Subcommittee on Natural Assessment of Fundamental Understanding of Isotopes of IUPAC

Summary Minutes of Meeting September 14 – 18, 2017, University of Groningen, Groningen, The Netherlands

IUPAC Project 2015-030-2-200
Assessment of fundamental understanding of isotopic abundances and atomic weights of the chemical elements (2016—2017)

1. Opening and Welcome

Dr. Holden welcomed the members of the Subcommittee on Natural Assessment of Fundamental Understanding of Isotopes (SNAFUI) to Groningen, The Netherlands. The following members were in attendance:

Dr. N. E. Holden (Chair), Brookhaven National Laboratory, Upton, New York, USA
Dr. T. B. Coplen (Secretary), U.S. Geological Survey, Reston, Virginia, USA

Dr. J.K. Böhlke (U.S. Geological Survey, Reston, Virginia, USA) and Prof. M. E. Wieser (University of Calgary, Calgary, Alberta, Canada) attended parts of the meeting via email and telephone.

2. Agenda

The principal objectives of SNAFUI (Subcommittee hereafter) are to (1) review fundamental issues and concerns that have been raised by members of the Commission on Isotopic Abundances and Atomic Weights (Commission) and IUPAC members, (2) discuss these issues at length for time periods not available during Commission meetings, and (3) present recommendations to the Commission on solutions to problems that will help to provide future direction for their work on atomic weights and isotopic abundances of the chemical elements. The following issues were discussed during this meeting.

- An Interdivisional Committee on Terminology, Nomenclature, and Symbols (ICTNS) review of the Commission's recent publications indicated that the term "normal material" needs an updated definition. This term is fundamental to both the Table of Standard Atomic Weights (TSAW) and the Table of Isotopic Compositions (TICE).
- According to guidelines on expression of uncertainty defined by the Joint Committee for Guides in Metrology (JCGM), which is a part of the International Bureau of Weights and Measures (BIPM), the expression of standard atomic weight in a format such as "78.971(8)" suggests to users that 0.008 is the standard uncertainty of the value 78.971 [1]. This requires discussion by the Subcommittee because the value 0.008 in this

example was never intended to be understood by users of the TSAW and TICE as the standard uncertainty.

- A PowerPoint titled "Definitions and Meaning of Terms: Changing Traditions & Protocols of the Commission" and a Technical document titled "Clarification of the term 'normal material' and a table of standard atomic weights 2015 having curly brackets (IUPAC Technical Report)" was prepared and shared with members of the Commission on Isotopic Abundances and Atomic Weights.

3. Normal Material

From its inception in 1919, the International Union of Pure and Applied Chemistry (IUPAC) took over the careful evaluation and dissemination of atomic weights from critically assessed, published information through its Commission on Isotopic Abundances and Atomic Weights. Each standard atomic weight value reflects the best knowledge of evaluated, published data [2, 3] of normal materials. The implied range of each standard atomic weight is intended to apply to all sources of normal materials of that element. In the Commission's 1969 report [4], a "normal" material was defined as:

> ". . . 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; or
> (e) a rare geological occurrence in small quantity."

This definition for normal material in the 1969 Commission report [4] resulted in several decrees:

- "In assessing variations in isotopic composition, the Commission will continue to disregard other than 'normal' materials."
- "To arrive at the recommended value for an atomic weight the Commission will use weighting procedures so that the value will be optimized for materials in world science, chemical technology and trade, rather than represent an estimated geochemical average [of the Earth]."
- "The Commission must attempt to state the atomic weight values so that they are as precise as possible. At the same time, they must be sufficiently imprecise so that all normal specimens fall within the implied tolerance range. In other words, large quantities of available materials should not lie outside the tolerance range. The difficult judgment has to be made when only a small fraction of normal material falls outside the tolerance range. The Commission has decided in such cases not to discard useful accuracy applicable to the great majority of practical condition, but to exclude from the definition of 'normal', geological oddities."

This definition was updated in the 1971 TSAW [5], where "artificial alteration" was updated to "artificial isotopic fractionation" and "mutation" was updated to "artificial nuclear reaction." In

1984, the Commission revised the definition of a normal material to a material from a terrestrial source that satisfies the following criteria [2]:

> "The 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."

Consideration of this definition of normal materials by the Commission has resulted in several changes in standard atomic weights in the last three decades, for example:

1. The uncertainty value of the standard atomic weight of boron was expanded in 1995 (from 10.811(5) to 10.811(7)) to include boron in sea water because it was decided that boron in sea water was a normal material [6].
2. In 1995, the Commission decided it could reduce the uncertainty value of the standard atomic-weight of carbon from 12.011(1) to 12.0107(8), noting that specimens outside these limits could be covered by footnote "g" for rare geological occurrences in small quantities [6].
3. In 1999, the Commission recognized that the standard atomic weight of nitrogen did not include a substantial fraction of naturally occurring materials in the terrestrial environment, and the Commission changed the standard atomic weight from 14.006 74(7) to 14.0067(2) [7].

Although this definition of normal material has served the Commission for the last three decades [8], a revised definition is needed, in part, because the clause "its isotopic composition has not been modified significantly in a geologically brief period" is not clear to many readers. Considering the intended meaning of normal materials since the 1960s, the Subcommittee suggests that confusion in its definition could be reduced by revising this definition to the following:

> "**Normal materials** include all substances, except (1) those subjected to substantial deliberate, undisclosed, or inadvertent artificial isotopic modification, (2) extraterrestrial materials, and (3) isotopically anomalous specimens, such as ~~Oklo~~ natural nuclear reactor products from Oklo (Gabon) or other rare terrestrial occurrences."

This revised definition of normal material no longer includes the exclusion that "its isotopic composition has not been modified significantly in a geologically brief period." This modification recognizes the fact that much of the atomic-weight variation of some elements is caused by isotopic fractionation processes that operate on many different time scales.

The revised definition also anticipates that materials with radiogenic or nucleogenic isotopic variability may no longer be excluded in the definition of a normal material, except in very exceptional situations, such as the occurrence of ^{87}Sr in a pure rubidium sample. For example, with this revised definition of normal materials, based on the recent evaluation of argon (Fig. 1) by Böhlke [9], the standard atomic weight of argon might be changed from the current value of 39.948 ± 0.001 [10] to [39.7931, 39.9624], when expressed as an interval, to include naturally occurring sources having nucleogenic and radiogenic isotopic variation. Similar evaluations of other such elements (e.g., strontium) are underway by the IUPAC project titled "Evaluation of Radiogenic Abundance Variations in Selected Elements (#2009-023-1-200)." The chair of this project is M. E. Wieser.

After discussion, the following definition was accepted by the Commission:

> "**Normal materials** include all substances, except (1) those subjected to substantial deliberate, undisclosed, or inadvertent artificial isotopic modification, (2) extraterrestrial materials, and (3) isotopically anomalous specimens, such as natural nuclear reactor products from Oklo (Gabon) or other unique occurrences."

To explain and document this change in definition of normal materials, it was decided that an article titled "Clarification of the term 'normal material' used for standard atomic weights (IUPAC Technical Report)" would be prepared and submitted by the Subcommittee to *Pure and Applied Chemistry*.

4. Expression of Uncertainties of Standard Atomic Weights

The 1984 Element by Element Review [2] states:

> "The Commission aims at disseminating value pairs [A_r(E), U_r(E)] such that it can claim at a high level of confidence that any element in question in all known normal sources will have an atomic weight that will not differ from the relevant A_r(E) by more than U_r(E). At an even much higher level of confidence, bordering on complete certainty, any chemist sampling any given "normal" (see Section 4) material, be it any ore in trade, or any product at a chemical plant, or any substance at any chemical laboratory, shall be justified in expecting all elements in that material to possess atomic weights within the implied tabulated ranges of the standard atomic-weight values."

The quantity A_r(E) – U[A_r(E)] denotes the lower bound of standard atomic weight, and the quantity A_r(E) + U[A_r(E)] denotes the upper bound of standard atomic weight. The difference between the upper and lower bounds is the range and is 2 × U[A_r(E)]. The distribution of atomic-weight values may not be Gaussian.

At the 1983 Commission meeting in Lyngby, Denmark [11], a Working Party was formed to examine the procedures that had been used to assign uncertainties to atomic weights and to report to the Commission at the next meeting on those and other procedures, which might be used in the future. The Working Party provided recommendations at the 1985 Commission meeting in Lyon, France [12]. One of the recommendations of the Working Party was that uncertainties be quoted (or implied) by single digit values (1–9) applicable with both signs to the last decimal of each tabulated standard atomic weight. For example, the standard atomic weight of selenium, which is 78.971 having a decisional uncertainty of ± 0.008, would be tabulated as 78.971(8). This single digit provides the Commission's decisional uncertainty of standard atomic-weight values, and the selenium standard atomic-weight value of 78.971(8) is intended to be applicable to the vast majority of normal materials containing selenium.

The decisional uncertainty (e.g. ±0.008 for selenium) is an expanded uncertainty and is the product of a combined standard measurement uncertainty and a factor larger than the number one. This factor is referred to as the coverage factor, and a coverage factor is usually symbolized by k [1, 13]. Although the Commission declines to specify the coverage factor [2], the lower and upper bounds are assigned so that standard atomic weights are highly reliable and have great certitude [2]. For example, the coverage factor for the approximately 20 elements having one stable isotope is six (k = 6) [4]. Additionally, the expansion of the uncertainties of atomic masses by six by the Commission resulted in only one stable isotope out of 294 stable isotopes being inconsistent between the 2003 and 2012 Atomic Mass Evaluations [14, 15], namely lithium-7

[10]. For elements having two or more stable isotopes (or radioactive isotopes that contribute to the standard atomic weight), the Commission intentionally has declined to specify the coverage factor [2], but De Bièvre et al. [16] state, "The aim of IUPAC has been fulfilled by which any chemist – taking any natural sample from research, industry, or commerce can confidently expect his or her true sample atomic weight to lie within the tabulated range with a probability far in excess of 95 %." If needed for their own statistical purposes, it will be up to users of the table to select an appropriate coverage factor, *k*, based on these principles.

The expression of a standard atomic weight as 78.971(8) is confusing because the Commission never intended that the value in parentheses be a standard uncertainty. The Subcommittee evaluated reducing this confusion by presenting decisional uncertainty values in another format. Three formats considered at the meeting, or in subsequent emails, included:

1. Expressing the decisional uncertainties of A_r(E) values as half-ranges in a separate column. For example, "78.971(8)" would be divided into two columns named "value" and "half-range" with entries of "78.971" and "0.008," respectively. In text, a value would be expressed, for example, as A_r(Se) = 78.971 ± 0.008.
2. Expressing A_r(E) values and their decisional uncertainties in curly brackets, following the last significant digit to which they are attributed. For example, "78.971(8)" would be printed as "78.971{8}."
3. Expressing A_r(E) values and their decisional uncertainties in square brackets, following the last significant digit to which they are attributed. For example, "78.971(8)" would be printed as "78.971[8]."

The Subcommittee noted that expressing decisional uncertainties of A_r(E) values as half-ranges could add confusion if applied to elements with no known range of atomic-weight variation. Likewise, the format "78.971[8]" might confuse readers thinking that "[8]" represents a reference, which is the standard method to identify references in *Pure and Applied Chemistry*. Although the format 78.971{8}" was preferred by the Subcommittee, the Commission decided upon the format having the ± symbol, e.g., A_r(Se) = 78.971 ± 0.008.

Since the 2009 TSAW, the word "decisional" has appeared in the rubric to indicate that standard atomic weight values and their uncertainties decided by consensus [10, 17, 18]. To emphasize that tabulated uncertainties in the new uncertainty column in the TSAW are consensus values, not GUM-evaluated values, the Subcommittee proposed that a new footnote be added to the TSAW. The Subcommittee proposed that the symbol for the footnote be the symbol double dagger (‡), recognizing that the symbol single dagger had been used between the 1997 and 2007 TSAWs to indicate that "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." The column heading "Uncertainty" will appear as "Uncertainty‡" in the TSAW. This new footnote in the TSAW is the first in more than two decades: [8]

‡ For 71 elements, A_r(E) values and their decisional uncertainties are given for normal materials and include evaluations of measurement uncertainty and variability. The atomic weight of a normal material should lie between the lower and upper bounds of the standard atomic weight with great certitude. If a more accurate A_r(E) value for a specified material is required, it should be determined.

5. Definitions and Meaning of Terms: Changing Traditions & Protocols of the Commission

A PowerPoint titled "Definitions and Meaning of Terms: Changing Traditions & Protocols of the Commission" was prepared and shared with members of the Commission on Isotopic Abundances and Atomic Weights (see Appendix A). This PowerPoint is of benefit to new and younger members of the Commission, and it addresses the following:

(1) Why does the CIAAW continue to produce a Table of Standard Atomic Weights when the values are not weights, but are dimensionless? Why not produce a Table of Standard Relative Atomic Masses?

(2) Historically, how has the CIAAW set the lower and upper standard atomic weight bounds of elements?

(3) How did the one-digit uncertainty for standard atomic weights arise?

(4) Why is a mineral survey important for consideration of a new standard atomic weight?

(5) The Subcommittee on Isotopic Abundance Measurements (SIAM) is responsible for evaluation of best measurements of isotopic composition. How does a best measurement of a material relate to a new standard atomic weight?

(6) From where did the adoption of the 6s uncertainty in the standard atomic weights of some elements arise?

(7) Why did the CIAAW decide not to assign standard atomic weights to many radioactive elements?

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APPENDIX A: Definitions and Meaning of Terms: Changing Traditions & Protocols of the Commission

Definitions and Meaning of Terms: Changing Traditions & Protocols of the Commission

DR. N.E. HOLDEN, DR. T.B. COPLEN, PROF. M.E. WIESER AND DR. J.K. BÖHLKE

Responsibility of a Standards Commission

Approximately a half century ago, H. Steffen Peiser, (Commission Secretary) stated “the work of the Atomic Weights Commission requires special continuity to ensure that today’s considerations are a logical and a consistent development of a tradition that goes back over fifty years”.

Responsibility of a Standards Commission - Continued

Norman N. Greenwood (Commission Chairman) argued that atomic weights are consensus values enunciated by uniquely qualified experts and not subject to statistical concepts.

Paul De Bièvre introduced the term, ‘decisional uncertainties’, based on Greenwood’s argument.

The 1987 Commission report emphasizes that the collective judgement and experience of the Commission members are its most valuable asset, which must be applied in each case.

Terms/Issues to be Discussed

1. Atomic Weight Values, Uncertainties, Isotopic Variations;

2. ‘Normal’ Materials- Trace Elements, Radiogenic Isotope;

3. Use of Intervals (Upper and Lower Bounds) in lieu of Separate Values and Uncertainties, SNIF diagrams;

4. Radioactive and Synthetic Elements;

5. Internationally Distributed Isotopic Reference Material Preferred for the Acceptance of the Best Measurement.

Definition of Atomic Weight

The Commission's main purpose is to provide accurate atomic weight values for chemical calculations. Atomic Weights considered to be a universal constant of nature with a 'true value' for each element.

Values determined from chemical stoichiometric data. By 1950s, the values are derived from the isotopic compositions of the elements.

Isotopic variations in nature eliminates the concepts of 'constants of nature' and 'one true value'. Any sample can have an atomic weight.

In 1961, Commission recommends 'change atomic weights to relative atomic mass'. Over-ruled by IUPAC higher authorities.

Definition of Atomic Weight (Continued)

1973: atomic weight is ratio of average mass per atom of a natural nuclidic composition to 1/12 of the mass of an atom of nuclide ^{12}C.

The IDCNS rules omitting the phrase ‘relative atomic mass’ probably justified because of elements with more than one stable isotope.

1979: atomic weight of an element from a specified source is “ratio of average mass per atom of element to 1/12 of an atom of ^{12}C”. Atomic weight can be defined for any sample; Average mass/atom in specified source is the total mass of the element divided by the total number of atoms of that element.

Atomic Weight Uncertainties

The Commission has **never** treated their uncertainty as a standard deviation.

The 1949 Commission chairman preferred neither experimental uncertainties nor indication of any variability, fearing users might lose confidence in the remarkable reliability of the values. The 1969 chairman argued atomic weight values were considered consensus values enunciated by uniquely qualified experts and could not be subject to statistical concepts.

At a level bordering on **complete certainty**, the 1984 Commission claimed that any chemist sampling any given 'normal material' shall be justified in expecting all elements in that material to possess an atomic weight within the implied tabulated (uncertainty) ranges of the standard atomic weight value.

Normal Materials

The preamble to atomic weight tables from 1961 to 1967 noted that atomic weights applied to elements as they exist in nature, without artificial alteration of their isotopic composition and to natural mixtures that do not include isotopes of radiogenic origin. Technical Policy of Commission: Specimens suspected of significant radioactive change in recent past excluded from atomic weight.

1969: ‘Normal Material’ introduced; must contain element as a MAJOR constituent of a specimen. A trace element in a material with isotopic variation significantly different from accepted value in the Table would be disregarded.

Normal Materials (Continued)

2017 SNAFUI-preferred definition: ‘Normal Materials’ includes all substances, except (1) those subjected to substantial deliberate, undisclosed, or inadvertent artificial isotopic modification; (2) extra-terrestrial materials; and (3) anomalous isotopic specimens, such as natural nuclear products from the Oklo mine-site in Gabon, South-west Africa or other rare terrestrial occurrences.

Restriction on normal materials to have no trace element data and no radiogenic isotope data is eliminated. Information on radiogenic data not incorporated yet; still under investigation.

Intervals in Lieu of Values & Uncertainties

The Commission requires symmetric uncertainties only. When asymmetric variations of isotopic fractionations in nature were recommended by SNIF, the value of atomic weight shifted from best measured value to mid-point of extreme ranges of values calculated from extreme isotopic abundance values.

This led to recommended values, which did not correspond to any known specimen of a normal material of that element. The result does not conform to ISO/GUM rules. The Commission introduces ‘intervals’ to encompass the total range of all normal materials of the element with upper and lower bounds. The value may not be selected as the mid-point of the interval or the previous problem remains. The atomic weight interval is the standard atomic weight and is the best knowledge of atomic weights of natural terrestrial sources.

Radioactive and Synthetic Elements

These elements are produced in the laboratory rather than discovered in nature. Listing atomic numbers is inconsistent with primary purpose of TSAW to provide accurate values for use in chemical calculations. There is no general agreement on which of the isotopes is, or is likely to be ‘important’, which one is most stable, which one is produced in quantity, or which one is used commercially. (1) Use of mass numbers too imprecise for analytical work; (2) users know enough about their source to have best useable knowledge of atomic weight; (3) new half-life determinations may change the listed isotope; (4) isotope of longest half-life in some instances is not the one most widely available, e.g., technetium, plutonium and californium.

The argument for inclusion in the TSAW is users do not like to see open spaces for known elements but this blank space provides an opportunity to better educate users about atomic-weight values. Fact that Standard Atomic Weight values must apply to all terrestrial samples of an element is probably not appreciated by most users of TSAW.

Radioactive Elements - continued

Etienne Roth wanted TICE to include the longest-lived isotope of every radioactive element either synthetic or naturally occurring, as well as the atomic mass and the half-life of the isotope. He argued that TICE should include information on radioactive isotopes of stable elements such as potassium-40, rubidium-87, carbon-14 and tritium . He also wanted additional entries in Table 3 on selected radionuclides for many of these elements, where there is only one entry for some elements and multiple entries for other elements.

Isotopic Reference Materials

Use of an internationally accepted IRM (if available) is recommended for acceptance of a ‘best’ measurement.

Use of an IRM provides assurance that reported data are of high quality; match matrix of samples before MS analysis.

Isotope Ratios of Reference Materials have uncertainties that must be included in any statement of overall uncertainties of experimental data.

Acceptance of the ‘Best’ Measurement

Commission evaluates the mass spectrometric parameters:

Abundance Sensitivity (greater for high *Z* elements)

Isobaric Interferences; (for absence, check another isotope of possible interfering element)

Linearity of ion conversion/measurement system

Isotope Fractionation, time dependent Correction Factor must be calculated and applied to measured isotopic data.

Conclusions

The Standard Atomic Weight satisfies an element's value for all of the specimens of elements in nature. Users should have complete certainty that sampling any given normal material should expect all elements to possess values within the implied tabulated uncertainty range Commission never treated atomic weight uncertainties as a standard deviation. Uncertainty described as expanded under ISO/GUM terminology.

Normal materials are redefined as all substances, except those subjected to substantial artificial isotopic modification, extra-terrestrial materials and anomalous isotopic specimens or other terrestrial occurrences.

Conclusions – continued (1)

Commission provides dual task of highest precision in TSAW and disseminates the most reliable data. For practical considerations, Commission may slightly compromise in the precision of the tabulated data but not with their perceived reliability.

The atomic weight interval is the standard atomic weight and is the best knowledge of the atomic weights of natural terrestrial normal materials.

The atomic weight of an interval element **may not** be selected as the mid-point of the atomic weight interval.

Conclusions – continued (2)

Listing atomic numbers of radioactive and synthetic elements in TSAW is inconsistent with the primary purpose to provide accurate values for chemical calculations.