_{Pb}(D)_{rel.\%}$ [% rel.]	D_{rel} [% rel.]
1	**BAM**	0,0016	0,0333	2,4	0,12
2	**CENAM**	0,0036	0,0482	3,5	0,26
3	**INM**	-0,0364	0,0991	7,3	-2,68
4	**INMETRO**				
5	**INTI**	0,0596	0,0333	2,4	4,38

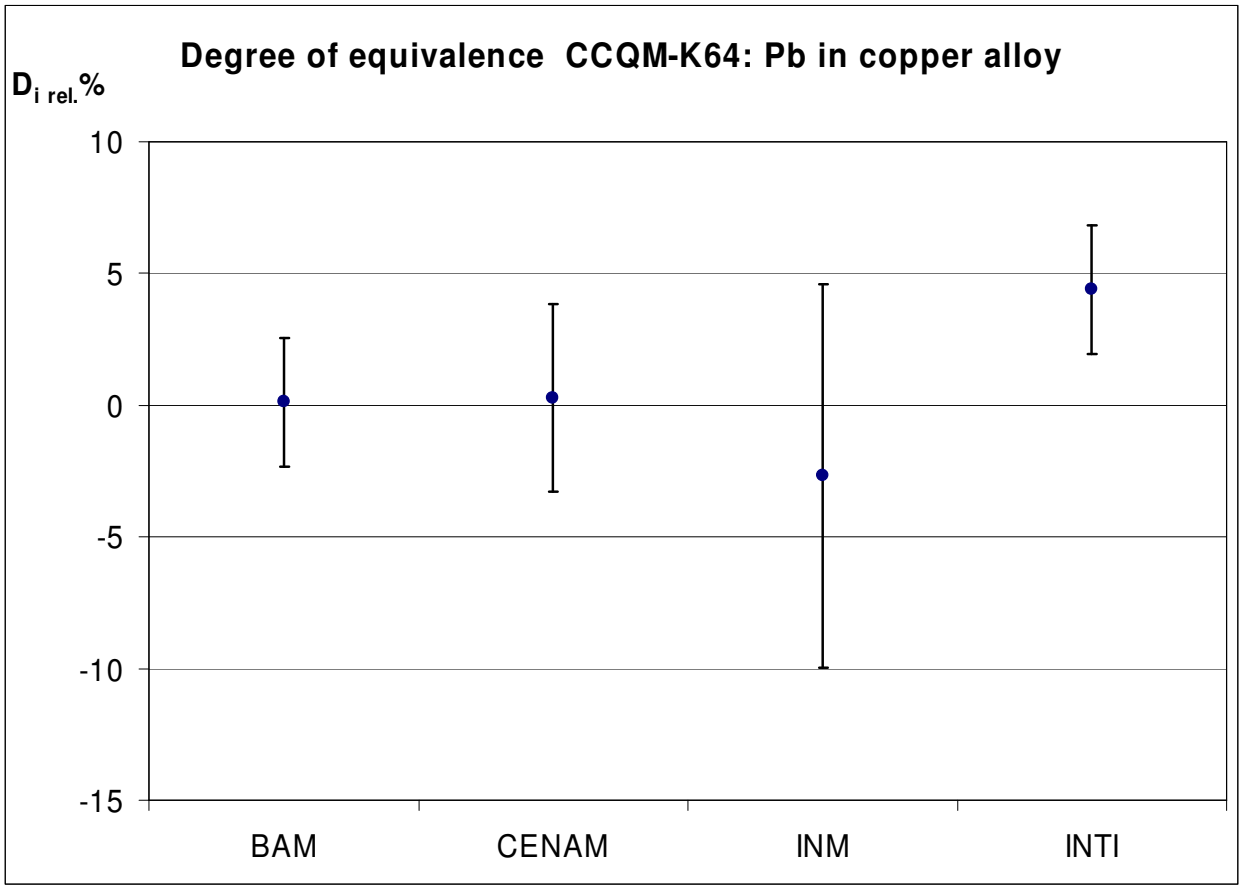

Fig. 7: Relative degree of equivalence of the participating laboratories for the element Pb

Tab. 11: Degree of equivalence for the element Fe

KCRV(Fe)	**0,1723**
***u*[KCRV(Fe)]**	**0,0014**

CCQM-K64 copper alloy
Degree of equivalence Analyte x: **Fe**

1	2	3	4	5	6
No.	Participant	$D = w$(Fe) - KCRV(Fe) [% abs.]	U_{Fe}(D) [% abs.]	$U_{Fe}(D)_{rel.\%}$ [% rel.]	D_{rel} [% rel.]
1	**BAM**	0,0030	0,0066	3,9	1,75
2	**CENAM**	-0,0014	0,0085	4,9	-0,81
3	**INM**	0,0001	0,0066	3,9	0,06
4	**INMETRO**				
5	**INTI**	-0,0016	0,0044	2,5	-0,92

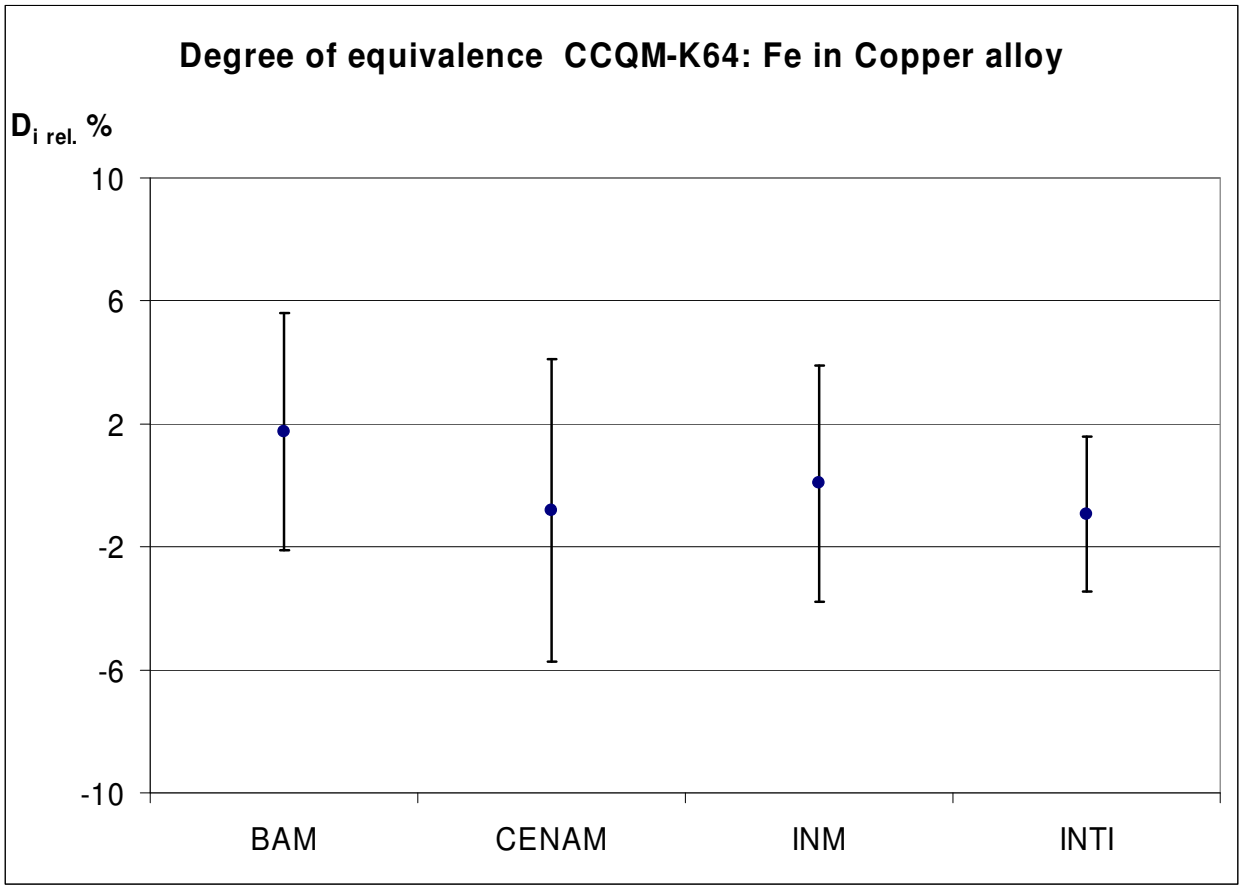

Fig. 8: Relative degree of equivalence of the participating laboratories for the element Fe

Tab. 12: Degree of equivalence for the element Ni

KCRV(Ni)	**0,0665**
***u*[KCRV(Ni)]**	**0,00026**

CCQM-K64 copper alloy
Degree of equivalence Analyte x: **Ni**

1	2	3	4	5	6
No.	Participant	$D = w$(Ni) - KCRV(Ni) [% abs.]	U_{Ni}(D) [% abs.]	$U_{Ni}(D)_{rel.\%}$ [% rel.]	D_{rel} [% rel.]
1	**BAM**	-0,0016	0,0021	3,2	-2,44
2	**CENAM**	0,0001	0,0051	7,7	0,12
3	**INM**	0,0002	0,0061	9,2	0,27
4	**INMETRO**				
5	**INTI**	-0,0034	0,0015	2,2	-5,14

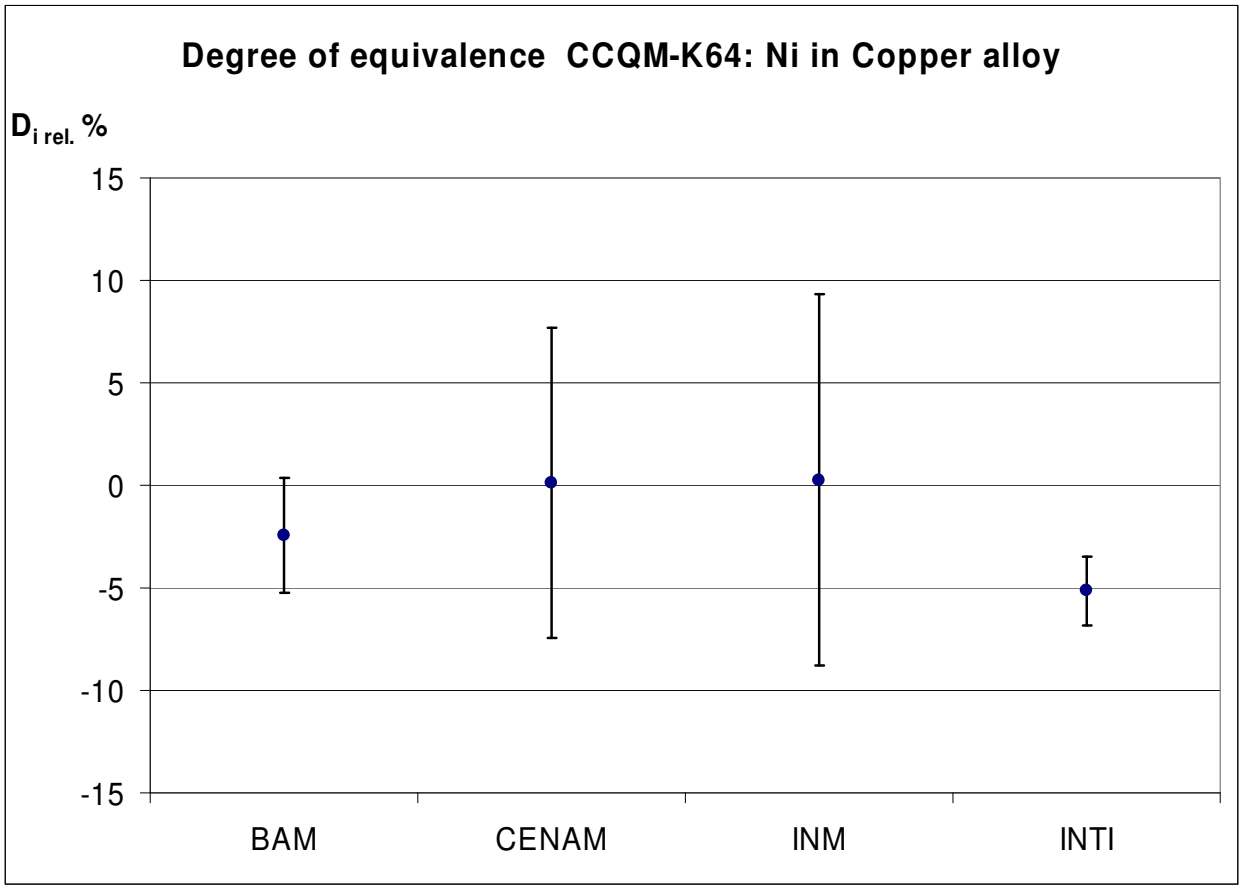

Fig. 9: Relative degree of equivalence of the participating laboratories for the element Ni

Tab. 13: Degree of equivalence for the element Sn

KCRV(Sn)	**0,0302**
***u*[KCRV(Sn)]**	**0,00005**

CCQM-K64 copper alloy
Degree of equivalence Analyte x: **Sn**

1	2	3	4	5	6
No.	Participant	$D = w(\mathrm{Sn}) - \mathrm{KCRV(Sn)}$ [% abs.]	$U_{\mathrm{Sn}}(D)$ [% abs.]	$U_{\mathrm{Sn}}(\mathrm{D})_{\mathrm{rel.\%}}$ [% rel.]	D_{rel} [% rel.]
1	**BAM**	-0,0019	0,0024	8,1	-6,19
2	**CENAM**	-0,0001	0,0013	4,3	-0,23
3	**INM**				
4	**INMETRO**				
5	**INTI**				

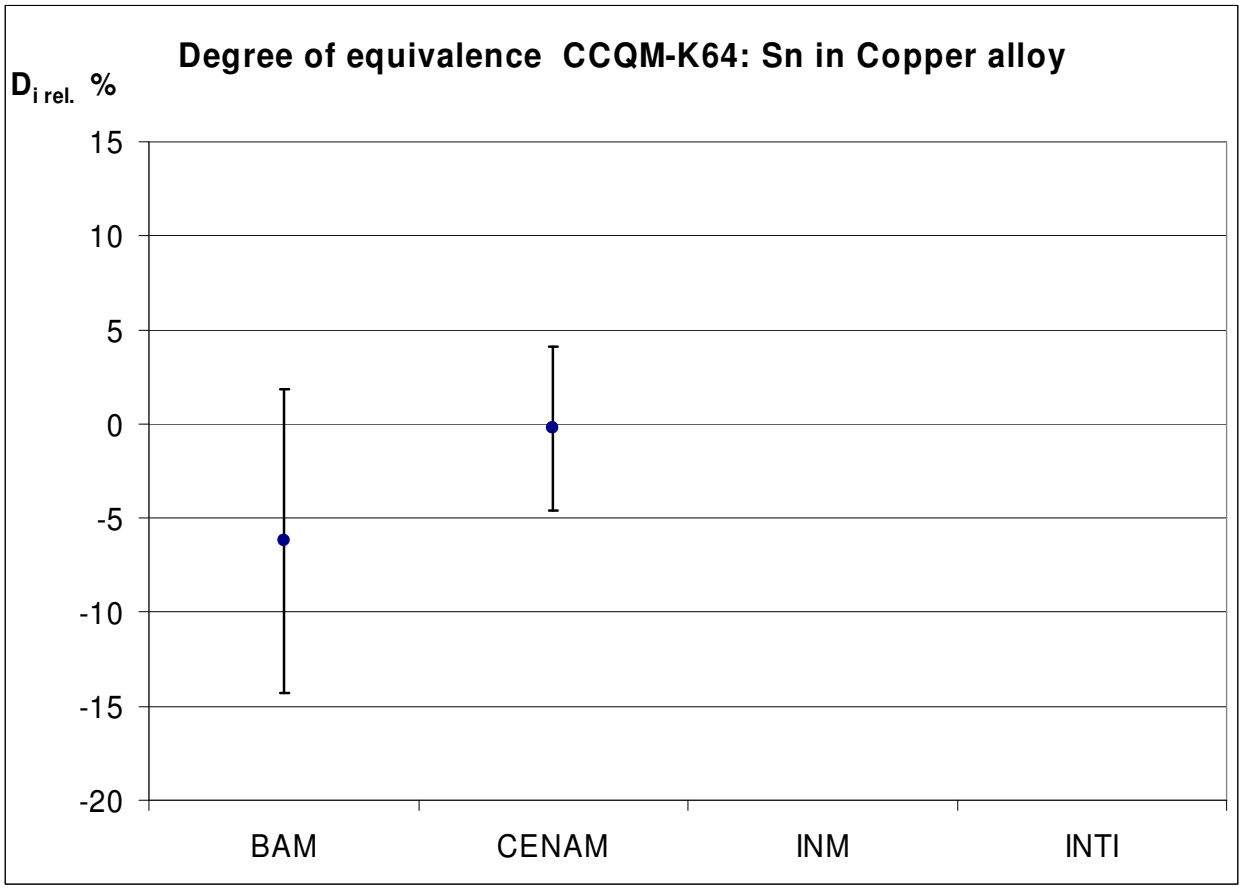

Fig. 10: Relative degree of equivalence of the participating laboratories for the element Sn

7 Discussion

Five NMIs participated in CCQM-K64 Determination of Cu, Pb, Fe, Ni and Sn in a copper alloy (brass). Three of five participants reported results for all five elements, the other two for all elements except tin. One participant reported a second set of results for the element Pb for information. This set was not included in any evaluation. All participants were requested to report an uncertainty estimation but only four participants did so. Therefore the standard deviation of the single results were taken as uncertainty estimation of the fifth laboratory. For this participant no degree of equivalence was calculated.

For the element copper, which was determined by all participants using the primary method electrogravimetry the mean value of all laboratories‘ means was taken as KCRV. All results for copper were fully consistent with the KCRV and with the results of the other participants respectively. The most important contribution to the uncertainty of the KCRV for this element came from homogeneity testing where a method (ICP OES) was used which was not ideal for this purpose.

For the element lead only three results were consistent with the KCRV. The other two results were not inconsistent with all of these results taking into account their uncertainty ranges. However, the relative degrees of equivalence were < 5 % for all results.

For the elements Fe and Ni four of five results were consistent with the KCRVs, the fifth results were too low in both cases, i.e. the relative degrees of equivalence were > 5 %. These results only partly overlaped with the results of other laboratories taking into account their uncertainty ranges.

For the element tin only three of the participants reported results. Two of them were consistent with the KCRV considering their uncertainty ranges. The third result was too high and did not overlap with the two other results, its relative degree of equivalence was > 10 %.

8 Conclusions

There is no doubt that copper and copper alloys are very important materials in different areas of industry and research and that the chemical composition can significantly influence their properties and performance characteristics. Therefore a global harmonization of the analytical results is of high technical and economical interest.

The results of CCQM-K64 show that the determination of copper in copper alloys using electrogravimetry is well proficient by the participating laboratories.

In case of the other elements there is at least one result which was not consistent with the KCRV of the respective elements.

9 Acknowledgement

Many thanks to Dr. Jochen Vogl and his group for establishing the KCRVs for the elements Pb, Fe, Ni and Sn.

Appendix A - Technical protocol

CCQM-K64 Analysis of a Copper Alloy

Technical protocol

Introduction

Cu-alloys are very important basic materials for producing several consumer goods, the range of commercial copper alloy materials is very large. Thus, it has been a challenge to identify the appropriate measurement activity for the CCQM in this area. This proposed study is the first key comparison in the field of copper and its alloys and follows CCQM-P76. It is piloted by Federal Institute for Materials Research and Testing (BAM).

Samples

Each participant will receive one bottle containing about 30 g of small chips of leaded brass. The homogeneity of the material will be checked based on determinations using a sample size of about 0,5 g.

Elements to be determined are

Cu	approx. 58 % mass fraction
Pb	approx. 1.4 % mass fraction
Sn	approx. 0.03 % mass fraction
Fe	approx. 0.15 % mass fraction
Ni	approx. 0.05 % mass fraction

in copper-alloy (brass). All elements are related to material standards for lead containing brasses.

Methods of Measurement

Each participant can use any suitable method(s) of measurement. The use of primary methods (ID-MS, Gravimetry, Titration) as well as activation analysis is appreciated. CCQM members are invited to join this comparison or to designate a competent laboratory in their coutries. Four measurements of each element are to be carried out by each participant.

Reporting

The results should be reported in % mass fraction of each measurand to BAM, accompanied by a full uncertainty budget. Reporting the details of the procedure, traceability links (calibration substances), and the instrument(s) used is desirable. An Excel-sheet for reporting the results will be distributed to all participants by email.

Uncertainty budget

According to the Guide to Expression of Uncertainty in Measurement (GUM) an uncertainty budget should be calculated considering all known influencing paramaters (especially contributions from calibration!) which can cause a bias of the analytical result (e.g. weighing parameters, temperatures, dispersion of measuring values, volumes etc.).

In that context it should be noted that there are two groups of influencing parameters: The

parameters of the "Type A" are based on frequency distributions. The parameters of the "Type B" are based on data of former results or experiences.

Time schedule

Deadline of registration of participation:	September 15, 2007
Dispatch of the samples:	November 2007
Deadline for receiving the report:	March 31, 2008
Draft report:	May 2008
Final report:	August 2008

Participants

Participation is open to all interested CCQM members and official observers who can perform the determination. The CCQM members and official observers. Please inform Dr. Recknagel of the contact person and the shipping address.
Because of the limited number of sample bottles, the number per economy might have to be restricted. However, we do not anticipate such oversubscription. We would like to ask CCQM members and official observers to coordinate participation within their economies including inviting participants, shipping samples, and receiving the reports.

Pilot laboratory

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Appendix B – Overview of the methods used by the participants

Tab. B1: Methods used for the determination of Cu by the participants of CCQM-K64

NMI	Analytical Method	Material used for calibration	Sample intake in g	Dissolution reagents	
BAM	electrogravimetry FAAS (residual copper)	--- Cu-metal (>99.99%)	1	15 ml HNO_3	
CENAM	electrogravimetry FAAS (residual copper)	--- Cu-solution (DMR-17f)	0.5	3.5 ml HNO_3	
INM	electrogravimetry	---	0.5	HNO_3	
INMETRO	FAAS	Cu-solution (NIST 3114)	0.5	HNO_3	
INTI	electrogravimetry FAAS (residual copper)	--- Cu-solution (Merck)	1	10 ml HNO_3	

Tab B2: Methods used for the determination of Pb by the participants of CCQM-K64

NMI	Analytical Method	Material used for calibration	Sample intake in g	Dissolution reagents	Matrix matching
BAM	FAAS	Pb-metal (>99.99%)	0.38	15 ml HNO_3	Cu
CENAM	FAAS	Pb-solution (DMR-63d)	0.5	3.5 ml HNO_3	
INM	FAAS	Pb-solution (Merck)	0.18 - 0.45	HNO_3 + HCl	yes
INMETRO	FAAS	Pb-solution (NIST 3128)	0.5	HNO_3	
INTI	1) electrogravimetry 2) FAAS	--- Pb-solution (Merck)	1 0.5 - 1	10 ml HNO_3 10 ml HCl	

Tab. B3: Methods used for the determination of Fe by the participants of CCQM-K64

NMI	Analytical Method	Material used for calibration	Sample intake in g	Dissolution reagents	Matrix matching
BAM	FAAS*	Fe-metal (>99.9%)	1	15 ml HNO_3	
CENAM	FAAS	Fe-solution (NIST 3126)	0.5	3.5 ml HNO_3	
INM	FAAS	Fe-solution (Merck)	0.18 – 0.45	HNO_3 + HCl	yes
INMETRO	FAAS	Fe-solution (NIST 3126a)	0.5	HNO_3	
INTI	FAAS	Fe-solution (Merck)	0.5 - 1	10 ml HCl	

*after electrolytic separation of copper

Tab. B4: Methods used for the determination of Ni by the participants of CCQM-K64

NMI	Analytical Method	Material used for calibration	Sample intake in g	Dissolution reagents	Matrix matching
BAM	FAAS*	Ni-metal (BAM RS4)	1	15 ml HNO_3	
CENAM	FAAS	Ni-solution (DMR-40d)	0.5	3.5 ml HNO_3	
INM	FAAS	Ni-solution (Merck)	0.18 – 0.45	HNO_3 + HCl	yes
INMETRO	FAAS	Ni-solution (NIST 3136)	0.5	HNO_3	
INTI	FAAS	Ni-solution (Merck)	0.5 - 1	10 ml HCl	

*after electrolytic separation of copper

Tab. B5: Methods used for the determination of Sn by the participants of CCQM-K64

NMI	Analytical Method	Material used for calibration	Sample intake in g	Dissolution reagents	Matrix matching
BAM	FAAS after extraction	Sn-metal (>99.9%)	1	40 ml HCl	
CENAM	ICP-MS	Sn-solution (NIST 3161a)	0.5	3.5 ml HNO_3	
INM	---	---	---	---	
INMETRO	FAAS	Sn-solution (NIST 3161a)	0.5	HNO_3	
INTI	---	---	---	---	