

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: **Antimony standard for ICP**

Fluka product no.: 73495 (Lot 1409574, Filling Code 53808197)

Composition: Antimony semimetal (high purity quality) in 2% HNO₃ and <0.1% HF (prepared from HNO₃ TraceSELECT[®], HF TraceSELECT[®] and water TraceSELECT[®] Ultra, 18.2 MΩ·cm, 0.22 μm filtered)

Density at 20°C: $\rho = 1009.9 \text{ kg m}^{-3}$ $u_c(\rho) = 0.5 \text{ kg m}^{-3}$

Intended use: Calibration of ICP-spectrometry, AAS, spectrophotometry 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 to minimize transpiration rate. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. We highly recommend using this reference material no longer than 15 months after the aluminum bag was opened.

Expiry date: **28. August 2012** (unopened bottle in aluminized bag)

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 value at 20°C ^[4]	Expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Antimony	999 mg L⁻¹	2 mg L⁻¹
	989 mg kg⁻¹	2 mg kg⁻¹

1. CONCEPT OF CERTIFICATION AND TRACEABILITY STATEMENT

To guarantee top reliability of the values for this TraceCERT[®] certified reference material three independent procedures were followed. The values have to agree in the range of their uncertainties, but the impurity corrected value from the gravimetric preparation has been chosen as certified value^[5].

1. Gravimetric preparation using pure materials is a practical realization of concentration units, through conversion of masses and mole fraction to mass fraction^[5]. 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 TraceCERT[®] reference materials is based on this approach and directly traceable to the SI unit kilogram.

Therefore comprehensively characterized materials of highest purity are used (see paragraph 2). 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 6 hours. A peristaltic pump with perfluorinated polymer tubings was used for bottling. Detailed information about the long-term stability of the bottled solution is given in paragraph 5 of this certificate.

2. 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.
3. Whenever applicable the bottled TraceCERT[®] calibration solution is compared to a second reference (e.g. from NIST, BAM or EMPA) which is independent from the first reference.

2. PURITY 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 under supervision of H. Hoffmann at Sigma-Aldrich Laborchemikalien, Seelze (Germany).

Water *TraceSELECT*[®] Ultra (18.2 MΩ·cm; 0.22 μm filtered, all metallic traces at ng kg⁻¹-level) and acid in *TraceSELECT*[®] quality was used for preparation.

3. TRACE IMPURITIES IN BOTTLED SOLUTION

Up to 75 trace impurities were determined with ICP-OES, ICP-MS and AAS. Some of the impurities are determined in the starting material and calculated for the solution (e.g. for rare earth elements contamination during the preparation is rendered impossible). Other elements are determined both in the starting material as well as in the bottled solution.

All values listed below are given in mg kg⁻¹ (ppm), <X = below detection limit, m = matrix, n.a. = not analyzed:

Li	Be												B	C	N	O	F	Ne
<0.010	<0.001												<0.050	n.a.	n.a.	n.a.	n.a.	n.a.
Na	Mg												Al	Si	P	S	Cl	Ar
<0.050	<0.005												<0.025	<0.10	<0.020	<0.010	n.a.	n.a.
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
<0.005	<0.010	<0.001	<0.010	<0.010	<0.025	<0.005	<0.050	<0.010	<0.050	<0.025	<0.010	<0.001	<0.050	<0.01	<0.010	n.a.	n.a.	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
<0.001	<0.005	<0.001	<0.050	<0.001	<0.010	n.a.	<0.001	<0.001	<0.001	<0.010	<0.005	<0.001	<0.050	m	<0.001	n.a.	n.a.	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
<0.001	<0.010	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.020	<0.001	<0.050	0.005	n.a.	n.a.	n.a.	
Fr	Ra	Ac																
n.a.	n.a.	n.a.																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			<0.005	<0.001	<0.001	n.a.	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001		
			Th	Pa	U													
			<0.001	n.a.	<0.001													

4. TRACEABILITY MEASUREMENTS

Only internationally accepted reference materials e.g. from NIST (USA), BAM (Germany) or EMPA – Material Science & Technology (Switzerland) have been carefully selected to provide the basis for traceability to the SI unit mole. When no such reference is available, an elemental metal or an adequate salt of highest available purity is used to confirm traceability to this pure material (and therefore to the SI unit kg).

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:

NIST SRM 3102a / ICP-OES

Reference and applied technique used for traceability measurements of the bottled solution:

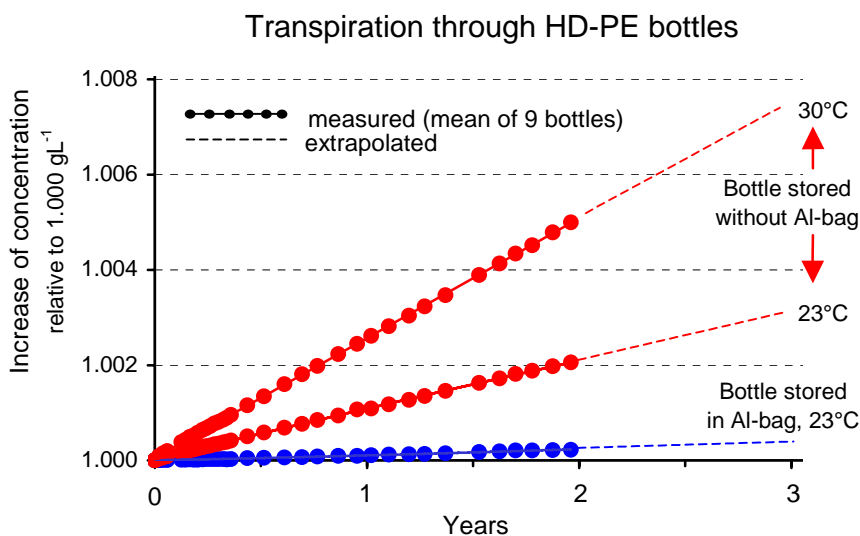
NIST SRM 3102a / ICP-OES

5. 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:

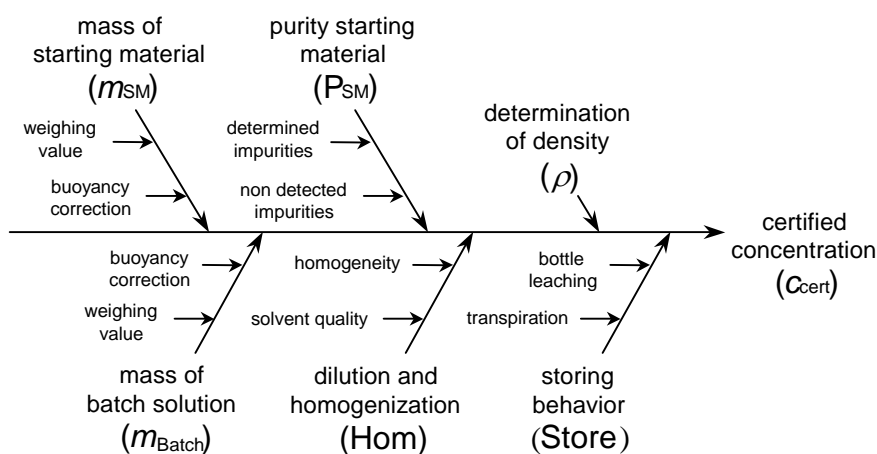
1. The leach out of trace impurities from HD-PE bottles was determined with HR-ICP-MS after leaching the bottles with 2% nitric acid. Maximum contamination levels were found in the ng L^{-1} level for 12 elements.

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 to open the bag until the solution is needed. Once the bottle is opened the solution should be stored at reduced temperature (4°C) to reduce transpiration.



6. 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 the uncertainty contributions are illustrated by the following cause-effect diagram [6]:



Typical contributions:

$u(m_{SM})$	< 0.01 %
$u(m_{Batch})$	< 0.01 %
$u(P_{SM})$	< 0.05 %
$u(H_{om})$	< 0.03 %
$u(Store)$	< 0.09 %
$u(\rho)$	< 0.05 %

Combined uncertainty [7]:

$$u_c(C_{cert}) < 0.1\%$$

Expanded uncertainty:

$$U(C_{cert}) < 0.2\%$$

Certification laboratory	Certification body	Date of release	Quality systems
 J. Wuethrich	 K.-D. Schmidt, Ph.D.	October 9 th 2008	

- [1] ISO Guide 31, 1-7, 2nd Ed. (2000), "Reference materials - Contents of certificates and labels"
 [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] The mg kg^{-1} value is the certified value whereas the mg L^{-1} value is calculated with the density
 [5] Eurachem/CITAC Guide, 1-37, 1st Ed. (2003) "Traceability in chemical measurement"
 [6] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R., "The uncertainty of weighing data obtained with electronic analytical balances", Microchimica Acta (2004) 148: 133-141.
 [7] Calculated by combination of the squared contribution values