

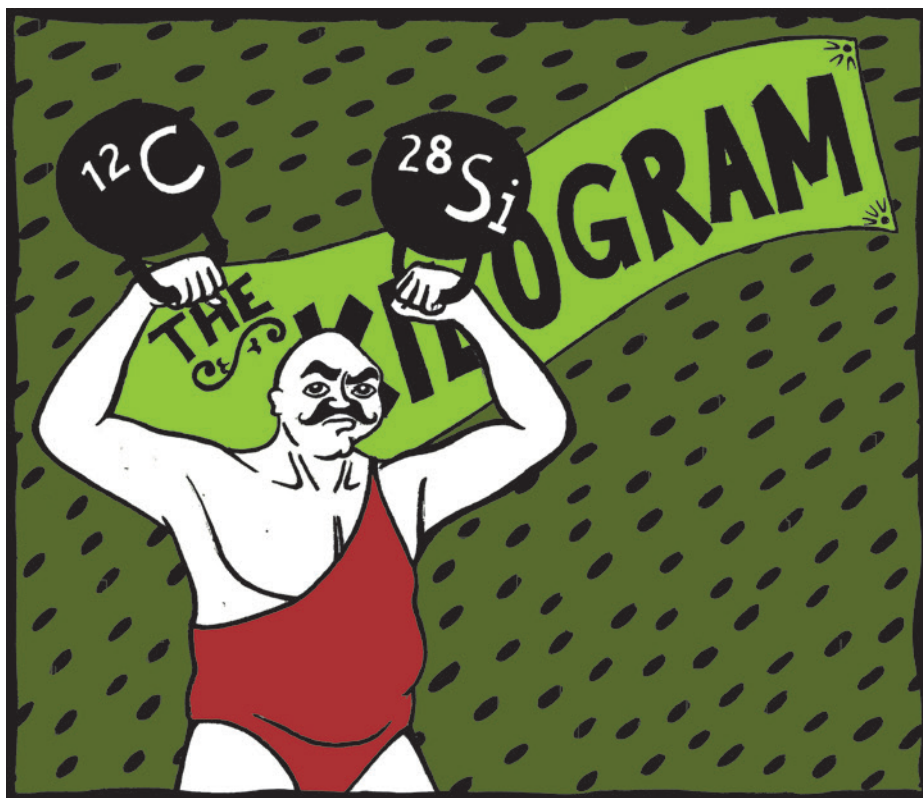
An ode to the atomic weights

They might not be fundamental constants of nature, but atomic weights are one of the foundations on which modern chemistry is built, explains **Juris Meija**.

One hundred years ago the Harvard University chemist Theodore William Richards was awarded the 1914 Nobel Prize in Chemistry for his accurate determination of the atomic weights of many elements. This was the first in what has become a long line of Nobel Prizes in Chemistry received by American scientists. A century ago the atomic weights were considered sacrosanct ‘constants of nature’, and it was ‘a much agitated question’ whether or not the atomic weights of nickel and cobalt were inexplicably identical¹. In contrast, today’s periodic tables portray variations of atomic weights in nature, and the eighth digit of the atomic weight of silicon in the grapefruit-sized multimillion-dollar silicon-28 crystal sphere is under intense scrutiny in support of the impending redefinition of the kilogram². These disparate examples from this century and the last are a testament to the advances in science over this period. It also shows that the interest in atomic weights remains unabated.

Atomic weight is part of the fabric of chemistry, much like J. S. Bach is when it comes to classical music. The concept of atomic weights appears on classical science curricula, and plays its small, yet important, role in popular culture. Think of the episode of *The Simpsons* television series in which Edna Krabappel asks “who can tell me the atomic weight of bolognium”, or the final clue in Dan Brown’s debut novel *Digital Fortress*, which has to do with the atomic weight of uranium.

One frequently asked question about atomic weights concerns the utility of the numerous decimal digits. Paraphrasing what the Nobel Laureate Steven Chu had to say during the 125th anniversary celebrations of the Metre Convention, the short answer is that new science begins at the next decimal place. Indeed, many fascinating discoveries in the history of science can be recounted to illustrate this point. In his 1934 Nobel Lecture, for example, Harold Urey recounts how the fourth-digit discrepancy in the atomic weight of hydrogen led him to the discovery of deuterium (soon thereafter, heavy water played a vital role in the Manhattan Project)³. Likewise, in 1972 the small discrepancy in the abundance of uranium-235, 0.003% less than the normal



abundance of 0.720%, led to the discovery of a natural nuclear reactor in Oklo (Gabon), which was active two billion years ago⁴. A more recent example of 0.0001% bias in the atomic-weight estimate of silicon led to a decade of standstill in the ongoing redefinition of the kilogram and the mole⁵. When it comes to the impact of such measurements in popular culture, although many will not appreciate the science behind the headlines, a doping test can be declared positive if the atomic weight of carbon — as measured by the ratio of its two isotopes — differs by more than 0.0003% between a pair of steroids in an athlete’s urine.

The Avogadro and Planck constants are both slated to become integral parts of the International System of Units (SI). These two constants are related through the Rydberg constant, which enables comparison between them. The Avogadro constant obtained from the X-ray crystal density measurements of silicon in the early 2000s did not agree well with the Planck constant obtained from

watt balances. While this disagreement of a few parts-per-million is now known to have arisen from an overlooked error in the calibration of the atomic-weight measurements, at the time it questioned the validity of two phenomena that led to Nobel Prizes in Physics — the quantum Hall and Josephson effects^{6,7}. Several other fundamental constants of nature are determined with the help of high-precision atomic-weight measurements. For example, the atomic weight of silver has an influence on the quality of the best measurement of the Faraday constant⁸, as does the atomic weight of argon in the best measurement of the Boltzmann constant⁹.

Natural variations of the isotopic composition of oxygen and hydrogen have significance well beyond the atomic weight of these elements. In the mid-1990s, for example, it was noticed that isotopic variations associated with New Zealand water gave rise to measurable differences in temperature readings from

water triple-point cells¹⁰. As a consequence, the General Conference on Weights and Measures revised the definition of the kelvin in 2007 by specifying the isotopic composition of the water for which the triple-point is defined as 273.16 K exactly¹¹. Owing to the ever-greater prominence of natural variations in the atomic weights of some elements — simply because of our ability to measure them — in 2009 IUPAC recommended a new format for expressing standard atomic-weight values by using intervals in these cases¹².

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Atomic weights also play a role in 'everyday' science. As an example, comparison of weights of dissimilar materials in air is affected by buoyancy, and the correction for this effect typically requires knowledge of the atomic weight of air (which determines its density). Air buoyancy is, if uncorrected, often the largest source of error in weighing. If Richards had ignored this effect when determining the atomic weight of hydrogen, he would have obtained 1.003 instead of 1.008 (ref. 13) and errors of this magnitude would certainly not have distinguished him with the 1914 Nobel Prize in Chemistry. Perhaps much less widely known is that atomic weights are used to calculate standard densities of all metals from X-ray crystallography data. This, in fact, created a 'nerd-alert' of sorts some twenty years ago when the atomic-weight revisions by the Commission on Isotopic Abundances and Atomic Weights (<http://ciaaw.org/>) promoted osmium over iridium as the densest metal¹⁴.

In October 2011, the General Conference of Weights and Measures resolved to proceed with the redefinition of all SI base units in terms of fundamental invariants of nature¹⁵. Chemists have, in fact, adopted this strategy ever since John Dalton published his table of atomic weights in 1808. In his book *A New System of Chemical Philosophy* he writes "in all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity". Whether expressed in terms of the mass of hydrogen, later oxygen, and now carbon-12 atoms, atomic weights have always been expressed in terms of the mass of an atom (and therefore always remained outside the SI). Dalton's ingenious introduction of the atomic unit of mass at the time when the very idea of atoms was fiercely contested,

catapulted quantitative chemistry to new heights. It made it possible, for the first time, to establish a practical connection between mass measurements and chemical stoichiometry. The use of atomic weights, in conjunction with the mass measurements of substances, still remains a common means for stoichiometric calculations in chemistry.

The Newtonian constant of gravitation has been widely regarded as 'a constant too difficult to measure'¹⁶. Atomic weights, albeit not constants, do most certainly fit this bill. For a large number of elements, measurement science is not mature enough to allow for calibrated measurements of atomic weights or isotope ratios, let alone high-precision measurements. A vivid example of this was the 'drastic' change of the standard atomic weight of zinc in 2007 arising from inadequate prior measurements. In fact, zinc became the first element whose standard atomic weight fell outside the conservative uncertainty bounds of the previous value in the century-long history of the Atomic Weights Commission.

Advances in measurement precision often lead to a new understanding of the world, and isotope-ratio measurements are no exception to this. Determination of atomic weights in the nineteenth century was a journey towards the gradual elimination of impurities¹⁷. The twentieth century saw the development of mass spectrometry, and the painstaking gravimetric measurements of the past were soon superseded by this technique. Standard atomic weights of all but one element (tellurium) are now based on mass spectrometry. These measurements are no longer limited by impurities, but rather by the calibration of the mass spectrometers because they are not faithful in preserving the isotope ratios. Lighter ions travel faster than the heavier ones and their ratios are therefore altered as they traverse the various regions of the instruments from the sample introduction inlet to the detector. To obtain accurate results, a standard with a known isotope ratio is required.

Before the 1950s, the accuracy of mass spectrometry measurements were ascertained by comparison to the atomic weights obtained by means of classical wet chemistry. Indeed, for many elements the mass spectrometry results agreed well with the chemical methods¹⁸. Starting in the 1950s, gravimetrically prepared mixtures of two near-pure isotopes were used to calibrate isotope-ratio measurements. This ensured an independence of mass spectrometry measurements from the chemical methods of the past. More than fifty years later, however, the calibration of isotope-ratio measurements still remains a challenge¹⁹. A case in point is

that a calibrated measurement of a three-isotope system (silicon) was performed only recently, and was greatly aided by the resources of the colossal International Avogadro Project²⁰. In the absence of standards with known isotope ratios, isotopic measurements for some thirty elements, including oxygen, are performed using standards with values agreed upon by scientists. Accurate isotope-ratio measurements depend not only on the availability of standards, however, but also on the validity of the underlying calibration procedures. Since its introduction in the 1960s, so-called double-spike calibration has remained a common method in geological sciences, although the impact of its underlying mathematical assumptions is not yet fully understood²¹.

Atomic-weight research has witnessed a natural progression. The nineteenth-century chemists set out on the quest to determine the atomic-weight values, which indeed culminated with the 1914 Nobel Prize in Chemistry for Richards. The twentieth century was largely shaped by the quest to understand these values, which led to the discovery of isotopes and the realization that the atomic-weight values of many elements do vary in nature. It is premature to judge what the twenty-first century will bring, but the quest to measure atomic weights and isotope ratios with ever-increasing precision is bound to reveal new phenomena. □

*Juris Meija is the Chairman of the IUPAC Commission on Isotopic Abundances and Atomic Weights and is at the National Research Council Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada.
e-mail: Juris.Meija@nrc-cnrc.gc.ca*

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