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EMPA

Key comparison CCQM-K29

Anion calibration solutions

Final report

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0. Table of content

1. Abstract

In this key comparison anion calibration solutions of chloride and phosphate were investigated. The contents of both solutions were about 1 g/kg relative to the anion mass. For the chloride comparison 10 participants provided results by the following 3 analytical techniques: coulometry, titrimetry and ion chromatography. The phosphate amount content was determined by 10 NMIs whereby the following 6 techniques were applied: ion chromatography, titrimetry, ICP-OES, gravimetry, UV-Vis and ion-exchange followed by coulometry. The following institutes participated in this key comparison:

BAM and PTB (Germany)

BNM-LNE (France)

CENAM (Mexico)

EMPA (Switzerland)

GUM (Poland)

INTEC (Chile)

KRISS (Korea)

NMIJ (Japan)

NRCCRM (China)

SMU (Slovakia)

With one exception all results were found within the range of ± 0.25% with respect to the gravimetric value. The variability (RSD) of the results is below 0.1% for both the chloride and the phosphate solution (chloride without CENAM result). Compared to the pilot study CCQM-P32 the results of CCQM-K29 were significantly better. This is especially true for the phosphate comparison.

2. Introduction

Aqueous solutions of anions are widely used for the calibration in analytical chemistry. Therefore they are a decisive factor for the reliability of measurement results. This is especially true in the field of environmental and medicinal investigation. The mass concentration of the analyte in commercial standards is often declared as 1.000 g/L with an uncertainty of 0.002 – 0.005 g/L. In practice, deviations up to several percent of the declared value can be found. Therefore, the CCQM inorganic working group proposed the analysis of some typical anionic calibration solutions within the pilot study CCQM-P32 (accepted in April 2000). This key comparison CCQM-K29 was agreed by the Inorganic Analysis Working Group of CCQM in April 2002 and it was carried out similarly to CCQM-P32 with EMPA as the pilot laboratory.

3. Participants

The following 11 institutes participated in CCQM-K29:

Institute / Organisation	Country	Contact
BAM Bundesanstalt für Materialforschung und Prüfung	Germany	M. Breitenbach
BNM-LNE Bureau National de Métrologie - Laboratoire National d'Essais	France	C. Rivier
CENAM Centro National de Metrologia	Mexico	R. Arvizu Torres
EMPA Federal Laboratories for Materials Testing and Research	Switzerland	J. Wüthrich
GUM Central Office of Measures	Poland	W. Kozlowski
INTEC Instituto Tecnológico de Chile, Centro de Metrologia Quimica Fundacion Chile	Chile	G. Massiff
KRISS Korean Research Institute of Standards and Science	Korea	E. Hwang
NMIJ National Metrology Institute of Japan	Japan	A. Hioki
NRCCRM National Research Center for Certified Reference Materials	China	M. Liandi
PTB Physikalisch-Technische Bundesanstalt	Germany	D. Schiel
SMU Slovak Institute of Metrology	Slovakia	M. Máriássy

4. Samples

For each analyte a gravimetric solution of a mass fraction of about 1 g/kg (relative to the anion) was prepared using a high purity salt and ultrapure water. About 250 mL of each solution were provided. The solutions were not stabilized, bottled into polypropylene bottles, sealed and welded into mylar bags. The type of bottles and bags were the same as used in former comparisons. Detailed information about transpiration losses can be found in the final report of key comparison CCQM-K8.
Potassium chloride was provided by NIST (SRM 999a). It was dried at 500 °C for 4 hours. The phosphate solution was prepared by using disodium hydrogenphosphate provided by EMPA. The salt was dried for 3 hours at 150 °C. All weighing operations were performed in a weighing room fulfilling the requirements of OIML Class E2.
A homogeneity study was performed in both cases and the data were included into the uncertainty budgets of the gravimetric values (analogue to CCQM-K8, see Appendix B of CCQM-K8 report).
Detailed information and handling instructions are given in Appendix A (technical protocol) of this report.

5. Gravimetric target values

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

Chloride:	w_{Cl} = 0.98854 g/kg	$U(w_{Cl})$ = 0.00024 g/kg (k=2)
Phosphate:	w_{PO4} = 1.00447 g/kg	$U(w_{PO4})$ = 0.00066 g/kg (k=2)

6. Methods of measurement

The following measurement methods were applied by the participants:

Participant	Chloride solution	Phosphate solution
BAM	coulometry	-
BNM-LNE	titrimetry	titrimetry
CENAM	titrimetry	gravimetry
EMPA	titrimetry	ICP-OES
GUM	titrimetry	titrimetry
INTEC	titrimetry / IC	IC / UV-Vis
KRISS	coulometry / IC	IC / ICP-OES
NMIJ	titrimetry	IC
NRCCRM	coulometry	gravimetry
PTB	-	IC
SMU	coulometry	ion exchange + coulometry
Total results	10	10

7. Results

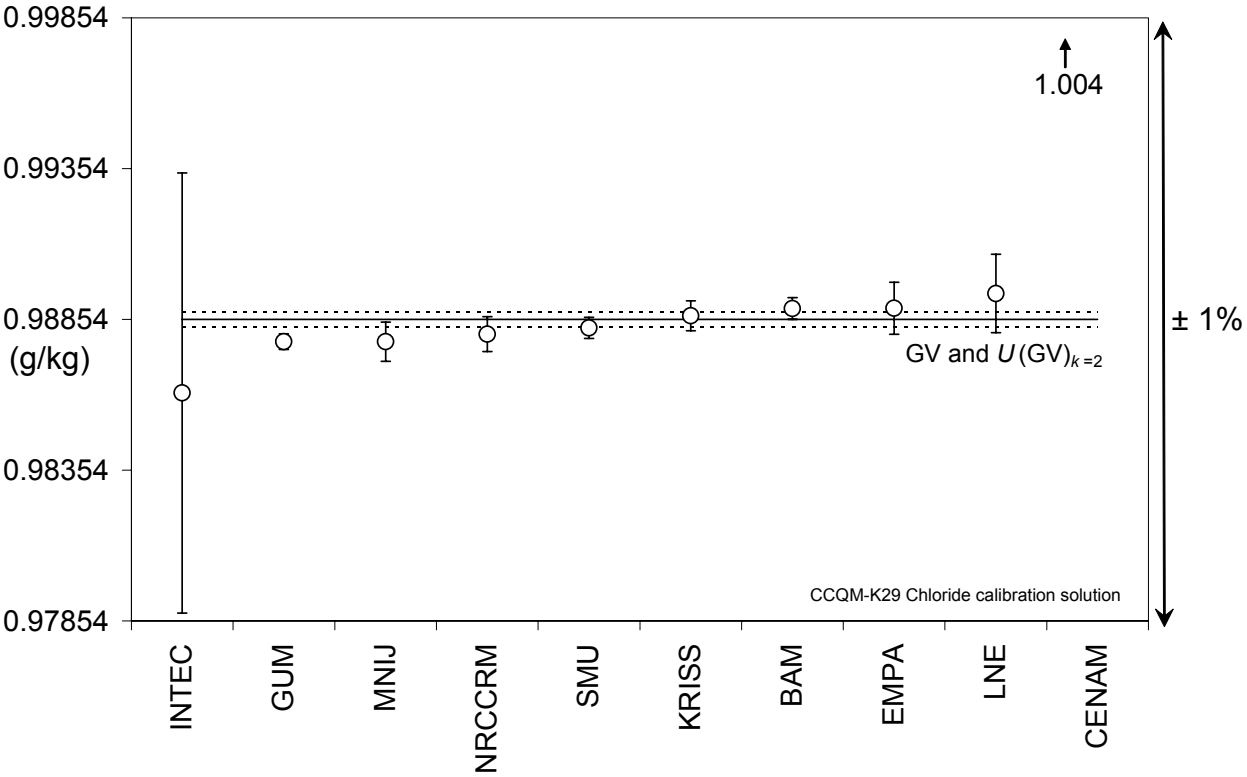
Within the chloride comparison 10 participants submitted results by 3 different methods. INTEC and KRISS reported mean results by 2 different methods. For the phosphate sample 10 participants submitted results by 6 different methods whereby INTEC and KRISS also reported mean values from 2 different methods. SMU reported its phosphate result from a coulometry measurement following ion exchange. The following tables gives the results including the uncertainty statement given as expanded uncertainties (k=2):

Participant	Results of **chloride** comparison given as mass fraction w_{Cl}	Expanded uncertainty $U(w_{Cl})$; k=2
INTEC	0.9861	0.0073
GUM	0.9878	0.00026
NMIJ	0.9878	0.00065
NRCCRM	0.98805	0.00058
SMU	0.98826	0.00035
KRISS	0.98866	0.00050
BAM	0.98890	0.00036
EMPA	0.98891	0.00086
BNM-LNE	0.9894	0.0013
CENAM	1.0040	0.0036

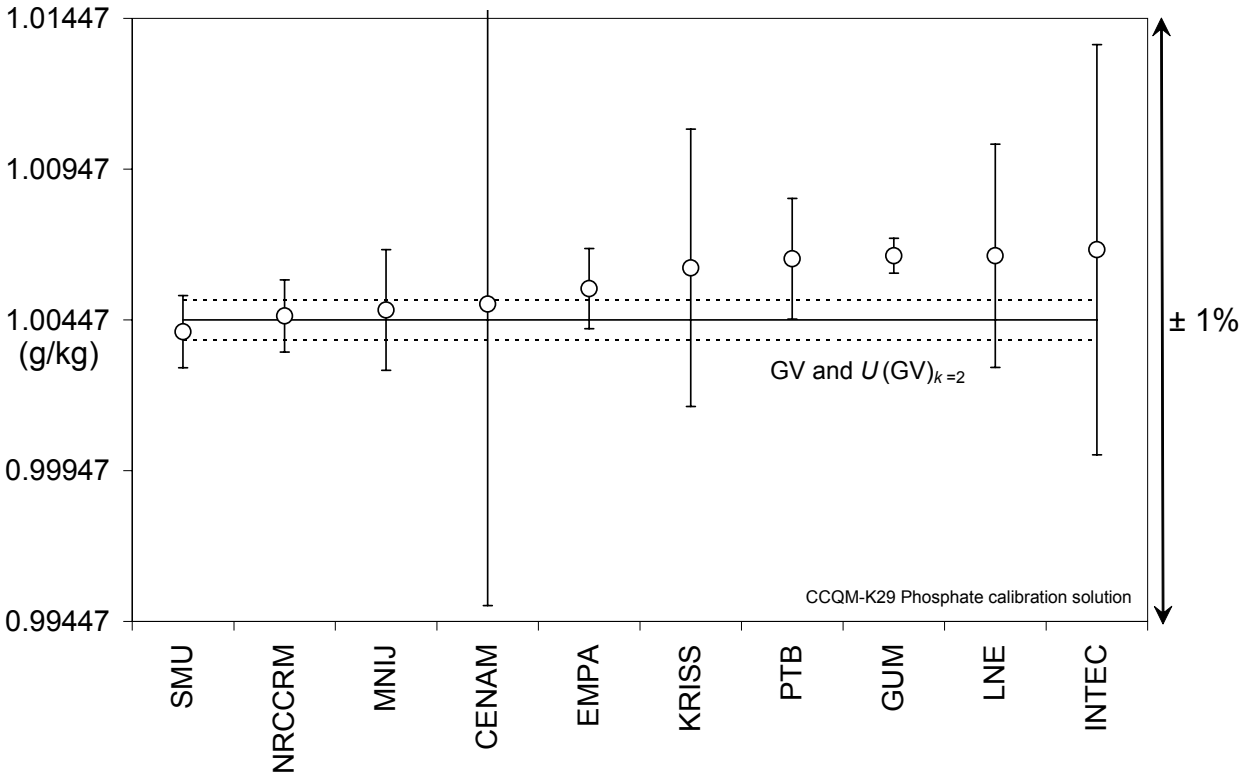
Participant	Results of **phosphate** comparison given as mass fraction w_{PO4}	Expanded uncertainty $U(w_{PO4})$; k=2
SMU	1.00408	0.0012
NRCCRM	1.0046	0.0012
NMIJ	1.0048	0.0020
CENAM	1.005	0.010
EMPA	1.00551	0.00133
KRISS	1.00620	0.0046
PTB	1.0065	0.0020
GUM	1.0066	0.00058
BNM-LNE	1.0066	0.0037
INTEC	1.0068	0.0068

8. Graphs

CCQM K29 anion calibration solutions - graph of **chloride** comparison:



CCQM K29 anion calibration solutions - graph of **phosphate** comparison:



9. Equivalence statements

The degree of equivalence of each laboratory with respect to the reference value D_i and its combined standard uncertainty (k = 2) U_i (both expressed in g/kg) are given by the equations:

$D_i = (x_i - x_{grav})$ and $U_i^2 = 2^2(u_i^2 + u_{grav}^2)$

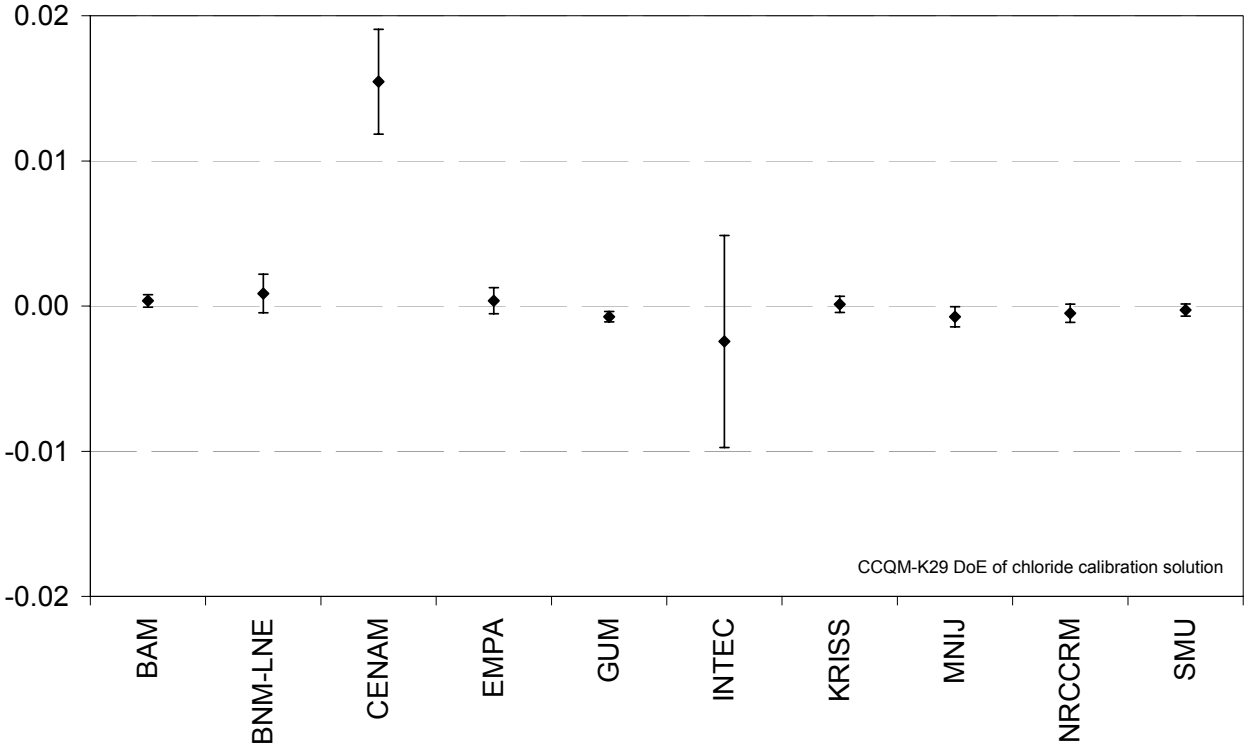
The degree of equivalence between two laboratories and its combined standard uncertainty (k = 2), both expressed in g/kg, are given by the equations:

$D_{ij} = D_i - D_j = x_i - x_j$ and $U_{ij}^2 = 2^2(u_i^2 + u_j^2)$

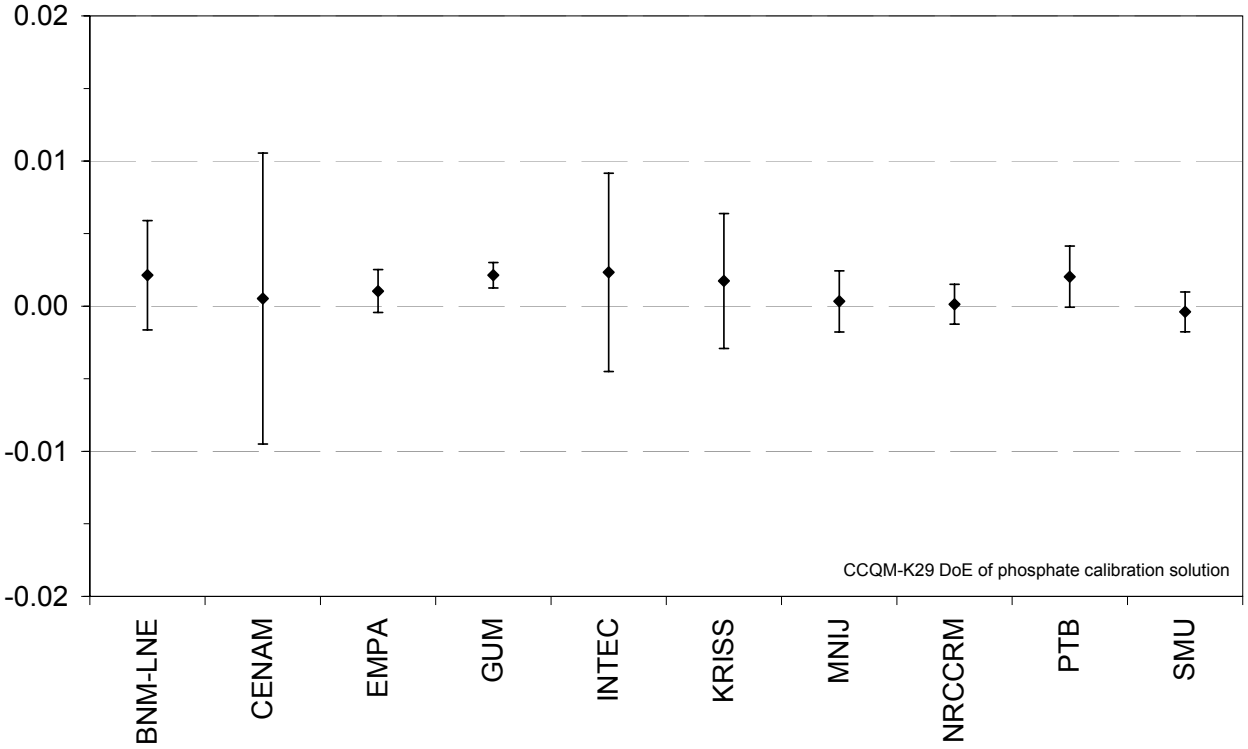
Participant *i*	D_i of **chloride** comparison	U_i of **chloride** comparison
INTEC	-0.00244	0.00730
GUM	-0.00074	0.00035
NMIJ	-0.00074	0.00069
NRCCRM	-0.00049	0.00063
SMU	-0.00028	0.00042
KRISS	0.00012	0.00055
BAM	0.00036	0.00043
EMPA	0.00037	0.00089
BNM-LNE	0.00086	0.00132
CENAM	0.01546	0.00361

Participant *i*	D_i of **phosphate** comparison	U_i of **phosphate** comparison
SMU	-0.00039	0.00137
NRCCRM	0.00013	0.00137
NMIJ	0.00033	0.00211
CENAM	0.00053	0.01002
EMPA	0.00104	0.00148
KRISS	0.00173	0.00465
PTB	0.00203	0.00211
GUM	0.00213	0.00088
BNM-LNE	0.00213	0.00376
INTEC	0.00233	0.00683

Graphical display of the equivalence statements for **chloride** of the participating institutes (alphabetical order; $U = ku_c$, k=2)



Graphical display of the equivalence statements for **phosphate** of the participating institutes (alphabetical order; $U = ku_c$, k=2)



10. Discussion and conclusions

Compared to CCQM-K8 (monoelemental solutions) and CCQM-P32 (pilot study on anion calibration solutions) the results from this key comparison are significantly better with regard to the comparability of results.

Analyte	Total results	Comparison	RSD between participants [%]
Chloride	16	P32	0.13
Phosphate	11	P32	0.26
Aluminium	13	K8	0.33
Copper	14	K8	0.13
Iron	13	K8	0.27
Magnesium	14	K8	0.29
Anions	27	P32	0.19
Cations	54	K8	0.26
All ions	81	P32 + K8	0.24
Chloride	**10**	**K29**	**0.10***
Phosphate	**10**	**K29**	**0.10**

* without CENAM result (including CENAM result leads to an RSD of 0.51%)

The uncertainties reported by the NMIs in K29 show a very good overlapping compared to the former comparisons K8 and P32. So it can be stated that participants improved their measurement skills from 2002 (CCQM-P32) until today (CCQM-K29).

The presence of diphosphate was unexpected by the participants, so many of them used methods which were not selective to species of interest only (i.e.phosphate). In atomic spectrometry (ICP-OES) and titration methods, both compounds are determined together. Also in gravimetric determination as phosphomolybdate the diphosphate is coverted to phosphate in the course of the procedure. In one case although a selective method - ion chromatography was used, the same material was used for calibration as was used for preparation of the samples yielding same bias in the result. It can be concluded that the present results of these institutes do not fully reflect the capabilities of the institutes in measurements of pure phosphate samples without phosphorus containing impurities. Thus in evaluation of CMC claims it should be taken into account that the results of LNE, GUM, NRCCRM and PTB ould be lower by the diphosphate contribution; for KRISS by half of it.

11. Acknowledgement

Many thanks to:

Dr. Michal Máriássy from SMU for helpful discussions concerning the purity determination of hydrogenphosphate salts and his measurements of the diphosphate impurity in the phosphate comparison starting material; NIST for providing potassium chloride; Dr. Mike Sargent from LGC for chairing the IAWG meetings.

Special thanks to the EMPA crew Monika Val, Karl Kehl, Jürg Wüthrich, Sergio Rezzonico, Dr. Giusepino Fortunato and Dr. Samuel Wunderli for doing a great job.

Appendix A - Technical protocol

Samples

Analytes/Matrix: The analytes in K29 are chloride (Cl^- from KCl) and phosphate (PO_4^{3-} from Na_2HPO_4) provided as monoanion solutions in water. The solutions of about 1 g/kg (mass fraction relative to Cl^- and PO_4^{3-}, not HPO_4^{2-}!) are prepared gravimetrically. At least 250 mL of each 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 labelling: 250 mL PP bottles are precleaned 2 times (48 h leaching) with ultrapure water and dried in a clean atmosphere. After bottling the samples were closed with a screw cap, sealed and welded in mylar foil to avoid transpiration during transport. Each sample was labelled with an individual sample code.

Distribution: One bottle of each anion 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 mylar bags until they are used. After receipt they shall be shaked rigorously. The bottles should not 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.

Reporting

Because K29 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 fractions of chloride (Cl^-) and phosphate (PO_4^{3-}) should be reported. No other forms of the analyte such as hydrogenphosphate HPO_4^{2-} should be reported.

Calculation of the uncertainty should be expressed as expanded uncertainty U for 95% confidence (i.e. $k = 2$ or reporting degrees of freedom). 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), informations 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.

Methods of measurement

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

Reference value

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

Proposed time schedule

The samples are distributed to participants by end of September 2003. The results should be returned to EMPA by the end of January 2004.

Participants

Participation is open to all interested CCQM members and official observers who have sufficient experience in this type of measurement. If the CCQM member or observer does not participate itself another competent institute may be nominated.

Appendix B - Weighing data and gravimetric values

Calculation of gravimetric value for CCQM-K29 chloride solution

Weighing of KCl starting material:

balance type	Mettler AT 201
air density (ρ_{air})	1.103754 kgm^{-3}
KCl density (ρ_{KCl})	1984 kgm^{-3}
weighing value KCl (W_{KCl})	22.7392 g
buoyancy correction factor (b_{KCl})	1.000419
mass KCl (m_{KCl})	**22.7487 g**
KCl purity (w_{KCl})	0.999817
chloride mass fraction	0.47546
mass Chloride (m_{Cl})	**10.8162 g**

Weighing of KCl aqueous solution:

balance type	Mettler KA 32S
air density (ρ_{air})	1.103754 kgm^{-3}
solution density (ρ_{SolnCl})	999.1 kgm^{-3}
weighing value solution (W_{Soln})	10931.2 g
buoyancy correction factor (b_{SolnCl})	1.000968
mass solution (m_{Soln})	**10941.6 g**

calculated mass content of chloride in CCQM-K29 solution

mass fraction $w_{Cl} = m_{Cl}/m_{Soln}$ **0.98854 g/kg**

Calculation of gravimetric value for CCQM-K29 phosphate solution

Weighing of Na_2HPO_4 starting material:

balance type	Mettler AT 201
air density (ρ_{air})	1.1070 kgm^{-3}
Na_2HPO_4 density ($\rho_{Na2HPO4}$)	1530 kgm^{-3}
weighing value Na_2HPO_4 ($W_{Na2HPO4}$)	15.9258 g
buoyancy correction factor ($b_{Na2HPO4}$)	1.000586
mass Na_2HPO_4 ($m_{Na2HPO4}$)	**15.9351 g**
Na_2HPO_4 purity [1] ($w_{Na2HPO4}$)	0.999925
Na_2HPO_4 purity [2]	0.999145
phosphate mass fraction [3]	0.66901
mass phosphate (m_{PO4}) [4]	**10.6516 g**

Weighing of Na_2HPO_4 aqueous solution:

balance type	Mettler KA 32S
air density (ρ_{air})	1.1070 kgm^{-3}
solution density ($\rho_{SolnPO4}$)	999.2 kgm^{-3}
weighing value solution (W_{Soln})	10593.9 g
buoyancy correction factor ($b_{SolnPO4}$)	1.000971
mass solution (m_{Soln})	**10604.2 g**

calculated mass content of phosphate in CCQM-K29 solution

mass fraction $w_{PO4} = m_{PO4}/m_{Soln}$ **<u>1.00447 g/kg</u>**

1) Purity with regarding all traces except sodium diphosphate as an impurity

2) Purity with regarding sodium diphosphate as an impurity

3) calculated from the purity value regarding all impurities (including sodium diphosphate)

4) calculated as follows: 15.9351 g · 0.999145 · 0.66901

Appendix C - Uncertainty budgets of gravimetric values

A detailed uncertainty calculation was made for both gravimetric values. The budgets are calculated according to the EURACHEM/CITAC Guide. Details of the calculations of weighing values, buoyancy correction factors and homogeneity factors can be found in Appendix B of report CCQM-K8. The following uncertainty contributions were considered:

Uncertainty contribution	Symbol	Chloride solution	Phosphate solution
Weighing Salt	$u_{rel}(W_{Salt})$	$2 \cdot 10^{-5}$	
Buoyancy correction of weighing salt	$u_{rel}(b_{Salt})$	$4 \cdot 10^{-6}$	
Solution weighing	$u_{rel}(W_{Soln})$	$1.2 \cdot 10^{-5}$	
Buoyancy correction of solution weighing	$u_{rel}(b_{Soln})$	$4.3 \cdot 10^{-6}$	
Purity of salt	$u_{rel}(P_{Salt})$	$4.0 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$
Hygroscopy	$u_{rel}(Hyg)$	--	$4.7 \cdot 10^{-6}$
Homogeneity	$u_{rel}(H)$	$1.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$
Evaporation Correction	$u_{rel}(V)$	$5 \cdot 10^{-5}$	
Comb. uncertainty of mass fraction	$u_{c,rel}(w_{Salt})$	**$1.2 \cdot 10^{-4}$**	**$3.3 \cdot 10^{-4}$**
Exp. uncertainty of mass fraction (k=2)	$U_{rel}(w_{Salt})$	**$2.4 \cdot 10^{-4}$**	**$6.6 \cdot 10^{-4}$**

Appendix D - Purity determination of the starting materials

Purity of potassium chloride

Potassium chloride was from NIST (SRM 999a). A chloride content (mass fraction) of 47.546% is reported in the NIST certificate. This material was used in earlier times for CCQM Study P8. Details of the certification procedure and data of impurities can be found in the NIST certificate of SRM 999a.

Purity of disodium hydrogenphosphate

Disodium hydrogenphosphate was provided by EMPA (inhouse certification ARF-005). Impurities were quantified by HR-ICP-MS, ICP-OES and IC and titration. Measurements of diphosphate were done at SMU with IC. More than thirty metals and 5 anions have been quantified as impurities. Only the most relevant impurities are listed in the following table:

	List of significant impurities in disodium hydrogenphosphate (EMPA certificate ARF-005)	
	quantified	smaller than (mg/kg)
Aluminium	1 mg/kg	-
Boron	-	1
Bromide	-	20
Calcium	-	20
Chloride	16 mg/kg	-
Chromium		2
Fluoride	6 mg/kg	-
Iron	-	2
Lead	-	2
Magnesium	-	1
Nitrate	-	35
Potassium	-	10
Sulfate	3 mg/kg	-
Thallium	-	2
Others (24 metals)	-	0.1 - 0.5 each
Sodium diphosphate	0.078 % (w/w)	-

Hygroscopy: Dry Na_2HPO_4 (after 3 h at 150 °C and storage over anhydrous magnesiumperchlorate) shows a slow hygroscopy leading to an increase of mass of 0.029% per hour (300 mg dry Na_2HPO_4 monitored at 22 °C and 50% rel. humidity during 12 hours on a Mettler Toledo UMT-5; readability 0.1 μg). For the relevant time span for the weighing operation of approx. 1 minute this implicates a bias of $4.7 \cdot 10^{-6}$. This effect was included into the uncertainty budget of the gravimetric phosphate value.

Dihydrogenphosphate: In CCQM-P32 dihydrogenphosphate as an impurity was assumed following acidimetric titration of the starting material. The observed but marginal underconsumption of acid (titration of the hydrogenphosphate to the dihydrogenphosphate) would be a sign of an increase of the phosphate mass content of +0.022%. Nevertheless, it never could be clearly demonstrated that dihydrogenphosphate really exists in the starting material. To account for this unclarity an additional uncertainty contribution of 0.022% was included into the uncertainty budget of the gravmetric phosphate value of CCQM-K29.

Diphosphate: Although thermogravimetric analysis revealed no significant loss of mass within 180 minutes at 150 °C (< 0.01%) it could be demonstrated that a significant polycondensation takes place under the chosen drying conditions. Further IC measurements (by M. Máriássy from SMU) revealed a content of 0.078% sodium diphosphate in the starting material. The gravimetric value was corrected for this effect and an uncertainty contribution of 20% relative to the diphosphate content was included into the uncertainty budget of the gravmetric phosphate value of CCQM-K29.

Buchs, May 2005

Michael Weber

Dr. Michael Weber