TraceCERT™
Traceable Certified Reference Materials

BAM

Certificate

Fluka
Riedel-de Haën®

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

Object of certification: **Nitrate, certified anion standard solution**

Fluka Product No.: 86576 (Lot 1311195)

Composition: $NaNO_3$ (high purity quality) diluted in water *Trace***SELECT**™Ultra (18.2 MΩ cm, 0.22 µm filtered)

Density at 20°C: ρ = 999.1 kg m^{-3} $u_c(\rho)$ = 0.5 kg m^{-3}

Intended use: Calibration of ion chromatography or any other analytical technique

Storing and handling: This reference material shall be stored in the original closed bag between 5 °C and 30 °C. After opening the bottle should be stored at reduced temperature. The bottle's temperature must be 20°C and the bottle has to be shaken well before every use. We highly recommend using this reference material no longer than 15 months after the aluminum bag was opened.

Expiry date: **25. May 2011** (unopened bottle in aluminized bag, latest use = exp. date + shelf life)

Bottle opening date: _____ (recommended shelf life after opening: 8 months)

Declaration of value and uncertainty according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]			
Constituent	Certified value at 20°C	Expanded uncertainty [$U = k\,u_c$; k = 2]	Methods of certification
Nitrate	**1001 mg L^{-1}** **1002 mg kg^{-1}**	**2 mg L^{-1}** **2 mg kg^{-1}**	gravimetric preparation and precipitation

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1. Concept of Certification and Traceability Statement

To guarantee highest reliability this certified reference material is certified by two independent certification bodies[4]:

1. Gravimetric preparation using pure materials is a practical realization of concentration units, through conversion of masses and mole fraction to mass fraction [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 this reference material is based on this approach and directly traceable to the SI unit kilogram. The starting material is measured against a certified reference material (i.e. NIST, BAM or EMPA) 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.

2. The bottled solution is certified by BAM (Federal Institute for Materials Research and Testing) using precipitation analysis. The measurements are traced directly to base SI unit: mass and mole.

3. Both values were combined for the certified value of this anion standard solution.

2. NITRATE CONTENT DETERMINATION

2.1 Nitrate content by gravimetric preparation

For high purity materials (*P* >99.9%) the most appropriate way of purity determination is to quantify the impurities (i,found) and to subtract the sum from 100%. Impurities below the detection limit (j,*DL*) are considered with a contribution of half of the detection limit (*DL*). Up to 75 trace impurities were determined in the high purity material using ICP OES, ICP-MS, AAS, IC and wet chemical methods.

$$P = 100\% - \sum_{i} w_{i,found} - \sum_{j} \left(\frac{DL_{j,DL}}{2} \right)$$

Sigma-Aldrich Production GmbH, Switzerland produced the nitrate standard solution by dissolving high purity $NaNO_3$ (content calculated as described above) in ultra-pure water (18.2 MΩ cm; 0.22 µm filtered). The starting material was dried for 8h at 290°C to absolute dryness and stored over magnesium perchlorate prior to use. Balances used for the gravimetric batch production 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 6 hours. A total number of 150 HDPE flasks were each filled with 100 mL of batch material under clean room conditions.

Nitrate content of the standard by gravimetric preparation	**1000.5 mg kg^{-1}**
Standard uncertainty u_{SIAL}	**0.04 mg kg^{-1}**

2.2 Nitrate content by precipitation analysis

This fundamental method connects the content (in fraction by mass) with the corresponding base SI units: mass and mole. The content of the solution was established by precipitating the nitrate as nitron-nitrate ($C_{20}H_{16}N_4$ x HNO_3) in acidified media at nearly boiling temperature [5]. Nitrate losses in the filtrate due to the solubility of nitron-nitrate were analysed by ion chromatography. The result is based on one determination of the content of each of the eighteen randomly chosen bottles.

Nitrate content of the standard by precipitation analysis	**1002.2 mg kg^{-1}**
Standard uncertainty u_{BAM}	**0.73 mg kg^{-1}**

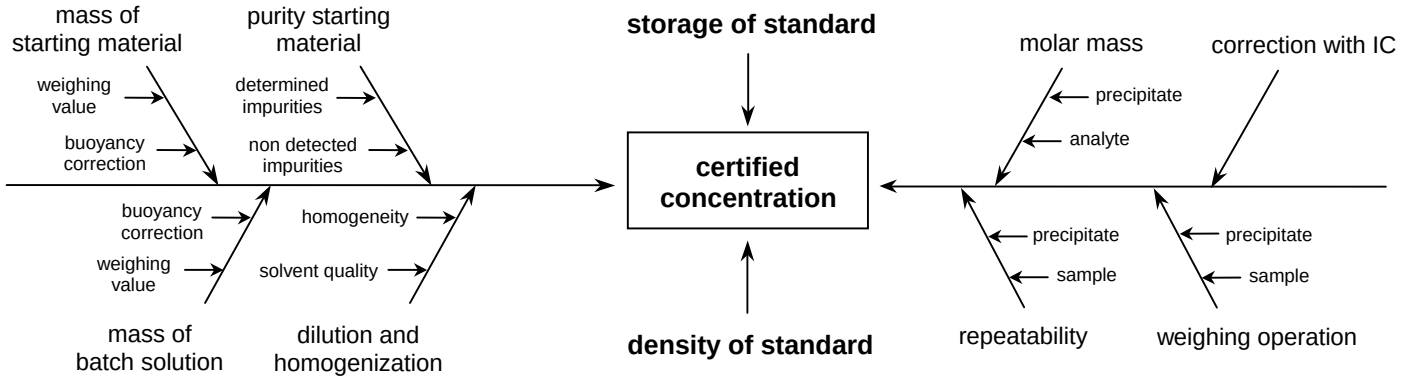
The certified value (CV) has been adjusted upward by 0.40 mg L^{-1} to compensate transpiration losses of solvent during the period of validity of the unopened bag (see also storage behavior).

CV = ($Value_{SIAL}$ + $Value_{BAM}$)/2 + transpiration losses = (1000.5 + 1002.2)/2 + 0.40 = 1001.8 mg kg^{-1}

CV (at 20°C) = 1001.8 mg kg^{-1} x 0.9991 kg L^{-1} = 1000.9 mg L^{-1}

2.3 UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide[3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation[6] and titrimetric measurements the uncertainty contributions are illustrated by the following cause-effect diagram:



gravimetric preparation by Sigma-Aldrich **precipitation analysis by BAM**

The uncertainty of the transpiration correction has been modeled as a uniform distribution covering a 4 year period of validity in which the maximum expected transpiration varies between 0 mg L^{-1} and 0.80 mg L^{-1}. The standard deviation is taken as having a rectangular distribution and therefore calculated as:

$u_{Transpiration} = 0.40 / \sqrt{3}$ mg L^{-1} = 0.23 mg L^{-1}

The combined standard uncertainty is calculated as:

$$u_c = \sqrt{u_{SIAL}^2 + u_{BAM}^2 + u_{Transpiration}^2} + u_{Bias} = \sqrt{0.04^2 + 0.73^2 + 0.23^2} + 0.20 * = \mathbf{0.97\ mg\ kg^{-1}}$$

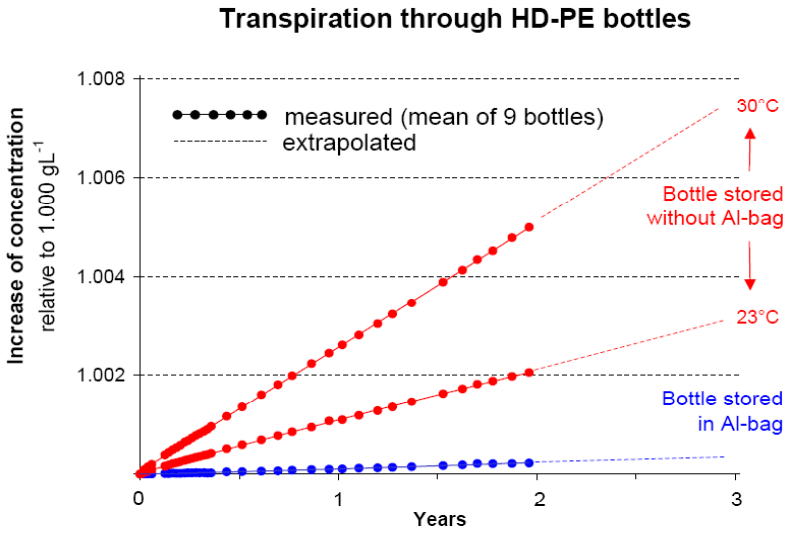
* : Systematic differences between methods are also taken into account.

3. Storing Behavior

The storage behavior of standard solutions is of greatest importance with regard to the certified value. Therefore the two most important effects were investigated by in-depth studies in a cooperation with EMPA, St. Gallen:

1. The leach out of trace impurities from HDPE bottles was determined with HR-ICP-MS by leaching the bottles with 2% nitric acid. Maximum contamination levels were found in the ng kg^{-1} level for 12 elements.

2. To avoid significant loss of mass through transpiration the bottle is delivered in aluminum coated bags. After the bottle has been removed from the bag, transpiration will occur at an accelerated rate (see figure). We highly recommend not opening the bag until the solution is needed. Once the bottle is opened the solution should be stored at reduced temperature to minimize transpiration.



4. Trace Impurities in Bottled Solution

The relevant anion impurities were determined with ion chromatography by Sigma-Aldrich, Buchs. The following anions were measured as possible impurities:

Chloride, Fluoride, Iodide, Nitrite, Phosphate, Sulfate	< 0.010 mg L^{-1} each
Bromide	< 0.050 mg L^{-1}

Berlin, 25. May 2007
BAM Berlin/Germany
Head of Division Inorganic Chemical Analysis;
Reference Materials

Dr. R. Matschat

Buchs, 25. May 2007
Sigma-Aldrich Production GmbH
R&D Manager

M. Weber

SQS Reg. No. 16368-02

[1] ISO Guide 31, 1-7, 1st Ed. (1981), "Contents of certificates of reference materials"
[2] ISO Guide 35, 1-64, 3rd Ed. (2006), "Reference materials – general and statistical principles for certification"
[3] Eurachem/CITAC Guide, 1-120, 2nd Ed. (2000), "Quantifying uncertainty in analytical measurement"
[4] Eurachem/CITAC Guide, 1-37, Draft Ed. (2003) "Traceability in chemical measurement"
[5] A. Hioki, T. Watanabe, K. Terajima, N. Fudagawa, M. Kubota and A. Kawase, Analytical Sciences (1990) Vol. 6, No. 5, p.757-762
[6] 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.