

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), SO4 (23)
NaCl	99.980	0.015	K (5), Br (30)
CaCO ₃	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_2HPO_4 is used as starting material for phosphate calibration solutions. During the evaluation of a



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particular batch of Na_2HPO_4 , 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_2PO_4 , 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.

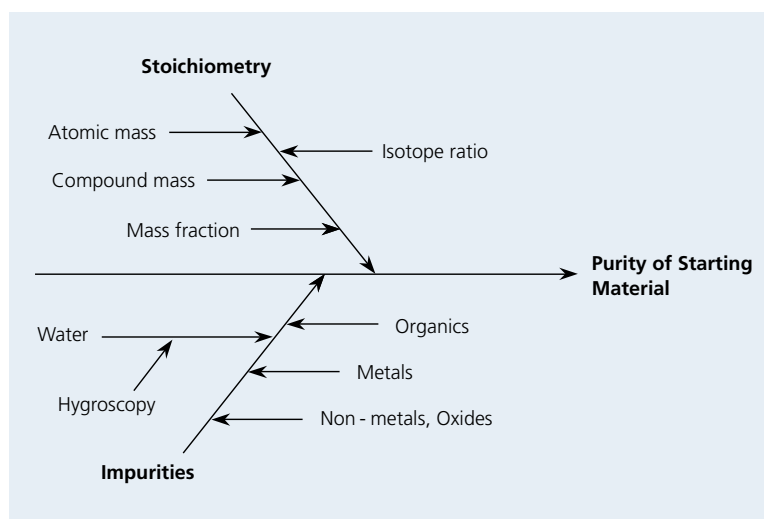
Problem No. 3: Isotope ratio and atomic mass

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 ${}^6\text{Li}$ to ${}^7\text{Li}$ is approximately 7.6% to 92.4%. When using Li_2CO_3 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*TM 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*TM 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_{measured}*). In addition, contributions for „investigated but not found“ impurities (those below detection limit, *I_{unfound}*) and expected but not investigated impurities (*I_{estimated}*) are considered in the purity assessment. This conservative approach leads to more reliability and surety of *TraceCERT*TM calibration standards and reference materials.

For most of the *TraceCERT*TM 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_{measured}*). For non-detected impurities, a contribution of half of the detection limit is estimated and also subtracted (*I_{unfound}*). Last but not least, an estimated contribution (also as a mass fraction) by impurities that were not investigated is also considered (*I_{estimated}*).

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*TM starting materials without accepting any compromises.

For more information, please visit our *TraceCERT*TM Web site: www.sigma-aldrich.com/tracecert

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