

3. Certified purities of primary materials

Primary material	Difference analysis approach		Content verification		Difference
	Purity _{DAA} ^[2] (%)	<i>U</i> (P _{DAA}) ^[3] (%)	Purity _{CV} ^[4] (%)	<i>U</i> (P _{CV}) ^[3] (%)	
NaF	99.973	0.081	99.833	0.061	0.140 ⁵
NaCl	99.986	0.082	99.981	0.015	0.005
NaBr	99.967	0.082	99.941	0.091	0.026
NaNO ₃	99.985	0.081	99.93	0.36	0.06
Na ₂ HPO ₄	99.988	0.081	100.06	0.24	-0.07
Na ₂ SO ₄	99.987	0.081	99.999	0.064	-0.012

The primary materials have to be dried prior to use as followed: NaCl and NaBr for 15 h at 500°C, NaF and Na₂SO₄ for 10 h at 500°C, Na₂HPO₄ for 3 h at 150°C and NaNO₃ for 10 h at 290°C. Storage over anhydrous magnesium perchlorate.

Berlin, 19 December 2003



BAM Berlin/Germany
Head of Division Inorganic Chemical Analysis
Reference Materials

R. Matschat

Dr. R. Matschat

St. Gallen, 19 December 2003



EMPA St. Gallen/Switzerland
Head of the Chemical Metrology Group

Michael Weber

Dr. M. Weber

1 Detailed information about the measured content or detection limit of an individual trace impurity is available on request at EMPA.

2 DAA = Difference analysis approach calculated by using the equation given under paragraph 1 of this report.

3 Expanded measurement uncertainty (*k*=2) according to Eurachem / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", 2nd Ed., 2000. A contribution of 0.08% is included regarding non detected impurities.

4 CV = Content verification by direct measurement (ICP-OES measurement of Na in NaF; coulometric determination of halides in NaCl and NaBr; mean value of gravimetric determination of NO₃ in NaNO₃ and ICP-OES determination of Na in NaNO₃; content of Na₂HPO₄ determined by an intercomparison of 11 national metrological institutes (CCQM-P32), ion-exchange/coulometric determination of Na in Na₂SO₄).

5 The difference between DAA and CV analysis results for NaF is caused by the limits of high accuracy analysis of fluoride. Nevertheless, the difference of 0.14% is significantly smaller than the reported uncertainty for fluoride content (0.2%) and therefore this does not reduce the PM quality.

PRIMUS

Primary Multiion Standards

Certificate

A Cooperation Project of



This certificate is designed in accordance with ISO Guide 31^[1] and comprises four pages.

Primary multianion standard solution

Production: Sigma-Aldrich Production GmbH, Industriestrasse 25, CH-9471 Buchs/Switzerland

Object of certification: **Primary multianion standard solution** in *TraceSELECT*[™] Ultra water (18.2 MΩ·cm, 0.22 μm filtered) in precleaned 50 mL HDPE bottles, sealed in an aluminized bag

Fluka product no.: 89886

Lot and filling code: 1265008, 10606286

Density at 22°C: ρ = 997.9 kgm⁻³ u(ρ) = 0.2 kgm⁻³

Intended use: This reference material is intended to be used for calibration of ion chromatography or any other analytical technique needing a calibration with anion standard solutions.

Expiry date: 15. February 2009

Storing and handling: This reference material shall be stored in the original closed bag in a temperature range of 5°C to 30°C. Before opening, the bottle's temperature must be 22 ± 2°C.

1. Certified values

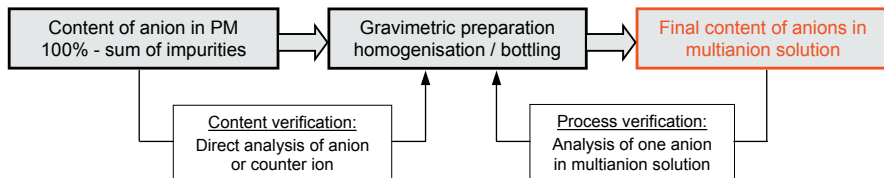
Certified value and uncertainty according to ISO Guide 35 ^[2] and Eurachem/CITAC Guide ^[3]		
Constituent (formula) ^[4]	Certified value	Combined expanded uncertainty [<i>U</i> = <i>k</i> · <i>u_c</i> ; <i>k</i> = 2]
Bromide (Br⁻)	10.01 mg kg⁻¹	± 0.02 mg kg⁻¹
Chloride (Cl⁻)	10.00 mg kg⁻¹	± 0.02 mg kg⁻¹
Fluoride (F⁻)	10.00 mg kg⁻¹	± 0.02 mg kg⁻¹
Nitrate (NO₃⁻)	10.01 mg kg⁻¹	± 0.02 mg kg⁻¹
Phosphate (PO₄³⁻)	10.00 mg kg⁻¹	± 0.02 mg kg⁻¹
Sulfate (SO₄²⁻)	10.00 mg kg⁻¹	± 0.02 mg kg⁻¹

2. Concept of certification and traceability statement

The certified contents of anions (given as mass fractions) in this multianion solution are calculated from gravimetric preparation values using **BAM/EMPA certified primary materials** (PMs, see page 4). The following basic materials are used: NaF, NaCl, NaBr, NaNO₃, Na₂HPO₄, Na₂SO₄. The anion contents in the PMs are calculated by subtracting the below listed impurities from 100% (=difference analysis approach).

A **content verification** was performed for all the PMs by high precision analysis of either the anion or its counterion. The content verification strongly indicates that no significant impurities are missed in the difference analysis approach (i.e. organics or residual water). In addition, the content verification underpins the correct PM stoichiometry.

A final **process verification** for the production process was performed using high precision ICP-OES measurements of phosphorus in the bottled multianion solution.



3. Gravimetric production of primary multianion standard solution

Sigma-Aldrich Production GmbH produced the primary multianion standard solution gravimetrically by dissolving certified PMs in *TraceSELECT*[™] Ultra water (18.2 MΩcm, 0.22 μm filtered). All balances are certified by DKD and calibrated with OIML Class E2 (up to 12 kg) and F2 (up to 64 kg) weights. The bulk solution was homogenized by overhead tumbling in a PVDF container for at least 12 hours. A total of 1060 precleaned 50 mL HDPE bottles were each filled under clean room conditions.

4. Calculation of Anion content in multianion standard solution

$$w_{Anion} = \frac{m_{Anion}}{m_{Soln}} = \frac{W_{PM} \cdot b_{PM} \cdot w_{Anion\ in\ PM} \cdot f_{Cross}}{W_{Soln} \cdot b_{Soln}}$$

W_{PM} , W_{Soln} Weighing values for primary material (PM) and solution
 b_{PM} , b_{Soln} Air buoyancy correction factors for PM and solution
 f_{Cross} Correction factor for anion content from other PM (cross contamination)
 $w_{Anion\ in\ PM}$ Mass fraction of anion in PM
 w_{Anion} Final content of anion in multianion solution (mass fraction)

5. Uncertainty calculation

The standard uncertainty contributions of the following parameters are included in the uncertainty budgets of gravimetric values^[3] (approx. contributions in % are given in parentheses): Weighing operations (for masses of primary material and batch) including air buoyancy correction (≤ 0.07); purity of primary material (≤ 0.04); relative molecular masses^[5] (≤ 0.004); transpiration rate^[6] (0.035); cross contaminations for analyte impurities from other PMs (≤ 0.01) and stoichiometry effects (0.008; only for Na₂HPO₄). In addition, an estimated uncertainty contribution of 0.08% was included to account for not determined impurities including residual water (estimation according to drying behavior, TGA and TGA-MS data and content verification measurements).

Reviewing chemist	Certification body	Date of release	Quality system
 K.-D. Schmidt, Ph.D.	 J. Wuethrich	February 15 th 2006	 SQS Reg. No. 16368-02

[1] ISO Guide 31, 1-7, 1st Ed. (1981), "Contents of certificates of reference materials"
 [2] ISO Guide 35, 1-7, (2000), "Certification of reference materials – general and statistical principles"
 [3] Eurachem / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", 2nd Ed., 2000.
 [4] Chloride is the only anion in this solution (with exception of anionic trace impurities; for details see certification of primary materials).
 [5] Relative molecular mass: Pure & Appl. Chem., Vol. 75, No. 8, pp. 1107-1122, 2003.
 [6] Data based on long term stability tests at 30°C at EMPA. After the HDPE bottle has been removed from the bag, transpiration will occur at an accelerated rate. Storage of a partially used bottle is not recommended. If storage is necessary, the bottle should be stored at a reduced temperature (e.g. refrigerator) to slow down the rate of transpiration.

Certification of primary materials by BAM and EMPA

1. Purity determination of primary materials

The primary material (PM) content is calculated as 100% minus the sum of impurities ($w_{i,found}$), whereas for impurities ($w_{i,unfound}$) below the detection limit (DL), a contribution of half of the detection limit was considered. The contribution for not determined impurities ($w_{i,nd}$) was assumed to be zero, whereas its uncertainty was estimated to 0.08%. The equations for the calculation of PM purity w_{PM} and its combined uncertainty $u(w_{PM})$ are given below (where $w_{i,found}$ = mass fraction of found impurity i):

$$w_{PM} = 100\% - \sum_i w_{i,found} - \sum_i \left(\frac{DL_{i,unfound}}{2} \right) - \sum_i w_{i,nd}$$

$$u(w_{PM}) = \sqrt{\sum_i u(w_{i,found})^2 + \sum_i \left(\frac{DL_{i,unfound}}{2} \cdot \frac{1}{\sqrt{3}} \right)^2 + \sum_i u(w_{i,nd})^2}$$

2. Trace analysis

Measurements at EMPA were carried out between 2 April 2003 and 18 December 2003. Trace element measurements were performed by K. Grieder under the supervision of Dr. G. Fortunato using HR-ICP-MS and ICP-OES. Anion measurements by IC and titration were performed by K. Kehl under the supervision of J. Wuethrich. Analysis of water traces and observation of drying behavior were performed by J. Wuethrich using TGA and TGA-MS. Measurements of C, N and O using carrier gas hot extraction/combustion analysis were carried out by T. Giray under the supervision of Dr. H. Kipphardt at BAM between 14 September 2003 and 7 November 2003 whereby coulometry measurements were performed at BAM by Ch. Oberroeder under the supervision of Dr. M. Breitenbach.

Impurities¹ in NaF

≤ 1 mg/kg	Ag	Be	Ca	Cd	Ce	Co	Cs	Dy	Er	Eu	Gd	Hf	Ho	In	La	Lu	Mg	Mn	Nd	Pr	Rb	Sc	Sm	Ta	Tb	Tm	U	V	Y	Yb
1-5 mg/kg	Al	Au	B	Bi	Cr	Cu	Fe	Ge	Hg	Ir	Li	Mo	Nb	P	Pd	Pt	Re	Rh	Ru	S	Sb	Sn	Te	Th	Ti	Tl	Zr			
5-10 mg/kg	As	Ba	Cl	I	K	Ni	NO ₂	Pb	Se	Sr	Zn	10-65 mg/kg	Br	C	N	PO ₄	Si	SO ₄												

Impurities¹ in NaCl

≤ 1 mg/kg	As	B	Bi	Ce	Cr	Cs	Cu	Fe	In	La	Li	Lu	Mg	Nb	Ni	P	Rb	Re	Rh	Ru	S	Sc	Sr	Ta	Th	Ti	Tl	Tm	Y
1-5 mg/kg	Ag	Al	Au	Ba	Be	Cd	Co	Ga	Hf	Ir	Mn	Mo	Nd	Pb	Pd	Pt	Sb	Sm	Te	U	V	Zr							
5-10 mg/kg	Ca	Ge	Hg	NO ₂	Pd	Si	Sn	SO ₄	Zn	10-55 mg/kg	Br	C	F	I	K	N	NO ₂	PO ₄	Se										

Impurities¹ in NaBr

≤ 1 mg/kg	Ag	As	Au	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Li	Lu	Mg	Mn	Mo
	Nb	Nd	Ni	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	S	Sb	Sc	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	Y	Yb	Zn	Zr	
1-5 mg/kg	Al	K	P	Se	5-10 mg/kg	B	Si	10-55 mg/kg	C	F	I	N	NO ₂	NO ₃	PO ₄	SO ₄	210 mg/kg	Cl													

Impurities¹ in NaNO₃

≤ 1 mg/kg	Ag	As	Au	B	Ba	Be	Bi	Ca	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Li	Lu	Mn	Mo	Nd
	Ni	Pb	Pr	Rb	Re	Rh	Ru	Sb	Sc	Sm	Sr	Tb	Th	Ti	Tl	Tm	U	V	Y	Yb	Zn	Zr									
1-5 mg/kg	Al	F	Mg	Nb	P	Pd	Pt	Se	Sn	Ta	Te	5-10 mg/kg	Hg	NO ₂	S	Si	10-55 mg/kg	Br	C	Cl	I	K	PO ₄	SO ₄							

Impurities¹ in Na₂HPO₄

≤ 1 mg/kg	Ag	As	Au	Ba	Be	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Ga	Gd	Ge	Hf	Ho	In	Ir	La	Li	Lu	Mg	Mn	Mo	Nb	Nd	Ni
	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	Sb	Sc	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	Y	Yb	Zr						
1-5 mg/kg	Al	B	Bi	Cl	F	Fe	S	Se	Si	Zn	5-10 mg/kg	Hg	10-55 mg/kg	Br	C	K	NO ₃	SO ₄													

Impurities¹ in Na₂SO₄

≤ 1 mg/kg	Ag	Al	As	Au	B	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Li	Lu	Mg	Mn	Mo	Nb
	Nd	Ni	P	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	Sb	Sc	Sm	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	Y	Yb	Zn	Zr			
1-5 mg/kg	Ca	Dy	Er	F	K	Se	Sn	5-10 mg/kg	NO ₂	10-55 mg/kg	Br	C	Cl	N	NO ₃	PO ₄	Si														

by HR-ICP-MS by ICP-OES by IC by carrier gas hot extraction/combustion analysis