CCQM-K30: Lead in wine

Final Report

Revised February 2008

Setting standards
in analytical science

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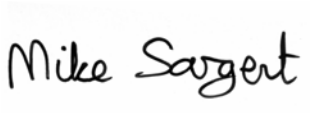

Date: 4 February 2008

Setting standards in analytical science

Contents

1. Summary

Key comparison CCQM-K30 was performed to demonstrate and document the capability of interested national metrology institutes in the determination of the mass fraction of lead in wine. This comparison was an activity of the Inorganic Analysis Working Group of the Comité Consultatif pour la Quantité de Matière and was co-ordinated by LGC (Teddington, UK).

Twelve national metrology institutes (NMIs) registered to participate in the key comparison but only eleven NMIs submitted results.

2. Introduction

Following consultation with CMQ Fundacion Chile, LGC proposed a key comparison (CCQM-K30) to analyse Pb in wine after successful completion of the pilot study, CCQM-P12 [1] (co-ordinated by IRMM). This was proposed in October 2004, at the Inorganic Analysis Working Group (IAWG) of the Comité Consultatif de la Quantité de Matière (CCQM) meeting in Mexico. It was agreed that the pilot study, CCQM-P12.1, would run in parallel to the key comparison and would include Pb, Fe, Cu and Cd, using the same sample.

The sample prepared is a Chilean red wine (Cabernet Sauvignon, vintage 2003) with naturally occurring concentrations of the elements of interest. Sample preparation and treatment has been carried out by CMQ and followed the experimental procedure used in CCQM-P12 [2]. Each sample is contained in a 0.1L glass bottle covered with PTFE/silicone septa sealed with aluminium crimp tops. Homogeneity studies were carried out following internationally accepted tests (1-way ANOVA). There is no evidence that the material is not homogeneous. Stability has also been determined by CMQ following LGC guidelines [3]. The measurements indicate that there should not be stability problems for the duration of the CCQM-K30/P12.1 reporting period.

At the time of this study, CMQ were not a designated NMI and therefore the comparison was officially co-ordinated by LGC.

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. 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 as pilot study CCQM-P12. Following the successful conclusion of that study, it was agreed that it should be succeeded by a key comparison. The IAWG also agreed to conduct a parallel pilot study for Pb as well as Fe, Cu and Cd (CCQM-P12.1), to assist newer NMIs less experienced in the analysis, and to extend it to include new work on additional elements of interest for international trade. The same sample is to be used for the key comparison and the pilot study. Details of CCQM-P12.1 are reported separately. Only one other invited laboratory participated for Pb in the pilot study.

3.1 Participation in CCQM-K30

The NMIs that registered for CCQM-K30 are listed in Table 1.

4. Instructions to participants

A protocol was sent to all participants on 27th September 2006. The samples were sent directly from CMQ to all registered participants for the key comparison and the parallel pilot study during September – October 2006.

On the 4th October 2006, all participants were sent a revised results report and protocol (Appendix A) with an amended concentration range for Pb. Participants were also advised of storage conditions on this date. Participants were free to use the method of their choice.

The original deadline for submission of results was 31st January 2007. Some participants experienced delays in receiving the samples and, therefore, the deadline was extended to 12th March 2007.

Table 1. CCQM-K30 participants

INSTITUTE / ORGANIZATION	COUNTRY	CONTACT
CSIR National Metrology Laboratory	South Africa	Dr. A. Barzev
INM National Institute of Metrology (INM)	Romania	Dr. M. Buzoianu
INMETRO Instituto Nacional de Metrologia	Brazil	Dr. T. de Oliveira Araujo
INTI * Instituto Nacional de Tecnologia Industrial	Argentina	Dr. L. Valiente
IRMM Institute for Reference Materials & Measurements	Belgium	Dr. C. Quetel
KRISS Korea Research Institute of Standards and Science	Republic of Korea	Dr. E. Hwang
LGC Limited	UK	Dr. R. Santamaria-Fernandez
LNE	France	Dr. G. Labarraque
NIM	China	Dr. J. Wang
NMIA	Australia	Dr. D. Saxby
NMIJ National Metrology Institute of Japan	Japan	Dr. A. Hioki (Dr. Masaki Ohata)
PTB	Germany	Dr. D. Schiel (Dr Olaf Reinitz)

* INTI registered for the key comparison, but they were unable to report a result since the Pb concentration was below their quantification limit.

5. Methods and instrumentation used

Nine of the key comparison participants used isotope dilution ICP-MS. The remaining two NMIs used ICP-MS with external calibration (INMETRO) and graphite furnace AAS (INM). An overview of the measurement and sample preparation methods used by each participant is given in Appendix B.

6. CCQM-K30 participants' results

The CCQM-K30 participants' results for Pb, as reported to the co-ordinating institute (LGC), are given in Table 2. All data are reported as $ng.g^{-1}$ of Pb in the sample as received. These results are also displayed in Figure 1. Figure 2 shows only the IDMS results.

Table 2. CCQM-K30 participants' measurement results for Pb

Participant	*Reported result ng g^{-1}*	*Reported expanded uncertainty ng g^{-1}*	*% expanded uncertainty*	*k=*
CSIR	3.001	0.136	4.5%	2
INM	7.71	1.98	26%	2
INMETRO	1.62	0.088	5.4%	2
IRMM	2.940	0.033	1.1%	2
KRISS	2.893	0.044	1.5%	2.13
LGC	3.00	0.10	3.4%	2
LNE	3.13	0.12	3.8%	2
NIM	3.07	0.17	5.5%	2
NMIA	2.98	0.20	6.7%	1.99
NMIJ	2.936	0.025	0.85%	2
PTB	2.96	0.08	2.7%	2.4
INTI	Not reported			

7. Discussion

The two NMIs that did not use IDMS, have results that appear to be outliers. INM subsequently reported a number of technical reasons why their result was high. These included inconsistent blank subtraction, precipitate in digest samples and the effect of time between sample preparation and measurement. They performed some repeat measurements, results for which were in the range 2.35 – 2.85 ng/g, which overlap with several of the IDMS results. INM results can, therefore, be justifiably excluded from the calculation of the KCRV. INMETRO subsequently reported a mass calibration problem with their ICP-MS instrument and recommended that their results were not included in the KCRV calculations.

The agreement between the nine NMIs that used IDMS is excellent with almost all results overlapping with all others. Most reported uncertainties for the IDMS results were in reasonable agreement with the majority in the range 1-4%. The range of uncertainties reported for CCQM-K30 was not significantly different from those reported by CCQM-P12 participants.

There was no apparent correlation between the sample digestion (Appendix B) and the IDMS results.

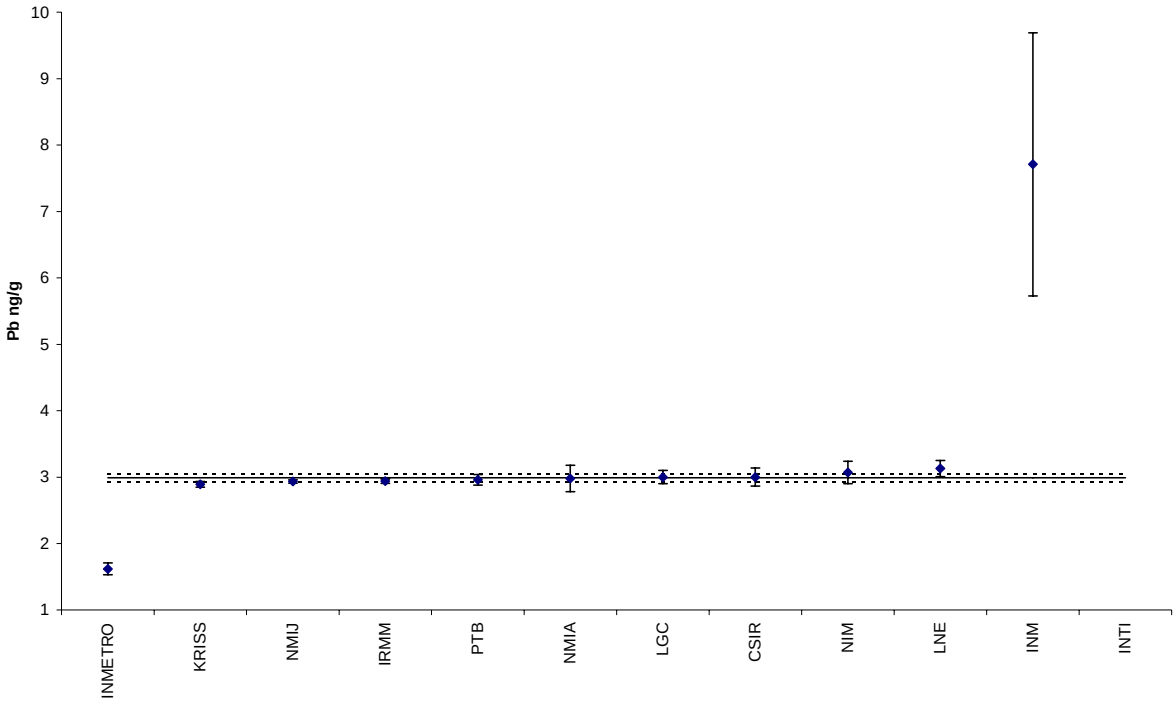

Figure 1 Participants' results for CCQM-K30. The horizontal lines represent the proposed KCRV and associated uncertainty.

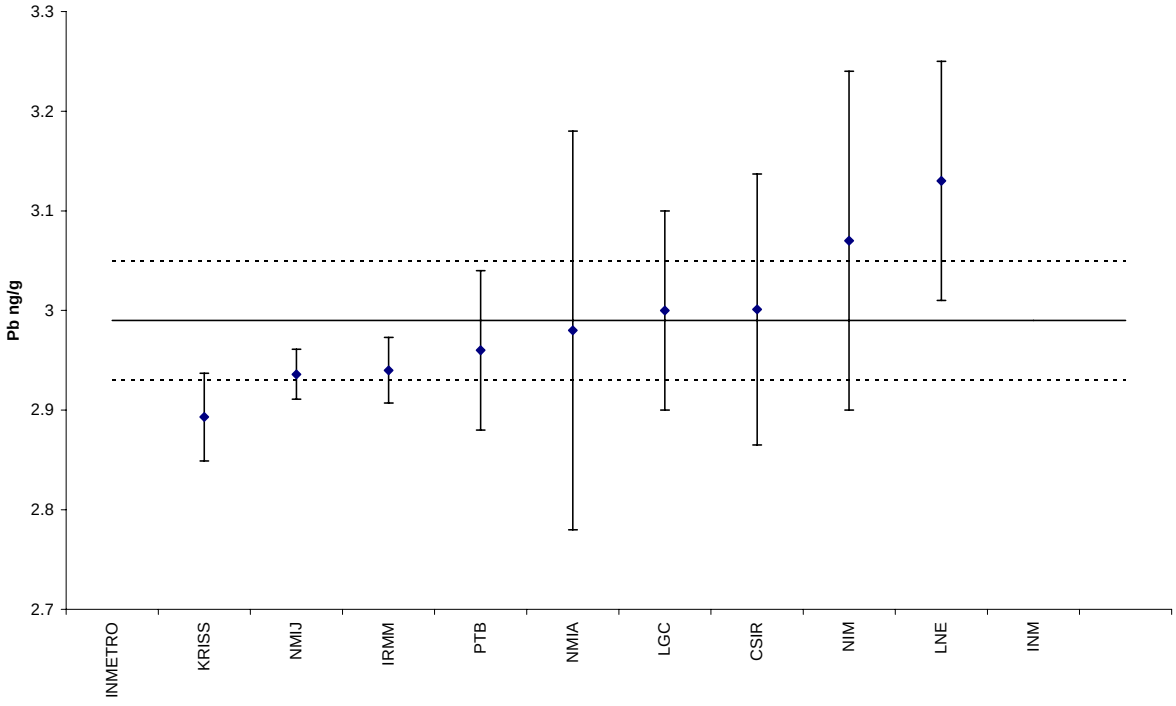

Figure 2 IDMS results for CCQM-K30. The horizontal lines represent the proposed KCRV and associated uncertainty.

8. KCRV Calculations

With reported uncertainties that do not account fully for the observed dispersion, it is inappropriate to use the reported uncertainties as weights in calculating a consensus value. Table 3 shows the mean and median of the results with associated uncertainties. Since the uncertainties are based on 8 effective degrees of freedom, an expansion factor k of 2.3 is recommended.

Table 3 KCRV calculations for CCQM-K30

Method	KCRV	Expanded Uncertainty (k=2.3)
Mean	2.99	0.06
Median	2.98	0.06

The reported values for the data remaining after agreed exclusions are approximately normally distributed with no apparent outliers; under these circumstances, the mean and standard deviation of the mean of the data provide a justifiable basis for the KCRV and its uncertainty.

Therefore, the proposed KCRV is 2.99 ± 0.06 ng.g^{-1}.

9. Equivalence Statements

The equivalence statements have been calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

$$D_i = x_i - x_R \qquad U_i = 2 \cdot \sqrt{\left(u_i^2 + u_R^2\right)}$$

where D_i is the degree of equivalence between the NMI result x_i and the KCRV x_R, and U_i is the expanded uncertainty (k = 2) of the D_i calculated by combining the uncertainties (k = 1) of the NMI result u_i and the uncertainty (k = 1) of the KCRV u_R.

The equivalence statements for CCQM-K30 are given in Table 4. The equivalence statements for the IDMS results (ie those used in the calculation of the KCRV) are displayed in Figure 3.

Table 4: Equivalence Statements for CCQM-K30

	D_i (ng g^{-1})	U_i (ng g^{-1})
CSIR	0.01	0.14
INM	4.72	1.98
INMETRO	-1.37	0.10
IRMM	-0.05	0.06
KRISS	-0.10	0.06
LGC	0.01	0.11
LNE	0.14	0.13
NIM	0.08	0.18
NMIA	-0.01	0.21
NMIJ	-0.05	0.05
PTB	-0.03	0.08

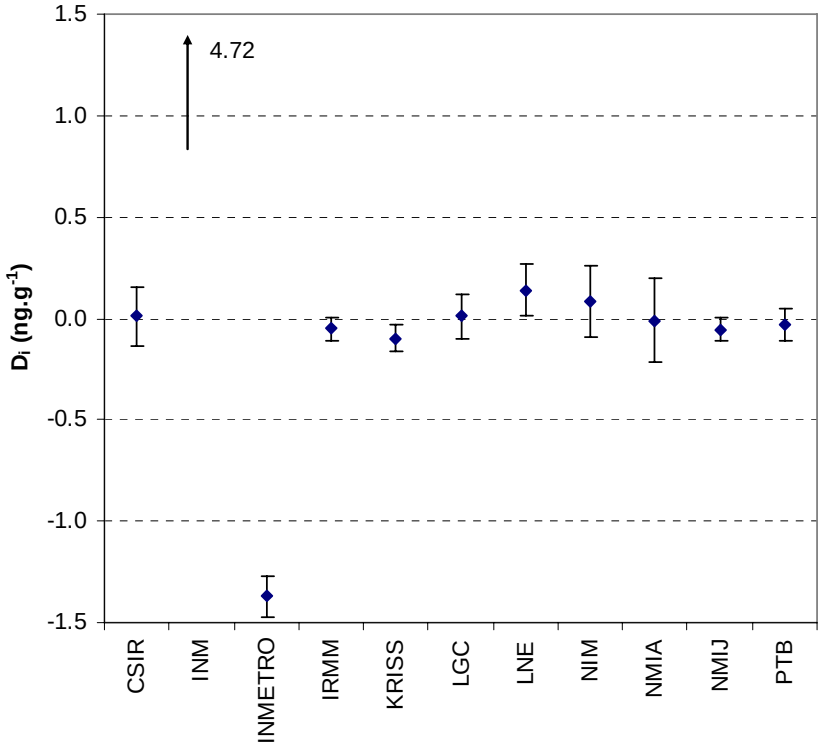

Figure 3: Graph of equivalence statements for CCQM-K30

The degree of equivalence (and its uncertainty) between two NMI results is calculated according to the following equations:

$$D_{ij} = x_i - x_j \qquad U_{ij} = 2 \cdot \sqrt{\left(u_i^2 + u_j^2\right)}$$

Where D_{ij} is the degree of equivalence between the two NMI result x_i and x_j, and U_{ij} is the expanded uncertainty (k = 2) of the D_{ij} calculated by combining the uncertainties (k = 1) of the two NMI result u_i and u_j.

The equivalence statement between the CCQM-K30 participants is given in Table 5.

10. Acknowledgements

The work described here contains the contributions of many scientists as detailed in Table 1.

Sample preparation, homogeneity and stability testing and sample distribution was organised by Gabriela Massiff and the researchers of CMQ Fundacion, Chile. Rita Harte, LGC assisted with the collection of participants reports.

The co-ordination of this study at LGC was supported by the Department for Innovation, Universities & Skills as part of the National Measurement System Chemical & Biological Metrology Knowledge Base Programme.

11. References

1 C. R. Quétel, S. M. Nelms, L. Van Nevel, I. Papadakis and P. D. P. Taylor, *J. Anal. At. Spectrom.***,** 2001, **16**, 1091 - 1100

2 Quétel et.al., Protocol for the production of IMEP-16 wine test samples, IRMM, 2001

3 Stability testing and predicting the shelf-life of reference materials; LGC/VAM/2002/019

lab $j \rightarrow$	CSIR		INM		INMETRO		IRMM		KRISS		LGC	
lab $i \downarrow$	Di	Ui	Di	Ui	Di	Ui	Di	Ui	Di	Ui	Di	Ui
CSIR			-4.71	1.98	1.38	0.16	0.06	0.14	0.11	0.14	0.00	0.17
INM	4.71	1.98			6.09	1.98	4.77	1.98	4.82	1.98	4.71	1.98
INMETRO	-1.38	0.16	-6.09	1.98			-1.32	0.09	-1.27	0.10	-1.38	0.13
IRMM	-0.06	0.14	-4.77	1.98	1.32	0.09			0.05	0.05	-0.06	0.11
KRISS	-0.11	0.14	-4.82	1.98	1.27	0.10	-0.05	0.05			-0.11	0.11
LGC	0.00	0.17	-4.71	1.98	1.38	0.13	0.06	0.11	0.11	0.11		
LNE	0.13	0.18	-4.58	1.98	1.51	0.15	0.19	0.12	0.24	0.13	0.13	0.16
NIM	0.07	0.22	-4.64	1.99	1.45	0.19	0.13	0.17	0.18	0.17	0.07	0.20
NMIA	-0.02	0.24	-4.73	1.99	1.36	0.22	0.04	0.20	0.09	0.21	-0.02	0.22
NMIJ	-0.06	0.14	-4.77	1.98	1.32	0.09	0.00	0.04	0.04	0.05	-0.06	0.10
PTB	-0.04	0.15	-4.75	1.98	1.34	0.11	0.02	0.07	0.07	0.08	-0.04	0.12

lab $j \rightarrow$	LNE		NIM		NMIA		NMIJ		PTB	
lab $i \downarrow$	Di	Ui	Di	Ui	Di	Ui	Di	Ui	Di	Ui
CSIR	-0.13	0.18	-0.07	0.22	0.02	0.24	0.06	0.14	0.04	0.15
INM	4.58	1.98	4.64	1.99	4.73	1.99	4.77	1.98	4.75	1.98
INMETRO	-1.51	0.15	-1.45	0.19	-1.36	0.22	-1.32	0.09	-1.34	0.11
IRMM	-0.19	0.12	-0.13	0.17	-0.04	0.20	0.00	0.04	-0.02	0.07
KRISS	-0.24	0.13	-0.18	0.17	-0.09	0.21	-0.04	0.05	-0.07	0.08
LGC	-0.13	0.16	-0.07	0.20	0.02	0.22	0.06	0.10	0.04	0.12
LNE			0.06	0.21	0.15	0.23	0.19	0.12	0.17	0.14
NIM	-0.06	0.21			0.09	0.26	0.13	0.17	0.11	0.18
NMIA	-0.15	0.23	-0.09	0.26			0.04	0.20	0.02	0.21
NMIJ	-0.19	0.12	-0.13	0.17	-0.04	0.20			-0.02	0.07
PTB	-0.17	0.14	-0.11	0.18	-0.02	0.21	0.02	0.07		

Table 5: Matrix of equivalence between CCQM-K30 participants.

12. Appendix A: Protocol distributed to participants

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

Protocol

Introduction

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 as pilot study CCQM-P12. Following the successful conclusion of that study, it was agreed that it should be succeeded by a key comparison. The IAWG also agreed to conduct a parallel pilot study for Pb, to assist newer NMIs less experienced in the analysis, and to extend it to include new work on additional elements of interest for international trade. The same sample is being used for the key comparison and the pilot study.

Sample

The sample prepared is a Chilean red wine (Cabernet Sauvignon, vintage 2003) with naturally occurring concentrations of the elements of interest. Sample preparation and treatment has been carried out by Fundacion Chile and followed the experimental procedure used in CCQM-P12 (Quétel et.al., Protocol for the production of IMEP-16 wine test samples, IRMM, 2001). Each sample is contained in a 0.1L glass bottle covered with PTFE/silicone septa sealed with aluminium crimp tops. Homogeneity studies were carried out following internationally accepted tests. (1-way ANOVA). There is no evidence that the material is not homogeneous. Stability has also been determined by Fundacion Chile following LGC guidelines (Stability testing and predicting the shelf-life of reference materials; LGC/VAM/2002/019). The measurements indicate that there should not be stability problems for the duration of the CCQM-K30/P12.1 reporting period.

Measurands

The key comparison will be for Pb (0.002-0.035 μg/g) only. Participants may choose to participate in the pilot study for Pb as well as Fe (1-5 μg/g), Cu (0.05-0.3 μg/g) and Cd (0.1-1 μg/g).

Please note: the concentration range indicated for Pb is different from the values in previous correspondence.

Method of analysis

At least three replicate analyses should be carried out. Participants are free to use any suitable method but **please include a full description of your method of analysis** when reporting the

results. It is recommended that preparation and dilution of solutions be carried out by weighing. A full uncertainty budget should also be included with your results, as indicated below.

Uncertainty Evaluation

Each laboratory should make an assessment of the experimental uncertainty according to ISO principles (Guide to the Expression of Uncertainty in Measurement, ISO, Geneva, 1993, ISBN 92-67-10188-9). Each variable contributing to the uncertainty of the results should be identified and quantified in order to be included in the combined standard uncertainty of the result. A full uncertainty budget must be included, as part of the results.

Contributions to the overall uncertainty will arise from the repeatability of the sample preparation, the repeatability of instrumental determination, determination of masses and volumes, concentration of primary and internal standards, and any other parameter specific to each method of analysis chosen by the participant.

Reporting

Results should be submitted using the results report form provided and sent to **Rita Harte (E-mail: Rita.Harte@lgc.co.uk) at LGC**, by post, e-mail or fax, **no later than 31 January 2007.**

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13. Appendix B: Overview of the methods used by the participants

Table 6: Overview of the methods used by the participants in CCQM-K30

NMI	Technique	Instrument	Preparation	Sample aliquot (g)	Digest reagents	Number of replicates
CSIR	double IDMS	Magnetic sector ICPMS	microwave	5	2ml HNO_3, 0.5ml H_2O_2	3
INM	multi-point external calibration	GFAAS	microwave	5	5ml HNO_3, 2ml H_2O_2	4
INMETRO	multi-point external calibration	ICP-MS	room temp for 20hr	2	3ml HNO_3	6
LGC	double IDMS	Magnetic sector ICPMS	water bath digestion	4	3ml HNO_3	12
NMIJ	double IDMS	Q ICP-MS	microwave	3-5	3ml or 0.5ml HNO_3, 3ml or 5ml or 0.5ml H_2O_2	10
KRISS	IDMS	ICP-MS	microwave	5	6ml HNO_3, 2ml H_2O_2	7
LNE	double IDMS	Magnetic sector ICPMS	graphite hotplate	5	10ml HNO_3, 1ml H_2O_2	9
NMIA	double IDMS	Q ICP-MS	water bath digestion	3	1.5ml HNO_3	6
IRMM	one-way IDMS	Q ICP-MS	microwave	5	0.5ml HNO_3, 1ml H_2O_2	5
PTB	double IDMS	MC-ICP-MS	hot plate	3	10.5ml HNO_3, 1.5ml H_2O_2	8
NIM	IDMS	MC-ICPMS	sealed vessel	5	HNO_3 + H_2O_2	6