*Trace*CERT™ – Traceable Certified Reference Materials. Part 4: Production, Handling and Storage of High-Precision Calibration Solutions ..... This is the fourth article of a series on Certified Reference Materials to appear in Analytix

By Michael Weber, Manager R&D Europe, Sigma-Aldrich Switzerland ... michael.weber@sial.com
and Jürg Wüthrich, Senior Scientist R&D Europe, Sigma-Aldrich Switzerland ... juerg.wuethrich@sial.com

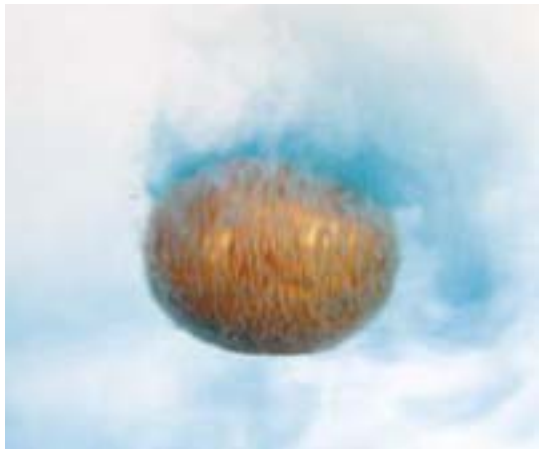

Figure 1 ..... Etching of high purity copper shot as an example for starting material pretreatment

In the last issue of this series on ***Trace*CERT**™ reference materials, we discussed the challenge of properly selecting and characterizing high purity starting materials [1-3]. Although the composition of the starting material is critical to produce highly accurate standard solutions, it can be even more challenging to get the starting material into solution. Neither loss of material nor contamination with trace impurities is allowed during the entire production process and during shipment and storage. The high-precision solution must arrive in the customer's hand with all the quality measures in terms of certified value, uncertainty and impurity specifications fulfilled. Consequently, only highly sophisticated equipment and well-defined production procedures make it possible to produce calibration solutions with uncertainties of 0.2%. Even the bottles and the packaging are important when these specifications are to be guaranteed over years of storage. The equipment used for the production of ***Trace*CERT**™ reference materials was designed by the Swiss Federal Institute for Materials Science and Technology (EMPA). EMPA used the equipment for the production of samples for interlaboratory comparisons at the highest metrological stage [4, 5]. When EMPA discontinued their metrological activities in 2005, Sigma-Aldrich Switzerland acquired this cutting-edge technology as well as their unique know-how.

Pretreatment of starting materials

With few exceptions (gold, palladium, etc.) the surface of all metallic starting materials are pre-cleaned by acid etching. Diluted ultrapure nitric acid or hydrochloric acid is used in most cases. The etched metal shots are transferred into high purity water through washing with water several times and transferred into acetone. Finally, the shiny metal shots are dried under argon. These procedures are all performed in a clean room environment to avoid contamination with dust.

When salts are used as a starting material, they normally are dried in large, flat-bottomed borosilicate glass or Vycor dishes under specified drying conditions. The air supply to the high temperature oven is connected to a clean room bench. The dried salt is then brought to room temperature in a desiccator over anhydrous magnesium perchlorate.

High precision weighing: More challenging than you might expect!

It goes without saying that high precision balances are essential tools for accurate weight measurements. However, the environment around the balance as well as operator technique and know-how are also of critical importance (**Figures 2, 3**) [6].

Figure 2 ..... High precision balances on a 1,000 kg granite weighing table with static discharge unit and climate monitoring instrument for air buoyancy correction

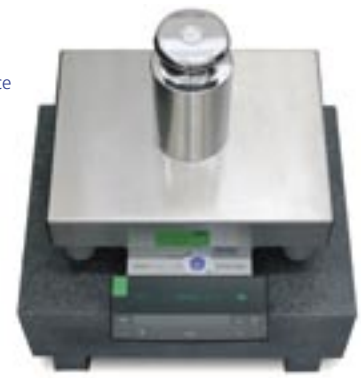

Figure 3 ..... High precision 64 kg balance with 0.1 g readability for batch weighing

For the gravimetric production of ***Trace*CERT**™ standards, we built a special weighing room. The balances stand on three-point supported granite tables weighing up to 1000 kg. Vibrations cannot affect the weighing results and maximum performance is therefore obtained from the balances.

Static electricity can be a source of weighing errors. Whenever possible we use aluminum rather than plastic vessels since the latter does suffer from problems associated with electrostatic discharge. Nevertheless, we still use a high voltage static charge dissipater to help ensure accurate weight measurement. This device is especially useful when weighing dry salts.

Ambient conditions also affect weighing accuracy. We closely monitor temperature, humidity and barometric pressure in the weighing room since these data are necessary to calculate the air buoyancy bias. Air buoyancy bias has to be taken into account since the balances are calibrated with reference weights having a density of 8000 kg/m^3 while many starting materials have higher or lower density. As a consequence, the displacement of air during calibration and sample weighing is different (calibration weights and sample do not displace the same amount of air because they do not have the same volume per mass ratio). The approximately 1.2 kg/m^3 density of air can affect the weighing result up to 0.1%. Since many ***Trace*CERT**™ standards are certified with 0.2% total uncertainty, the air buoyancy correction is of critical importance.

Of course, all the weighing data are directly traceable to the SI unit kg by calibration the balances with SI-traceable calibration weights. Only calibration weights fulfilling OIML class E2 and F1 are used to ensure highest quality of the weight measurements. Besides the normal calibration weights (density 8000 kg/m^3) we also have calibration weights with a density of 2760 kg/m^3 (anticorrodal). This allows us to double-check the air buoyancy correction.

All of the high-precision balances used to produce ***Trace*CERT**™ standards are on regular maintenance schedules, being periodically checked and calibrated by a third party and certified according to DKD guidelines. Only by maintaining all of these stringent conditions and continually improving our infrastructure can we cover full weight range from 1 mg to 65 kg with very low uncertainties.

Dissolving, homogenization and bottling

Every starting material is dissolved in high purity acid (mostly nitric or hydrochloric acid) following procedures specific for the material. This is important since the reaction behavior of metals can differ greatly from one metal to another. Some of the metals are passivated immediately by surface oxidation when they come into contact with concentrated nitric acid and the dissolution reaction is stopped. For example, nickel can be dissolved overnight in diluted nitric acid at higher temperatures while other metals, such as magnesium, are much more reactive and dissolution in concentrated acid leads to uncontrolled and vigorous aerosol formation. A loss of starting material would be the negative consequence. Metals showing such a dissolution behavior are normally dissolved very slowly in dilute acids followed by cooling for several hours. Since the already low acid concentration decreases during the dissolution process, the reaction is driven to completion by the addition of more concentrated acid to the stock solution at the end of the process. Obviously, all the dissolution reactions are done in totally inert bottles comprised of materials such as FEP or PFA.

After dissolution, the so-called stock solution containing the total amount of dissolved analyte is quantitatively transferred into a 65L PVDF container. While the mixing container is standing on the balance, the batch is filled with high purity water until the calculated total mass of the final solution is reached. This gravimetric approach allows a highly precise adjustment of the final concentration of the calibration solution. The solution is then homogenized by overhead tumbling of the PVDF container for several hours (**Figure 4**). With this technique it can be assured that the solution has no measurable inhomogeneity; this was demonstrated by EMPA in an in-depth study when this equipment was used for the preparation of samples for interlaboratory comparisons at the highest metrological stage [7].

Last but not least, the solution must be placed into the final container bottles without any contamination during the transfer process. This is accomplished by bottling the standards under clean room conditions using PTFE-tubing and an inert peristaltic pump.

Figure 4 .....
The 60L PVDF containers for overhead tumbling of ***Trace*CERT**™ standards guarantee the complete homogenization and ensure that no contamination from container wall into the solution and also no adsorption of analyte on the container wall can occur.

Storage and stability

The ideal container for standard solutions is totally inert, will not adsorb analyte, does not leach impurities into the solution, is impermeable toward the solvent and atmosphere, and is easy to handle and store. It is likely that no container material will ever meet all of these requirements and still be affordable. We found the most suitable material available today was high-density polyethylene (HDPE) bottles in combination with aluminum-coated bag typs, and chose them to bottle and package our ***Trace*CERT**™Ultra standards for ICP.

HDPE bottles fulfill the demand for the absence of trace contaminants; most elements cannot be detected even at ng/L concentration levels when the bottles are leached with 2% nitric acid. Some omnipresent contaminations (*e.g.* calcium and sodium ions) might be found at very low µg/L levels, which is not typically a problem for 1g/L standards. In the ***Trace*CERT**™Ultra standards, up to 70 trace impurities are specified in the certificate. The reported values for trace impurities include contributions from the starting material, the matrix (water, acid and/or base) and from leaching out of the container.

HDPE bottles are known to lose solvent through transpiration through the container wall. The rate and extent of loss depends on temperature, thickness of the wall, its shape and surface. Solvent is depleted more rapidly when the surface-to-volume ratio is high. Consequently, attention should be paid to storage conditions when small bottles are used. To avoid the loss of solvent from the 100 mL ***Trace*CERT**™Ultra bottles, we weld them into aluminum-coated bags. Only with this packaging technique can we guarantee the ambitious specification of 0.2% uncertainty for the certified value over the entire shelf life of the standard. The solvent transpiration rate of 100 mL HDPE bottles with and without the aluminum-coated bag at 23°C and 30°C has been investigated comprehensively during an EMPA study (**Figure 5**).

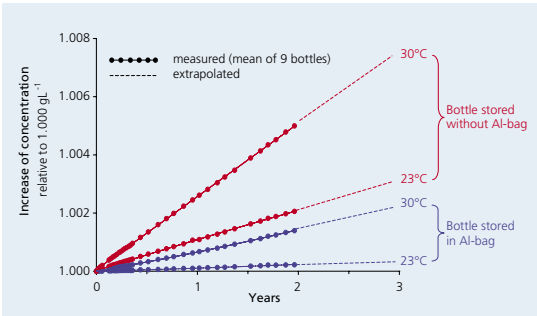

Figure 5 ..... Transpiration behavior of an aqueous calibration solution in a 100 mL HDPE bottle at different temperatures

During the preparation of this article, we realized that there are many more issues on which we could write. Many aspects of preparing high-quality reference materials that seem simple or irrelevant turn out to be of crucial importance. We hope that, through this series of four articles, we have shown how important it is to choose the right CRM supplier, one whose expertise and equipment are equal to the challenge of handling of sensitive raw materials and producing high purity standards suitable for today's sensitive analytical methods. CRM production really is a special task within the world of chemical reagents and standards. At Sigma-Aldrich, we are committed to meeting and exceeding your expectations as a quality CRM provider.

To view the ***Trace*CERT**™ line, please visit our web site: **www.sigma-aldrich.com/tracecert**

Figure 6 ..... Packaging of ***Trace*CERT**™Ultra standards for ICP to ensure ±0.2% expanded uncertainty for the certified value. Only when using specially selected Al-coated bags the specifications of the CRM can be guaranteed to have a shelf life of up to 4 years

References

[1] ***Trace*CERT**™ – Traceable Certified Reference Materials. Part 1: Swiss precision meets analytical competence. Analytix, Vol. 5, 2006.

[2] ***Trace*CERT**™ – Traceable Certified Reference Materials. Part 2: What uncertainty really means. Analytix, Vol. 1, 2007.

[3] ***Trace*CERT**™ – Traceable Certified Reference Materials. Part 3: Challenges in the characterization of high-purity starting materials. Analytix, Vol. 2, 2007.

[4] Felber H.; Weber, M. Final report on key comparison CCQM-K8 of monoelemental calibration solutions. Metrologia **2002**, 39, Tech. Suppl., 08002.

[5] Weber M., Wüthrich J., Key comparison CCQM-K29: Anion calibration solutions: final report. Metrologia **2006**, 43, Tech. Suppl., 08012.

[6] Reichmuth A., Wunderli S., Weber M., Meyer V.R., The uncertainty of weighing data obtained with electronic analytical balances, Microchimica Acta **2004**, 148 (3-4), 133-141.

[7] Weber M., Wüthrich J., High Precision Titrimetry, Ion Chromatography and ICP-Optical Emission Spectrometry for the Estimation of Inhomogeneities in Aqueous Calibration Solutions for Metrological Purposes, **2004**, 146 (2), 165-171