METROLOGY in CHEMISTRY
for the 21st Century

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Extended abstract

1. Meeting the need for intercontinentally understood Concepts and associated intercontinentally agreed Terms for Metrology in Chemistry:

The 2006/2007 edition of the
International Vocabulary of Metrology (VIM)
Basic Concepts and associated Terms

To prevent war, be very precise in your speaking
[Kongfutze 551-479 B.C.]

For the first time in history, chemical measurement, including measurements in laboratory medicine (the world of clinical measurement) and in any field of biochemistry have been systematically fully considered in a revision of the International Vocabulary of Basic and General Terms in Metrology (VIM), in its revision 1997-2006/2007. Similarly, nominal properties (so-called qualitative measurements) have been addressed. During this revision, it became clearer than ever, that the perception of the VIM in the past had been too much that of being a compilation of terms (cf the word 'terminology', sometimes disposed off as 'semantics'), whereas in reality it is a set of mutually consistent concepts from

which the terms are only the labels. It was also revealed that many of these concepts had to be examined and, in many cases, (re-)defined. Hence the 3rd edition of the VIM (2006/2007) might be renamed: 'International Vocabulary of Metrology', 'Basic and General Concepts and associated Terminology (VIM)'. Unambiguous and consistent concepts and associated terms such as measurand, measurement result, calibration hierarchy, metrological traceability, metrological comparability, validation, metrological compatibility, target measurement uncertainty, and many more, must govern the description of results of chemical measurements (and not only chemical measurements!) in order to enable valid *comparisons* of these results amongst each other i.e. making them *comparable* (hence the need to define *comparability*). That is not yet the case as chemical literature continuously displays and as numerous workshops over the last decade have shown world-wide. For international trade in food and feed to be fair, for border-crossing implementation of environmental regulations to be the same for all parties concerned, for interchangeability of results of clinical measurements to become a reality, for any border-crossing interpretation of chemical measurement results to be possible, intercontinentally understood and intercontinentally agreed, mutually accepted, concepts and associated terms are a condition 'sine qua non'.

Similarly, the translation of a term from one language -English- into 30-40 other languages, must be made unambiguously, and that is not possible without a common and verified understanding of the concept concerned from which the term is the label. People using native English as common language have not yet fully realized that they are at a considerable advantage over people using non-native English in cultures or ountries where correctly translated terms

describing concepts may not yet be available, let alone be understood. People in the latter countries are therefore at a considerable disadvantage in all cases where chemical measurements are involved, such as in global trade, business and tourism.

The revision of the VIM is of primordial importance for good understanding within and between measurement communities world-wide.

2. Implications for society

Measurement units have been established for practical use in technology, trade and science. In all these applications, measurement standards are required which are 'realizations', or 'embodiments' of certified values of the measurands, selected by the customer for any particular measurement. These measurement standards have themselves to be metrologically traceable to the definition of the measurement unit chosen for the expression of the measurement result, through a 'realization', or an 'embodiment' of that definition. Thus, a careful customer or user of a measurement standard needs not only to know the metrological traceability chain of his/her own measurement result (to a specified measurement standard) to earn credibility. (S)he also needs to understand the metrological traceability chain of that measurement standard at the laboratory that 'realizes' or 'embodies' in a measurement standard the (definition of the) measurement unit concerned. In other words: the good measurement laboratory wants to give proof to its customer of the real authority of its measurement result as expressed in a given measurement unit and using a measurement standard really 'embodying' that unit.

3. The ongoing redetermination of the Avogadro constant through the Si route (1980-2009)

Since many years, two major international attempts are going on to improve the Avogadro constant, i.e. to reduce its uncertainty, yet the uncertainty aimed for ($2.10^{-8}N_A$) will be extremely difficult to achieve and take many years.

One of the continuing redetermination of the Avogadro constant, makes use of a one kilogram near-perfect Si spherical single crystal of the highest chemical purity and natural isotope composition, as well as of an extremely simple measurement model.

$$\{N_A\} = V_m(E) / V_o(E) \qquad [1]$$

where E (for element or entity) is Si in the Si approach to the Avogadro constant -it could be another element- , V_m is the molar volume of Si and V_o is the atomic volume of Si: the volume.of one Si atom.

In this approach, only a few measurements are made, but then with the smallest possible measurement uncertainty:

1) **SI-traceable length measurements to determine the lattice constant in the Si single crystal, leading to a_o , the interatomic distance of Si atoms in the unit cell which in turn, leads to the volume V_o (Si) of the unit cell and, hence, to the volume of one atom of Si (there are 8 atoms of Si in a unit cell):**

$$V_o\,(\mathrm{Si}) = a_o^3 / 8 \qquad [2]$$

2) **SI-traceable length measurements to determine the diameter of the sphere enabling to calculate an SI-traceable value for the volume V_{sph} of the sphere, and mass measurements to derive an SI-traceable value for the mass m_{sph} of the sphere. These two measurements lead to an SI-traceable value for the density of the crystal (i.e. of the Si constituting the sphere):**

$$\rho = m_{sph} / V_{sph} \qquad [3]$$

The molar volume is then accessible as:

$$V_m(\text{Si}) = M(\text{Si}) / \rho$$

3) **SI-traceable values for the isotope abundances $x(^{i}\text{Si}) / \Sigma\, x(^{i}\text{Si})$ enabling to calculate an SI-traceable value for the molar mass (atomic weight) M(Si) of the Si in the sphere:**

$$M(\text{Si}) = \Sigma\, x(^{i}\text{Si})\, M(^{i}\text{Si})$$

$$= \Sigma\, [R_{i/28} \cdot M(^{i}\text{Si})] / \Sigma\, R_{i/28} \qquad [4]$$

Note that the measurement of the abundance ratios $R = x(^{i}\text{Si}) / x(^{28}\text{Si}$ of the Si isotopes is an amount-of-substance measurement:

$$x(^{i}\text{Si}) / x(^{28}\text{Si}) = n(^{i}\text{Si}) / n(^{28}\text{Si}) = R_{\ i/28} \qquad [5]$$

which is a number ratio of Si isotope atoms, measured in a high precision mass spectrometer, therefore called an amout comparator.

The ratio molar volume to atomic volume yields the Avogadro constant, as described in Eq [1].

A first (multiannual) attempt (1985-2004) has led to a value for N_A of 6,022 1353(31) x 10^{23} mol^{-1} i.e. with a combined measurement uncertainty on N_A of 3,1 x 10^{-7} N_A. A second (multiannual) attempt (2204-2009) has started recently using the same measurement model, but the Si constituting the sphere is isotopically highly enriched ^{28}Si (>99,99 %), and is produced in the ultracentrifuge installations of Zentrotech in St Peterburg. This attempt is expected to yield a reduction of the combined relative uncertainty on N_A of about a factor of ten, hence putting the ultimate goal on the horizon, which is $2.10^{-9} N_A$. The project structure is described. It is fully integrated both in budget and management, not a daily occurrence in international collaboration.

4. Defining the Avogadro Constant? Or the Avogadro Number?

It is hardly possible to overestimate the importance of the Avogadro constant N_A , and an enormous amount of effort has been spent in the course of the last centuries on its determination and improvement.

As a "constant" it enters very important relationships between fundamental *constants*, yet there are still big programmes to *measure* it.

It is now a key to a possible new definition of the kilogram, the measurement unit for mass, yet it is not known with sufficiently small uncertainty to make the transition from the old definition of the unit kilogram to a new one.

It is related to the definition of the mole, yet it is not mentioned in that definition. It makes people think about a 'number of things', consistent with the particulate nature of matter, a fundamental characteristic known as "numerosity" of matter, yet the definition relates it to the definition of the unit of mass, a property of matter which has nothing to do with "numerosity" but with "inertia". Its numerical value is held to relate ratios of quanties measured on the macroscopic scale to ratios of the same quantities on the atomic scale; that does not sound as a "fundamental constant of nature", but as a "scaling factor". Chemists do work so much with these balances by means of which they measure mass ratios of material, that they sometimes forget that the old chemists, more than 100 to 200 years ago, found out that by means of balances, the particulate nature of matter, could be conceived and indeed described. They found out that ratios of mass values could be converted to ratios of integer numbers of atoms and molecules (i.e. number ratios), by conceiving and applying the concept of 'atomic weight' (molar mass). The discovery that matter is indeed of

“particulate” nature, built up by a discrete numbers of entities constituting each specified substance, was an extremely useful new feature in our model of nature. It gave birth to the concept “amount-of-substance” and the possibility of its measurement: an amount of a specified substance can be measured in terms of a number of entities of that substance rather than being described in terms of its inertia i.e. its mass.

All chemical reactions go with numbers of atoms and molecules. In the human body, it are the number of entities which poison (e.g. Pb) or cure (e.g. acetylsalicylic acid), not their mass. This concept is applicable to bacteria, where -again- the number of entities are important, not their mass. Rather than looking for traceability of chemical measurement results to an “inertial” measurement unit such as the kilogram, it is much simpler to look for metrological traceability to a measurement unit based an the “particulate” nature of matter (and of bacteria!): one entity for each specified substance, or, a fixed multiple of one such entity.

Any measurement, is the evaluation, on a measurement scale, of the number ratio of an unknown number, representing the magnitude of a quantity, to a given number, defining the agreed measurement unit. In other words, any measurement results in fact in a number ratio with measurement unit in the denominator. In a chemical measurement, that is particularly relevant: any unknown number of entities can be ratio-ed to a known number of entities, agreed as measurement unit. That measurement unit could be $\{N_A\}$ entities in the denominator

In many chemical measurements, we transform the problem of a difficult-to-measure quantity (an amount ratio involving the unknown sample and the

chosen measurement standard) into the measurement of an easy-to-measure quantity (an electric current ratio involving the unknown sample and the chosen measurement standard). The conversion factor *K*, more or less close to one, can be measured by means of a *measurement standard* (that is why we need measurement standards) and, hence, carries its own measurement uncertainty. We like to use measurements of electric current ratios because they are in fact ratios of the outputs of very fast counters. Thus, we encounter again the concept of numbers and number ratios. This is also very convenient, as in many chemical samples, the entities (e.g. molecules) lose their chemical identity as they disappear in some form of chemical reaction. When we count number (ratios), we do not have to worry about this loss of identity: the job of counting has been passed over to count ions or electrons. Thus, in a chemical measurement, we first separate specified, identical entities by mass (as in mass spectrometry), or by frequence (as in light absorption and light emission spectrometry) represented on the abscissa of the spectrum, before measuring a number proportional to amount represented on the ordinate of the spectrum.

With these insights, we look for other measurements in the SI system which are based on "numerosity". We find time measurements as being very analogous and inspiring for proper metrological organisation of chemical measurement results because both measurements can be described in almost identical terms:

1 sec is the duration of 9 192 631 770 electronic transitions in the ^{133}Cs atom (a natural unit because believed to be constant in nature under any circumstances), each of a duration of one period.

1 mole is the amount-of-substance constituted by 6 022 141 5 specified, identical entities (one entity is a natural unit because each entity, such as an atom or a

molecule, of a specified substance, is believed to be identical).

In the time example, we have the 'numerosity' of events as basis for defining an appropriate measurement unit, in the amount-of-substance example, we have the 'numerosity' of entities (the particulate nature of matter) as basis for defining an appropriate measurement unit.

5. Redefining the mole?

The Avogadro constant serves as a scaling factor the unit for amount-of-substance measurements and its numerical value serves as a scaling factor between quantities measured on the macroscopic scale and the same quantities measured on the atomic scale. The question is raised whether the Avogadro constant should not be fixed as an exact number,once further improvement of its determination has been achieved to a combined measurement uncertainty of $2 \cdot 10^{-8} N_A$, the goal which is pursued now. The question is, of course, based on our perception of the "particulate" nature of matter and the ensuing concept of "numerosity". A definition of the Avogadro *number* as basis for the unit for amount-of-substance measurement, would be very useful for chemical measurement and for the SI as well. It would not only simplify the establishment of metrological traceability of chemical amount measurement results to the SI (i.e. to the definition of the SI unit for amount-of-substance), but also enable to establish metrological traceability to the SI of microbiological measurements and a variety of other biochemical measurement results, many of which are a matter of *counting entities*. However, we need a combined measurement uncertainty of $2 \cdot 10^{-8} N_A$ to redefine the unit kilogram (as the mass of a fixed number of unified atomic mass units u (1 u = 1/12th of the mass of a ^{12}C atom). The obvious choice for that number is of course the Avogadro number $\{N_A\}$.

A new definition of the mole could then be as follows:

The mole is the unit of amount of substance. It is equal to 6,022 141 5 10^{23} of specified identical entities exactly. The entities may be atoms, ions, molecules or other particles.

(The number quoted is the latest CODATA value for N_A , the actual number in the definition would be the result of the ongoing determinations).

Compared with the present definition of the mole, it makes clear that the unit mol is equal to a number of entities $\{N_A\}$, an option that leaves out any relation to mass and the kilogram. The proposal has been made previously.

It may be useful to remember that the chemist does not count numbers like $\{N_A\}$, but is interested in ratios of numbers of different entities. These are used in various kinds of spectrometry or by electrolytic measurements such as coulometry without requiring a value for the mass of one mole or, in many cases, not even requiring an exact value for $\{N_A\}$ (when number ratios are used).

Only in gravimetry must the relative atomic mass or the molar mass of the substance under investigation be known. This approach would remain perfectly possible too.

By the next International Conference of Weights and Measures, CGPM 2007, new definitions of the measurement units mole and kilogram are not ready, but they might by CGPM 2011.

As one can see, the introduction of more metrological thinking i.e. of 'Metrology in Chemistry' surely will modify the landscape for chemists in the early part of the 21st century.