Report of the key comparison CCQM-K88
Determination of lead in lead-free solder containing silver and copper

(Final Report)

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Abstract

The CCQM-K88 key comparison was organised by the Inorganic Analysis Working Group of CCQM to test the abilities of the national metrology institutes to measure the mass fraction of lead in lead-free solder containing silver and copper. National Metrology Institute of Japan (NMIJ), National Institute of Metrology P. R. China (NIM) and Korea Research Institute of Standards and Science (KRISS) acted as the coordinating laboratories. The participants used different measurement methods, though most of them used inductively coupled plasma optical emission spectrometry (ICP-OES) or isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). Accounting for relative expanded uncertainty, comparability of measurement results was successfully demonstrated by the participating NMIs for the measurement of the mass fraction of lead in lead-free solder at the level of 200 mg/kg.

It is expected that metals at mass fractions greater than approximately 100 mg/kg in lead-free solder containing silver and copper can be determined by each participant using the same technique(s) employed for this key comparison to achieve similar uncertainties mentioned in the present report.

1 Introduction

Solder is a ubiquitous industrial material and recent interest in lead-free solders has arisen from the viewpoint of the RoHS directive. Therefore, accurate measurements of lead in lead-free solders, especially containing silver and copper, are important. To date, only low alloy steel (P25 and K33+P56) and a copper alloy (P76 and K64) have been used as materials for CCQM comparisons in the field of metals and metal alloys. Since the main constituent of solders is usually tin, the pilot study CCQM-P119 extended the field of comparisons to another important type of metals and metal alloys.

Following the pilot study CCQM-P119, National Metrology Institute of Japan (NMIJ), National Institute of Metrology P. R. China (NIM) and Korea Research Institute of Standards and Science (KRISS) proposed a key comparison of "Determination of lead in lead-free solder containing silver and copper" at the Inorganic Analysis Working Group (IAWG) meeting held April 13-14, 2010. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K88 and NMIJ, NIM and KRISS were designated as coordinating laboratories. The element in this comparison was lead in the solder matrix at a mass-fraction between 100 mg/kg and 600 mg/kg. Each participant could use any suitable method(s) of measurement. Four measurements of the element had to be carried out by each participant. The homogeneity of the material used in this study had been investigated prior to the comparison. This is the first CCQM key comparison in the field of tin-based alloy analysis. The comparison results were discussed at the IAWG meetings held April 11-12, 2011, November 1-2, 2011 and April 16-17, 2012.

It was decided that a parallel pilot study designated CCQM-P125 would be conducted, in which the same samples measured by the CCQM-K88 participants would also be used.

2 List of Participants

Table 1 contains the full names of all participating NMIs.

In the context of the current concept of the CIPM-MRA, different CMCs which refer to the same key comparison should be acceptable. Therefore, there is no problem with both BAM and PTB participating in this key comparison provided they do not both have CMCs for the same measurements.

Table 1 List of participating NMIs

No.	Participant	Country
1	**BAM** Federal Institute for Materials Research and Testing	Germany
2	**INMETRO** National Institute of Metrology, Standardization and Industrial Quality	Brazil
3	**INTI** National Institute of Industrial Technology	Argentina
4	**KRISS** Korea Research Institute of Standards and Science	Rep. of Korea
5	**NIM** National Institute of Metrology P. R. China	P. R. China
6	**NIST** National Institute of Standards and Technology	USA
7	**NMIJ** National Metrology Institute of Japan	Japan
8	**NRC** National Research Council Canada	Canada
9	**PTB** Federal Institute of Physical and Technical Affairs	Germany
10	**VNIIM** All-Russia D. I. Mendeleev Scientific and Research Institute for Metrology	Russia

3 Samples

The comparison material is a lead-free solder (Sn 96.5 %, Ag 3 % and Cu 0.5 %) containing between 100 mg/kg and 600 mg/kg of lead. The measurand to be determined is the mass fraction of lead. The material consists of short pieces (less than 0.1 g each) made by cutting long wires. Each participant received approximately 10 g of the lead-free solder and were instructed to keep the material at ambient laboratory temperature after receipt. No special treatment of the sample, such as drying, was required before use; however, it was noted that it should be kept in a silica-gel desiccator before weighing.

The homogeneity of the material, expressed as the relative standard deviation (RSD) of the mass fraction of lead, was 0.13 % (RSD) according to results for determination of lead by isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS or IDMS) using a sample size of about 0.2 g. Though the homogeneity indicated in the technical protocol was 0.8 % (RSD) based on analysis by inductively coupled plasma optical emission spectrometry (ICP-OES or OES), it was substantially better according to the more precise ID-ICP-MS measurements. Based on the sample size for the homogeneity test, the use of more than 0.2 g sample for each measurement was strongly recommended. The homogeneity value was expressed for a single sub-sampling of 0.2 g; it should be divided by the square root of 4 for the homogeneity corresponding to the average arising from four sub-samplings.

The samples were distributed to the participants from NMIJ by EMS mail in July, 2010, except for BAM, PTB and KEBS (in August, 2010). Finally, all samples reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of the participants

Participant	Contact person
BAM	Sebastian Recknagel
INMETRO	Rodrigo Caciano de Sena
INTI	Mónica Borinsky
KRISS	Kyung Haeng Cho
NIM	Ma Liandi
NIST	Gregory Turk
NMIJ	Akiharu Hioki
NRC	Ralph Sturgeon
PTB	Olaf Rienitz
VNIIM	L.A. Konopelko

4 Technical Protocol

The technical protocol, attached as Annex A, instructed participants concerning treatment of the samples, methods of measurement, reporting of results and the time schedule. The deadline for the reporting of results was originally intended to be September 20, 2010 in the protocol; it was, however, postponed to December 31, 2010.

5 Methods of Measurement

Participants were allowed to use any suitable method(s) of measurement. Though most of the results were obtained by ICP-OES or ID-ICP-MS, isotope-dilution thermal ionization mass spectrometry (ID-TIMS) and glow dishcarge mass spectrometry (GDMS) were also employed by one participant each. The number of results by each method is summarized in Table 3.

Table 3 Number of results by each method for CCQM-K88

Method	Number of results reported
ICP-OES	4
ID-ICP-MS	4
ID-TIMS	1
GDMS	1
Total number	10

6 Results

Results, given in Table 4, include information on the measurement methods; results are illustrated graphically in Figure 1. The half of the bar of each data in the Figure 1 indicates the reported combined standard uncertainty ($k = 1$). The Figure contains a solid, horizontal line representing the median of the IDMS or ID-TIMS data. The uncertainty of the median was based on the estimate according to median($|x_i$-median$|$)/0.6745, where x_i is each reported value. The dashed, horizontal lines indicate the range of the combined standard uncertainty ($k = 1$) of the median. The median for the IDMS or ID-TIMS data and its expanded uncertainty ($k = 2$) are 197.2 mg/kg and 0.93 mg/kg; the expanded uncertainty 0.9 mg/kg was used for calculating the uncertainty of the degree of equivalence (*vide infra*). The arithmetic mean of the IDMS or ID-TIMS data for the measurand is also represented in Figure 1. The half of the bar of the arithmetic mean indicates the combined standard uncertainty ($k = 1$) based on the standard deviation of the mean. The reference value (RV) is discussed in the following section

Table 4 Results for lead of CCQM-K88

| Participant	Measurement Method	Decomposition Method	Materials used for calibration	Reported value / mass fraction (mg/kg)	Combined standard uncertainty / mass fraction (mg/kg) (k=1)
INMETRO	ICP-OES	HCl:H_2O_2 (3:2); microwave digestion; no Pb detected in precipitation	Pb standard solution (NIST SRM 3128)	179	2
VNIIM	ICP-OES, with external calibration	HNO3:HF (5:1) digestion	CRM of Pb solution (GSO 7447-98)	194.2	5
NIM	ID-ICP-MS (207/208, Q-ICP-MS)	H_2O_2/HF digestion	NIM primary assay standard of Pb	195.8	1.3
NMIJ	ID-ICP-MS	HNO_3/HF digestion	NMIJ primary standard solution	196.7	0.76
KRISS	ID-ICP-MS (Q-ICP-MS)	HNO_3/HCl digestion	KRISS primary assay standard of Pb	197.2	1.0
PTB	ID-ICP-MS (HR-ICP-MS)	HCl/HNO_3 digestion	calibration standard (BAM-A-primary-Pb-1)	197.9	0.95
BAM	ID-TIMS	HNO_3 digestion by high pressure asher	primary reference material BAMY004	198.29	0.25
INTI	ICP-OES, calibration/matrix matching	HNO_3/HF 5+1 digestion	Pb standard solution (NIST SRM 3128)	199	2
NIST	ICP-OES, standard addition calibration	HNO_3/HF digestion	NIST SRM 3128 standard solution (CRM for Pb)	199.43	0.35
NRC	GDMS	Direct measurement	calibrated against lead-free solder CRM with similar composition (NMIJ CRM 8203-a)	202.4	9.3
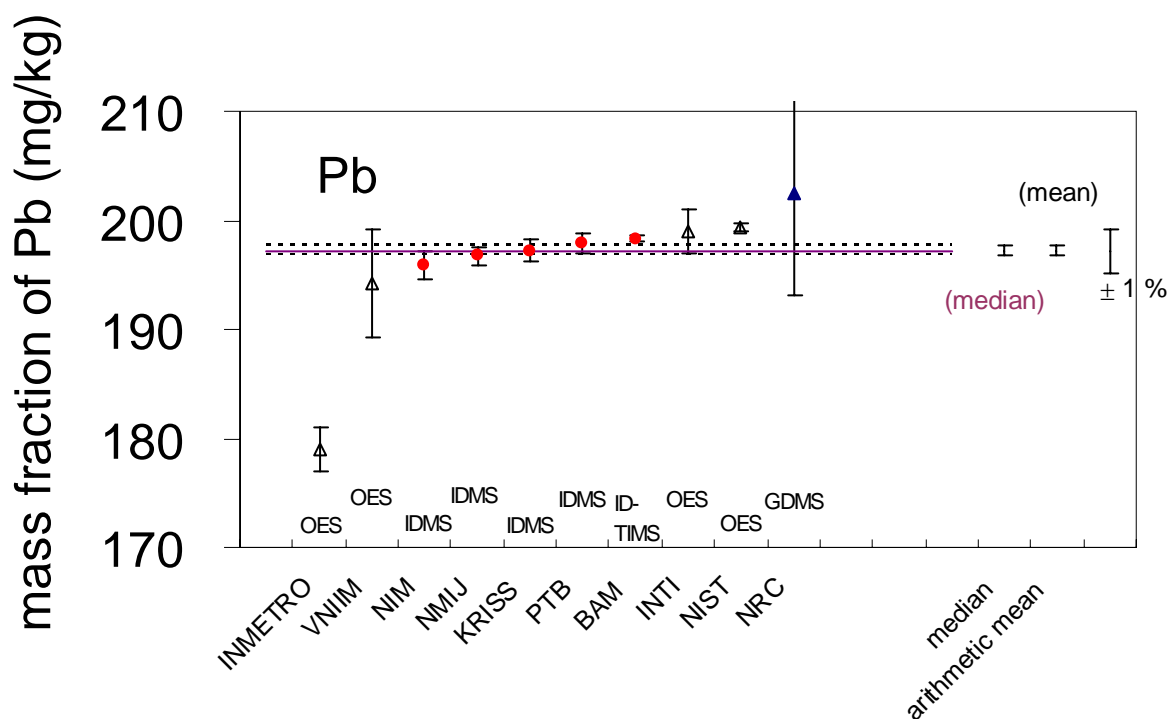
Fig. 1 Results for Pb of CCQM-K88
The half of each bar indicates the combined standard uncertainty (k =1).

7 Discussion

No clearly observed differences among the measurement methods (including the acids used for digestion) employed are evident from the results. Most of the reported data are within ±2 % relative to the median, except for a limited number of results.

In order to easily compare the results with each other, the reference value (RV) was estimated and an equivalence statement was made. At the IAWG meeting held April 11-12, 2011, it was decided that the RV should be estimated from the IDMS data, including the ID-TIMS value. For reference, some candidates for the RV are shown in Table 5; n=10 indicates that all submitted results were used for calculating the estimate. The variance due to heterogeneity was not included in the calculation of each expanded uncertainty. From the viewpoint of simplicity and robustness, the median is recommended as the RV for this comparison. If the homogeneity corresponding to the average from four sub-samplings is included, the expanded uncertainty of the median, for example, becomes 0.96 mg/kg.

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Table 5. Candidates for an RV of lead for CCQM-K88

		Value / mass fraction (mg/kg)	Expanded uncertainty (k=2) / mass fraction (mg/kg)
Mean (only IDMS & ID-TIMS)	*1	197.2	0.9
Mean (n=10)	*1	196.0	4.0
Median (only IDMS & ID-TIMS)	*2	197.2	0.9
Median (n=10)	*2	197.6	1.5
MMmedian (only IDMS & ID-TIMS)	*3	197.3	0.9
MMmedian (n=10)	*3	197.5	1.5
Weighted mean (usual weight) (n=10)	*4	198.2	0.4
Weighted mean (mild weight) (n=10)	*5	197.3	0.5

*1 The expanded uncertainty was based on the standard deviation of the mean.
*2 The uncertainty of the median was based on the estimate from median($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*3 The MMmedian was calculated according to the following:
David L. Duewer, "A robust approach for the determination of CCQM key comparison reference values and uncertainties", Working document CCQM/04-15, BIPM, 2004, (www.bipm.info/cc/CCQM/Allowed/10/CCQM04-15.pdf).
    The uncertainty of the MMmedian was based on the estimate from median ($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*4 The square of reciprocal of reported uncertainty was used as a weight.
*5 The reciprocal of reported uncertainty was used as a weight.

The degree of equivalence (DoE) and its uncertainty between a participant result and the KCRV is calculated according to the following equations:
$$D_i = (x_i - x_R)$$
$$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2)$$
where D_i is the DoE between the participant's result x_i and the KCRV, x_R, and U_i is the expanded uncertainty (coverage factor $k = 2$) of D_i calculated from both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R. The calculation results are shown in Table 6 and Figure 2. The half of each bar in the Figure indicates U_i.

Table 6 Degree of equivalence for lead (CCQM-K88)*

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)	D_i / relative value (%)	U_i / relative value (%)
RV	197.2	0.9	$k=2$				
INMETRO	179	4	$k=2$	-18.2	4.1	-9.2	2.1
VNIIM	194.2	10	$k=2$	-3.0	10.0	-1.5	5.1
NIM	195.8	2.6	$k=2$	-1.4	2.8	-0.7	1.4
NMIJ	196.7	1.52	$k=2$	-0.5	1.8	-0.3	0.9
KRISS	197.2	2	$k=2$	0.0	2.2	0.0	1.1
PTB	197.9	1.9	$k=2$	0.7	2.1	0.4	1.1
BAM	198.29	0.5	$k=2$	1.1	1.0	0.6	0.5
INTI	199	4	$k=2$	1.8	4.1	0.9	2.1
NIST	199.43	0.7	$k=2$	2.2	1.1	1.1	0.6
NRC	202.4	18.6	$k=2$	5.2	18.6	2.6	9.4

* Data from Table 4.

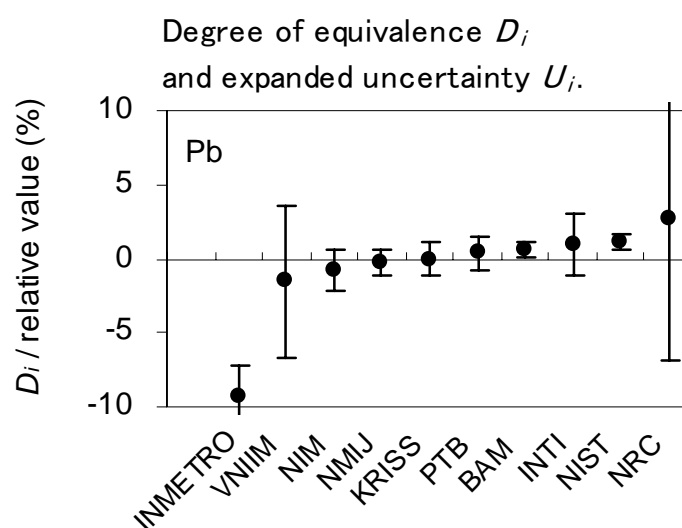Degree of equivalence D_i and expanded uncertainty U_i.

Fig. 2 Degree of equivalence for Pb
The half of each bar indicates U_i.

8 Demonstrated Core Capabilities

The four tables of demonstrated core capabilities are attached as Annex B.

At the IAWG meeting held November 1-2, 2011, it was decided to have a '**how far does the light shine**' (HFDTLS) statement in the report as well as the tables of demonstrated core capabilities. With regard to HFDTLS, CMC claims based on determination of lead in this key comparison may be applied to other tin-based solders containing silver and copper provided that the concentration range of lead is 100 mg/kg to 2000 mg/kg and that those of silver and copper are less than 4 % and 6 % (mass fractions), respectively. The HFDTLS statement can be used for the participating institute to demonstrate ability to comply with the European WEEE and RoHS regulations, which was a major reason for organising this key comparison.

9 Acknowledgement

Annex A - Technical Protocol
CCQM-K88 & P125 Key comparison and pilot study
on determination of lead in lead-free solder
containing silver and copper

Call for participants and technical protocol
(revised on July 14, 2010)

Introduction

Solder is one of ubiquitous materials in industry and elsewhere, and many people have recently been interested in lead-free solders from the viewpoint of the RoHS directive. Therefore, accurate measurements of lead in lead-free solders, especially containing silver and copper, are important. As the materials of CCQM comparisons in the field of metals and metal alloys, only low alloy steel (P25 and K33+P56) and copper alloy (P76 and K64) have been used. Since the main constituent of solders is usually tin, the recent pilot study P119 extended the field of comparisons to another important type of metals and metal alloys. The present key comparison K88 is a follow-up comparison of P119, and is carried out in parallel with the pilot study P125.

Samples

The comparison material is a lead-free solder (Sn 96.5 %, Ag 3 % and Cu 0.5 %) containing 100 mg/kg -600 mg/kg level of lead. The measurand to be determined is the mass fraction of lead. The material consists of short pieces (less than 0.1 g each) made by cutting long wires. Each participant will receive approximately 10 g of the lead-free solder. The homogeneity of the material was 0.8 % (rsd) according to the results of Pb based on ICP-OES determination using a sample size of about 0.2 g. Therefore, the use of more than 0.2 g sample for each measurement is strongly recommended. The sample after receiving should be kept at the laboratory temperature. No special treatment of the sample such as drying is required before use; however, it should be kept in a silica-gel desiccator before weighing. The CCQM-P125 sample is the same as the sample for CCQM-K88.

Methods of Measurement

Each participant can use any suitable method(s) of measurement. NMIs or officially designated institutes are welcome to participate in this comparison using primary methods of measurement. Four measurements for lead are to be carried out by each participant. The calibrations should be carried out by using standards with metrological traceability.

Each participant's capability of lead determination (approximately several hundred mg/kg) under the condition of the coexistence of tin and silver will be examined by the present comparison. The reference value will be probably a median of the submitted data from NMIs and officially designated institutes, though it will be decided after discussion in an IAWG meeting.

Reporting

The result should be reported as the mass fraction of lead to NMIJ (Akiharu Hioki), accompanied by a full uncertainty budget. Any participant that chooses to use multiple methods shall decide only one composite result (e.g., an average value from different methods).

Reporting the details of the procedure (including details of sample treatment/digestion), the calibration standard and the traceability link, and the instrument(s) used is required. A reporting form will be distributed to participants. Furthermore, please choose a suitable Core Capability table from the attached example forms and the filled-out table should be submitted together with the measurement result; if there is no suitable table, please make a suitable one depending on the measurement method.

Time schedule

Deadline of registration of participation: July 26, 2010
Dispatch of the samples: at the beginning of August, 2010
Deadline for receiving the report: December 31, 2010

Participants

Participation is open to all interested NMIs or officially designated institutes that can perform the determination. An NMI or an officially designated institute is recommended to participate in the key comparison rather than in the pilot study as far as possible. An NMI or an officially designated institute may nominate other institutes or laboratories to participate in the pilot study. Please inform NMIJ (Akiharu Hioki) of the contact person, the shipping address, and so on using the attached registration form. Even if you do not wish to participate, please inform NMIJ of it.

We would like to ask NMIs or officially designated institutes to coordinate participation within their economies including inviting participants in the pilot study, shipping samples, and receiving the reports. The coordinating laboratories might invite some expert laboratories directly to participate in the pilot study.

Coordinating laboratories

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Annex B - Tables of Demonstrated Core Capabilities

Demonstrated Inorganic Core Capabilities (1)

CCQM-K88, Lead in Lead-Free Solder

Analyte: Pb

Methodology: ID-ICP-MS

Participating Institutes: NMIJ, NIM, KRISS, PTB

Instructions: *List institutes demonstrating capabilities*

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	Lead remains a common contaminant at trace levels demanding use of clean reagents, vessels and hyandling procedures to not only minimize the blank, but generate a consistent one.
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.*	All		No organic components within this sample
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.*		All	Co-existence of tin and silver should be considered in order to determine the optimal digestion approach; precipitation of tin oxides and silver halides may be problematic
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	All		The measurand is not volatile with respect to the sample processing conditions and no losses are expected, especially when digestion is undertaken in high pressure closed vessels.
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		No preconcentration or matrix separation techniques were needed as the amount content of the measurand was sufficient to allow for simple dilution of the digested matrix.
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.*	All		Direct sample introduction techniques were used.
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.*	All		No preconcentration or matrix separation techniques were needed as the amount content of the measurand was sufficient to allow for simple dilution of the digested matrix.
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*		All	ID-MS requires spike equilibration to ensure identical behaviour of the endogenous and added forms of lead from the start of any sample processing.
Signal detection *The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low*		All	The amount content of the measurand was sufficient to generate good signal-to-noise characteristics

Capabilities/Challenges	Not Tested	Tested	Specific Challenges Encountered
isotopic abundance, or that are poorly ionized.			
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		All	Lead does not suffer significant memory effects with standard sample introduction systems but care should be exercised when alternating between spiked solutions containing enriched isotopes and the unspiked sample
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 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.*		All	Alhough the 200 Da region of the mass spectrum is relatively free of background counts and interferences from molecular ions, these need to be carefully checked, along with elemental isobaric interferences and corrections made when required
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*		All	Standard deadtime correction equations were utilized to correct response.
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		All	Determination of the isotope composition of Pb in the sample is required.Usually isotopic ratio and matrix component of spike sample and those of isotopic standard solution (*e.g.*, NIST SRM 982) are different. Therefore, careful handling of these solutions is necessary; for example, insertion of washing stage between the solutions to reduce memory effect.
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		All	Careful assessment of the amount content of the enriched spike is required, using a reverse ID-MS approach and a traceable calibration standard of known iostopic composition

Demonstrated Inorganic Core Capabilities (2)

CCQM-K88, Lead in Lead-Free Solder

Analyte: Pb

Methodology: ID-TIMS

Participating Institutes: BAM

Instructions: *List institutes demonstrating capabilities*

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.*		BAM	Lead remains a common contaminant at trace levels demanding use of clean reagents, vessels and hyandling procedures to not only minimize the blank, but generate a consistent one.
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.*	BAM		No organic components within this sample
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.*		BAM	Co-existence of tin and silver should be considered in order to determine the optimal digestion approach; precipitation of tin oxides and silver halides may be problematic
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*		BAM	ID-MS requires spike equilibration to ensure identical behaviour of the endogenous and added forms of lead from the start of any sample processing.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*		BAM	The measurand is not volatile with respect to the sample processing conditions and no losses are expected.
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.*		BAM	TIMS requires careful separation of matrix components without perturbation of the isotopic composition of the measurand
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_2S_3 for sulfur measurements.*	BAM		Standard procedure for Pb measurements has been used, this point has been tested during procedure development and validation
Filament preparation chemistry and loading *Techniques and procedures used to load the analyte onto filaments and prepare them for measurement.*	BAM		Standard procedure for Pb measurements has been used, this point has been tested during procedure development and validation
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.*	BAM		Standard procedure for Pb measurements has been used, this point has been tested during procedure development and validation
Ion signal generation *Procedures for warm up, filament heating and measurement procedures*	BAM		Standard procedure for Pb measurements has been used, this point has been tested during procedure development and

Capabilities/Challenges	Not Tested	Tested	Specific Challenges Encountered
			validation
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.*		BAM	Checked for interferences, but no interferences oc cur
Detector deadtime correction *Measurement of and correction for the deadtime of ion counting detectors if applicable.*	BAM		Not applicable as Faraday detectors have been used
Correction of mass fractionation *Techniques used to determine, monitor, and correct for instrumental and procedural mass fractionation.*		BAM	Determination of the isotope composition of Pb in the sample is required.
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		BAM	Double IDMS applied

Demonstrated Inorganic Core Capabilities (3)

CCQM-K88, Lead in Lead-Free Solder

Analyte: Pb

Methodology: ICP-OES

Participating Institutes: INMETRO, VNIIM, INTI, NIST

Instructions: *List institutes demonstrating capabilities*

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	Lead remains a common contaminant at trace levels demanding use of clean reagents, vessels and hyandling procedures to not only minimize the blank, but generate a consistent one.
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.*	All		No organic components within this sample
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.*		All	Co-existence of tin and silver should be considered in order to determine the optimal digestion approach; precipitation of tin oxides and silver halides may be problematic and result in loss of measurand
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	All		The measurand is not volatile with respect to the sample processing conditions and no losses are expected, especially when digestion is undertaken in high pressure closed vessels.
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		No preconcentration or matrix separation techniques were needed as the amount content of the measurand was sufficient to allow for simple dilution of the digested matrix.
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.*	All		Direct sample introduction techniques were used.
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.*	All		No preconcentration or matrix separation techniques were needed as the amount content of the measurand was sufficient to allow for simple dilution of the digested matrix.
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		All	Calibration standards prepared from traceable reference materials, requires accurate (gravimetric) dilution.
Signal detection *The detection and recording of the analyte signals. The degree of difficulty increases for analytes present at low concentrations, or that are have weak emission lines..*		All	Good signal-to-noise ratio must be achieved. Lead is not a particularly sensitive element by atomic emission.

Capabilities/Challenges	Not Tested	Tested	Specific Challenges Encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		All	Lead does not suffer significant memory effects with standard sample introduction systems but care should be exercised when alternating between samples, calibrants and blanks
Complex spectral backgrounds *Any techniques used to remove, reduce, or mathematically correct for interferences caused by the overlap of analyte emission lines with atomic, ionic, or molecular emission from matrix components. The relative concentrations and sensitivities of the analyte and the interfering species will affect the degree of difficulty. Samples containing high concentration matrix components with large numbers of emission lines or molecular bands may increase the measurement challenge.*		All	The Pb(II) 220.353 nm line is realtively free of major interferences from other lines but care must be exercised in establishing baseline levels for intensity evaluations.
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.*		All	The relatively low concentration of Pb requires low sample dilution factors and thus greater susceptibility to matrix interference.

<p style="text-align:center">Demonstrated Inorganic Core Capabilities (4)</p>

<p style="text-align:center">CCQM-K88, Lead in Lead-Free Solder</p>

Analyte: Pb

Methodology: GD-MS

Participating Institutes: NRC

Instructions: *List institutes demonstrating capabilities*

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.*		NRC	Chemical surface etching of sample under clean conditions followed by sputter cleaning of sample surface in the GD.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NRC		The measurement technique utilizes the solid sample for testing and losses are not possible.
Sample preparation *Techniques and procedures used to render the test sample into a form compatible with GD pin cell geometry, including machining, cutting, pressing , forming (e.g., Ga) or otherwise mounting (e.g., pressing onto In) to achieve required geometry.*		NRC	Pin geometry identical to matrix matched standard used for calibration
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.*	NRC		Solid sampling is undertaken with no dissolution or matrix separation.
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		NRC	Calibration in this exercise performed with matrix matched "standard" NMIJ CRM 8203-a
Signal detection *The detection and recording of the analyte signals. The degree of difficulty increases for analytes present at low concentrations, or that are have weak emission lines..*		NRC	Ratioing technique between ion and faraday detectors with cross-calibration using Ar ions
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		NRC	Cells pre-sputtered for each sample prior to data collection
Complex spectral backgrounds *Any techniques used to remove, reduce, or mathematically correct for interferences caused by the overlap of analyte emission lines with atomic, ionic, or molecular emission from matrix components. The relative concentrations and sensitivities of the analyte and the interfering species will affect the degree of difficulty. Samples containing high concentration matrix components with large numbers of emission lines or molecular bands may increase the measurement challenge.*		NRC	"Medium" resolution (4000) MS measurements performed with sector field instrument to separate molecular ion interferences
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.*		NRC	Ratioing technique with calibration against matrix matched standard for this exercise (NMIJ CRM 8203-a)

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