Isotopic Abundances and Atomic Weights

History of IUPAC Commission II.1 in the Service of Chemistry*

by John R. De Laeter

tomic weights are of fundamental importance in science, technology, trade and commerce. In particular, atomic weights relate mass to molar quantities. It is therefore not surprising that the measurement of atomic weights has played a central role in the development of chemistry and continues to be a key component in the progress of discipline.

By the middle of the 19th century the atomic theory and its implications for the chemical elements had taken firm hold. Nature was seen to be using remarkably few types of elementary "building blocks" for all materials. With an understanding of simple-number valencies of these "elements", the stage was set for chemistry to emerge as a science based on measurement of the interactions between "atoms" of the elements in simple mass proportions. Chemical reactions, energies, and products, could now all be represented by simple formulae and equations. With newly developed balances of high precision, the relative mass values of the atoms of the elements could be determined. When scaled to the mass of hydrogen equal to one, or oxygen equal to sixteen, these relative elemental masses became known as "atomic weights."

Quantitative chemical analysis of materials with uncertainties a little better than 1 % became possible and widely practiced. However, there was an increasing need to determine the ratios between these constants with higher reliability than could be achieved by chemical analysis. To determine atomic weights to the highest possible accuracy, Berzelius and others developed the quantitative gravimetric study of the most stoichiometric compounds and the most complete reactions for each known element. Often the compounds and reactions involved oxygen, less frequently hydrogen, chlorine, bromine, or silver. Atomic weights, scaled to hydrogen or oxygen, and the oxygen/hydrogen mass ratio in water, were measured with great skill under carefully controlled conditions of purity and freedom from contaminations. New and better atomic-weight determinations by classical chemical methods also drove progress in chemistry, for instance in purification and recovery methodologies and insight into isotropy. The scientists, among them Richards, Brauner, Urbain, Hönigschmid, and Baxter who measured atomic weights, were rightfully accorded the highest honor among professional scientists.

As early as 1872 Frank W. Clarke, chief chemist at the US Geological Survey, recognized that measurement compatibility between laboratories made uniformly recognized atomic weights desirable. Under his leadership the best contemporary knowledge of the atomic weights became the primary task of the American Chemical Society's Committee on Atomic Weights, formed at the start of the 20th century, and of which the IUPAC Commission on Isotopic Abundances and Atomic Weights [CIAAW or Commisssion II.1] is the direct descendent.

An elaborate international election of 57 chemists from many nations was organized by W. Ostwald, and, as a result, the Commission was initially entrusted to just three members who had obtained the highest number of election votes: F. W. Clarke, K. Siebert from Germany, and T. E. Thorpe from England. There was a strong feeling that France, a leader in the promotion of rational unification in measurement science, had to be represented on the Commission. So first H. Moissan and, after his death, G. Urbain of France joined the Commission. It preserved continuity through World War I despite problems in contacting German colleagues through Switzerland, as is documented in our Commission archives.

Nevertheless, after World War I the Commission flourished. It subordinated itself to the International Union of Pure and Applied Chemistry when that organization was established (in 1919). IUPAC saw the Commission's mandate at the heart of its own responsibilities to the world's science community. Indeed, no data set of science and technology has been or is now used more extensively or in as many disciplines, technologies, and commercial transactions, as is the IUPAC table of recommended atomic weights, now called the standard atomic weights. Reproduction of the table is encouraged by IUPAC and all cognate data are freely available in print or online.

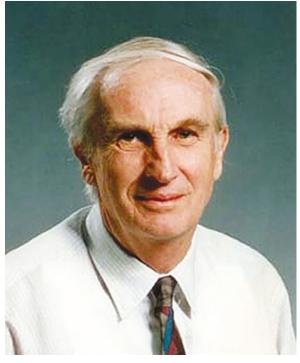
In 1921 it was decided to reorganize and enlarge this Commission by giving it the responsibility of advising on the existence of radioactive and stable isotopes, as well as on atomic weights. It was renamed the

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Committee on Chemical Elements. Two members of the Committee were Francis Aston and Frederick Soddy, both of whom had received Nobel Prizes for their work on isotopes. Altogether six Nobel Prize laureates have served on the Commission and two of them have chemical elements named after them (Curie and Flerov). In 1930 the Committee on Chemical Elements was subdivided into three parts, one of which became the Atomic Weights Committee. In 1979 this Committee became the Commission of Atomic Weights and Isotopic Abundances (CA-WIA), which has the role of evaluating new isotope abundance and other relevant data and providing the outcome of such investigations to the scientific

community on a regular basis.



John Robert de Laeter (1933-2010) served as the 11th Chairman of the CIAAW from 1988-1991, prior to which he also served as the CIAAW Secretary from 1983-1987. He remained active member of the CIAAW and attended his last CIAAW meeting in 2009 (Vienna).

In the second half of the 20th century, the Commission has not only evaluated and reported best knowledge of atomic weights on a biennial basis, but has also made wider retrospective evaluations of improvements achieved in the data set and in the reliability of the data. The precision and reliability of the tabulated values of atomic weights show considerable improvements during all periods of this century. The objective is for users to be confidently assured that the atomic weight of an element from any source, be it taken from laboratory shelves, from a manufacturing process, or from nature, will truly be in the guoted interval. The Commission in its reports highlights the causes for exceptional atomic-weight values. When in future years the precision of tabulated values improves further, the Commission will need to expand the statements on exceptions. At all times during the 20th century, atomic weights have been of adequate precision for the vast majority of concurrent relevant applications. Among the memorable events was Mattauch's and Wichers' persuasion of the physics and chemistry communities respectively to use the mass of carbon-12 isotope for the atomic weights scale. In addition, in 1971 the international community, under the Metre Convention, defined the number of carbon-12 atoms in 12 g of carbon-12 as the unit of amount of substance of any chemical entity. That new unit was called the mole, a well-known term in chemistry, though previously it carried a slightly differing definition.

Two major reviews of the atomic weights of the elements have been published. The first was published in 1962, in which the existing chemical and physical determinations of the atomic weights of all the elements were reviewed in the light of the new reference nuclide carbon-12 (Wichers and Cameron, 1962). A second element-by-element review, which critically examined the changes

that had occurred in the atomic weights of each element since the first report, was published in 1984 (Peiser *et al.*, 1984). A third review, which evaluated all the changes that have taken place in atomic weight in the 20th century was published in 2003 (de Laeter *et al.*, 2003).

Most of the determinations of atomic weights in the first half of this century were based on gravimetric procedures in which the mass ratio of the chloride or bromide of the elements to the chemically equivalent amount of silver or the corresponding silver halide was measured. The relationship of silver to the primary oxygen standard was established by accurately measuring the silver-silver nitrate ratio. This technique became known as the "Harvard Method". The discovery of isotopes led to an alternative "physical" method of determining atomic weights, and since the 1940s very few chemical determinations have been carried out. The predominant method for determining atomic weights is now based on the isotopic composition of the element combined with the relevant atomic masses. CIAAW uses published tabulations of the atomic masses in determining atomic weights by the Atomic Mass Evaluation Group.

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In 1969 there was a serious move within IUPAC to eliminate the Atomic Weights Commission. Not that atomic weights were not needed—not that the Commission had performed badly—no, it was because atomic weights were then thought to be so accurate that any further improvement was at most an 'academic' exercise of no interest or relevance to professional chemists, or chemical technology, and certainly not to commerce. The physical method of determining atomic weights was so successful, that chemists were not fully able to utilize the accuracy which had so painstakingly been achieved.

In the 1980s it became clear that the very techniques that gave more accurate atomic weights could be employed to do chemical analyses and other chemical measurements to equal accuracies. New applications sprang into prominence, among them the ability to use subtle differences in sample atomic weights for identifying sources of materials, influences from manufacturing processes, and mechanisms of biological reactions. So in atomic-weight measurements we have come around full circle. From the classical emphasis on better atomic weights, higher and no longer needed accuracies were achieved, that in turn are being applied to novel, practically important measurements that now drive us once again to aim at values that have significantly better accuracies than can now be achieved from the best modem analytical measurements.

While the Commission made such progress in atomic weight determinations and assessments, the more universal art of measurement at the highest achievable accuracy also advanced. That field, called metrology, received wide recognition especially in physics and engineering. A world-wide agreement came into use on an international system of units of measurements (SI). The previously mentioned mole is an SI base unit, namely that for quantities of amount-of-substance. Other new insights and conventions of metrology are actively disseminated by the International Organization for Standardization with participation by IUPAC. Some of these may be found applicable to the work of the Commission. Among these is the concept that the estimated uncertainty of a measurement is its sole quantitative measure of quality. With only a slight problem with the definition, the Commission has in fact pioneered uncertainty estimates since 1969.

The metrological importance of reference standards with certified values has equally been recognized by the Commission as playing a key role in the determination of the atomic weights in specific

samples. Reference materials enabled laboratories with sensitive instruments to make 'traceable' (accurate, absolute) determinations from relative measurements of similar uncertainty without a reference value. The Commission in the years ahead may find itself involved with uncertainties, reference materials, and other concepts of metrology, such as statistical evaluations and choices in nomenclature in cooperation with IUPAC Interdivisional Committee on Terminology, Nomenclature and Symbols.

In more recent years, the Commission has undertaken additional responsibilities. Most important is that of publishing tables of isotopic compositions of the elements consistent with the standard atomic weights, if not necessarily with their respective uncertainties. The Commission also makes a substantial effort in abstracting and summarizing literature information on the isotopic compositions of non-terrestrial materials. The rapidly increasing knowledge and diversity of available information might eventually outgrow the Commission's ability to fulfill this function. At the present time (1999) the Commission has a Subcommittee for Natural Isotopic Fractionation, which is charged with the responsibility of investigating the impact of naturally occurring fractionation processes on the isotopic abundances and atomic weights of the elements—particularly with respect to the uncertainties which these processes impose.

However, the primary work of the Commission is to continually evaluate the literature on isotopic abundances and atomic weights so as to provide accurate information to the scientific community on a regular basis. This data is accepted as the authoritative information in the field and is used for many purposes—including the refinement of fundamental constants.

References

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For more historical information, please read Atomic Weights and the International Committee—A Historical Review by N.E. Holden. *Chem. Int.* **26**(1), 4-7 (2004); http://dx.doi.org/10.1515/ci.2004.26.1.4