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CCQM-K29.1

Anion calibration solution

Final report

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Summary

This bilateral comparison between CENAM and SMU was carried out in order to confirm improved CENAM performance in analysis of chloride calibration solution investigated. The mass fraction of chloride was about 1 g/kg. The deviation from reference value based on preparation was less than 0.1%.

1 Introduction

In the key comparison CCQM-K29, carried out in 2003/4, CENAM chloride result was found to be an outlier. The reason for this was identified and procedure corrected. At the October 2004 meeting of the Inorganic Analysis Working Group of CCQM CENAM requested a bilateral comparison on chloride sample to confirm its improved measurement capability. SMU agreed to coordinate this comparison, as EMPA as the original coordinating laboratory cut its activities in this field.

2 Participants

The following institutes participated in CCQM-K29.1:

Institute	***Country***	***Contact***
CENAM Centro Nacional de Metrologia	Mexico	Judith Velina Lara-Manzano
SMU Slovak Institute of Metrology	Slovakia	Michal Máriássy

3 Samples

About 1 L of solution with a known chloride mass fraction of about 1 g/kg was prepared by weight using a high purity potassium chloride (NIST SRM 999a, the same as in CCQM-K29) and ultrapure water. Potassium chloride was dried at 500 °C for 4 hours. The solution was not stabilized. It was bottled into polypropylene bottles (the same as used in CCQM-K29 comparison), sealed and sealed into mylar type bags. About 250 mL of solution were provided.

The sample was sent to CENAM by Fedex on January 24. The sample receipt was confirmed on 28 January 2005 without any indication of damage.

4 Reference value

The reference value resulting from the preparation is given in mass fraction (w in g/kg) including a complete uncertainty statement. Details of the calculation of the reference value and its uncertainty are described in Appendix B of this report.

Transpiration losses were estimated from the mass change of the bottles from the filling to the end of the measurement period and were less or equal to 0.01%. A homogeneity study carried out on 3 from 4 prepared bottles using high-accuracy coulometry did not reveal any significant inhomogeneity. Uncertainty due to transpiration and inhomogeneity was included into the uncertainty budget of the reference value.

Reference value for chloride:

w_{Cl} = 1.00065 g/kg U (w_{Cl}) = 0.00024 g/kg (k=2)

5 Methods of measurement

The principles of measurement methods applied by the participants were the same as in CCQM-K29:

Participant	**Method**
CENAM	titrimetry
SMU	coulometry

6 Results

The following table gives the results including the uncertainty statement given as expanded uncertainties (k = 2):

Institute	***Date results reported***	***Reported mass fraction w_{Cl}***	***Expanded uncertainty U (k=2)***	***Standard deviation***
CENAM	14.3.2005	0.9999 g/kg	0.0048 g/kg	0.0035 g/kg
SMU	15.3.2005	1.00116 g/kg	0.00034 g/kg	0.00007 g/kg

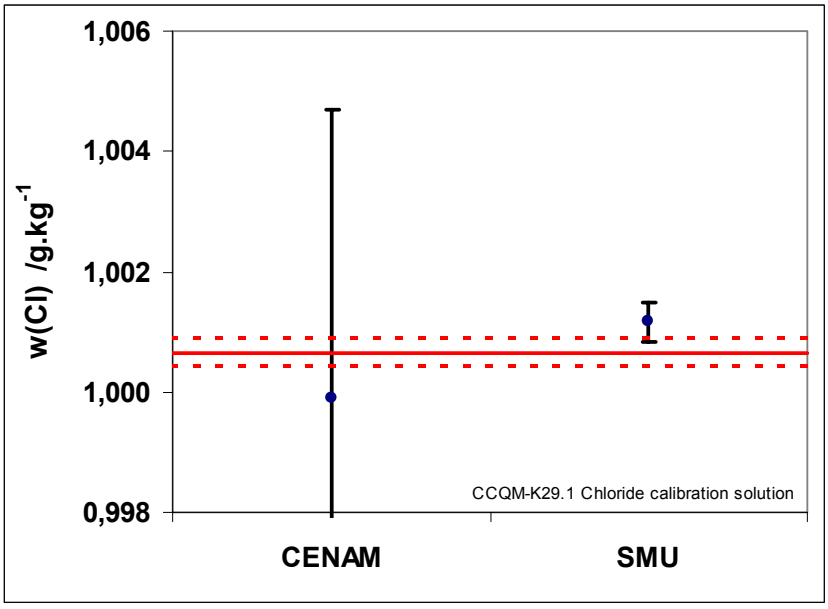

Fig. 1 Results of CCQM-K29.1

7 Link to CCQM-K29

Both in the key comparison CCQM-K29 and the subsequent bilateral are the key comparison reference values based on sample preparation. The relative difference between the reference values is very small, and therefore the link to the reference value of CCQM-K29 is straightforward. The CENAM result linked to the original CCQM-K29 reference value is presented in Figure 2.

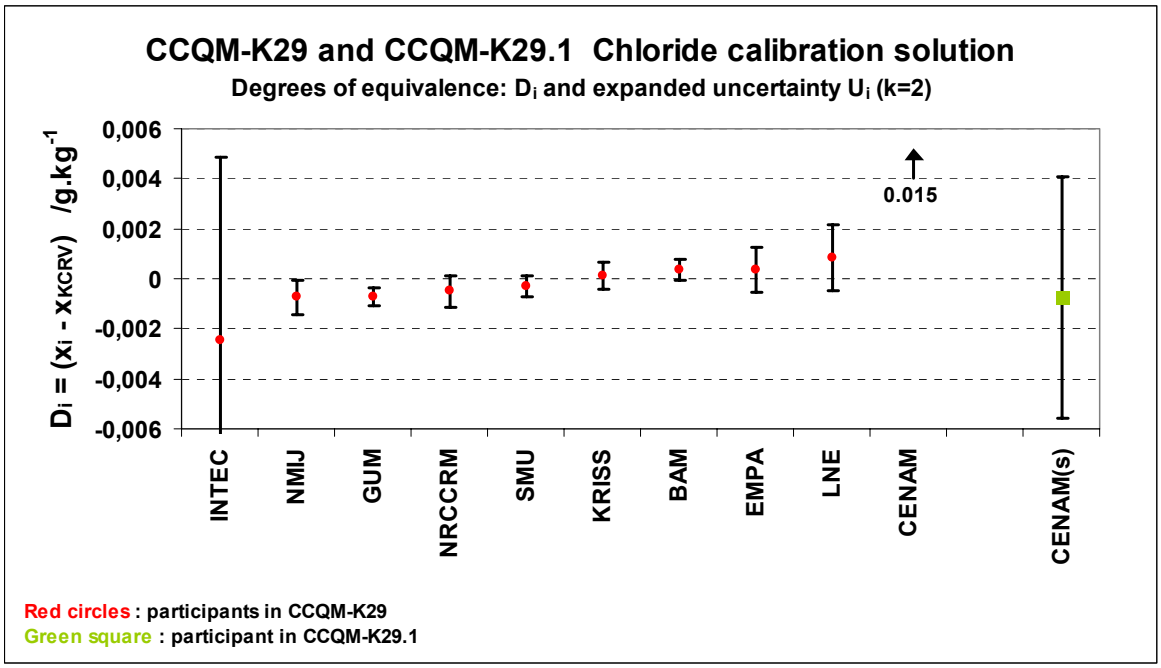

Fig. 2 CCQM-K29.1 linked to CCQM-K29

8 Discussion and conclusions

This key comparison confirmed improved performance of CENAM in chloride determination. The relatively high uncertainty seems to be related to the very small samples used (1 g of solution), so that the endpoint determination becomes a significant uncertainty source. This is supported by the high standard deviation of the results. If larger samples are used, better results can be expected.

9 Acknowledgements

The coordinating laboratory wishes to express its gratitude to M. Weber from EMPA for conducting the original CCQM-K29 comparison and NIST for providing the source material for preparation of samples.

Key Comparison CCQM-K29.1 "Anion Calibration Solutions"

Technical Protocol

1. Introduction

In 2003/4 the CCQM inorganic working group organized a key comparison CCQM-K29 with anion calibration solutions. CENAM result for chloride was an outlier and after identification of the reasons requested a bilateral comparison for chloride. The request was accepted at the WG meeting in October 2004 and it is carried out analogue to CCQM-K29 with SMU as pilot laboratory.

2. Samples

Analytes/Matrix: The analyte in K29.1 is chloride (Cl^- from KCl) provided as monoanion solution in water. The solution of about 1 g/kg (mass fraction relative to Cl^-) is prepared by weight. At least 250 mL of solution is provided. The solutions are not stabilized. The origin and purity of the primary material used for the preparation is given in CCQM-P32 report.
Packaging and labeling: 250 mL PP bottles are precleaned (24 h leaching) with ultrapure water and dried in a clean atmosphere. After bottling the samples are closed with a screw cap, sealed and welded in mylar type foil to avoid transpiration during transport. Each sample is labeled with an individual sample code.
Distribution: One bottle is dispatched to the participants by an adequate mail service. The participants will be informed by the pilot laboratory about the date of dispatching the samples. Participants are required to **confirm the receipt of the sealed samples** by e-mail or fax. In case of any damage of the packaging and the samples the pilot laboratory should be informed.
Handling and storing instructions: To avoid transpiration the samples shall be kept in the aluminized bags until they are used. After receipt they shall be shaken rigorously. The bottles should not be kept open longer than needed for taking the required sample aliquot. Participants are expected to handle the samples in a way that any contamination by air, the dilutant or the used equipment is avoided.

3. Reporting

Because K29.1 is a key comparison, only one result per NMI can be reported. Each NMI is allowed to report its result as an average value from different methods. Detailed information of all the applied methods are required in this case.
A detailed description of the applied method of measurement is required including the complete calculation of the result and reporting corrections e.g. of blanks and interferences.
Mass fraction of chloride (Cl^-) should be reported.
Calculation of the uncertainty should be expressed as **expanded uncertainty *U*** ($k = 2$). This must include the complete specification of the measurand, especially the identification and quantification of all uncertainty sources (list or table).
A description of the used equipment (e.g. type, technical specifications), information about sample preparation and the reference material used for calibration (origin, purity) or any other material used during the analytical procedure should be reported too.

4. Methods of measurement

The participants are free to choose one or more suitable methods of measurement (see note at 3. Reporting).

5. Reference value

The reference value resulting from the preparation by weight will be given in g/kg including a complete uncertainty statement.

6. Proposed time schedule

The samples will be distributed to participants in mid January 2005. The results should be returned to SMU by **March 15, 2005**. Draft A of the report will be sent to participants two weeks before the next scheduled working group meeting.

7. Participants

This comparison is organized as bilateral between SMU and CENAM.

8. Correspondence

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Appendix B - Weighing data and values from preparation

Calculation of reference value for CCQM-K29.1 chloride solution

Weighing of KCl starting material:

balance type	Mettler AG285
air density	1.178 kg m^{-3}
KCl density	1980 kg m^{-3}
balance reading for KCl	2.10601 g
buoyancy correction factor	1.00045
KCl mass	**2.10696 g**
chloride mass fraction	0.475463
chloride mass (m_{Cl})	**1.00178 g**

Weighing of aqueous KCl solution:

balance type	Mettler PR1203
air density	1.178 kg m^{-3}
solution density	1000 kg m^{-3}
balance reading for solution	1000.095 g
buoyancy correction factor	1.00103
solution mass (m_{Soln})	**1001.125 g**

Calculated mass fraction of chloride in CCQM-K29.1 solution

mass fraction $w_{Cl} = m_{Cl}/m_{Soln}$	**1.00065 g/kg**

The uncertainty budget is calculated according to GUM analogously to the CCQM-K29 key comparison. The following uncertainty contributions were considered:

Uncertainty component	Relative standard uncertainty
Salt weighing	$2.04 \cdot 10^{-5}$
Salt weighing buoyancy correction	$2 \cdot 10^{-6}$
Solution weighing	$3.5 \cdot 10^{-6}$
Solution weighing buoyancy correction	$4 \cdot 10^{-6}$
Chloride assay in the salt	$4.2 \cdot 10^{-5}$
Evaporation, homogeneity	$1.0 \cdot 10^{-4}$
Combined uncertainty of mass fraction	**$1.2 \cdot 10^{-4}$**