

## TraceCERT™ Traceable Certified Reference Materials. Part 1: Swiss Precision Meets Analytical Competence .....

This is the first of a series of articles on Certified Reference Materials (CRMs) to appear in the upcoming issues of Analytix

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### Sigma-Aldrich now brings metrological excellence directly to your lab

Due to the increasing demand for certified reference materials (CRM), Sigma-Aldrich established partnerships with several metrological institutes that serve as certifying bodies. For certified elemental and anion calibration solutions, we maintained a long-standing partnership with Swiss Federal Institute for Materials Science and Technology (EMPA). However, EMPA terminated all their activities in chemical metrology in 2004 and no longer acts as a national metrological institute.

Recognizing that EMPA's exit created the need for first-class CRM supplier in the market, Sigma-Aldrich made a strategic decision to acquire the metrological competency from EMPA and transfer it to our Buchs, Switzerland site. Cutting no corners, we began in 2005 to replicate the EMPA metrological environment in order to provide a seamless transition. First, we purchased from EMPA the unique equipment which was custom-designed to produce intercomparison samples of the highest metrological level. Second, we built a special, dedicated laboratory at the Buchs site where the high-precision weighing capabilities, homogenization and clean room

bottling equipment were installed. Third, and perhaps most importantly, we acquired technical know-how and experience by hiring two key EMPA personnel: the former Heads of EMPA's Metrological Reference and Certification Labs.

Now, barely a year after beginning the transfer of EMPA's competency to Sigma-Aldrich, we are proud to introduce the first CRMs developed and produced at our new Buchs facility: thirteen new TraceCERT™Ultra (ICP) and thirteen new TraceCERT™ (AAS) standards (**Table 1**).

### Buying analytical standards is a matter of trust

Any measurement is only as good as the reference standard used to calibrate the system. Although other components of the system contribute to the uncertainty of the analysis, the calibration and reference solutions also contribute. When the accuracy of your measurement matters, it is important to start every analysis with a fresh vial of the highest quality, certified reference or calibration standards. TraceCERT™ standards, an abridgment of Traceable and CERTified, meet these requirements and bring a wealth of security and reliability to your analytical results.

TraceCERT™ products are characterized by

- Unique (metrological) level of accuracy and lot-specific values
- Traceability to at least two independent references (i.e. NIST, BAM or SI unit kg)
- Certification according to ISO Guide 35
- Highest-purity starting materials available
- Comprehensive documentation including proper uncertainty calculation, expiry date and storage data
- Certificates of ICP standards list up to 70 trace impurities
- ICP standards packaged in light- and gas-tight aluminum foil bags
- Competitively priced

**Table 1** ..... Newly-available Fluka TraceCERT™Ultra calibration standards for ICP and TraceCERT™ calibration solutions for AAS\*

| Element   | Starting Material   | Cat. No.<br>TraceCERT™Ultra<br>ICP Standard | Cat. No.<br>TraceCERT™<br>AAS Standard |
|-----------|---|---|--|
| Aluminum  | Al(NO <sub>3</sub> ) <sub>3</sub> × 9H <sub>2</sub> O + HNO <sub>3</sub>          | 61935                                       | 39435                                  |
| Arsenic   | As <sub>2</sub> O <sub>3</sub> + NaOH + HNO <sub>3</sub>                          | 01969                                       | 39436                                  |
| Cadmium   | Cd metal + HNO <sub>3</sub>   | 36379                                       | 51994                                  |
| Calcium   | CaCO <sub>3</sub> + HNO <sub>3</sub>  | 19051                                       | 69349                                  |
| Chromium  | (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + HNO <sub>3</sub> | 68131                                       | 02733                                  |
| Cobalt    | Co metal + HNO <sub>3</sub>   | 30329                                       | 05202                                  |
| Copper    | Cu metal + HNO <sub>3</sub>   | 68921                                       | 38996                                  |
| Iron      | Fe metal + HNO <sub>3</sub>   | 43149                                       | 16596                                  |
| Lead      | Pb(NO <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub>                              | 41318                                       | 16595                                  |
| Magnesium | Mg metal + HNO <sub>3</sub>   | 30083                                       | 42992                                  |
| Mercury   | Hg metal + HNO <sub>3</sub>   | 28941                                       | 16482                                  |
| Nickel    | Ni metal + HNO <sub>3</sub>   | 28944                                       | 42242                                  |
| Zinc      | Zn metal + HNO <sub>3</sub>   | 18562                                       | 18827                                  |

\* ICP standards supplied in 100 mL HDPE bottles and sealed in an aluminum bag, including certificate. AAS standards supplied in 250 mL HDPE bottles, except for Hg which is bottled in 100 mL borosilicate white glass bottle.

**Special Offer: 50% off**  
on your first order on  
**TraceCERT™Ultra ICP Standards**

Please quote promotion code T98 when placing your order.  
Valid until January 31<sup>st</sup> 2007.

**Figure 2** .....  
Example of Zinc  
*TraceCERT™Ultra*  
certificate (front  
page out of three  
pages)



Our well-defined approach to CRM production leads to multiple-traceability and, as a further benefit, ensures that significant biases and systematic deviations are excluded to the fullest extent possible.

#### The rationale behind this series of CRM articles

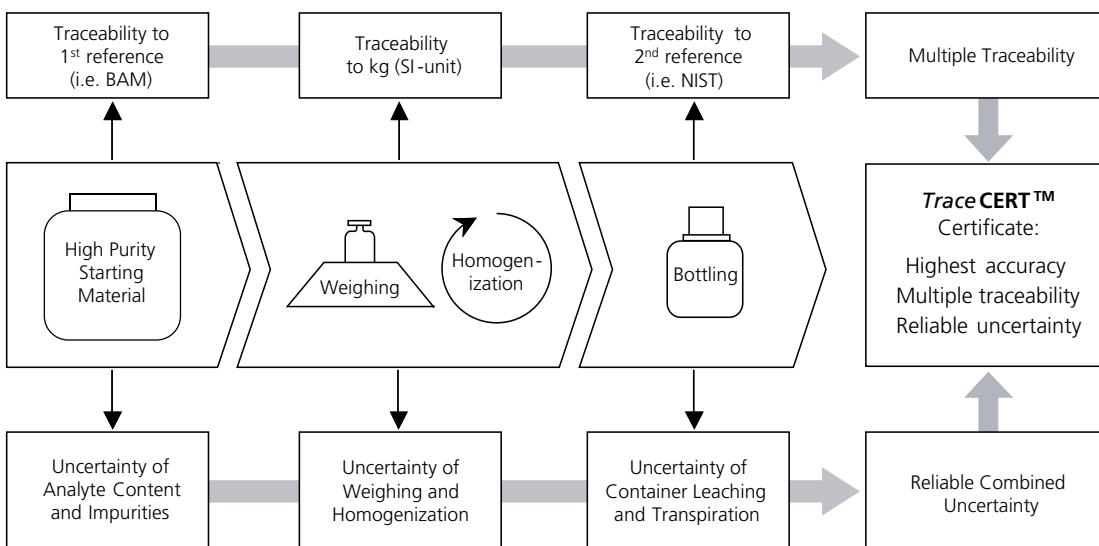
There is much confusion and many misconceptions over traceability, uncertainty calculation and the proper use of reference materials. In the next six issues of *Analytix*, we will attempt to enlighten interested readers on the meaning behind important CRM-related terms and concepts, including

- What does traceability really mean?
- The proper method to calculate uncertainty
- Characterization and purity statement of high-purity starting materials
- Production, liquid handling and packaging on a metrological level
- Certification and accreditation
- Certification of custom standards

To actually produce CRMs that meet all these criteria, the entire development process, beginning from the selection of an appropriate starting material to the choice of a purpose-specific packaging, must be highly sophisticated. **Figure 1** (see below) shows an overview of the production and certification process we employ. Not only is the bottled solution compared to a reference material (NIST, BAM, etc.), the starting material is checked against a second, independent reference. A key step is that the weighing operation leads to direct traceability to the SI unit kilogram. Gravimetric preparation using pure materials is a practical and, in many cases, the most accurate calculation of concentration units, through conversion of mass and mole fraction to mass fraction. As a final step, we provide detailed, lot-specific information in the Certificate of Analysis supplied with every *TraceCERT™* product (**Figure 2**).

Our intention with these articles is to clearly demonstrate that the technical experts at our new facility in Buchs are firmly grounded in the science behind the production of high-quality analytical reference materials. This is the reason why we link our *TraceCERT™* line with the image of high-precision Swiss chronographs (courtesy of IWC Schaffhausen).

We realize that buying and using analytical standards is a measure of your trust in the supplier. In the upcoming series of technical articles, we hope to answer most of your questions about certified reference materials.



**Figure 1** ..... Schematic representation of the production design and certification of Sigma-Aldrich *TraceCERT™* products. This approach was established for the preparation of intercomparison samples at the highest metrological stage.

## TraceCERT™ – Traceable Certified Reference Materials. Part 2: What Traceability Really Means .....

This is the second article of a series on Certified Reference Materials to appear in Analytix

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Figure 1 .....

The international prototype of the kilogram, an artifact made of platinum-iridium, is kept at the International Bureau of Weights and Measures in Paris.



### Establishment of SI units and NMIs: A historical perspective

Prior to standardization of weights and measures, enormous variation existed between nations, regions and even individual vendors. For example, in earlier times people could not get the same amount of potatoes when they bought them at different market stands because there was not an established reference for mass. The situation between nations became very confusing, and resulted in the Meter Convention being signed in Paris in 1875 by seventeen nations [1]. The purpose of this treaty was to ensure world-wide uniformity of measurements and their traceability to the International Systems of Units (SI), ultimately established in 1948. Today, fifty-one member states signed this diplomatic treaty. After the adoption in 1954 of the first six base units, the mole was introduced in 1973 as the base unit for amount of substance. Currently, all units of measurement on earth are derived from this set of seven base units (Table 1).

Table 1 ..... The seven base units of the International Systems of Units (SI)

| Property            | Base Unit | Symbol |
|---------------------|-----------|--------|
| Mass                | Kilogram  | kg     |
| Length              | Meter     | m      |
| Time, Duration      | Second    | s      |
| Electric Current    | Ampere    | A      |
| Temperature         | Kelvin    | K      |
| Luminous Intensity  | Candela   | cd     |
| Amount of Substance | Mole      | mol    |

To provide oversight, each member country established a National Metrological Institute (NMI), one per country with a few exceptions. NMIs have responsibility within the respective country for the realization of SI base units and to ensure comparability of measurement results between the member nations. The supply of national standards and reference materials is therefore of crucial importance. Although there are many NMIs that provide the highest level of reference materials and certification services, perhaps the most well-known are the US National Institute of Standardization and Technology (NIST), the European Institute of Reference Materials and Measurement (IRMM) and the German Federal Institute for Materials Research and Testing (BAM).

### Metrological background of the traceability concept

The International Vocabulary of Basic and General terms in Metrology (VIM) defines traceability 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* [2].” Analysts often report their results as traceable to NIST or to another NMI. This is not literally correct, for, as one consequence of the above definition of traceability, a measurement result is not traceable to an NMI but to a reference material certified by an NMI. Because of the Mutual Recognition Arrangement (MRA) a certified reference material issued by one NMI (e.g. NIST SRM 915, CaCO<sub>3</sub>) must always be comparable, within the stated degree of equivalence, to a second NMI (e.g. BAM RS3, CaCO<sub>3</sub>). One is not more traceable than the other.

### Practical realization of traceability in chemistry

Compared to other base units there is one big difference in the realization of the mole: there is no extant prototype of the mole since it is defined as a multiple of the mass of carbon-12 atoms! So how can we realize traceability in chemistry in practice? Traceability to the SI system can be achieved by traceability to one of the other six base units. Such measurements are called „primary methods.“ The following methods are accepted as primary: isotope dilution with mass spectrometry (IDMS), coulometry, gravimetry, titrimetry and determination of freezing point depression [3]. The result of a primary method (analytical technique) is not expressed in moles but in one of the other six base units.

Coulometry, for example, gives a direct traceability from the amount of a certain species (i.e. the analyte concentration in a solution) to the SI base unit ampere.

Another appropriate way to achieve traceability to the SI system is by the weighing of high purity compounds. This follows from an almost unique feature of chemical measurement: 100% purity forms a natural reference value which cannot be exceeded. Coupled with widely available and excellent reference data for atomic and molecular weight, and often with additional data on physical parameters such as density, a high purity

material represents a local, practical realization of concentration units through conversion of mass to molar quantity. Calibration with materials of well-established purity is accordingly a valid means of establishing traceability [4].

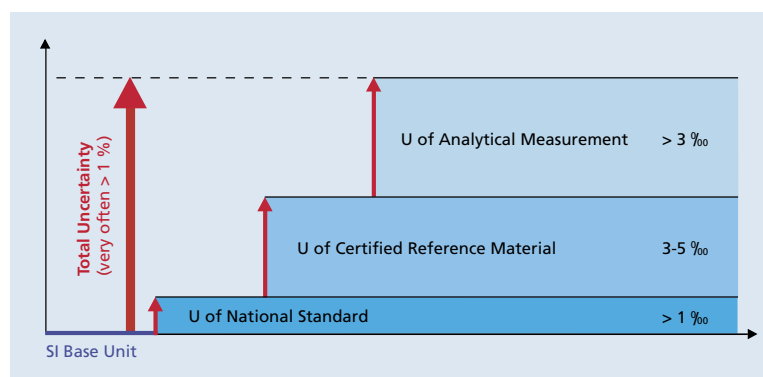
### Key comparisons and the limits of analytical measurements

In addition to the supply of reference materials, it is also important to evaluate the trans-national comparability of measurement results. Toward this end, periodically the NMIs are invited to participate in so-called Key Comparisons. Key Comparisons are proficiency tests, also called round robin tests, on the highest metrological stage. Only NMIs are invited to participate.

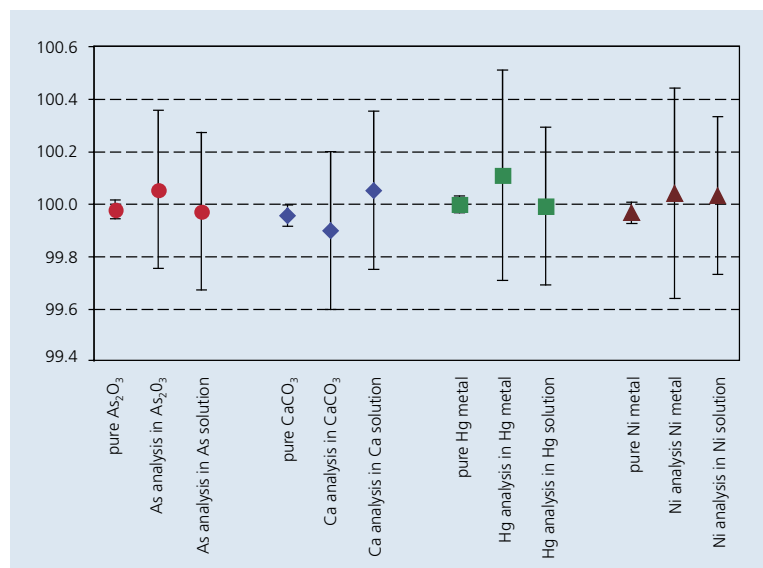
Since the results of these intercomparisons represent national measurement capabilities, the NMIs often expend intense effort in terms of technical equipment and time employing multiple techniques and many replicates. As a consequence, a single result from such a high precision measurement often takes days or weeks.

Round robin results are posted by the Bureau International des Poids et Mesures (BIPM) at <http://kcdb.bipm.org>. A closer look into this database reveals the limits of analytical measurements for many different applications [5-7]. For simple analytical tasks (matrix-free elemental or anion solutions at 1 g/L) the uncertainties of the NMIs are in the range of 0.1-0.4%, with the best values having uncertainties below 0.05%. It is important to remember that these data are collected at the highest metrological stage, which you certainly do not want to pay for when buying a simple elemental standard! Ergo: With very few exceptions it is quite normal to obtain combined, expanded uncertainties of 0.5% and higher under ordinary laboratory conditions (Figure 2).

**Figure 2** ..... Increasing uncertainty along the traceability chain. When individual parts of an uncertainty budget are calculated together analysts end up easily with a measurement uncertainty of >0.5%.



**Figure 3** ..... Examples of the purity of *TraceCERT*<sup>™</sup> starting materials (arsenic trioxide, calcium carbonate, mercury and nickel metal) determined by calculation 100% minus all traces (analyzed using ICP-MS, ICP-OES, AAS and IC). The values “X analysis in X” show the purity of the starting materials by direct titrimetric measurement traceable to NIST SRM. The values “X analysis in X solution” show direct titrimetric measurements (traceable to BAM CRM) of *TraceCERT*<sup>™</sup> standard solutions and are relative to the certified content of the gravimetrically-produced standard.



### The new „triple traceability“ approach with *TraceCERT*<sup>™</sup>

There are many approaches to establish traceability to different reference standards in analytical chemistry. For *TraceCERT*<sup>™</sup> reference materials and calibration standards, we decided to establish a new concept called “triple traceability.” Standards made according to this concept are characterized by independent traceability chains to three different references (Figure 3):

#### *Traceability chain No. 1:*

The starting material is measured against a certified reference material (e.g. NIST) followed by gravimetric preparation of the solutions 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.

#### *Traceability chain No. 2:*

The bottled **TraceCERT™** solution is directly compared to a second reference (e.g. BAM or EMPA) which is independent from the first reference.

#### *Traceability chain No. 3:*

Since only comprehensively characterized starting materials of highest purity are used (>70 trace impurities checked in **TraceCERT™**) the calculation of the gravimetric value using the molar mass of the analyte leads to direct traceability to the SI base unit kilogram. As previously discussed, this value is the most accurate; uncertainties of less than 0.2% can be achieved only with this method. Of course, during the preparation of all **TraceCERT™** solutions we prevent material loss and contamination and all balances are certified by DKD (Deutscher Kalibrierdienst) and calibrated with OIML (International Organization of Legal Metrology) Class E2 (up to 12 kg) and F1 (up to 64 kg) weights.

Last but not least, an analysis of variance (ANOVA) is made with the whole dataset. Only when all the values overlap is the **TraceCERT™** batch certified. Further details about the uncertainty calculation and traceability concept are found in the certificates of analysis provided with our **TraceCERT™** products, an example of which is shown in **Figure 4**.

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**Figure 4** .....

Packaging and certificate of analysis included with the new **TraceCERT™**Ultra (ICP) standards. Certificates for **TraceCERT™** (AAS) solutions are available as internet downloads.

**Special Offer: 50% off**  
on your first order on  
**TraceCERT™**Ultra ICP Standards

Please quote promotion code X91 when placing your order.  
Valid until April 30<sup>th</sup> 2007.

An up-to-date list of **TraceCERT™** standards can be found at [www.sigmaaldrich.com/tracecert](http://www.sigmaaldrich.com/tracecert)

## TraceCERT™ – Traceable Certified Reference Materials. Part 3: Challenges in the characterization of high-purity starting materials ..... This is the third article of a series on Certified Reference Materials to appear in Analytix.

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**Figure 1** .....  
Selected high purity  
metals as starting  
materials for  
TraceCERT™ standard  
solutions



### How to determine >99.9% purity

In the last article of this series about CRMs (Certified Reference Materials) we discussed the almost unique feature of chemical measurement that a 100% pure material would form a natural reference value which cannot be exceeded [1, 2]. Therefore, the calibration with high purity materials is accordingly a valid method of establishing traceability in analytical chemistry [3]. It goes without saying that with this traceability approach, a comprehensive characterization of the starting material is of crucial importance. So, when a chloride reference is made from sodium chloride, the exact sodium content of the salt can be determined with very high accuracy. However, the purity determination of a substance with more than 99.95% purity (salt or metal)

requires an analytical method with much less than 0.05% measurement uncertainty. This is practically impossible for most analytical techniques.

As a consequence, the common sense method for characterization of high purity materials is the so-called impurity approach whereby as many impurities as possible are measured in a certain material by as many different analytical techniques as necessary. The sum of all the impurities (and also the contribution from the potential impurities below their detection limit) is then subtracted from the maximum purity of 100%. With this approach, it is possible to assign a reliable purity statement to high purity materials, even for very high purity grades (>99.99 %). Of course, this approach gives reliable results only when much effort is put into the impurity investigations. For example, it makes no sense to look for the thirty most common metallic impurities in a high purity sodium chloride, while at the same time overlooking the major impurities, bromide and water. How the various types of impurities contribute to the overall starting material purity is diagrammed in **Figure 2**.

### From m6N to t3N materials or about apples and oranges

When considering high purity materials, one should always look closely at the details, especially how the purity is defined. The following nomenclature has been established: When a material is assigned to be >99.99% pure based on metallic impurities only, this is declared as an m4N material. Here, the „m“ signifies that only metallic impurities are identified, and the “4N” stands for the „four nines“ (99.99%) purity of the material. In some cases, such „m-characterized“ materials are also defined as „metals base.“ It is important to remember that the number of investigated elements is of great importance. All too often, certificates of analyses report only a very few number of trace metals.

A more reliable purity statement is provided when not only metallic impurities are identified, but also nonmetals, anions, oxides and residual water. In this case a „t“ (for total) replaces the „m“ (for metals only). It should come as no surprise that in many cases the reported purity (number of nines) is lower when the sum of all impurities, not only the metals, is reported. A material declared as a 99.9999% (m6N) purity can be

**Table** ..... Selected starting materials used for TraceCERT™ standard solutions

| Starting material | Purity (%) | Uncertainty (%) | Detected major impurities (ppm)                |
|-------------------|------------|-----------------|--|
| NaBr              | 99.881     | 0.052           | Cl (932), K (44), F (43), SO <sub>4</sub> (23) |
| NaCl              | 99.980     | 0.015           | K (5), Br (30)                                 |
| CaCO <sub>3</sub> | 99.954     | 0.033           | Sr (44), Mg (40), Na (36)                      |
| Zinc metal        | 99.975     | 0.012           | K (5)  |
| Cobalt metal      | 99.951     | 0.018           | Ni (420), P (30), Fe (5), Sn (5)               |
| Magnesium metal   | 99.991     | 0.010           | Zn (40), Mn (18), Fe (10), Al (9)              |

„downgraded“ to a 99.9% (t3N) when also taking nonmetal impurities into account [4]. Of course, the total impurity approach requires more analytical effort and is more costly. On the other hand, the approach leads to greater reliability.

When we source high quality starting materials for **TraceCERT™** calibration solutions, we often find that the purity is actually lower than what is reported on the supplier's certificate of analysis. This is due to the fact that manufacturers typically test for only a few impurities, and the contribution of nonmetals and anions to purity is often overlooked. We have concluded that it is not a trivial pursuit to find starting materials on the market with accurately reported purity values of >4N or >5N.

### Challenges particular to high purity salts and metals

There are many challenges and also knock-out criteria during the process of evaluating and choosing appropriate starting materials.

#### Problem No. 1: Water

When using NaCl as the starting material for a chloride calibration solution, drying at 110 °C for 4 hours followed by cooling over anhydrous magnesium perchlorate is not sufficient to ensure complete dryness of the salt. Investigations with TGA-MS show that only above 450 °C does NaCl completely lose its water. Since the amount of water can be as high as 20,000 ppm (0.2%), failure to remove it has a significant impact on the purity results. To guarantee complete dryness, NaCl has to be dried at 500 °C for at least 4 hours [5].

#### Problem No. 2: Stoichiometry

Na<sub>2</sub>HPO<sub>4</sub> is used as starting material for phosphate calibration solutions. During the evaluation of a



Just as with high-precision watches, our CRM customers expect attention to detail in all quality parameters.

particular batch of Na<sub>2</sub>HPO<sub>4</sub>, HR-ICP-MS, ICP-OES (for metals), TGA-MS (for water), IC (for anions) and combustion analysis (for carbon) were used to measure purity. Even though 73 different impurities were identified, one significant impurity was missed. When a second IC method was run, significant levels of the dihydrogen analog, NaH<sub>2</sub>PO<sub>4</sub>, were found in the starting material. This affected the total content of phosphate in the starting material due to the different stoichiometry of the impurity.

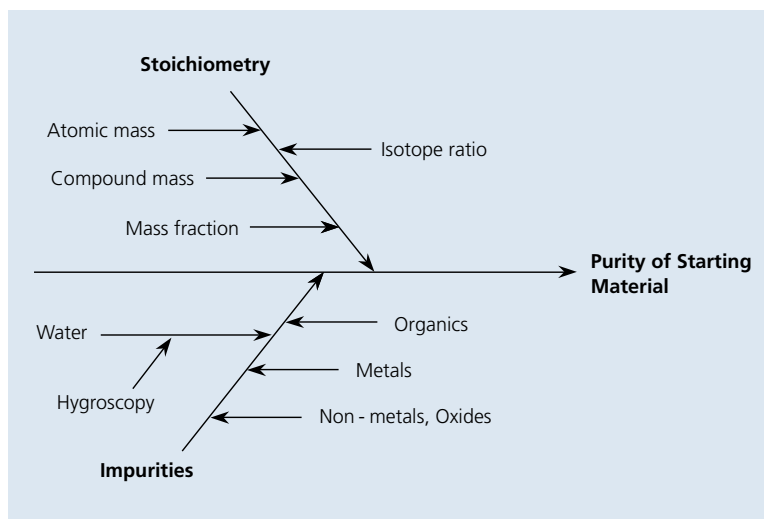
#### Problem No. 3: Isotope ratio and atomic mass

Most elements, rather than being naturally monoisotopic, exist in a natural isotopic ratio. Since this ratio is not constant, it leads to significant variation in the atomic mass for different materials. The most important example might be lithium where the natural isotope ratio of <sup>6</sup>Li to <sup>7</sup>Li is approximately 7.6% to 92.4%. When using Li<sub>2</sub>CO<sub>3</sub> as a starting material for a lithium calibration solution, this can lead to variation of the Li content up to 0.6% in the final solution.

#### Problem No. 4: Oxides

With pure metal starting materials, it is usually necessary to take into account oxide impurities. Oxygen, often at a few hundred ppm but rarely exceeding 1000 ppm, is found associated with many high purity metals. In terms of the „tXN“ nomenclature, this means that a t4N purity (>99.99%) is mostly not possible unless the standard is produced under an inert, oxygen-free atmosphere. On the other hand, for certain types of metals the content of oxide impurities is not relevant. However, more often than not their existence must be considered. Since the quantitative determination of oxide impurities in metals is rather difficult, it may be acceptable to not account

**Figure 2** .....  
Visualization (cause-effect diagram) of relevant contributions to starting material purity



for the oxygen content itself, but to introduce an estimated contribution into the uncertainty budget of the purity calculation.

#### Implications for the evaluation of *TraceCERT*<sup>TM</sup> starting materials

The problems outlined previously drive home a few important lessons with regard to evaluating high purity starting materials.

1. Whenever possible and feasible, choose a pure metal over a salt as a starting material. Metals avoid problems with stoichiometry, residual water and hygroscopy. Also, because of their manufacturing process, metals normally do not contain appreciable amounts of nonmetallic, anionic or organic impurities. Another advantage of using metals is that they can be weighed more easily than salts and powders and there is no risk of electrostatic discharges during the weighing step. Even if the surface leaching and the dissolution of metals in acids take longer, using pure metals normally leads to higher accuracy.
2. If a salt must be used as a starting material, it is of utmost importance to eliminate all of the above-mentioned problems. Check for traces of residual water, control hygroscopy, know the stoichiometry and conduct comprehensive analysis of metallic, nonmetallic and anionic impurities. With this information, it is possible to properly characterize the salt. However, for the above-mentioned reasons, high purity salts tend to have higher uncertainties than metals.

#### *TraceCERT*<sup>TM</sup> purity assurance

Each starting material undergoes specific pre-treatment procedures. For metals this usually involves pre-cleaning with several different solvents followed by acid etching of the surface and drying over an argon atmosphere. Non-metallic compounds such as salts, carbonates, oxides, etc. are dried by individual drying procedures before the high-purity material is brought to the high-precision weighing room.

$$\text{Purity} = 100\% - \sum w(I_{\text{measured}}) - \sum \frac{1}{2} \cdot \text{DL}(I_{\text{unfound}}) - \sum w(I_{\text{estimated}})$$

**Figure 3** ..... Equation for the calculation of a purity statement of high-purity materials: Quantified impurities expressed as mass fraction (*w*) are subtracted from 100% (*I<sub>measured</sub>*). In addition, contributions for „investigated but not found“ impurities (those below detection limit, *I<sub>unfound</sub>*) and expected but not investigated impurities (*I<sub>estimated</sub>*) are considered in the purity assessment. This conservative approach leads to more reliability and surety of *TraceCERT*<sup>TM</sup> calibration standards and reference materials.

For most of the *TraceCERT*<sup>TM</sup> starting materials, more than 70 metallic impurities are analyzed using either ICP-OES or ICP-MS in combination with AAS with flame or hydride generation. In addition, several anions are determined using ion chromatography or wet chemical methods. Water-containing materials are dried to absolute dryness by individual drying conditions up to 600 °C. When drying is impossible due to decomposition, water is determined by high-precision KF-titration.

The purity of the material is calculated as 100% minus the sum of the impurities that are actually found (*I<sub>measured</sub>*). For non-detected impurities, a contribution of half of the detection limit is estimated and also subtracted (*I<sub>unfound</sub>*). Last but not least, an estimated contribution (also as a mass fraction) by impurities that were not investigated is also considered (*I<sub>estimated</sub>*).

Classification of materials by this conservative method (**Figures 2 and 3**), may yield pessimistic purity results and the purity may be actually higher than reported. Consequently, only very few materials are found on the market with a proven purity of more than 99.9% (t3N). However, for reference materials, the reliability of the certified value is the most important issue and we therefore decided to apply this approach for all *TraceCERT*<sup>TM</sup> starting materials without accepting any compromises.

For more information, please visit our *TraceCERT*<sup>TM</sup> Web site: [www.sigma-aldrich.com/tracecert](http://www.sigma-aldrich.com/tracecert)

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## TraceCERT™ – 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

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



In the last issue of this series on *TraceCERT*™ 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 *TraceCERT*™ 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 **TraceCERT™** 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<sup>3</sup> 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<sup>3</sup> density of air can affect the weighing result up to 0.1%. Since many **TraceCERT™** 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<sup>3</sup>) we also have calibration weights with a density of 2760 kg/m<sup>3</sup> (anticorrosive). This allows us to double-check the air buoyancy correction.

All of the high-precision balances used to produce **TraceCERT™** 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 **TraceCERT™** 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.



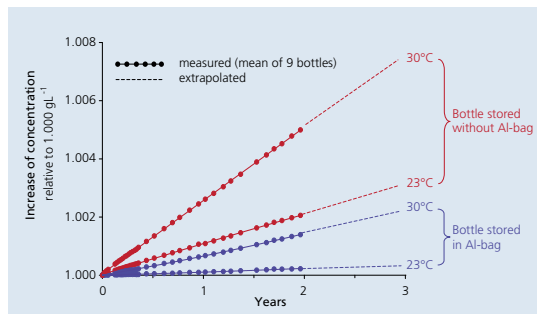
### Storage and stability

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 types, and chose them to bottle and package our *TraceCERT*<sup>TM</sup>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 *TraceCERT*<sup>TM</sup>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 *TraceCERT*<sup>TM</sup>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 *TraceCERT*<sup>TM</sup> line, please visit our web site: [www.sigma-aldrich.com/tracecert](http://www.sigma-aldrich.com/tracecert)



**Figure 6** ..... Packaging of *TraceCERT*<sup>TM</sup>Ultra standards for ICP to ensure  $\pm 0.2\%$  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

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## TraceCERT™ – Traceable Certified Reference Materials. Reliability is a matter of proper uncertainty calculation

**Part 5** – This is the fifth and final article in the series on Certified Reference Materials to appear in Analytix.

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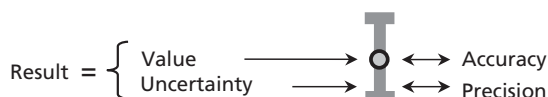


In addition to the concept of traceability as it applies to analytical chemistry, the concept of uncertainty is also poorly understood. It is not uncommon for chemists to hesitate when they are asked for the uncertainty budgets of their measurement values. Although there are published guidelines on how to deal with this issue [1–2], admittedly the calculation of uncertainty can be a real challenge. As is true for makers of fine watches, who must know how even the smallest component contributes to the overall mechanism, it is crucial for analysts to have a detailed understanding of the entire measurement process in order to calculate a true and reliable uncertainty budget. It is not possible to present in this short article a comprehensive discourse on the subject. However, we will use this space to provide some basic understanding and show how we calculate and report the uncertainty values for our TraceCERT™ reference materials.

### Uncertainty vs. error

Confusion often arises because of the incorrect use of the terms uncertainty and error. Whereas error is not quantifiable, being a blunder or a mistake, uncertainty can be estimated or calculated and therefore expressed as an actual number. The uncertainty characterizes the variability that can reasonably be attributed to the measurand, the physical parameter being quantified by measurement. Consequently, each measurement result consists of two components: the *value* (predominantly the average of replicate measurements) and the *uncertainty* (the attributed variability), as shown in Figure 1.

**Figure 1** A measurement value without an uncertainty budget is not a measurement result

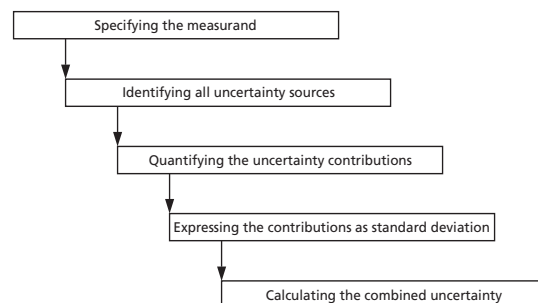


### Calculating the uncertainty budget: Empiric vs. bottom-up

Generally, there are two approaches to obtain an uncertainty budget for a measurement: the empiric approach and the so-called “bottom-up” approach. The empiric approach is based on historical data, such as proficiency test performance (round robins), control charts or validation data. Hence, uncertainties calculated by the empiric approach are based on actual experience. The empiric approach is also called the top-down estimation. Typically it is not necessary to know in detail all of the influence parameters since the uncertainty estimation is based on the analysis of the whole process. In some cases the empiric approach may lead to meaningful results. However, because it is based on a snapshot in time, it cannot be assumed to be representative of future measurements.

A more sophisticated approach is the so-called “bottom-up” approach. Here, the uncertainty of a process or a measurement is calculated by summing all contributing influence parameters. Hence, all the details of the process must be identified and quantified individually (Figure 2). Obviously, the bottom-up approach is much more challenging and, in some cases, is not even possible due to lack of information. However, there is greater confidence in uncertainty calculations that use the bottom-up approach since by definition all sub-processes at the actual time of measurement are fully known and understood.

**Figure 2** Step-by-step procedure of an uncertainty evaluation by the bottom-up approach



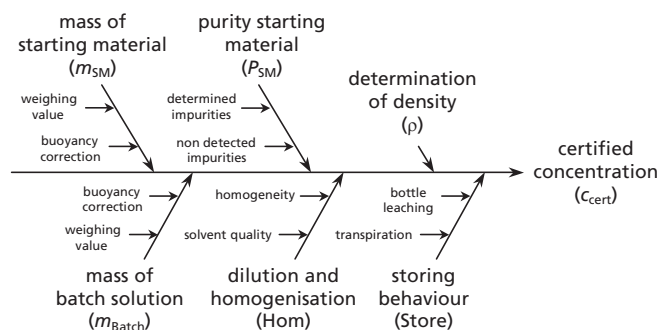
### Combined uncertainty, $u_c$

After specification of the measurand and identification of the influence parameters, the individual influence parameters (contributors to the uncertainty budget) must be quantified. There are many different ways input data on the individual influence parameters of a process can be obtained. They might include min/max tolerance values from instrument specifications, nonlinearity data, any repeatabilities, and so forth. However, for these various data to be summed they must be first converted to standard deviation values (SD). Only SDs can be added by applying mathematical rules to get the combined uncertainty. Besides triangular or rectangular distributions, there are other methods to convert data into SDs [1]. After all influence parameters are converted to SDs, the combined uncertainty  $u_c$  can be calculated by applying the mathematical rules of uncertainty propagation. **Figure 3** shows the two basic algorithms. With the help of a cause-effect (Ishikawa or fishbone) diagram, like that shown in **Figure 4**, the influence parameters can be visualized to give an overview of the uncertainty determination. This tool is very helpful, especially when analyzing highly-complex processes.

**Figure 3** Uncertainty propagation rules. In the case of additive parameters the absolute uncertainties are combined (square root of the sum of the squared contributions). In the case of multiplicative contributions the relative uncertainty contributions are combined

|                            |   |
|----------------------------|---|
| Additive parameters:       |   |
| $M = a + b$                | $u_c(M) = \sqrt{u^2(a) + u^2(b)}$   |
| Multiplicative parameters: |   |
| $M = a \cdot b$            | $\frac{u_c(M)}{M} = \sqrt{\left(\frac{u(a)}{a}\right)^2 + \left(\frac{u(b)}{b}\right)^2}$ |

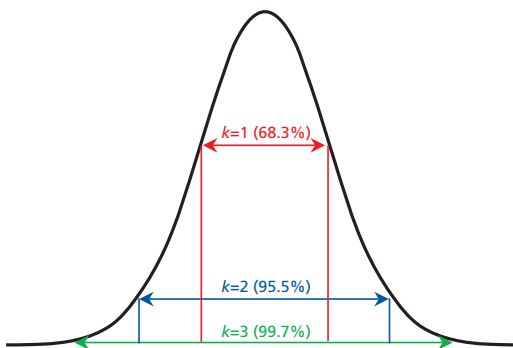
**Figure 4** Cause effect diagram of the preparation procedure of TraceCERT™ reference materials. Only first and second order influence parameters are shown



### Expanded uncertainty, $U$

Since the combined uncertainty,  $u_c$ , is a single standard deviation, the associated confidence level is only 68% (based on a Gaussian distribution, **Figure 5**). However, because a reported uncertainty value is meaningful only when the underlying level of confidence is adequate, it is quite common to expand  $u_c$  with an expansion factor,  $k$ , equaling 2. Assuming that a Gaussian distribution is fulfilled, the reporting of a double SD ( $k=2$ ) leads to a confidence level of 95%. It is therefore important avoid at all costs citing an uncer-

**Figure 5** Gaussian distribution showing the increase in confidence level with increasing expansion factor,  $k$  (number of standard deviation units)



tainty value based on a single SD since it can lead to misunderstandings and overly-optimistic uncertainty values. Instead, it is recommended to report the expanded uncertainty,  $U$ , which is equal to  $k \cdot u_c$ , where  $k$  is the number of standard deviation units (expansion factor).

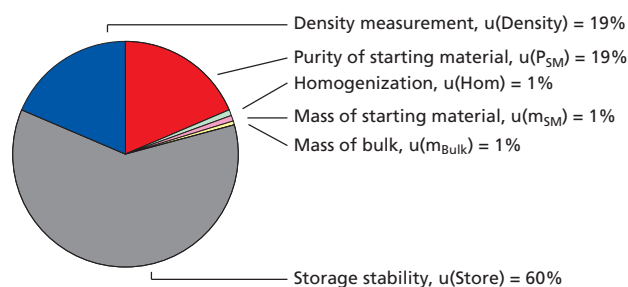
### Evaluation of TraceCERT™ CRM uncertainties

In the previous four installments of this series of technical articles on TraceCERT™ reference materials, we discussed the manufacturing, analysis and storage effects [3]. Without going into mathematical details, in this article we want to give an overview of the key influence parameters to the uncertainty calculation of TraceCERT™ CRMs and discuss their relevance to the overall uncertainty budget. In **Figure 4**, the identified key influence parameters are shown as a cause-effect diagram. Each of the primary parameters (vertical arrows) is composed of a set of secondary parameters (horizontal arrows). For clarity, we have shown only the major effects. It should be noted that most of the secondary influence parameters comprise multiple minor influence parameters (tertiary parameters). For example, the secondary influence parameter “weighing value” (left upper corner in **Figure 4**) is made up of the following contributions: repeatability of weighing, readability, nonlinearity and eccentric load of balance, uncertainties of the calibration weights and temperature coefficient. This is a good example of how the bottom-up approach for uncertainty calculation is only possible with a deep understanding of the details of the measurement process.

Of course not all of the influence parameters are of equal importance in terms of their contribution to the overall uncertainty budget. Only when the whole uncertainty calculation is done can the relevance of the individual parameters be analyzed. **Figure 6** shows the primary influence parameters of the uncertainty budget of a TraceCERT™ Ultra, a CRM for ICP calibration, including the storage effects. By including the storage

effects into the uncertainty budgets of all *TraceCERT*<sup>™</sup> products, we can guarantee that the certified value is not only within specification at the time of production, but also when the bottle is first opened by the end-user. Two major contributions will be explained in more detail in the next section: the uncertainty calculation of the starting material purity statement and the storage effect contribution.

**Figure 6** Partitioning of the uncertainty budget of *TraceCERT*<sup>™</sup> Ultra reference materials relative to the total uncertainty (expanded uncertainty usually is 0.2% relative to the certified value)



### Uncertainties of starting material purity and storage effects

We discussed in a previous article of this series how the “100% minus sum of impurities” approach is the best method for the characterization of materials with high purity (>99.8%). In this case, the found trace impurities and an estimated contribution from the non-found impurities (below detection limit, DL) are subtracted from 100%. These two different impurities (real found and below DL) are also treated in separate ways in terms of their contribution to the uncertainty budget. For the real found impurities, an individual uncertainty contribution is considered for each element. For trace analysis with ICP-OES or ICP-MS, these contributions are typically in the range of several percent relative to the found value. For all the unfound impurities (below DL) a contribution of half of the DL is applied to the uncertainty budget.

The storage effects arise primarily from the loss of solvent by transpiration through the container wall [3]. Hence, the associated uncertainty contribution of this effect depends to a great extent on the container and the packaging material (aluminized bag vs. “naked” bottle). Long-term studies have yielded maximum transpiration rates for each individual type of bottle/packaging under various storage conditions and solvent systems. These data are considered in the uncertainty budget, and also are used to calculate the expiry date and the maximum storage temperature for the product.

We hope that this series of technical articles gave you an inside look into the production, testing and certification of our *TraceCERT*<sup>™</sup> reference materials. Since buying an analytical standard is a matter of trust, it is our intention to bring as much transparency as possible to our customers. As a consequence of the continuous improvement in our production of certified reference materials and our extensive experience in the CRM field, our laboratories will soon be accredited by the Swiss Accreditation Service according to both EN-ISO/IEC 17025 (general requirements for the competence of testing and calibration laboratories) and also ISO Guide 34 (general requirements for the competence of reference material producers). We look forward to supplying your need for CRMs, in terms of application, composition and quality, long into the future.

To view the entire *TraceCERT*<sup>™</sup> line, please visit our web site [www.sigmaaldrich.com/tracecert](http://www.sigmaaldrich.com/tracecert)

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## Increasing the reliability and value of analytical results

Sigma-Aldrich achieves "Gold Standard" double accreditation according to both ISO/IEC 17025 and ISO Guide 34, and now offers a unique class of CRM

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

Following long-lasting cooperation with different metrological institutes, such as Switzerland's EMPA and Germany's BAM, Sigma-Aldrich has built-up a broad knowledge base in the field of CRM production. In the newly-built laboratories equipped with specialized instruments at our Buchs, Switzerland site, we developed a series of CRMs for the analytical market. After two years of continuous development, our Buchs facility was ready to be audited by the Swiss Accreditation Service (SAS) and receive the highest achievable quality assurance level for CRM producers: the double accreditation as both a testing lab (ISO/IEC 17025) and a CRM producer (ISO Guide 34). This combination is also called the „Gold Standard“ accreditation for CRM producers.

### Accreditation vs. Certification

Confusion often arises over the proper meaning and differences between the terms accreditation and certification. Accreditation means that an authoritative body formally recognizes that an organization or individual is competent to execute a specific service as described in the scope of accreditation. Certification, on the other hand, means that an independent third party has confirmed in writing that a product, procedure or service fulfils the prescribed requirements.

The difference between the two seemingly similar definitions lies in the fact that with accreditation, the formal recognition of competence is based on proven technical knowledge and therefore requires the consultation of a technical expert for the scope to be accredited, while certification primarily involves ensuring conformity to a given norm. For example, certification according to ISO 9001 targets the general management, processes and data-handling within a company. Therefore, ISO 9001

certification is not linked to a technical competence. Although both ISO 9001 certification and ISO/IEC 17025 accreditation do have some overlap, they are more-or-less independent [1].

### ISO/IEC 17025 for testing labs

The particular aspects of this type of accreditation are described in ISO/IEC 17025 „General requirements for the competence of testing and calibration laboratories [1].“ In addition to the basic management requirements of ISO 9001, the following topics are crucial for ISO/IEC 17025 compliance:



- Instrument qualification
- Validation of analytical methods
- Traceability statements
- Evaluation of measurement uncertainty
- Ongoing education of personnel
- Periodic participation in proficiency tests to demonstrate technical capability

Analytical results produced in laboratories fulfilling ISO/IEC 17025 can be labeled with a special quality logo that confirms the reliability of the results. In every country there is at least one official body that is responsible for accreditation, and each has its own design for their quality logos. In Switzerland, it is the Swiss Accreditation Service (SAS) that gives the permission to the accredited laboratories to use the „Swiss Testing“ logo. This logo and the individual registration number of the laboratory must appear on the certificate. Furthermore, the scope of each accredited laboratory is published on the web sites of the responsible accreditation bodies.

In most cases, ISO/IEC 17025 is associated with a well-defined analytical technique and a stated measurement range comprising analyte, matrix and concentration range. This is called the scope of the accreditation. For example, Laboratory A is accredited to perform ICP-OES measurements of lead in plastics in the range of 0.1 up to 1000 mg/kg with a stated relative uncertainty of 2 up to 5%. Due to the wide variety of analytical techniques and analytes, there are many laboratories worldwide already having an ISO/IEC 17025 accreditation, each for a very specific analytical scope. Since this accreditation is an assignment of a technical competence, it goes without saying that it is strictly linked to the specified staff and

infrastructure of the accredited laboratory and can not be moved from one location to another.

### ISO Guide 34 as the relevant guide for CRM producers

A CRM producer is defined as a “technically competent body that is fully responsible for the supply of the CRM and authorizes the property values assigned to the CRM.” The most appropriate document dealing with CRM production is ISO Guide 34 “General requirements for the competence of reference materials producers [2].”



This guide outlines the quality system requirements under which reference materials can be produced. It is intended to be used as part of the reference material producer's general quality assurance procedures.

The organization and management requirements, for example quality system, documentation, services and supplies, preventative and corrective actions, audits and reviews, are usually covered when the laboratory already is certified according to ISO 9001 or accredited under ISO/IEC 17025. In ISO Guide 34, there are a few additional requirements that deal with the production of CRMs:

- Production planning and maintenance of a suitable environment
- Starting materials selection and pre-treatment
- Assignment of a CRM's property values, uncertainty and traceability
- Assessment of CRM homogeneity and stability
- Assurance of adequate packaging and storage
- Certificates that include detailed information

Because many aspects of CRM production require precise measurements, for example homogeneity and stability testing, and proper data evaluation is an integral part of the certification process, a CRM producer under ISO Guide 34 must also comply with ISO Guide 31 (contents of certificates and labels) and ISO Guide 35 (general and statistical principles for certification) [4, 5].

### Double accreditation: The „Gold Standard“

As mentioned previously, ISO/IEC 17025 is the common standard in analytical chemistry, while ISO Guide 34 is more relevant to CRM producers. Nevertheless, the quality of most CRMs also depends on analytical measurement capabilities. Therefore, the double accreditation achieved by following both of these guidelines is the highest achievable quality and confidence level for CRM producers. It is therefore also called the “Gold Standard” for CRM producers. In 2004, the International Laboratory Accreditation Cooperation (ILAC) began recommending this double accreditation for all CRM producers. However, only a very small group of institutes and companies worldwide are working at this level of certified quality today.

### Accreditation @ Sigma-Aldrich

After receiving ISO 9001 certification in 1994, we have systematically improved and expanded our quality management systems and skills. The technical competence for CRM production at Sigma-Aldrich Switzerland is a consequence of the long-standing cooperation between our R&D group and various metrological institutes.

In mid-2007, we achieved ISO/IEC 17025 accreditation for the two scopes „mass determination through high-precision weighing“ and “gravimetric preparation of homogeneous solutions from high-purity starting materials.” By the end of 2007, we attained our second accreditation as “Producer of Certified Reference Materials” according to ISO Guide 34 in combination with ISO/IEC 17025. The scope is specified for homogeneous solutions in the concentration range of 0.5 mg/kg to 20,000 mg/kg using gravimetric preparation.

**Figure 1** When climbing up the “quality ladder,” only with ISO Guide 34 (in combination with ISO/IEC 17025) can CRM producers achieve the highest level of reliability.



(continued on page 6)

### TraceCERT® CRM launched

The first products developed and produced under these doubly-accredited conditions are our recently-launched *TraceCERT* calibration standards for spectrometry and ion chromatography. The name *TraceCERT* stands for Traceability and CERTified, and means that these CRMs are suitable for even the most challenging analytical applications. They also fulfill all the needs of our customers who work in regulated environments. Key characteristics of these new CRMs are:

- Unique level of accuracy and lot-specific values
- Produced in our doubly-accredited laboratory that fulfils ISO/IEC 17025 and ISO Guide 34
- Traceable to at least two independent references (NIST, BAM or SI unit kg)
- Sophisticated packaging and comprehensive documentation, including proper uncertainty calculation, expiration date and storage information

The quality of a CRM strongly depends on the quality of the starting materials and, therefore, their characterization is very important. *TraceCERT* starting materials are characterized by two different approaches: the direct measurement of the purity by the most accurate method (e.g. titrimetry) and the purity assignment by the „100% minus impurities“ approach. The combination of these two purity assignments leads to two independent traceability chains, and results in higher reliability of the CRM.

**Figure 2** Only well-characterized and high-purity starting materials are used for *TraceCERT* calibration standards (clockwise from upper left: copper, zinc, nickel and gold).



More information on issues related to CRM quality and production can be obtained by reading the series of Analytix articles we published in 2006 and 2007 [6]. This series covered traceability and uncertainty assignment, handling of high-purity starting materials, production, packaging and stability studies.

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