Eidgenössische Materialprüfungs- und Forschungsanstalt
Laboratoire fédéral d'essai des matériaux et de recherche
Laboratorio federale di prova dei materiali e di ricerca
Institut federal da controlla da material e da retschertgas
Swiss Federal Laboratories for Materials Testing and Research

Lerchenfeldstrasse 5
Postfach 755
CH-9014 St. Gallen
Tel. +41-71-274 74 74
Fax +41-71-274 74 99

EMPA

International Intercomparison

Pilot Study CCQM-P32
on
Anion Calibration Solutions

Final Report
2003

Michael Weber
Jürg Wüthrich

1. Abstract

In CCQM-P32 pilot study two 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 11 participants provided 16 results by the following analytical techniques: coulometry (7), titrimetry (5) and ion chromatography (4). The phosphate amount content was determined by 9 NMIs and 11 results were submitted. For phosphate ion chromatography was the most used technique (4) followed by titrimetry (2), ICP-OES (2), gravimetry (1) and ion-exchange-coulometry (1).
All results were found within the range of ± 0.5% with respect to the gravimetric value. The variability (RSD) of the results is 0.13% for the chloride solution and 0.26% for the phosphate solution. Compared to the results of CCQM-K8 (monoelemental solutions, average RSD 0.25%) these results are quite similar. No significant deviation between the mean of all measured values and the gravimetric value were found in both samples. A key comparison is planned for 2003.

2. Rationale of this Study

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. Similar to monoelemental calibration solutions as investigated in CCQM-K8 and CCQM-P30, 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 as a study.
The study was accepted by the CCQM in April 2000. It was carried out by EMPA as pilot laboratory.

3. Participants

The following institutes participated in this study:

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
KRISS Korean Research Institute of Standards and Science	Korea	E. Hwang
NIST National Institute for Standards and Technology	USA	J. Smeller
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 anion 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. No stabilization of the solution was made. The solution was bottled into polypropylene bottles, sealed and welded into mylar bags. The type of bottles and bags were the same as used in CCQM-K8. Detailed information about transpiration losses can be found in the CCQM-K8 report.
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. Both samples are matrix free and they only content chloride or phosphate as anions (except the specified impurities listed in Appendix C).
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)

5. Instructions to Participants

Participants were instructed to open the bags immediately before the measurements to avoid evaporation. The solutions were not stabilized and therefore participants were instructed to do the measurements as soon as possible to prevent any effects of degradation. It was recommended to check the sealing of the caps to ensure that the bottles were not opened at any time during the transportation. The method of measurement was free of choice to the participants. It was allowed to do the measurements with more than one analysis method. Analysis results from different techniques were treated individually.
All results (values and uncertainties) must be given as mass fractions in g/kg with respect to chloride and phosphate. A detailed uncertainty budget was required for each result.

6. 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 are described in Appendix B.

Chloride: w_{Cl} = 1.00892 g/kg $U(w_{Cl})$ = 0.000366 g/kg (k=2)

Phosphate: w_{PO4} = 0.98953 g/kg $U(w_{PO4})$ = 0.000448 g/kg (k=2)

7. Methods of Measurement

The following measurement methods were applied by the participants:

Participant	Chloride solution
BAM	coulometry
CENAM-1	titrimetry
CENAM-2	coulometry
EMPA-1	titrimetry
EMPA-2	IC
GUM	titrimetry
KRISS-1	coulometry
KRISS-2	IC
LNE	titrimetry
NIST-1	IC
NIST-2	coulometry
NMIJ	titrimetry
NRCCRM	coulometry
PTB	IC
SMU-1	ion exchange + coulometry
SMU-2	coulometry
No. of results	16

Participant	Phosphate solution
EMPA-1	ICP-OES
EMPA-2	IC
GUM	titrimetry
KRISS-1	ICP-OES
KRISS-2	IC
LNE	titrimetry
NIST	IC
NMIJ	IC
NRCCRM	gravimetry
PTB	IC
SMU	ion exchange + coulometry
No. of results	11

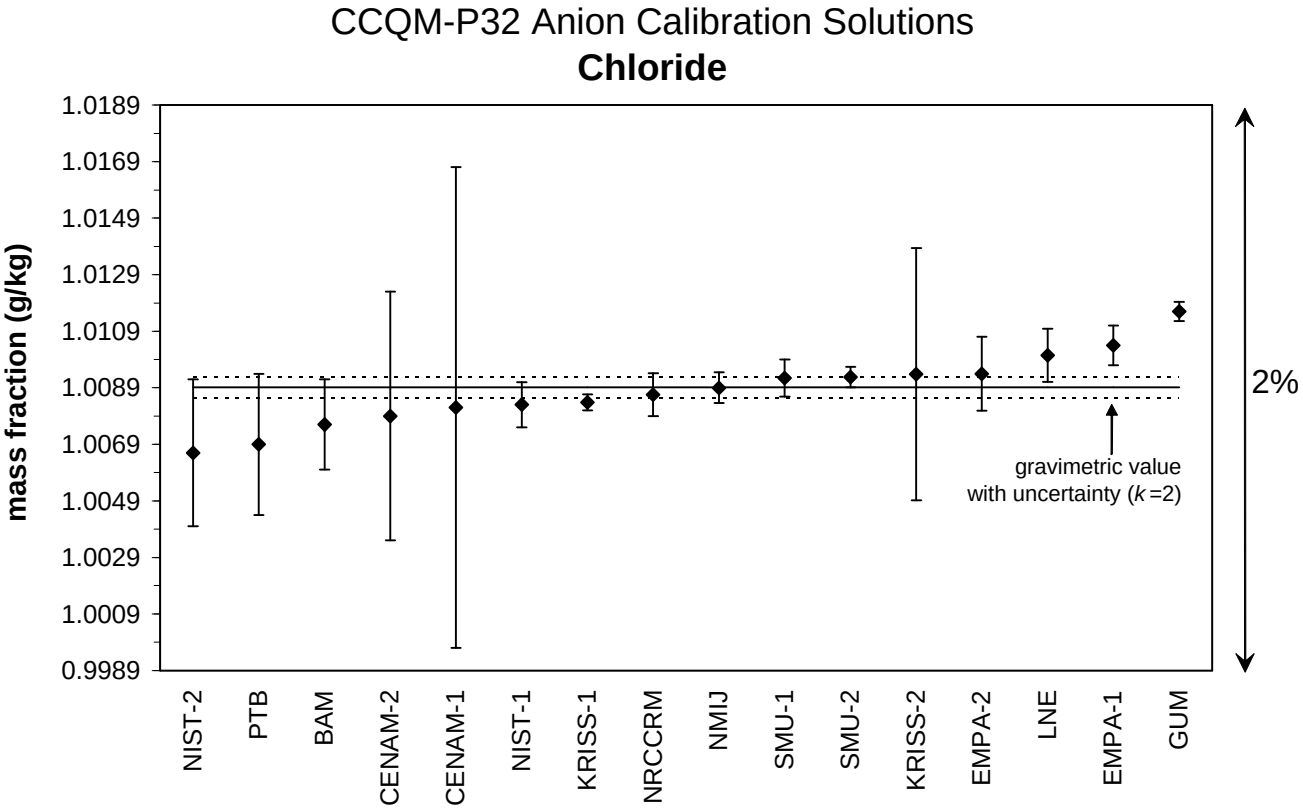
8. Results

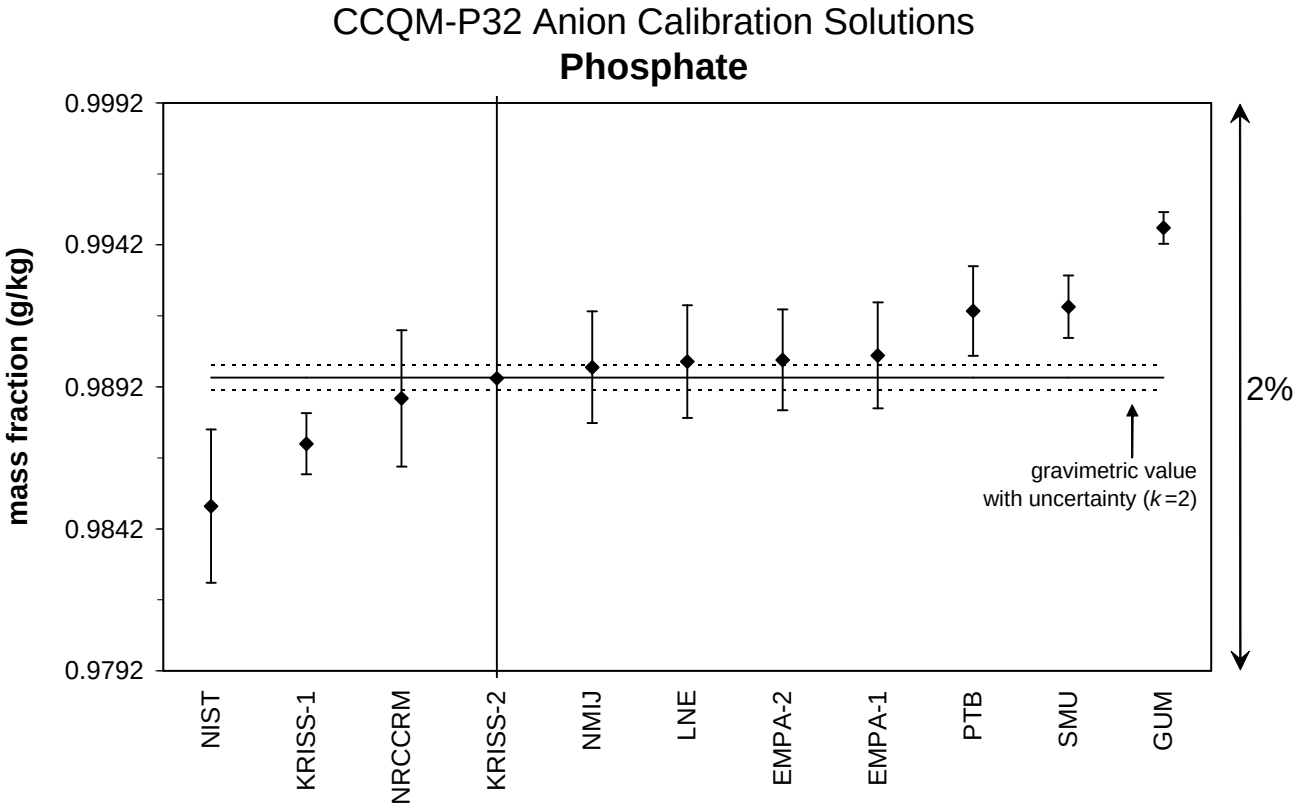
11 participants submitted 16 results for the chloride comparison. 5 of them reported two results due to different analytical methods. Therefore a total of 16 results were obtained in the chloride comparison. For the phosphate sample 9 participants submitted 11 results and two of them reported two results by different methods. This leads to a total of 11 results in the phosphate comparison.
The following tables give 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
NIST-2	1.0066	0.0026
PTB	1.0069	0.0025
BAM	1.0076	0.0016
CENAM-2	1.0079	0.0044
CENAM-1	1.0082	0.0085
NIST-1	1.0083	0.0008
KRISS-1	1.00839	0.00028
NRCCRM	1.00866	0.00076
NMIJ	1.0089	0.00054
SMU-1	1.00924	0.00066
SMU-2	1.00928	0.00036
KRISS-2	1.00938	0.00446
EMPA-2	1.0094	0.00131
LNE	1.01005	0.00094
EMPA-1	1.0104	0.00069
GUM	1.0116	0.00034

Participant	Results of **phosphate** comparison given as mass fraction w_{PO4}	Expanded uncertainty U (w_{PO4}); k=2
NIST	0.9850	0.0027
KRISS-1	0.9872	0.00108
NRCCRM	0.9888	0.0024
KRISS-2	0.9895	0.0109
NMIJ	0.98989	0.00197
LNE	0.99009	0.00198
EMPA-2	0.99015	0.00178
EMPA-1	0.99031	0.00186
PTB	0.99187	0.00158
SMU	0.99202	0.0011
GUM	0.9948	0.00056

9. Graphs


CCQM-P32 Anion Calibration Solutions
Chloride
mass fraction (g/kg)
1.0189
1.0169
1.0149
1.0129
1.0109
1.0089
1.0069
1.0049
1.0029
1.0009
0.9989
2%
gravimetric value
with uncertainty (k=2)
NIST-2
PTB
BAM
CENAM-2
CENAM-1
NIST-1
KRISS-1
NRCCRM
NMIJ
SMU-1
SMU-2
KRISS-2
EMPA-2
LNE
EMPA-1
GUM


CCQM-P32 Anion Calibration Solutions
Phosphate
mass fraction (g/kg)
0.9992
0.9942
0.9892
0.9842
0.9792
2%
gravimetric value
with uncertainty (k=2)
NIST
KRISS-1
NRCCRM
KRISS-2
NMIJ
LNE
EMPA-2
EMPA-1
PTB
SMU
GUM

10. Discussion and Conclusions

Compared to CCQM-K8 (monoelemental solutions) the results from this anion study are of about the same quality in regard to the comparability of results. Following CCQM-K8 in this study no significant deviations are found between the gravimetric values and the corresponding median of participant results.

Analyte	RSD between participants [%]	Relative deviation of median from grav. value [%]
Al	0.34	0.041
Cu	0.11	0.021
Fe	0.28	0.011
Mg	0.28	0.077
Chloride	0.13	0.014
Phosphate	0.26	0.057

The uncertainties reported by the NMIs do not overlap perfectly. Regarding the diversity of the applied measurement techniques this is not surprising. Nevertheless in many cases the measurement uncertainties are rather underestimated than conservative.
This study raised the discussion about purity determination of salts and its limits. It was shown that for many inorganic salts such as disodium hydrogenphosphate it is quite difficult to determine the exact stoichiometry. This is certainly also true for a large number of inorganic salts such as sulfates, carbonates etc.

Finally the results of CCQM study P32 are quite satisfying for chloride as well as phosphate and therefore the CCQM agreed to launch key comparison CCQM-K29 in 2003. EMPA will act as pilot laboratory again.

11. Acknowledgement

Many thanks to:

Dr. Michal Máriássy from SMU for the helpful discussion concerning the purity determination of hydrogenphosphate salts; 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 - Weighing Data and Gravimetric Values

Calculation of gravimetric value for CCQM-P32 chloride solution

KCl weighing:

balance type	Mettler AT 201
air density (r_{air})	1.1127 kgm^{-3}
KCl density (r_{KCl})	1984 kgm^{-3}
weighing value KCl (W_{KCl})	19.02577 g
buoyancy correction factor (b_{KCl})	1.000422
mass KCl (m_{KCl})	19.03380 g
KCl purity (w_{KCl})	0.999817
chloride mass fraction	47.5463%
mass Chloride (m_{Cl})	**9.04987 g**

Solution weighing

balance type	Mettler KA 32S
air density (r_{air})	1.1127 kgm^{-3}
solution density (r_{SolnCl})	999.1 kgm^{-3}
weighing value solution (W_{Soln})	8961.2 g
buoyancy correction factor (b_{SolnCl})	1.000976
mass solution (m_{Soln})	**8969.9 g**

calculated mass content of chloride in CCQM-P32 solution

mass fraction $w_{Cl} = m_{Cl}/m_{Soln}$ **1.00892 g/kg**

Calculation of gravimetric value for CCQM-P32 phosphate solution

Na_2HPO_4 weighing:

balance type	Mettler AT 201
air density (r_{air})	1.1110 kgm^{-3}
Na_2HPO_4 density ($r_{Na2HPO4}$)	1530 kgm^{-3}
weighing value Na_2HPO_4 ($W_{Na2HPO4}$)	14.89835 g
buoyancy correction factor ($b_{Na2HPO4}$)	1.000588
mass Na_2HPO_4 ($m_{Na2HPO4}$)	14.90711 g
Na_2HPO_4 purity [1] ($w_{Na2HPO4}$)	0.999925
Na_2HPO_4 purity [2]	0.9987
phosphate mass fraction [3]	66.915%
mass phosphate (m_{PO4}) [4]	**9.9743 g**

Solution weighing

balance type	Mettler KA 32S
air density (r_{air})	1.1110 kgm^{-3}
solution density ($r_{SolnPO4}$)	999.2 kgm^{-3}
weighing value solution (W_{Soln})	10070.100 g
buoyancy correction factor ($b_{SolnPO4}$)	1.000974
mass solution (m_{Soln})	**10079.909 g**

calculated mass content of phosphate in CCQM-P32 solution

mass fraction $w_{PO4} = m_{PO4}/m_{Soln}$ **0.98953 g/kg**

1) Purity without regarding NaH_2PO_4 as an impurity

2) Purity with regarding NaH_2PO_4 as an impurity

3) A content of 0.12% NaH_2PO_4 was determined by acidimetric titration of the Na_2HPO_4 starting material. This leads to an increase of the phosphate content of 0.022%. The phosphate mass fraction of 66.915% is calculated for a mixture of 99.88% Na_2HPO_4 and 0.12% NaH_2PO_4.

4) Calculated as follows: 14.90711 g · 0.999925 · 0.66915

Appendix B - Uncertainty Budgets of Gravimetric Values

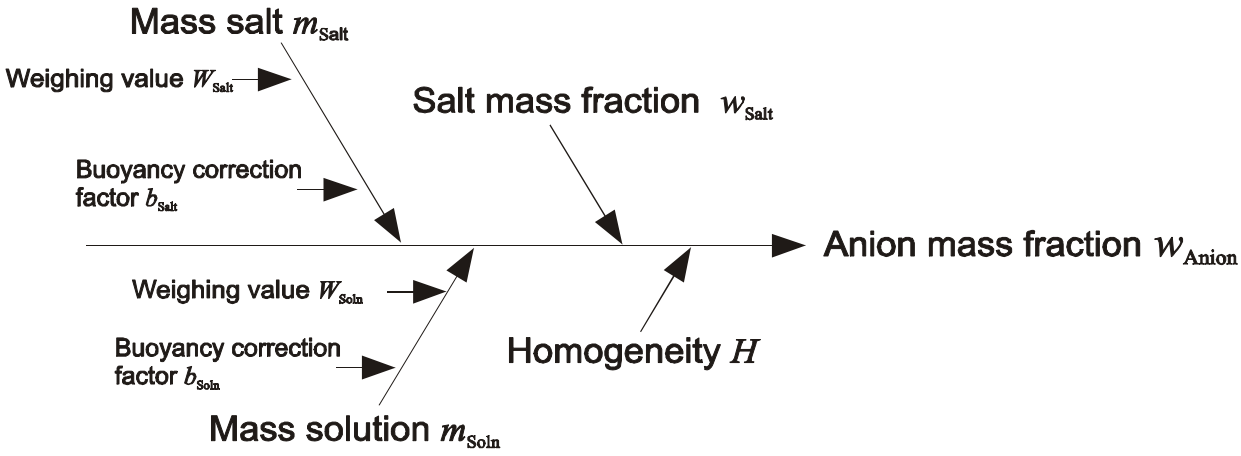
A detailed uncertainty calculation was made for both gravimetric values. The budgets are calculated according to the EURACHEM/CITAC Guide. Details of the calculations of weighing values, buoyancy correction factors and homogeneity factors can be found in Appendix B of report CCQM-K8.

The equation for mass fraction of an anion in a solution is given as follows:

$$w_{Anion} = \frac{m_{Anion}}{m_{Soln}} = \frac{W_{Salt} \cdot b_{Salt} \cdot w_{Salt} \cdot H}{W_{Soln} \cdot b_{Soln}}$$

w_{Anion}	mass fraction of anion in solution
m_{Anion}, m_{Soln}	masses of anion and solution
W_{Salt}, W_{Soln}	weighing values of salt and solution
b_{Salt}, b_{Soln}	buoyancy correction factors of salt and solution
H	factor for homogeneity (H=1; u(H)>0)

leading to the following cause effect diagram:



The following table gives a detailed listing of the uncertainty contributions:

Uncertainty contribution		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	$u_{rel}(P_{Salt})$	$4.0 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$
Correction for NaH_2PO_4 content	$u_{rel}(Stoech)$	--	$8 \cdot 10^{-5}$
Hygroscopy	$u_{rel}(Hyg)$	--	$4.7 \cdot 10^{-6}$
Homogeneity	$u_{rel}(H)$	$1.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Evaporation Correction	$u_{rel}(V)$	$5 \cdot 10^{-5}$	
Comb. uncertainty of mass fraction	$\boldsymbol{u_{c,rel}(w_{Salt})}$	$\mathbf{1.83 \cdot 10^{-4}}$	$\mathbf{2.24 \cdot 10^{-4}}$
Exp. uncertainty of mass fraction ($k=2$)	$\boldsymbol{U_{rel}(w_{Salt})}$	$\mathbf{3.66 \cdot 10^{-4}}$	$\mathbf{4.48 \cdot 10^{-4}}$

Appendix C - Purity Determination of the Salts

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

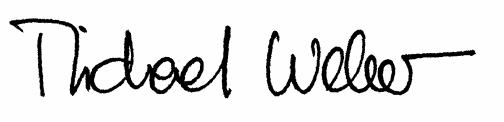
Disodium hydrogenphosphate was provided by EMPA (inhouse certification ARF-005). Impurities were quantified by HR-ICP-MS, ICP-OES and IC and titration. More than thirty metals and 5 anions have been quantified as impurities. Only the most relevant impurities are listed in the following table:

	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 dihydrogenphosphate	0.12% (w/w)	-

In addition, dihydrogenphosphate as an impurity was determined by acidimetric titration of the hydrogenphosphate salt (3 sets of eight titrations; relative combined uncertainty 0.04%). It was found that 0.12% less acid was used to titrate the hydrogenphosphate. Assuming that this effect originates only from the presence of dihydrogenphosphate leads to an increase of the phosphate mass content of +0.022%. The corrected phosphate mass content in the salt (mass fraction) is 66.915% (see note on page 10).

Thermogravimetric analysis revealed a loss of mass of approx. 0.35% in 15 minutes when raising the temperature up to 150 °C. After that no significant loss of mass was detected within 180 minutes (< 0.01%). Therefore it is supposed that no polycondensation takes place under the chosen drying conditions. Dry Na_2HPO_4 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 value.

St. Gallen, September 2003



Dr. Michael Weber
EMPA
Metrology in Chemistry
Lerchenfeldstrasse 5
9014 St. Gallen
Switzerland

michael.weber@empa.ch