

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] (%)	Purity _{DAA} - Purity _{CV}
Li ₂ CO ₃	99.984	0.081	99.996	0.020	-0.012
NaCl	99.986	0.082	99.981	0.015	0.005
KCl	99.987	0.081	100.009	0.005	-0.022
CaCO ₃ ^[5]	99.79	0.05	---	---	---
MgO ^[6]	60.19	0.02	---	---	---

The primary materials have to be dried prior to use as followed: NaCl and KCl for 10 h at 500°C, Li₂CO₃ for 4 h at 450°C, CaCO₃ for 3 h at 110°C and MgO for 1 h at 1000°C. Storage over anhydrous magnesium perchlorate (except CaCO₃ and MgO in a desiccator without drying agent)

Berlin, 19 December 2003



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- Detailed information about the measured content or detection limit of an individual trace impurity is available on request at EMPA.
- DAA = Difference analysis approach calculated by using the equation given under paragraph 1 of this report.
- 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 for Li₂CO₃, NaCl and KCl regarding non-detected impurities.
- CV = Content verification by coulometric determination of Cl in NaCl/KCl and acidimetric titration of Li₂CO₃.
- Certified reference material by Bundesanstalt für Materialforschung und -prüfung (BAM) and Verein deutscher Eisenhüttenleute (VDEh): CaCO₃ "Zertifiziertes Referenzmaterial Reinstoff Nr. 3, 99.79%; measurement uncertainty 0.05% (95% level)".
- Certified reference material by Bundesanstalt für Materialforschung und -prüfung (BAM) and Verein deutscher Eisenhüttenleute (VDEh): MgO "Zertifiziertes Referenzmaterial Reinstoff Nr. 6A, 60.19% Magnesium; measurement uncertainty 0.02% (95% level)".
- ISO Guide 31, 1-7, 1st Ed. (1981), "Contents of certificates of reference materials"

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 multication standard solution

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

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

Fluka product no.: 89316

Lot and filling code: 1265017, 10606285

Density at 22°C: $\rho = 998.2 \text{ kgm}^{-3}$ $u(\rho) = 0.2 \text{ kgm}^{-3}$

Intended use: This reference material is intended to be used for calibration of ion chromatography or any other analytical technique needing a calibration with cation 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 $22 \pm 2^\circ\text{C}$.

1. Certified values

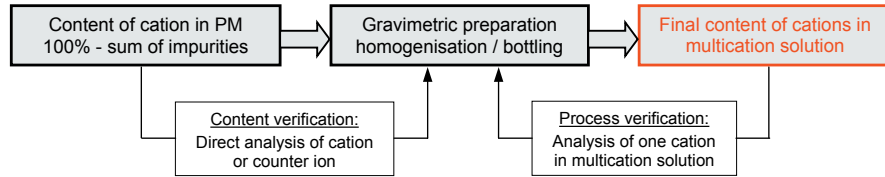
Certified value and uncertainty according to ISO Guide 35 ^[2] and Eurachem/CITAC Guide ^[3]		
Constituent (formula) ^[4]	Certified value	Combined expanded uncertainty $[U = k \cdot u_c; k = 2]$
Calcium (Ca ²⁺)	10.00 mg kg ⁻¹	± 0.02 mg kg ⁻¹
Lithium (Li ⁺)	10.00 mg kg ⁻¹	± 0.02 mg kg ⁻¹
Magnesium (Mg ²⁺)	10.00 mg kg ⁻¹	± 0.02 mg kg ⁻¹
Potassium (K ⁺)	10.00 mg kg ⁻¹	± 0.02 mg kg ⁻¹
Sodium (Na ⁺)	10.00 mg kg ⁻¹	± 0.02 mg kg ⁻¹

2. Concept of certification and traceability statement

The certified contents of cations (given as mass fractions) in this multication solution are calculated from gravimetric preparation values using **BAM/EMPA certified primary materials** (PMs, see page 4). The following basic materials are used: Li₂CO₃, NaCl, KCl, CaCO₃, MgO. The cation contents in the PMs (except CaCO₃, MgO) are calculated by subtracting the analyzed impurities from 100% (= difference analysis approach). The contents of CaCO₃ ("Zertifiziertes Referenzmaterial ZRM – Reinstoff Nr. 3") and MgO ("Zertifiziertes Referenzmaterial ZRM – Reinstoff Nr. 6A") are taken from certification reports by Bundesanstalt für Materialforschung und -prüfung (BAM) and Verein deutscher Eisenhüttenleute (VDEh).

A **content verification was performed at EMPA for all the PMs** (except CaCO₃, MgO) by high precision analysis of either the cation 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 by Sigma-Aldrich Production GmbH using high precision ICP-OES measurements of calcium in the bottled multication solution.



3. Gravimetric production of primary multication standard solution

Sigma-Aldrich Production GmbH produced the primary multication standard solution gravimetrically by dissolving certified PMs in **TraceSELECT™** Ultra hydrochloric acid and **TraceSELECT™** Ultra water (18.2 MΩ·cm, 0.22 μm filtered). The pH of the primary multication standard solution is 2.0 ± 0.1. 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 1100 precleaned 50 mL HDPE bottles were each filled under clean room conditions.

4. Calculation of cation content in multication standard solution

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

$W_{\text{PM}}, W_{\text{Soln}}$ Weighing values for primary material (PM) and solution
 $b_{\text{PM}}, b_{\text{Soln}}$ Air buoyancy correction factors for PM and solution
 f_{Cross} Correction factor for cation content from other PM (cross contamination)
 $w_{\text{Cation in PM}}$ Mass fraction of cation in PM
 w_{Cation} Final content of cation in multication 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 (≤ 0.05); 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 (0.01; only for Li₂CO₃). 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 ($w_{i,\text{found}}$), whereas for impurities ($w_{i,\text{unfound}}$) below the detection limit (DL), a contribution of half of the detection limit was considered. The contribution for not determined impurities ($w_{i,\text{nd}}$) 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 $u(w_{\text{PM}})$ are given below (where $w_{i,\text{found}}$ = mass fraction of found impurity i):

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

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

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.

Impurities^[1] in Li₂CO₃

≤ 1 mg/kg	Ag	As	Au	B	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	Ir	La	Lu	Mg	Mn	Nb	
	Nd	Pb	Pd	Pr	Pt	Re	Rh	Ru	Sb	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	Yb	Zn	Zr							
1-5 mg/kg	Ca	K	Mo	Ni	Rb	S	Se	5-10 mg/kg	Al	Na	NO ₃	P	10-50 mg/kg	Br	Cl	F	NH ₄	PO ₄	SO ₄												

Impurities^[1] in NaCl

≤ 1 mg/kg	As	B	Bi	Ce	Cr	Cs	Cu	Fe	In	La	Li	Lu	B	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 ₃	Pd	Si	Sn	SO ₄	Zn	10-55 mg/kg	Br	C	F	I	K	N	NO ₂	PO ₄	Se											

Impurities^[1] in KCl

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

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

Impurities^[1] in CaCO₃

An elaborately characterisation of this PM was made at BAM by difference analysis approach at the highest metrological level. All the trace impurities were determined by at least two different independent techniques. Detailed information is available at BAM (see footnote 5).

Impurities^[1] in MgO

An elaborately characterisation of this PM was made at BAM by difference analysis approach at the highest metrological level. All the trace impurities were determined by at least two different independent techniques. Detailed information is available at BAM (see footnote 6).