Reliable analysis results in IC through traceability to certified reference materials

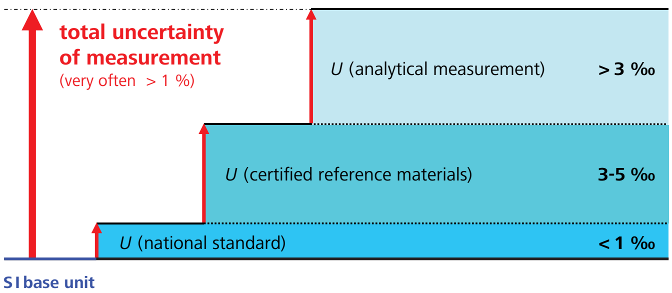
The International Prototype Kilogram, made of an alloy of platinum and iridium, is kept at the Bureau International des Poids et Mesures in Paris, France. Every determination of weight in the world relates ultimately to this cylinder under the two glass domes.

In a networked world, many companies use a variety of markets for raw material procurement and production. To make work with products and services safer, it is very important to set uniform standards and ensure they are put into practice. Because the philosophy of «tested once – accepted everywhere» has become established in many places, reliable and, above all, comparable measurement results are now more important than ever.

To ensure comparability of analysis results it is crucially important that the various measurements are based on internationally recognized reference materials or standards. The strategy of linking results to such standards is known as traceability. According to the «International Vocabulary of Basic and General Terms in Metrology»[1] traceability is defined as:

the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.*

To ensure the reliability of measurement results, recognized quality assurance standards (including ISO/IEC 17025, ISO 9001 and EN 45001) call for complete traceability of measurement results. For example, in the case of ISO/IEC 17025 (general requirements for test laboratories) the accreditation bodies require evidence of the traceability of measurement results to internationally recognized standards and, in addition, an indication of the measurement uncertainty.



In accordance with the definition of traceability, the extended measurement uncertainty U of an analysis result increases along the traceability chain.

*The term «standards» denotes metrological reference items, metrological reference materials or precise measuring instruments that are used to calibrate other measuring instruments.

The role of the metrological institutes

The national metrological institutes (NMIs) are responsible for ensuring that the seven base units of the International System of Units (SI = Système international) are adopted in their countries and that there is comparability of measurement results between the different countries (based on the Meter Convention of 1875). The provision of national standards and reference materials by the NMIs is therefore of crucial importance. There are some well-known NMIs, such as the National Institute of Standards and Technology (NIST) in the United States, the Bundesamt für Materialforschung und -prüfung (BAM) in Germany, the Institute for Reference Materials and Measurements (IRMM) in Belgium etc., which offer a wide range of reference materials of the highest possible metrological quality.

Practical implementation of traceability

Certified reference materials (CRM) play an essential role in analytical chemistry as reference points that can be traced back to an internationally recognized standard, such as the CRM of an NMI or, even better, directly to SI units. One appropriate way of achieving traceability to the SI system is to weigh high-purity, very well characterized compounds[2], since, with 100% purity, these constitute a natural reference value that cannot be exceeded.

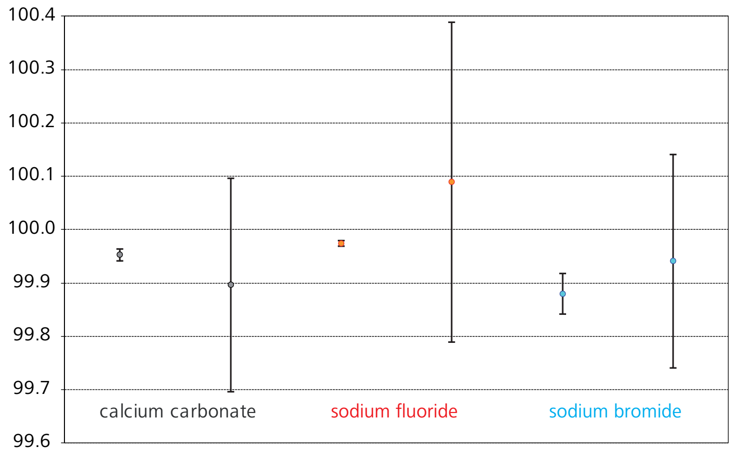
The following equation applies:

$$100\% - \sum w(I_{DET}) - \sum \frac{1}{2} \cdot DL(I_{ND}) - \sum w(I_{EST})$$

If, for example, the copper content in high-purity copper is to be determined (as the starting material for a copper standard solution), any method (titration, spectrometry, etc.) that establishes the copper content directly is much more inaccurate than the «100% minus traces» approach. Here the content of copper is calculated as 100% minus the sum of all impurities that are actually found (I_{DET}). For undetected impurities, half of the detection limit is estimated as the additional possible contamination and also subtracted (I_{ND}). Ultimately, if necessary, a contribution from unanalyzed (but possible) impurities is also estimated (I_{EST}) and subtracted. In certain metals these could be, for example, oxygen, nitrogen, hydrogen or noble gases.

Many manufacturers of ultrapure materials declare their products to be 99.999% pure, if they have found less than 10 ppm of impurities. The fact that the detection limits are in some cases very high or that a search has only been carried out for a few impurities is something they prefer not to mention. The use of such low-quality ultrapure materials can lead to measurement data incorrectly showing too high a content, so the effective content in the sample is in fact considerably lower.

The starting materials for the *Trace***CERT**® standard solutions from Sigma-Aldrich are analyzed for more than 70 metallic and ionic impurities at trace concentrations. For this, ICP-OES, ICP-MS, AAS and IC analytical methods are used as well as wet-chemical methods. The analyte content is calculated using the above formula. Additionally, the analyte in the starting material is measured directly against an internationally recognized reference (see graph below). This combination of the two content determinations leads to two independent traceability chains and thus to the greatest possible reliability of the starting materials used.



The value on the left in the particular color shows the content of *Trace***CERT**® starting material through calculation «100% minus all traces». The value on the right indicates the result from direct determination against a NIST reference material.

*Trace*CERT® standards for IC

In 2007, Sigma-Aldrich started developing new, improved calibration standards for ion chromatography and spectrometry. In this connection the name *Trace***CERT**® stands for certified reference materials of the highest quality. These reference materials also satisfy the requirements in highly regulated areas (GMP, ISO/IEC 17025, etc.), as they are produced and certified under ISO/IEC 17025 in combination with ISO Guide 34[3].

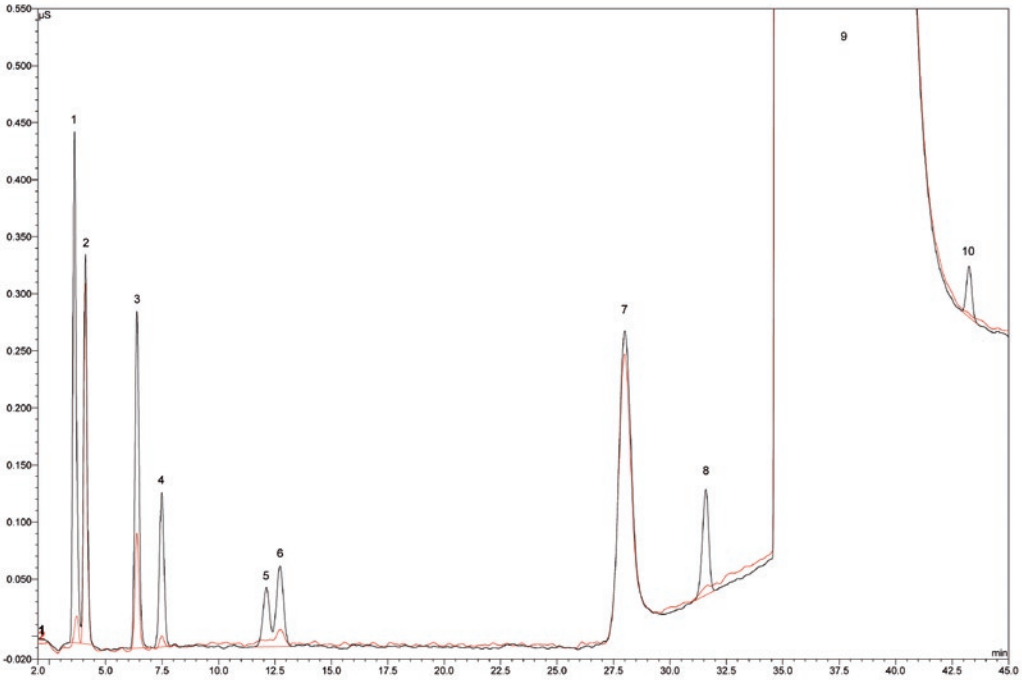
The CRM certificates for ion chromatography are issued according to ISO Guide 31[4] and contain, amongst other things, the following information:

- certified content (expressed in mg/kg and mg/L)
- measurement uncertainty (calculated according to international standard[5])
- traceability to internationally recognized references
- relevant trace impurities
- expiry date
- density
- composition, handling and storage

An up-to-date list of available *Trace***CERT**® reference materials for ion chromatography can be found at www.sigma-aldrich.com/tracecert.

Greater reliability through accreditation

Because most measurement results are influenced directly by the quality of the reference material through calibration, the choice of the appropriate CRM producer is a matter of trust. An important indicator of the technical and administrative expertise of a CRM producer is accreditation and inspection by an independent authority. Sigma-Aldrich Production GmbH in Buchs, Switzerland, is accredited by the Swiss Accreditation Service as a reference material producer in accordance with ISO Guide 34 (General requirements for the competence of reference material producers) and also ISO/IEC 17025 (general requirements for the competence of testing and calibration laboratories). This dual accreditation is described as the «gold standard» for CRM producers and represents the highest achievable level in quality assurance. So the conclusion is: you can always rely on the reference materials from Sigma-Aldrich!



The relevant trace impurities as well as the corresponding ion chromatogram are given in the cerificate supplied with a *Trace***CERT**® standard for IC.
Red line = anion chromatogram of an iodide standard (diluted to 200 mg iodide/kg).
Black line = sample spiked with 10 µg/kg of each anions: (1) fluoride, (2) acetate, (3) chloride, (4) nitrite, (5) bromide, (6) nitrate, (8) sulfate, (9) iodide, (10) phosphate; (7) system peak.

Literature

- [1] International Vocabulary of Basic and General Terms in Metrology (VIM = Vocabulaire international des termes fondamentaux et généraux de métrologie), 2008
- [2] Traceability in chemical measurement, Eurachem/CITAC Guide, 2003
- [3] General requirements for the competence of reference material producers, ISO Guide 34, 2000
- [4] Reference materials – contents of certificates and labels, ISO Guide 31, 2000
- [5] Quantifying uncertainty in analytical measurement, Eurachem/ CITAC Guide, 2000