TraceCERT®
Traceable Certified Reference Materials

SIGMA-ALDRICH®

Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO Guide 34

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification: **Cation Calibration Standard for MARGA (Metrohm Air Monitoring Instrument)**

Product No.: 73638 Lot: BCBQ2744V

Composition: High-purity starting materials in 0.02% HNO_3 (prepared with HNO_3 suitable for trace analysis and high-purity water, 18.2 MΩ·cm, 0.22 µm filtered).

Density at 20°C: ρ = 998.3 kg m^{-3} $u_c(\rho)$ = 0.5 kg m^{-3}

Intended use: Calibration and quality control of Metrohm Air Monitoring Instrument (MARGA).

Storing and handling: This reference material shall be stored between 5 °C and 30 °C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.

Expiry date: **JUN 2017** (unopened bottle)

Certificate issue date: 20 JUL 2015

Bottle opening date: _____

Certified value traceable to SI unit kg and uncertainty according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]		
Constituent	Certified values at 20°C and expanded uncertainty [$U = k \cdot u_c$; k = 2]	
Ammonium (NH_4)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**
Calcium (Ca)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**
Lithium (Li)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**
Magnesium (Mg)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**
Potassium (K)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**
Sodium (Na)	**0.25 mg kg^{-1} ± 0.02 mg kg^{-1}**	**0.25 mg L^{-1} ± 0.02 mg L^{-1}**

1. Concept of Certification and Traceability Statement

To guarantee top reliability of the values for this *Trace***CERT**® certified reference material two independent procedures were followed. The values have to agree in the range of their uncertainties, but the value from the gravimetric preparation has been chosen as certified value [4]:

1. Gravimetric preparation using pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. If the purity of the materials is demonstrated and if contamination and loss of material is strictly prevented this approach allows highest accuracy and small uncertainties. The certified value of *Trace***CERT**® reference materials is based on this approach and directly traceable to the SI unit kilogram. Therefore comprehensively characterized materials of high purity are used. All balances are certified by DKD and calibrated with OIML Class E2 (up to 12 kg) and F2 (up to 64 kg) weights.
2. The starting material is measured against a certified reference material (i.e. NIST or BAM) followed by gravimetric preparation using balances calibrated with SI-traceable weights. Consequently the value calculated by this unbroken chain of comparisons is traceable to the reference to which the starting material is compared.

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2. CONTENT OF STARTING MATERIALS

For high purity materials (P >99.9%) the most appropriate way of purity determination is to quantify the impurities (w_i) and to subtract the sum from 100%. Impurities below the detection limit are considered with a contribution of half of the detection limit (DL_j).

$$P = 100\% - \sum_i w_i - \sum_j \left(\frac{DL_j}{2} \right)$$

Water containing materials were dried to absolute dryness by individual drying conditions (up to 600°C). When drying is impossible due to decomposition water was determined by high-precision KF-titration.

3. TRACEABILITY MEASUREMENTS

Only internationally accepted reference materials e.g. from NIST (USA) or BAM (Germany) have been carefully selected to provide the basis for traceability to the SI unit Mole. To underpin the certified gravimetric value all traceability measurements are performed with the most accurate and precise analytical technique available. Therefore titrimetry measurement series are applied whenever possible (corrected for trace impurities). When no titrimetric technique is available, the traceability measurements are performed with another analytical technique, e.g. ICP-OES or AAS.

Reference and applied technique used for traceability measurements of the starting material:

Constituent	**Starting material**	**Reference**	**Method**
Ammonium (NH_4)	NH_4Cl	NIST SRM 999	Argentometric titration
Calcium (Ca)	$CaCO_3$	NIST SRM 728	Complexometric titration
Lithium (Li)	Li_2CO_3	NIST SRM 924	ICP-OES
Magnesium (Mg)	$Mg(NO_3)_3$ x 6 H_2O	NIST SRM 728	Complexometric titration
Potassium (K)	KNO_3	NIST SRM 3141	ICP-OES
Sodium (Na)	$NaNO_3$	NIST SRM 3152	ICP-OES

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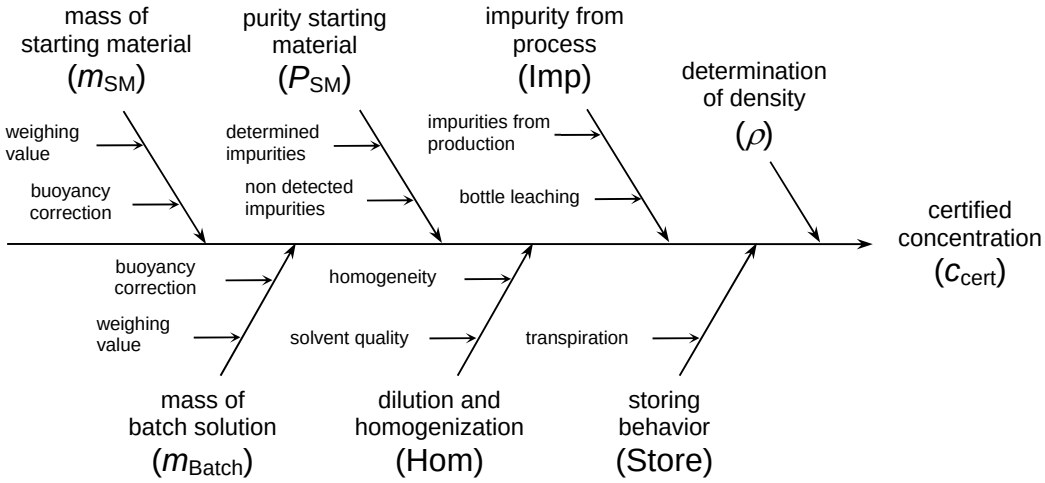
4. UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level.

The relative standard uncertainty from the individual gravimetric steps are below 0.01%, the uncertainty from dilution and homogenization is estimated to be less than 0.1%, the uncertainty of the analyte mass fraction for each starting material is below 0.1%, the uncertainty for storing behavior (transpiration of solvent through the HDPE bottle) is below 0.5% and the density measurement is performed with an uncertainty of 0.05%.

Due to the low analyte concentrations the major contribution for the combined measurement uncertainty adds from potential trace impurities from the overall process. This includes impurities from matrix materials (water and nitric acid), all production and filling steps and also leaching from the bottle into the solution. It is conservatively estimated to be less than 4%.

For this gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [5]:



CRM operations: S.Matt

S.Matt

Certification body: K.-D. Schmidt, Ph.D.

ISO Guide 34 **ISO/IEC 17025** **ISO 9001**

[1] ISO Guide 31:2000, "Reference materials - Contents of certificates and labels"
[2] ISO Guide 35:2006, "Reference materials - General and statistical principles for certification"
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), "Quantifying uncertainty in analytical measurement"
[4] Eurachem/CITAC Guide, 1st Ed. (2003) "Traceability in chemical measurement"
[5] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R. (2004), "The uncertainty of weighing data obtained with electronic analytical balances", Microchimica Acta 148: 133-141.

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