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THE ROLE OF MASS SPECTROMETRY IN ATOMIC WEIGHT DETERMINATIONS

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The 1914 Nobel Prize for Chemistry was awarded to Theodore Richards, whose work provided an insight into the history of the birth and evolution of matter as embedded in the atomic weights. However, the secret to unlocking the hieroglyphics contained in the atomic weights is revealed by a study of the relative abundances of the isotopes. A consistent set of internationally accepted atomic weights has been a goal of the scientific community for over a century. Atomic weights were originally determined by chemical stoichiometry—the so-called "Harvard Method," but this methodology has now been superseded by the "physical method," in which the isotopic composition and atomic masses of the isotopes comprising an element are used to calculate the atomic weight with far greater accuracy than before. The role of mass spectrometry in atomic weight determinations was initiated by the discovery of isotopes by Thomson, and established by the pioneering work of Aston, Dempster, and Nier using sophisticated mass spectrographs. The advent of the sector field mass spectrometer in 1947, revolutionized the application of mass spectrometry for both solids and gases to other fields of science including atomic weights. Subsequently, technological advances in mass spectrometry have enabled atomic masses to be determined with an accuracy better than one part in 10^7, whilst the absolute isotopic composition of many elements has been determined to produce accurate values of their atomic weights. Conversely, those same technological developments have revealed significant variations in the isotope abundances of many elements caused by a variety of physiochemical mechanisms in natural materials. Although these variations were initially seen as an impediment to the accuracy with which atomic weights could be determined, it was quickly realized that nature had provided a new tool to investigate physiochemical and biogeochemical mechanisms in nature, which could be exploited by precise and accurate isotopic measurements. Atomic weights can no longer be regarded as constants of nature, except for the monoisotopic elements whose atomic weights are determined solely by the relative atomic mass of that nuclide. Stable isotope geochemists developed mass spectrometric protocols by the adoption of internationally accepted reference materials for the light elements, to which measurements from various laboratories could be compared. Subsequently, a number of heavy elements such as iron, molybdenum and cadmium have been shown to exhibit isotope fractionation. The magnitude of such isotope fractionation in nature is less than for the light elements, but technological developments, such as multiple collector-inductively coupled plasma-mass spectrometry, have enabled such fractionation effects to be determined. Measurements of the atomic weights of certain elements affect the determination of important fundamental constants such as the Avogadro Constant, the Faraday Constant and the Universal Gas Constant. Heroic efforts have been made to refine the accuracy of the atomic weight of silicon, with the objective of replacing the SI standard of mass—the kilogram—with the Avogadro Constant. Improvements in these fundamental constants in turn affect the set of self-consistent values of other basic constants through a least-squares adjustment methodology. Absolute isotope abundances also enable the Solar System abundances of the s-, r-, and p-process of nucleosynthesis to be accurately determined, thus placing constraints on theories of heavy element nucleosynthesis. Future developments in the science of atomic weight determinations are also examined. © 2008 Wiley Periodicals, Inc., Mass Spec Rev 28:2–19, 2009

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> "If our inconceivably ancient universe even had any beginning, the conditions determining that beginning must even now be engraved in their atomic weights. They are the hieroglyphics which tell, in a language of their own, the story of the birth or evolution of all matter."
>
> T.W. Richards (Nobel Prize Lecture in Chemistry, 1914). (see Richards, 1966)

I. INTRODUCTION

Theodore Richards displayed an amazing understanding of the ultimate nature of atomic weights when he described them as being hieroglyphics of the past. And he was correct—in that atomic weights do tell a fascinating story of the birth *and*

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evolution of all matter. Sir Arthur Eddington expressed a similar sentiment when he proclaimed that ''what was happening in the Cavendish Laboratory (nuclear transformation, by Rutherford and his students), may not be too difficult in the Sun'' (Eddington, 1926). He based this observation on the fact that Aston (1919) had measured a mass loss of approximately 0.08% in the formation of helium from hydrogen, using a primitive mass spectrograph. This basic thermonuclear mechanism which converts hydrogen to helium, now known as ''Hydrogen Burning,'' is the source of energy which fuels Main Sequence stars such as the Sun. On the basis of this isotopic evidence, Eddington (1926) was also able to estimate that the Sun would keep on converting hydrogen to helium for another 10 billion years.

Although isotopes were only just becoming known in 1919, they held the secret of the hieroglyphics of atomic weights of the chemical elements, as the atomic weights of polyisotopic elements, are determined by their relative isotope abundances. The manifold variations in the isotopic composition of the elements is now known to depend on principles of nuclear physics, or more correctly nuclear astrophysics, because various nucleosynthetic processes occurring in stars have determined the present-day magnitude of the atomic weights, in an on-going creation story which commenced billions of years ago. Hydrogen, some helium and a little lithium are believed to have been produced at the time of the cataclysmic event we call the: ''Big Bang.'' The isotopes of the ''light'' elements (defined as those with an atomic number $Z < 28$) are synthesized by a combination of thermonuclear and neutron capture reactions, whilst the isotopes of the ''heavy'' elements (with $Z > 28$), in the main by neutron capture reactions. In fact, as Aston carried out his mass spectrographic determinations of the isotopic composition of an increasing number of elements, he began to realize the underlying implications of the relative isotope abundances in terms of nuclear physics. His development of the so-called ''Packing Fraction Curve'' which reflected the nuclear stability of the isotopes, led to a model of the nucleus which proved to be an effective description for over a decade. Aston's other great achievement was to re-instate the ''Whole Number Rule,'' which has stood the test of time (Aston, 1919). An examination of a present-day Table of Atomic Masses shows that apart from hydrogen, with an atomic mass of 1.00794, all the other atomic masses are within 1 part in 10^3 of the whole number. It is of interest to note that the atomic mass of helium is 4.002602, which enables three helium nuclei to be converted to ^{12}C in a process called ''Helium Burning'' which is the energy source which fuels Red Giant stars.

The composition of the isotopes controlling the magnitude of the atomic weight of an element was synthesized in a large number of stars at various stages of their stellar evolution. Main Sequence stars, Red Giant stars and Supernova are three important phases of a stars's life in which different nucleosynthetic processes dominated, until such time as this complicated assemblage of isotopic material was finally gathered together in the cloud of gas and dust which gave birth to the Sun and the Solar System. Thus, the material that constitutes the Earth–including the material in our own bodies–was synthesized in stars over a long period of time. The supernova explosion, which in all probability, triggered the collapse of the gaseous cloud which was to become the proto-Sun, gave birth to a new generation of stars, including our Sun, but only by its own cataclysmic death.

Most of this nuclear astrophysical information was not understood until 1957 when Burbidge et al. (1957) and Cameron (1957) independently laid the foundation of nuclear astrophysics, which explained the synthesis of the isotopes of the elements in stellar interiors. Measurements of the absolute isotopic composition of the polyisotopic elements enable the Solar System abundances of the isotopes for the various nucleosynthetic processes to be accurately determined, thus providing constraints on nucleosynthetic models. In retrospect, the insight of Richards some 38 years earlier, is even more astounding.

Atomic weights are one of the most fundamental sets of scientific data, since they enable mass to be related to amounts of substance, which is the basis of analytical chemistry. Atomic weights have a practical application as they are the basis of trade and commerce, as those transactions involve amounts of substance. The concept of atomic weights was advanced in the early part of the 19th century when John Dalton published a table showing ''the:relative weights of the ultimate particles in gaseous and other bodies'' (Dalton, 1805). Although Dalton had suggested that hydrogen be the basis of atomic weights, by the beginning of the 20th century it was generally accepted that the atomic weight scale be based on the weight of one atom of oxygen, being exactly equal to 16.

As early as 1872, Clarke recognized that measurement compatibility between laboratories was essential to develop a uniform set of atomic weights. Under his leadership, the best contempory knowledge of the atomic weights became the priority task of the American Chemical Society's Committee on Atomic Weights (Clarke, 1886). In 1902, the International Committee on Atomic weights was formed to coordinate this important field of science. However, it was not until 1920 that this international committee was formerly constituted as part of the International Union of Pure and Applied Chemistry (IUPAC). In 1921, this committee was re-named the Committee on the Chemical Elements, with the responsibility of advising on stable and radioactive isotopes as well as on atomic weights. In 1930, the Committee on the Chemical Elements was sub-divided into three groups, one of which became the Atomic Weights Committee. Forty-nine years later, it was given the title of the Commission on Atomic Weights and Isotopic Abundances (CAWIA), in recognition of the fact that atomic weights were now determined by isotope abundance and atomic mass measurements. More recently, in 2001, CAWIA was renamed the Commission on Isotopic Abundances and Atomic weights (CIAAW) in view of the dominant role of mass spectrometric measurements, not only in determining atomic weights, but in many other fields of science as well.

CIAAW has the role of evaluating new isotope abundance data and the implication of these new measurements to the magnitude and associated uncertainties of atomic weights, every 2 years, and then publishing a Table of Standard Atomic Weights incorporating these changes. CIAAW is also responsible for publishing a Table of the Isotopic Compositions of the Elements approximately every five years for the international scientific community. CIAAW and its numerous predecessors, probably represent the longest-serving international scientific body in existence. The importance of this body to science is exemplified by the fact that a number of Nobel Prize winners have served on the Atomic Weight Committee over the years.

II. THE DETERMINATION OF ATOMIC WEIGHTS

At the turn of the 20th century, the Harvard Method was used to determine the values of the atomic weights. This method was based on accurate gravimetric measurements using chemical stoichiometry, and is dependent on the mass relationships between the halide of the element concerned, silver or a soluble silver salt. The silver halide is precipitated from pure soluble salts of silver and the halide of that element. This method was developed by T.W. Richards at Harvard University, and he received the Nobel Prize in Chemistry in 1914 for his pioneering work. Richards, his successor at Harvard in Baxter, and Honigschmidt at the University of Munich, reported approximately 140 independent determinations of atomic weights using the Harvard Method (Richards & Lembert, 1914).

A major change in the methodology of determining atomic weights was initiated by the discovery that neon existed in at least two isotopic forms of mass 20 and 22 (Thomson, 1912). This crucial experiment explained why the measured atomic weight of neon was 20.2 rather than the expected whole number, since approximately 90% of the neon existed as ^{20}Ne. Thomson encouraged Aston to develop a mass analyzer with higher resolution than he had attained with his parabola method. Aston designed and constructed a series of increasingly sophisticated mass spectrographs (so named because of their similarity to an optical spectrograph), with which he determined the isotopic composition of most of the elements (Aston, 1942).

Other physicists, such as Dempster and Nier, designed other mass spectrographs and used them to measure, with increasing accuracy, the isotopic composition of gaseous and non-gaseous elements, and in the process U-Pb geochronology was established as an important tool in geology (Nier, Thompson, & Murphy, 1941). Dempsrer, in the early 1920s, measured the atomic weight of magnesium, potassium, zinc, calcium and lithium from his relative abundance measurements of these elements, assuming whole number mass values of the isotopes (Dempster, 1921, 1922). Thus began the ultimate demise of the chemical stoichiometry method of determining atomic weights.

The atomic weight $A_r(E)$ of a polyisotopic element, can be determined from a knowledge of the absolute isotope abundances, and the atomic masses of each of the isotopes as given in the equation:

$$A_r(E) = \sum[x(^iE)A_r(^iE)]$$

where $A_r(^iE)$ is the atomic mass of an isotope i of element E, and $x(^iE)$ is the molar fraction of isotope ^iE in a mole of element E; $x(^iE)$ is also called the abundance of isotope ^iE.

Isotope abundances which are free from all known sources of bias are referred to as ‘‘absolute’’ isotope abundances and, together with the relevant atomic masses, enable ‘‘absolute’’ atomic weights to be calculated. In order to produce such ‘‘absolute’’ isotope abundances, the mass spectrometer must be calibrated by means of gravimetric mixtures of a pair of enriched isotopes of the element in question. The measured bias can then be used to convert the ‘‘observed’’ or ‘‘relative’’ isotope abundances into ‘‘absolute’’ isotope abundances. Although a number of variants have been used to calibrate a mass spectrometer, the two basic procedures are those developed by the U.S. Bureau of Standards (now the National Institute of Standards and Technology, NIST), which is described by Powell and Murphy (1984), and that developed by the Institute of Reference Materials and Measurements (IRMM) as described by De Laeter, De Bièvre, and Peiser (1992). In assessing new experimental determinations of atomic weights, CIAAW evaluates evidence of the linearity of the detection system used in the analyses over the range of isotope ratios reported, the absence of any isobaric interferences, evidence that the mass resolution is sufficient to resolve adjacent isotopes, especially where a small isotope of mass M is followed by an abundant isotope $M+1$, as well as the estimation of the isotope fractionation determined by the calibration of the mass spectrometer.

However, the chemical method continued to be used until at least the 1970s. In 1969, an examination of the atomic weight of gallium by the Committee on Atomic Weights, adopted a chemically determined value of $A_r(Ga) = 69.735$, (CAWIA, 1970) despite the fact that a mass-spectrometrically determined value gave $A_r(Ga) = 69.72$ (Inghram et al., 1948). Two new mass spectrometer measurements by De Laeter (1972) and De Laeter and Rosman (1976) gave an atomic weight of $A_r(Ga) = 69.724 \pm 0.002$, which was in stark contrast to a precise couliometric assay of gallium and arsenic which gave a value of $A_r(Ga) = 69.737$ (Marinenko, 1977). The situation was finally resolved in favor of the physical method by a carefully calibrated mass spectrometric determination of the atomic weight to be $A_r(Ga) = 69.72307 \pm 0.00013$ (Machlan et al., 1986). Formal recognition of the demise of the chemical method in favor of the physical method of determining atomic weights finally ‘‘took’’ place in 1979 when IUPAC renamed the Committee on Atomic Weights the Commission on Atomic Weights and Isotopic Abundances (CAWIA).

The Isotope Science Laboratory at Curtin University of Technology became involved in atomic weight determinations in the 1970s through our experience with gallium, and when it became apparent that accurate isotope abundance measurements were the undisputed methodology for the future determination of atomic weights. The laboratory has subsequently been involved in the analysis of the isotope abundances of 16 polyisotopic elements which have lead to new and improved values of atomic weights.

III. ATOMIC WEIGHT SCALES

The advent of physicists into what was previously the sole domain of chemists, created an unexpected problem. Prior to the 20th century, two scales for atomic weights were in use—$A_r(H) = 1$, and $Ar(O) = 16$. In the early part of the 20th century the oxygen scale gained almost exclusive acceptance, because most elements form stoichiometrically reliable compounds with oxygen rather than with hydrogen. Then, in 1929, from an entirely different direction, it was discovered that atmospheric oxygen has three stable isotopes (Giague and Johnson, 1929). This led to the unsatisfactory situation in which chemists continued to use the $A_r(O) = 16$ scale whereas physicists adopted the $^{16}O = 16$ scale. This ambiguity in atomic weight scales required a conversion factor of 1.000275 to change the ‘‘physics’’ values into the chemical scale values. The situation became even more serious when it was discovered that the two mass scales were not even related by a fixed constant, since the isotopic composition and hence the atomic weight of oxygen was not invariant in nature. Thus, the two mass scales also created confusion in what were the true values of certain fundamental constants.

In 1957, Nier and Ölander independently suggested a solution to the dilemma between the chemical and physical atomic weight scales, if $A_r(^{12}C) = 12$ was adopted as the basis of the atomic weight scale. A few years later IUPAC and the International Union of Pure and Applied Physics (IUPAP), both accepted a unified atomic weight scale based on the atomic mass of $^{12}C = 12$ (Kohman, Mattauch, & Wapstra, 1959). This was a significant event in the history of atomic weights, as it resolved a dispute between the physics community and the chemists which had lasted 31 years. Duckworth and Nier (1988) have given a full account of the circumstances surrounding the debate and its final solution. The way was then clear for Cameron and Wichers (1962) to undertake an element by element review of the atomic weights under the unified atomic weight scale. At the time of this historic review, the atomic weights of 14 polyisotopic elements were still based on chemical determinations, although the remainder were based on mass spectrometric measurements.

In the period which has elapsed since the review by Cameron and Wichers (1962), the physical method of determining atomic weights has produced values which have now replaced the atomic weights of those elements which in 1962 were still determined on the basis of chemical stoichiometry. The last element to undergo a change was ytterbium, the atomic weight of which $A_r(Yb) = 173.04$, had remained unchanged since 1934. This chemically determined value was reconfirmed by the Cameron-Wichers review, despite the fact that three mass spectrometric determinations of the atomic weight of ytterbium had previously been made. It has only been with the advent of a new determination of the "absolute" isotopic composition of ytterbium which gives $A_r(Yb) = 173.054 \pm 0.001$ (De Laeter and Bukilic, 2006a), that CIAAW has now accepted the new value for the atomic weight of Yb. It is of interest to note that the physical value of ytterbium is in excellent agreement with the old chemically determined value. In fact, atomic weights determined by the Harvard Method have, in general, stood the test of time, highlighting the excellence of the work carried out by Richards and others in the first part of the 20th century.

IV. ATOMIC MASSES

As important as atomic weights are to the chemical community, so are atomic masses to physicists. The term atomic mass has also been referred to as "relative atomic mass," "nuclear mass," or "nuclidic mass" (Wapstra, 1995). The determination of the atomic weight of a polyisotopic element requires both the absolute isotopic composition of the element as well as the atomic mass of each isotope comprising that element. In the case of monoisotopic elements, the atomic weight is synonomous with the atomic mass.

Although the history of atomic weights extends back to the 19th century, the experiment by Thomson (1912), in demonstrating that at least two isotopes of neon existed, not only led to the initiation of the physical method of determining atomic weights, but was also the commencement point for determining atomic masses. In fact, the history of atomic masses is commensurate with the history of nuclear physics itself (Audi, 2006). Thomson's graduate student—Francis Aston—built a succession of mass spectrographs which were able to focus ions of the same species, independent of their velocity (energy) spread. The resolving power of Aston's first instrument was only 130, but this was sufficient to obtain a precision of one part in 10^3 in his measurements (Aston, 1919). His second mass spectrograph achieved a mass resolution of 600 and a precision of one part in 10^4 (Aston, 1927), whilst his third mass spectrograph achieved a mass resolution of 2000 (Aston, 1942).

In 1933, Bainbridge built a new type of mass spectrograph by combining a Wien-type velocity filter with a 180° magnet, to obtain a resolving power of 600 and a relative mass precision of one part in 10^4. He used this instrument to demonstrate the Einstein equivalence of mass and energy by measuring the atomic masses involved in the nuclear reaction:

$$^{1}_{1}\mathrm{H} + ^{7}_{3}\mathrm{Li} \rightarrow 2 \times ^{4}_{2}\mathrm{He} + Q$$

where Q is the reaction energy (Bainbridge, 1933).

In the mid-1930s, there was a burst of activity in developing instruments to measure atomic masses with greater precision. Double focusing mass spectrographs, in which both velocity and direction focusing occurred simultaneously, were constructed following the development of the theory of double focusing by Herzog (1934). Dempster, in 1935 at the University of Chicago, Bainbridge and Jordon in 1936 at Harvard University, and Mattauch and Herzog in 1936 in Vienna, all built sophisticated double focusing mass spectrographs capable of measuring atomic masses with precisions of one part in 10^5. In the 1950s, Henry Duckworth at McMaster University (Hogg & Duckworth, 1953), and Nier at the University of Minnesota (Johnson & Nier, 1953), continued the work on atomic masses by using electronic means of detection rather than photographic plates in measuring the separation between mass doublets. This enabled the precision of the measurements to be improved to one part in 10^7. The only double focusing mass spectrometer still in use is shown in Figure 1 (Barber et al., 1971).

The atomic mass values are linked directly to the binding energy of particles in the nucleus, and can be used to calculate the energy balance in nuclear reactions. A Table of Atomic Masses is published approximately every 10 years, with the support of the Commission on Symbols, Units, Nomenclature, Atomic Masses and Fundamental Constants (SUN-AMCO). The Atomic Mass Table constitutes a fundamental data set of the Commission on Data for Science and Technology (CODATA), of the International Council of Scientific Unions (ICSU). The establishment of the Atomic Mass Table is one of the great achievements of 20th century science. Mass spectrometry has played a key role in that the atomic masses of the isotopes can be measured to a precision of better than one part in 10^7.

Further improvements in the accuracy with which atomic masses can be determined have occurred subsequent to the

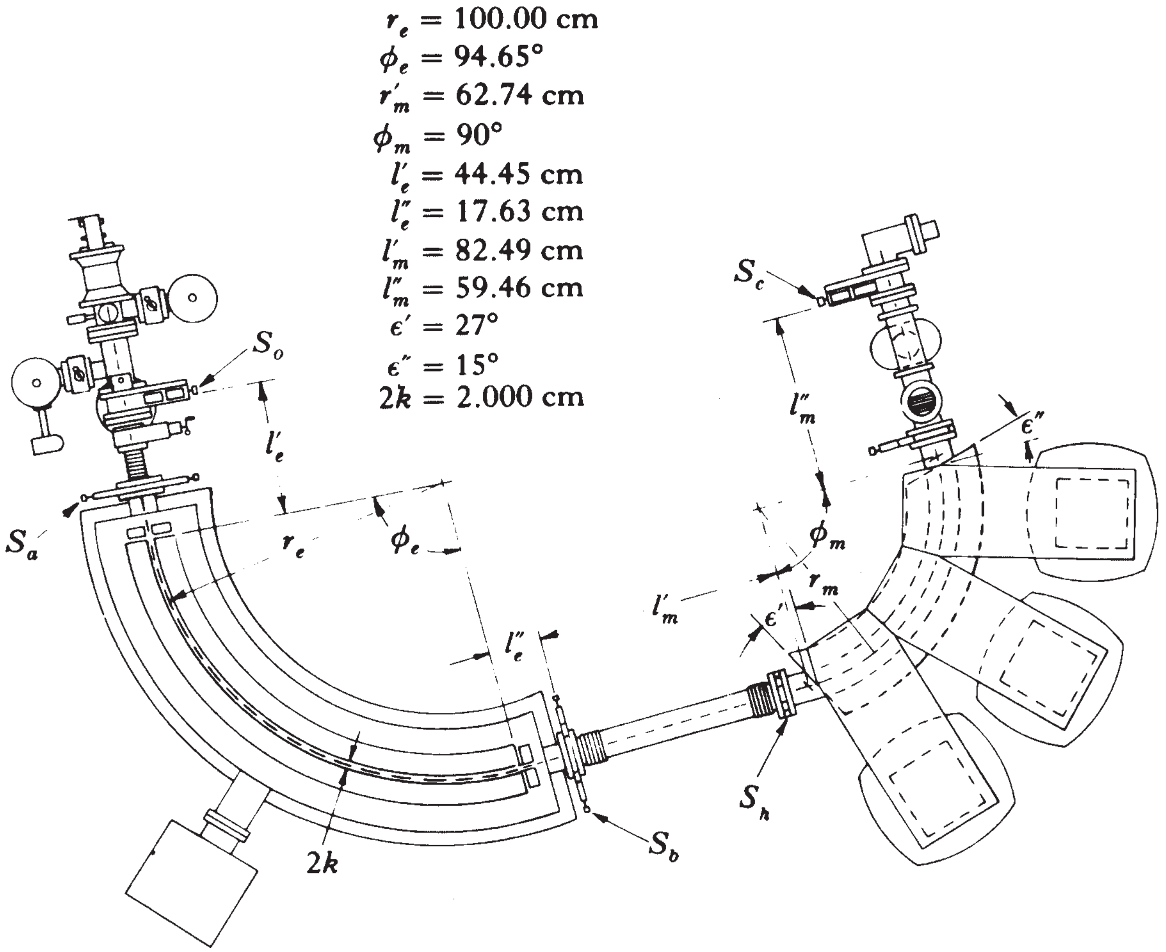

FIGURE 1. The Barber-Duckworth double focusing mass spectrometer. (Reproduced from De Laeter, De Bièvre, & Peister, 1992, with permission, John Wiley & Sons, Inc., Copyright 2003.)

double focusing mass spectrometer era, by the Penning Trap methodology (DiFillipo et al., 1994). An ion of the isotope under investigation, is isolated in the Penning Trap, and its cyclotron velocity in a constant magnetic field is determined with respect to a reference ion's motion. The ratio of the cyclotron frequencies determine their relative masses, which are then converted to a scale in which $^{12}C = 12$ (exactly). Thus both the Atomic Weight scale as well as the Atomic Mass scale are based on ^{12}C. The net effect of the Penning Trap methodology, was to improve the accuracy of the atomic masses by up to a factor of 100 beyond that achieved by conventional mass spectrometry. The atomic mass unit is defined as one twelfth of the mass of one free atom of ^{12}C in its atomic and nuclear ground state, namely 1 $\mu = M\ (^{12}C)/12$ - where the symbol μ is used to signify the unification between the physicist's use of $^{16}O = 16$, and the chemists' use of $O = 16$ which occurred between IUPAC and IUPAP in 1960 (Duckworth & Nier, 1988).

A good description of the evolution and achievements of atomic mass determinations is given by Wapstra (1995), who has been responsible for producing the Table of Atomic Masses since 1971 (Wapstra and Gove, 1971). The most recent compilation was published in 2003 by Audi, Wapstra, and Thibault (2003). A considerable effort has been made to measure the atomic mass of ^{28}Si, because of its importance in the determination of the Avogadro Constant N_A. The scientific objective is to replace the last non-microscopic SI unit, the kilogram, by the Avogadro Constant, provided N_A can be determined with sufficient accuracy to justify the change. The limitation in achieving this objective rests with an accurate determination of the atomic weight of silicon, rather than in the accuracy with which the atomic mass of ^{28}Si is attainable.

V. FUNDAMENTAL CONSTANTS

The responsibility for evaluating the experimental and theoretical research on the fundamental constants, and providing a self-consistent set of data for the fundamental constants and associated conversion factors falls to CODATA. The final data set is obtained from a least squares adjustment of hundreds of pieces of information including the Tables of Atomic Masses and Atomic Weights. Some of the fundamental constants are directly dependent on atomic masses and atomic weights, and these in turn affect the values of other fundamental constants through the least squares adjustment methodology, as shown in Figure 2. Three fundamental constants depend directly on atomic weight values—the Avogadro Constant N_A, the Faraday Constant F, and the Universal Gas Constant R.

An important objective of the scientific community over the past three decades or so has been to improve the accuracy of N_A to a few parts in 10^8, at which level of accuracy it may be possible to replace the kilogram as the SI unit of mass. The international prototype of the kilogram is a platinum-iridium cylinder which is maintained at the Bureau Internationale des Poids and Mesures in France. However, the kilogram gradually changes weight over time because of surface effects and cleaning, so that it is not the ideal basis for a SI unit. The kilogram is related to N_A by the equation

$$1(\mathrm{kg}) = 10^3 (N_A)\mu$$

The magnitude of N_A can be determined by the Bragg relation:

$$N_A = \eta A_r(E)/\rho V_C$$

where η atoms of average atomic weight $A_r(E)$ occupy a unit cell of volume V_C where ρ is the macroscopic density Bragg and Bragg (1913). Deslattes et al. (1974) measured the density and atomic weight of a pure silicon crystal. These values, when combined with optical interferometric measurements of the crystal lattice diameter, gave a value of $N_A = 6.0220943 \times 10^{23}$ mol^{-1}, with an uncertainty of 1.05 ppm. This experiment represented a 30-fold improvement in the previously-accepted value of N_A, but it fell far short of the desired level of accuracy.

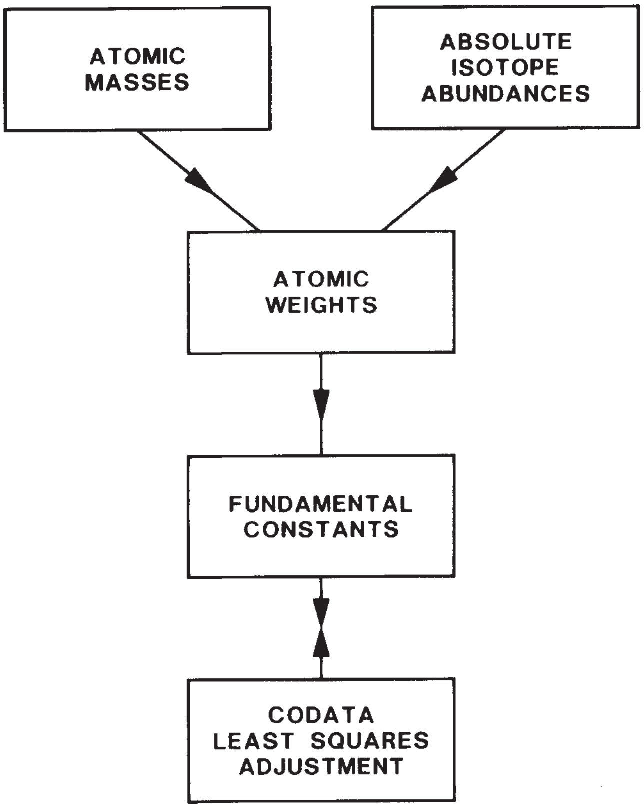

FIGURE 2. The dependence of some fundamental constants on atomic weights. (Reproduced from De Laeter, De Bièvre, & Peister, 1992, with permission, John Wiley & Sons, Inc., Copyright 2003.)

A new series of measurements has been carried out by the Physikalsch Technishe Bundesanstalt in Germany, and the IRMM in Belgium. Fortunately, the semiconductor industry can produce silicon crystals of great purity and physical perfection. Figure 3 shows a spherical sample of silicon produced by the Australian Commonwealth Scientific and Industry Research Organisation (CSIRO) Centre for Precision Optics, which has been used in a more accurate determination of N_A. In fact, a number of scientists, from many countries, have contributed to the task of improving the accuracy of N_A. Scanning tunneling microscopy, capable of detecting small surface imperfections, and new methods of detecting and measuring micro-voids, have led to an improvement in the uncertainty of N_A so that the 1998 CODATA value of $N_A = 6.02214199 \times 10^{23}$ mol^{-1}, with a relative uncertainty of 7.9×10^{-8} (Mohr & Taylor, 1999). More recently, essentially monoisotopic ^{28}Si has been produced in Russis and CSIRO's Centre for Precision Optics and is preparing spherical samples of ^{28}Si for further experiments to reduce the uncertainty in N_A to a few parts in 10^8 or less.

The Faraday Constant is defined as "the quantity of electricity associated with the transfer of $\{N_A\}$ electrons," where $\{N_A\}$ is the magnitude of the Avogadro Constant and can be determined from the equation:

$$F = \frac{A_r(A_g)}{E_{Ag}}$$

where E_{Ag} is the electrochemical equivalent of silver. The largest source of uncertainty in determining F is the atomic weight of silver. The U.S. National Bureau of Standards made a new measurement of the atomic weight of silver by calibrating a thermal ionization mass spectrometer (TIMS) to obtain a value of $A_r(Ag) = 107.86815 \pm 0.00011$ to give a marked improvement in the uncertainty of $A_r(Ag)$—(Bower et al., 1982). This enabled a revised value of F of 96.485309 C mol^{-1}, with a relative uncertainty of 0.30 ppm to be determined (Cohen & Taylor, 1987). The 1998 CODATA recommended value, determined in part, by the least squares adjustment of other fundamental constants, is $F = 96.4853415$ C mol^{-1} with a relative uncertainty of 4×10^{-8} (Mohr & Taylor, 1999).

The Universal Gas Constant R is not only an important fundamental constant in its own right, but its value directly affects both the Boltzman Constant and the Stefan-Boltzman constant. The magnitude of R can be determined by measuring the speed of sound in argon as a function of pressure, at the temperature of the Triple Point of water T_i, in a spherical acoustic resonator. The molar mass M of argon was determined by comparing the speed of sound in the working sample of argon to the speed of sound in a standard sample of argon of accurately known chemical and isotopic composition (Moldover et al., 1988). The Universal Gas Constant can be determined from the equation:

$$R = c_o^2 \frac{M}{T_i} \gamma_o$$

FIGURE 3. A photograph of a near perfect sphere, made from a single crystal of silicon made at the CSIRO's Australian Centre for Precision Optics, used in the determination of a more accurate value for the Avogadro Constant. The sphere is shown on the interferometric measurement bench of the National Measurement Institute. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where c_o^2 is the zero pressure limit of the speed of sound in argon, and γ is the ratio of the heat capacities C_p/C_v which is assumed to have the value $\gamma_o = 5/3$ for a dilute monatomic gas.

The best measurement of the isotopic composition of argon from a single terrestrial source (the atmosphere), together with the associated atomic weight as used by Moldover et al. (1988), was that of Nier (1950). Moldover et al. (1988) reported a value of $R = 8.314471\ \mathrm{J\,mol^{-1}\,K^{-1}}$ with an associated uncertainty of 1.7 ppm. This value represents a fivefold improvement in R to that of the previous determination by Colclough et al. (1979). Nier (1950) pioneered the concept of calibrating a TIMS by preparing volumetric mixtures of enriched isotopes of argon (prepared in Nier's own laboratory), and measuring these mixtures in a gas source, sector field mass spectrometer. The isotope abundances and atomic weight of argon measured by Nier (1950) have been the definitive data set for over 50 years. Lee et al. (2006) have recently re-determined the absolute isotopic composition of argon, and its associated atomic weight, by calibrating a TIMS with highly enriched isotopes of ^{40}Ar and ^{36}Ar. The new atomic weight of argon is $A_r(\mathrm{Ar}) = 39.9498 \pm 0.0002$ as compared to a value of $A_r(\mathrm{Ar}) = 39.9493 \pm 0.0003$ as determined by Nier (1950). Thus the new measurement of the atomic weight of argon has not significantly altered the presently accepted value of R, due in part, to the excellence of the earlier research of Nier (1950). CODATA will take into account the revised and more accurate value of $A_r(\mathrm{Ag})$ in its next re-evaluation of the fundamental constants.

VI. CONSTANTS OF NATURE

Atomic weights have traditionally been regarded as constants of nature in the same sense that Planck's Constant or the velocity of light in a vacuum are fundamental constants. The discovery of radioactivity by Becquerel (1896) and the delineation of the decay of uranium to lead and helium by Rutherford and Soddy (1902), caused the first ripple to surface in this long-standing hypothesis. However, it was argued that elements involved in radioactive decay were an exception to the rule, so that in the first part of the 20th century, the basic premise that the atomic weights were invariant in nature, remained a defendable hypothesis.

As mass spectrometric measurements improved in accuracy and precision, this hypothesis became more and more untenable. The discovery by Nier and Gulbransen (1939) that the isotopic composition of carbon varied in nature, with the minor isotope ^{13}C isotope varying by up to 5%, sounded the "death knell" of the hypothesis that atomic weights were constants of nature. Although this was initially seen as an obstacle to the science of atomic weights, in that the determination of more and more accurate values of the atomic weights would be impossible, it was soon realized that these variations in the isotope abundances of certain elements could be used to investigate the mechanisms which caused these variations. This posed a challenge for mass spectrometry, in that the natural variations were often small and therefore difficult to measure. In the case of carbon, biochemists quickly joined forces with the physicist/mass spectrometrist Al Nier, to tackle a number of biochemical problems using isotopic techniques (Wood et al., 1941).

White and Wood (1986) provide a graphic analogue of this phenomenon. They compare the situation of isotope fractionation as a vast information source akin to electromagnetic waves. Just as an electromagnetic carrier frequency transfers information only when modulated, so information retrieved from mass spectra depends on the countless variations in isotope abundances that characterize elements in nature. Although there are only 92 elements, there are over 300 stable and long-lived isotopes which carry information through their unique isotopic signatures. Mass spectrometry is therefore an indispensable ingredient in providing isotopic data, with high accuracy and precision, to enable scientists from different disciplines to decipher the mechanisms which generate this information base.

The term ''natural isotope fractionation'' is used to describe the mass-dependent variations in the isotopic composition of an element as observed in nature. The term is not used for specific anomalies caused for example by radioactive decay, neutron capture or nucleosynthetic processes. Instrumental isotope fractionation may be caused by the mass spectrometer itself—in the ion source, the mass analyzer or in the detecting system. Chemical fractionation may occur in the chemical separation process used to isolate the element under investigation from other contaminants, particularly if the efficiency of the chemical separation process is $<100\%$, but these are different processes than the isotope fractionation induced by natural mechanisms. Depending on the mechanism involved, the lighter isotopes may be enhanced with respect to the heavier isotopes or vice versa. These mechanisms include: isotope exchange reactions, subtle differences in solid and liquid solubilities of isotopes, and kinetic processes involving slightly differing reaction rates. These processes also include gaseous and thermal diffusion, evaporation, distillation, centrifugation, crystal growth and electrolysis. In most cases the isotope fractionation is mass dependent. Natural isotope fractionation can be distinguished from instrumental or chemical-induced isotope fractionation by the double spike technique (Russell, 1971). If MC-ICP-MS is used to measure the isotope ratios, element spiking or sample-standard bracketing techniques, as well as double spiking, can be used to distinguish natural isotope fractionation from instrumental isotope fractionation.

Of course some isotope fractionation effects are the result of industrial processes, uranium enrichment being a well-known example. The purification of elements may also result in the isotopes of that element being fractionated as is the case for gallium (Gramlich & Machlan, 1985). Thus the exploitation of natural isotope fractionation in order to understand the underlying mechanisms occurring in nature, is not without its challenges.

In 1972, an alert mass spectrometrist in France, recognized that certain samples of uranium ore from the Oklo mine-site in Gabon, West Africa, were slightly depleted in ^{235}U. It was later shown that these anomalous samples contained fission product isotopes in their rare earth elements, thus indicating that one or more nuclear reactors had operated at some time in the past. It has subsequently been proved that neutron-induced fission chain reactions occurred in a number of uranium-rich reactor zones approximately 2 billion years ago in the Oklo mine-site. An international study of a number of elements in the Zone 9 reactor was carried out on samples from the reactor zone itself, and from the surrounding rocks (Loss et al., 1988). The study was carried out by scientists at Curtin University, Los Alamos National Laboratory and the Idaho National Engineering Laboratory. The ^{235}U/^{238}U isotope ratio was approximately 3% 2 billion years ago, so that, given the correct environmental conditions, criticality could have occurred. Variations in a large number of elements caused by a combination of nuclear fission, neutron capture and radioactive decay have been identified in samples from the reactor zones or in the surrounding rocks (De Laeter & Hidaka, 2007). Anomalous isotope abundances, and in some cases atomic weights, are therefore present in nature. Fortunately, the Oklo natural reactors are unique in that they are the only such natural reactors identified anywhere in the world, although it is possible that other such reactors occurred in the past, but have not been preserved in their geological location over billions of years, as have the Oklo reactors. For this reason, the likelihood of encountering such anomalous material in normal circumstances is extremely small, so that CIAAW excludes Oklo-type material from consideration in assessing uncertainty constraints in evaluating atomic weight values.

In a similar sense, extra-terrestrial materials, such as meteorites and lunar samples, which show evidence of anomalous isotopic composition, are also excluded from consideration in atomic weight determinations. CIAAW, in determining data that may be included in the Table of Isotopic Compositions or Atomic Weight Tables, also exclude materials with deliberately altered isotopic composition, such as uranium which has been altered either by enrichment or by use in nuclear reactors. Thus, these CIAAW tables pertain to ''normal'' materials, with footnotes or annotations supplied in the tables for unusual materials.

Another example of an element with a industrially-altered isotopic composition is ^{6}Li, which is isotopically separated for use in tritium production and as a neutron absorber in nuclear fusion. Commercial lithium depleted by up to 80% in ^{6}Li is available, so that CIAAW has provided a footnote in the Table of Atomic Weights, to alert users of this potential problem. Of course, enriched isotopes are available for most of the polyisotopic elements which can be used in the isotope dilution mass spectrometric technique in analytical chemistry (De Bièvre et al., 1993). It is essential to keep supplies of these enriched isotopes isolated from materials of normal isotopic composition. A large-scale atmospheric isotopic effect occurred during the testing of thermonuclear bomb tests during the 1950s and 1960s, when tritium was released into the atmosphere. The resulting pulse of tritium has affected atmospheric water vapor and has subsequently been used to trace subsurface water movements in aquifers and the oceans (Jenkins, 1980).

VII. STABLE ISOTOPE GEOCHEMISTRY

Elements of low atomic number, such as hydrogen, lithium, boron, carbon, nitrogen, oxygen and sulfur are most susceptible to isotope fractionation, as the magnitude of the effect is related to the square root of the masses. The discipline of Stable Isotope Geochemistry, was developed in the 1950s to exploit these natural variations, initially using gas source, sector field mass spectrometry (Nier, 1947), which had sufficient sensitivity for the task. The stable isotope geochemistry of the gaseous elements was the most visible phenomenon of isotope fractionation in nature, at that time, but Rosman, De Laeter, and Kempt (1989) in a study of the isotopic composition of palladium in terrestrial samples, showed that a precious metal concentrate from the Bushveld Igneous Complex in South Africa is fractionated by

3.8‰ per mass unit, which gave an atomic weight for this sample of 106.434, which was significantly larger than the then accepted best value for the atomic weight of palladium. This led to the realization that the so-called ''heavy'' elements could also exhibit natural isotope fractionation effects, for example in ''non-traditional'' isotopes such as iron, molybdenum and cadmium.

The magnitude of isotope fractionation is commonly given with respect to a delta scale such that:

$$\delta({}^{i}E)_{\mathrm{Sa}} = \left(\frac{R_{\mathrm{Sa}}}{R_{\mathrm{RM}}}\right) - 1$$

where R_{Sa} and R_{RM} refer to the isotope abundance ratios ${}^{i}E/{}^{j}E$ in a sample Sa, and a reference material RM respectively, for isotopes *i* and *j* from a given element *E*. The differences in isotope ratios between the sample and the reference material are more useful than the actual values, provided both are measured under similar mass spectrometric conditions. It is therefore essential that a common, internationally recognized reference material be adopted for each element to ensure consistent normalization procedures to be adopted, and inter-laboratory comparisons to be accomplished.

The advent of MC-ICP-MS has provided an impetus to the study of isotope abundance variations in nature for non-traditional stable isotopes such as iron, molybdenum and cadmium, because of their potential value in investigating biogeochemical processes. Of all the non-traditional elements, iron, being incorporated in a range of biochemical processes, has been the subject of considerable investigations (Anbar, 2004a). The ^{56}Fe/^{54}Fe ratios found in iron-bearing phases precipitated in sedimentary deposits vary from + 0.9‰ to −1.6‰, whereas similar phases in igneous rocks show no measurable isotope fractionation effects (Beard et al., 1999). These authors argue that biogenetic processes have caused the isotope fractionation in sedimentary deposits, and that it may be possible to trace the distribution of micro-organisms in modern and ancient earth using isotope fractionation processes in the isotopes of iron (Beard et al., 1999).

Molybdenum is a redox-sensitive trace metal of particular value in palaeo-oceanography (Siebert et al., 2003). It is also of importance in nitrogen fixation, nitrate reduction and sulfite oxidation (Anbar, 2004b). A study of the isotope fractionation of this element in molybdenites, using the double spike technique to distinguish between instrumental and natural isotope fractionation has revealed a range in isotope fractionation from −0.1‰ per mass unit to +0.55‰ per mass unit in 20 samples of known age and widespread geographic locations (Hannah et al., 2007). In contrast, no variations in the isotopic composition of molybdenum could be found in rocks from the continental crust. This implies that the isotopic composition of molybdenum delivered to the oceans is uniform both geographically and through geological time. There is also evidence that kinetic isotope fractionation may explain variations of up to 0.34‰ per mass unit in some molybdenite ore deposits (Hannah et al., 2007). A sensitive high resolution ion probe mass spectrometer (SHRIMP) developed at the Australian National University, originally for geochronology was successfully applied to sulfur geochemistry to enable the isotope abundances of sulfur to be measured in mineral separates, as well as in the whole rock sample itself (Eldridge et al., 1987).

A classic example of isotope variability in nature came to prominence through a problem in the nuclear industry at a time when power reactors were being installed in the 1950s. Boron is used in reactor physics experiments as a reference standard for thermal neutron capture cross-section measurements, because of the (n, γ) neutron capture reaction on ^{10}B, one of two isotopes of boron. Inconsistent neutron cross-section results were being measured in different reactor sites, with a large discrepancy between American and European reactor sites. It eventuated that the cause of the problem was not nuclear in nature, but rather geochemical, as it was shown that natural variations in the ^{11}B/^{10}B isotope ratio existed, and differed by 1.5% in commercial boron (De Bièvre, Debus, & Spaepen, 1963). Thus it was important to know the isotopic composition of the boron being used in reactor physics measurements. An important source of boron in North America was from Searle's Lake which gave an atomic weight of $A_r(B) = 10.811 \pm 0.003$ (McMullen, Cragg, & Thode, 1961), but more comprehensive studies of the atomic weight of boron gave an $A_r(B) = 10.811 \pm 0.007$ to reflect the range of values found in nature (Coplen, 1996). The geochemical explanation for the variability of boron in nature is that isotope fractionation in aqueous solutions is caused by differences in inter-atomic vibrational energy and symmetry between the triagonal species $B(OH)_3$ and the tetragonal anion $B(OH)_4^-$.

The profound influence of oxygen on the history of atomic weights has already been noted in this review, including the discovery that oxygen had three isotopes (Giague & Johnson, 1929). It was later shown that the isotopic composition of oxygen varied in nature as shown in Figure 4 for a number of oxygen-bearing materials. The data in Figure 4 are plotted with respect to a Reference Material called VSMOW, a water sample, which is used as an inter-laboratory standard by laboratories around the world. The horizontal lines represent the range in measured oxygen isotope ratios in δ^{18}O in permil (‰) deviations relative to VSMOW (Vienna Standard Mean Ocean Water), or alternatively in mole fractions of ^{18}O relative to VSMOW. The effect on the atomic weight of oxygen as a result of the variability of oxygen in nature is also shown. The variation in δ^{18}O in water for example varies from −62.8‰ in Antarctic waters to +31.3‰ in a desert basin in the Western Sahara (Coplen et al., 2002). As pointed out above, the stable isotope geochemistry community has successfully used designated reference materials in their mass spectrometric protocols for many decades, in that it is better to measure the isotope ratio of a sample against an in-house reference material of similar matrix, than attempt to measure the absolute isotopic composition of that sample. Other reference materials for oxygen are SLAP and VPDB, details of which are given in Coplen et al. (2002).

VIII. SOLAR SYSTEM ABUNDANCES

The landmark paper by Burbidge et al. (1957) gave a canonical framework for the nucleosynthesis of the chemical elements and their isotopes in stellar sources. The three basic processes in synthesizing the isotopes of the elements with $Z > 28$ (the heavy

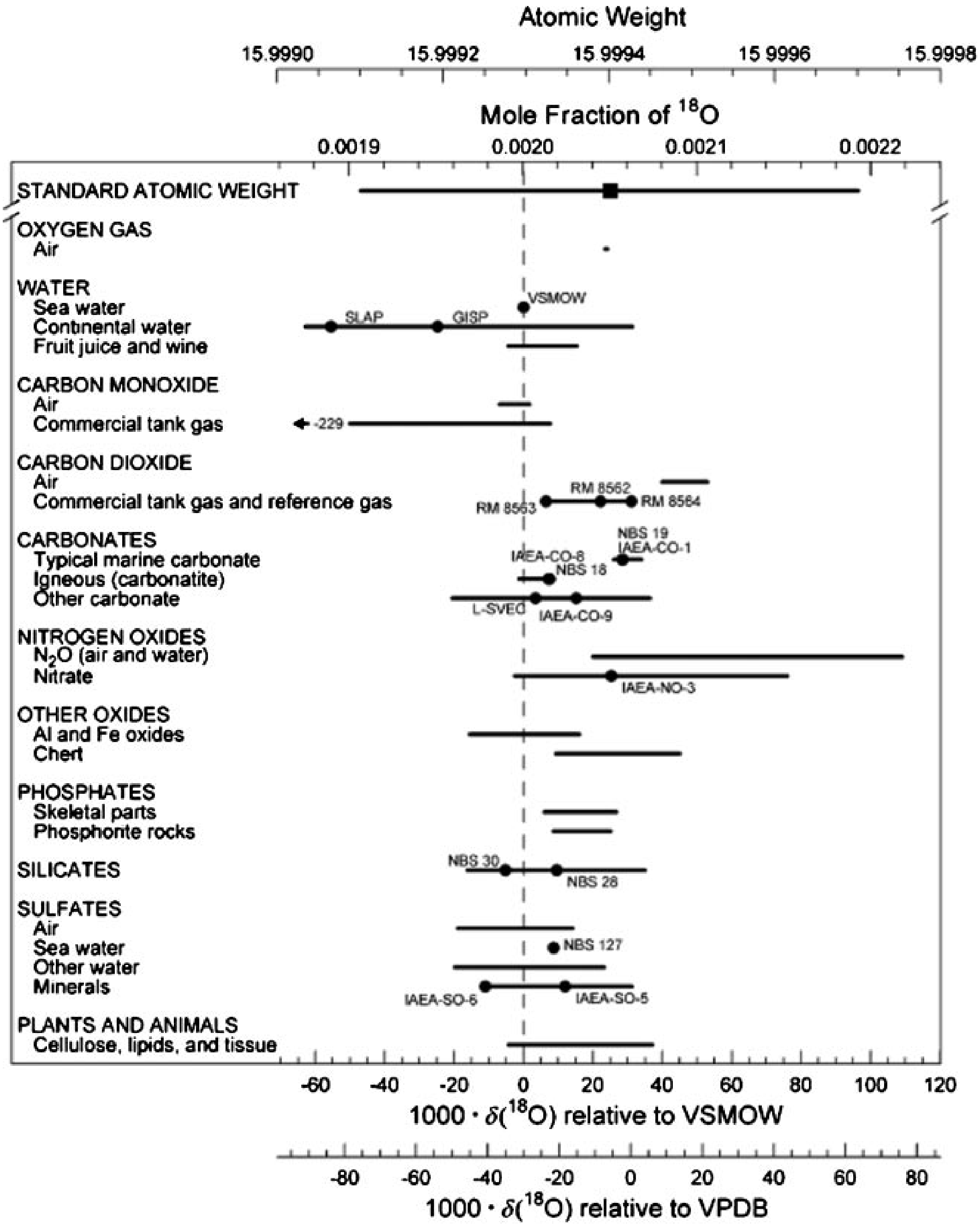

FIGURE 4. Oxygen isotopic compositions and atomic weights of selected oxygen-bearing materials with respect to the internationally recognized reference material VSMOW. (Reproduced from Coplen et al., 2002, with permission of Pure and Applied Chemistry, Copyright 2002.)

elements), are the slow s- and rapid r-neutron capture processes, and the p-process, which is largely responsible for synthesizing the rare, neutron deficient nuclides on the neutron-poor side of the valley of stability. In order to test nucleosynthetic models, it is necessary to know, as accurately as possible, the Solar System abundances of the s-, r-, and p-process nuclides. Of particular importance are the p-process Solar System abundances, since the nucleosynthesis of these isotopes is not well understood, and because their abundances are mostly small. Thus, these abundances are not as well characterized as the neutron process-produced isotopes. A knowledge of the Solar System abundances of the elements is derived from their abundances in primitive carbonaceous meteorites (Anders & Grevesse, 1989; Lodders, 2003) and photospheric abundances.

Two rare p-process isotopes in ^{138}La and ^{180}Ta are both of importance in assessing the abundance predictions of models of nucleosynthesis against measurements of the Solar System abundances. The p-process isotope ^{180}Ta is an odd-odd nuclide which is unique in possessing a long-lived isomeric state ^{180}Ta^{m}, and a short-lived ground state. ^{180}Ta^{m} is the rarest isotope of nature's rarest element. Only two uncalibrated mass spectrometric determinations of tantalum have been reported, with widely different results. White et al. (1955) measured the ^{181}Ta/^{180}Ta ratio to be 8,120 ± 200, and Palmer (1958) measured the same ratio as 8,546 ± 460. Recently, a partially calibrated measurement of the isotopic composition of tantalum has been reported using TIMS (De Laeter & Bukilic, 2005a). These authors reported a ^{181}Ta/^{180}Ta ratio of 8325 ± 43. The isotope abundance of ^{180}Ta^{m} can be derived as 0.0001201 ± 0.000006%, which gives a Solar System abundance of 2.49×10^{-6} with reference to silicon = 10^6 atoms, using the Solar System abundance of tantalum of 0.0207 (Anders & Grevesse, 1989). This incredibly small abundance imposes incredibly tight constraints on p-process models of nucleosynthesis. The atomic weight calculated from this absolute isotopic composition is 180.947878 ± 0.000002 (De Laeter & Bukilic, 2005a) in which the uncertainties in the atomic masses of ^{180}Ta and ^{181}Ta are a limiting factor in the determination of the atomic weight rather than the mass spectrometric measurements themselves.

The rare, odd–odd nuclide ^{138}La is another crucial test case for nucleosynthetic theorists, in that this isotope is also under-produced in conventional models of p-process nucleosynthesis. The under-production of ^{138}La in p-process calculations is due to the unfavorable balance between its production from the reaction ^{139}La(γ, n) ^{138}La and its mass destruction by ^{138}La(γ, n) ^{137}La (Arnould & Coriely, 2003). De Laeter and Bukilic (2005b) have recently measured the ^{139}La/^{138}La ratio to be 1125 ± 3 which gives an isotope abundance of ^{138}La = 0.000888 ± 0.000002%. Using the Solar System abundance table of Anders and Grevesse (1989) in which La = 0.4460 with respect to silicon = 10^6 atoms, the Solar System abundance of ^{138}La can be calculated from the absolute isotope abundance of lanthanum to be 0.000386.

At the low atomic number end of the "heavy" elements, there exists another dilemma for p-process theorists. The p-process produced isotopes of molybdenum and ruthenium, are significantly overabundant in terms of nucleosynthetic theory, and no convincing theory has yet been given to explain the situation. Molybdenum is a particularly interesting element from a nucleosynthetic perspective in that ^{92,94}Mo are produced solely by the p-process, ^{95,97,98}Mo by a mixture of the s- and r-process, ^{96}Mo solely by the s-process, and ^{100}Mo solely by the r-process (see Fig. 5). As a general rule, the p-process produced isotopes are much smaller than the s- and r-process produced isotopes. However, in the case of molybdenum, the p-process isotopes, ^{92,94}Mo have similar isotope abundances to the other molybdenum isotopes. A coherent theory of p-process nucleosynthesis has been a controversial topic since Burbidge et al. (1957) proposed that they were produced in the hydrogen-rich layers in type 11 supernovae, where (p, γ) and (γ, n) reactions occurred on the more abundant s- and r-process seed nuclei. Hayakawa et al. (2005) have examined a number of processes which have been proposed for the origin of the p-process nuclides.

A recent experiment has measured the absolute isotopic composition of molybdenum using a TIMS which was calibrated

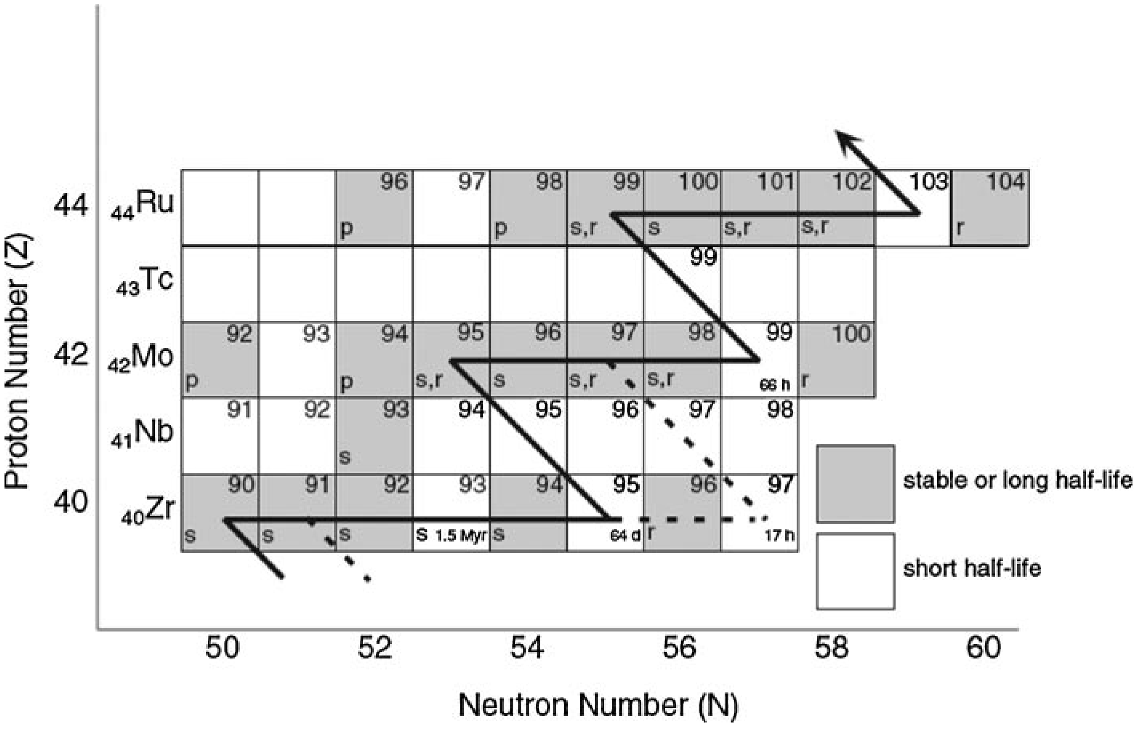

FIGURE 5. Chart of the Nuclides in the mass region of molybdenum showing the s-, r-, and p-process nuclides. (Reproduced from Wieser & De Laeter, 2007, with kind permission of The American Physical Society, Copyright 2007.)

by gravimetric mixtures of enriched $^{92.98}$Mo isotopes. The resultant isotope abundances of ^{92,94}Mo are 14.5246 ± 0.0015% and 9.1514 ± 0.0074% respectively (Wieser & De Laeter, 2007). If one adopts the Solar System abundance of Mo = 2.51 with respect to silicon = 10^6 atoms (Anders & Grevesse, 1989), the Solar System abundances of ^{92,94}Mo are 0.364 ± 0.012 and 0.230 ± 0.008 respectively. These abundances are lower than the previously accepted values of the p-process abundances of ^{92,94}Mo which are 0.378 ± 0.021 and 0.236 ± 0.013 respectively, and have a much smaller uncertainty. These new values are lower than the earlier values and are therefore a shift in the correct direction as far as p-process theorists are concerned.

These accurately determined Solar System abundances provide a much improved set of molybdenum p-process produced nuclides on which models of nucleosynthesis can be assessed. It should be noted that existing tables of isotopic Solar System abundances (Arnould & Coriely, 2003) invariably overestimate the abundance of the p-process nuclides, because TIMS measurements enhance the lighter isotopes due to Rayleigh-type evaporation mechanisms in the ion source, and of course, p-process nuclides are always the isotopes with the lowest mass numbers.

Calibrated absolute isotopic composition experiments not only improve the quality of Solar System abundance measurements of the p-process nuclides, but also the s- and r-process nuclide abundances. The s-only process isotope ^{176}Lu, is an important nuclide in nucleosynthesis in that it is of thermochronological significance (De Laeter et al., 1988). De Laeter and Bukilic (2006b) have reported a partially calibrated TIMS experiment which has enabled the isotope abundance of ^{176}Lu to be determined to be 2.5987 ± 0.0012% to give a Solar System abundance of 0.0347918 ± 0.0000004 based on the Solar System abundance of lutetium of 0.0367 as compared to silicon = 10^6 atoms (Anders & Grevesse, 1989). This calibrated value should now be used in nuclear astrophysics calculations rather than the existing value.

Thus, absolute isotope abundance experiments such as those described above, enable the Solar System abundances of s-only, r-only and p-process produced nuclides to be obtained with greater accuracy than uncalibrated mass spectrometric measurements. In the past, the emphasis of CAWIA was on measuring the absolute isotopic composition of elements in order to determine the atomic weight with higher accuracy. However the emphasis of CIAAW is now based primarily on determining the isotopic composition of an element as accurately as possible, not only to calculate the atomic weight, but because of their intrinsic value to science. The importance of determining accurate Solar System abundances, particularly for the p-process nuclides, is a good example of this scenario. An emerging dependable data set of Solar System abundances will enable models of nucleosynthesis to be tested against more accurate and reliable data than in the past.

IX. THE FUTURE OF ATOMIC WEIGHT DETERMINATIONS

There have been two conflicting points of view in the evaluation and publication of atomic weights. The first, which we will call the ‘‘Metrological Viewpoint,’’ is that we should endeavor, at every means at our disposal, to measure and report the most accurate values possible for the atomic weights of each polyisotopic element. This implies the adoption of the data contained in the most recent Table of Atomic Masses, despite the fact that changes may only be a few parts in 10^7, or less. In one sense, this metrological culture has its roots in the early 20th century concept that atomic weights were ‘‘constants of nature,’’ and therefore should be treated in the same way as are fundamental constants, in which we strive collectively for the best possible values.

The opposing point of view, which we will call the ‘‘Working Scientists’ Viewpoint,’’ is that the discovery that the atomic weights of many elements are affected by natural isotope fractionation processes, implies that there is no universal atomic weight for any of the polyisotopic elements which can be determined with greater and greater accuracy. In fact, rather the reverse, in that as further experiments are undertaken, with more sophisticated mass spectrometry, the uncertainties associated with each atomic weight is likely to increase rather than decrease. A more important argument by the working scientists is that they simply do not require the latest value of the atomic weights to the *n*th decimal place in order to carry out their work. They want to know the range in values of the atomic weights of materials they will encounter in the laboratory—in reagent bottles, in ores of that element, or from a spectroscopically pure sample of the element concerned. The Working Scientists’ Viewpoint is that CIAAW and its predecessor CAWIA have kept changing the atomic weights of a few elements every 2 years, even though there seems little advantage in making the change. Even worse, after each new publication of the Atomic Mass Table, the atomic weight of each monoisotopic element is changed at a level of accuracy which is of no consequence to the working scientist.

It seems that a single Table of Atomic Weights cannot possibly satisfy these two opposing viewpoints. A working party of CIAAW is presently examining this inherent difficulty. A possible scenario for the future is to generate two Tables of Atomic Weights, one which is essentially the same as the present table for the working scientists, and a second ‘‘Metrological Table,’’ which will provide the most accurate and up-to-date values possible—but for each polyisotopic element this value would be connected directly to a selected reference material of that element. Reference materials already exist for many elements, and more are becoming available with the passage of time. However, the present method of selecting reference materials is somewhat haphazard. Such reference materials should be available in large quantity, be of high purity and homogeneity, and be available in a suitable form over a long period of time, for use as a laboratory standard in laboratories around the world. The isotopic composition of each reference material should be determined by a proven method of calibration, and the experimental data accepted by CIAAW for that reference material to be designated as an international isotopic calibrated reference material (De Bièvre et al., 1993). Thus, each of these reference materials would be used routinely for isotope abundance inter-laboratory comparison purposes. In this scenario, the Metrological Table of Atomic Weights would be a direct outcome from the absolute isotopic composition of each isotopic reference material.

The ‘‘Metrological Table’’ should be published every 2 years, after each CIAAW meeting has evaluated the new experimental work. This table is not designed for the working scientist, but rather for the metrological community. The eventual outcome of this metrological table is that each polyisotopic element will have its own internationally recognized reference material (including the atmosphere, if appropriate, for the gaseous elements), whose absolute isotopic composition has been established by a calibration procedure whose methodology and experimental procedures have been evaluated by CIAAW. In time, this Metrological Table of Atomic Weights will become an accepted data set for CODATA. On the other hand, the Working Scientists’ Table of Atomic Weights should only be published every 5 years or so in tandem with the Table of the Isotopic Compositions of the Elements. Changes should be kept to a minimum and the magnitudes and uncertainties of each atomic weight be commensurate not only with the quality of the experimental data, but also reflecting the uncertainties introduced by natural isotope fractionation processes. This Table would also include footnotes as necessary, to bring attention to any unusual sample that might be encountered in the laboratory.

In examining the future of atomic weight determinations, another important consideration is that of instrumentation. The sector-field mass spectrometer has been the instrument of choice for atomic weight determinations since Nier (1950) first used a calibration technique to determine the atomic weights of five elements. It has been regarded as ‘‘the gold standard’’ for absolute isotopic composition measurements. However in the last decade or so, multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become a viable alternative to TIMS, as MC-ICP-MS can produce high precision isotopic data and is of particular advantage in analyzing elements of high ionization potential which may be difficult to analyze by TIMS. A comprehensive determination of the atomic weight of zinc has recently been carried out at IRMM by MC-ICP-MS (Ponzevera et al., 2006). One advantage of MC-ICP-MS as compared to TIMS is that the mass discrimination, although large, is invariant with time, which is of importance in such calibration experiments. The net result of the IRMM experiment on the atomic weight of zinc, is that the MC-ICP-MS results are in good agreement with a companion TIMS determination to give a value of $A_r(Zn) = 65.37777 \pm 0.00022$ for the reference material IRMM-3702.

The future of atomic weight determinations of the polyisotopic elements lies solely with the mass spectrometric measurements of their absolute isotopic abundances. The application of accurate and precise isotope abundances have diversified to such an extent, as new and more advanced technological instrumentation have become available, that it has penetrated into a wide cross-section of science. Radioactive decay schemes are of particular importance, not only in geochronology, but as a tracer of geological processes. In the case of the U, Th-Pb decay series, the daughter isotopes of lead have an isotopic composition that reflects the chemical composition and age of the parent material. Lead isotopes can therefore be used as isotopic fingerprints, which have found application in ice core studies in climate change (Rosman & Chisholm, 1996) and health-related studies (Gulson, 1996). Many other examples of the relevance of isotopic studies could be given, including the regulatory procedures in nuclear safeguards which will become of more importance as nuclear energy becomes even more important in power production in many countries.

Thus, isotope abundance measurements will continue to flourish and diversify, whereas atomic weights will no longer occupy its previously held pre-eminent position. Whereas chemists once dominated the determination of atomic weights, a large number of scientists from many disciplines are now engaged routinely in measuring the relative abundance of isotopes to answer questions in their own field of interest. Science and technology are related endeavors. Subsequent advances in mass spectrometric instrumentation will undoubtedly enable new applications in science to be pursued. In contrast to Aston’s contention that mass spectrometry would diminish in importance (Svec, 1985), the 21st century beckons isotope abundance studies on to new and exciting horizons.

X. CONCLUSIONS

The 20th century witnessed a transformation in the science of atomic weights, through the interdisciplinary interaction of chemists, physicists, and other scientists. No longer is the Harvard Method of determining atomic weights the supreme and unrivalled methodology. The stoichiometric method has been superseded by the physical method, based on accurate mass spectrometric measurements of the isotopic composition of the polyisotopic elements and their atomic masses. In fact, the establishment of the Atomic Mass Table has been one of the success stories of 20th century science, with the atomic masses being known to a few parts in 10^8. Another major change which occurred during the 20th century was the realization that atomic weights, with the exception of the monoisotopic elements, are no longer ‘‘constants of nature.’’ The polyisotopic elements may be affected by a variety of physiochemical and biogeochemical isotope fractionation processes that affect the magnitude and/or uncertainty of their atomic weight. This means that the atomic weight of a polyisotopic element does not possess a universal value, rather the atomic weight is specific to a particular sample. Whilst it was originally feared that this variability in nature would restrict the accuracy to which atomic weights could be measured, it was quickly realized that fractionation effects can be a window to our understanding of nature. Gradually the realization led to the acceptance that the future of the science lies with isotopic abundance measurements, and that atomic weights are simply the outcome of absolute isotopic composition determinations. This change in emphasis has led IUPAC to rename CAWIA to CIAAW. This change does not reduce the significance of atomic weights, but emphasizes the priorities of the future.

It may appear that the development of the science of isotope abundance and atomic weight measurements throughout the 20th century has been remarkably slow. In comparison to many areas of science, this is indeed the case. It can be explained in part, by the very demanding technological advances, as well as the time-consuming nature of changing accepted ideas and concepts—in effect a change in culture. A good example has been that it took 31 years for chemists and physicists to agree on the use

TABLE 1. A century of progress in atomic weight determinations

Element name	1900	2001	Element name	1900	2001
Aluminium	27.1	26.981538(2)	Neon	Not measured	20.1797(6)
Antimony	120.4	121.760(1)	Nickel	58.7	58.6934(2)
Argon	Not measured	39.948(1)	Niobium	93.7	92.90638(2)
Arsenic	75.0	74.92160(2)	Nitrogen	14.0	14.0067(2)
Barium	137.40	137.327(7)	Osmium	191.0	190.23(3)
Beryllium	9.1	9.012182(3)	Oxygen	16.000	15.9994(3)
Bismuth	208.1	208.98038(2)	Palladium	107.0	106.42(1)
Boron	11.0	10.811(7)	Phosphorus	31.0	30.973761(2)
Bromine	79.95	79.904(1)	Platinum	194.9	195.078(2)
Cadmium	112.4	112.411(8)	Potassium	39.11	39.0983(1)
Calcium	40.1	40.078(4)	Praseodymium	140.5	140.90765(2)
Carbon	12.0	12.0107(8)	Protactinium	Not known	231.03588(2)
Cerium	139	140.116(1)	Rhenium	Not known	186.207(1)
Cesium	132.9	132.90545(2)	Rhodium	103.0	102.90550(2)
Chlorine	35.45	35.453(2)	Rubidium	85.4	85.4678(3)
Chromium	52.1	51.9961(6)	Ruthenium	101.7	101.07(2)
Cobalt	58.93	58.933200(9)	Samarium	150.3	150.36(3)
Copper	63.6	63.546(3)	Scandium	44.1	44.955910(8)
Dysprosium	Not known	162.500(1)	Selenium	79.2	78.96(3)
Erbium	166.0	167.259(3)	Silicon	28.4	28.0855(3)
Europium	Not known	151.964(1)	Silver	107.92	107.8682(2)
Fluorine	19.05	18.9984032(5)	Sodium	23.05	22.989770(2)
Gadolinium	157.0	157.25(3)	Strontium	87.6	87.62(1)
Gallium	70.0	69.723(1)	Sulfur	32.07	32.065(5)
Germanium	72.5	72.64(1)	Tantalum	182.8	180.9479(1)
Gold	197.2	196.96655(2)	Tellurium	127.5	127.60(3)
Hafnium	Not known	178.49(2)	Terbium	160	158.92534(2)
Helium	Not measured	4.002602(2)	Thallium	204.15	204.3833(2)
Holmium	Not known	164.93032(2)	Thorium	232.6	232.0381(1)
Hydrogen	1.008	1.00794(7)	Thulium	170.7	168.93421(2)
Indium	114	114.818(3)	Tin	119.0	118.710(7)
Iodine	126.85	126.90447(3)	Titanium	48.15	47.867(1)
Iridium	193.1	192.217(3)	Tungsten	184.0	183.84(1)
Iron	56.0	55.845(2)	Uranium	239.6	238.02891(3)
Krypton	Not measured	83.798(2)	Vanadium	51.4	50.9415(1)
Lanthanum	138.6	138.9055(2)	Xenon	Not measured	131.293(6)
Lead	206.92	207.2(1)	Ytterbium	173.2	173.04(3)
Lithium	7.03	6.941(2)	Yttrium	89.0	88.90585(2)
Lutetium	Not known	174.967(1)	Zinc	65.4	65.409(4)
Magnesium	24.3	24.3050(6)	Zirconium	90.4	91.224(2)
Manganese	55.0	54.938049(9)			
Mercury	200.0	200.59(2)			
Molybdenum	96.0	95.94(2)			
Neodymium	143.6	144.24(3)			

A comparison of the atomic weights in 1900 with those of 1999. The atomic weights of 1900 are scaled to $A_r(O) = 16$, whereas those in 1999 are scaled to $A_r(^{12}C) = 12$. (Reproduced from De Laeter and Peiser, 2003, with permission, Springer-Verlag GnbH, Copyright 2003.)

of the ^{12}C isotope as the basis for the unified scale for atomic weights. After this agreement was reached in 1960, it enabled the field to make some rapid advances.

Another controlling factor in the progress of the field has been that of metrology. A metrological measurement implies the necessity of the quantification of a property with reference to a unit, and the estimated reliability of that value. The determination of atomic weights has been increasingly affected by metrological procedures, not only in the determination of the magnitude of the atomic weight but also in the estimation of all possible errors which make up the uncertainty in the value. CIAAW therefore undertakes a rigorous metrological assessment of all new experimental data. Table 1 is a comparison of atomic weight values at the beginning of the 20th and 21st centuries. Since the year 2002, further improvements have been made to the Table of Atomic Weights, the most recent report being that of Wieser (2006). The improvements in the accuracy of the atomic weights from 1969 to 2001 are shown in Figure 6.

In addition to publishing a Table of Atomic Weights every two years, CIAAW also publishes a Table of the Isotopic Composition of the Elements every five years or so, the most recent Table being that of Böhkle et al. (2005). Major reviews have been published in 1962 (Cameron & Wichers, 1962), in 1984 (Peiser et al., 1984) and in 2003 (De Laeter et al., 2003). On occasions, Five Figure Tables of the Atomic Weights, suitable for educational purposes, have been produced by the Commission.

The values of three important fundamental constants—the Avogadro Constant N_A, the Universal Gas Constant R and the Faraday Constant F, are based directly on the atomic weights of silicon, argon and silver respectively. There has been an intense international scientific effort to improve the accuracy of N_A to a few parts in 10^8 when it could replace the SI unit of mass, the kilogram. The value of R also directly influences the magnitude and uncertainty of the Boltzmann Constant and the Stefan-Boltzmann Constant. A recent redetermination of the atomic weight of argon Lee et al. (2006), will enable CODATA to reassess the value of R, which has previously used the atomic weight of argon determined by Nier (1950). The atomic weight of silver is one of the most accurately known of all the atomic weights, and this is reflected in the low uncertainty of F by CODATA. Accurate determinations of the absolute isotopic

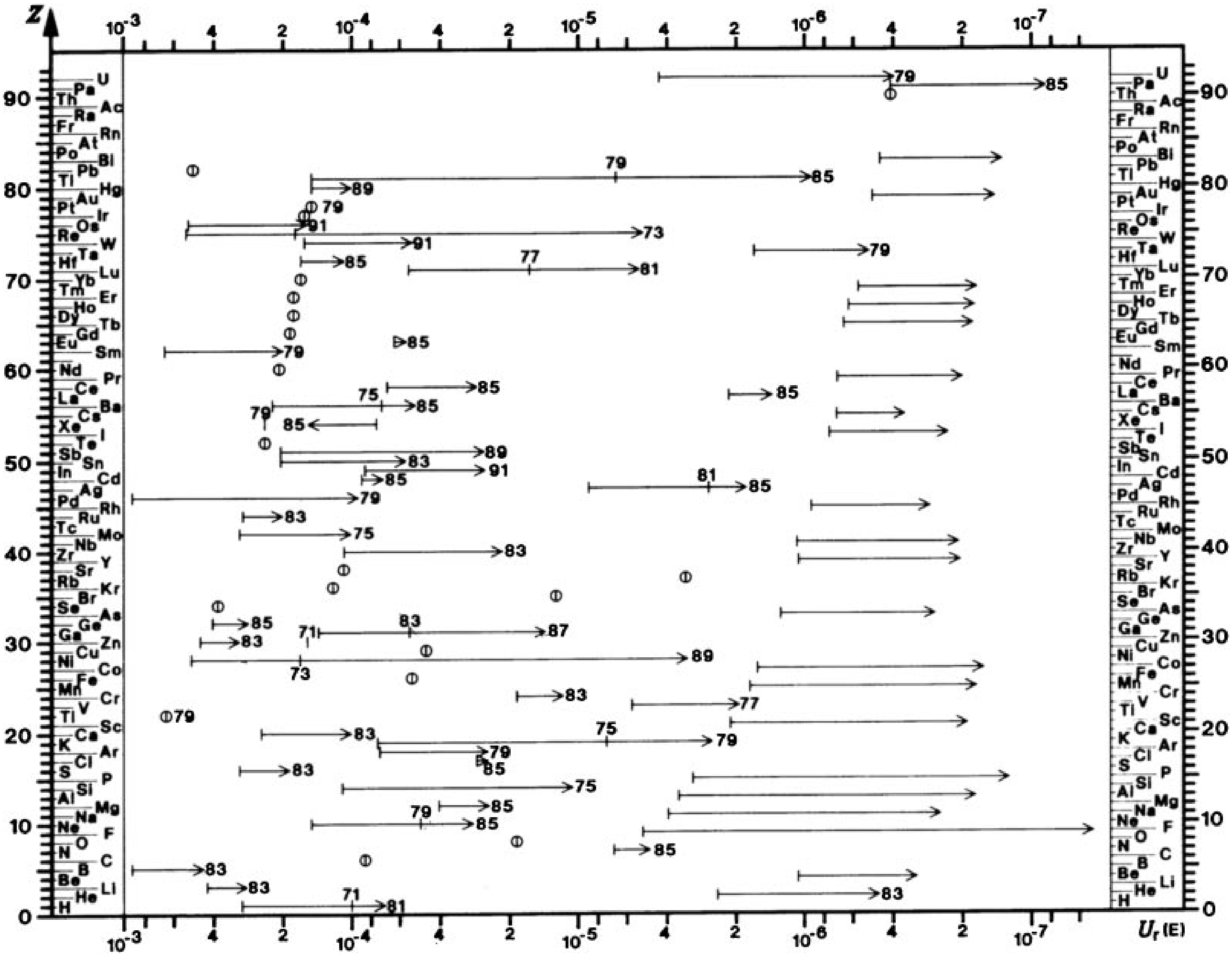

FIGURE 6. Changes in relative uncertainties of the IUPAC-recommended atomic weights from 1969 to 2001. (Reproduced from De Laeter et al., 1992, with permission of John Wiley & Sons, Inc., Copyright 2003.)

compositions of the elements can provide a significant input to nuclear astrophysics in that accurate values of the Solar System abundances of s-, r-, and p-process nuclides can be derived which can be used as a test-bed against which models of nucleosynthesis can be tested. This is particularly true for the p-process nuclides.

The future of atomic weight determinations will be dominated by isotope abundance measurements which will be used in a wide range of scientific fields. In that sense atomic weights will simply be an outcome of isotopic measurements. Characterization by isotopic composition will be applied to a range of materials derived from manufacturing or laboratory synthesis and to those materials submitted to regulatory authorities. Thus, there will be continuing pressure to attain more precise and accurate isotope abundance measurements. The continuing role of CIAAW in providing direction and oversight to such measurements is assured.

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