Accred Qual Assur (2011) 16:591–596
DOI 10.1007/s00769-011-0849-z

EDITORIAL

Looking back at two decades of “Metrology in Chemistry”

Paul De Bièvre

Published online: 15 November 2011

In this Editorial, I am announcing the end of my 16 years of formal responsibility for this Journal as I am becoming slightly subject to biological boundary conditions imposed by mother nature.

During that time period—and even prior to that—I was privileged to be in a position from where I could observe a growing interest for the introduction of metrological principles in chemical measurement and could follow this evolution closely at many stages and in many environments. Maybe this is a good time to look back on these years and offer some thoughts for the future of “Metrology in Chemistry”, a concept quoted so many times in this Journal.

Somewhere in the period 1985–1990, an important change in thinking and attitude must have occurred within the SI [1] about chemical measurement. It must have been a difficult undertaking since it took quite some time after the introduction in 1971 of an SI unit intended for chemical measurement, the mole. For much longer, other measurement units such as length, mass, time, electric current, thermodynamic temperature, and luminous intensity, were part of the SI structure through Consultative Committees to the CIPM (see “Appendix”). The change in thinking eventually resulted in the foundation of the CCQM (see “Appendix”) which had its first session in 1995 [2, 3] 24 years later. It is noteworthy that the name “CCQM” contains “amount-of-substance”, a not well described nor commonly well understood quantity amongst chemists, not then and not until this very day. A broader view was reflected by the addition of “metrology in chemistry” in the name of CCQM in 2002. That seemed to include, at least implicitly, any “chemical measurement”. However, no in-depth conceptual discussion about the ambiguous quantity “amount-of-substance” nor about “chemical measurement” has taken place in the CCQM as yet.

Such a discussion is very necessary and therefore highly recommended.

“Amount-of-substance” is a base quantity of the international system of quantities ISQ. For lack of a better term, it is sometimes described as “the quantity for which the mole is the unit”, a remarkable reasoning as long as “amount-of-substance” is commonly not well understood. Actors in the field of physical chemistry, especially in thermodynamics, seem to have been the main if not only proponents of a unit “mole” in 1971, involving the Physical Chemistry Division of the IUPAC (see “Appendix”). Analytical Chemistry was not really involved—nor did analytical chemists involve themselves—very much. Neither are they very noticeable in the presently ongoing discussions on the re-definition of the mole. However, the development of chemical measurement techniques exploded over the last 40 years because of the broad use of chemical measurement results in intercontinental trade and commerce, caused by possible pollution of food and drinks, and of the environment in general. Thus, fast instrumental measuring systems were needed as well as an answer to the question “when are results of chemical measurements comparable throughout the world and, if so, what is their degree of equivalence?” (concept 5-4 in [4]). This (r)evolution has been achieved by analytical chemists mostly outside the “metrological community/structures”. The technical development was based on the particulate nature of atoms and molecules that were converted into charged particles or light emission/absorption quanta in an essentially one-to-one ratio, in all kinds of spectrometers. Thus, the concept “number-of-entities” was confirmed again to be a highly relevant quantity because it was the

P. De Bièvre (✉)
Kasterlee, Belgium
e-mail: paul.de.bievre@skynet.be

output quantity of the measurement function (entry 2.49 in [5]) used in these techniques. The quantity with associated unit to be used on the ordinate of these spectra was to be proportional to a number *N* of entities to express measurement results. A much wider and simpler base concept 'number-of-entities' with associated base unit (i.e. a defined number-of-entities) was intuitively felt as very appropriate for the expression of results of chemical measurements.

This (r)evolution in instrumental measurement methods could be one of the basic reasons for the present diverging opinions—or even heated discussions—on the international scene. The 1971 definition of the mole seems to have been coined as a concept for use with continuous quantities (such as length, mass and time) on the macroscopic level, whereas this unit should probably have been built on the concept of discrete, i.e. discontinuous, 'number-of-entities' for use at the atomic level, imposed by the particulate nature of matter (atoms and molecules), another basic property of matter [6, 7] together with mass. Such a transparent concept would also cover a measurement interval from the smallest integer number "1" to any large but still integer number-of-entities at the macroscopic level. A good and fully transparent rule for the definition of a measurement unit should thereby be kept in mind: a value of a quantity is selected and defined as the measurement unit for the expression of later measurement results obtained for the same quantity. A shining example of the application of that rule is the definition of the second as a the duration of a defined number of electronic transitions in the ^{133}Cs atom which had first been measured to a sufficiently small measurement uncertainty; see section 2.1.1.3 in [1].

It seems that CCQM took note of that in its sessions 2010 and 2011:

- *"noting that "the level of awareness of the proposal to redefine the mole is low in the relevant community" and "support for the proposal is not yet unanimous"*
- …
- *"recommends that any decision be deferred until full consideration is given to the interests of the chemical measurement community"* [8]

and IUPAC noted that

- *"the name of the ISQ base quantity 'amount-of-substance' has been a source of much confusion"*

and recommended, through its ICTNS (see "Appendix") [9], that

- *"the greatest effort should be made to change the name of the ISQ base quantity "amount-of-substance" at the same time that a new definition of the mole is approved"*

The President of the CCU (see "Appendix") understandably admits himself "that 'amount-of-substance' is a difficult concept, but it is kept because of the lack of a better and accepted/acceptable alternative". The IUPAC requirement does not seem to have been fulfilled as of today.

Wasn't this an invitation to analytical chemistry-orientated organizations such as IUPAC, EURACHEM (see "Appendix"), CITAC (see "Appendix") and EuCheMS (see "Appendix") to provide a better concept and associated term than what it meant in the eyes of the authors of the concept in 1971 and nowadays in the eyes of the CCU itself?

Eventually at the IUPAC General Assembly 2011 (San Juan, July/August), the initiation of a project on the re-definition of the mole was discussed including making it "interdivisional" thus enabling every Division, and in particular the Analytical Chemistry Division, to consider the proposals for re-definition of the mole and to reflect on them against the background of the exploding developments and applications of chemical measurement techniques.

In 1961, we started developing and applying metrological principles in chemical and isotope measurements at CBNM/IRMM (see "Appendix"), driven by the task to deliver to the international nuclear measurement community primary measurement standards (entry 5.4 Example 3 in [5]), i.e. realizations of SI units for the international control of nuclear materials, given as task by an International Diplomatic Treaty to EURATOM (see "Appendix") for six countries in W Europe, and later to the IAEA (see "Appendix") by the United Nations for the world. The request by the PTB (see "Appendix") to join the Avogadro project through the silicon route in 1981 generated even more in-depth thinking about basic concepts and terms needed to prepare "primary" measurement standards at the frontline of conceptual and technical measurement capabilities for elements and isotopes. Because of the overriding need to achieve the smallest possible "measurement uncertainties" for certified quantity values embodied in these standards, as well as in the scientific contributions to the Avogadro project, units of the existing system of units, the SI had to be used, thus making these results "traceable to the SI". At the frontline of chemical measurement capabilities, they had to have the smallest possible measurement uncertainties to be fit for the intended use.

A metrological programme that had a wide distribution and echo was started at CBNM in 1986 under the name IMEP (see "Appendix") after a similar programme RE-IMEP (see "Appendix") had been conceived and started in 1976 for U and Pu measurements. Probably for the first time, these were large Interlaboratory Comparison ILCs (see a definition in the concept 7.1-1 in [4]) for chemical measurements in which a reference quantity value was made available that was totally independent from the participants' results (no "consensus mean") and exclusively based on metrological principles. The IMEP and REIMEP ILCs are still continued today. Their metrological principles have been borrowed for many Key Comparisons by CCQM/BIPM.

All of this resulted in the first International Workshop on "Traceability and Comparability in measurements of amount-of-substance", organized at CBNM/IRMM in November 1992 and patronized by the newly born EURACHEM.

Another important tool to promote the introduction of metrological principles in chemical measurement was this Journal [10, 11], started in 1996. It was—and still is—an almost ideal instrument for establishing the connection to the SI of chemical measurement results obtained through measurements of elements, isotopes and molecular compounds.

A real milestone in this process of change was attained with the publication of a set of consistent basic concepts in measurement in the form of an "International vocabulary of metrology-VIM" [5]. These concepts were identified, discussed and, ultimately, defined in the period 1998–2008 by the JCGM Working Group 2 on the VIM. The 2008 VIM and its "Corrigendum 200:2008" released in 2010, was the third edition of the VIM, the first one having been released in 1983 [12] and the second one in 1993/1995 [13]. However, in the third edition, chemical measurement was now explicitly considered for the first time in history. This edition had a revolutionary modified title compared with its two predecessors [5]. René Dybkaer and later Françoise Pontet had been delegated to the WG from IFCC (see "Appendix") and myself from IUPAC. We were the only Delegates with professional chemical and clinical background amongst about fifteen members, the others being delegated from other measurement fields: electrical, mechanical and physical as well as from other international organisations. Chemical (and other) measurements now have available an internationally agreed set of consistently defined concepts, an absolute necessity for communication on the intercontinental (and therefore intercultural) scene in a time of intercontinental trade. Also, comparison of results of chemical measurements and ensuing evaluation of their (lack of) "metrological equivalence" (concept 2.6-1 in [4]) can now be done on a sound and common conceptual basis since "metrological comparability of measurement results" has been defined unambiguously in this VIM (entry 2.46 in [5]). Such comparisons require, of necessity, establishing "metrological traceability" (entry 2.41 in [5]) of the results as a matter of course, as well as evaluation of their "measurement uncertainty", an insight either not explicitly realized, or, alas, still partially ignored in the chemical measurement community at large. It was a great step forward because

a set of consistent definitions of "basic concepts with their associated terms" (*taken from the title of the VIM* [5]), *is a prerequisite for translating the terms used in measurement, including analytical measurement, into various languages; this essential and logical requirement is only fulfilled since 2008; prior to that, this requirement was largely ignored in settling disputes in which chemical measurement results were involved*

The other—equally important—means to promote integration of chemical measurement into the SI were the numerous lectures and seminars on this matter we were asked to give by organizers on the five continents over the last 20 years. Next to the opportunity to explain "metrological traceability" to the audiences, they provided an extremely useful possibility to obtain insights and understanding of the real situation in the field through a direct contact possibility with the "analysts at the bench".

To promote the use of the SI for the expression of chemical measurement results, has proven to be a difficult task until this very day. The SI structure did not want it before 1990, most analysts ware not clear in their own mind about the quantity 'amount-of-substance' and the **Avogadro constant** N_A (having the dimension of reciprocal 'amount-of-substance'; also it is an incorrectly used symbol since N is the symbol for a *number*). They satisfied themselves in their daily work with their own interpretation of it as a number N of entities (entry 8 Note 4 in [5]). Such a number could be symbolized correctly by, e.g. N_L which is a correct symbol for a number (called Loschmidt *number*, a well known and historically more correct concept than the Avogadro *number*).

The 1971 mol seems to be built on the concept of an "aggregate of entities" (similar to a "dozen", a bunch of twelve entities), whereas the unit the analysts have in mind, can be the smallest 'number-of-entities'—one (entity) —up to whatever large number needed. If anything, they use the mole without thinking too much about the underlying and not well described quantity "amount-of-substance" and interpreted it as a "number-of-entities". In practice, many analytical chemists worked (and still work) much more using the SI base quantity "mass" with its base unit kilogram as well as with the derived SI quantities "mass/mass" or "mass/volume" with their derived units (kilo)gram/(kilo)gram or (kilo)gram/litre. They arrive at "molar" results by converting experimentally obtained mass values by means of Atomic Weights, the concept conceived more than about 200 years ago thanks to the work of a number of famous groundbreaking chemists (Lavoisier, Proust, Dalton, Avogadro, Prout, Perrin, …). Remarkably enough, also the (International) Commission on Isotope Abundances and

Atomic Weights (CIAAW) was absent from these discussions until September 2011 when they took a position in the matter, although this Commission has released ratios of number-of-entities (atomic weight values relative to 1/12th of the mass of a ^{12}C atom), for more than a hundred years.

In general, real metrological thinking, or application of basic metrological principles, is making slow progress in chemical measurement. It would be worth research in a university department of History of Chemistry or History of Science, to investigate as to how and why all of the above has happened and took so long.

Maybe, CCQM should take up as part of its field of formal competence the task of reflecting on the basic concepts needed in chemical measurement to provide *conceptual guidance*. Maybe ISO TC 12 (see "Appendix"), the formal international authority on "Quantities and Units" ought to take up the task of proposing an alternative for the quantity "amount-of-substance" as the jurisdiction of the CIPM/BIPM, formally speaking, is limited to the SI units.

Of core importance is the backbone of every (chemical and other) measurement, i.e. the "metrological traceability" (entry 2.41 in [5]) of the measurement result, traceable through a transparent "metrological traceability chain" (entry 2.42 in [5]) to a "metrological reference" (concept 2.6-1 in [4]). When numbers of things are involved, a simple and natural base quantity 'number-of-entities' is available (entry 1.4 Note 3 in [5]) as well as an associated base unit "one" (entry 1.10 Note 3 in [5]), an integer. It is always possible to take a defined multiple of that, hence also an integer. And for the latter, it is indicated to take the Avogadro *number* (better: the Loschmidt *number* as we will see further). From these the numerous derived quantities and associated units can be obtained that analysts need. There is a large amount of literature about this, but it is not the purpose of this Editorial to be an exhaustive scientific study.

However, it is easy to predict that, unless these questions are discussed fully and openly, they will not go away for chemists whatever the CIPM/CGPM may finally decide in 2013.

Finally, a note on "teachability". Quantities and units ought to be simple, consistent, transparent and "teachable". We will not reach the measurement community "at the bench" nor interest students (at whatever level) if we do not fulfil these requirements. That is true for the quantity 'amount-of-substance' and the 1971 definition of its unit mole. It is not at present.

That should not only be the case for any unit used in analytical chemistry. It should also be the case for all SI units. Quantities should be clearly described and associated measurement units defined unambiguously in a simple and transparent way. It is to be feared that the present proposals in the "new SI" are not meeting that requirement, and chemists may turn away from the present SI unit "mole" more than ever. That would not be good. Basic concerns have been voiced in this Journal by various authors [14] and still recently by Johansson [15], Hill [16], Censullo et al. [17], and Leonard [18]. Attempts to address them have been made [19, 20], but are not convincing and many questions still remain. Many of them have not yet been addressed by the SI authorities.

Future contributions to ACQUAL from my side may become more occasional, the above-mentioned biological influences permitting.

It gave me great pleasure and intellectual satisfaction to interact with many colleagues-chemists all over the world. That was a highly enjoyable "intercontinental" experience, an adjective I have increasingly used since 2000 as the twenty-first century required to be shaped.

I have been very privileged in my professional career by having had the opportunity to build up -and work for- an international Institute at CBNM/IRMM in Geel, Belgium, in the twentieth century, then for an intercontinental Journal in the twenty-first century.

I sincerely say "thank you" to the entire readership of ACQUAL with whom I had so much interaction. I wish all of them the very best in their professional life and family.

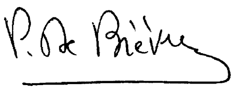
I want to remember Prof Helmut Günzler and Dr Peter Enders, Editor for Chemistry at SPRINGER. We were "allies" in 1994/1995 forming a team that launched this Journal at SPRINGER's invitation. It was a pioneering task to work on that challenge: a Journal which, through its subtitle, implied that measurement results in chemistry might not be as "reliable" as was generally believed and might be in need of (metrological) improvement, a disagreeable but necessary observation to bring. That remains valid as proven by the still running IMEP rounds as well as by other ILCs.

I explicitly wish to express my deep gratitude and appreciation to Dr Heiner Korte who took the succession of Prof Helmut Günzler in 2005 after his passing away at the end of 2004. He has so diligently picked up Helmut's role and heritage, and contributed intensely to what is now looking as a set of 16 volumes of the Journal. Together we formed an excellent and integrated team, built on complementarity.

This Founding Editor-in-Chief, will henceforth concentrate on further introduction and implementation of metrological principles in chemical measurement, now known as MiC (Metrology in Chemistry), including doing that in, and for, ACQUAL. Chances are that he will stay in contact with some of you for some time.

That would be delightful.

Thank you for that in advance and … I wish all of you a relaxing Christmas and New Year time.



Paul De Bièvre
Editor-in-Chief
until 2011–12–31

Appendix: List of acronyms

Organizations under the Metre Convention

CGPM, Conférence Générale des Poids et Mesures—General Conference on Weights and Measures, http://www.bipm.org/en/convention/cgpm/ accessed on 31 October 2011; met in October 2011, next meeting in 2013 (exceptionally 1 year earlier)

CIPM, Comité International des Poids et Mesures—International Committee for Weights and Measure, http://www.bipm.org/en/committees/cipm/ accessed on 31 October 2011

BIPM, Bureau International des Poids et Mesures—International Bureau of Weights and Measures, http://www.bipm.org/en/bipm/ accessed on 31 October 2011

CCQM, Comité Consultatif pour la Quantité de Matière—Métrologie en Chimie—Consultative Committee for Amount-of-Substance—Metrology in Chemistry (to CIPM), http://www.bipm.org/en/committees/cc/ccqm/ accessed on 31 October 2011

CCU, Comité Consultatif des Unités—Consultative Committee for Units (to CIPM). http://www.bipm.org/en/committees/cc/ccu/ accessed on 31 October 2011

Scientific Organizations, Institutions and Programmes

CBNM, Central Bureau for Nuclear Measurements of the European Commission in GEEL (Belgium), renamed 1993 as IRMM (see there)

CITAC, Cooperation on Traceability in Analytical Chemistry, http://www.citac.cc accessed on 31 October 2011

EuCheMS, The European Association for Chemical and Molecular Sciences, http://www.euchems.org accessed on 31 October 2011

EURACHEM, A Focus for Analytical Chemistry in Europe, http://eurachem.org

IFCC, International Federation of Clinical Chemistry and Laboratory Medicine http://www.ifcc.org accessed on 31 October 2011

EURATOM (1957) European Atomic Energy Community, International Diplomatic Treaty, Art 8, para 1, http://www.ec.europa.eu/energy/nuclear/safeguards/safeguards_en.html

IAEA (1957) International Atomic Energy Agency to the UNO (United Nations Organization) given the tasks in 1970 of inspecting nuclear material in the world through the Non-Proliferation Treaty (NPT), http://www.iaea.org/Publications/Documents/Treaties/npt.html accessed on 31 October 2011

IMEP, International Measurement Evaluation Programme, run by CBNM/IRMM (see above in this "Appendix") since 1986, http://irmm.jrc.ec.europa.eu/interlaboratory_comparisons/imep/Pages/index.aspx accessed on 31 October 20

IRMM Institute for Reference Materials and Measurements (of the Joint Research Center of the European Commission), http://irmm.jrc.ec.europa.eu accessed on 31 October 2011

ISO TC 12, International Organization for Standardization, Technical Committee 12 on Quantities and Units, http://iso.org/iso/home.html accessed on 31 October 2011

IUPAC, International Union of Pure and Applied Chemistry, http://iupac.org/ accessed on 31 October 2011

ICTNS, Interdivisional Committee on Terminology, Nomenclature and Symbols, http://www.iupac.org/web/ins/027/ accessed on 31 October 2011

JCGM, Joint Committee for Guides in Metrology, now chaired by Director BIPM 2011–2013, http://www.bipm.org/en/committees/jc/jcgm/ accessed on 31 October 2011

JCGM Working Group 2 on VIM

PTB, Physikalisch-Technische Bundesanstalt (the National Metrology Institute of Germany), http://www.ptb.de accessed on 31 October 2011

REIMEP, Regular European Interlaboratory Measurement Evaluation Programme, run by CBNM/IRMM (see above in this "Appendix") since 1976, http://irmm.jrc.ec.europa.eu/interlaboratory_comparisons/reimep/Pages/index.aspx accessed on 31 October 2011

References

1. SI, Le Système international d'unités—The International System of Units SI, edn 8, BIPM 2008, ISBN 92-822-2213-6; http://www.bipm.org/en/si/ accessed on 31 October 2011
2. BIPM (1995) Report of the first meeting of CCQM, Paris-Sèvres (not accessible on website on 31 October 2011)
3. De Bièvre P (1996) Report on the first meeting of the CCQM, 19–21 April 1995 at the BIPM, Paris-Sèvres. Accred Qual Assur 1:37–39
4. De Bièvre P, Dybkaer R, Fajgelj A, Hibbert B (2011) Metrological traceability of measurement results in chemistry—concepts and implementation. Pure Appl Chem 83:1871–1933. doi:10.1351/PAC-REP-07-09-39IUPAC
5. BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML (2008 corrigendum 2010) International vocabulary of metrology; basic

and general concepts and associated terms—VIM, edn 3, JCGM 200:2008/corrected 2010 at http://www.bipm.org/vim accessed on 31 October 2011
6. De Bièvre P (2007) Numerosity versus mass. Accred Qual Assur 12:221–222
7. Rocha-Filho R C (1990) A proposition about the quantity of which the mole is the SI unit. J Chem Educ 67:139–140
8. CCQM (2010) Report 16th meeting at http://www.bipm.org/en/committees/cc/ccqm/ accessed on 31 October 2011
9. IUPAC (2009) General Assembly, Glasgow at http://iupac.org/web/ins/027/ accessed on 31 October 2011
10. De Bièvre P (1996) Introducing a new journal. Accred Qual Assur 1:1–2
11. De Bièvre P, Kaarls R, Peiser HS, Rasberry SD, Reed WP (1996) Measurement principles for traceability in chemical analysis. Accred Qual Assur 1:3–13
12. BIPM, IEC, ISO, OIML (1983) International vocabulary of basic and general terms in metrology (VIM), ISO Geneva (not accessible on website on 31 October 2011)
13. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1993/1995) International vocabulary of basic and general terms in metrology, edn 2, ISO Geneva (not accessible on website on 31 October 2011)
14. The re-definition of the mole must be of high quality. Accred Qual Assur 16:117–174
15. Johansson I (2011) The mole is not an ordinary measurement unit. Accred Qual Assur 16:467–470
16. Hill T (2011) Criticisms of the proposed "new SI". Accred Qual Assur 16:471–472
17. Censullo AC, Hill TP, Miller J (2011) From the current "Kilogram Problem" to a proposed definition. Chem Int 33:9–12
18. Leonard BP (2011) Accred Qual Assur 16:577–581
19. Milton M (2011) Reasonable scope for change. Accred Qual Assur 16:575–576
20. Mills I (2011) Explicit-constant definitions for the kilogram and the mole. Chem Int 33:12–15