

CCQM-K98 Pb isotope amount ratios in bronze

Draft B

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1	BAM	2	KRISS	3	LGC	4	NIM	5	NIST
6	NMIJ	7	РТВ	8	SYKE	9	TÜBÍTAK UME		

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1. Motivation

Isotope amount ratios (hereafter referred to as simply isotope ratios) are proving useful in an ever increasing array of applications that range from studies unravelling transport processes, to pinpointing the provenance of specific samples as well as trace element quantification by using isotope dilution mass spectrometry (IDMS). These expanding applications encompass fields as diverse as archaeology, food chemistry, forensic science, geochemistry, medicine and metrology. However, to be effective tools, the isotope ratio data must be reliable and traceable to enable the comparability of measurement.

The importance of traceability and comparability in isotope ratio analysis has already been recognized by the Inorganic Analysis Working Group (IAWG) within the CCQM. Three pilot studies have focused on the quality of isotope ratio determinations (P48 "U isotope ratios in urine", P75 "stable isotopes in Methionine", P105 "⁸⁷Sr/⁸⁶Sr in wine"). Moreover, isotope ratio measurements are fundamental to IDMS amount of substance determinations. For example, when Pb quantification using IDMS is undertaken, this requires the measurements of Pb isotope ratios. While the requirements for isotope ratio accuracy and precision in the case of IDMS are generally quite modest, "absolute" Pb isotope ratio measurements for geochemical age dating and source rock characterization as well as forensic provenance and fingerprinting studies require Pb isotope ratio determinations, a Key Comparison was urgently needed. Therefore, it was decided at the IAWG meeting in Paris in April 2011 that a Key Comparison on the determination of Pb isotope amount ratios in a pure Pb solution and in a bronze sample should be organized.

Measuring Pb isotope amount ratios in a pure Pb solution, while seemingly straight forward, rigorously tests the ability of analyst to correct for any instrumental effects (such as mass discrimination and blank correction) on the measured ratios. Pb, present in trace amounts in a metal matrix sample (e.g. Pb in bronze), provides a real world test of the whole chemical and instrumental procedure, from chemical separation and sample purification to analysis and subsequent correction of appropriate instrumental effects on the separated samples.

A suitable bronze material with a Pb mass fraction between 10 and 100 $\text{mg}\cdot\text{kg}^{-1}$ was available at BAM. A high purity solution of Pb with a mass fraction of approximately 100 $\text{mg}\cdot\text{kg}^{-1}$ was also available. By comparing the Pb isotope ratio results obtained for the bronze sample with the Pb isotope ratio results from the Pb solution, potential biases arising from the processing of the bronze sample could be effectively identified and separated from the instrumental effects arising from the measurement and data processing protocol.

2. Framework & predefinitions of the comparison

2.1 Measurand and reporting

Mandatory measurands in sample A and B

- > Isotope amount ratio $n(^{206}Pb)/n(^{204}Pb)$
- Isotope amount ratio n(²⁰⁷Pb)/n(²⁰⁴Pb)
- > Isotope amount ratio $n(^{208}Pb)/n(^{204}Pb)$
- Isotope amount ratio n(²⁰⁸Pb)/n(²⁰⁶Pb)

The first three isotope ratios are commonly reported in Pb isotopic studies, while the last isotope ratio is typically measured when doing Pb quantitation by IDMS involving a ²⁰⁶Pb spike.

While each participant in the Key Comparison was asked to provide, for each sample, a single value for each of the mandatory measurands, this number was to be the average of at least three (3) independent values for sample A and three (3) independent values for each unit of sample B. An independent value was defined as being a value measured on a new sample and not just a new measurement on an already processed sample. The results were to be reported using the questionnaire and reporting form, which was provided after registration.

2.2 Methods of measurement

Each participant was free to use any method they deemed suitable for measuring the individual isotope ratios. When several methods could be used by a participant, only one composite result was to be reported.

Methods involving instrumentation capable of producing results of the highest metrological quality, such as multi-collector TIMS or ICPMS, were preferred; but results from single collector ICPMS and TIMS as well as solid sampling procedures in combination with mass spectrometry (e.g. laser ablation ICPMS) were also acceptable. A key requirement for all analytical procedures was the production of an uncertainty budget and a traceability statement. The use of a Pb-matrix separation procedure was also encouraged.

2.3 Guidance values and target uncertainty

The materials were selected so that the Pb isotopic compositions of the samples were within the natural range of the Pb isotopic compositions as tabulated by IUPAC [1]. The Pb mass fraction in sample A (water) was approximately 100 mg·kg⁻¹, while the Pb mass fraction of sample B (bronze) was between 10 and 100 mg·kg⁻¹.

Because this type of isotope ratio analysis is typically used to determine isotope variations in natural materials where important differences can range from a few percent to less than a few thousandths of a percent, the target uncertainty for all ratios was set to 0.2 %, relative (k=1).

2.4 Key comparison reference value (KCRV)

The Key Comparison Reference Values (KCRV) were to be calculated from results that had undergone analyte-matrix separation and also met the target uncertainty requirements. In the event that these criteria proved too rigorous (e.g. too few results met these requirements), the process to establish a KCRV was to be revisited and a suitable alternative approach for setting this value would be chosen.

2.5 Time schedule of the comparison

The key comparison was agreed upon by the IAWG in April 2011. Additionally, it was agreed that before starting the key comparison, a questionnaire would be circulated amongst all interested institutes to obtain feedback. The responses from the questionnaire (see Annex I) were discussed at the April 2012 meeting, after which the key comparison was started. The final schedule for the project is shown in Table 1.

Table 1: Time scale of CCQM-K98.

Action	Deadline
Call for participants	May 2012
Registration of participants	31 st of July 2012
Sample shipment	End of September 2012
Results reporting	30 th of June 2013
Report A:	End of September 2013
Report B:	End of December 2013

3. Participants

A total of nine (9) NMIs or designated institutes (DI) participated in CCQM-K98 and provided nine (9) independent data sets. The participating institutes are listed in Table 2 in alphabetical order. All measurement results and the details of analytical procedures were reported on time.

Table 2:Participants in CCQM-K98.

Abbrev.	Institute	Responsible/Contact	Country
BAM	Federal Institute for Materials Research and Testing	Jochen Vogl	DE
KRISS	Korea Research Institute of Standards and Science	Yong-Hyeon Yim	KR
LGC	Laboratory of the Government Chemist	Heidi Goenaga-Infante	UK
NIM	National Metrology Institute P.R. China	Tongxiang Ren	CN
NIST	National Institute of Standards and Technology	Robert D. Vocke, Jr.	US
NMIJ	National Metrology Institute of Japan	Naoko Nonose	JP
PTB	Physikalisch-Technische Bundesanstalt	Olaf Rienitz	DE
SYKE	Finnish Environment Institute	Teemu Näykki	FI
TÜBÍTAK	TÜBÍTAK UME National Metrology Institute	Nilgün Tokman	TR

4. Samples

4.1 Sample material and instructions for use

For this key comparison, two different sample types were provided. Each participant received one unit of sample A (Pb solution) and two units of sample B (Pb in bronze):

- Sample A was a solution of pure Pb in dilute nitric acid (approximately 6 % v/v) with a Pb mass fraction of approximately 100 mg·kg⁻¹. Each unit contained a least 20 mL of solution. Sample A was delivered in a PFA bottle sealed in a plastic bag.
- Sample B consisted of approximately 1 g of bronze swarf, sealed in glass ampoules. The bronze consisted of approximately 94 % (w/w) Cu and 6 % (w/w) Sn with Pb dispersed as a trace component with a mass fraction between 10 to 100 mg·kg⁻¹. Pb isotopic homogeneity was confirmed for a sample amount of approximately 100 mg.

No specific instructions for use were provided.

4.2 Homogeneity of the sample material

Based on theoretical considerations and confirmed by own measurements the Pb isotopic composition was expected to be homogenously distributed in sample A (water). Sample B (bronze) was also assumed to have a homogenous Pb isotopic composition. This latter assumption was however tested, because the bronze turnings (swarf) had been produced from solid bronze cylinders.

The homogeneity of the Pb isotopes in the bronze needed to be assessed at a level comparable to the best analytical methods (i.e. those with extremely tight reproducibility) that would be later used in the key comparison. Therefore, the homogeneity test was carried out using thermal ionization mass spectrometry (TIMS) with Pb-matrix separation. The procedure described in ref. [2] was followed, however the separation protocol using the Pb-spec resin was replaced by a two stage separation, the first using AG1-X8 (BioRad) and the second involving Sr-Spec resin. In the first stage the Pb was fixed on the AG1-X8 resin and Cu eluted using hydrochloric acid (1 mol/L). Pb was then stripped from the column with 0.01 mol/L HCl. In the second stage (Sr-Spec), the Pb fraction was separated from any remaining impurities.

The homogeneity analysis of the material was carried out at BAM by M. Koenig and J. Vogl using the described procedure. From a population of 317 ampoules, 8 ampoules were randomly selected. From each of these ampoules, three (3) subsamples with sample masses around 100 mg were taken and processed independently. Each subsample was then measured at least twice. The results are listed in Tables 3 through 6.

Sample	Isotope amount ratio n(²⁰⁶ Pb)/n(²⁰⁴ Pb)							
	Aliquot 1	Aliquot 2	Aliquot 3	Mean	Std. dev.			
Amp 23	18.0700	18.0745	18.0743	18.0729	0.0025			
Amp 73	18.0746	18.0768	18.0782	18.0765	0.0018			
Amp 98	18.0734	18.0716	18.0706	18.0719	0.0014			
Amp 138	18.0761	18.0859	18.0800	18.0807	0.0049			
Amp 166	18.0799	18.0763	18.0803	18.0788	0.0022			
Amp 236	18.0752	18.0782	18.0810	18.0781	0.0029			
Amp 287	18.0730	18.0806	18.0805	18.0781	0.0043			
Amp 317	18.0754	18.0764	18.0760	18.0759	0.0005			

Table 3: Isotope amount ratio $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ for the isotopic homogeneity assessment as analyzed by TIMS in three (3) independent aliquots taken from each of eight (8) units of the bronze sample B.

Table 4: Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$ for the isotopic homogeneity assessment as analyzed by TIMS in three (3) independent aliquots taken from each of eight (8) units of the bronze sample B.

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Table 5: Isotope amount ratio $n(^{208}\text{Pb})/n(^{204}\text{Pb})$) for the isotopic homogeneity assessment as analyzed by TIMS in three (3) independent aliquots taken from each of eight (8) units of the bronze sample B.

Sample	Isotope amount ratio n(²⁰⁸ Pb)/n(²⁰⁴ Pb)							
	Aliquot 1	Aliquot 2	Aliquot 3	Mean	Std. dev.			
Amp 23	38.067	38.087	38.087	38.080	0.012			
Amp 73	38.090	38.094	38.110	38.098	0.011			
Amp 98	38.100	38.082	38.079	38.087	0.011			
Amp 138	38.093	38.118	38.114	38.108	0.014			
Amp 166	38.110	38.110	38.107	38.109	0.002			
Amp 236	38.082	38.103	38.097	38.094	0.011			
Amp 287	38.089	38.117	38.110	38.105	0.015			
Amp 317	38.104	38.089	38.081	38.092	0.012			

Table 6:The overall means of the lead isotope ratios of the bronze sample B material listed
in Tables 3-5 with the corresponding F-values.

	Isotope amount ratio						
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)					
Mean	18.0766	15.5852	38.097				
Std. dev.	0.0037	0.0040	0.014				
Rel. Std. dev. in %	0.021	0.026	0.036				
F-value tested *	3.126	2.720	2.497				
F-value tabulated *	4.026	4.026	4.026				

* significance level 1%, v_1 =k-1=7, v_2 =N-k=16

Note that both, the relative standard deviations of the mean of each ampoule and the relative standard deviations of the overall means are similar in magnitude and are less than a standard deviation of 0.05 %, typical for routine TIMS Pb isotopic analyses. The F-test from a one way ANOVA on these data are significantly smaller than the tabulated F-value for a nested design,

F(0.01,7,16)=4.026. Applying a conservative relative standard deviation of 0.05 % to all the measured Pb isotopic ratios and the ampoule mean values, the tested F-values are significantly smaller than the tabulated F-values even at a 10 % significance level. Therefore, the bronze material can be regarded as homogeneous for lead isotope ratios when a sample mass of 100 mg is used. This also means that there is no extra uncertainty contribution for inhomogeneity that needs to be added to the KCRV uncertainty.

5. Results and discussion

5.1 Reference values for KCRV

As described in section 2.4, the KCRV for each of the Pb isotope amount ratios was to be calculated from results that had undergone both an analyte-matrix separation step and met the target uncertainty of 0.2 % (k=1). For this reason all the results from SYKE and TÜBÍTAK UME were not considered when calculating the KCRV, as both participants did not separate the Pb analyte from the matrix. Moreover, the Pb isotope ratio values reported by SYKE did not meet the target uncertainty (Tables 7 and 8). All other results have been used to calculate an arithmetic mean as the basis for the KCRV.

SYKE and TUBITAK UME, and are the bases for the KCRV.									
	Isotope amount ratios in sample A (water)								
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)					
Mean (all)	21.147	15.976	39.96	1.8897					
U _{Mean-a}	0.035	0.037	0.13	0.0028					
u _{Mean-a} in %	0.17	0.23	0.32	0.15					
Mean (restricted)	21.1139	15.9439	39.8502	1.887397					
U _{Mean-r}	0.0012	0.0011	0.0031	0.000045					
<i>u</i> _{Mean-r} in %	0.0059	0.0070	0.0078	0.0024					
Median	21.1140	15.94340	39.8490	1.887400					
U _{Median}	0.0011	0.00062	0.0019	0.000050					
u _{Median} in %	0.0053	0.0039	0.0047	0.0026					
KCRV	21.1139	15.9439	39.8502	1.887397					
U KCRV	0.0012	0.0011	0.0031	0.000045					
U _{KCRV} (<i>k</i> =2)	0.0025	0.0022	0.0062	0.000089					

Table 7: Isotope ratio values for sample A (water) calculated from the results reported by the participants, with associated uncertainties. The restricted mean excludes data from SYKE and TÜBÍTAK UME, and are the bases for the KCRV.

from SYKE and TUBITAK UME, and are the bases for the KCRV.								
	lso	otope amount ratios	in sample B (bronz	ze)				
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)				
Mean (all)	18.096	15.623	38.21	2.1116				
U _{Mean-a}	0.033	0.059	0.18	0.0061				
u _{Mean-a} in %	0.18	0.38	0.46	0.29				
Mean (restricted)	18.0723	15.5776	38.0751	2.10685				
U _{Mean-r}	0.0027	0.0025	0.0078	0.00017				
<i>u</i> _{Mean-r} in %	0.015	0.016	0.020	0.0082				
Median	18.0718	15.5790	38.0790	2.10686				
U _{Median}	0.0038	0.0019	0.0060	0.00022				
u _{Median} in %	0.021	0.012	0.016	0.011				
KCRV	18.0723	15.5776	38.0751	2.10685				
U KCRV	0.0027	0.0025	0.0078	0.00017				
<i>U</i> _{КСRV} (<i>k</i> =2)	0.0055	0.0049	0.016	0.00034				

Table 8: Isotope ratio values for sample B (bronze) calculated from the results reported by the participants, with associated uncertainties. The restricted mean excludes data from SYKE and TÜBÍTAK UME, and are the bases for the KCRV.

For completeness, the mean and the median of all results, which include SYKE and TÜBÍTAK UME, have been calculated and included in Tables 7 and 8. When examining the different average values in these tables, it is clear that the means of all results(Mean(all)) give a significantly larger uncertainty than the restricted means (Mean(restricted)) and the medians. The difference is at least an order of magnitude larger. In addition, the mean values of all results differ markedly from the restricted means and the medians of all results. Note that the restricted means and the medians of all results. Note that the means of all results were biased values.

These data demonstrate two important points. First, by using objective and analytically-based qualifying parameters for selection of inputs for the computation of the KCRV the robustness and uncertainty of this statistic can be significantly improved. Secondly, when qualifying parameters are not available and the number of participants is relatively small and/or the distribution is asymmetric the median remains a very suitable and robust estimator for the KCRV

Standard uncertainties are calculated following the CCQM guidelines for calculating KCRVs.

Standard uncertainty of the Mean [3]:

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

Standard uncertainty of the Median [3]: $u_{Median}^2 = \frac{\pi}{2n} \cdot \hat{\sigma}^2$ with $\hat{\sigma} = MAD_E = 1.483 \cdot MAD$ eqn. 2

5.2 Results as reported from the participants

For the summaries as given in Tables 9 and 10 the following applies:

- Results and combined standard uncertainties were taken from the participant's reporting sheet without any modification.
- > The data shown in Tables 9 and 10 have been used for all calculations.
- Combined standard uncertainties are given in brackets and apply to the last digits of the value

Table 9:	Summary c	of the	results	for	CCQM-K98	sample	А	(water)	as	reported	by	the
	participants											

Institute	Isotope amount ratios in sample A (water)						
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)			
BAM	21.1197 (73)	15.9491 (64)	39.865 (17)	1.88758 (39)			
KRISS	21.1122 (133)	15.9432 (119)	39.8481 (311)	1.8874 (6)			
LGC	21.114 (13)	15.944 (14)	39.849 (35)	1.8874 (7)			
NIM	21.112 (7)	15.942 (6)	39.846 (16)	1.8874 (4)			
NIST	21.1143 (40)	15.9434 (37)	39.8495 (104)	1.88732 (61)			
NMIJ	21.1129 (53)	15.9424 (54)	39.8457 (168)	1.88727 (39)			
PTB	21.1124 (68)	15.9430 (60)	39.848 (15)	1.88741 (37)			
SYKE	21.39 (22)	16.23 (19)	40.84 (55)	1.909 (12)			
TÜBITAK	21.131 (25)	15.946 (18)	39.858 (66)	1.8862 (21)			

Table 10: Summary of the results for CCQM-K98 sample B (bronze) as reported by the participants

Institute	Isotope amount ratios in sample B (bronze)					
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)		
BAM	18.0780 (63)	15.5843 (62)	38.097 (15)	2.10741 (46)		
KRISS	18.0802 (114)	15.5799 (99)	38.0853 (241)	2.1065 (4)		
LGC	18.073 (12)	15.579 (14)	38.079 (34)	2.1070 (8)		
NIM	18.062 (9)	15.567 (10)	38.043 (25)	2.1063 (8)		
NIST	18.0718 (23)	15.5794 (23)	38.0790 (57)	2.10710 (42)		
NMIJ	18.0699 (45)	15.5760 (53)	38.0693 (160)	2.10676 (43)		
PTB	18.0710 (58)	15.5774 (58)	38.073 (15)	2.10686 (41)		
SYKE	18.32 (15)	16.03 (15)	39.43 (40)	2.154 (10)		
TÜBITAK	18.037 (28)	15.532 (32)	37.922 (87)	2.1025 (28)		

For all subsequent Tables in this report the following modifications to the reported data have been applied:

- If the reported value shows one digit less than the reported combined standard uncertainty, a zero is appended to the results value.
- Combined standard uncertainties with more than two significant digits were rounded to two significant digits and the value was rounded accordingly.
- Combined standard uncertainties with only one significant digit were left unmodified

5.3 Summary of reported measurement details

The reported measurement details give a large amount of information that would require many pages to list completely. Therefore, this summary will be limited to the principal factors controlling the quality of the measurements. These include descriptions of the mass spectrometric techniques, the separation procedures, the corrections for mass fractionation/discrimination, the traceability links and the major uncertainty contributions (Tables 11 and 12).

Note, that different mass spectrometric techniques were used by each participant. In one case (NIM) more than one technique was used, however composite results were reported.

Institute	MS technique	MS type	Matrix separation	Recovery in %	Procedure blank	Correction for ²⁰⁴ Hg	Fractionation correction
BAM	MC-TIMS	Sector 54	AG 1X8 Sr Spec	80 ± 10	2.8 ng	No	K-factor
KRISS	MC-ICPMS	Neptune	AG 1X8	tested	0.6 ng	No	K-factor
LGC	MC-ICPMS	Neptune	AG 1X8	> 90 %	0.49 ng	No	²⁰⁵ TI/ ²⁰³ TI
NIM	MC-ICPMS MC-TIMS	Isoprobe Isoprobe T	AG 1X8	> 98 %	45 ng	No	K-factor
NIST	MC-ICPMS	Neptune	Pb Spec	~ 90 %	6 ng	Yes	²⁰⁵ TI/ ²⁰³ TI
NMIJ	MC-ICPMS	Neptune	MetaSEP AnaLig Pb-02	~ 100 %	5 µg/kg	Yes	²⁰⁵ TI/ ²⁰³ TI
PTB	MC-ICPMS	Neptune	Triskem Pb resin PB-C50-A	complete	tested	Yes	K-factor
SYKE	ICP-QMS	Elan DRC II	No	n.a.	Not tested	Yes	K-factor
TÜBITAK	ICP-SFMS	Element 2	No	n.a.	tested	Yes	²⁰⁵ TI/ ²⁰³ TI

Table 11: Overview of the analytical techniques and analytical procedures used by the different participants (abbreviations are explained below).

Abbreviations:

- n.a.: not applicable K-factor: correction factor with K=certified ratio/observed ratio
- ²⁰⁵TI/²⁰³TI: use of TI for correcting mass discrimination

Institute	Traceability	Reprodu-	Major uncertainty contribution			
		cibility *	n(²⁰⁸ Pb)/n(²⁰⁴ Pb)	n(²⁰⁷ Pb)/n(²⁰⁴ Pb)	n(²⁰⁶ Pb)/n(²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)
BAM	NIST SRM 981	0.04 % 0.07 %	204/206 cert. 208/206 cert. Separation	204/206 cert. 207/206 cert. Separation	204/206 cert. Separation 206/204 obs.	208/206 cert. Separation 208/206 obs.
KRISS	NIST SRM 981	0.04 % 0.03 %	obs. ratio sample obs. ratio CRM CRM unc.			
LGC	NIST SRM 981	0.003 % 0.003 %	208/204 cert. 208/204 sa ²⁰⁵ TI/ ²⁰³ TI sa	207/204 cert. 207/204 sa 207/204 st	206/204 cert. 206/204 sa ²⁰⁵ TI/ ²⁰³ TI sa	208/206 cert. 208/206 sa ²⁰⁵ Tl/ ²⁰³ Tl sa
NIM	NIST SRM 981	0.04 % 0.04 %	CRM unc. Blank std. dev.	CRM unc. Blank std. dev.	CRM unc. Blank std. dev.	CRM unc. Blank std. dev.
NIST	NIST SRM 981	0.001 % 0.001 %	208/204 cert. 208/204 st ²⁰⁵ Tl/ ²⁰³ Tl st	207/204 cert. 207/204 st ²⁰⁵ Tl/ ²⁰³ Tl st	206/204 cert. 206/204 st ²⁰⁵ TI/ ²⁰³ TI st	208/204 cert. 206/204 cert. 208/204 st
NMIJ	NIST SRM 981	0.002 % 0.002 %	EDTA matrix CRM unc. repeatability	EDTA matrix CRM unc. ratio sa	EDTA matrix CRM unc. ratio sa	EDTA matrix CRM unc. repeatability
PTB	NIST SRM 981	0.005 % 0.009 %	204/206 cert. 208/206 cert. 208/204 st	204/206 cert. 207/206 cert. 207/204 st	204/206 cert. 206/204 st 206/204 sa	208/206 cert. 208/206 st 208/206 sa
SYKE	NIST SRM 981	1.8 % 1.7 %	Int. 204 sa Int. 208 st	Int. 204 sa Int. 208 st	Int. 204 sa Int. 208 st	Int. 208 sa Int. 208 st
TÜBITAK	NIST SRM 981	0.07 % 0.20 %	Reproducibility unc. 1 st rep. unc. 2 nd rep.			

Table 12: Overview of the traceability links and the major uncertainty contributions to the results reported by the different participants (abbreviations are explained below).

* maximum reproducibility of all isotope ratios given as standard deviation for individually prepared samples; first value for sample A, second value for sample B

Abbreviations:

cert.:	certified value of NIST SRM 981
Int.:	Intensity in cps
rep.:	replicate
sa:	sample
st:	standard, here observed values for NIST SRM 981
unc.:	uncertainty

5.4 Comparisons by measurand

5.4.1 Explanation

The individual results of the nine (9) data sets reported by the participants are grouped in ascending order of the value of the measurand. Also listed are the mean values, the median and the reference values/KCRV for each measurand. These data are listed for each measurand separately in Tables 13 through 20 and plotted in Figures 1 through 8. The displayed uncertainties are combined standards 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.

Each isotope ratio reported by the participants for samples A and B was compared to the appropriate KCRV and target uncertainty.

Consistency of a measurement result with the KCRV within the target standard uncertainty of 0.2 % was calculated according to eqn. 3, irrespective of the reported uncertainty. A consistent result was expressed as a "+" (Yes) and an inconsistent result as a "-" (No) and are tabulated in the columns marked "T" of Tables 13 through 20.

$$|(w_i - w_{Ref})|/(0.002 \cdot w_{Ref})^?$$

eqn. 3

The column headed with a "U" indicates whether the reported measurement uncertainty is below the target uncertainty of 0.2 % or not. Again, a result below the target uncertainty was expressed as a "+" (Yes) and a results above as a "-" (No).

The compatibility of the measurement results with the corresponding reference values is also a very important assessment criteria. The "Degree of Equivalence" (DoE) gives a concise and accepted assessment of the compatibility of the reported result with the KCRV values.

5.4.2 Isotope ratio $n(^{206}Pb)/n(^{204}Pb)$ in sample A (water)

Institute	Isotope	ratio	U _{rel}	Т	U
-	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>U</i> _c			
NIM	21.112	0.007	0.033 %	+	+
KRISS	21.112	0.013	0.063 %	+	+
PTB	21.1124	0.0068	0.032 %	+	+
NMIJ	21.1129	0.0053	0.025 %	+	+
LGC	21.114	0.013	0.062 %	+	+
NIST	21.1143	0.0040	0.019 %	+	+
BAM	21.1197	0.0073	0.035 %	+	+
TÜBITAK	21.131	0.025	0.12 %	+	+
SYKE	21.39	0.22	1.0 %	-	-
Mean (all)	21.147	0.035	0.17 %		
Median (all)	21.1140	0.0011	0.0053 %		
Mean (restricted)	21.1139	0.0012	0.0059 %		

Table 13: Results for $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ in sample A, water (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{206}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ in sample A is judged excellent.

5.4.3 Isotope ratio $n(^{207}Pb)/n(^{204}Pb)$ in sample A (water)

Institute	Isotope	ratio	U _{rel}	Т	U
	<i>n</i> (²⁰⁷ Pb) <i>/n</i> (²⁰⁴ Pb)	Uc	_		
NIM	15.942	0.006	0.038 %	+	+
NMIJ	15.9424	0.0054	0.034 %	+	+
PTB	15.9430	0.0060	0.038 %	+	+
KRISS	15.943	0.012	0.075 %	+	+
NIST	15.9434	0.0037	0.023 %	+	+
LGC	15.944	0.014	0.088 %	+	+
TÜBITAK	15.946	0.018	0.11 %	+	+
BAM	15.9491	0.0064	0.040 %	+	+
SYKE	16.23	0.19	1.2 %	-	-
Mean (all)	15.976	0.037	0.23 %		
Median (all)	15.94340	0.00062	0.0039 %		
Mean (restricted)	15.9439	0.0011	0.0070 %		
15.98 (qd _{b02}) <i>u</i> /(qd _{b02})	MC-ICPMS Neptune MC-ICPMS + TIMS TIMS HR-ICPMS Q-ICPMS Proposed KCRV KCRV + u KCRV - u	Т	Ţ	T	16.23
15.95 -					

Table 14: Results for $n(^{207}Pb)/n(^{204}Pb)$ in sample A, water (for an explanation of T & U see 5.4.1).



KRISS

PTB

sotope a

15.93

15.92

NIM

NMIJ

All reported isotope ratios $n(^{207}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree guite well.

NIST

LGC

TÜBITAK

BAM

SYKE

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{207}Pb)/n(^{204}Pb)$ in sample A is judged excellent.

5.4.4 Isotope ratio $n(^{208}Pb)/n(^{204}Pb)$ in sample A (water)

Institute	Isotope	ratio	U _{rel}	Т	U
-	<i>n</i> (²⁰⁸ Pb) <i>/n</i> (²⁰⁴ Pb)	Uc			
NMIJ	39.846	0.017	0.042 %	+	+
NIM	39.846	0.016	0.040 %	+	+
PTB	39.848	0.015	0.038 %	+	+
KRISS	39.848	0.031	0.078 %	+	+
LGC	39.849	0.035	0.088 %	+	+
NIST	39.850	0.010	0.026 %	+	+
TÜBITAK	39.858	0.066	0.17 %	+	+
BAM	39.865	0.017	0.043 %	+	+
SYKE	40.84	0.55	1.3 %	-	-
Mean (all)	39.96	0.13	0.32 %		
Median (all)	39.8490	0.0019	0.0047 %		
Mean (restricted)	39 8502	0.0031	0 0078 %		

Table 15: Results for $n(^{208}Pb)/n(^{204}Pb)$ in sample A, water (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{208}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{208}Pb)/n(^{204}Pb)$ in sample A is judged excellent.

5.4.5 Isotope ratio $n(^{208}Pb)/n(^{206}Pb)$ in sample A (water)

Institute	Isotope ratio		U _{rel}	Т	U
-	<i>n</i> (²⁰⁸ Pb) <i>/n</i> (²⁰⁶ Pb)	Uc	-		
TÜBITAK	1.8862	0.0021	0.11 %	+	+
NMIJ	1.88727	0.00039	0.021 %	+	+
NIST	1.88732	0.00061	0.032 %	+	+
KRISS	1.8874	0.0006	0.032 %	+	+
LGC	1.8874	0.0007	0.037 %	+	+
NIM	1.8874	0.0004	0.021 %	+	+
PTB	1.88741	0.00037	0.020 %	+	+
BAM	1.88758	0.00039	0.021 %	+	+
SYKE	1.909	0.012	0.63 %	-	-
Mean (all)	1.8897	0.0028	0.15 %		
Median (all)	1.887400	0.000050	0.0026 %		
Mean (restricted)	1.887397	0.000045	0.0024 %		

Table 16: Results for $n(^{208}Pb)/n(^{206}Pb)$ in sample A, water (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{208}Pb)/n(^{206}Pb)$ are in good agreement except those from SYKE, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{208}Pb)/n(^{206}Pb)$ in sample A is judged excellent.

5.4.6 Isotope ratio *n*(²⁰⁶Pb)/*n*(²⁰⁴Pb) in sample B (bronze)

Institute	Isotope	Isotope ratio		Т	U
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	Uc			
TÜBITAK	18.037	0.028	0.16 %	+	+
NIM	18.062	0.009	0.050 %	+	+
NMIJ	18.0699	0.0045	0.025 %	+	+
PTB	18.0710	0.0058	0.032 %	+	+
NIST	18.0718	0.0023	0.013 %	+	+
LGC	18.073	0.012	0.066 %	+	+
BAM	18.0780	0.0063	0.035 %	+	+
KRISS	18.080	0.011	0.063 %	+	+
SYKE	18.32	0.15	0.82 %	-	-
Mean (all)	18.096	0.033	0.18 %		
Median (all)	18.0718	0.0038	0.021 %		
Mean (restricted)	18.0723	0.0027	0.015 %		

Table 17: Results for $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ in sample B, bronze (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{206}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{206}Pb)/n(^{204}Pb)$ in sample B is judged excellent.

5.4.7 Isotope ratio $n(^{207}Pb)/n(^{204}Pb)$ in sample B (bronze)

Institute	Isotope ratio		U _{rel}	Т	U
	<i>n</i> (²⁰⁷ Pb) <i>/n</i> (²⁰⁴ Pb)	Uc			
TÜBITAK	15.532	0.032	0.21 %	-	-
NIM	15.567	0.010	0.064 %	+	+
NMIJ	15.5760	0.0053	0.034 %	+	+
PTB	15.5774	0.0058	0.037 %	+	+
LGC	15.579	0.014	0.090 %	+	+
NIST	15.5794	0.0023	0.015 %	+	+
KRISS	15.5799	0.0099	0.064 %	+	+
BAM	15.5843	0.0062	0.040 %	+	+
SYKE	16.03	0.15	0.94 %	-	-
Mean (all)	15.623	0.059	0.38 %		
Median (all)	15.5790	0.0019	0.012 %		
Mean (restricted)	15.5776	0.0025	0.016 %		

Table 18: Results for $n(^{207}\text{Pb})/n(^{204}\text{Pb})$ in sample B, bronze (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{207}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE and TÜBÍTAK UME, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{207}\text{Pb})/n(^{204}\text{Pb})$ in sample B is judged excellent.

5.4.8 Isotope ratio $n(^{208}Pb)/n(^{204}Pb)$ in sample B (bronze)

Institute	Isotope	e ratio	U _{rel}	Т	U
-	<i>n</i> (²⁰⁸ Pb) <i>/n</i> (²⁰⁴ Pb)	Uc			
TÜBITAK	37.922	0.087	0.23 %	-	-
NIM	38.043	0.025	0.066 %	+	+
NMIJ	38.069	0.016	0.042 %	+	+
PTB	38.073	0.015	0.039 %	+	+
LGC	38.079	0.034	0.089 %	+	+
NIST	38.0790	0.0057	0.015 %	+	+
KRISS	38.085	0.024	0.063 %	+	+
BAM	38.097	0.015	0.039 %	+	+
SYKE	39.43	0.40	1.0 %	-	-
Mean (all)	38.21	0.18	0.46 %		
Median (all)	38.0790	0.0060	0.016 %		
Mean (restricted)	38.0751	0.0078	0.020 %		
38.30 38.25 38.20 38.20 38.15		Ţ	Ţ	T	39.43
⁸ , ^{38.10} – – – –	<u>1</u>	F		•	<u> </u>
it 38.05 -	Ť	<u>I</u>	<u>t</u>		
38.00			* • •	MC-ICPMS MC-ICPMS TIMS HR-ICPMS	Neptune + TIMS

Table 19: Results for $n(^{208}Pb)/n(^{204}Pb)$ in sample B, bronze (for an explanation of T & U see 5.4.1).



PTB

37.85

37.80

TÜBITAK

NIM

NMIJ

All reported isotope ratios $n(^{208}Pb)/n(^{204}Pb)$ are in good agreement except those from SYKE and TÜBÍTAK UME, which exceed the target uncertainty and are thus incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

LGC

NIST

KRISS

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{208}Pb)/n(^{204}Pb)$ in sample B is judged excellent.

Q-ICPMS Proposed KCRV

--- KCRV + u ----- KCRV - u

BAM

SYKE

5.4.9 Isotope ratio n(²⁰⁸Pb)/n(²⁰⁶Pb) in sample B (bronze)

Institute	Isotope	ratio	U _{rel}	Т	U
	<i>n</i> (²⁰⁸ Pb) <i>/n</i> (²⁰⁶ Pb)	Uc			
TÜBITAK	2.1025	0.0028	0.13 %	-	+
NIM	2.1063	0.0008	0.038 %	+	+
KRISS	2.1065	0.0004	0.019 %	+	+
NMIJ	2.10676	0.00043	0.020 %	+	+
PTB	2.10686	0.00041	0.019 %	+	+
LGC	2.1070	0.0008	0.038 %	+	+
NIST	2.10710	0.00042	0.020 %	+	+
BAM	2.10741	0.00046	0.022 %	+	+
SYKE	2.154	0.010	0.46 %	-	-
Mean (all)	2.1116	0.0061	0.29 %		
Median (all)	2.10686	0.00022	0.011 %		
Mean (restricted)	2.10685	0.00017	0.0082 %		

Table 20: Results for $n(^{208}Pb)/n(^{206}Pb)$ in sample B, bronze (for an explanation of T & U see 5.4.1).





All reported isotope ratios $n(^{208}Pb)/n(^{206}Pb)$ are in good agreement except those from SYKE and TÜBÍTAK UME, which are incompatible with the KCRV within the target uncertainty. Note that the median and the restricted mean (KCRV) agree quite well.

All reported results meeting the predefined requirements (target uncertainty and matrix separation) agree with each other within the combined standard uncertainty. Therefore, the overall result for measurements of $n(^{208}Pb)/n(^{206}Pb)$ in sample B is judged excellent.

5.5 Degrees of Equivalence

eqn. 6

 $E_{\rm n} = \frac{|d_{\rm i}|}{U(d_{\rm i})}$

to zero.

The degree of equivalence (DoE), d_i , between an individual NMI result, x_i , and the KCRV, x_{KCRV} , and its uncertainty $u(d_i)$ are calculated using eqns. 4 and 5 [3]. The resultant DoEs are listed together with their associated uncertainties in Table 21 through 28 and are plotted in Figures 9 through 16. The normalized error E_n (eqn. 6) is also added to these tables. For $E_n \leq 1$ the participant's result is compatible with the KCRV.

$$d_i = x_i - x_{KCRV}$$
 eqn. 4
 $u^2(d_i) = u^2(x_i) + u^2(x_{KCRV}) - 2 \cdot cov(x_i, x_{KCRV})$ eqn. 5

The KCRV was calculated as described in section 5.1. Correlations between a single participant's result and the mean as well as correlations between the participants' results were not considered, because the bases for quantitating such correlations were unclear, even considering the common use of NIST SRM 981. Therefore the covariances in eqn. 5 were set

5.5.1 DoE for the isotope ratio $n(^{206}Pb)/n(^{204}Pb)$ in sample A (water)

Table 21: Isotope ratios x_i ($n(^{206}Pb)/n(^{204}Pb)$ in sample A (water)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute		Isotope ratio n(²⁰⁶ Pb)/n(²⁰⁴ Pb)						
	Xi	<i>u_c</i> (x _i)	U(x _i)	d _i	<i>u</i> (<i>d</i> _i)	k	<i>U</i> (<i>d</i> _i)	<i>E</i> n
NIM	21.112	0.007	0.014	-0.0019	0.0071	2	0.014	0.14
KRISS	21.112	0.013	0.027	-0.002	0.013	2	0.027	0.065
PTB	21.1124	0.0068	0.014	-0.0015	0.0069	2	0.014	0.11
NMIJ	21.1129	0.0053	0.011	-0.0010	0.0054	2	0.011	0.094
LGC	21.114	0.013	0.027	0.000	0.013	2	0.026	0.0027
NIST	21.1143	0.0040	0.0080	0.0004	0.0042	2	0.0084	0.044
BAM	21.1197	0.0073	0.015	0.0058	0.0074	2	0.015	0.39
TÜBÍTAK	21.131	0.025	0.051	0.017	0.025	2	0.050	0.34
SYKE	21.39	0.22	0.43	0.28	0.22	2	0.44	0.63



Fig. 9: Plot of the DoE data for $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ in sample A (water) listed in Table 21. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.2 DoE for the isotope ratio $n(^{207}Pb)/n(^{204}Pb)$ in sample A (water)

Table 22: Isotope ratios x_i ($n(^{207}Pb)/n(^{204}Pb)$ in sample A (water)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute		Isotope ratio <i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)						
	Xi	<i>u_c</i> (x _i)	U(x _i)	di	<i>u</i> (<i>d</i> _i)	k	<i>U</i> (<i>d</i> _i)	<i>E</i> _n
NIM	15.942	0.006	0.012	-0.0019	0.0061	2	0.012	0.15
NMIJ	15.9424	0.0054	0.011	-0.0015	0.0055	2	0.011	0.13
PTB	15.9430	0.0060	0.012	-0.0009	0.0061	2	0.012	0.071
KRISS	15.943	0.012	0.024	-0.001	0.012	2	0.024	0.028
NIST	15.9434	0.0037	0.0074	-0.0005	0.0039	2	0.0077	0.061
LGC	15.944	0.014	0.027	0.000	0.014	2	0.028	0.0046
TÜBÍTAK	15.946	0.018	0.037	0.002	0.018	2	0.036	0.059
BAM	15.9491	0.0064	0.013	0.0052	0.0065	2	0.013	0.40
SYKE	16.23	0.19	0.38	0.29	0.19	2	0.38	0.75



Fig. 10: Plot of the DoE data for $n(^{207}\text{Pb})/n(^{204}\text{Pb})$ in sample A (water) listed in Table 22. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.3 DoE for the isotope ratio $n(^{208}Pb)/n(^{204}Pb)$ in sample A (water)

Table 23: Isotope ratios x_i ($n(^{208}Pb)/n(^{204}Pb)$ in sample A (water)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute		Isotope ratio <i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)						
	Xi	<i>u_c</i> (x _i)	<i>U</i> (x _i)	di	<i>u</i> (<i>d</i> _i)	k	<i>U</i> (<i>d</i> _i)	E n
NMIJ	39.846	0.017	0.034	-0.004	0.017	2	0.034	0.13
NIM	39.846	0.016	0.030	-0.004	0.016	2	0.033	0.13
РТВ	39.848	0.015	0.031	-0.002	0.015	2	0.031	0.071
KRISS	39.848	0.031	0.062	-0.002	0.031	2	0.063	0.033
LGC	39.849	0.035	0.070	-0.001	0.035	2	0.070	0.017
NIST	39.850	0.010	0.021	-0.001	0.011	2	0.022	0.032
TÜBÍTAK	39.858	0.066	0.13	0.008	0.066	2	0.13	0.059
BAM	39.865	0.017	0.033	0.015	0.017	2	0.035	0.43
SYKE	40.84	0.55	1.1	0.99	0.55	2	1.1	0.90



Fig. 11: Plot of the DoE data for $n(^{208}\text{Pb})/n(^{204}\text{Pb})$ in sample A (water) listed in Table 23. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.4 DoE for the isotope ratio $n(^{208}Pb)/n(^{206}Pb)$ in sample A (water)

Table 24: Isotope ratios x_i ($n(^{208}Pb)/n(^{206}Pb)$ in sample A (water)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute		Isotope ratio <i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)						
	Xi	<i>u_c</i> (x _i)	U(x _i)	di	u(d i)	k	U(d _i)	E n
TÜBÍTAK	1.8862	0.0021	0.0041	-0.0012	0.0021	2	0.0042	0.28
NMIJ	1.88727	0.00039	0.00078	-0.00013	0.00039	2	0.00079	0.16
NIST	1.88732	0.00061	0.0012	-0.00008	0.00061	2	0.0012	0.063
KRISS	1.8874	0.0006	0.0012	0.00000	0.00060	2	0.0012	0.0024
LGC	1.8874	0.0007	0.0014	0.00000	0.00070	2	0.0014	0.0020
NIM	1.8874	0.0004	0.0008	0.00000	0.00040	2	0.00080	0.0035
PTB	1.88741	0.00037	0.00074	0.00001	0.00037	2	0.00075	0.017
BAM	1.88758	0.00039	0.00077	0.00018	0.00039	2	0.00079	0.23
SYKE	1.909	0.012	0.024	0.022	0.012	2	0.024	0.90



Fig. 12: Plot of the DoE data for $n(^{208}\text{Pb})/n(^{206}\text{Pb})$ in sample A (water) listed in Table 24. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.5 DoE for the isotope ratio $n(^{206}Pb)/n(^{204}Pb)$ in sample B (bronze)

Table 25: Isotope ratios x_i ($n(^{206}Pb)/n(^{204}Pb)$ in sample B (bronze)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute	Isotope ratio <i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)							
	Xi	<i>u_c</i> (x _i)	U(x _i)	di	u(d _i)	k	U(d _i)	E n
TÜBÍTAK	18.037	0.028	0.056	-0.035	0.028	2	0.056	0.63
NIM	18.062	0.009	0.019	-0.0103	0.0094	2	0.019	0.55
NMIJ	18.0699	0.0045	0.0090	-0.0024	0.0053	2	0.011	0.23
PTB	18.0710	0.0058	0.012	-0.0013	0.0064	2	0.013	0.099
NIST	18.0718	0.0023	0.0046	-0.0005	0.0036	2	0.0071	0.066
LGC	18.073	0.012	0.023	0.001	0.012	2	0.025	0.030
BAM	18.0780	0.0063	0.013	0.0057	0.0069	2	0.014	0.42
KRISS	18.080	0.011	0.023	0.0079	0.012	2	0.023	0.34
SYKE	18.32	0.15	0.29	0.25	0.15	2	0.30	0.83



Fig. 13: Plot of the DoE data for $n(^{206}\text{Pb})/n(^{204}\text{Pb})$ in sample B (bronze) listed in Table 25. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.6 DoE for the isotope ratio $n(^{207}Pb)/n(^{204}Pb)$ in sample B (bronze)

Table 26: Isotope ratios x_i ($n(^{207}Pb)/n(^{204}Pb)$ in sample B (bronze)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute	Isotope ratio <i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)							
	X i	<i>u_c</i> (x _i)	U(x _i)	di	u(d _i)	k	<i>U</i> (<i>d</i> _i)	E n
ΤÜΒĺΤΑΚ	15.532	0.032	0.064	-0.046	0.032	2	0.064	0.71
NIM	15.567	0.010	0.019	-0.011	0.010	2	0.021	0.51
NMIJ	15.5760	0.0053	0.011	-0.0016	0.0058	2	0.012	0.13
PTB	15.5774	0.0058	0.012	-0.0002	0.0063	2	0.013	0.014
LGC	15.579	0.014	0.027	0.001	0.014	2	0.028	0.050
NIST	15.5794	0.0023	0.0046	0.0018	0.0034	2	0.0067	0.27
KRISS	15.5799	0.0099	0.020	0.002	0.010	2	0.020	0.11
BAM	15.5843	0.0062	0.012	0.0067	0.0067	2	0.013	0.50
SYKE	16.03	0.15	0.29	0.45	0.15	2	0.30	1.5



Fig. 14: Plot of the DoE data for $n(^{207}\text{Pb})/n(^{204}\text{Pb})$ in sample B (bronze) listed in Table 26. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.7 DoE for the isotope ratio $n(^{208}Pb)/n(^{204}Pb)$ in sample B (bronze)

Table 27: Isotope ratios x_i ($n(^{208}Pb)/n(^{204}Pb)$ in sample B (bronze)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute	Isotope ratio <i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)							
	Xi	<i>u_c</i> (x _i)	U(x _i)	ď	<i>u</i> (<i>d</i> _i)	k	<i>U</i> (<i>d</i> _i)	E n
TÜBÍTAK	37.922	0.087	0.17	-0.153	0.087	2	0.17	0.88
NIM	38.043	0.025	0.050	-0.032	0.026	2	0.052	0.61
NMIJ	38.069	0.016	0.032	-0.006	0.018	2	0.036	0.16
PTB	38.073	0.015	0.029	-0.002	0.017	2	0.034	0.062
LGC	38.079	0.034	0.068	0.004	0.035	2	0.070	0.056
NIST	38.0790	0.0057	0.011	0.004	0.010	2	0.019	0.20
KRISS	38.085	0.024	0.048	0.010	0.025	2	0.051	0.20
BAM	38.097	0.015	0.031	0.022	0.017	2	0.034	0.65
SYKE	39.43	0.40	0.80	1.35	0.40	2	0.80	1.7



Fig. 15: Plot of the DoE data for $n(^{208}\text{Pb})/n(^{204}\text{Pb})$ in sample B (bronze) listed in Table 27. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.5.8 DoE for the isotope ratio $n(^{208}Pb)/n(^{206}Pb)$ in sample B (bronze)

Table 28: Isotope ratios x_i ($n(^{208}Pb)/n(^{206}Pb)$ in sample B (bronze)) with their associated combined ($u_c(x_i)$) and expanded uncertainties ($U(x_i)$), together with the Degrees of Equivalence d_i , the associated combined ($u(d_i)$) and expanded uncertainties ($U(d_i)$), and the normalized error E_n , are listed for each participant.

Institute	Isotope ratio <i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)							
-	X i	<i>u_c</i> (x _i)	U(x _i)	ď	<i>u</i> (<i>d</i> _i)	k	<i>U</i> (<i>d</i> _i)	<i>E</i> n
TÜBÍTAK	2.1025	0.0028	0.0057	-0.0043	0.0028	2	0.0056	0.77
NIM	2.1063	8000.0	0.0015	-0.00055	0.00082	2	0.0016	0.33
KRISS	2.1065	0.0004	0.0008	-0.00035	0.00044	2	0.00087	0.40
NMIJ	2.10676	0.00043	0.00086	-0.00009	0.00046	2	0.00093	0.094
РТВ	2.10686	0.00041	0.00082	0.00001	0.00044	2	0.00089	0.014
LGC	2.1070	0.0008	0.0016	0.00015	0.00082	2	0.0016	0.093
NIST	2.10710	0.00042	0.00084	0.00025	0.00045	2	0.00091	0.28
BAM	2.10741	0.00046	0.00093	0.00056	0.00049	2	0.0010	0.57
SYKE	2.154	0.010	0.020	0.047	0.010	2	0.020	2.4



Fig. 16: Plot of the DoE data for $n(^{208}Pb)/n(^{206}Pb)$ in sample B (bronze) listed in Table 28. 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 $U(d_i)$. Results that encompass zero within their uncertainty interval are considered to be consistent with the KCRV.

5.6. Observations and conclusions on the overall result

When comparing all isotope ratios for both samples, the following observations can be made:

- When the results are grouped in ascending order of measurand value, the same sequence of participants often occurs for different isotope ratios for one specific material.
- The relative uncertainty for all isotope ratios ratioed to ²⁰⁴Pb can be divided into four groups: group 1 (NIST) less than 0.02 %, group 2 (NMIJ, PTB, BAM) at 0.04 %, group 3 (NIM, LGC, KRISS) at 0.06 to 0.08 % and group 4 (SYKE, TÜBÍTAK UME) greater than 0.1 %.
- KCRVs could be established with expanded uncertainties less than 0.05 %, relative.
- For the water sample (sample A), all results are compatible with the KCRV within the participant's expanded uncertainty; for the bronze sample (sample B), the results reported by SYKE are not compatible with the KCRV within the expanded uncertainty.
- The uncertainties obtained by mass spectrometry using multi-collector technology for the ratio $n(^{208}\text{Pb})/n(^{206}\text{Pb})$ range between 0.02 % and 0.04 % and are very consistent.
- The uncertainties for the restricted mean and the median obtained for the isotope ratios of the bronze sample are significantly larger than those for the water sample, by at least by a factor of 2.
- Singe collector instruments can provide compatible results, however with significantly larger uncertainties (see TÜBÍTAK UME sample A).
- Analytical procedures without matrix separation produce biased results, which however might be covered by a realistic uncertainty statement.
- All results obtained with a Neptune-type MC-ICPMS show very narrow ranges of values for all isotope ratios.
- NIM China kindly provided their single MC-ICPMS and MC-TIMS data (see Annex VI). For sample A the MC-TIMS data are slightly lower, for sample B the MC-TIMS data are slightly higher than the MC-ICPMS data. It was also noted that all MC-TIMS data from NIM China are lower than all data obtained with a Neptune-type MC-ICPMS.

From these observations the following conclusions can be drawn:

- In this comparison TIMS data show a larger spread of results compared to the MC-ICPMS data.
- Single collector instruments can provide accurate Pb isotope ratio results in real samples; however matrix separation must be carried out. When doing so, the achievable expanded uncertainties are often larger than the uncertainties which are necessary for the accurate and precise determination of Pb isotope variations. Single collector instruments are suitable for Pb-IDMS applications which require a more modest overall uncertainty.
- MC-ICPMS and MC-TIMS data are consistent with each other and agree to within 0.05 %. The corresponding uncertainties can be considered as realistic uncertainties and mainly range from 0.02 % to 0.08 %.
- NMIs/DIs reported comparable and compatible results for the determination of Pb isotope ratios; the overall result is excellent.

5.7 Applicability of this key comparison to CMC claims

The analytical challenge was the determination of accurate, bias-free isotope ratios, also called "absolute isotope ratios" in a metal matrix sample. The matrix cannot be removed by a digestion or precipitation step and therefore an analyte-matrix-separation has to be carried out. The analyte mass fraction range is in the 100 mg·kg⁻¹ range and the isotope ratios refer to the least abundant isotope ²⁰⁴Pb (isotope abundance \approx 1 %), which additionally has an isobaric interference with ²⁰⁴Hg in the case of ICP ion sources.

The successful participation in this key comparison supports CMC claims for isotope ratios of elements such as Cd, Pt and Pb, which show isobaric interferences. Such CMC claims should apply to reference solutions such as acidified waters as well as organic and inorganic matrices (e.g. metals and minerals), where analyte-matrix-separations are required.

6. Outlook

Isotope ratios are being increasingly used in different fields ranging from trace element quantitation using IDMS to biogeochemical and geochronological applications as well as atomic weight determinations requiring absolute isotope ratios of the highest quality. The use of relative isotope ratios (artefact-based delta-values) is even more wide spread, enabling studies that were not even thought possible a decade ago. Improvements in mass spectrometry and the user-measurement interface have only served to accelerate the application of these powerful tools in the research and commercial arenas. Despite the improvements and availability of new mass spectrometers and the deceptive ease with which users can generate large amounts of seemingly precise data, the metrology of unbiased isotope ratio measurements remains very challenging. For these and other reasons, further comparisons are urgently needed, and should be designed to also engage scientist outside the NMI/DI community.

Possible follow-ups studies that could be conducted as Pilot and/or Key comparison are:

- Isotope systems important for environmental and technical applications, e.g. B
- Isotope systems applicable to food traceability or for detecting illegal timber, e.g. ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, and the CNOHS elements such as δ^2 H, δ^{13} C, δ^{15} N, δ^{18} O δ^{34} S.
- Delta measurements of important "non-traditional" stable isotope elements such as Mg, Fe, Se, and Mo.
- Isotope ratio analyses of selected elements in seawater that supports studies examining global issues such as Climate Change. These include isotope ratio measurements of elements like Li, B, Mg, Ca, Si, Sr and Mo.

References

- [1] M. Berglund, M.E. Wieser, Isotopic compositions of the elements 2009 (IUPAC Technical Report), Pure Appl Chem, 83 (2011) 397-410.
- [2] Vogl J, Paz B, Völling E, Koenig M, Pritzkow W, A modified lead-matrix-separation procedure shown for lead isotope analysis in Trojan silver artefacts as an example, Anal Bioanal Chem, 405 (2013) 2995-3000.
- [3] CCQM/13-22: CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 2013-04-12.

Annex I: Tables of demonstrated core capabilities

Inorganic core capabilities (1)

CCQM-K98, Lead isotope amount ratios in bronze

Analyte(s): Pb

Methodology: ICP-MS, isotope ratio

Participating institutes: KRISS, LGC, NIM, NIST, NMIJ, PTB, SYKE, UME

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.		All	No specific challenges
Digestion/dissolution of organic matrices All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.	N/A		
Digestion/dissolution of inorganic matrices All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.	NIM	KRISS LGC NIST NMIJ PTB SYKE UME	Sn may form precipitates depending on the digestion procedure applied.
Volatile element containment All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	N/A		
Pre-concentration Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	All		
Vapor generation Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.	N/A		
Matrix separation Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion- exchange, extraction, precipitation procedures, but not vapor generation procedures.	SYKE UME	KRISS LGC NIM NIST NMIJ PTB	Different chromatographic separation procedures were applied; potential Sn precipitates required consideration
Signal detection The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.	LGC NIM NMIJ UME	KRISS NIST PTB SYKE	The low isotope abundance of ²⁰⁴ Pb required signal adjustment which, however, is no specific challenge
Memory effect Any techniques used to avoid, remove or reduce the carry- over of analyte between consecutively measured standards and/or samples.	NIM NMIJ PTB	KRISS LGC NIST SYKE UME	No specific challenges
Correction or removal of isobaric/polyatomic interferences Any techniques used to remove, reduce, or mathematically	NIM	KRISS LGC NIM	No specific challenges: The isobaric interference of ²⁰⁴ Hg on ²⁰⁴ Pb was monitored via ²⁰² Hg.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.		NIST NMIJ PTB SYKE UME	However no relevant Hg impurity was present in the samples.
Detector deadtime correction Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	KRISS LGC NIM NIST NMIJ PTB	SYKE UME	No specific challenges
Mass bias/fractionation control and correction Techniques used to determine, monitor, and correct for mass bias/fractionation.		All	No specific challenges; NIST SRM 981 was used to correct for mass discrimination

Inorganic core capabilities (2)

CCQM-K98, Lead isotope amount ratios in bronze

Analyte(s): Pb

Methodology: TIMS, isotope ratio

Participating institutes: BAM, NIM

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.		All	No specific challenges
Digestion/dissolution of organic matrices All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for subsequent analyte-matrix separation.			N/A
Digestion/dissolution of inorganic matrices All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for subsequent analyte-matrix separation.	NIM	BAM	Sn may form precipitates depending on the digestion procedure applied.
Volatile element containment All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.			N/A
Matrix separation Techniques and procedures used to remove the sample matrix and isolate the analyte element for subsequent loading on the filament. Includes evaporation, ion-exchange, extraction, precipitation procedures or others. Test of recovery and potential mass fractionation.		All	Different chromatographic separation procedures were applied; potential Sn precipitates required consideration
Conversion to chemical form for TIMS Techniques and procedures to convert the analyte into a chemical form required for TIMS measurements, e.g. conversion of sulfate into As ₂ S ₃ for sulfur measurements.			N/A
Filament preparation chemistry and loading Techniques and procedures used to load the analyte onto filaments and prepare them for measurement.	NIM	BAM	No specific challenges
Signal detection The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.	NIM	BAM	No specific challenges
Ion signal generation Procedures for warm up, filament heating and measurement procedures	NIM	BAM	No specific challenges
Correction or removal of isobaric/polyatomic interferences Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes warm up and filament heating procedures, high resolution mass spectrometry, or mathematical corrections. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	All		
Detector deadtime correction Measurement of and correction for the deadtime of ion counting detectors if applicable.			N/A
Correction of mass fractionation Techniques used to determine, monitor, and correct for instrumental and procedural mass fractionation.		All	No specific challenges; NIST SRM 981 was used to correct for mass fractionation

Please return before 30/11/2011 to: jochen.vogl@bam.de



CCQM Inorganic Analysis Working Group

Questionnaire to all NMIs / DIs for a Key Comparison and parallel Pilot Study on Pb isotope abundance ratios: CCQM-K98 & P134

Description of the planned Key Comparison / Pilot Study:

Already 3 pilot studies on isotope ratio determinations (U isotope ratios in urine, stable isotopes in Methionine, ⁸⁷Sr/⁸⁶Sr in wine) have been conducted in the Inorganic Analysis Working Group (IAWG). To support present and future CMCs on isotope ratio determinations a related Key Comparison is required.

BAM volunteers for organizing this Key Comparison. At the IAWG meeting 2011 in Paris it was decided to go for "Pb isotope abundance ratios in bronze", because there is a broad range of applications. Isotope abundance ratios in general are the basis of isotope dilution mass spectrometry (IDMS) and Pb isotope abundance ratios specifically are required for Pb quantification. Furthermore Pb isotope abundance ratios are used in geochemical research and for investigating the provenance of artefacts in archaeology or forensic science. BAM has a suitable bronze material available with a Pb mass fraction between 10 and 100 mg/kg. The solid bronze cylinders will be chipped and the resulting bronze swarf with a few mg per single piece will be bottled in crimp vials (borosilicate glass) containing approximately 4 g sample. Usually the homogeneity of the Pb isotopic composition can be assumed. Nevertheless the homogeneity will be verified by BAM.

Additionally to the bronze sample a mono-element solution with a Pb mass fraction of approximately 100 mg/kg will be provided. By comparing the results obtained for the bronze sample with the results obtained for the mono-element solution, remaining matrix effects may be detected.

For all samples the isotope abundance ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, which are used for provenance studies, shall be determined. Additionally ²⁰⁸Pb/²⁰⁶Pb shall be determined, as a representative isotope abundance ratio for IDMS.

The target standard uncertainty for all isotope abundance ratios is 0.1 %.

The preliminary schedule is as follows:

Questionnaire deadline:	30/11/2011
Sample preparation:	10/2011
Homogeneity test:	12/2011
Call for participants:	02/2012
Registration deadline:	04/2012
Sample shipment:	05/2012
Results deadline:	09/2012

Please enter your answers into the shaded fields, save the questionnaire by extending the filename with the abbreviation of your institute and **return it before 30/11/2011** to: jochen.vogl@bam.de

Please give your contact details

(e.g. Institute, contact person, e-mail)

Are you interested in participation? (Yes/No)

What is the technique you are presumably going to use?

(e.g. SF-ICPMS, MC-ICPMS, MC-TIMS etc.)

Are you performing a Pb-matrix separation prior to measurements?

What technique for correcting mass fractionation / mass discrimination effects do you use?

- a) Correction (K-)factor obtained by measurement of a Pb Isotope Reference Material
- b) Correction via TI using the linear, exponential or power law model
- c) Double-spike technique
- d) Other

Which Isotope Reference Material do you typically use?

- a) For correcting mass fractionation / mass discrimination?
- b) For validating the whole procedure?

Do you have the isotope reference material NIST SRM 981 available in your lab? (Yes/No)

What is your typical relative standard uncertainty for the above mentioned isotope abundance ratios? (in %)

- a) ²⁰⁶Pb/²⁰⁴Pb
 - a) FU/FU
- b) ²⁰⁷Pb/²⁰⁴Pb
- c) ²⁰⁸Pb/²⁰⁴Pb
- d) ²⁰⁸Pb/²⁰⁶Pb

Are you additionally interested in $\delta\mbox{-values}$ versus NIST SRM 981?

Which isotope abundance ratio?

Do you agree with the schedule? (Yes/No)

If no, please provide comment

Do you know expert labs (non-NMIs) in your country, which might participate?

Please give address and contact person

Thank you for submitting your questionnaire.

Annex III: Invitation

BAM Federal Institute for Materials Research and Testing Berlin, Germany



Berlin, 2012-05-16

To CCQM members, official observers and other interested parties,

Invitation to participate in the key comparison CCQM-K98 and/or in the pilot study CCQM-P134 on the measurement of Pb isotope amount ratios in bronze

Dear colleagues,

we kindly invite you to participate in the CCQM key comparison K98 and/or in the CCQM pilot study CCQM-P134 "Pb isotope amount ratios in bronze". In the attached files, you can find the registration form and the technical protocol.

When you decide to participate in CCQM-K98/P134, please send us the completed registration form by regular mail, e-mail or fax before **31st July 2012**. Although several institutes showed their interest already, we ask all participants to register by fax or e-mail.

After the registration deadline the samples will be shipped to all participants. All related details can be found in the technical protocol.

The schedule of the study can be taken from the technical protocol. Once the deadline for submitting the results has been passed, the results of the study will be presented in the subsequent IAWG meeting. In parallel a report will be prepared and will be circulated between the participants for comments and corrections. 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, Jochen Vogl

BAM Federal Institute for Materials Research and Testing Division 1.1 Unter den Eichen 87 12205 Berlin GERMANY

Contact for scientific issues: Jochen Vogl Phone: +49 30 8104 1144 Fax: +49 30 8104 3527 E-Mail: jochen.vogl@bam.de Contact for organizational issues: Ms Dorit Becker

Fax: +49 30 8104 3527 E-Mail: <u>dorit.becker@bam.de</u>

Annex IV: Registration Form

REGISTRATION FORM

CCQM-K98 / P134

"Pb isotope amount ratios in bronze"

Name (contact person):			
Institute:			
Shipping address:			
Telephone:			
Fax:			
E-Mail:			<u></u>
Participation CCQM-K98:	Yes	No	
Participation CCQM-P134:	Yes	No	
Signature:			
Date:			

Please return the completed form by regular mail, e-mail or fax no later than 31st July 2012 to:

Ms Dorit Becker		
BAM Federal Institute for Materials Research and Testing		
Unter den Eichen 87		
12205 Berlin	Fax	+49-30-8104-3527
Germany	E-Mail:	<u>dorit.becker@bam.de</u>

Annex V: Technical Protocol

BAM Federal Institute for Materials Research and Testing Berlin, Germany



CCQM-K98 / P134 "Pb isotope amount ratios in bronze"

Technical Protocol

1. Introduction

Isotope ratio determinations have been increasingly used in the past decades, either to unravel transport processes, gain information on the provenance of specific samples, for quantification by applying isotope dilution mass spectrometry (IDMS) or others. Due to the broad field of applications ranging from archaeology, food chemistry, forensic science and geochemistry to medicine and metrology, reliable and traceable isotope data are necessary to enable the comparability of measurement results obtained e.g. by analyzing different ore deposits in geochemistry or different hair samples in forensic science.

The importance of traceability and comparability in isotope analysis has been recognized in the Inorganic Analysis Working Group (IAWG) within CCQM and already 3 pilot studies on isotope ratio determinations (P48 "U isotope ratios in urine", P75 "stable isotopes in Methionine", P105 "⁸⁷Sr/⁸⁶Sr in wine") have been conducted in the past. To support present and future CMCs on isotope ratio determination a Key Comparison is urgently needed. Therefore it was decided at the IAWG meeting in Paris in April 2011 to organize a Key Comparison on the determination of Pb isotope amount ratios in bronze. Isotope amount ratios in general are the basis of IDMS and Pb isotope amount ratios specifically are required for Pb quantification. Furthermore Pb isotope amount ratios are used in geochemical research and for investigating the provenance of artefacts in archaeology or forensic science. A suitable bronze material with a Pb mass fraction between 10 and 100 mg/kg is available at BAM. Additionally to the bronze sample a mono-element solution with a Pb mass fraction of approximately 100 mg/kg will be provided. By comparing the results obtained for the bronze sample with the results obtained for the mono-element solution, remaining matrix effects may be detected.

For all samples the isotope abundance ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, which are used for provenance studies, shall be determined. Additionally ²⁰⁸Pb/²⁰⁶Pb shall be determined, as a representative isotope abundance ratio for IDMS.

2. Samples

Within this study 2 different samples will be provided. Each participant will receive one unit of sample A and two units of sample B: *Sample A* is a solution of pure Pb in dilute nitric acid with a Pb mass fraction of approximately 100 mg/kg. Each unit contains a least 20 mL of the described solution. Sample A comes in a PFA bottle sealed in a plastic bag. *Sample B* consists of bronze swarf filled in glass ampoules each containing approximately 1 g bronze. The bronze consists of approximately 94 % Cu and 6 % Sn and contains Pb in the range of 10 to 100 mg/kg. Homogeneity of the samples has been confirmed for a sample intake of approximately 100 mg.

Every participant is asked to confirm the delivery of the samples by regular mail, e-mail or fax as soon as the samples have arrived. A form for confirmation of the delivery will be provided together with the samples.

3. Measurand and reporting

Mandatory measurands for sample A and B in CCQM-K98 are as follows:

- Isotope amount ratio $n(^{206}Pb)/n(^{204}Pb)$,
- Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$,
- Isotope amount ratio $n(^{208}Pb)/n(^{204}Pb)$ and
- Isotope amount ratio $n(^{208}Pb)/n(^{206}Pb)$.

Mandatory measurands for sample A and B in CCQM-P134:

- Isotope amount ratio $n(^{206}Pb)/n(^{204}Pb)$,
- Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$,
- Isotope amount ratio $n(^{208}Pb)/n(^{204}Pb)$ and
- Isotope amount ratio $n(^{208}Pb)/n(^{206}Pb)$.

Otpional measurands for sample A and B in CCQM-P134:

- Delta value: δ^{208} Pb versus NIST SRM 981 following eqn. 1 and
- Molar mass of Pb in sample A and B.

$$\delta^{208} P b_{NIST SRM 981} = \left(\frac{\left(\frac{n(208 Pb)}{n(206 Pb)}\right)_{sample}}{\left(\frac{n(208 Pb)}{n(206 Pb)}\right)_{NIST SRM 981}} - 1 \right) \cdot 10^3$$
eqn. 1

Please also provide single values for the mandatory results. At least 3 single values for sample A and 3 single values for each unit of sample B are requested.

The results shall be reported using the questionnaire and reporting form, which will be provided after registration.

4. Target values and target uncertainty

The materials are selected such that the isotopic composition of Pb is within the natural range of the Pb isotopic composition as tabulated by IUPAC. The target uncertainty for all isotope measurements is 0.2% relative (k=1).

5. Methods of measurement

The participants are free to choose any suitable method (e.g. TIMS, ICPMS...), although procedures including analyte-matrix separation and enabling smaller uncertainties are encouraged. In case of CCQM-K98 participants are advised to use NIST SRM 981 for correcting mass fractionation / mass discrimination in order to obtain a more consistent set of data. It is allowed to submit more than one set of results to CCQM-K98. However, participants are encouraged to submit only one result to K98 and submit all additional results to P134. Additional results can be obtained by using an alternative instrument, by using an alternative method for correcting mass fractionation or by using / not using matrix separation procedures. If more than one result will be submitted to CCQM-K98, participants are obliged to state beforehand which result shall be used for the calculation of the KCRV.

6. Key comparison reference value

It is intended to use those results being obtained after analyte-matrix separation and meeting the target uncertainty for the calculation of the Key Comparison Reference Value (KCRV). Should it prove unsuccessful, because e.g. too few results meet these requirements, this has to be revisited and other requirements have to be set or an alternative approach has to be used (e.g. Median of <u>all</u> results).

7. Planned time schedule

Call for participants:	May 2012
Registration deadline:	31 July 2012
Sample shipment:	by end of September 2012
Deadline for reporting of results:	31 May 2013
Issue of draft A report:	by end of September 2013
Issue of draft B report:	by end of December 2013

8. Pilot laboratory

Contact for scientific issues:

BAM Federal Institute for Materials Research and Testing Division 1.1 "Inorganic Trace Analysis"

Contact for Coloritino Icoaco.		
Jochen Vogl		
Unter den Eichen 87	Phone:	+49 30 8104 1144
12205 Berlin	Fax:	+49 30 8104 3527
GERMANY	E-Mail:	jochen.vogl@bam.de

Contact for organizational issues:(e.g. registration, sample shipment, submission of results)Ms Dorit BeckerUnter den Eichen 8712205 BerlinFax:449 30 8104 3527GERMANYE-Mail:

Annex VI: Reporting Form

CCQM-K98

Measurement of "Pb isotope amount ratios in bronze"

Results Report

Lab Identification:	name institute address	:
	country e-mail tel. number fax number	: : : :

Practical work done by:

Sample	Isotope amount ratio			
	Ratio	Value	Std. unc. <i>u</i> c *	Exp. unc. <i>U</i> **
	•			·
A (water)	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)			
A (water)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)			
A (water)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)			
A (water)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)			
B (bronze)	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)			
B (bronze)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)			
B (bronze)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)			
B (bronze)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)			

* Combined standard uncertainty (coverage factor *k*=1) according to ISO/GUM guidelines.

** Expanded uncertainty $U(U=u_c\cdot k)$; coverage factor k should be given in brackets: e.g. (k=2)

Date:

Signature:

CCQM-K98

Measurement of "Pb isotope amount ratios in bronze"

Details

Lab Identification: name : institute :

1. Mass spectrometric technique used: e.g. ICPMS, TIMS

2.	Instrument type used:	e.g. MC-ICPMS Neptune
3.	Digestion method used:	e.g. open digestion on hot plate with HCI/H_2O_2
4.	Analyte-matrix separation:	e.g. ion exchange procedure with Pb spec
5.	Procedure blank:	Tested / Not tested; if tested provide the total blank of the analytical procedure in ng Pb
6.	Recovery of separation:	Tested / Not tested; if tested please specify
7.	Interference correction:	Yes/No; if yes specify what isotope has been corrected for which interference
8.	Validation of analytical procedure:	Tested / Not tested; if tested please specify
9.	Correction of mass fractionation:	Type of correction
10.	Reference materials used:	e.g. NIST SRM 981
11.	Traceability:	e.g. to SI via NIST SRM 981
12.	Experimental reproducibility:	Please provide sample standard deviation

Please replace text in italics by your own description.

CCQM-K98 "Pb isotope amount ratios in bronze"

Details on uncertainty calculation

Please list the major uncertainty contributions (max. number of contributions 5) for the following measurands together with an indication on their percentage:

a) n(²⁰⁸Pb)/n(²⁰⁴Pb): 1) 2) 3) 4)́ 5) *b) n*(²⁰⁷Pb)/*n*(²⁰⁴Pb): 1) 2) 3) 4) 5) *c) n*(²⁰⁶Pb)/*n*(²⁰⁴Pb): 1) 2)́ 3) 4) 5) *d) n*(²⁰⁸Pb)/*n*(²⁰⁶Pb): 1) 2)́ 3) 4) 5)́

CCQM-K98 "Pb isotope amount ratios in bronze"

Please provide single values of separately processed samples

Sample	Unit no.	Isotope amount ratio			
		<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)
A (water)					
A (water)					
A (water)					
B (bronze)					
B (bronze)					
B (bronze)					
B (bronze)					
B (bronze)					
B (bronze)					

Annex VII: Additional Information

NIM China reported a composite result calculated from MC-ICPMS and TIMS values. Additionally NIM China kindly provided the single MC-ICPMS and TIMS results, which are displayed in the following table.

MS technique	Isotope amount ratios in sample A (water) as reported by NIM China			
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)
MC-ICPMS	21.1127 (70)	15.9436 (58)	39.849 (16)	1.88746 (48)
MC-TIMS	21.1108 (74)	15.9403 (65)	39.841 (19)	1.88723 (47)
MS technique	Isotope amount ratios in sample B (bronze) as reported by NIM China			
	<i>n</i> (²⁰⁶ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁷ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁴ Pb)	<i>n</i> (²⁰⁸ Pb)/ <i>n</i> (²⁰⁶ Pb)
MC-ICPMS	18.0613 (62)	15.5656 (62)	38.041 (18)	2.10624 (60)
MC-TIMS	18.0662 (58)	15.5719 (58)	38.053 (17)	2.10639 (69)