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Summary of a meeting of SNAFUI 30 July 2015, Vienna, Austria

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Abstract

SNAFUI recommends the CIAAW publish two separate atomic-weight tables, with a table for the general science community with abridged atomic-weight values and uncertainty, listed first; SNAFUI recommends the CIAAW to publish a second table with atomic-weight values based on best measurements of certified reference materials including atomic-weight intervals based on isotope abundance variation ranges and all detailed footnotes for measurement experts; SNAFUI examined the definition of "normal' materials, carriers of measured atomic weight values, and recommends a more extensive review via a new Project Proposal from SNAFUI; SNAFUI examined CIAAW uncertainties and a possible linking of Tables on Atomic Weights and Isotopic Composition of the Elements and recommends further study of both subjects.

Introduction

During the International Union of Pure and Applied Chemistry (IUPAC) General Assembly at Beijing in 2005, the Commission on Isotopic Abundances and Atomic Weights (CIAAW) created the Subcommittee for the Natural Assessment of Fundamental Understanding of Isotopes (SNAFUI) to consider significant problems of CIAAW. It serves as a "brain-storming think tank" that provides the "institutional memory" of CIAAW since the five former chairmen and/or secretaries account for more than one and one half centuries of service to IUPAC and CIAAW.

The Commission's names (describing its tasks) changed with time. The Commission was initially named International Commission on Atomic Weights (ICAW). With the effort slowly evolving to the evaluation of the isotopic composition of the elements, the name was changed to the Commission on Atomic Weights and Isotopic Abundances (CAWIA). Finally, the increasing importance of the isotopic composition work led to the present name Commission on Isotopic Abundances and Atomic Weight (CIAAW). In this report, the acronym CIAAW is used to refer to the Commission under all of its names, both the previous ones and the present one.

SNAFUI met in Vienna, Austria on July 30, 2015, prior to the CIAAW's 2015 sessions. The topics on the agenda included the following:

[1] Sent apologies for being unable to attend the meeting.

A. Review the term “normal” material, which is defined by CIAAW and was questioned by reviewers of the 2013 atomic weights report.
B. Review the contribution by the late Professor Etienne Roth (a former CIAAW chairman) on the issue of the isotope delta-zero scale, as requested by the present CIAAW chairman.
C. Review the issue of CIAAW having two separate and significant audiences as reflected by the metrological atomic weights table for measurement specialists and the abridged atomic weights table for the scientific community, in general, and the educational community, in particular.
D. Review the issue of measurement uncertainties used by CIAAW.
E. Review the two tables produced by CIAAW and consider linking the standard atomic weights and the isotopic composition of the elements.

The last three topics were added by the SNAFUI chairman.

Early in the meeting the task group undertook a discussion of strategies to improve existing tables of standard atomic weights. SNAFUI members learned from Peter Mahaffy (past chairman of CCE) and others that TSAW 2009 and TSAW 2011 are being ignored because of the lack of understanding of interval atomic-weight values. The first few rows of the 2013 TSAW are shown below:

2013 Unabridged Table of Standard Atomic Weights

Element name	Symbol	Atomic number	Standard atomic weight	See also figure	Foot-notes
hydrogen	H	1	[1.007 84, 1.008 11]	2	m
helium	He	2	4.002 602(2)		g r
lithium	Li	3	[6.938, 6.997]	3	m
beryllium	Be	4	9.012 1831(5)		
boron	B	5	[10.806, 10.821]	4	m
carbon	C	6	[12.0096, 12.0116]	1	
nitrogen	N	7	[14.006 43, 14.007 28]	5	
oxygen	O	8	[15.999 03, 15.999 77]	6	
ununoctium*	Uuo	118	–		

We do not want the TSAW 2015 ignored. Therefore, we propose to modify Table 1 to the following:

Proposed Unabridged Table of Standard Atomic Weights

Symbol	Atomic number	Standard atomic weight	Atomic-weight interval	See also figure	Foot-notes
H	1	1.007 981 75(5)	[1.007 84, 1.008 11]	2	m
He	2	4.002 602(2)			g r
Li	3	6.9400(2)	[6.938, 6.997]	3	m
Be	4	9.012 1831(5)			
B	5	10.8118(2)	[10.806, 10.821]	4	m
C	6	12.011 09(3)	[12.0096, 12.0116]	1	
N	7	14.006 726(5)	[14.006 43, 14.007 28]	5	
O	8	15.999 305(2)	[15.999 03, 15.999 77]	6	
Uuo	118	–			

Note that a new column, "Atomic-weight interval", has been added. To make room for this column, the Element name column has been omitted. For the 12 elements with interval atomic weights, atomic-weight values with (very) small measurement uncertainties of the isotope-delta zero materials (or virtual materials) have been determined from TICE "best measurements" and added to the standard atomic weight column. The column on figures refer to SNIF diagrams.

Advantages of this method of recommending TSAW values are the following:

1) We additionally provide users of the Table with an evaluated calibrated atomic-weight value (and associated uncertainty). This avoids the criticism that users are unable to derive an atomic-weight value from the interval.

2) The atomic weight is connected to a specific material. Therefore, the new atomic weight with its calibrated isotope-abundance values will enable users to determine atomic weights of a sample on an absolute scale by using delta measurements of that sample and then deriving absolute isotopic abundances, eliminating the need for absolute isotope-abundance measurements of their sample.

3) There should be fewer changes to atomic-weight values (a continuing complaint about presently published TSAW tables) unless there are improved zero delta scale measurements for an element.

4) Atomic-weight intervals will no longer have an impact on recommended standard atomic-weight values.

5) Atomic-weight intervals continue to be provided to indicate to users that standard atomic weights of elements with two or more stable isotopes are not constants of nature.

6) Standard Atomic-Weight intervals seem to invite scientists to report new record delta values to be cited in the next TSAW, TSAW in its current form will be obsolete

whenever such a measurement is reported; maybe such data would be better incorporated separately from the Standard Atomic Weight

A disadvantage of this method of recommending TSAW values is that the standard atomic weight would no longer be applicable to all normal materials.

Rationale of this approach to recommending TSAW values is the following:

1) A delta zero material has an isotopic composition that is often near the midpoint of isotopic composition observed for normal materials. Therefore, the new recommended standard atomic weights are commonly representative of major natural occurrences of an element that might be encountered in the laboratory or in trade and commerce.

2) This proposal to use calibrated isotope-amount-ratio measurements for each element's "delta zero scale measurement standard" as a best measurement in TICE tables and as a recommended standard atomic weight value in TSAW tables was suggested year after year by Etienne Roth (the Commission's longtime delta expert).

3) A single delta measurement is sufficient (as shown in the SNIF diagrams) to enable users to determine an atomic weight value with smaller uncertainty than at present. This is a straightforward process for elements with only two stable isotopes. For elements with three or more stable isotopes, knowledge of a delta value for one isotope-amount ratio enables one to calculate an atomic weight, when delta values for all other isotope-amount ratios are known or assumed to follow mass-dependent isotope-fractionation laws. This is the case when the isotope-abundance variation is due to physical or chemical effects. One also needs to calculate the uncertainty in the atomic-weight value from the uncertainty of the best measurement of isotopic abundances and associated measurement uncertainty in a delta measurement. In this case, the uncertainty is relatively small and will not cover ranges of isotope-abundance variations of natural substances, but it has the advantage that the atomic-weight is a value with (very) small uncertainty and should remain unchanged for many years.

4) It is possible to determine calibrated atomic weight and isotope-abundance values of a sample by measuring the delta value relative to a *secondary* isotopic measurement standard. This is because the secondary measurement standard has a known delta value relative to the value embodied in an isotopic measurement standard that anchors the delta scale. Primary and secondary measurement standards remain indispensable because few laboratories can perform calibrated isotope-number ratio measurements, but their delta values would be expressed on a scale that, anchored in calibrated values, would not change when new standards are introduced.

5) Since the best measurement of the value of the anchor of the delta zero scale elements is the measurement with the smallest uncertainty available, it shows the user the smallest measurement uncertainty obtainable because the enlargement of the uncertainties due to natural variability is not considered.

> Some users have expressed to the Commission that the recommendation of an interval means that they can no longer rely on the information provided in the TSAW. Users are demanding a single authoritative best value for an atomic weight.

In 2013, the Commission published:

Table 2 Standard atomic weights 2013 abridged to five significant digits.

Element name	Symbol	Atomic number	Abridged standard atomic weight	Foot-notes
hydrogen	H	1	[1.0078, 1.0082]	m
helium	He	2	4.0026	
lithium	Li	3	[6.938, 6.997]	m
beryllium	Be	4	9.0122	
boron	B	5	[10.806, 10.821]	m
carbon	C	6	[12.009, 12.012]	
nitrogen	N	7	[14.006, 14.008]	
oxygen	O	8	[15.999, 16.000]	
ununoctium*	Uuo	118	–	

SNAFUI proposes that this table be updated to the following in TSAW 2015.

Table 2 Practical atomic weights 2015

[Scaled to $A_r(^{12}C) = 12$, where ^{12}C is a neutral atom in its nuclear and electronic ground state.] The atomic weights of many elements are not invariant, but depend on the origin and treatment of the material. Thus, these practical atomic-weight values and their associated uncertainties have been selected so that most atomic-weight variations in normal materials are covered. The values of atomic weight, $A_r(E)$, and the uncertainties (in parentheses, following the last significant digit to which they are attributed) apply to elements from normal materials. The last significant figure of each tabulated value is considered reliable to ±1 except when a larger single digit uncertainty is inserted in parentheses following the atomic weight. An atomic-weight value is not shown for elements that have no stable isotope or no radioactive isotope having a characteristic isotopic composition in normal materials. A double dagger (‡) indicates elements in specimens from unusual geological environments or materials that have been subjected to an undisclosed or inadvertent fractionation of isotopes, resulting in atomic-weight values outside the tabulated values below. Additional information on these deviations can be found in the "Footnotes" column of the full Table of Standard Atomic Weights. Names and symbols of elements with atomic number 113, 115, 117, and 118 are provisional; they have been reported in the peer-reviewed, scientific literature, but they have not yet been officially named.

Element name	Symbol	Atomic number	Practical atomic weight
hydrogen‡	H	1	1.0079(2)
helium	He	2	4.0026
lithium	Li	3	6.94†
beryllium	Be	4	9.0122
boron‡	B	5	10.814(8)
carbon	C	6	12.011(2)
nitrogen	N	7	14.007
oxygen	O	8	15.999
ununoctium	Uuo	118	–

†Commercially available Li materials have atomic weights that range between 6.939 and 6.996; if a more accurate value is required, it must be determined for the specific material.

Values in the practical atomic weight column of Table 2 have been calculated from the SNIF diagrams for each element, using the total range to provide a five figure atomic weight value and uncertainty which covers the entire interval in SNIF.

A. ‘Normal’ Material

In 1957, CIAAW stated that the primary purpose of CIAAW was to provide accurate atomic weights for any calculation in chemistry.

In 1969, CIAAW stated it would use weighting procedures to optimize atomic weights for materials in science, chemical technology and trade, rather than represent an estimated average value for use in geochemistry. The estimated uncertainty was taken as three times the standard deviation of measured values increased by the maximum difference between stated values and that for any reliably observed normal material. No treatment of systematic measurement uncertainties was included.

In 1969, CIAAW noted that a “normal” material is one that contains as a major constituent a specified element with an atomic weight value that does not display a significant difference from the accepted value of that atomic weight because of a) its radiogenic source, b) its extraterrestrial origin, c) artificial alteration, d) mutation, e) a rare geological occurrence in small quantity.

In 1971, CIAAW modified its definition of “normal” material to slightly revise item c) artificial isotopic fractionation, and d) artificial nuclear reaction.

In 1975, CIAAW commented that Commission members use “normal” (material) in the sense of “terrestrial (material) with isotopic composition unaltered in its geological past”. CIAAW proposed to publish a Table of Standard Atomic Weights defined by isotopic composition with an atomic weight that in the judgment of the Commission is most probably encountered by chemists.

In 1977, CIAAW members tended to use “terrestrial” with isotopic composition of material that was the most abundant source of the element.

In the 1984 Element by Element Review, CIAAW stated that “normal” material is a reasonably possible source for this element or its compounds in commerce, for industry or science; the material is not itself studied for some extraordinary anomaly and its isotopic composition has not been modified significantly in a geologically brief period.

In 1985, CIAAW attached a footnote ‘g’ to boron to account for seawater boron because it was considered unlikely that it would become a source of commercial boron and impact the atomic weight value.

In 1991, CIAAW chose a ‘radiogenic’ osmium measurement result as the standard atomic weight value.

In 2009, in 2011, and in 2013, CIAAW again quoted, in its reports, the identical meaning of a “normal” material from the 1984 Element by Element Review article above.

There are continuing references, between 1975 and 2011, to the term ‘normal’ material as defined by the CIAAW to material with isotopic composition unaltered in its geological past or whose isotopic composition has not been modified significantly in a geologically brief period. There is no definition by CIAAW of what constitutes the ‘geological past’ or a ‘geologically brief period’. The wording that a specimen’s isotopic composition was not changed in a brief geological period, which a pair of geologists from Europe and the United States indicated was somewhat vague, but would mean approximately one million years or longer. How would this issue affect isotopic variations, which are incorporated into the data considered when a standard value is recommended by CIAAW? SNAFUI has concluded that no recommendation about "normal" material can be made at this time because of the potential impact of the geologically brief period and because of contradictory decisions that have been made in the past, such as excluding elements whose atomic weight is affected by its radiogenic source and the acceptance of a standard atomic weight for an element, whose atomic weight is affected by its radiogenic source. What is the future for elements with radiogenic isotopes? Should results of radiogenic project evaluations be incorporated into the tables? This issue will require more detailed study, possibly via a new SNAFUI Project Proposal to resolve what "normal" material should be after considering past statements.

B. Etienne Roth's Proposals Dealing with Isotope Delta Zero Scales

Over the years, Etienne had made many comments about the delta scale, including a proposal to use measurement of isotopic composition as the best measurement in the Isotopic Compositions of the Elements (TICE) tables and as a recommended atomic weight value in the Table of Standard Atomic Weights (TSAW). He commented that data are published as measurements of relative difference of isotope ratios (delta values) for most isotopic work, but these deltas do not facilitate inter-laboratory comparisons, nor do they tie results to an atomic weight scale. There is a limited stock of isotopic standard reference material samples that are available from various agencies. When they are exhausted, new reference materials are prepared. One can keep the scale of deltas unchanged by measuring sample delta values relative to the new reference material and combining results with the delta value of the new reference in the old scale. If an agency discontinues the distribution of a reference material, laboratories have to rely on their own references or borrow certified samples, which make the comparison of results less reliable. Not knowing the "absolute" compositions of the zero delta reference prevents laboratories from calculating better isotope abundances (and atomic weights) of samples from delta measurements, even for those samples that do not show mass independent fractionation. Measuring calibrated isotope-number ratios instead of relative differences and expressing results in calibrated number fractions, when necessary and justified, would provide answers to the above issues.

During the years when new extreme values were published for variations of isotopic compositions, the Commission's procedure would be to calculate new averages of the extremes and change the atomic weight values to a new mid-point, Etienne suggested that the Commission choose as a reference the value (embodying a material) that was used as the zero of the delta scale. One could use the Subcommittee on Natural Isotopic Fractionation (SNIF) reports on isotopic variations to work out atomic weights of materials other than the reference, without needing to make calibrated abundance measurements. A single delta determination would be sufficient as SNIF reports display figures, where atomic weights can be read versus delta values. It is straight forward for elements with only two isotopes. In the case of multiple isotope elements, knowing delta for one isotope enables one to calculate an atomic weight, when deltas for all isotopes are known to follow a linear mass law, as is the case when the range is due to purely physical effects. When nuclear phenomena produce the range, the linear mass fractionation law does not apply. Etienne had previously provided sulfur as an example of a multiple isotope element and he determined the various isotope ratios and isotope abundances after applying the mass fractionation law.

Etienne suggested tabulating atomic weight samples that are the origin of delta scales. If necessary, one should reconsider the choice of these samples so that their availability were guaranteed for a long period of time and calibrated isotope abundance has been determined. One would attach to the atomic weight the measurement uncertainty it deserves. The uncertainty will be small, because it will not cover natural ranges and no footnotes will apply. This procedure has the advantage that this entry will stay unchanged for many years. CIAAW should consider establishing the origin of delta values (used for natural isotopic abundance measurements) on a calibrated basis. This will affect calibrated values for every material. An approach of this kind started when the standard reference materials, standard mean ocean water (SMOW) and standard light Antarctica precipitate (SLAP), were measured for calibrated deuterium contents. Establishing atomic weights on the basis of a reference sample and published SNIF reports enables one to select atomic weights relative to the material under study with a lower uncertainty than at present. This procedure would reduce measurement uncertainty of isotope dilution mass spectrometry (IDMS) measurement results. The origin of atomic weight values would be the origin of delta values. One would need to follow these steps:

1. Complete the SNIF tables for elements with only two stable isotopes. Work out how to deal with poly-isotopic elements.
2. Apply the new method of tabulating atomic weights to elements for which SNIF tables are completed.
3. Work out new atomic weights for poly-isotopic elements. Publish atomic weights of reference sample and choose those samples that serve as the origin of the delta scale. The choice is not obvious for all elements. It will need discussion and the origin may need to shift for some elements.

For the case of hydrogen, Etienne suggested defining delta values not versus material samples, but on a scale anchored in SMOW (now Vienna-Standard Mean Ocean Water, VSMOW). For every element, by using a calibrated isotopic composition to characterize the origin of deltas, results could be expressed independently of the values of measurement or reference measurement standards. Reference standards would remain indispensable because few laboratories can measure calibrated ratios, but their delta would be expressed in a scale that, resting on a calibrated value, would not change when new reference measurement standards were introduced. Under this concept, ‘standards’ would only be useful if they could be procured. Their role would be that of a measurement sample carrying a certified delta value. Knowing the isotopic composition of the origin of delta values enables one to derive isotope abundances from delta values and vice versa.

Understanding Etienne’s suggestions on the use of the delta zero scale, SNAFUI decided to work out the details and attempt to produce such a system and provide an example of such a table of recommended atomic weight values for some of the chemical elements. After seeing the results of Etienne’s suggested system, SNAFUI decided to recommend this system to CIAAW and to replace the present ‘Standard’ Atomic Weights by these recommended atomic weight values. SNAFUI recognizes that the adoption of this strategy would require a redefinition of standard atomic weight.

C. Two Significant, Separate Audiences of CIAAW

CIAAW noted as early as the 1970s that there were two separate audiences for its table. When questioned about the number of significant digits included in the atomic weight values quoted for mono-nuclidic elements, it was stated that one cannot predict potential future uses of atomic weight values and the most accurate values should therefore be quoted, whether required at the present time or not.

During the SNAFUI meeting at the Bureau International des Poids et Mesures (BIPM) in 2007, SNAFUI concluded during discussions that CIAAW had two separate and significant audiences for their recommended atomic-weight tables. The measurement specialists required a metrological (full or complete) table and the general science community, including educators, wanted an abridged atomic weight table.

In 1957, former CIAAW chairman, the late Edward Wichers, stated that the primary purpose of the CIAAW was to provide accurate atomic weights for chemical calculations.

In 1975, CIAAW stated their task was to publish a table of standard atomic weights derived from its isotopic composition and consistent with that atomic weight which in the judgment of the CIAAW is most probably encountered by chemists.

In 1985, CIAAW added footnote ‘g’ to boron because they determined that seawater boron was unlikely to become a source of commercial boron, an indication that the users of the table would not be interested in that source of boron.

The above is an indication that CIAAW has always acknowledged a user community beyond that of measurement specialists.

In recent years, CIAAW has always presented the full table. On occasion one or two abridged versions would be provided with the full table front and center. Because the vast majority of users of the CIAAW tables do not require the details of the full table, SNAFUI recommends that CIAAW should provide the abridged table first in their reports and the full table with all of its details as the second table. This approach would enable the majority of users to obtain their information quickly. Any users from that community who desired more details and the measurement specialists could read further and receive the complete picture of the status of the best atomic weight values with all appropriate additional information.

SNAFUI recommendations for the publication of atomic weight tables

SNAFUI recommends that CIAAW publish two tables of atomic weight values in their report; the abridged table for the general science community should be the first table presented in the publication.

D. Issue of Uncertainties used by CIAAW

In 1969, CIAAW stated that their estimated uncertainty is taken as three times the standard deviation of experimental measurements and the maximum difference between stated values and that for any reliably observed normal material. This would indicate that the CIAAW viewed their aim as providing values at the 99 percent confidence level.

There are two distributions that CIAAW has discussed relative to atomic weight values. One is the Gaussian (Normal) distribution and the other is the Rectangular distribution. For the Gaussian distribution, there are various types of uncertainties:
1. A ‘standard’ uncertainty implies a 1s Gaussian distribution.
2. A ‘combined’ uncertainty means that the uncertainty has been calculated using error propagation.
3. An ‘expanded’ uncertainty is obtained by multiplying the combined standard uncertainty by a coverage factor, *K*, and is denoted by *U*. The factor used to be 3 or 6 but lately CIAAW has used any factor in order to cover the range deemed necessary. $U = K \cdot u_c$, where *K* is the coverage factor and u_c is the combined standard uncertainty. This implies a standard distribution (which CIAAW cannot always guarantee).
The results of a measurement is $Y = y \pm U$; the best estimate of the value attributed to measurand Y is y. $y - U$ to $y + U$ is an interval expected to encompass a large fraction of the distribution of values reasonably attributed to Y. (Large fraction is not defined, although CIAAW has indicated 99%, see above).

A rectangular distribution implies that CIAAW does not know the distribution. The probability that the value of the atomic weight lies within the interval ‘value minus uncertainty’ to ‘value plus uncertainty’ for all practical purposes is equal to one. The probability that the atomic weight lies outside this interval is essentially zero (according to GUM). A rectangular distribution implies that all values within that distribution are equally probable. This is a reasonable assumption with regard to the uncertainty range from an experimental measurement. An interval to cover variations in nature, where there are experimentally discrete values may not be in the same category.

The former CIAAW chairman, the late Professor John de Laeter, in discussing uncertainties, stated that the CIAAW aimed to provide a table of atomic weights that were accurate at the 99 percent confidence level based on the premise of a normal distribution. Metrologists are correct in referring to rectangular distributions rather than Gaussian distributions. However, the scientists to whom we are presenting the information will not be statistical wizards, in general. We must state the atomic weight data in a way in which most people easily understand our evaluated data tables. The idea of confidence limits based on a notion of normal distributions is something that most people can intuitively grasp and IUPAC should recognize this. If we are writing for the metrological community and not the general scientific community, we could take a different approach, but while we only have one data set, then we must appreciate the limitations imposed on us by our readership.

Etienne Roth has commented on the issue of the general readership by noting that in the TICE tables, annotations C, F, L flag values, whose accuracies have been ascertained by different methods. Knowing the differences between the methods is useful (for metrologists), but not for the general scientific public. These readers would be satisfied with a statement such as ‘accuracy has been checked’. Details would come from the references.

SNAFUI recommendation on the treatment of uncertainties

SNAFUI recommends that a further examination of the best method for treating uncertainties in CIAAW reports be made, possibly via a SNAFUI Project Proposal to insure that all material is presented in a manner which is appropriate for each of the two CIAAW audiences, particularly when two separate tables are presented.

E. A Tale of Two Tables

More than a decade ago, CIAAW proposed creating a comprehensive table of all data. Perhaps it is time to put TSAW and TICE together, rather than produce them separately and give all of the different evaluated quantities in all relevant terms.