Certification Report

for the

Isotopic Reference Materials

ERM-AE142 and ERM-EB400

A pure Pb solution and a bronze material, both certified for their Pb isotope amount ratios

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1. Summary

Lead (Pb) isotope amount ratios are commonly used in applications ranging from archaeology and forensic sciences to terrestrial and extra-terrestrial geochemistry. Despite their utility and frequency of use, only three certified isotope amount ratio reference materials are currently available for Pb: NIST SRMs 981, 982 and 983. Because SRM 981 has a natural Pb isotopic composition, it is mainly used for correcting instrumental mass discrimination or fractionation. This means that, at present, there are no other certified isotope reference materials with natural Pb isotopic composition that could be used for validating or verifying an analytical procedure involving the measurement of Pb isotope amount ratios.

To fill this gap, two new reference materials, both certified for their Pb isotopic composition, have been produced together with a complete uncertainty assessment. These new reference materials offer SI traceability and an independent means of validating or verifying analytical procedures used to produce Pb isotope amount ratio measurements.

ERM-EB400 is a bronze material containing a nominal Pb mass fraction of 45 mg/kg. ERM-AE142 is a high purity solution of Pb with a nominal mass fraction of 100 mg/kg. Both materials have been specifically produced to assist analysts in verifying or validating their analytical procedures. Note that while one of these reference materials requires the chemical separation of Pb from its matrix (ERM-EB400), the other does not (ERM-AE142). Details on the certification of these isotope reference materials are provided in this report.

Certified quantity	Unit	Certified value	Uncertainty *
ERM-EB400			
Isotope amount ratio $n(^{206}Pb)/n(^{204}Pb)$	mol/mol	18.072	0.017
Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$	mol/mol	15.578	0.018
Isotope amount ratio $n(^{208}Pb)/n(^{204}Pb)$	mol/mol	38.075	0.046
Isotope amount ratio $n(^{208}Pb)/n(^{206}Pb)$	mol/mol	2.1068	0.0014
Isotope amount fraction $n(^{204}Pb)/n(Pb)$	mol/mol	0.013 7504	0.000 0098
Isotope amount fraction $n(^{206}Pb)/n(Pb)$	mol/mol	0.248 50	0.000 24
Isotope amount fraction $n(^{207}Pb)/n(Pb)$	mol/mol	0.214 20	0.000 24
Isotope amount fraction $n(^{208}Pb)/n(Pb)$	mol/mol	0.523 55	0.000 35
Molar mass M(Pb)	g/mol	207.209 68	0.000 57
ERM-AE142			
Isotope amount ratio $n(^{206}Pb)/n(^{204}Pb)$	mol/mol	21.114	0.017
Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$	mol/mol	15.944	0.017
Isotope amount ratio $n(^{208}Pb)/n(^{204}Pb)$	mol/mol	39.850	0.044
Isotope amount ratio $n(^{208}Pb)/n(^{206}Pb)$	mol/mol	1.8874	0.0010
Isotope amount fraction $n(^{204}Pb)/n(Pb)$	mol/mol	0.012 8357	0.000 0083
Isotope amount fraction $n(^{206}Pb)/n(Pb)$	mol/mol	0.271 01	0.000 23
Isotope amount fraction $n(^{207}Pb)/n(Pb)$	mol/mol	0.204 65	0.000 21
Isotope amount fraction $n(^{208}Pb)/n(Pb)$	mol/mol	0.511 50	0.000 32
Molar mass M(Pb)	g/mol	207.177 83	0.000 53

* Expanded uncertainty $U = k \cdot u_c$ with $k = 2$

2. Introduction

Lead (Pb) isotope amount ratios (hereafter referred to as Pb isotope ratios) are proving useful in an ever increasing array of applications that span fields as diverse as archaeology, food chemistry, forensic science, geochemistry, medicine and metrology. The measurement of Pb isotope ratios is also necessary for the quantification of Pb at trace levels when using isotope dilution mass spectrometry (IDMS). However, to be an effective tool, the Pb isotope ratio data must be reliable and traceable to ensure its comparability with other measurements.

In order to generate reliable and traceable Pb isotope ratio data, users need suitable isotope reference materials (iRMs) for determining and correcting instrumental mass fractionation or discrimination. They also require independent iRMs for validating their analytical procedures, especially the sample preparation and analyte isolation steps. For determining instrumental mass fractionation / discrimination, NIST SRM 981 (Catanzaro *et al.* 1968) is typically used. It comes in the form of solid Pb wire and has certified Pb isotope ratios that lie within the natural Pb isotopic spectrum. There are also a Pb iRM enriched in ^{206}Pb (SRM 983: Radiogenic Lead) and a Pb iRM with a $n(^{208}\text{Pb})/n(^{206}\text{Pb}) = 1.000\ 16$ (SRM 982: Equal Atom Lead), each with certified Pb isotope ratios. However, because some of the Pb in both of these iRMs was separated from U ore, both contain minute amounts of radioactive ^{210}Pb (SRM 983: Certificate of Analysis, 2004 and SRM 982: Certificate of Analysis, 2004). Needless to say, both of these last two Pb iRMs do not have Pb isotope ratios that lie within the natural Pb isotopic spectrum.

Matrix reference materials certified for their Pb isotopic composition, which can be used for validation of analytical procedures, are not yet available. While reference samples exist within the geochemical community, their value assignments are based on compilations of published Pb isotope ratio data from reviews or databases (GeoReM). While quite useful, these reference materials provide only composite means of the three Pb isotope ratios that do not take into account possible measurement biases as well as the stability and homogeneity of the materials. This means that there can be no metrologically sound assessment of their measurement uncertainties.

To meet this need, a bronze material (ERM-EB400) has been produced that contains a Pb mass fraction of 45 mg/kg and has been characterized for its Pb isotopic composition. In addition, a solution containing pure Pb at a nominal mass fraction of 100 mg/kg (ERM-AE142) has been produced and also characterized for its Pb isotopic composition. It has a Pb atomic weight at the lower end of the natural range in Pb isotope ratio variations. Both materials were specifically produced to assist analysts in validating their analytical procedures. Details on the characterization of these new iRMs as well as the certification procedure used to make them certified reference materials under the ERM® label are described here in detail.

3. Experimental Section

3.1. Chemicals, Reagents and Lab-ware Used for Processing the Candidate iRMs

All dilutions carried out at BAM to produce these candidate iRMs used ultrapure water from a Milli-Q Advantage A10 water purification system. Nitric acid and hydrochloric acids (originally of p.a. grade) were further purified by a two-stage sub-boiling distillation process (1st stage: quartz still, 2nd stage: Teflon still).

Hydrogen peroxide was purchased at Suprapure grade. Only quartz, fluorinated ethylene propylene (FEP), perfluoralkoxy polymer (PFA) or polypropylene (PP) lab-ware were used for the preparation of both candidate materials, preparing them for the subsequent Pb isotope ratio measurements at BAM.

3.2. Candidate Material Characterizations, Processing and Bottling

ERM-AE142 was produced from a high purity Pb that had been fully characterized as Primary Reference Material BAM-Y004, with a purity (expressed as Pb mass fraction) of 0.999 92(6) kg/kg, with the associated expanded uncertainty in brackets and referring to the last digit. All metal impurity mass fractions, excepting Bi (< 2 mg/kg), are below 1 mg/kg. The Hg mass fraction was even lower (< 0.2 mg/kg). An exactly weighed piece of approximately 0.49 g BAM-Y004 was dissolved in 5 mL of high purity nitric acid (≈ 7 mol/L). Then 490 g of dilute nitric acid (1 mol/L) was added to reach a final nitric acid concentration of approximately 1 mol/L. The resulting Pb mass fraction was 998.223(16) mg/kg, with its associated expanded uncertainty shown in brackets. This stock solution was then further diluted approximately ten-fold to produce a Pb mass fraction of 99.969(21) mg/kg in the final solution that became ERM-AE142. This solution was then transferred to more than 100 PFA bottles, each containing 20 mL of solution. The bottles were labelled and sealed in polyethylene-aluminium-composite foil bags. Ten units, randomly selected, were distributed for the CCQM Key Comparison K98 and the Pilot Study P134 (Vogl *et al.* 2014). A representative unit of ERM-AE142 is shown in Fig. 1a.

Fig. 1: Photographs of the candidate reference materials ERM-AE142 (a) and ERM-EB400 (b)

ERM-EB400 was produced from an existing bronze reference material, ERM-EB377, which was certified for the elemental mass fractions listed in Table 1 (Recknagel & Meyer 1999). Three solid bronze cylinders were machined in an oil-free and contamination-free manner, producing small swarfs with masses ranging between 1 mg and 40 mg. These swarfs were homogenized by manual mixing. More than 300 glass vials with crimp closures were filled with the bronze swarfs, each vial containing approximately 1 g of material. The filled crimp vials were then labelled and sealed in PE bags. Twenty units, randomly selected, were used for CCQM Key Comparison K98 and Pilot Study P134 (Vogl *et al.* 2014). Three representative units of ERM-EB400 are shown in Fig. 1b.

Table 1: Mass fraction reference values for analytes in ERM-AE142 and ERM-EB400 with their expanded uncertainties ($U = k \cdot u_c$ with $k = 2$); Pb mass fraction in ERM-AE142 represents the gravimetric value and elemental mass fractions in ERM-EB400 represent certified mass fractions for ERM-EB377, which is the base material of ERM-EB400 (Recknagel & Meyer 1999)

Mass fraction	Unit	Value	Expanded uncertainty
ERM-AE142			
Pb mass fraction	mg/kg	100.0	2.0
ERM-EB400			
Cu mass fraction	kg/kg	0.9404	0.0005
Sn mass fraction	kg/kg	0.0592	0.0013
Bi mass fraction	mg/kg	42.2	1.5
Pb mass fraction	mg/kg	44.9	2.3

3.3. Homogeneity

ERM-AE142 has been produced by dissolution of a pure Pb Primary Reference Material followed by subsequent dilutions. Such solutions of target elements are, in principle, homogenous for their mass fractions. More importantly though, these solutions are also homogeneous with respect to their isotopic composition regardless of any variations in their mass fractions. Therefore, the solution of ERM-AE142 is taken to be homogeneous for its intended use as an iRM. Contamination issues are also not relevant because 1) the laboratory blank levels at BAM for Pb are in the pico-gram range (Vogl *et al.* 2013) and 2) any added contaminant would have a natural Pb isotopic composition which would have a minimal effect when mixed with the natural Pb isotopic composition already in solution. Moreover, after mixing and equilibration, the resultant solution will itself be homogeneous with respect to its Pb isotopes, regardless of their source. The characterization study, which was carried out on 10 units spread over the whole filling sequence, supports this because there was no hint of variations due to inhomogeneity. An uncertainty contribution for inhomogeneity has therefore not been added to the overall uncertainty for this iRM.

The base material for **ERM-EB400** comes from a bronze CRM, ERM-EB377 (Recknagel & Meyer 1999), which was certified for its elemental mass fractions (Table 1). It has already been tested for homogeneity. For elements at trace levels, homogeneity can be presumed because the relative standard deviations for the elemental mass fractions measured during the homogeneity tests were $\leq$1 %. Even though no inhomogeneity was observed for ERM-EB377, a homogeneity test was also carried out on ERM-EB400 because the material had undergone additional processing. The homogeneity of the Pb isotopes in the bronze needed to be assessed at a level of precision comparable to the best analytical methods available (i.e. those with extremely tight reproducibility). For this purpose 8 units were randomly selected from the whole batch. Each of these units was sampled 3 times, resulting in 24 samples. With sample masses around 100 mg, all samples were processed independently and measured using thermal ionization mass spectrometry (TIMS) after Pb-matrix separation. The procedure described by Vogl *et al.* 2013 was followed, however the separation protocol using the Pb-spec resin was modified by a two stage separation, the first stage 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 further purified. The resulting 24 Pb fractions were then measured at least twice. The results are listed in Tables 2 through 5.

Table 2: Isotope amount ratio n(^{206}Pb)/n(^{204}Pb) for the isotopic homogeneity assessment of three (3) independent aliquots taken from each of eight (8) units of ERM-EB400

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(^{207}Pb)/n(^{204}Pb) for the isotopic homogeneity assessment of three (3) independent aliquots taken from each of eight (8) units of ERM-EB400

Sample	Isotope amount ratio $n(^{207}Pb)/n(^{204}Pb)$				
	Aliquot 1	Aliquot 2	Aliquot 3	Mean	Std. dev.
Amp 23	15.5769	15.5830	15.5823	15.5808	0.0033
Amp 73	15.5822	15.5849	15.5883	15.5851	0.0030
Amp 98	15.5844	15.5806	15.5796	15.5816	0.0025
Amp 138	15.5841	15.5927	15.5895	15.5888	0.0044
Amp 166	15.5892	15.5879	15.5883	15.5885	0.0006
Amp 236	15.5814	15.5866	15.5871	15.5851	0.0032
Amp 287	15.5827	15.5907	15.5910	15.5881	0.0047
Amp 317	15.5861	15.5842	15.5810	15.5838	0.0026

Table 4: Isotope amount ratio n(^{208}Pb)/n(^{204}Pb) for the isotopic homogeneity assessment of three (3) independent aliquots taken from each of eight (8) units of ERM-EB400

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 5: The overall means of the lead isotope ratios of the bronze material ERM-EB400 listed in Tables 2-4 with their corresponding F-values.

Parameter	Isotope amount ratio		
	$n(^{206}Pb)/n(^{204}Pb)$	$n(^{207}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{204}Pb)$
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
MS_{within}	0.00000854	0.00001058	0.00012968
$MS_{between}$	0.00002668	0.00002879	0.00032382
s_{bb}	0.00246	0.00246	0.00804
s_{bb} rel.	0.0136 %	0.0158 %	0.0211 %
u^*_{bb}	0.00100	0.00112	0.00391
u^*_{bb} rel.	0.0055 %	0.0072 %	0.0103 %

* Significance level 1%, ν_1=k-1=7, ν_2=N-k=16

The Pb isotope ratio results based on measurements of 3 aliquots from 8 ampoules were then used to test for potential inhomogeneity and to calculate the corresponding uncertainty contribution. As a result from these data the test criterion, the F-value, was smaller than the critical (tabulated) value. Thus, no significant inhomogeneity was detected and the material could be considered as homogenous. Nevertheless, an undetected inhomogeneity might be hidden by the repeatability of the applied analytical procedure. The corresponding uncertainty contribution, caused by the insufficient repeatability of the analytical procedure, can be expressed as u^*_{bb} according to the ISO Guide 35. The equations used for this calculation are listed in Appendix 1. For the three tested isotope ratios, u^*_{bb} is approximately 40 % to 48 % of the standard deviation for all measurements. Additionally, u^*_{bb} increases from 0.0055 % for $n(^{206}Pb)/n(^{204}Pb)$ to 0.0103 % for $n(^{208}Pb)/n(^{204}Pb)$. This suggests that u^*_{bb} still reflect artifacts from the replications of the measurements themselves, because the isotope ratios are all normalized to ^{204}Pb, are thus correlated and logically cannot show different levels of homogeneity.

Following common practice, the larger value of the two uncertainty estimates s_{bb} and u^*_{bb} is chosen as uncertainty contribution for homogeneity/inhomogeneity. For the isotope ratio $n(^{208}Pb)/n(^{206}Pb)$, which has not been tested for homogeneity, but is correlated with the tested isotope ratios, the largest value of s_{bb} (0.0211 %) was chosen as uncertainty contribution for homogeneity/inhomogeneity.

3.4. Stability

Experience acquired over two decades of using various BAM isotopic spikes and calibration solutions as well as work carried out at the *Institute for Reference Materials and Measurements* (IRMM, Geel, Belgium) and the *National Institute of Standards and Technology* (NIST, Gaithersburg, Maryland USA) demonstrate that acidified aqueous solutions containing one element with mass fractions in the mg/kg range can be stored

under normal laboratory conditions for long periods with no measurable change in the isotopic composition of the solutions.

The factors which can affect the stability of both the mass fraction and the isotopic composition of such solutions are contamination, adsorption on container walls, evaporation of solvent and redox-reactions. Contamination, until first use at the customer's lab, is excluded by the use of PFA bottles. The PFA material of these bottles also prevents adsorption on the container walls. Evaporation is reduced to a minimum by sealing the bottles in polyethylene-aluminium-composite foil bags. Redox reactions cannot take place as no suitable oxidation and/or reducing agents are present. Therefore, ERM-AE142 is assumed to be stable regarding its isotopic composition and no extra uncertainty is applied. Note that even if there was some evaporative solvent loss through the PFA material despite the additional foil bag seal that causes the mass fraction of Pb to change slightly over 10 years, this loss of solvent cannot change the Pb isotope amount ratios. The possible changes in the Pb mass fraction are covered by the expanded uncertainty of 2 % (Table 12). Note that the mass fraction is reported as an indicative value and not a certified quantity. The minimum shelf life of ERM-AE142 is 10 years from the issue of the certificate.

ERM-EB400 is a chipped bronze in solid form and thus should remain stable indefinitely. The certificate of ERM-EB400 is valid until 2037 for units with unbroken seal stored under required conditions. The validity is based on the Certificate and the Certification report of the base material ERM-EB377 (Recknagel & Meyer 1999).

3.5. Value Assignment Using the Results from CCQM-K98

CCQM is the Consultative Committee for "Amount of Substance: Metrology in Chemistry and Biology" within the Metre Convention (BIPM 2015). Its main task is to establish global comparability of measurement results through promoting traceability to the SI and to contribute to the establishment of a globally recognized system of national measurement standards. In order to fulfill this, CCQM runs different projects and comparisons such as Key Comparisons, where National Institutes such as NIST, PTB or BAM compare their measurement results at highest metrological level, whereby measurement uncertainty and traceability are a mandatory prerequisite. Such comparisons build the technical basis for global comparability of measurement results.

The candidate materials ERM-AE142 and ERM-EB400 were used as samples for the key comparison CCQM-K98 (Vogl *et al.* 2014). The results from this Key Comparison, which were used for establishing the Key Comparison Reference Value (KCRV) were also used for the value assignment of the Pb isotope amount ratios of these iRMs. The measurements were made at the seven different National Metrology Institutes (NMI) listed in Table 6. All results met a target uncertainty of < 0.2% for the three reported Pb isotope ratios. While the Pb solution, ERM-AE142, only required dilution before analysis, the bronze iRM, ERM-EB400, required that each NMI processes the sample through column chromatography to separate the Pb from the matrix (Table 7). The measurement details reported by the participating NMIs are extensive. Therefore, a summary is provided in tabular form which presents the principal factors controlling the quality of these measurements. These include descriptions of the mass spectrometric techniques, the separation procedures, the corrections for mass fractionation/discrimination, the traceability links and the reproducibility of the procedures as well as the individual results. More details on specific procedures can be obtained from

the CCQM-K98 report (Vogl *et al.* 2014). Note, that different mass spectrometric techniques were used by each NMI. In one case (NIM), more than one technique was used, however composite results were reported.

Table 6: National Metrology Institutes participating in the characterization and certification of Pb isotope amount ratios in ERM-AE142 and ERM-EB400.

BAM	Bundesanstalt für Materialforschung und –prüfung	Berlin, Germany
KRISS	Korea Research Institute of Standards and Science	Daejeon, South Korea
LGC	Laboratory of the Government Chemist	Teddington, United Kingdom
NIM	National Institute of Metrology	Beijing, People's Republic of China
NIST	National Institute of Standards and Technology	Gaithersburg, Maryland USA
NMIJ	National Metrology Institute of Japan	Tsukuba, Japan
PTB	Physikalisch-Technische Bundesanstalt	Braunschweig, Germany

Table 7: Overview of the analytical techniques and analytical procedures used by the different participants (abbreviations are explained below).

Institute	MS Instrument [1]	MS type	Matrix separation	Correction for ^{204}Hg	Fractionation correction [2]	Source of traceability	Reproducibility [3]
BAM	MC-TIMS	Sector 54	AG 1X8 Sr Spec	No	K-factor	NIST SRM 981	AE142 0.04 % EB400 0.07 %
KRISS	MC-ICPMS	Neptune	AG 1X8	No	K-factor	NIST SRM 981	AE142 0.04 % EB400 0.03 %
LGC	MC-ICPMS	Neptune	AG 1X8	No	^{205}Tl/^{203}Tl	NIST SRM 981	AE142 0.003 % EB400 0.003 %
NIM	MC-ICPMS MC-TIMS	Isoprobe Isoprobe T	AG 1X8	No	K-factor	NIST SRM 981	AE142 0.04 % EB400 0.04 %
NIST	MC-ICPMS	Neptune	Pb Spec	Yes	^{205}Tl/^{203}Tl	NIST SRM 981	AE142 0.001 % EB400 0.001 %
NMIJ	MC-ICPMS	Neptune	MetaSEP AnaLig Pb-02	Yes	^{205}Tl/^{203}Tl	NIST SRM 981	AE142 0.002 % EB400 0.002 %
PTB	MC-ICPMS	Neptune	Triskem Pb resin PB-C50-A	Yes	K-factor	NIST SRM 981	AE142 0.005 % EB400 0.009 %

[1] MC-TIMS: Multi Collector-Thermal Ionization Mass Spectrometry; MC-ICPMS: Multi Collector-Inductively Coupled Plasma Mass Spectrometer

[2] K-factor: correction factor with K=certified ratio/observed ratio; ^{205}Tl/^{203}Tl: use of Tl for correcting mass discrimination

[3] the maximum reproducibility of all isotope ratios is given as a relative standard deviation for individually prepared samples; first value for ERM-AE142, second value for ERM-EB400

The certified values of the Pb isotope amount ratios in ERM-AE142 were calculated from the reported results that met the target uncertainty of < 0.2 % (*k*=1). As mentioned earlier, this iRM required no additional processing steps other than further dilution. All results fulfilling these requirements are listed in Table 8 arranged in alphabetical order of the NMI's initials. The arithmetic means of all results are listed as well as their associated uncertainties $u_{c,c}$ (eqn. 1).

$$u_{c,c} = \bar{u} = \sqrt{\frac{\sum u_i^2}{n}} \qquad \text{eqn. 1}$$

Table 8: Summary of the results for ERM-AE142 (solution) as reported by the different NMIs; all standard uncertainties are enclosed in brackets and apply to the last digits of the value

Institute	Isotope amount ratios in ERM-AE142			
	$n(^{206}Pb)/n(^{204}Pb)$	$n(^{207}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{206}Pb)$
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)
Mean	21.1139	15.9439	39.850	1.88740
Standard deviation	0.0027	0.0024	0.0067	0.00010
$u_{c,c}$	0.0087	0.0084	0.022	0.00051

The certified values of the Pb isotope amount ratios in ERM-EB400 were calculated from the reported results that also met the target uncertainty of <0.2 % (k=1). Unlike ERM-AE142, this iRM required that the Pb in the bronze be separated from all other matrix elements and therefore underwent chromatographic separation. The results of these measurements are listed in Table 9, arranged in alphabetical order of the NMI's initials. The arithmetic means of all results were calculated as well as their associated uncertainties $u_{c,c}$ (eqn. 1).

Table 9: Summary of the results for ERM-EB400 (bronze) as reported by the different NMIs; all standard uncertainties are enclosed in brackets and apply to the last digits of the value.

Institute	Isotope amount ratios in ERM-EB400			
	$n(^{206}Pb)/n(^{204}Pb)$	$n(^{207}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{206}Pb)$
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)
Mean	18.0723	15.5776	38.075	2.10685
Standard deviation	0.0059	0.0053	0.017	0.00037
$u_{c,c}$	0.0081	0.0084	0.021	0.00056

4. Certification

For the certification of a reference material in general all data altering or affecting the quantity value to be certified or its combined uncertainty have to be collected and used for establishing the certified quantity value. Commonly, the results from homogeneity, stability and characterization are combined. The here described reference materials are certified on the basis of values obtained in a CCQM Key Comparison, which fulfil the highest metrological requirements, especially in terms of measurement uncertainty and traceability.

Table 10: Isotope amount ratios of ERM-AE142 and ERM-EB400 with their final combined uncertainties

Description	Isotope amount ratios			
	$n(^{206}Pb)/n(^{204}Pb)$	$n(^{207}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{204}Pb)$	$n(^{208}Pb)/n(^{206}Pb)$
ERM-AE142	21.1139	15.9439	39.850	1.887 40
$u_c = u_{c,c}$	0.0087	0.0084	0.022	0.000 51
ERM-EB400	18.0723	15.5776	38.075	2.106 85
$u_{c,c}$	0.0081	0.0084	0.021	0.000 56
$u_{c,c}$ rel.	0.045 %	0.054 %	0.055 %	0.026 %
u_{bb} rel.	0.014 %	0.016 %	0.021 %	0.021 %
u_c	0.0084	0.0088	0.023	0.000 71

As explained above possible homogeneity issues apply only to ERM-EB400 and instability issues do not apply to either of these new iRMs. Consequently, the certified values and their associated uncertainties are taken from Table 8 for ERM-AE142. In the case of ERM-EB400, the uncertainty contribution of the homogeneity test has to be folded in. The resulting isotope amount ratios for ERM-AE142 and ERM-EB400 are displayed in Table 10 together with their associated uncertainties.

From the isotope amount ratios in Table 10 the isotope amount fractions (also called isotopic abundances) and the molar masses for both materials can be calculated. The certified isotope amount ratios, isotope amount fractions and molar masses of ERM-AE142 and ERM-EB400 are listed in Table 11 and Table 12. The dominant contributor to the uncertainties of all these certified quantity values comes from the propagated uncertainties of the certified iRM (NIST SRM 981), which has been used for correcting instrumental mass fractionation/mass discrimination.

Table 11: Certified quantity values of ERM-AE142 with their associated combined uncertainties u_c and their associated expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Quantity	Unit	Value	u_c	U	U_{rel} in %
$n(^{206}Pb)/n(^{204}Pb)$	mol/mol	21.1139	0.0087	0.017	0.082
$n(^{207}Pb)/n(^{204}Pb)$	mol/mol	15.9439	0.0084	0.017	0.11
$n(^{208}Pb)/n(^{204}Pb)$	mol/mol	39.850	0.022	0.044	0.11
$n(^{208}Pb)/n(^{206}Pb)$	mol/mol	1.887 40	0.000 51	0.0010	0.054
$n(^{204}Pb)/n(Pb)$	mol/mol	0.012 8357	0.000 0041	0.000 0083	0.064
$n(^{206}Pb)/n(Pb)$	mol/mol	0.271 01	0.000 12	0.000 23	0.085
$n(^{207}Pb)/n(Pb)$	mol/mol	0.204 65	0.000 11	0.000 21	0.10
$n(^{208}Pb)/n(Pb)$	mol/mol	0.511 50	0.000 16	0.000 32	0.062
$M(Pb)$	g/mol	207.177 83	0.000 26	0.000 53	0.000 26

Table 12: Certified quantity values of ERM-EB400 with their associated combined uncertainties u_c and their associated expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Quantity	Unit	Value	u_c	U	U_{rel} in %
$n(^{206}Pb)/n(^{204}Pb)$	mol/mol	18.0723	0.0084	0.017	0.093
$n(^{207}Pb)/n(^{204}Pb)$	mol/mol	15.5776	0.0088	0.018	0.11
$n(^{208}Pb)/n(^{204}Pb)$	mol/mol	38.075	0.023	0.046	0.12
$n(^{208}Pb)/n(^{206}Pb)$	mol/mol	2.106 85	0.000 71	0.0014	0.067
$n(^{204}Pb)/n(Pb)$	mol/mol	0.013 7504	0.000 0049	0.000 0098	0.072
$n(^{206}Pb)/n(Pb)$	mol/mol	0.248 50	0.000 12	0.000 24	0.097
$n(^{207}Pb)/n(Pb)$	mol/mol	0.214 20	0.000 12	0.000 24	0.11
$n(^{208}Pb)/n(Pb)$	mol/mol	0.523 55	0.000 17	0.000 35	0.067
$M(Pb)$	g/mol	207.209 68	0.000 28	0.000 57	0.000 27

These certified isotopic reference materials (CRM) are traceable to the International System of units (SI) in the most direct way possible, by calibration of all mass spectrometers against a SI-traceable calibrator, NIST SRM 981.

5. Storage and Handling

ERM-AE142 should be stored under normal laboratory conditions (between 5 °C and 25 °C). Once opened, the bottle lid should be left open as little as possible. Its weight should be monitored to track any evaporative losses during storage. These losses however will only affect the nominal Pb mass fraction in the solution and not affect the certified Pb isotope amount ratios. The introduction of any contaminant to this solution may change the Pb isotope ratios, and will therefore render these certified values null and void.

ERM-EB400 should be stored under normal lab conditions in a tightly sealed container. No specific precautions are necessary aside from exposure to any contaminants

6. References

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7. Appendix 1: Equations used for the calculation of u_{bb}

$$SS_{\text{within}} = \sum_{i=1}^{k} (N_i - 1) \cdot s_i^2$$

$$SS_{\text{between}} = \sum_{i=1}^{k} N_i \cdot \left(\overline{X}_i - \overline{X}\right)^2$$

$$MS_{\text{between}} = \frac{SS_{\text{between}}}{k-1}$$

$$MS_{\text{within}} = \frac{SS_{\text{within}}}{N-k}$$

$$F_{\text{test}} = \frac{MS_{\text{between}}}{MS_{\text{within}}}$$

$$s_{\text{wb}} = \sqrt{MS_{\text{within}}}$$

$$s_{\text{bb}} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n}}$$

$$u_{bb}^{*} = \sqrt{\frac{MS_{\text{within}}}{n}} \cdot \sqrt[4]{\frac{2}{k \cdot (n-1)}}$$

$$u_{\text{bb}} = \sqrt{s_{\text{bb}}^2 + \frac{MS_{\text{within}}}{N} \cdot \sqrt[4]{\frac{2}{\nu_{\text{MSwithin}}}}}$$

With

k *number of selected samples*

n *number of replicate measurements for one sample*

N *Total number of measurements* $N = n \cdot k$