CCQM-K30.1: Lead in Wine

Final Report

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CMQ-Fundacion Chile

February, 2013

The individuals who contributed the measurements described in this report are listed in Table 2.

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CCQM-K30.1: Lead in Wine

1. Summary

The CCQM-K30.1 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 wine. CMQ-Fundacion Chile acted as the coordinating laboratory. Twelve institutes registered to participate in the key comparison but only eleven submitted results. One of these agreed that its result should not be included in the KCRV and another indicated after completion of the study that it had recalculated its uncertainty. The participants used different measurement methods, though the most common was isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). Accounting for the achieved uncertainty, comparability of measurement results was successfully demonstrated by the majority of participating NMIs for this measurement. Participants were also asked to indicate the core capabilities required for their measurements and these are summarised in the report. This comparison may be directly used to support CMCs for Pb in wine and indirectly by institutes wishing to support appropriate CMCs via the core capability route.

2. Introduction

Key comparison CCQM-K30.1 was performed to demonstrate and document the capability of national metrology (NMIs) and designated (DIs) institutions in the assessment of the mass fraction of lead in wine.
This study was agreed in 2009 by the Inorganic Analysis Working Group (IAWG) of the Comité Consultatif pour la Quantité de Matière (CCQM) and was coordinated by the Centre of Chemical Metrology (CMQ-Fundación Chile), Santiago, Chile.
This comparison is subsequent to the CCQM-K30 study of lead in wine that was agreed upon in October 2004 with a final report issued on January 2008. The CCQM–K30 was coordinated by LGC (Teddington, UK) with experimental support of CMQ that, at the time of this study, was not an officially designated institute.
The IAWG also agreed that a pilot study CCQM-P12.2 would run in parallel to the key comparison and would include Pb, Fe, Cu and (initially) Cd using the same sample. The progress report on the pilot study is presented separately.

3. Rationale of this comparison

Analysis of heavy metals and other toxic elements in wine is essential for regulatory control and to comply with the requirements of international trade in wine. Thus, the availability of traceable measurements supported by NMIs through appropriate calibration and measurement capabilities is an important requirement in many countries. An earlier pilot study CCQM-P12 of Pb in wine [14.1] was successfully followed by the above mentioned CCQM-K30 and CCQM-P12.1 that, in addition to Pb, also included the analysis of native concentrations of Fe, Cu and Cd in red wine.

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Some NMIs/DIs that did not participate in the latter studies asked the IAWG to perform a new, subsequent study on the same metals included in the CCQM-K30/CCQM-P12.1, aiming to demonstrate and document their measurement capabilities.
The IAWG agreed to perform such subsequent studies and the coordination of these comparisons (CCQM-30.1 and CCQM-P12.2) was assigned to CMQ- Fundacion Chile, Santiago, Chile.

4. Sample

The sample prepared for both studies was a Chilean red wine (Cabernet Sauvignon, vintage 2009) with naturally occurring concentrations of the elements of interest.
Sample preparation and treatment followed the experimental procedure used in the CCQM-P12 and CCQM-K30 [14.1,14.2]. Each sample is contained in 100ml amber glass bottle covered with PTFE/silicone septa sealed with aluminium crimp tops.

- **Homogeneity and stability study**

  Bottles of the testing material were randomly selected from the prepared bottles of sample. Two test portions were taken from each bottle for analysis. The test portions were digested using microwave-assisted digestion. The digested samples, control samples and method blanks were analysed using ICP-MS.
  ANOVA technique was applied to assess the between bottle heterogeneity and the standard uncertainty originated from the between bottle heterogeneity was calculated using the formula (1) given below in accordance with ISO Guide 35:2006 [14.3]. The results of single ANOVA calculation and applying the formula for estimation of the uncertainty originated from between bottles heterogeneity u_{bb} are reported in Table 1.

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{\nu MS_{within}}} \qquad (1)$$

where:
u_{bb} is the standard uncertainty due to between bottles heterogeneity;
MS_{within} is the mean square of within bottles variance;
$\nu_{MSwithin}$ is the degree of freedom of MS_{within};
n is the number of replicates.

Table 1. Summary of homogeneity study results

Measurand	ANOVA test on heterogeneity		u_{bb} (%)
	F-statistics	Critical value	
Pb	1.10	5.19	0.68

The homogeneity study results reported in Table 1 shows that no significant heterogeneity was observed and the sample quality fits the purpose of this comparison.

- **Stability**

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A study for long-term stability was determined of the test material under storage conditions of participating laboratories. This study was conducted at 20ºC and covered the period from the distribution of test material to the deadline for submission of results.
Following international guidelines of ISO Guide 35:2006, the trend-analysis technique was applied to assess the stability of the test material using a model as:

$$Y = \beta_0 + \beta_1 X + \varepsilon$$

where β_0 and β_1 are the regression coefficients and ε denotes the random error component.
With appropriate t-factors, β_1 can be tested for significant deviation from zero.
P-value of 0.68 was obtained for Pb, indicating that β_1 value was not significantly different from zero at a confidence limit of 95%. In other words, no instability was observed for the test material, during the reporting period and the sample stability fits the purpose of this comparison.

5. Participation in CCQM-K30.1

The NMIs/DIs registered for CCQM-K30.1 are listed in Table 2

Table 2 CCQM-K30.1 participants

INSTITUTE/ ORGANIZATION	COUNTRY	CONTACT
INMETRO Instituto Nacional de Metrología, Qualidade e Tecnología	Brasil	Dr. Marcelo Dominguez de Almeida
Jozef Stefan Institute	Slovenia	Dr. Milena Horvat
LGC Limited	United Kingdom	Dr. Heidi Goenaga-Infante
NMIA National Measurement Institute Australia	Australia	Dr. David Saxby
NMISA National Metrology Institute of South Africa	South Africa	Dr. Angelique Botha
TUBITAK UME National Metrology Institute of Turkey	TURKEY	Dr. Oktay Cankur
Bulgarian Institute of Metrology, National Centre of Metrology, Chemical Measurements Department	Bulgaria	Dr. Boriana Kotzeva
EXHM/GCSL-EIM Hellenic Metrology Institute/ Designated Institute for Metrology in Chemistry	Greece	Dr. Elias Kakoulidis
HSA Health Sciences Authority	Singapore	Dr. Richard Shin
INDECOPI	Perú	Dr. Christian Uribe

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INM National Institute of Metrology	Romania	Dr. Mirella Buzoianu
CMQ Center of Chemical Metrology, F. Chile	Chile	Dr. Gabriela Massiff

6. Instructions to participants

Each participant received two labelled bottles (100 ml) of the wine material. They were advised to mix the sample thoroughly before processing. The technical protocol and example of the reporting forms used in this study (see Appendix A) were sent to all of the registered participants.
Participants were free to choose any analytical methods for examination. Participants were requested to perform three independent measurements on three separate portions of the sample. The participants were asked to report the mean value of 3 independent measurements of the mass fractions of Pb in ng/g and its associated and expanded uncertainty.
Remittance of the samples and protocol took place on October 2011. The original established deadline was set at 30 January 2012 but some unexpected delays occurred and the final deadline was February 29th 2012.

7. Methods and instrumentation used

Four of the key comparison participants used ICP-MS, while five of them used isotope dilution ICP-MS. Only one laboratory used ETAAS. An overview of the measurement and sample preparation methods used by each laboratory is shown in Appendix B.

8. CCQM-K30.1 participants' results

The CCQM-K30.1 participants' results for Pb, as reported to the co-ordinating institute (CMQ) are shown in Table 3. All data are reported as ng g^{-1} of Pb in the sample as received. These results are also presented in Figure 1.

Table 3. CCQM-K30.1 participants results for Pb

Participant	Reported result ng g^{-1}	Reported standard uncertainty ng g^{-1}	Reported expanded uncertainty ng g^{-1}	% relative expanded uncertainty	k
NMIA	12.14	0.12	0.24	2.0	2.03
INMETRO	11.8	0.14	0.28	2.4	2
CMQ	12.31	0.06	0.13	1.1	2
EXHM	11.424	0.153	0.306	2.7	2
INDECOPI	12.16	0.3	0.59	4.9	2
HSA	12.3	0.25	0.49	4.0	2
IJS	10.45	0.13	0.26	2.5	2
NMISA	12.08	0.16	0.32	2.6	2

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UME	11.88	0.32	0.64	5.4	2
LGC	12.12	0.155	0.31	2.6	2

Bulgarian Institute of Metrology did not send results. INM from Romania agreed that their results will not be used in the KCRV estimation.

INMETRO sent revised values on September 25th 2012: 11.85 ± 0.50 ng/g, but the KCRV calculations were carried out with the original values.

9. Discussion

After preliminarily discussing the participants' results of Pb in the IAWG meeting last April 2012, it was decided that the median of IDMS results and its uncertainty should be taken as the KCRV and associated uncertainty for this study. Thus, the consensus reference value (solid line) and the expanded uncertainty (dashed lines) are shown in Figure 1 together with each participant's reported average value, associated uncertainty and the technique used.
On the right hand vertical axis of Fig. 1 the % deviation of each individual result relative to the KCRV is shown. It can be seen that results obtained by most of the participants are satisfactory.

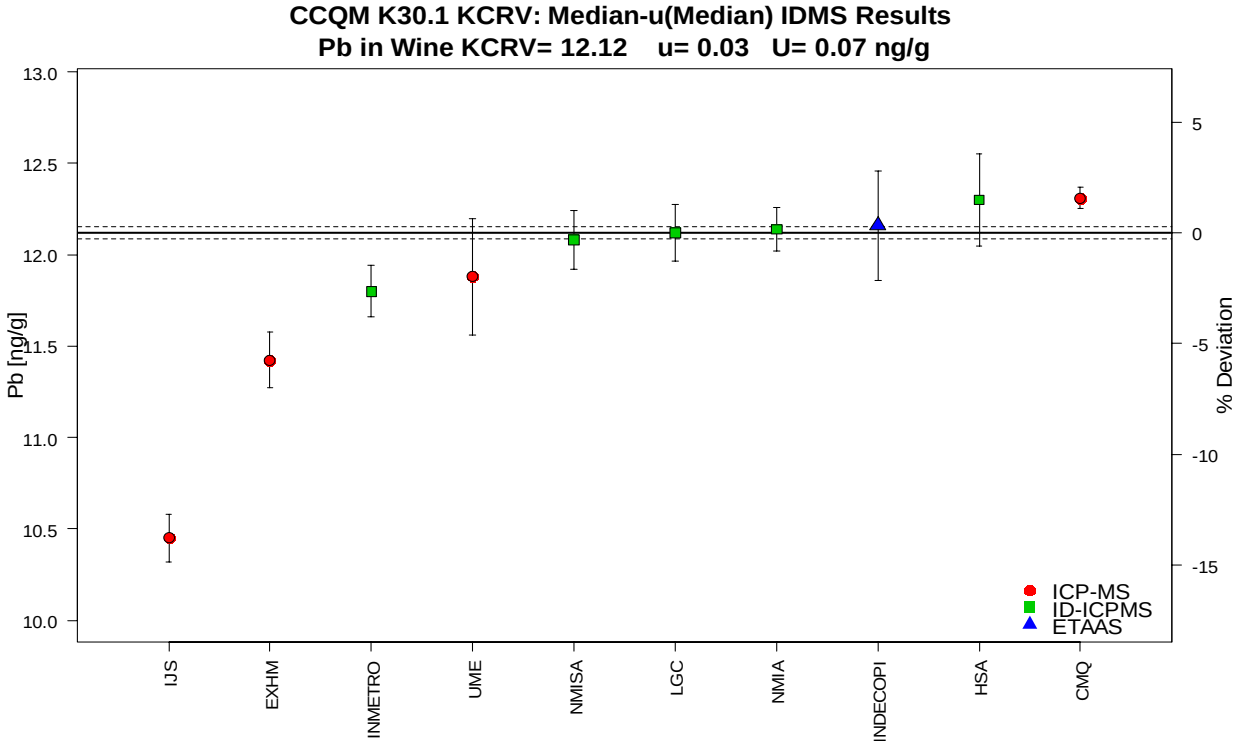

Figure 1: Participants results with standard uncertainties and KCRV proposed (solid line) and its standard uncertainty (dotted lines)

During the study two comments were received from EXHM and HSA, related to the appearance of a precipitate on the inner wall of a bottle.

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HSA noted that in one of the bottles ("affected bottle"), a layer of precipitate had uniformly deposited on the inner wall of the vessel. Due to the dark coloration of the wine sample and the container, the deposited layer was not obvious when the bottle was full. However, the precipitate was found to contain negligible amount of Pb which may explain why its concentration was not affected in each of the 2 bottles.

EXHM informed the presence of a film adhering strongly to the inner walls of the vial and after April IAWG meeting EXHM proceeded as follows (mail August 13th):
"*In a separate study, the wine was decanted from the containers and the presence of a film as well as thick sediment adhering strongly to the bottom of the vials was observed. Using two 2 mL of conc. HNO_3 the solid material was dissolved and transferred into digestion vials, where additionally 2 mL conc. HNO_3 and 1 mL of H_2O_2 were added. The samples were digested using exactly the same procedure employed for the analysis of the wine. The digests were made up to 100 g (the approximate weight of the original wine content) and analyzed for Pb with HR-ICP-MS, obtaining a Pb content 0.570 ± 0.015ng/g.*"

At the April 2012 IAWG meeting, it was pointed out that the uncertainty reported by INMETRO for CCQM.K30 was likely underestimated. INMETRO revised its uncertainty budget and made a different approach for some sources, especially for the analysis repeatability. INMETRO considered that this new approach was more consistent and sent new values for Pb: 11.85 ± 0.50 ng/g. However, KCRV calculations were carried out with the original values

10. KCRV calculations

According to CCQM document "Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence" Version 6, 2010, information is provided on procedures used to assess the KCRV, evaluate the associated standard uncertainty, and the Degrees of Equivalence (DoEs) for the evaluation of Key Comparisons. All the calculations were carried out with R Statistical Program v2.15 using *metRology* package [14.4].

Several ways of estimating the KCRV and associated uncertainties were presented and discussed at the IAWG meeting on April 16, 2012. Taking into account that the individual reported uncertainties did not account fully for the observed dispersion (Table 3), attempts to use reference values based on uncertainties weights were discarded. The median and associated u (median) of the ID-ICPMS results was selected as the best estimator of the KCRV. .
Table 4 shows the mean and the median of results with associated uncertainties excluding IJS´ results. According to the CCQM document mentioned above [Consensus_ KCRV_v6.2.doc:2010-03-01], the uncertainty of the median for *m* results was calculated as:

$$u = \sqrt{\frac{\pi}{2m}}\hat{\sigma}$$

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Where $\hat{\sigma}$ is a robust estimate of standard deviation, usually based on the median absolute deviation. After discussions at IAWG, it was agreed to consider only IDMS results for KCRV calculations ('candidate set').

Table 4: KCRV for K30.1 Pb in lead (Median IDMS), together with the mean and median of all the results

	KCRV ng/g	u ng/g	u rel	U ng/g
Mean[a]	12.02	0.09	0.74%	0.21
Median[a]	12.12	0.11	0.91%	0.22
Median IDMS(KCRV)	12.12	0.03	0.27%	0.07

[a]: Excluding JSI

Therefore, the recommended KCRV and its standard uncertainty is 12.12 ± 0.03 ng/g

11. Equivalence statements

The equivalence statements were calculated according to the BIPM guidelines. The degree of equivalence between an NMI/DI and the KCRV is calculated according to the following equations:

$$D_i = x_i - x_{KCRV} \qquad U_i = 2 * \sqrt{u_i^2 + u_{KCRV}^2}$$

Where D_i is the the difference between the NMI/DI result and the KCRV value, while U_i is the expanded uncertainty (k=2) of the D_i calculated by combining the uncertainties (k=1) of the NMI/DI result u_i and the uncertainty (k=1) of the KCRV u_{KCRV}.
The equivalence statements for CCQM-K30.1 are given in Table 5.

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Table 5. Equivalence statements for CCQM-K30.1

Institution	D_i (ng g^{-1})	U_i (ng g^{-1})	Di/Ui	D_i relative % (D_i/X_{KCRV})	U_i relative % (U_i/X_{KCRV})
NMIA	0.02	0.247	0.08	0.17	2.04
INMETRO	-0.32	0.286	-1.12	-2.64	2.36
CMQ	0.19	0.134	1.42	1.57	1.11
EXHM	-0.696	0.312	-2.23	-5.74	2.57
INDECOPI	0.04	0.603	0.07	0.33	4.98
HSA	0.18	0.504	0.36	1.49	4.16
IJS	-1.67	0.267	-6.26	-13.78	2.21
NMISA	-0.04	0.326	-0.12	-0.33	2.69
UME	-0.24	0.643	-0.37	-1.98	5.31
LGC	0.00	0.316	0.00	0.00	2.61

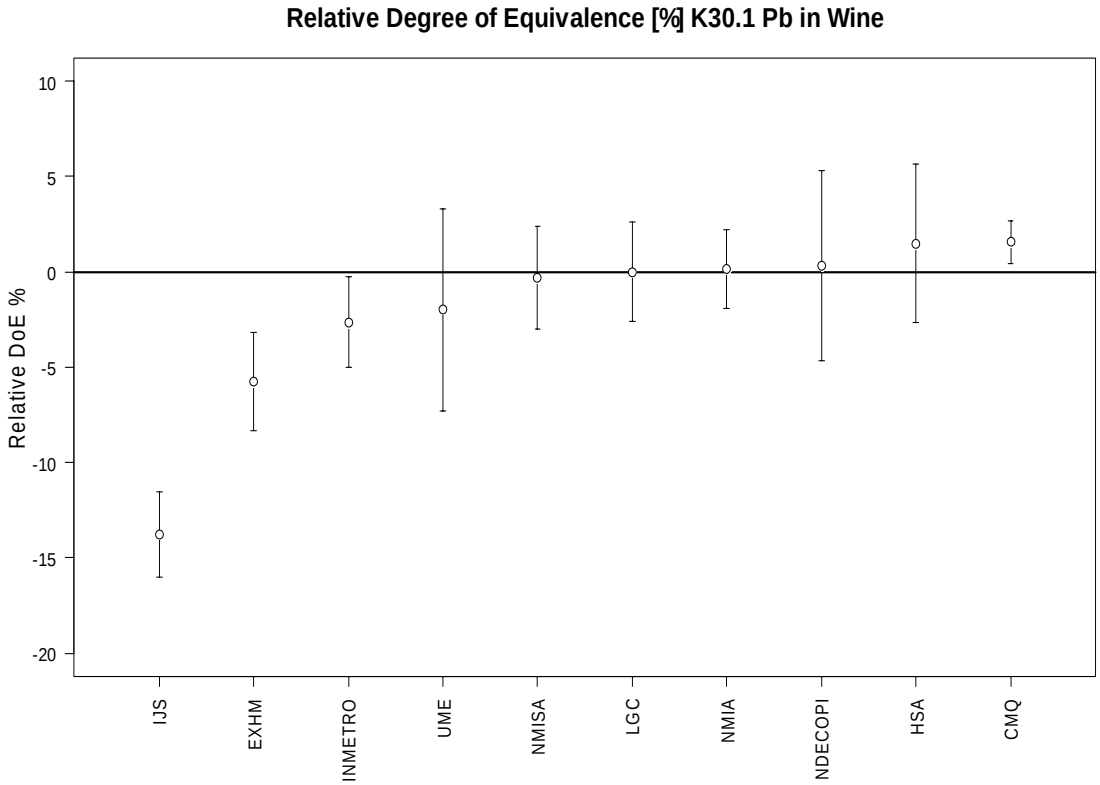

Figure 2: Degrees of equivalence, D_i and expanded uncertainty U_i at 95% level of confidence, expressed in %.

12. Demonstration of core capabilities

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As agreed in previous IAWG meetings, a system of Core-Capabilities (CC) for inorganic analysis will be employed in Key Comparisons starting from CCQM-K75 onward. This strategy is to improve the efficiency and effectiveness of Key Comparisons to support CMC claims. With the use of this system, new CMC claims can be supported by describing which core capabilities are required to provide the claimed measurement capability. In this study the recently modified CC form will be used [14.5].

13. Acknowledgements

This study contains the contribution of many scientists as detailed in Table 2.

14. References

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5. G.Turk and M. Sargent. “A System to Interpret the Results of Key Comparisons in Support of CMCs for Inorganic Analysis Based on Demonstrations of Core Capabilities”. White paper sent to IAWG members; March 2012.

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Appendix A

Key Comparison CCQM-K30.1 Analysis of Pb in Wine
Pilot Study CCQM-P12.2 Analysis of Pb, Fe, Cu and Cd in Wine

Protocol

Background

Analysis of heavy metals and other toxic elements in wine is essential for regulatory control and to comply with the requirements of international trade in wine. As such, the availability of traceable measurements supported by NMIs through appropriate calibration and measurement capabilities is an important requirement in many countries. Analysis of Pb in wine was previously addressed by the IAWG Key Comparison study CCQM-K30. The IAWG also agreed to conduct a parallel pilot study for Pb, Cu, Fe and Cd. The same sample is to be used for the key comparison and the pilot study.

Sample material

The sample prepared is a Chilean red wine (Cabernet Sauvignon, vintage 2009) with naturally occurring concentrations of the elements of interest. Sample preparation and treatment has been carried out by Fundación Chile and followed the experimental procedure used in CCQM-K30.
The homogeneity study was performed on a representative number of bottles randomnly selected and analyzed, at least, in duplicates. The internationally accepted statistical criteria showed that there is no evidence that the material is not homogeneous. The stability of the material was also determined. Results show that the material is stable over the time period of the current study. Both studies were carried out using ICP-MS.

Distribution

Each participant will receive two samples of 100 ml each. Participants should confirm the reception of sealed samples sending an acknowledgment of receipt to CMQ by either e-mailed message or fax. In case that any damage of the samples is apparent, please get in touch with CMQ immediately.

Handling and storing

To avoid any decomposition, the samples should be kept sealed until they are used. They should be stored at room temperature in its original bottle, tightly capped and not exposed to intense direct light.

Measurands

The key comparison will be for Pb and the pilot study for Pb as well as Fe, Cu, and Cd in red wine sample.

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Participants will receive two sample units for the CCQM K-30.1 and P-12.2. One sample can be used for preliminary assessments and the other for performing the measurements that will be reported. The analytes and mass fraction information are shown in Table 1.

Table 1

Analyte	Expected mass fraction
Lead	2 – 25 ng/g
Iron	1 – 5 ug/g
Copper	40 – 200 ng/g
Cadmium	0.1 – 1 ng/g

Methods/Procedures

Participants may use any method of their choice. Participants are requested to perform three (3) independent measurements on three separate portions of the sample and to determine the mass fractions of the analytes of interest. The sample should be mixed thoroughly before processing and it is recommended that preparation and dilution of solutions be carried out by weighing.

Reporting of results

- The mean value of 3 independent measurements and its associated uncertainties
- The value of the results and their associated uncertainties must be expressed in ng/g for copper, lead and cadmium. For iron, the result and their associated standard uncertainty must be expressed in ug/g

In order to allow a sufficient evaluation of the comparison, the report must include:

- A detailed description of the applied method of measurement.
- Information about sample digestion (used acid and quantity, digestion program, etc.), extraction (used solvent and quantity, extraction program etc.) and preparation.
- Information about the reference material used for calibration purposes (origin, standard value and uncertainty) or other materials used in the analytical procedure. For IDMS, indicate reference and spiked isotopes used.
- Calculation of the uncertainty expressed as a combined standard uncertainty and an expanded uncertainty. It must include:
  - The complete specification of the measurement equation
  - The identification and quantification of all significant uncertainty sources
  - Calculate the combined standard uncertainty (uc)

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- The values for the coverage factor and the expanded uncertainty U

Results should be sent to:

Gabriela Massiff
CMQ, Fundación Chile
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Santiago, Chile

☎ 56-2-2428180
Fax: 56-2-2428182
E-Mail: gmassiff@fundacionchile.cl

Time schedule

Deadline for registration of participants:	30 September 2011
Shipment of samples:	October 2011
Deadline for delivery of results:	30 January 2012
Draft A report:	October 2012
Final report:	April 2013

15. Appendix B

Overview of the methods used for Pb by the participants in CCQM-K30.1

NMI/DI	Measurement Technique	Sample Preparation/digestion procedure	Sample aliquot (g)	Number of replicates
NMIA	Double IDMS	Graphite digestion block (90min at 90°C), 1ml HNO_3 + 4ml H_2O_2	8	6
INMETRO	ID-ICPMS	Direct determination. Dilution with HNO_3 2%.	n/r	3
CMQ	ICP-MS (standard addition)	Microwave assisted digestion, 6ml HNO_3 + 1ml H_2O_2	7	3
EXHM	ICP-MS (standard addition)	Microwave assisted digestion, 1ml HNO_3 + 1ml H_2O_2	2.5	3
INDECOPI	ETAAS (standard addition)	Direct determination	n/a	3
HSA	ID-ICPMS	Microwave assisted digestion, 1ml HNO_3 + 1ml H_2O_2	2	8
IJS	ICPMS (external calibration)	No digestion was applied. Sample was diluted with MilliQ water in the ratio 1:10	n/a	3
NMISA	Double IDMS	Microwave assisted digestion, 2ml HNO_3	5	3
TUBITAK UME	ICP-MS (standard addition)	Microwave assisted digestion, 3ml HNO_3 + 0.5ml H_2O_2	2.5	3
LGC	ID-ICPMS	Heating in a water bath for at least 3 hrs, 3ml HNO_3	4	9

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16. Appendix C : Inorganic Core Capabilities Table

ID-ICP-MS
ICP-MS
ETA-AAS

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Inorganic Core Capabilities
Summary Table

CCQM Study: □ CCQM-K30.1

Institute(s): HSA, INMETRO, LGC, NMIA, NMISA

Method: *ID-ICP-MS*

Analyte(s): Pb

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

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.*		HSA, INMETRO, LGC, NMIA, NMISA	The very low Pb concentration requires precautions to avoid contamination problems especially when using microwave digestion. NMIA reported specific trace analysis precautions including using a clean room.
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.*		HSA, INMETRO, LGC, NMIA, NMISA	All participants using ID incorporated a microwave digestion step to facilitate spike equilibration. INMETRO used sample evaporation and re-dissolution in acid.
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.*	HSA, INMETRO, LGC, NMIA, NMISA		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	HSA, INMETRO, LGC, NMIA, NMISA		
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.*	HSA, INMETRO, LGC, NMIA, NMISA		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample*	HSA, INMETRO, LGC,		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
as a gas for introduction into the ICP.	NMIA, NMISA		
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.*	HSA, INMETRO, LGC, NMIA, NMISA		
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*		HSA, INMETRO, LGC, NMIA, NMISA	
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.*		HSA, INMETRO, LGC, NMIA, NMISA	Good signal intensity is required to improve isotope ratio precision.
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	HSA, INMETRO, LGC, NMIA, NMISA		
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.*		HSA, INMETRO, LGC, NMIA, NMISA	Possible interference includes ^{204}Hg on ^{204}Pb (corrected by measuring ^{202}Hg) but this can be avoided by using an alternative Pb isotope.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*		HSA, INMETRO, LGC, NMIA, NMISA	Most participants matched the sample and calibration blend intensities to reduce the significance of this effect.
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		HSA, INMETRO, LGC, NMIA, NMISA	
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		HSA, LGC, NMISA, INMETRO, NMIA	Most participants used double IDMS which provides indirect spike calibration but NMIA calibrated against NIST 3128.

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Inorganic Core Capabilities
Summary Table

CCQM Study: □ CCQM-K30.1

Institute(s): CMQ, EXHM, IJS, TUBITAK UME

Method: ICP-MS (without Isotope Dilution)

Analyte(s): Pb

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

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.*		CMQ, EXHM, IJS, TUBITAK UME	The very low Pb concentration requires precautions to avoid contamination problems.
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.*	IJS	CMQ, EXHM, TUBITAK UME	Relatively high levels of organic content make the digestion more difficult. It is necessary to adjust acid/sample ratio and the other parameters for efficient digestion.
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.*	CMQ, EXHM, TUBITAK UME		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	CMQ, EXHM, TUBITAK UME		
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.*	CMQ, EXHM, TUBITAK UME		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the*	CMQ, EXHM,		

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Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
sample as a gas for introduction into the ICP.	TUBITAK UME		
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.*	CMQ, EXHM, TUBITAK UME		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		CMQ, EXHM, TUBITAK UME	Matrix matched calibration standards were used for calibration since the sample contains high levels of organics and also the acid concentration in the final sample solution is relatively high.
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.*		CMQ, EXHM, TUBITAK UME	
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	CMQ, EXHM, TUBITAK UME		
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.*		CMQ, EXHM, TUBITAK UME	Possible interference includes ^{204}Hg on ^{204}Pb (corrected by measuring ^{202}Hg) but this can be avoided by using an alternative Pb isotope.
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.*		CMQ, EXHM, TUBITAK UME	Matrix matching or standard addition for calibration to minimise errors.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	CMQ, EXHM, TUBITAK UME		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	CMQ, EXHM, TUBITAK UME		

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Inorganic Core Capabilities
Summary Table

CCQM Study: □ CCQM-K30.1

Institute(s): INDECOPI

Method: ETA-AAS (or GF-AAS)

Analyte(s): Pb

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

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.*		*X*	The very low Pb concentration requires precautions to avoid contamination problems.
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 ETA-AAS.*	X		NB. Direct determination of the sample was used.
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 ETA-AAS.*	X		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	X		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ETA-AAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	X		
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.*	X		
Hydride preconcentration/matrix separation	X		

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Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*			
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures. Also use of matrix-matched standards to minimize effect of interferences.*		X	Standard addition calibration.
Signal detection *The detection and recording of the absorption signals of analytes. The degree of difficulty increases for analytes present at low concentrations, of low atomic absorption coefficient. Requires selection of operating conditions such as light source, absorption line, Zeeman background correction conditions. Includes selection of signal processing conditions (peak area or height).*		X	
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	X		
Optimization of the furnace temperature program *Optimization of temperature and duration of steps for sample drying, pyrolysis to remove (residual) organics, and atomization. Furnace temperature program to minimize analyte loss in the drying/pyrolysis steps, while maximizing analyte vaporization in the atomization step.*		X	
Correction or removal of matrix effects or interferences *Chemical or instrumental procedures used to avoid or correct for spectral and non-spectral interferences. Includes effects of differences in viscosity and chemical equilibrium states of analyte between the standard and sample. Selection of matrix modifier to adjust volatility of analyte and/or matrix to eliminate these effects is also included. Addition of reactive gases (eg oxygen) to the carrier gas to improve matrix separation. Also included is Zeeman or other background correction techniques to remove interference due to absorption and scattering from coexisting molecules/atoms in the sample.*		X	

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