

# Certificate

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

This certificate is designed in accordance with ISO Guide 31<sup>[1]</sup>.

Object of certification: **Citrate standard for IC**  
 Product no.: **96068**  
 Lot no. **BCBP1992V**  
 Composition: Citric acid (high purity quality) in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.  
 Intended use: Calibration of ion chromatography or any other analytical technique.  
 Storing and handling: This reference material shall be stored between 5°C and 30°C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25°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: **JAN 2018**  
 Certificate issue date: 18 FEB 2015  
 Bottle opening date: -----

The certified values and uncertainties are according to ISO Guide 35<sup>[2]</sup> and Eurachem/CITAC Guide<sup>[3]</sup>

Constituent	Certified value at 20°C and expanded uncertainty [ $U = k u_c; k = 2$ ]	
<b>Citrate</b>	<b>1'001 mg kg<sup>-1</sup> ± 4 mg kg<sup>-1</sup></b>	<b>1'000 mg L<sup>-1</sup> ± 4 mg L<sup>-1</sup></b>
Traceability <sup>[4]</sup>	NIST SRM 84i, Potassium Hydrogen Phthalate	

Measurand	Certified value and expanded uncertainty [ $U = k u_c; k = 2$ ]
<b>Density at 20°C</b>	<b>0.9988 g mL<sup>-1</sup> ± 0.0005 g mL<sup>-1</sup></b>

CRM operations: <i>S. Matt</i>	  
Certification body: <i>Klaus Ditsch Klaus</i>	
K.-D. Schmidt, Ph.D.	<b>ISO Guide 34</b> <b>ISO/IEC 17025</b> <b>ISO 9001</b>

## 1. CONCEPT OF CERTIFICATION

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetric production and from the analytical results determined using high-resolution quantitative NMR, which is recognized as primary measurement method.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance<sup>[4]</sup>. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025<sup>[5]</sup> and also ISO Guide 34<sup>[6]</sup>. Storage stability, leaching and homogeneity tests are also considered for certification.

## 2. STARTING MATERIAL CONTENT BY qNMR

The absolute content of starting material is measured by high-resolution quantitative NMR measurements on a Bruker 600 MHz Avance III NMR spectrometer.

The certification of the content is performed using 7 separate samples which are each spiked with an adequate amount of internal reference and then immediately dissolved in deuterated solvent. In most cases 16 scans are recorded for every sample with a 1H relaxation time of  $d1 = 60$  seconds. Quantification of the content is directly calculated from the 1H-NMR peak areas and the initial weights of the sample and reference substance. After ANOVA the resulting standard deviation is included into the uncertainty calculation of the certified value.

Extensive stability and homogeneity tests are considered for certification.

**Stability stress test** is performed with samples which are stored above the recommended storing temperature (mostly at 45 °C) and q-NMR double determinations after 1 and 3 months.

**Long term stability test** is performed with samples which are stored at the recommended storing temperature and q-NMR double determination after 3, 9 and 24 or 36 months.

**Homogeneity** of the material is tested by q-NMR measurements using 7 subsamples which are taken from different positions in the entire bulk material. The recommended minimal sample size is taken for all the homogeneity test samples. Analysis of variance (ANOVA) results are included into the calculation of content uncertainty of this CRM.

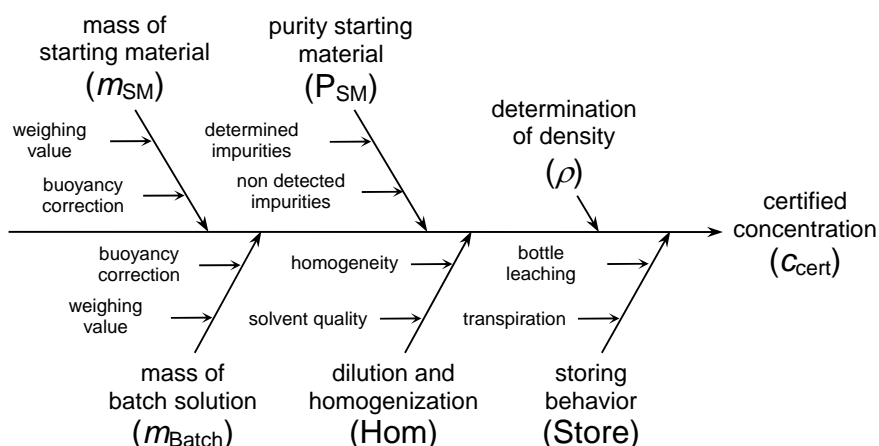
Starting material	Starting material content with expanded uncertainty	Traceable to
<b>Citric acid</b> P/N 94676 Lot BCBL8376V	<b>99.6 % ± 0.1 %</b>	NIST SRM 84I, potassium hydrogen phthalate

## 3. DENSITY MEASUREMENT

The density measurement is carried out according to ISO 15212-1<sup>[7]</sup> and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

## 4. UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide <sup>[3]</sup> 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 <sup>[8]</sup>:



Typical contributions:

$u(m_{SM})$	< 0.01 %
$u(m_{Batch})$	< 0.01 %
$u(P_{SM})$	< 0.05 %
$u(Hom)$	< 0.03 %
$u(Store)$	< 0.20 %
$u(\rho)$	< 0.05 %

Combined uncertainty <sup>[9]</sup>:

$u_c(C_{cert})$	< 0.2 %
-----------------	---------

Expanded uncertainty:

$U(C_{cert})$	< 0.4 %
---------------	---------

### References

- [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, 3<sup>rd</sup> Ed. (2012), "Quantifying uncertainty in analytical measurement"
- [4] Eurachem/CITAC Guide, 1<sup>st</sup> Ed. (2003) "Traceability in chemical measurement"
- [5] ISO/IEC 17025, 2<sup>nd</sup> Ed. (2005), "General requirements for the competence of testing and calibration laboratories"
- [6] ISO Guide 34:2009, "General requirements for the competence of reference material producers"
- [7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
- [8] 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.
- [9] Calculated by combination of the squared contribution values