

Failures of the global measurement system. Part 1: the case of chemistry

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Abstract This discussion puts a case of *advocatus diaboli*: that the Treaty of the Metre, its associated administrative apparatus and the International System of measurement units (SI) has basically failed for chemical measurement and is largely irrelevant to modern analysis, much of practical measurement in modern economies and much of recent technology. The practical use of the chemical unit termed the mole, the introduction to the SI units of the thermodynamic mole and the invention of a new physical quantity called “amount of substance” are each reviewed with the conclusion that the current means of expressing the results of chemical measurements are unsatisfactory in both practice and theory and are imposing large and readily avoidable costs on all advanced economies.

Keywords Treaty of the metre · Mole · Amount of substance · Metrology

Introduction and disclaimer

The propositions I raise for discussion will cause expressions of horror. They have also have been common subject for tutorials in chemical analysis and lunch time discussion in laboratories for over four decades. The propositions are that the Treaty of the Metre, its associated administrative apparatus and the SI system of measurement units have

failed for chemical measurement and are of only incidental relevance to modern analysis, much of practical measurement in modern economies and much of recent technology. This failure stems from multiple and systemic sources is long term, and the prospects for reform are negligible. The question for chemical measurement is how to retrieve for the purposes of practical analysis those aspects of the system that are useful and coherent with chemical measurement practice and to develop simple, unambiguous, concise and commonly understood means of communicating the results of chemical measurements.

This is not undertaken lightly and must not be misunderstood as belittling the vital functions that measurements have today. Most discussions of the economics of measurement vastly underestimate its economic functions and usually quote some small but significant percentage of GDP to illustrate the value of measurement infrastructure to a modern economy. Poposki, Majcen and Taylor [1] have recently made a useful contribution to this literature. However, cost benefit approaches must be of limited usefulness when it comes to those most basic of mechanisms for economic co-ordination, currencies and measures.

The global financial crisis has focussed intense attention on global institutions for economic co-ordination. Measurement systems are instruments of economic co-ordination *par excellence*. We all need to think of the integrity of measurement results as being at least as important as the integrity of currencies and other financial instruments and apportion our critical faculties accordingly—for the stakes are indeed that high. That measurements are of vast economic significance is really beyond dispute. One needs only to reflect that the counterparties to any trade anywhere in the world at any level, from multinational to street corner bazaar, involving material goods all depend utterly on trust in measurements:

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the “other side of the coin” to our means of exchange. Not only the quantities that form the basis of the exchange, their amounts and their pricing but also the qualities of those goods are determined by the available measurement capabilities, as is the capacity to produce the goods and to deliver them. It is impossible to engage in commerce in our world without a trusted measurement system of some sort, and the degree of sophistication of that measurement infrastructure—and its integrity—is in a direct relation to the available possibilities in that economic system. Measurement systems are facilitators—they enable new things and new activities. But when they break down, when trust is compromised, Gresham’s Law applies as ruthlessly as it does to currencies. Bad measure drives out good.

The Convention of the Metre: a success

The Convention of the Metre was signed in 1875 and was intended to evolve as the basis of a global measurement system for those nineteenth century technologies based on classical mechanics. Its core was to be a system of National Measurement Laboratories whose representatives in various administrative organs were to develop a “rational, scientific” system of measurement units meant to form the basis of an evolving global measurement structure.

There were many successes. The example of electrical measurements is instructive. In the early nineteenth century, when electrical experimenters wanted to share results, they sent each other lengths of wire or explained how to construct the type of battery they used. The colossally expensive failure of the 1858 transatlantic telegraph convinced commercial interests of the need to set up a system of electrical standards, which developed in the ensuing decades just as the nascent electrical industry began its very early growth. In 1901, proposals were made to combine mechanical measurement units with practical electrical units in the MKSA system. By 1911, there were in existence banks of standard cells and resistors which were the basis of electrical measurements throughout the industrialised world. In 1949, the US National Bureau of Standards could report that [2]:

“...for the 37 years from 1911 to 1947 inclusive the national standardising laboratories, with invaluable coordinating service from the International Bureau of Weights and Measures, succeeded in maintaining throughout the civilised world a system of electrical units that did not vary in time ... by more than 0.1 of 1%”

And a failure...

Contrast that triumph with the case of chemical measurement. The chemists’ unit the mole was in use by the end of

the nineteenth century. A thermodynamic unit termed “the mole” was made a unit of the SI only in 1971, in a manner incoherent with most actual chemical measurement practice. The first action to implement that decision was the creation of a Consultative Committee (CCQM) a quarter of a century later. In the mean time, legal metrology authorities had been expressing grave concerns about chemical measurements, and growing disquiet among analysts was reflected in the creation of EURACHEM (a focus for analytical chemistry in Europe) and Co-operation in International Traceability for Analytical Chemistry (CI-TAC). Another sign of concern was the creation of Accreditation and Quality Assurance: this journal for quality, comparability and reliability in chemical measurement or ACQUAL. The International Measurement Evaluation Program (IMEP), now undertaken by the European Union’s Institute for Reference Materials and Measurements, was originally developed in 1976 for measurements of nuclear materials and arms control. In 1986, it turned its attention to non-nuclear chemical measurements, with disturbing results. The reader should examine the cover and logo of the journal you are now reading, ACQUAL. It is a globe superimposed with a representation of an IMEP. You do not need to be an expert to understand that something is very wrong. More recent results have shown much is still to be desired of the state of analysis, and laboratory managers still complain that needs continue to outstrip capabilities in exponential fashion. Incremental improvement is not nearly enough [3]. Despite this, analysts just get on with the job as best they can with the tools they have. They can rarely ask what might be and what new game-changing capabilities may arise should chemical measurement enjoy that global system of trust, assurance and transparency that for example anchors the gradations on any child’s school ruler and the indicators of any airliner’s navigation system anywhere in our world to a constant speed of light and a stable frequency of a certain radiation—and does so for cost virtually infinitesimal.

Yet, large-scale chemical industry and the need for reliable, trustworthy, practical chemical measurement *predated* the electrical industrial revolution by more than a century. The signatories of the Convention all wore suits whose dyes were the product of that industry, their shoes were shined with the products of that industry and their pens used ink made in that industry. The industrial manufacture and use of chemicals surrounded them; it was a pre-eminent economic story of their age. The measurement system that made it possible was based on growing knowledge of stoichiometry and the circulation of samples of pure materials. The growth of our understanding of stoichiometry, chemical reactions and later, bonding were basic advances in chemical thought, all largely ignored by the Treaty due to the absence of chemical thinking within

its structures from its very beginning. Well over a century later, in the light of subsequent non-events, it is not unreasonable to conclude that it is simply a fact of history that the organs of the Treaty have failed in the matter of chemical measurement—deeply regrettable as this may be.

Practical measurement

Chemical measurement is pre-eminently practical measurement. Analysts are very aware of the need to address fitness for an intended use or purpose—a longstanding weights and measures concept—and the complexity, specificity and dependence on particular circumstances and identity so characteristic of chemical measurements are also hallmarks of practical measurements as understood by weights and measures, legal metrology, trade measurement and practical industrial measurement. This is of major significance.

The fundamental failure of the Treaty of the Metre in practical measurements is also a simple matter of historical record. In 1955, the industrial nations that were signatories of the Convention of the Metre acknowledged formally that no common system of abstract quantities paired with a corresponding system of unit conventions could alone ensure harmony of practical measurement within or between their economies. They signed another Treaty that created separate but complementary institutions with international responsibilities for practical metrology—the International Organisation of Legal Metrology (OIML). From the beginning and despite the effusive rhetoric of co-operation, the relations between the institutions of “pure scientific” measurements and those for practical measurements were problematic. Many nations at the time well understood that there was potential for significant conflicts of interest and commercial sensitivities and set up separate national organisations for legal or practical metrology and linked them to the national weights and measures or trade measurement systems. The national measurement laboratories kept the standards; the national practical metrology organisations such as the legal metrology and accreditation authorities disseminated them.

However, economic rationalism and financial circumstance brought about amalgamations at national levels so that the representatives of practical measurement are increasingly of the same institutions and culture responsible for the Treaty of the Metre. The oft-noted cultural difference between physical and chemical measurement pales to insignificance compared to that between pure scientific measurements on the one hand and on the other weights and measures, legal metrology, trade measurements and practical measurements in industry and the economy. An indication of this cultural difference is

readily gained by looking at the contents pages of their respective official journals, *Metrologia* and the *OIML Bulletin*. It has not been an ideal of science and trade, equal open and co-operative partners, striding hand in hand to the future.

Much remains to be debated as to what a better architecture for a global measurement system might be, but history alone tells us the present one based on the institutions of the Treaty of the Metre has failed not only in the specific case of chemistry, but in practical measurement more generally. That is not to deny past substantial achievements in other areas.

The two moles

I turn now to the specific of chemical measurement. Let us be clear about measurement units. Whatever else they may be, measurement units are first and primarily instruments for the *linguistic communication* of measurement results [4, 5]. Units that cannot be understood by a general audience of their users, that are inconsistent, ambiguous, incoherent with common practice, confused in their conception of what is being measured, or simply not what they purport to be, are very much worse than useless. The base measurement unit for chemical analysis is the mole. There are two quite different “moles” in use today. On any level, practical or theoretical, this is not good metrology and is a source of deeply rooted confusion.

The first mole, the chemical mole, came into practical use at the end of the nineteenth century. Despite some now obsolete terms which allowed confusions with mass, such as gram-atom and gram-molecule, the basic concept proved to be a simple, elegant, effective and readily understood means of communicating chemical measurement results. Analysts were routinely taught to always work in (chemical) moles throughout the solution of an analytical problem and only convert results to mass at the end and only if required by the user. Working and thinking in (chemical) moles made complex problems simple and transparent, a sharp difference to the confusions of thinking in terms of mass when stoichiometry is concerned. For example, think of the complexity of using mass for a simple acid–base titration and the simplicity and clarity gained from merely thinking in terms of numbers of the chemical species of interest.

The chemists’ mole was simply an Avogadro number of things. The things need to be carefully specified—this is the chemical part of chemical analysis. One did not need to know a value (and uncertainty) for the Avogadro number (although it can be useful). The key point was that it was a number of things that, even if unknown to the last digit, was easily reproduced (within an evaluated uncertainty) in a multitude of ways and with a multitude of things—it was

superbly fit for the analyst's purpose. All one really needed to know was that it established the connection between a number of things, the identity of the things and the international units for mass and electrical quantities (if required by the user). That number of things was the number of hydrogen molecules (H_2) in 2 g of hydrogen (^1H), of oxygen molecules (O_2) in 32 g of oxygen (^{16}O), of carbon atoms in 12 g of carbon (^{12}C), of carbon dioxide molecules in 44 g of $^{12}\text{C}^{16}\text{O}_2$, of electrons in a faraday of charge and so forth. It was simple, straightforward and readily explained to the user. The arithmetic used to count very large numbers of things used that number as a multiplier simply so as to cohere with the other physical measurement units in common use, but in essence, chemical analysis was concerned with numbers of things because that is the way that things interact chemically. It is the chemical properties of things that nourish or poison us or damage the environment or release carbon dioxide or are important to industrial processes. It is the chemical properties of things that inform the object or purpose of most practical chemical measurement.

The second mole, the thermodynamic mole, was officially invented by administrative fiat in 1971 along with an entirely new physical quantity called "amount of substance", an ad hoc construction the likes of which had not graced text books since the times of phlogiston and the electromagnetic aether. In order to conserve formal consistency, Avogadro's number was separately transmuted and promoted by administrative decree to a physical constant of nature with unit mol^{-1} . The essence of the official definition states that the mole is the *amount of substance* of a system that contains as many elementary entities as there are atoms in 12 g of ^{12}C . Note that the phrase "as many entities" presupposes the concept of a number of things. Yet there is a new concept, amount of substance. What is the purpose of these superfluous words and concept? What are the users of chemical measurements to make of them? They seem to be unnecessary semantic obfuscation since nobody has yet explained in clear and simple terms to the general user of chemical measurements exactly what is an amount of substance, let alone what is its relevance to patients with cancer seeking to know what their blood tests really *mean*.

However, simple algebra and arithmetic as well as official pronouncements tell us unambiguously what amount of substance is not. It cannot be a number of things, any more than we can have three quarters of an atom. It is the wrong sort of number and the wrong sort of stuff.

The thermodynamic mole

It is not well understood that the SI versions of the mole and amount of substance are redundant and artificial

constructions of statistical thermodynamics. Jan De Boer, the architect of the SI system, was very clear on this in his reasoning for the introduction to the SI of the mole and amount of substance [6]. They were introduced for the purpose of making thermodynamic measurements. He did not mention chemistry, analysis or any related synonyms. For four decades, this not received the attention it deserves. The relevance to practical chemical measurement of the thermodynamic mole remains to this day tenuous. Recently, there was an authoritative attempt by Mills and Milton [7] to explain it. The explanation requires of its audience an education in thermodynamics. Even for the technically literate, it is not credible for reasons given below. For the average user of chemical measurements, it is simply incomprehensible. It does, however, resolutely confirm De Boer's view and proceeds to build an artificial thermodynamic construct called "amount of substance" whose unit is called "the mole". The authors admit that the name "amount of substance" is not well chosen. Although the name is wanting in many respects, it is the concept itself that is the larger problem, for what is omitted is any believable explanation of its relevance—however named—to practical chemical measurement. Like De Boer's account, the word "redundant" is missing but its presence is heavy in both papers. Mills and Milton acknowledge that the functions of the quantity, amount of substance, could equally be undertaken by another, more commonly understood quantity: number of entities. They offer three reasons for preferring the thermodynamic artifice. None of them are credible. The first two are *non sequiters*.

The first alleged reason for preferring "amount of substance" to number of things is that with the former, we can measure in (thermodynamic) moles without knowing the value for the Avogadro *constant*. But this is equally the case for the quantity number of things, and there was a time—before 1971—when analysts everyday measured in (chemical) moles without knowing the value of the Avogadro *number*. That is what the chemical mole is—it is a name for a given number of things, and even if we do not know what the number is, we can reproduce it, easily, simply, transparently. With this simple tool, we may count very large numbers of things indeed and the principles behind this sort of economy of arithmetic are a commonplace for all of humanity. That is why the second, allegedly practical reason given to prefer thermodynamics to chemistry is also beside the point. It is not necessary to report numbers of things at the human scale with numbers of the order of 10^{23} , as is alleged—the very terminology used to express it contradicts its own assertion and shows by example why humans invented the practical conventions of arithmetic to concisely convey the meanings of large numbers of things.

The third reason that is given to prefer artifice to practical number is a confusion of a different hue. It has two parts. The first part is the claim that amount of substance is necessary to extend the power of dimensional analysis to chemistry. The reference to dimensional analysis is surprising given the general aversion that the SI system has had for the principles of dimensional analysis and their alleged inconsistency with the quantity calculus. It is an allegation this writer regards as quite unproven but what is absolutely clear as simple historical fact is that many generations of analysts without any knowledge of “amount of substance” happily and usefully applied dimensional analysis to chemical equations in all their variety. Indeed, before the invention of “amount of substance” in 1971, a grounding in dimensional analysis was a common requirement of students in analytical chemistry to progress beyond basic levels of understanding. It is simply factually wrong to say that dimensional analysis cannot be applied to chemistry without “amount of substance”. The second part of this reason consists in the assertion that whereas “amount of substance” is a base quantity with its own dimension, a number of things are a dimensionless quantity. Assertion is not proof. There is a very simple test that can be applied to determine unequivocally whether a number of things is a dimensionless quantity or not. It is to enquire as to the kind of number that may be used to model or represent values of the quantity. It will be recalled that the “so-called dimensionless quantities” are by definition derived quantities having the general form of x divided by x , a ratio of similars. Therefore, they must of necessity be represented with the rational numbers, which are ratios of integers. The rational numbers form a continuum, and coherence requires that a dimensionless quantity be continuous. But a number of things is not expressible with a rational number. It requires whole, integral numbers. There can be no such thing as half an atom—it ceases to be an atom. A number of discrete things cannot be a continuous quantity. A number of things cannot be a dimensionless quantity because it cannot be expressed in the kind of number required for a dimensionless quantity. The claim that a number of things is a dimensionless quantity is self evidently false and with its falsity goes the final reason for preferring “amount of substance” to a number of things for the purpose of reporting chemical measurement results. On the other hand, very good reasons for avoiding “amount of substance” are that it is redundant, ad hoc, at best ambiguous, at worst self-contradictory [8]. Any proposal to reform the mole that retains reference to amount of substance [9] or any invented synonym is not credible as a means of communicating the results of practical chemical measurements. Teachers know only too well how difficult it is to explain the current definitions of the (thermodynamic)

mole. Some proposals for new definitions are virtually unteachable. In contrast, number of things is a concept well understood by the common run of humanity.

Exactly what is “amount of substance”?

Whatever the purpose of introducing the thermodynamic mole may have been, it cannot have been for the purpose of reporting the results of chemical measurements. The time has long passed when this should have been made very plain. We are paying a large price in technological opportunities foregone by this confusion. It is metrological absurdity to have two different units for two different quantities which share the same name. Clarity and simplicity in the communication of results is everything [10]. Ambiguity of this sort is simply not indefinitely sustainable, and it should not surprise that the mole is relatively less used in day to day practical analysis now than it was in 1971; the reason being that it is now simply inexplicable. It is notable for instance that even “key comparisons” for chemical measurements between national metrology facilities report results in terms of mass rather than “amount of substance”—a truly damning admission [11]. There is a heavy responsibility on the administrators of the Treaty of the Metre to carefully explain what exactly is an amount of substance in manner simply understood by politicians, juries, law enforcers, doctors, their patients and any citizen of any background who may have an interest in for example matters of the environment.

Despite being signatories to the Treaty of the Metre, some nations maintain two systems of units for common quantities such as mass or length throughout their economy and industry. Some of these are the most technologically advanced countries in the world, and the 1999 loss of an expensive spacecraft by one was a spectacular example of the need to ensure, for instance, that the data of navigation is expressed in the same units as the data for propulsion systems [12]. That sort of confusion, between kilometre and mile or kilogram and pound, compounds exponentially when added to the circumstance of two moles for two different quantities. Consider the hapless analyst who might work in ounces for mass [13] and the inconsistencies into which she must be led. For exactly the same sample, if she works in ounces, her quantity value (numerical value multiplied by units) in “ounce- (thermodynamic) moles” is different to the result of working in grams and official SI (thermodynamic) moles, even though mass does not appear in the final expressed result. In both cases, the actual number of entities in her sample stubbornly remains exactly the same. Amount of substance appears to be a strange sort of base physical quantity that none the less varies according to the particular mass units used. It is like

saying that a piece of meat varies in its weight depending on whether the ambient temperature is measured in degrees Celsius or degrees Fahrenheit (let alone whether the butcher weighs it in pounds or kilograms). This can of course be artificially rendered consistent by such semantic artistry as inventing more physical constants for just this purpose (and even in the post-modernist fashion, a meta-physical constant) and then making the corresponding and increasingly unbelievable arithmetic adjustments elsewhere, but verbal conjury of this sort contributes nothing whatever for the clear and concise and simple and comprehensible expression of results to users.

Just what is amount of substance? Why is it preferable to a number of things as a means of communicating chemical measurement results?

A number of things and the forms of unity

The simple fact is that the primary quantity of interest for chemical measurement is a number of things, identified and specified according to the purpose of the measurement [14]. The number must be a whole or integral number. You cannot have half an atom. Any given sample will possess its number of entities whatever particular measurement system for any other physical quantities the analyst chooses to use—that is the unique thing about the quantity number of things. The number may often be large but it is always finite and it is amenable to estimation and measurement within evaluated uncertainties. That is the primary feature of chemical measurement whatever other units may be combined with it to produce derived units for particular purposes. That has been the (usually very explicit) common presupposition of introductory textbooks on chemical analysis for more than a century. It is a simple concept, much discussed. Recent examples are [8, 14, 15, 16, 17]. But more often still it is just taken for granted. It is not a concept to be found in the SI.

Whilst it is a great advantage that the common quantity number of things is independent of which other particular measurement unit conventions may be chosen, it has an even greater virtue. It is a logically necessary part of any system of measurement units used to express measurement results. A number of things, small or large, is the universal quantity common to all possible consistent measurement systems. The SI, however, is curiously coy about whether counting should be so dignified as to merit description with the term measurement. There has been a low bustle of controversy in the halls of metrology for many decades concerning the status of unity as a unit. Many contentions and suggestions have been made but of agreement there has been none [8, 18, 19, 20, 21].

As analysts, we need to cut this particular Gordian knot with a bit of plain speaking. Any system of measurement units by their definition forms a group in the mathematical sense. It is required by definition that all groups include a form of unity. There are many forms of unity—or identity element to use the mathematical term—according to the type of group. There is plain one, as in one carbon atom or one rhinoceros or one event. This unity is a whole and positive number and the unitary basis of the idea of a whole, finite, countable number of things. It is the basic form of unity taken as a given by all other forms. Then, there is minus one. Then, there are the uncountably many unities having a general form of x divided by x . These are the rational unities, ratios of like with like. By definition, and as discussed previously, they are derived quantities—the “so-called dimensionless quantities”. Then, there are many other more complicated forms involving square roots and imaginary forms and other elegant constructions of mathematics and number theory which do not generally disturb most measurement users.

The form of unity which primarily concerns analysts is the plain everyday basic version understood by all—one identified thing. It is missing as a base unit from the SI, which as a consequence cannot of its nature, accommodate coherently the practical realities of chemical measurement. It is a simple but unfortunate truth that counting the quantity that it measures (number of things) and that quantity's base unit (one thing) do not currently form a basic part of the SI system.

We cannot reasonably ask of any unit system that it be complete. Consistency, however, is a very modest ambition.

Consequences beyond chemistry

This singular logical failure of the SI has serious consequences outside of metrology in chemistry. As the history shows, our current global measurement system was based on the fundamental assumptions of nineteenth century classical mechanics and evolved following the footsteps of the development of that branch of physics. Even here there were troubling indications. For example, the conceptual changes wrought by special relativity have been accommodated, albeit uneasily, but general relativity and the quantum revolution not at all, despite clever particular practical uses of the Hall effect and quantum devices. This is important for we now know that many quantities the subject of intense technological interest, some once thought to be continuous, have now proved with finer discrimination to be granular and that below a certain level, an amount of such a quantity has no meaning, just as half an atom is not a possibility. The assumption of continuity of

quantity values that underlies the idea of a “rational scientific” system of units has been shown to be not the case, by scientific means. Note that I am using “rational” in its correct metrological sense of pertaining to ratios. The assumption of a rational measurement system is that all quantity values must be expressed using rational numbers which form a continuum, as opposed to the natural or counting numbers which are quantised. Today, in addition to chemistry and all its associated technologies, we have information and communication technologies and sciences, nanotechnologies, biotechnologies, genomics, genetics, molecular biology, micro biology, quantum computing, molecular engineering and a “digital culture”. None of these can be coherently accommodated by any measurement system that fails to openly include counting as a bona fide base measurement.

Conclusion: an unsatisfactory present state of communication

We currently have a global measurement system that is failing in respects that are vital to the needs of both global trade and the technological and industrial futures of the signatories of the Treaty of the Metre. Measurement system failures of these kinds happen slowly, almost imperceptibly, cause vast damage which is only ever be fully understood long after the fact, and take many decades to rectify. The current unsatisfactory means of expressing chemical results has lingered for many decades. Chemists have largely been silenced by a general fear that what cannot be understood might haply be true. That suspicion may or may not be correct, but what is absolutely indisputable is that what cannot be understood must never, ever, be used to express and communicate measurement results.

It is clear that there are systemic cultural and institutional factors at play in this matter and the next part of this discussion will examine recent strategic reviews by the governing body of the Treaty, assess the likelihood of reform from this source and discuss the possibilities for simple and effective means to communicate with clarity and understanding chemical measurement results without the ambiguities and irrelevancies surrounding the SI (thermodynamic) mole.

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