Establishment of SI units and NMs: 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>
<thead>
<tr>
<th>Property</th>
<th>Base Unit</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Kilogram</td>
<td>kg</td>
</tr>
<tr>
<td>Length</td>
<td>Meter</td>
<td>m</td>
</tr>
<tr>
<td>Time, Duration</td>
<td>Second</td>
<td>s</td>
</tr>
<tr>
<td>Electric Current</td>
<td>Ampere</td>
<td>A</td>
</tr>
<tr>
<td>Temperature</td>
<td>Kelvin</td>
<td>K</td>
</tr>
<tr>
<td>Luminous Intensity</td>
<td>Candela</td>
<td>cd</td>
</tr>
<tr>
<td>Amount of Substance</td>
<td>Mole</td>
<td>mol</td>
</tr>
</tbody>
</table>

To provide oversight, each member country established a National Metrological Institute (NMI), one per country with a few exceptions. NMs 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 NMs 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 (IRMIM) 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, CaCO₃) must always be comparable, within the stated degree of equivalence, to a second NMI (e.g. BAM RS3, CaCO₃). 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.

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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™ 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™ standard solutions and are relative to the certified content of the gravimetrically-produced standard.

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**The new „triple traceability” approach with TraceCERT™**

There are many approaches to establish traceability to different reference standards in analytical chemistry. For TraceCERT™ 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.

**References**
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