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IUPAC Technical Report

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Interpreting and propagating the uncertainty of the standard atomic weights (IUPAC Technical Report)

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Abstract: In 2009, the Commission on Isotopic Abundances and Atomic Weights (CIAAW) of the International Union of Pure and Applied Chemistry (IUPAC) introduced the interval notation to express the standard atomic weights of elements whose isotopic composition varies significantly in nature. However, it has become apparent that additional guidance would be helpful on how representative values should be derived from these intervals, and on how the associated uncertainty should be characterized and propagated to cognate quantities, such as relative molecular masses. The assignment of suitable probability distributions to the atomic weight intervals is consistent with the CIAAW's goal of emphasizing the variability of the atomic weight values in nature. These distributions, however, are not intended to reflect the natural variability of the abundances of the different isotopes in the earth's crust or in any other environment. Rather, they convey states of knowledge about the elemental composition of "normal" materials generally, or about specific classes of such materials. In the absence of detailed knowledge about the isotopic composition of a material, or when such details may safely be ignored, the probability distribution assigned to the standard atomic weight intervals may be taken as rectangular (or, uniform). This modeling choice is a reasonable and convenient default choice when a representative value of the atomic weight, and associated uncertainty, are needed in calculations involving atomic and relative molecular masses. When information about the provenance of the material, or other information about the isotopic composition needs to be taken into account, then this distribution may be non-uniform. We present several examples of how the probability distribution of an atomic weight or relative molecular mass may be characterized, and also how it may be used to evaluate the associated uncertainty.

Keywords: atomic weights; atomic-weight intervals; beta distribution; delta scale; delta value; fractionation; Gaussian distribution; interval arithmetic; measurement uncertainty; normal; probability distribution; rectangular distribution; relative molecular mass; standard atomic weight; uncertainty; uncertainty propagation; uniform distribution.

1 Introduction

At its 2009 meeting in Vienna, the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) resolved to express the standard atomic weight of ten elements – including hydrogen, carbon,

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and oxygen – by means of intervals that characterize the span of their atomic-weight values in so-called “normal” materials.

We use the term “atomic weight” interchangeably with, and as shorthand for “relative atomic mass”, consistently with the historically customary usage recognized in the IUPAC *Green Book* [1, 2.10(8),6.2].

The CIAAW defines “normal” material as any terrestrial material that “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” [2]. Concerning the provision that the isotopic composition of a “normal” material should not have been modified significantly in a geologically brief period, John Böhlke (2015, personal communication) has pointed out that “high and low atomic weight values of light elements commonly are due to isotopic fractionation processes that are happening every day,” as arise in respiration, evaporation, and dissolution.

The CIAAW explained that expressing the standard atomic weights as intervals serves to emphasize that the atomic weights are not constants of nature [3–5]. This choice was reaffirmed when the CIAAW published the 2011 version of the atomic weights, and added bromine and magnesium to the list of elements whose standard atomic weights are expressed as intervals [6]. The same approach has been used in the 2013 version of the standard atomic weights [7]. The 2009 recommendation to use interval notation did achieve the valuable educational goal of drawing attention to the fact that isotopic composition can vary among natural materials, hence so do the atomic weights [8].

The expression “constant of nature” is used informally, generally referring to values of properties of natural entities or processes that are believed to remain invariant in time and space. Examples include $m_a(^{11}\mathrm{B})$, the atomic mass of $^{11}\mathrm{B}$, and the Newtonian gravitational constant G. According to Audi *et al.* [9], $m_a(^{11}\mathrm{B}) = 11.009\,305\,4$ Da, where $1\ \mathrm{Da} = m_a(^{12}\mathrm{C})/12 = 1.660\,539\,040 \times 10^{-27}$ kg is the unified atomic mass unit [10]. The relative atomic mass of this isotope, $A_r(^{11}\mathrm{B}) = m_a(^{11}\mathrm{B})/(m_a(^{12}\mathrm{C})/12) = 11.009\,305\,4$, and the relative atomic masses of all the other isotopes, are believed to be constants of nature.

The atomic weight of element E in material P is a weighted average of the relative atomic masses of the element’s isotopes present in material P, where the weights (of this weighted average) are the amount fractions of the isotopes of element E in material P [5]. Therefore, the atomic weight of element E is a collective property of the set of isotopes of E in material P that depends on the isotopic composition of material P, hence typically will have a different value in different materials.

1.1 Expressions of uncertainty for atomic weights

Because the atomic weight of an element in a material depends on the isotopic composition of the material, in the absence of specific knowledge about this isotopic composition the uncertainty surrounding an atomic weight usually is much larger than the uncertainty surrounding an isotopic mass. For example, the standard uncertainty (1σ) associated with the isotopic mass of $^{11}\mathrm{B}$ is $u(m_a(^{11}\mathrm{B})) = 0.000\,000\,4$ Da [11, table I], hence the isotopic mass of $^{11}\mathrm{B}$ is known to better than 0.04 parts per million. However, boron has standard atomic weight [10.806, 10.821], indicating that the atomic weight of boron in a generic “normal” material is known to no better than 0.7 parts per thousand.

The 2009 Technical Report prepared by the CIAAW did not offer guidance on the practical use of the new interval notation [5]. The present Technical Report illustrates how the standard atomic weights may be interpreted probabilistically, how such interpretation may be used in uncertainty evaluation, and how the uncertainty associated with the atomic weights may be propagated to relative molecular masses and to other quantities that depend on the atomic weights.

IUPAC’s 1951 report on the Standard Atomic Weights for the first time included a reference to uncertainty, recommending the standard atomic weight of sulfur as 32.066 ± 0.003 [12]. The CIAAW explained in 1951 that the “±0.003” represents the range of the atomic-weight values of sulfur due to natural variations in the abundance of its isotopes [12]. Coplen and Peiser [13, 14] discuss the use of uncertainties in this context, and their interpretation. By 1969, standard atomic weights were qualified with uncertainties [15].

Until the introduction of the standard atomic weights for selected elements as intervals in 2009, the uncertainties used to qualify the standard atomic weights had been expanded uncertainties as defined in the

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Guide to the expression of uncertainty in measurement (GUM) [16], and they were understood as follows: "any user of the atomic-weight data would, with high probability, find the atomic weight of any element in any normal sample to be in the range indicated by the uncertainty for the recommended standard atomic weight" [6, Page 1048].

For all the other elements, Meija *et al.* [7, table 1] give the standard atomic weight as a single value qualified with a *decisional uncertainty* that is conventionally denoted using a parenthetic notation. For example, the standard atomic weight of molybdenum is 95.95(1) [7], which means that $A_r(\text{Mo}) = 95.95$ and that the associated decisional expanded uncertainty is $U[A_r(\text{Mo})] = 0.01$. In general, the interval from $A_r(\text{E}) - U[A_r(\text{E})]$ to $A_r(\text{E}) + U[A_r(\text{E})]$ is believed to encompass the atomic weight values of element E in essentially all "normal" materials.

Molybdenum is one of several elements that have two or more stable isotopes whose relative abundances are known to vary among "normal" materials, but whose variability does not exceed the evaluated measurement uncertainty of the atomic weight derived from the best measurement of the isotopic abundances of the element. For elements in this category (and indeed for all elements in categories 2–5 as defined in Section 1.4 of Wieser *et al.* [6]), the decisional uncertainty $U[A_r(\text{E})]$ is given in parentheses following the last significant figure to which it is attributed.

It should be noted that the interval notation expresses the same sources of uncertainty, and has the same general meaning as the conventional, parenthetic notation. However, the interval indicates that the variablity of the atomic weight in "normal" materials is the dominant source of uncertainty, whereas the parenthetic notation indicates that other sources of uncertainty dominate. The interval notation also avoids suggesting a particular value as possibly being the "best estimate" of the atomic weight. The CIAAW determines whether a particular element belongs in one category or the other based on published information and on the CIAAW's best judgment, similarly to how the CIAAW determines whether each atomic weight should be qualified by a particular footnote ("g", "m", or "r"). Therefore, the result of such determination may change over time, from one release of the atomic weights to the next.

The standard atomic weight values for elements like molybdenum are obtained by averaging experimental results obtained from many samples, hence the variations in isotopic compositions are incorporated automatically, yet measurement uncertainty currently still is at least as large as these natural variations. And molybdenum, in particular, currently has its atomic weight qualified with a footnote "g", indicating that "geological materials are known in which the element has an isotopic composition outside the limits for normal material", and that "the difference between the atomic weight of the element in such materials and that given in the table may exceed the stated uncertainty" [7, table 1].

It should be noted that the aforementioned decisional expanded uncertainty differs essentially from the "expanded uncertainty" defined in the GUM, where an uppercase U is also used to denote the latter. According to the GUM (2.3.6), the expanded uncertainty is a multiple of the combined standard uncertainty, the multiplier (*coverage factor*) being chosen so that the interval centered at the estimate of the measurand, and of half-width equal to U, is believed to include the true value of the measurand with a specified probability.

From 2009 onward, the standard atomic weights of selected elements have been specified in such a way that the corresponding intervals are intended to encompass measured atomic weight values in all "normal" materials, both when the intervals are given explicitly (for example, [10.806, 10.821] for boron, which does not identify any particular value within this interval as "best" in any sense), or implicitly as a single value qualified by the associated uncertainty (for example, 40.078(4) for calcium, which is equivalent to [40.074, 40.082] except that it gives 40.078 as the "best" estimate).

The CIAAW derives these intervals by pooling the expert knowledge of its members taking into account the published information about isotopic abundances, in what effectively is an informal elicitation exercise [17].

In this conformity, when probability distributions are employed to describe states of knowledge about the values of the atomic weights, it is acceptable to assume that the distributions are essentially concentrated either in the standard atomic weight intervals, or in the intervals that are specified implicitly using the parenthetic notation. "Essentially concentrated" means that the probability is either zero or very close to zero that any "normal" material will have atomic weight outside of the standard atomic weight interval [6].

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A concise (parenthetic) notation for uncertainties has a long history, but it has been interpreted differently in different contexts. For example, CODATA [10] has adopted the concise form $1.660\,539\,040(20)\times10^{-27}$ kg to express the value of the (unified) atomic mass constant m_u and its associated uncertainty. In this case, the digits between parenthesis specify the standard measurement uncertainty (sometimes described informally as a "1σ" uncertainty), $u(m_u)=0.000\,000\,020\times10^{-27}$ kg, *not* an expanded uncertainty. The probabilistic interpretation of 1σ uncertainty is commonly made by reference to a Gaussian distribution, hence, and in this case, suggesting that the true value of m_u lies within $u(m_u)$ of the estimate of m_u published by CODATA with approximately 68 % probability.

The uncertainties reported by the CIAAW, using this parenthetic notation or any other, for the atomic weights and isotopic abundances, are expanded uncertainties corresponding to several different values of the coverage factor or of the coverage probability. Since some uncertainty statements, for example resulting from Monte Carlo uncertainty evaluations, do not involve application of coverage factors, a comparably effective, and indeed preferable alternative characterization consists of specifying the coverage probability. However, neither the assignment of values to the standard atomic weights, nor the evaluations of their associated uncertainties, are within the scope of this contribution: Meija and Possolo [18] describe a rigorous framework for the corresponding calculations.

In all cases, the important requirement to satisfy is that the probability assigned to particular intervals – be they standard atomic weights that are expressed as intervals, or coverage intervals generally – should be stated explicitly whenever intervals are reported that have a probabilistic interpretation, to remove all ambiguity and to ensure comparability of results. When, for example, the intention is to state that the probability is zero for values outside of an interval of finite length, then a probability distribution with correspondingly bounded support will have to be used, for example rectangular, triangular, rescaled and shifted beta (reviewed in §5.3, following the description of Algorithm S), etc.

If a distribution with unbounded support is used, for example a Gaussian (or, normal) distribution, then its standard deviation will have to be tuned so that the distribution assigns the intended probability to the interval in question, and this probability should be stated explicitly.

The expression of standard atomic weights using interval notation has emphasized the variability of the atomic weights in nature, while also capturing the measurement uncertainty associated with delta values (reviewed in §4) and with the relative atomic masses of the isotopes [6, Page 1053]. Such intervals were conceived as notational and educational devices, not as computational tools. However, this was achieved at the expense of deemphasizing the actual form of the underlying dispersion of values and how to use it in practical calculations.

To characterize the uncertainty associated with a standard atomic weight expressed as an interval, it is necessary to specify a probability distribution on the interval: this distribution may be uniform (or, rectangular), or it may be some other distribution. The incomplete knowledge that this distribution reflects may be dominated by measurement uncertainty, as it is for tellurium, or its principal source may be ignorance about the origin of the material, as it is for lithium. The same applies to the full characterization of the uncertainty associated with an atomic weight expressed using the parenthetic notation.

1.2 Notational conventions

We have adopted the following notational conventions, which are generally consistent with the guidance provided in the IUPAC *Green Book*. We note that different notation has been used in recent IUPAC Technical Reports, and that the current IUPAC Recommendation on definitions of terms relating to mass spectrometry [19] does not address several of the topics mentioned here.

- $A_{r,P}(\mathrm{E})$ denotes the atomic weight (relative atomic mass) of element E in material P. For example, $A_{r,\mathrm{SEAWATER}}(\mathrm{B})$ denotes the atomic weight of boron in seawater.
- $A_r(\mathrm{E})$ denotes the atomic weight of an element or isotope E disregarding the provenance of the element, hence effectively averaged over all "normal materials". For example, $A_r(\mathrm{H})=[1.007\,84,\ 1.008\,11]$, and

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$A_r(\text{Mo}) = 95.95(1)$ [7]. When E designates an isotope, $A_r(\text{E})$ is invariant across all materials. For example, $A_r(^{16}\text{O}) = 15.994\,914\,619\,566(179)$ [11, table A].
- $M_{r,P}(\text{S})$ denotes the relative molecular mass of substance S as it occurs in material P. For example, in §6.4 we compute $M_{r,\text{HUMAN}}(\text{TESTOSTERONE}) = 288.4289$, but also refer to it as the value of a random variable M_H whose probability distribution we use as a model for the associated uncertainty. The subscript P generally may be any string that denotes the relevant material: for example, in §4.3 we use "C" in this role because several quantities that we consider there pertain to a sample of colemanite.
- $M_r(\text{S})$ denotes the relative molecular mass of substance S disregarding the provenance of the material containing the substance. For example, in §6.1 we compute $M_r(\text{CO}_2) = 44.009\,40$.
- $x_P(\text{S})$ denotes the amount fraction of substance S in material P, where S may be a molecule, element or isotope. For example, $x_{\text{SRM951}}(^{10}\text{B})$ denotes the amount fraction of the isotope ^{10}B in NIST Standard Reference Material (SRM) 951.
- $w_P(\text{S})$ denotes the mass fraction of substance S in material P, where S may be a molecule, element or isotope. For example, in §2 we conclude that $w_{\text{H}_2\text{O}}(\text{O}) = \left[0.888\,083,\ 0.888\,114\right]$.
- $N_P(\text{S})$ denotes the number of entities S in material P. For example, $N_{\text{AVO28-S5}}(^{28}\text{Si})$ denotes the number of ^{28}Si atoms in silicon sphere AVO28-S5 [20].
- $R_P(^i\text{E}/^j\text{E})$ denotes the isotope-number ratio (also called *isotope ratio*) for isotopes ^iE and ^jE in material P: that is, $N_P(^i\text{E})/N_P(^j\text{E})$. Isotope ratios are discussed and used in §4. For example, the isotope ratio $R_{\text{VSMOW}}(^{18}\text{O}/^{16}\text{O})$ in the Vienna Standard Mean Ocean Water (VSMOW) is used in Listing 2.
- The delta value $\delta_{\text{STD},P}(^i\text{E}/^j\text{E})$ (where by convention ^iE is the heavier isotope and ^jE is the lighter one) denotes the relative difference of isotope ratios for a particular pair of isotopes of element E in material P and in a standard or reference STD (§4): $R_P(^i\text{E}/^j\text{E})/R_{\text{STD}}(^i\text{E}/^j\text{E}) - 1$.

Note that, in the notation that we adopt, the first (or only) subscript affecting the Greek letter δ designates the standard or reference. For example, $\delta_{\text{SRM951,SEAWATER}}(^{11}\text{B}/^{10}\text{B}) = +39.5$ ‰ [21, Page 15]: this means that the isotope ratio $R_{\text{SEAWATER}}(^{11}\text{B}/^{10}\text{B})$ is 1.0395 times larger than its counterpart for NIST SRM 951.

When an element has only two stable isotopes, occasionally we abbreviate the delta notation and mention only the heavier isotope. For example, in §3, where we state that $\delta_{\text{LSVEC}}(^7\text{Li})$ ranges from –10 ‰ to +56 ‰ among marine sources [21, table 5].

1.3 Overview

In Section 2 we review difficulties that the adoption of the interval notation has created for many users of the atomic weights, and discuss the limitations of an approach using interval arithmetic, which we therefore discourage. We believe that a probabilistic approach to the interpretation and use of the interval notation will be more useful than interval arithmetic, and that it will also be better aligned with the motivation for adopting the interval notation. Also, a probabilistic interpretation is consistent with the characterization of uncertainty promoted by the GUM.

In Section 3 we review the concept of uncertainty when it is applied to standard atomic weights, and its expression and interpretation. This serves as preparation for the illustrations provided in Section 5 of how the knowledge about the dispersion of isotopic compositions may be modeled probabilistically, followed by a discussion of how such models may be used to evaluate the uncertainty of relative molecular masses and of other quantities that depend on the values of the atomic weights.

In Section 4 we review the delta scales and notation commonly used to express relative differences in isotopic abundances, and show how, based on these scales, values and associated uncertainties can be obtained for atomic weights.

We provide an example of the evaluation of measurement uncertainty for the relative molecular mass of borax (Section 6), which shows that the choices the CIAAW has made regarding the standard atomic weights can co-exist with uncertainty characterizations, and that such co-existence: (i) on the one hand, satisfies the

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desideratum of the CIAAW to increase awareness about the natural variability of atomic weights; and (ii) on the other hand, also satisfies the practical requirements of those users that need to treat measurement results involving the atomic weights consistently with the provisions of the GUM.

2 Interval arithmetic

The interval notation is challenging for many users of the atomic weights because virtually all computations in science and technology involve single numbers, and neither intervals nor any other sets of numbers.

The question naturally arises of whether calculations involving the standard atomic weights (expressed as intervals) should be performed according to the rules of interval arithmetic, whose results also are intervals. Interval arithmetic has been used to bound rounding errors in mathematical computation, for uncertainty analysis, and for optimization [22]. For example, short of employing interval arithmetic, it is not obvious how to calculate the standard relative molecular mass of H_2O or how to obtain the ratio of the standard atomic weights of oxygen and hydrogen using the recommended interval values.

The following are commonly used rules of arithmetic involving two intervals, $[a_1, b_1]$ and $[a_2, b_2]$ (for example, representing the standard atomic weights of hydrogen and oxygen), where a_1, a_2, b_1, and b_2 denote real numbers such that $a_1 \leq b_1$ and $a_2 \leq b_2$, and the interval $[a_2, b_2]$ is assumed not to include 0 because standard atomic weight intervals never include 0, and we do not propose to use interval arithmetic for delta values (§4) [22]:

- **Addition:** $[a_1, b_1] + [a_2, b_2] = [a_1 + a_2, b_1 + b_2]$;
- **Subtraction:** $[a_1, b_1] - [a_2, b_2] = [a_1 - b_2, b_1 - a_2]$;
- **Multiplication:** $[a_1, b_1] \cdot [a_2, b_2] = [\min(a_1a_2, a_1b_2, b_1a_2, b_1b_2), \max(a_1a_2, a_1b_2, b_1a_2, b_1b_2)]$;
- **Division:** Since we assume that the interval $[a_2, b_2]$ does not include 0, it suffices to define $[a_1, b_1]/[a_2, b_2] = [\min(a_1/a_2, a_1/b_2, b_1/a_2, b_1/b_2), \max(a_1/a_2, a_1/b_2, b_1/a_2, b_1/b_2)]$.

Since the standard atomic weights of hydrogen and oxygen are [1.007 84, 1.008 11] and [15.999 03, 15.999 77] [7] (Table 1), the foregoing rules produce

$$\begin{aligned} M_r(H_2O) &= 2 \times [1.007\,84, 1.008\,11] + [15.999\,03, 15.999\,77] \\ &= [18.014\,71, 18.015\,99] \end{aligned}$$

for the standard relative molecular mass of H_2O. Likewise, the ratio of the standard atomic weights of oxygen and hydrogen will be

$$\begin{aligned} A_r(O) / A_r(H) &= [15.999\,03, 15.999\,77] \div [1.007\,84, 1.008\,11] \\ &= [15.870\,32, 15.875\,31] \end{aligned}$$

Now consider the problem of computing the mass fraction of oxygen in water,

$$w_{H_2O}(O) = \frac{A_r(O)}{M_r(H_2O)} = \frac{[15.999\,03,\ 15.999\,77]}{[18.014\,71,\ 18.015\,99]}. \tag{1}$$

Letting $a_1 = 15.999\,03$, $b_1 = 15.999\,77$, $a_2 = 18.014\,71$, and $b_2 = 18.015\,99$, then

$$\begin{aligned} w_{H_2O}(O) &= [\min(a_1/a_2, a_1/b_2, b_1/a_2, b_1/b_2), \max(a_1/a_2, a_1/b_2, b_1/a_2, b_1/b_2)] \\ &= [0.888\,046, 0.888\,150]. \end{aligned}$$

As it turns out, this interval is three times wider than it should be.

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On the other hand, since $w_{\mathrm{H_2O}}(\mathrm{O})$ may be rewritten as

$$w_{\mathrm{H_2O}}(\mathrm{O}) = \frac{1}{2A_\mathrm{r}(\mathrm{H})/A_\mathrm{r}(\mathrm{O})+1} \tag{2}$$

the same rules above now yield $w_{\mathrm{H_2O}}(\mathrm{O}) = [0.888\,083,\ 0.888\,114]$, which is the correct answer. Although not unique to interval arithmetic, this is an instance of the so-called *dependency problem*, which is widely recognized as posing a major obstacle to the application of interval arithmetic [25, 26].

Owing to the obvious practical difficulties associated with the use of interval arithmetic, and considering the desirability of quantifying and propagating uncertainties in calculations involving atomic weights, we recommend instead a probabilistic approach to the interpretation of the intervals, which we believe to be fully consistent with the motivation that led the CIAAW to adopt such notation. The rest of this report explains the basis and general procedures of such approach, and illustrates their application in concrete and substantial examples.

3 Uncertainty

Best practices in the reporting of measurement results, as explained in the "Guide to the expression of uncertainty in measurement" (GUM) [16], demand that measured values be qualified by statements of uncertainty: since these involve some underlying probabilistic interpretation, it is only natural that a conceptual apparatus be employed that facilitates such qualification consistently with the concept of atomic weights as intervals.

The evaluation of uncertainty associated with the atomic weights, and its propagation to derived quantities, including relative molecular masses, is necessary to characterize the uncertainty surrounding conversions between amount-of-substance and mass in analytical chemistry, and not only in scientific research but also in the fair trade of commodities like natural gas, and also for the proper characterization of compositions of mixtures, expressed as amount fractions, that are used as reference materials [27].

For example, suppose that one wishes to determine the amount of silicon in a pure sample of mass 75.000 kg. Using the conventional value of the atomic weight of silicon, 28.085 [7, table 3], and considering that the molar mass constant is $M_\mathrm{u} = 1\ \mathrm{g\ mol^{-1}}$, one obtains $75\,000\ \mathrm{g}/(28.085\ \mathrm{g\ mol^{-1}}) = 2\,670.5\ \mathrm{mol}$. If, in addition, and as we shall elaborate in §5, one were to model the uncertainty associated with $A_\mathrm{r}(\mathrm{Si})$ using a uniform (or, rectangular) distribution concentrated on the standard atomic weight of Si, which is the interval [28.084, 28.086], and assumed that the standard uncertainty associated with the mass is 2 g, then one would conclude that the standard uncertainty associated with the amount-of-substance is 0.1 mol. In this scenario, the atomic weight and the mass have relative standard uncertainties that are numerically quite close.

Our knowledge about the atomic-weights of the elements is limited by several different factors. One of these factors concerns the variability of values of the atomic weights across natural materials. Since it is impossible to sample adequately all potential sources of the elements for human use, there is an inherent ambiguity when providing standard atomic weight values for "representative materials".

Other factors constrain the ability to measure the value of the atomic weight in a particular material. Uncertainties of standard atomic weights are largely determined by one of these types of limitations. For example: for carbon, hydrogen, and oxygen, variations in natural isotope abundances greatly exceed the uncertainties of state-of-the-art measurements of the masses of their isotopes; for indium, germanium, and tellurium, however, it is the measurement capability that dominates the resulting uncertainty of the standard atomic weights.

Measurement uncertainty characterizes a state of knowledge about the value of a quantity [28, 29]. This state of knowledge may pertain to a particular person or to a group of persons, typically a scientific community. For example, Meija *et al.* [7] (Table 1) list $A_\mathrm{r}(\mathrm{Ge}) = 72.630(8)$. This conveys the belief (indeed the practically full certainty) of the CIAAW that the atomic weight of germanium in every sample of a "normal" material lies between 72.622 and 72.638. In §6.1, modeling the atomic weights of carbon and oxygen as independent random variables with uniform (or, rectangular) probability distributions over their standard atomic weight intervals, we conclude that the relative molecular mass of CO_2 lies between 44.008 04 and 44.010 76 with 95 % probability.

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Knowledge about the source of a material containing a particular element typically is informative about the atomic weight of the element in the material. Lithium provides a striking instance of this fact. Marine sources (seawater, hydrothermal fluids, foraminifera shells, carbonate sediments, brines, and pore water) have values of $\delta_{\text{LSVEC}}(^{7}\text{Li})$ between –10 ‰ and +56 ‰ [21, table 5] (the "delta" notation is described in §4). However, enrichment in ^{7}Li as high as +354 ‰ has been measured in ground water underlying West Valley Creek in Pennsylvania (USA), likely in consequence of the release of left-over lithium-7 into the environment from a nearby facility that produced ^{6}Li-enriched lithium for use in the nuclear industry [21, Page 13].

The fact that states-of-knowledge typically will vary between people and between communities, does not in any way detract from the value they add to the estimates of the corresponding quantities. On the contrary, their specificity and diversity is precisely what makes them useful in facilitating the fair comparison of different estimates of the same value of a quantity.

For example, NIST SRM 951a, a boric acid isotopic standard, is intended for use as an isotopic reference material for the calibration of mass spectrometers [30] (SRM 951a replaces SRM 951, which was exhausted, but the number fractions of the two stable isotopes of boron are the same in both materials). The corresponding certificate asserts that 19.827 % of the atoms of boron in the material are ^{10}B, with expanded uncertainty 0.013 %, meaning that, with 95 % probability, the proportion of ^{10}B atoms in the material is between 19.814 % and 19.840 %. (By default, NIST uses coverage factor $k = 2$ to compute expanded uncertainties corresponding to 95 % coverage.)

When a user of this reference material measures the isotopic composition of this boric acid in her laboratory, and finds that the proportion of ^{10}B atoms is 19.780 %, she cannot meaningfully compare this value with the certified value unless her determination is qualified with an evaluation of the measurement uncertainty associated with it.

In particular, it will be premature to conclude that her determination differs "significantly" from NIST's because the difference between the result of her determination and the certified value needs to be gauged taking into account not only the uncertainty associated with NIST's measured value, but also the uncertainty associated with her own determination [31]. More often than not these two uncertainties will be quite different, and reflect the different margins of doubt that NIST, and the user, have about the same measurand in the same material.

Suppose, for example, that the user's standard measurement uncertainty is 0.025 %. In these circumstances, the standardized difference between the measured value and the certified value is $(19.780-19.827)/\sqrt{(0.013/2)^2+0.025^2} = -1.8,$ which generally would not be interpreted as indicating a significant difference. A formal Student's *t* test cannot be applied here because there is no information about the numbers of degrees of freedom that the uncertainty evaluations are based on. However, even if the number of degrees of freedom were very large, and the relevant distribution were Gaussian, the standardized difference of –1.8 would fail to indicate a statistically significant difference in a test with significance level of 5 %: the *p*-value (the probability of a difference whose absolute value is this large or larger, on the assumption of no real difference, owing to the vagaries of sampling alone) would be 7.2 %.

The position that uncertainties should be interpreted probabilistically, and that probability distributions are effective devices to characterize and convey states of incomplete knowledge about measurands, is widely held. This viewpoint pervades not only the GUM and its supplements GUM-S1 and GUM-S2 [32], but also the guidance offered by Morgan and Henrion [33] and by Mastrandrea *et al.* [34], who address needs in very different fields.

4 Delta scale

4.1 Definition and realization

The isotope delta value (δ) is used to express the relative difference between the amount ratios of two isotopes of the same element in a material and in a standard. Generally adopting the terminology for stable

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isotope-ratio results suggested by Coplen [35] but not adopted by IUPAC, we define the isotope-number ratio (also called *isotope ratio*), $R_{\mathrm{P}}({}^{i}\mathrm{E}/{}^{j}\mathrm{E})$, for isotopes ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$ in material P (where by convention ${}^{i}\mathrm{E}$ is the heavier isotope and ${}^{j}\mathrm{E}$ is the lighter isotope), as

$$R_{\mathrm{P}}({}^{i}\mathrm{E}/{}^{j}\mathrm{E}) = \frac{N_{\mathrm{P}}({}^{i}\mathrm{E})}{N_{\mathrm{P}}({}^{j}\mathrm{E})}, \tag{3}$$

where $N_{\mathrm{P}}({}^{i}\mathrm{E})$ denotes the number of isotopes of mass number i of element E in material P. These isotope-number ratios are usually measured by mass spectrometry, as the ratio of ion currents or detector counts, and preferably calibrated using a mixture of isotopes prepared gravimetrically [36]. However, laser spectrometry is an increasingly important technique for the measurement of isotopic ratios for the lighter elements [37].

A relative difference of isotope ratios, also called *isotope delta*, or simply *delta value*, is usually defined relative to an international measurement standard (STD) as

$$\delta_{\mathrm{STD,P}}({}^{i}\mathrm{E}/{}^{j}\mathrm{E}) = \frac{R_{\mathrm{P}}({}^{i}\mathrm{E}/{}^{j}\mathrm{E})}{R_{\mathrm{STD}}({}^{i}\mathrm{E}/{}^{j}\mathrm{E})} - 1. \tag{4}$$

Isotope delta values are commonly quoted as per mill (parts per thousand, denoted ‰, meaning 1 ‰ = 0.001), the convention that we shall adopt. Positive values indicate an enrichment of the heavier isotope relative to its abundance in the standard, and negative values indicate a depletion. To improve the realization of isotope delta measurements of light elements, the CIAAW recommends two-point calibration [23]. Gonfiantini [38] explains how the two standards are used to realize such scales, and the advantages that accrue from such approach.

4.2 Delta values and atomic weights

The isotope ratio of an element in a given sample, and therefore the corresponding delta value, expresses the abundance of a heavier isotope relative to a lighter one, whence the number fractions of the isotopes, and the atomic weight of the sample may be calculated: for example, $R_{\mathrm{NBS19}}({}^{13}\mathrm{C}/{}^{12}\mathrm{C}) = 0.011\,202 \pm 0.000\,028$. Amount fraction is calculated from delta values by using isotope-abundance measurements of the reference for the delta scale, as will be illustrated below. The isotope ratio of the reference is "determined by isotope-ratio calibration using an international measurement standard, certified isotopic reference materials, or gravimetric mixtures of highly enriched (or depleted) isotopes" [35]. Coplen [35] provides a more formal and comprehensive review of all the relevant terminology, definitions, and computations.

In evaluating isotope ratios, the CIAAW includes system linearity, baseline correction, isobaric interferences, instrumental fractionation, and sample preparation in its determination of a so-called K-factor (defined as the true isotope ratio divided by the measured isotope ratio). When uncertainties are obtained for isotope ratios of sample and standard then the measurement uncertainty is propagated to isotope delta through Equation (4). The approach of taking "ratios of ratios" obtained in one instrument at one time causes many uncertainty factors to cancel, leaving mostly small, unpredictable components.

Uncertainties in measuring delta values and therefore in calculating atomic weights are much smaller than the variation in the isotopic abundances in nature of the elements for which the interval approach has been used. For example, Coplen *et al.* [23, Page 5] report that in meteoric waters (waters that originate as precipitation), $\delta_{\mathrm{VSMOW}}({}^{2}\mathrm{H}/{}^{1}\mathrm{H})$ values range from −495 ‰ in Antarctic ice to +375 ‰ in water from a well in the Lacq natural gas field in France, whereas the measurement uncertainty in $\delta_{\mathrm{VSMOW}}({}^{2}\mathrm{H}/{}^{1}\mathrm{H})$ is less than 1 %. The uncertainties in delta values are taken into account when deciding the upper and lower bounds of standard atomic weights expressed as intervals [7, Page 271].

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4.2.1 Example: atomic weight of boron in seawater

Consider boron, whose stable isotopes are ^{10}B and ^{11}B, with atomic weights $A_r(^{10}\mathrm{B}) = 10.012\,936\,9$ and $A_r(^{11}\mathrm{B}) = 11.009\,305\,4$ [11, table I]. By convention, the reference material for boron isotopes is NIST SRM 951, boric acid, whose amount fractions of ^{10}B and ^{11}B are $x_{\mathrm{SRM951}}(^{10}\mathrm{B}) = 0.198\,27$ and $x_{\mathrm{SRM951}}(^{11}\mathrm{B}) = 0.801\,73$ [30].

Seawater has a fairly constant boron isotope delta value $\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B}) = +39.5\,‰$ [21, Page 15]. From this information, the atomic weight of boron in seawater can be obtained as follows:

(a) Given the definition of $\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B})$, Equation (4), the boron isotope ratio in seawater is

$$\begin{aligned}R_{\mathrm{SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B}) &= (1+\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B}))R_{\mathrm{SRM951}}(^{11}\mathrm{B}/^{10}\mathrm{B})\\ &= (1+\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B}))\frac{x_{\mathrm{SRM951}}(^{11}\mathrm{B})}{x_{\mathrm{SRM951}}(^{10}\mathrm{B})}\\ &= (1+39.5\times 10^{-3})\frac{0.801\,73}{0.198\,27} = 4.2034\end{aligned}$$

Therefore, there are 4.2034 times more ^{11}B atoms in seawater than there are ^{10}B atoms.

(b) The proportion (isotopic abundance) of ^{11}B atoms in sea water is

$$x_{\mathrm{SEAWATER}}(^{11}\mathrm{B}) = \frac{R_{\mathrm{SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B})}{1+R_{\mathrm{SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B})} = \frac{4.2034}{1+4.2034} = 0.807\,82$$

The corresponding proportion (isotopic abundance) of ^{10}B atoms is $x_{\mathrm{SEAWATER}}(^{10}\mathrm{B}) = 1 - x_{\mathrm{SEAWATER}}(^{11}\mathrm{B}) = 1 - 0.807\,82 = 0.192\,18$.

(c) The atomic weight of boron in seawater is

$$\begin{aligned}A_{\mathrm{r,SEAWATER}}(\mathrm{B}) &= x_{\mathrm{SEAWATER}}(^{10}\mathrm{B})A_r(^{10}\mathrm{B}) + x_{\mathrm{SEAWATER}}(^{11}\mathrm{B})A_r(^{10}\mathrm{B})\\ &= 0.192\,18\times 10.012\,936\,9 + 0.807\,82\times 11.009\,305\,4\\ &= 10.817\,82.\end{aligned}$$

4.2.2 Example: atomic weight of oxygen in seawater

The atomic weights of the stable isotopes of oxygen are $A_r(^{16}\mathrm{O}) = 15.994\,914\,619\,566$, $A_r(^{17}\mathrm{O}) = 16.999\,131\,756\,500$, and $A_r(^{18}\mathrm{O}) = 17.999\,159\,612\,858$ [11, table A]. One of the the delta zero reference materials for oxygen is VSMOW, whose amount fractions of ^{16}O, ^{17}O, and ^{18}O are 0.997 620 6, 0.000 379 0, and 0.002 000 4, respectively [39].

For oxygen, matters are slightly more complicated than they were for boron in the previous subsection, because even though it has three stable isotopes, usually only one delta value is given. For example, oxygen in seawater has $\delta_{\mathrm{VSMOW,SEAWATER}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ between –1 ‰ and +0.6 ‰ [24, table 6]. For this example, we will use the midpoint of this interval, −0.2 ‰, as representative value. The other relevant delta value, $\delta_{\mathrm{VSMOW,SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O})$, usually is estimated using the approximate relation

$$\delta_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O}) \approx (1+\delta_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O}))^{\lambda} - 1, \tag{5}$$

derived by Meijer and Li [40], which expresses the equilibrium mass-dependent fractionation of ^{17}O. Based on a compilation of isotopic compositions of a large and varied collection of water samples, Meijer and Li [40] produced the estimate $\lambda = 0.5281$ with associated standard uncertainty $u(\lambda) = 0.0015$. More recently, Barkan and Luz [41] produced the estimate $\lambda = 0.5279$ with standard uncertainty 0.0001, using a different measurement method.

Although numerically distinct, these estimates are not significantly different from one another once their associated uncertainties are taken into account. Furthermore, Meijer and Li [40]'s is based on a much larger

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and diverse collection of waters than Barkan and Luz [41]'s, which lends their measurement result (measured value and associated uncertainty) a broader basis of evidential support.

Maybe for this reason, and possibly also because Barkan and Luz [41] used an intrinsically more precise measurement method, the uncertainty associated with the value measured by Meijer and Li [40] is 15 times larger than the uncertainty evaluated by Barkan and Luz [41], hence may be regarded as a more conservative, possibly safer and more generally applicable assessment.

Interestingly, the measurement result obtained by Meijer and Li [40] is also consistent (in the sense that the respective estimates of λ are not statistically significantly different) with the relationship between values of $\delta_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$ and $\delta_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ in materials radically different from those that Meijer and Li [40] used for their determinations: for example, in some of earth's oldest rocks, from the Isua region in Greenland [42]. However, and in general, igneous and metamorphic rocks need not lie on the same oxygen fractionation lines as meteoric waters or seawater [43, 44].

For these reasons, we shall use the value for λ measured by Meijer and Li [40], and its associated uncertainty, as we continue the example calculation of the atomic weight of oxygen in seawater. However, the estimates obtained by Barkan and Luz [41] and Luz and Barkan [45] would also be reasonable choices. In this conformity, Equation (5) yields the estimate

$$\delta_{\mathrm{VSMOW,SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O}) = (1-0.2\times10^{-3})^{0.5281} - 1 = -0.105625\,‰, \tag{6}$$

whence the atomic weight of oxygen in seawater can be computed by taking the following steps:

(a) The isotope ratios of oxygen in seawater are

$$\begin{aligned} R_{\mathrm{SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O}) &= (1+\delta_{\mathrm{VSMOW,SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O}))R_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O}) \\ &= (1+\delta_{\mathrm{VSMOW,SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O}))\frac{x_{\mathrm{VSMOW}}(^{17}\mathrm{O})}{x_{\mathrm{VSMOW}}(^{16}\mathrm{O})} \\ &= (1-0.105625\times10^{-3})\frac{0.000\,379\,0}{0.997\,620\,6} = 0.000\,379\,864 \\ R_{\mathrm{SEAWATER}}(^{18}\mathrm{O}/^{16}\mathrm{O}) &= (1-0.105625\times10^{-3})\frac{0.002\,000\,4}{0.997\,620\,6} = 0.002\,004\,77 \end{aligned}$$

(b) The corresponding amount fractions of the oxygen isotopes are

$$\begin{aligned} x_{\mathrm{SEAWATER}}(^{17}\mathrm{O}) &= \frac{R_{\mathrm{SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O})}{1+R_{\mathrm{SEAWATER}}(^{17}\mathrm{O}/^{16}\mathrm{O})} = 0.000\,379\,72 \\ x_{\mathrm{SEAWATER}}(^{18}\mathrm{O}) &= \frac{R_{\mathrm{SEAWATER}}(^{18}\mathrm{O}/^{16}\mathrm{O})}{1+R_{\mathrm{SEAWATER}}(^{18}\mathrm{O}/^{16}\mathrm{O})} = 0.002\,000\,76 \\ x_{\mathrm{SEAWATER}}(^{16}\mathrm{O}) &= 1 - x_{\mathrm{SEAWATER}}(^{17}\mathrm{O}) - x_{\mathrm{SEAWATER}}(^{18}\mathrm{O}) = 0.997\,62 \end{aligned}$$

(c) The atomic weight of oxygen in seawater is

$$\begin{aligned} A_{\mathrm{r,SEAWATER}}(\mathrm{O}) = {} & x_{\mathrm{SEAWATER}}(^{16}\mathrm{O})A_{\mathrm{r}}(^{16}\mathrm{O}) + x_{\mathrm{SEAWATER}}(^{17}\mathrm{O})A_{\mathrm{r}}(^{17}\mathrm{O}) \\ & + x_{\mathrm{SEAWATER}}(^{18}\mathrm{O})A_{\mathrm{r}}(^{18}\mathrm{O}) = 15.999\,31. \end{aligned}$$

4.3 Uncertainty evaluations involving delta scales

Suppose that the same, aforementioned user of NIST SRM 951a uses her mass spectrometer to measure the delta value $\delta_{\mathrm{SRM951,c}}(^{11}\mathrm{B}/^{10}\mathrm{B}) = +23\,‰$ in a sample C of colemanite, a borate that may occur in marine evaporitic sequences. The calculation of the atomic weight of boron in such sample is similar to the calculation done above, in §4.2.1, for seawater, and it yields $x_{\mathrm{c}}(^{10}\mathrm{B}) = 0.194\,68$, $x_{\mathrm{c}}(^{11}\mathrm{B}) = 0.805\,32$, and $A_{\mathrm{r,c}}(\mathrm{B}) = 10.8153$.

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Here and in later sections, choices need to be made of probability distributions to use to express uncertainty. The GUM, Possolo and Elster [46], and Possolo and Iyer [47], among several other references, discuss the issue at length, and provide examples. In the present context, and in the examples that we describe, we tend to use uniform (or, rectangular) distributions for quantities known only to take values in a specified interval of finite length. This ought not to be construed as the sole or best choice in all such cases. For example, where, in Step 1 of Algorithm A specified below, we have chosen a uniform distribution, others may prefer to use a Gaussian distribution, or a re-scaled and shifted beta distribution, and similarly in other examples.

The probability distribution that ought to be employed in each case should reflect, as accurately as possible, the state of knowledge about the quantity of interest: that is, it should be as informative as the knowledge in hand warrants. O'Hagan *et al.* [48] provide guidelines for how to elicit expert knowledge and distill it into a probability distribution. SHELF [49] and MATCH [50] are freely available software tools to assist in such process. O'Hagan [17] discusses elicitation specifically in the context of measurement science.

Now, suppose that the standard uncertainty associated with the measured isotope delta value is $u(\delta_{\text{SRM951,c}}(^{11}\text{B}/^{10}\text{B})) = 4$ ‰, and that one wishes to propagate it to evaluate the uncertainty associated with the atomic weight just computed. For this evaluation, one should also propagate the uncertainties associated with the isotopic abundances of ^{10}B and ^{11}B in the NIST SRM 951 standard, and with the atomic weights of these isotopes. This may be done by application of the Monte Carlo method of the GUM-S1, using the following ***Algorithm A*** for boron, whose implementation in the R language for statistical programming and graphics [51] is shown in Listing 1.

Given a delta value $\delta_{\text{SRM951,P}}(^{11}\text{B}/^{10}\text{B})$ for a material P, choose a suitably large sample size K_A (below we explain how to assess whether K_A is large enough), and repeat the following steps for $k=1,\ldots,K_\text{A}$:

(A1) Draw a value $\delta_{\text{SRM951,P},k}(^{11}\text{B}/^{10}\text{B})$ from a uniform (rectangular) distribution with mean $\delta_{\text{SRM951,P}}(^{11}\text{B}/^{10}\text{B})$ and standard deviation $u(\delta_{\text{SRM951,P}}(^{11}\text{B}/^{10}\text{B}))$;

(A2) Draw a value $x_{\text{SRM951},k}(^{11}\text{B})$ for the amount fraction of ^{11}B in SRM 951 from a Gaussian distribution with mean $x_{\text{SRM951}}(^{11}\text{B}) = 0.801\,73$ and standard deviation $u(x_{\text{SMR951}}(^{11}\text{B})) = 0.000\,13/2$;

(A3) Compute the corresponding amount fraction of ^{10}B in the SRM 951 standard, $x_{\text{SRM951},k}(^{10}\text{B}) = 1 - x_{\text{SRM951},k}(^{11}\text{B})$

(A4) Compute the isotope ratio of boron in material P as

$$R_{\text{P},k}(^{11}\text{B}/^{10}\text{B}) = (1+\delta_{\text{SRM951,P},k}(^{11}\text{B}/^{10}\text{B}))\frac{x_{\text{SRM951},k}(^{11}\text{B})}{x_{\text{SRM951},k}(^{10}\text{B})}$$

(A5) Compute the amount fraction of ^{11}B in material P as

$$x_{\text{P},k}(^{11}\text{B}) = \frac{R_{\text{P},k}(^{11}\text{B}/^{10}\text{B})}{1+R_{\text{P},k}(^{11}\text{B}/^{10}\text{B})}$$

(A6) The corresponding amount fraction of ^{10}B is $x_{\text{P},k}(^{10}\text{B}) = 1 - x_{\text{P},k}(^{11}\text{B})$

(A7) Draw a value $A_{\text{r},k}(^{11}\text{B})$ from a uniform (rectangular) distribution with mean $A_\text{r}(^{11}\text{B}) = 11.009\,305\,4$ and standard deviation $u(A_\text{r}(^{11}\text{B})) = 0.000\,000\,4$

(A8) Draw a value $A_{\text{r},k}(^{10}\text{B})$ from a uniform (rectangular) distribution with mean $A_\text{r}(^{10}\text{B}) = 10.012\,936\,9$ and standard deviation $u(A_\text{r}(^{10}\text{B})) = 0.000\,000\,4$

(A9) Compute a sample value from the resulting probability distribution of the atomic weight of boron in material P as

$$A_{\text{r,P},k}(\text{B}) = x_{\text{P},k}(^{10}\text{B})A_{\text{r},k}(^{10}\text{B}) + x_{\text{P},k}(^{11}\text{B})A_{\text{r},k}(^{11}\text{B})$$

Algorithm A produces a sample of size K_A from the probability distribution of the atomic weight of boron in material P that expresses uncertainty contributions from the following sources: measurement of the delta values, amount fractions of the two stable isotopes of boron in the standard, and atomic weights of the two boron isotopes.

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```
atomicWeight.Boron = function (deltaB11.x, deltaB11.u=NULL,
                               coverage=0.95, K=1e6)
{
  ## INPUT
  ## deltaB11.x = Measured delta value (for example, +39.5 per mill
  ## should be entered as 0.0395)
  ## deltaB11.u = Std. uncertainty for measured value
  ## NULL if not available
  ## coverage = Coverage probability (default = 0.95)
  ## K = Sample size (default = 1e6)

  ## OUTPUT Vector with 4 elements: estimate of atomic weight,
  ## associated standard uncertainty, and end-points of coverage
  ## interval (these end-points are the 100*(1-coverage)/2 and
  ## 100*(1+coverage)/2 percentiles of the bootstrap distribution of
  ## the atomic weight corresponding to the specified deltaB11 value

  B10.mass.x = 10.0129369; B10.mass.u = 0.0000004
  B11.mass.x = 11.0093054; B11.mass.u = 0.0000004

  B10.std.fraction = 0.19827 ; B10.std.fraction.u = 0.0001
  B11.std.fraction = 0.80173 ; B11.std.fraction.u = 0.0001

  B10.mass.boot = runif(K, min=B10.mass.x-sqrt(3)*B10.mass.u,
                        max=B10.mass.x+sqrt(3)*B10.mass.u)
  B11.mass.boot = runif(K, min=B11.mass.x-sqrt(3)*B11.mass.u,
                        max=B11.mass.x+sqrt(3)*B11.mass.u)

  boron.std.fractions.boot = cbind(
     rnorm(K, mean=B10.std.fraction, sd=B10.std.fraction.u),
     rnorm(K, mean=B11.std.fraction, sd=B11.std.fraction.u))
  boron.std.fractions.boot =
     sweep(boron.std.fractions.boot, 1,
           apply(boron.std.fractions.boot, 1, sum), FUN="/")
  B10.std.fraction.boot = boron.std.fractions.boot[,1]
  B11.std.fraction.boot = boron.std.fractions.boot[,2]

  deltaB11.sample.boot =
     if (is.null(deltaB11.u)) {rep(deltaB11.x, K)} else {
        runif(K, min=deltaB11.x-sqrt(3)*deltaB11.u,
                 max=deltaB11.x+sqrt(3)*deltaB11.u) }

  R.sample.boot = (1 + deltaB11.sample.boot) *
     (B11.std.fraction.boot/B10.std.fraction.boot)
  B11.sample.fraction.boot = R.sample.boot/(1+R.sample.boot)
  B10.sample.fraction.boot = 1 - B11.sample.fraction.boot

  atomicWeight.sample.boot =
     B11.sample.fraction.boot * B11.mass.boot +
     B10.sample.fraction.boot * B10.mass.boot

  out = c(mean(atomicWeight.sample.boot), sd(atomicWeight.sample.boot),
        quantile(atomicWeight.sample.boot,
                 probs=c((1-coverage)/2, (1+coverage)/2)))
  names(out) = c("Ar(B)", "u(Ar(B))", "Lwr95(Ar(B))", "Upr95(Ar(B))")
  return(out)
}
```

Listing 1: Implementation of Algorithm A as R function `atomicWeight.Boron`. Given a delta value (`deltaB11.x`) for ^{11}B in a material, and optionally also the standard uncertainty associated with this delta value (`deltaB11.u`), the function produces an estimate of the atomic weight of boron in the material, an evaluation of the associated standard uncertainty, and the endpoints of a coverage interval with the specified coverage probability (`coverage`), based on Monte Carlo samples of a given size (K). The factor `sqrt(3)` reflects the fact that the endpoints of a uniform (or, rectangular) probability distribution are $\sqrt{3}$ standard deviations away from the mean. The values of the atomic weights of the isotopes, and the associated uncertainties, are from Table I of Wang *et al.* [11]. The isotopic abundances, and the associated uncertainties, are from Meija *et al.* [39].

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```
atomicWeight.Oxygen = function (delta018.x, delta018.u=NULL,
                                coverage=0.95, K=1e6)
{
  ## INPUT
  ## delta018.x = Measured delta value (for example, +42 per mill
  ## should be entered as 0.042)
  ## delta018.u = Std. uncertainty for measured value
  ## NULL if not available
  ## coverage = Coverage probability (default = 0.95)
  ## K = Sample size (default = 1e6)

  ## OUTPUT Vector with 4 elements: estimate of atomic weight,
  ## associated standard uncertainty, and end-points of coverage
  ## interval (these end-points are the 100*(1-coverage)/2 and
  ## 100*(1+coverage)/2 percentiles of the bootstrap distribution of
  ## the atomic weight corresponding to the specified deltaB11 value

  016.mass.x = 15.994914619566; 016.mass.u = 0.000000000172
  017.mass.x = 16.999131756500; 017.mass.u = 0.000000000692
  018.mass.x = 17.999159612858; 018.mass.u = 0.000000000758

  016.mass.boot = runif(K, min=016.mass.x-sqrt(3)*016.mass.u,
           max=016.mass.x+sqrt(3)*016.mass.u)
  017.mass.boot = runif(K, min=017.mass.x-sqrt(3)*017.mass.u,
           max=017.mass.x+sqrt(3)*017.mass.u)
  018.mass.boot = runif(K, min=018.mass.x-sqrt(3)*018.mass.u,
           max=018.mass.x+sqrt(3)*018.mass.u)

  delta018.sample.boot =
      if (is.null(delta018.u)) {rep(delta018.x, K)} else {
          runif(K, min=delta018.x-sqrt(3)*delta018.u,
                max=delta018.x+sqrt(3)*delta018.u) }

  lambda.x = 0.5281; lambda.u = 0.0015
  lambda.boot = rnorm(K, mean=lambda.x, sd=lambda.u)
  delta017.sample.boot =
     (1+delta018.sample.boot)^lambda.boot - 1

  R018016.std.boot = rnorm(K, mean=2005.2e-6, sd=0.45e-6)
  R017016.std.boot = rnorm(K, mean= 379.9e-6, sd=0.8e-6)

  r018.sample.boot = (1 + delta018.sample.boot) * R018016.std.boot
  r017.sample.boot = (1 + delta017.sample.boot) * R017016.std.boot

  018.sample.fraction.boot = r018.sample.boot/(1+r018.sample.boot)
  017.sample.fraction.boot = r017.sample.boot/(1+r017.sample.boot)
  016.sample.fraction.boot =
      pmax(0, 1 - 018.sample.fraction.boot - 017.sample.fraction.boot)

  atomicWeight.sample.boot =
      016.sample.fraction.boot * 016.mass.boot +
      017.sample.fraction.boot * 017.mass.boot +
      018.sample.fraction.boot * 018.mass.boot

  out = c(mean(atomicWeight.sample.boot), sd(atomicWeight.sample.boot),
          quantile(atomicWeight.sample.boot,
                   probs=c((1-coverage)/2, (1+coverage)/2)))
  names(out) = c("Ar(O)", "u(Ar(O))", "Lwr95(Ar(O))", "Upr95(Ar(O))")
  return(out)
}
```

Listing 2: Modified version of Algorithm A as R function `atomicWeight.Oxygen` to compute the atomic weight of oxygen in a material P, and the associated uncertainty, given $\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O})$, and optionally also the standard uncertainty associated with this delta value. The values assigned to λ in eq. (6) and to $u(\lambda)$ are from Meijer and Li [40]. The values and associated uncertainties for the isotope ratios in the VSMOW standard are from Baertschi [53] and from Li *et al.* [54]. The values of the atomic weights of the isotopes, and the associated uncertainties, are from Table A of Wang *et al.* [11]. The amount fractions of the isotopes in the standard, and their associated uncertainties, are as compiled by Meija *et al.* [39].

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The mean of this set of values of the atomic weight of boron is an estimate of the atomic weight of boron in material P, the standard deviation is an evaluation of the associated combined standard uncertainty $u(A_{\mathrm{r,P}}(\mathrm{B}))$, and the 2.5th and 97.5th percentiles of this sample are the endpoints of a 95 % coverage interval for the atomic weight.

The question of how large K_{A} needs to be may be answered by determining the number of significant digits in the results that correspond to any particular value chosen for K_{A}. Suppose that the Monte Carlo sample $\{A_{\mathrm{r,P,1}}(\mathrm{B}),\ldots,A_{\mathrm{r,P},K_{\mathrm{A}}}(\mathrm{B})\}$ has average a and standard deviation s. The number of digits that $a-2s/\sqrt{K_{\mathrm{A}}}$ and $a+2s/\sqrt{K_{\mathrm{A}}}$ have in common is a fair estimate of the number of significant digits achieved with a sample of size K_{A}.

In general, one may be interested in some other function of the sample values, different from the average: for example, their standard deviation, or a percentile. Let $T=\tau(A_{\mathrm{r,P,1}}(\mathrm{B}),\ldots,A_{\mathrm{r,P},K_{\mathrm{A}}}(\mathrm{B}))$ denote such function. Partition the Monte Carlo sample $\{A_{\mathrm{r,P,1}}(\mathrm{B}),\ldots,A_{\mathrm{r,P},K_{\mathrm{A}}}(\mathrm{B})\}$ into L_{A} subsets of size $K_{\mathrm{A}}/L_{\mathrm{A}}$ each (with L_{A} equal to 100 or 1000, say), and compute the value of T based on each of these subsets, thus obtaining $\{T_1,\ldots,T_{L_{\mathrm{A}}}\}$ with average a and standard deviation s. Then, the number of digits that $a-2s/\sqrt{K_{\mathrm{A}}/L_{\mathrm{A}}}$ and $a+2s/\sqrt{K_{\mathrm{A}}/L_{\mathrm{A}}}$ have in common is a fair estimate of the number of significant digits achieved for T with a sample of size K_{A} [52].

For the case of the colemanite sample mentioned above, application of Algorithm A with $K_{\mathrm{A}}=1\times10^6$ yields a sample drawn from the probability distribution of $A_{\mathrm{r,c}}(\mathrm{B})$, whose average 10.8154 is an estimate of $A_{\mathrm{r,c}}(\mathrm{B})$, and whose standard deviation 0.0006 is the associated standard uncertainty. A 95 % coverage interval for the true value of the atomic weight of boron in this material ranges from 10.8143 to 10.8164.

Algorithm A is applicable only to elements with exactly two stable isotopes. To compute the atomic weight of oxygen in a material P whose $\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ is given, the algorithm requires a few modifications, implemented in Listing 2, which we describe next, referencing the line numbers of the R code in this listing.

Lines 22–27 Monte Carlo samples of the masses of $^{16}\mathrm{O}$, $^{17}\mathrm{O}$, and $^{18}\mathrm{O}$, are drawn from uniform distributions that describe the uncertainty surrounding their masses.

Lines 29–32 A Monte Carlo sample of $\delta_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ for the material of interest is drawn from a uniform (or, rectangular) distribution that describes the uncertainty surrounding this delta value, and whose standard deviation is the specified standard uncertainty. If no uncertainty is specified, then all the values in this sample are equal to the specified value of the delta value.

Lines 34–37 The value of $\delta_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$ in the material is imputed using the relationship in Equation (6).

Lines 39–40 The options for drawing Monte Carlo samples from the probability distributions that express the uncertainty surrounding the isotope ratios for the VSMOW standard $R_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ and $R_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$ are either (i) modeling the amount fractions that appear in the numerator and in the denominator as independent Gaussian random variables with means and standard deviations equal to the corresponding estimates for the amount fractions in VSMOW, or (ii) relying on the measurement results from Baertschi [53] for $R_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$, and from Li *et al.* [54] for $R_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$, which are listed in Wise and Watters [55].

Option (i) produces estimates of the isotope ratios essentially identical to the measured values, but standard uncertainties slightly larger than those reported in (ii). Since there is no cogent reason to prefer (i) over (ii), and the measurement results just mentioned are widely relied upon, for the Monte Carlo evaluation we model both isotope ratios as Gaussian random variables: $R_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$ with mean $2\,005.2\times10^{-6}$ and standard deviation 0.45×10^{-6} [53]; $R_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$ with mean 379.9×10^{-6} and standard deviation 0.8×10^{-6} [54].

Lines 42–43 Monte Carlo samples drawn from the probability distributions of the two isotope ratios for the material are computed as functions of the Monte Carlo samples for the delta values and for the isotope ratios for the VSMOW standard, as $R_{\mathrm{P}}(^{18}\mathrm{O}/^{16}\mathrm{O})=(1+\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O}))\,R_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$, and similarly for $R_{\mathrm{P}}(^{17}\mathrm{O}/^{16}\mathrm{O})$.

Lines 45–48 Monte Carlo samples of the amount fractions of $^{18}\mathrm{O}$ and $^{17}\mathrm{O}$ in the material are derived from the isotope ratios computed in the previous step, and the amount fraction of $^{16}\mathrm{O}$ is computed as the remainder needed to make the amount fractions add to 1.

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Lines 50–53 The atomic weight of oxygen in the material is computed as a weighted average of the relative atomic masses of the three isotopes, with weights equal to the corresponding amount fractions.

Now, consider the calculation of the atomic weight of oxygen, and of the associated uncertainty, in a material P whose $\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O}) = +42\,‰$, with associated standard measurement uncertainty $u(\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O})) = 6\,‰$, using either the Monte Carlo method of the GUM-S1 implemented in R function `atomicWeight.Oxygen` specified in Listing 2, or the conventional Gauss's formula (Equation (10) in the GUM), as implemented in the *NIST Uncertainty Machine* [56].

The measurement model according to the GUM expresses $A_{\mathrm{r,P}}(\mathrm{O})$ as the value (output quantity) of a function of seven input quantities: $\delta_{\mathrm{VSMOW,P}}(^{18}\mathrm{O}/^{16}\mathrm{O})$, λ, $R_{\mathrm{VSMOW}}(^{18}\mathrm{O}/^{16}\mathrm{O})$, $R_{\mathrm{VSMOW}}(^{17}\mathrm{O}/^{16}\mathrm{O})$, $A_{\mathrm{r}}(^{16}\mathrm{O})$, $A_{\mathrm{r}}(^{17}\mathrm{O})$, and $A_{\mathrm{r}}(^{16}\mathrm{O})$. We assume that the corresponding random variables have means and standard deviations equal to their estimates and standard uncertainties specified in Listing 2, and that they are uncorrelated.

In these circumstances, both R function `atomicWeight.Oxygen` and Gauss's formula produce the same results to within the number of significant digits reported here: $A_{\mathrm{r}}(\mathrm{O}) = 15.999\,483$ and $u(A_{\mathrm{r,c}}(\mathrm{O})) = 0.000\,025$. Where they differ is in the corresponding 95 % coverage intervals for the true value of $A_{\mathrm{r,c}}(\mathrm{O})$: the interval produced by `atomicWeight.Oxygen` is (15.999442, 15.999525), while the interval of the form $A_{\mathrm{r,P}}(\mathrm{O}) \pm 2u(A_{\mathrm{r,P}}(\mathrm{O}))$ (which is the interval that conventionally corresponds to the GUM calculation when there is no information about numbers of degrees of freedom associated with the standard uncertainties of the input quantities – *cf.* GUM 6.3.3) is (15.999433, 15.999534), hence about 1.2 times longer than the interval produced by `atomicWeight.Oxygen`.

In general, the Monte Carlo method is recommended, in particular for evaluations of uncertainty associated with non-linear functions of one or more input quantities, atomic weights in particular. Clearly, the Monte Carlo method is more demanding of assumptions than the approximate calculation of standard uncertainty specified in the GUM: application of the Monte Carlo method requires that the joint probability distribution of the input quantities be specified fully, while Gauss's formula in the GUM requires only that means, standard deviations, and correlation coefficients of the same joint distribution be specified.

If these assumptions are valid, then the Monte Carlo method is exact, in the sense that it can produce as many significant digits of the quantities of interest (standard uncertainty, endpoints of coverage intervals, etc.) as may be required. Not only this, it can also characterize the whole probability distribution of the output quantity based on an arbitrarily large sample drawn from it, while the original approach described in the GUM produces only an approximation to the standard deviation of this distribution. The Monte Carlo method enjoys these properties because it is a numerical (simulation-based) version of the change-of-variable formula of probability theory [57, 58].

The *NIST Uncertainty Machine* is an application available in the World Wide Web at uncertainty.nist.gov that implements both the conventional approximate method for uncertainty evaluation specified in the GUM, as well as the Monte Carlo method for the propagation of distributions [56].

The following Sections 5 and 6 describe how uncertainties associated with standard atomic weights and with relative molecular masses may be evaluated, and illustrates the corresponding calculations in several examples. But first we discuss how the dispersion or variability of atomic-weight values may be modeled.

5 Modeling the dispersion of atomic-weight values

5.1 Preamble

The approaches that we shall describe next, to model the dispersion of atomic-weight values (which for many elements is attributable to natural variations in isotopic abundances of the same element in different materials), are fully consistent with the meaning that the CIAAW gives to the intervals used to represent the standard atomic weights.

The probability distributions assigned to these intervals, to encapsulate various states of knowledge about atomic weights, may be rectangular (uniform) or not. The rectangular distribution is a default choice

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when there is no specific knowledge about the isotopic composition of the material, for example as may be inferred from its provenance, or when there is no compelling reason to use that specific knowledge even if it is available. One practical reason that may justify glossing over specific information about the material is the fact that atomic weights often are used in calculations whose results have uncertainties dominated by uncertainty contributions other than the uncertainties of the atomic weights, even when these are modeled in the most conservative fashion.

However, when results of the highest precision are required, then one will take pains to incorporate all information in hand about the isotopic composition of the materials involved. This often will involve consideration and manipulation of non-rectangular distributions for the atomic weights, as will be copiously illustrated in the following subsections. Or, if even greater precision than can be achieved by these means is required, then the isotopic composition of the sample should be determined.

5.2 Conveying simplicity

Historically, the standard atomic weights have served as convenient simplifications at the expense of forsaking the fine details of the variability of isotopic compositions in natural materials. Producing such internationally accepted codification of the atomic weight values has been the central task of the International Committee of Atomic Weights (now the CIAAW) since 1899.

The simplest possible probability distribution over the interval that defines a standard atomic weight is uniform (rectangular). Such probability distribution must not be interpreted as reflecting the diversity and relative abundances of the values that the atomic weight may have in nature. Instead, it is merely a deliberately simplistic description of a state-of-knowledge that, in this case, says that the atomic weight of the element in a sample of a "normal" material is equally likely to lie in any two sub-intervals of the standard atomic weight that are of the same length [59].

Such model typically leads to a coarse estimate of the value of an atomic weight and may yield a conservative evaluation of the associated uncertainty. The use of this conservative or "exaggerated" uncertainty requires no further effort from the user and is, in fact, fit-for-purpose in many applications.

More precise estimates of the atomic weight are achievable when further effort is spent eliciting relevant information about the dispersion of the relative abundances of the isotopes of the element in the material being studied. For example, this information may be about the provenance of the material, or it may comprise measurement results about the isotopic composition of the material. The latter approach is preferred by the National Metrology Institutes whereas the former approach might be found useful by those who lack designated atomic-weight measurement capabilities or do not wish to employ them.

Consider boron, with standard atomic weight $A_r(\mathrm{B}) = [10.806, 10.821]$. This interval means that any "normal" boron-containing material, likely to be encountered by a chemist, will have the atomic weight within this interval with high degree of confidence. With no further knowledge in hand, this fact can be expressed probabilistically by a uniform probability distribution that is concentrated on that interval.

The CIAAW points out, in the 2013 version of the Table of Standard Atomic Weights [7], that for some elements (including hydrogen, lithium, boron, nitrogen, oxygen, neon, and chlorine, among others) "modified isotopic compositions may be found in commercially available material because the material has been subjected to an undisclosed or inadvertent isotopic fractionation." In such materials, the atomic weight of the element may deviate substantially from that given in the table.

5.3 Conveying complexity

Although the primary goal of the standard atomic weights is to convey simple, easy-to-understand atomic-weight values, one can nevertheless take a closer look at the rather complex "machinery" underlying the recommended values and intervals, which we will do by considering again boron as an example.

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Table 1: Classes of sources of boron, and observed intervals of $\delta_{\mathrm{SRM951}}(^{11}\mathrm{B}/^{10}\mathrm{B})$ as listed by Coplen *et al.* [23, table 8] and Coplen and Shrestha [24, table 3].

j	Class		$\delta_{\mathrm{SRM951},j}(^{11}\mathrm{B}/^{10}\mathrm{B})$/‰	
			min	**max**
1	Marine	Seawater	+38.4	+40.4
2	Marine	Evaporated seawater	+36.5	+58.5
3	Marine	Hydrothermal fluids	+30.0	+36.8
4	Marine	Evaporite minerals	+18.2	+31.7
5	Marine	Carbonates	+4.0	+32.2
6	Non-marine	Rain water	+0.8	+35.0
7	Non-marine	Brines, surface ground waters	−21.3	+59.2
8	Non-marine	Hydrothermal fluids	−9.3	+29.1
9	Non-marine	Evaporite minerals	−31.3	+7.3
10	Rocks	Igneous	−17.0	−1.7
11	Rocks	Metamorphic	−34.2	−22.0
12	Rocks	Sediments	−17.0	+26.2
13	Organic	Boron	−12.0	+29.3

Boron isotopic reference material SRM 951 is certified by NIST as comprising 19.827 % of ^{10}B and 80.173 % of ^{11}B (amount-of-substance fractions), both with expanded uncertainty (for 95 % coverage) of 0.013 %, hence $R_{\mathrm{SRM951}}(^{11}\mathrm{B}/^{10}\mathrm{B}) = 4.044$, with expanded uncertainty (for 95 % coverage) of 0.003.

The problem of characterizing the state of knowledge available about atomic weights may be approached differently from how we have approached it above, when other sources of information are available and are exploited. For each element whose standard atomic weight is given in the interval notation, Coplen *et al.* [23, table 8] and Coplen and Shrestha [24, table 3] provide intervals of isotope delta values, $\delta_{\mathrm{SRM951}}(^{11}\mathrm{B}/^{10}\mathrm{B})$ in this case, for materials in different classes – seawater, marine carbonates, igneous rocks, etc. –, transcribed here in Table 1. Note that this particular collection of classes is used only to illustrate an algorithm described below (Algorithm S) to compute the atomic weight of an element. This algoritm may be applied to any partition of the "normal" materials into disjoint classes that are meaningful for a particular element.

Now suppose that a sample of unknown isotopic composition originates from class *j* with probability π_j, where $\sum_j \pi_j = 1$. Assume also that, given a particular class, the value of $\delta_{\mathrm{SRM951}}(^{11}\mathrm{B}/^{10}\mathrm{B})$ is uniformly distributed between the minimum and maximum values listed for the class (that is, it is described by a rectangular distribution whose endpoints are these minimum and maximum). In these circumstances – all of which are subject to the above assumptions, however unrealistic –, one can apply a statistical method suggested by Stone [60] and by Lindley [61] to form a sample of suitably large size K_S from the probability distribution of the atomic weight of boron across all such sources, and then summarize this sample to characterize the atomic weight of boron.

To produce such a sample, while also propagating the uncertainty associated with the isotopic composition of NIST SRM 951, and with the atomic weights of ^{10}B and ^{11}B, [39, 55, 62], apply the following ***Algorithm S***, where all the random variables involved are assumed to be mutually independent.

(S1) Draw a sample of size K_S from the the set of labels {1, 2,...,13} of the classes of materials listed in Table 1, with probabilities $\pi_1, \pi_2,...,\pi_{13}$;

(S2) For each j_k in that sample, compute $A_{\mathrm{r},k}(\mathrm{B})$ using Algorithm A (specified in §4.3) with the delta value set equal to the mid-point of the delta values for materials in this class, and with standard uncertainty corresponding to a uniform distribution of delta values over this class.

The resulting values $A_{\mathrm{r},1}(\mathrm{B}),\ldots,A_{\mathrm{r},K_\mathrm{S}}(\mathrm{B})$ are a sample of size K_S from the probability distribution of the atomic weight of boron. Since Algorithm A is executed K_A times for each j_k, the dispersion of values (or, scatter) of this sample also expresses the uncertainties associated with the atomic weights of both boron isotopes, and with their amount fractions in the reference standard (NIST SRM 951).

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The value of K_S chosen here need not be identical to the value of K_A used in Algorithm A: since the uncertainties that are associated with the atomic weights and with the amount fractions of the isotopes in the standard are much smaller than the variability of the atomic weights within and between the different classes of materials in Table 1, it is preferable that the value of K_S be substantially larger than the value of K_A that is used each time that Algorithm A is executed in step S2 of Algorithm S.

Obviously, Algorithm S may be much simplified (involving exactly 13 applications of Algorithm A) when the 13 classes all are deemed to be equally likely sources for the material. However, as written above, the algorithm may be immediately adapted to cases where the classes are not all equally likely. It should be noted that the results of Algorithm S are as reliable as the assumptions made in applying it: in particular, the relative contributions that the identified classes of sources of boron may make to the pool of boron atoms in "normal" materials, which are expressed in the probabilities $\{\pi_j\}$.

Application of Algorithm S with $K_S = 50\,000$ (using $K_A = 5\,000$ each time that Algorithm A was executed), produced a sample of values of the atomic weight of boron whose 2.5th and 97.5th percentiles were 10.807 and 10.820 which is very close to the endpoints of the standard atomic weight of boron.

Figure 1 shows an estimate of the probability density of the atomic weight of boron, produced by application of a kernel density estimator [63], implemented in R function `density`, to the sample of atomic weight values produced by Algorithm S. The same figure also depicts the probability density of a rescaled and shifted beta distribution with the same mean and standard deviation as that sample. In this case, the beta approximation is not particularly accurate, even though it improves on a rectangular distribution.

The beta distribution [64] is concentrated on the interval [0, 1], and is determined by two adjustable parameters. It includes the uniform (or, rectangular) distribution as a special case, and its probability density may be bell-shaped and symmetrical or skewed, J-shaped, L-shaped, or U-shaped [65, §1.3.6.6.17], affording a flexible model for the variability of proportions. If V denotes a random variable with a beta distribution, then the random variable $a + bV$ has a rescaled and shifted beta distribution, where a and $b > 0$ denote real numbers. Even greater modeling flexibility can be achieved by considering mixtures of several shifted and rescaled beta distributions.

5.4 Conveying further complexity

The isotopic composition of boron in the earth's mantle (approximately 2 900 km thick, underlying the crust, which is 5 km to 50 km thick) has $\delta_{\text{SRM951}}(^{11}\text{B}/^{10}\text{B}) \approx -10$ ‰ [66]. Boron can be readily mobilized by hydrother-

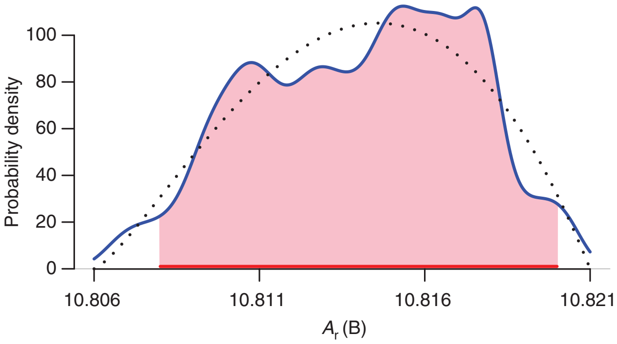

Fig. 1: Estimate of the probability density of A_r(B) (solid blue curve), and probability density of a rescaled and shifted beta distribution (dotted black line) that approximates that estimate. This approximant is concentrated on the standard atomic weight interval for boron and has the same mean and standard deviation of the sample of values of A_r(B) produced by Algorithm S. The multiple peaks and valleys in the blue curve are due to the fact that the corresponding distribution is a mixture of 13 different rectangular distributions. The horizontal axis has the same endpoints as the standard atomic weight interval for boron. The total area under any curve representing a probability density, or a smooth histogram that estimates a probability density, is always 1. The area of the region shaded pink amounts to 95 % of the area under the solid blue curve, therefore, its projection onto the horizontal axis (marked with a horizontal red line segment immediately above the horizontal axis) is a 95 % coverage interval for the true value of A_r(B).

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Table 2: Estimated snapshot of the global production of boron for 2001, specified in terms of equivalent mass of B_2O_3.

j	Country	Location	$m(B_2O_3)$/Gg	π/%	$\delta(^{11}B/^{10}B)$/‰	$u(\delta(^{11}B/^{10}B))$/‰	Source
1	USA	US Borax	575	38	0	5	[68, 69]
2	USA	IMC Chemicals	75	5	6	3	[68]
3	Turkey	Kirka	230	15	0	3	[70]
4	Turkey	Emet	150	10	−15	3	[70]
5	Turkey	Bigadic	80	5	−15	3	[70]
6	Turkey	Bigadic	60	4	0	5	[70]
7	Chile		120	8	−20	5	[71]
8	China		110	7	10	2	[72]
9	Argentina		60	4	0	2	[71]
10	Russia		60	4	−20	10	[73]
	Total		1 520				

Source: `boronturkey.com`, accessed on September 20, 2015. π_j is the proportion of the total production that originates from source j, for $j=1,\dots,10$. The column headed "$\delta(^{11}B/^{10}B)$" lists the values of $\delta_{SRM951}(^{11}B/^{10}B)$, and the column headed "$\sqrt{3}u(\delta(^{11}B/^{10}B))$" lists the values of one half of the range of the uniform (rectangular) distribution used to model the uncertainty associated with $\delta_{SRM951}(^{11}B/^{10}B)$. The values listed here are rough estimates largely guided by the work of Palmer and Helvaci [70].

mal fluids, captured in the precipitation of evaporites, and re-mobilized by weathering and other geological processes, all of which induce fractionation and produce materials with the wide range of isotopic compositions that have been observed [23]. The fractionation of boron in natural processes is determined mostly by whether boron is bound to oxygen or to hydroxyl groups in either trigonal or tetrahedral coordination because the corresponding bond lengths and vibrational frequencies are different in the two cases [67, Page 418].

Over 90 % of the boron that is mined worldwide originates from only eight natural deposits, which are located in the USA, Turkey, Chile, and China. The isotopic composition of boron from each of these sources is known, and so is their annual production (Table 2).

The simplistic assumption that the probability of a sample of boron used in a laboratory originating from a particular source is proportional to the mass of boron produced by that source, opens another avenue to evaluate the uncertainty associated with the atomic weight of boron. This evaluation, whose most comprehensive form is a probability distribution for $A_r(B)$, does not reflect natural abundances generally, but only abundances in those sources that are actively exploited and that produce materials that boron is extracted from. Figure 2 shows the corresponding probability density.

The sampling procedure and uncertainty propagation exercise that underlie the results depicted in Fig. 2 involves the probabilities assigned to the sources, which are proportional to the mass of boron that the source produced: for example, $\pi_1=575/1\,520\approx 0.378$ for US Borax. Table 2 lists $n=10$ sources, and we will use π_j to denote the probability corresponding to source $j=1,\dots,n$. The probability density shown in Fig. 2 has been derived from a set comprising $K=1\times 10^6$ isotopic compositions of hypothetical samples drawn from the sources listed. This set has been generated by repeating the steps S1–S2 specified above for $k=1,\dots,K$, except that step S1 is replaced by the following two steps:

(T1) Select one source at random, according to the source probabilities $\{\pi_j\}$, and suppose that it is source $j(k)$;

(T2) Simulate an outcome $\delta_{SRM951,k}(^{11}B/^{10}B)$ from a Gaussian random variable with mean $\delta_{SRM951,j}(k)(^{11}B/^{10}B)$ and standard deviation $u(\delta_{SRM951,j(k)}(^{11}B/^{10}B))$, which will be the values listed in row $j(k)$ of Table 2.

Figure 2 shows that the materials, whose provenance is one of the commercial sources listed in Table 2, have atomic weights concentrated on the lower half of the interval [10.806, 10.821] that represents the standard atomic weight of boron. This fact is not surprising considering that the non-marine evaporite deposits in California and Turkey are substantially depleted in ^{11}B relative to seawater [23, Page 1994].

Neither Fig. 1 nor Fig. 2 should be regarded as characterizating the uncertainty surrounding the atomic weight of boron. They serve only as illustrations of methods used to propagate uncertainty associated with

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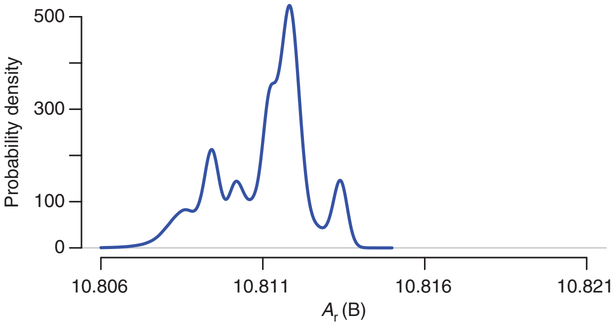

Fig. 2: Estimate of the probability density of A_r(B) (solid blue curve) for a material originating in one the sources listed in Table 2. The horizontal axis has the same endpoints as the standard atomic weight of boron. The same as in Fig. 1, the area under the curve is 1.

the atomic weights, including uncertainty components that are attributable to lack of knowledge about the provenance of the materials that are used as sources for boron. Figure 1, in particular, is contingent not only on the specific sampling and modeling assumptions already discussed, but also on the profile of boron mining, and on the channels of commerce that make such boron available throughout the world, both of which vary from year to year.

6 Uncertainty evaluation for relative molecular masses

6.1 Carbon dioxide

In many cases, the source of a molecular compound is known – for example, that a particular amount of CO_2 was extracted from the earth's atmosphere –, and the variability of the isotopic composition of the constituent elements in that source is documented. The uncertainty to be associated with the relative molecular mass can reflect the specific knowledge in hand about the provenance of the atoms present in the molecule.

At one end of the spectrum of possibilities, one makes no assumptions about the provenance of the carbon and oxygen in CO_2. The uncertainty associated with its relative molecular mass may be evaluated using rectangular distributions over the standard atomic weights of carbon and oxygen. In the terminology of the GUM, the output quantity is the relative molecular mass of CO_2, and it is a linear combination of two input quantities:

$$M_r(\mathrm{CO_2}) = A_r(\mathrm{C}) + 2A_r(\mathrm{O}) \tag{7}$$

Together with the assumption that the input quantities are independent random variables, we have

$$u^2(M_r(\mathrm{CO_2})) = u^2(A_r(\mathrm{C})) + 2^2u^2(A_r(\mathrm{O})) \tag{8}$$

Since $u^2(A_r(\mathrm{C})) = (12.0116 - 12.0096)^2/12$, and $u^2(A_r(\mathrm{O})) = (15.999\,77 - 15.999\,03)^2/12$, it follows that $u(M_r(\mathrm{CO_2})) = 0.000\,72$. This analysis, however, does not provide any additional information about the underlying probability distribution. The Monte Carlo method of the GUM-S1 may be employed to characterize the probability distribution that describes the dispersion of values of the relative molecular mass of CO_2. In this case, however, it is possible to derive this distribution analytically: it has the trapezoidal probability density [74] depicted in Fig. 3 (blue curve), with mean 44.009 40 and standard deviation 0.000 72. The shortest 95 % coverage interval ranges from 44.008 04 to 44.010 76 (computed using R function `qtrapezoid` defined in package `trapezoid` [75]).

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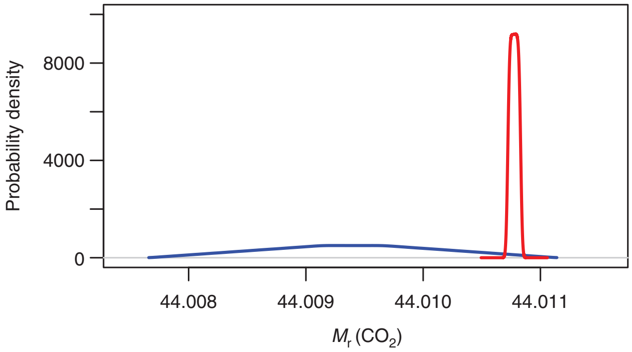

Fig. 3: Probability density characterizing the uncertainty associated with the relative molecular mass of CO_2: (i) when nothing is assumed known about the provenance of the compound (squat and blue trapezoid, with mean 44.009 40 and standard deviation 0.000 72); (ii) assuming atmospheric origin (tall and red curve), with mean 44.010 78 and standard deviation 0.000 03.

If a particular amount of CO_2 is known to be from the free troposphere without local source influences (often referred to as "background air"), then using this knowledge reduces the uncertainty of the relative molecular mass considerably (provided no fractionation takes place as CO_2 is extracted from the atmosphere). To evaluate it, we take into account the variability of the isotopic composition of carbon and oxygen in atmospheric CO_2 reported by Coplen *et al.* [21, tables 11 and 17]. Accordingly, $\delta_{\text{VPDB}}(^{13}\text{C}/^{12}\text{C})$ is modeled as a random variable uniformly distributed between −8.2 ‰ and −6.7 ‰ relative to the Vienna Peedee belemnite (VPDB), and $\delta_{\text{VPDB}}(^{18}\text{O}/^{16}\text{O})$ is modeled as a random variable uniformly distributed between +40 ‰ and +53 ‰ relative to Vienna Standard Mean Ocean Water (VSMOW).

In this case, owing to the non-linear relation between delta values and atomic weights, only the Monte Carlo method of the GUM-S1 is reliably practicable for the uncertainty evaluation. The procedures for carbon and for oxygen involve very much the same steps (S1–S2) listed above for boron. The version of Algorithm A to be used for carbon is a trivial modification of the version given in Listing 1 for boron whereas the version to be used for oxygen is given in Listing 2. The resulting distribution has mean 44.010 78 and standard deviation 0.000 03, and probability density depicted in Fig. 3 (tall, red curve).

6.2 Borax

The evaluation of the uncertainty associated with the relative molecular weight of sodium tetraborate decahydrate, $Na_2\,[B_4O_5\,(OH)_4] \cdot 8H_2O$ or $Na_2B_4O_7 \cdot 10H_2O$, a stable hydrated form of borax that is suitable for use as a primary standard in acid-base titrimetry, affords an opportunity for comparing the effects of different assumptions that may reasonably be made about the state of knowledge of the atomic weights.

We will consider three scenarios, in all of which we assume that the standard atomic weights are as listed by Meija *et al.* [7, table 1]: in scenario (i) (standard) the standard atomic weights are all the knowledge in hand; in scenario (ii) (commercial) the boron is assumed to have originated from one of the principal commercial sources listed in Table 2, with isotopic composition that varies between sources; and in scenario (iii) (marine) the boron is assumed to have originated from a marine source.

For the uncertainty evaluation in scenario (i), we will model the atomic weights of boron, hydrogen, and oxygen as independent random variables uniformly distributed over the intervals that define their corresponding standard atomic weights, and the atomic weight of sodium as a random variable independent of the others, and uniformly distributed between 22.989 769 28 − 0.000 000 02 and 22.989 769 28 + 0.000 000 02 (based on the entry for sodium in Meija *et al.* [7, table 1]).

For scenario (ii), we will make the same modeling assumptions that we made in (i) for hydrogen, oxygen, and sodium, but for boron we will assume that the value of its atomic weight is like an outcome of a random variable with the probability density illustrated in Fig. 2. The scenario (iii) is similar to scenario (ii) except

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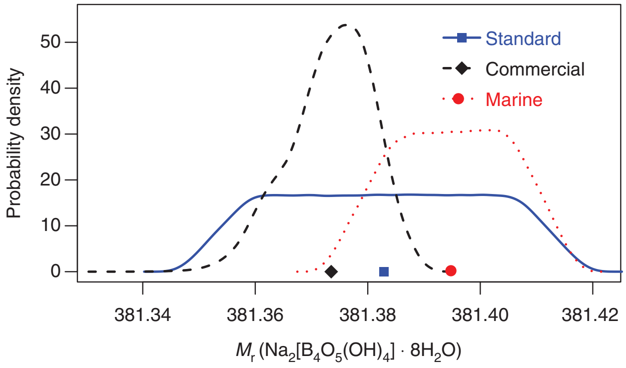

Fig. 4: Probability density of the relative molecular mass of borax under three modeling scenarios, and averages of the corresponding samples: (i) standard; (ii) commercial; and (iii) marine.

that the boron is assumed to have originated from a marine source with the values of $\delta_{SRM951}(^{11}B/^{10}B)$ ranging from +4.0 ‰ to +58.5 ‰. We assume that $\delta_{SRM951}(^{11}B/^{10}B)$ is a random variable with a uniform (rectangular) distribution over this interval.

The relative molecular mass of borax may, for the purpose of uncertainty evaluation, be expressed as a random variable $M = 2A_r(\text{Na}) + 4A_r(\text{B}) + 17A_r(\text{O}) + 20A_r(\text{H})$, where $A_r(\text{Na})$, $A_r(\text{B})$, $A_r(\text{O})$, and $A_r(\text{H})$ denote independent random variables with the distributions specified above for the atomic weights of these elements, in scenarios (i)–(iii).

Figure 4 depicts the results of the application of the Monte Carlo method of the GUM-S1, based on a sample of size 1×10^6 drawn from the probability distribution of M, summarized in kernel estimates of the corresponding probability density. The average value of M is (i) 381.38, (ii) 381.37, or (iii) 381.40, and the standard uncertainty $u(M)$ is (i) 0.018, (ii) 0.007, or (iii) 0.010, depending on the scenario. Furthermore, 95 % coverage intervals for M are (i) [381.35, 381.41], (ii) [381.36, 381.39], or (iii) [381.38, 381.41]. Note that in the more informative scenarios, (ii) and (iii), the standard uncertainty is smaller and the coverage interval is shorter than in scenario (i).

6.3 Ammonium nitrate

The relative molecular mass of ammonium nitrate, NH_4NO_3, may be computed using at least two different methods, and the resulting evaluations of the associated measurement uncertainty also turn out different.

First, we assume that the atomic weights of hydrogen, nitrogen, and oxygen, are like independent random variables with rectangular distributions over the intervals that are their respective standard atomic weights.

Second, we take into account the fact that the industrial production of ammonium nitrate involves two different fractionation trajectories for the two nitrogen atoms in the molecule: the Haber-Bosch process produces ammonia; and the Ostwald process produces nitric acid [76]. When the ammonia reacts with nitric acid in a concentrated aqueous solution, the isotopic composition of the hydrogen equilibrates and is likely to end-up resembling the isotopic composition of naturally occurring fresh water.

The assumptions for this second approach are these: (i) hydrogen as in naturally occurring fresh water, with $\delta_{VSMOW}(^2H/^1H)$ ranging from −495 ‰ to +129 ‰ [24, table 1]; (ii) oxygen with same isotopic composition as in air, $\delta_{VSMOW,AIR}(^{18}O/^{16}O) = +23.88$ ‰; (iii) half of the nitrogen has isotope delta values in the same range as nitrogen in ammonium present in synthetic reagents and fertilizers, $\delta_{AIR,AMMONIUM}(^{15}N/^{14}N) = [-5, +11]$ ‰ [21]; and (iv) the other half of the nitrogen has the isotope delta values of nitrogen in nitrates from synthetic reagents and fertilizers, $\delta_{AIR,NITRATES}(^{15}N/^{14}N) = [-23, +15]$ ‰.

The results, where the uncertainties were evaluated by application of the Monte Carlo method of the GUM-S1 using samples of 1×10^6 replicates in each case, are these: for the first method, the standard relative molecular mass is 80.0438 with standard uncertainty 0.00087; and for the second method, the relative

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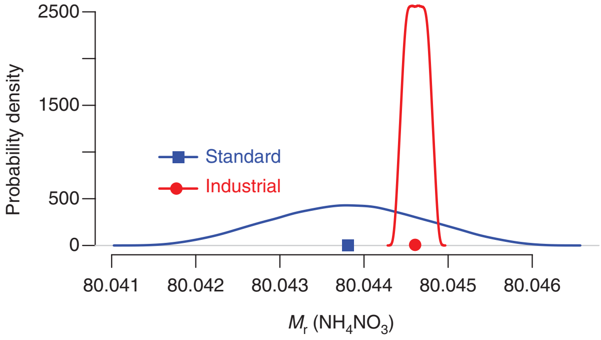

Fig. 5: Kernel estimates [63] of the probability density of the relative molecular mass of ammonium nitrate under two modeling scenarios. Both here and in Fig. 4, one of the probability densities is roughly bell-shaped, and one or more are roughly trapezoidal. The former tends to arise when there are multiple sources of uncertainty, that is, multiple elements in the compound, and they make comparable contributions to the uncertainty of the relative molecular mass. The latter emerges when the uncertainty of the relative molecular mass is dominated by two elements whose atomic weights effectively have rectangular distributions concentrated on fairly narrow ranges, similarly to the case of CO_2 illustrated in Fig. 3.

molecular mass of “industrial” ammonium nitrate is 80.0446 with standard uncertainty 0.00012. Even though the numerical difference between the last two estimates of the relative molecular mass is small, the corresponding probability distributions are strikingly different (Fig. 5).

6.4 Testosterone

Testosterone, with formula $C_{19}H_{28}O_2$, is a steroid hormone derived from cholesterol along natural biochemical pathways. Since synthetic testosterone is often synthesized from sterols obtained from soybean (*Glycine max*), which is significantly depleted in ^{13}C, its consumption is detectable based on differences in values of $\delta(^{13}C/^{12}C)$ of testosterone metabolites and metabolites of other endogenous steroidal hormones in urine [77].

Measurements of $\delta_{VPDB}(^{13}C/^{12}C)$ made by de la Torre *et al.* [78], in pharmaceuticals containing testosterone esters, had average –27.43 ‰ and standard deviation 76 ‰, while measurements in endogenous natural human testosterone and its main metabolites excreted into the urine in non-consumers of synthetic testosterone had $\delta_{VPDB}(^{13}C/^{12}C)$ values between –24.4 ‰ and –21.3 ‰. Determinations of testosterone and related compounds made by Munton *et al.* [79] are generally consistent with those values.

Even though discrimination between natural and synthetic testosterone is based on the examination of $\delta_{VPDB}(^{13}C/^{12}C)$ values [78], here we illustrate how the aforementioned differences produce easily perceptible differences between the relative molecular mass of synthetic ($M_S = M_{r,SYNTHETIC}$(TESTOSTERONE)) and endogenous human ($M_H = M_{r,HUMAN}$(TESTOSTERONE)) testosterone, and evaluate the associated uncertainties. For this purpose, we define the random variables $M_S = 19A_{r,S}(C) + 28A_r(H) + 2A_r(O)$ and $M_H = 19A_{r,H}(C) + 28A_r(H) + 2A_r(O)$, where $A_{r,S}(C)$, $A_{r,H}(C)$, $A_r(H)$ and $A_r(O)$ denote independent random variables. The first two represent the atomic weights of carbon in synthetic and human testosterone, and the last two represent the atomic weights of hydrogen and oxygen in seawater [21, tables 3, 17].

The distributions of these random variables are determined using the Monte Carlo method, similarly to how it was applied in preceding examples. All of these distributions recognize and express the uncertainty of the atomic weights of the relevant isotopes, and the uncertainty of their amount fractions.

For hydrogen and oxygen, uniform distributions were assigned to their delta values in seawater: [–2.5 ‰, +3.2 ‰] for hydrogen, and [–1 ‰, +6 ‰] for oxygen [21, tables 3, 17]. For carbon in synthetic testosterone, the delta value was modeled as a Gaussian random variable with mean $\delta_{VPDB}(^{13}C/^{12}C) = -27.43$ ‰ and standard deviation 0.76 ‰. For carbon in human testosterone, the delta value was modeled as uniformly distributed between –24.4 ‰ and –21.3 ‰.

Figure 6 depicts the probability densities of M_S and of M_H, and indicates the corresponding mean values: 288.4279 for the synthetic testosterone and 288.4289 for the human testosterone. The 95 % coverage intervals

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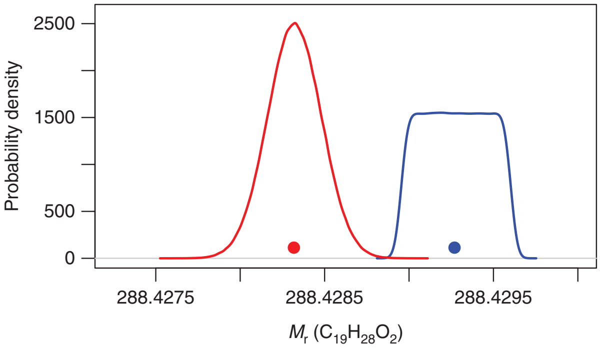

Fig. 6: Probability densities of the relative molecular mass of human (trapezoidal blue line) and synthetic (bell-shaped red line) testosterone, and corresponding averages (blue and red dots).

derived from samples of size 10^7 drawn from the probability distributions of M_S and of M_H are [288.4273, 288.4285] for the synthetic testosterone, and [288.4282, 288.4295] for the human testosterone.

7 Mixtures of molecules

In many calculations, the relative molecular masses of multiple components in a mixture need to be considered simultaneously. These relative molecular masses are often calculated based on the standard atomic weights and the stoichiometry of the molecules involved. Once the standard atomic weights are modeled probabilistically, the atomic weights of molecules with common elements become dependent random variables, possibly with quite strong correlations [27], and their joint distribution is not necessarily multivariate Gaussian.

Since the relative molecular masses are linear functions of the atomic weights, matrix algebra as employed in the GUM-S2 facilitates the evaluation of standard measurement uncertainty in closed form, taking into account those correlations. To characterize the corresponding joint probability distributions fully, however, requires application of the Monte Carlo method for multivariate quantities, as described in the GUM-S2.

The (column) vector $\boldsymbol{M}$ whose elements are the relative molecular masses of the N_c components in the mixture, can be related to the (column) vector $\boldsymbol{A}$ whose elements are the atomic weights of the N_e constituent elements of those components as $\boldsymbol{M}=\boldsymbol{\nu}\boldsymbol{A}$. The entries of the $N_c \times N_e$ matrix $\boldsymbol{\nu}$ are the stoichiometric numbers: ν_{ij}, in row i and column j, indicates the number of atoms of element j that appear in each molecule of component i in the mixture. For the $N_c=8$ principal components of a typical natural gas listed in Table 3, the matrix $\boldsymbol{\nu}$ is

$$\begin{array}{c|cccc|}
 & \mathrm{H} & \mathrm{C} & \mathrm{N} & \mathrm{O} \\
\mathrm{CH_4} & 4 & 1 & 0 & 0 \\
\mathrm{C_2H_6} & 6 & 2 & 0 & 0 \\
\mathrm{C_3H_8} & 8 & 3 & 0 & 0 \\
\mathrm{C_4H_{10}} & 10 & 4 & 0 & 0 \\
\mathrm{C_5H_{12}} & 12 & 5 & 0 & 0 \\
\mathrm{N_2} & 0 & 0 & 2 & 0 \\
\mathrm{CO_2} & 0 & 1 & 0 & 2 \\
\mathrm{O_2} & 0 & 0 & 0 & 2
\end{array}$$

The covariance matrix associated with $\boldsymbol{M}$ is obtained by applying the law of propagation of uncertainty from the GUM-S2 to $\boldsymbol{M}=\boldsymbol{\nu}\boldsymbol{A}$, which yields $\boldsymbol{U}(\boldsymbol{M})=\boldsymbol{\nu}\boldsymbol{U}(\boldsymbol{A})\boldsymbol{\nu}^{\mathrm{T}}$, where $\boldsymbol{\nu}^{\mathrm{T}}$ denotes the transpose of $\boldsymbol{\nu}$, and $\boldsymbol{U}(\boldsymbol{A})=\mathrm{diag}\{u^2(A_1),\, u^2(A_2),\ldots,u^2(A_{N_e})\}$ denotes the covariance matrix associated with $\boldsymbol{A}$, on the reasonable

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Table 3: Correlation matrix of the standard relative molecular masses of select substances in natural gas.

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	N_2	CO_2	O_2
CH_4	1.000	0.994	0.989	0.986	0.984	0.000	0.707	0.000
C_2H_6	0.994	1.000	0.999	0.998	0.997	0.000	0.745	0.000
C_3H_8	0.989	0.999	1.000	1.000	0.999	0.000	0.756	0.000
C_4H_{10}	0.986	0.998	1.000	1.000	1.000	0.000	0.762	0.000
C_5H_{12}	0.984	0.997	0.999	1.000	1.000	0.000	0.765	0.000
N_2	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
CO_2	0.707	0.745	0.756	0.762	0.765	0.000	1.000	0.595
O_2	0.000	0.000	0.000	0.000	0.000	0.000	0.595	1.000

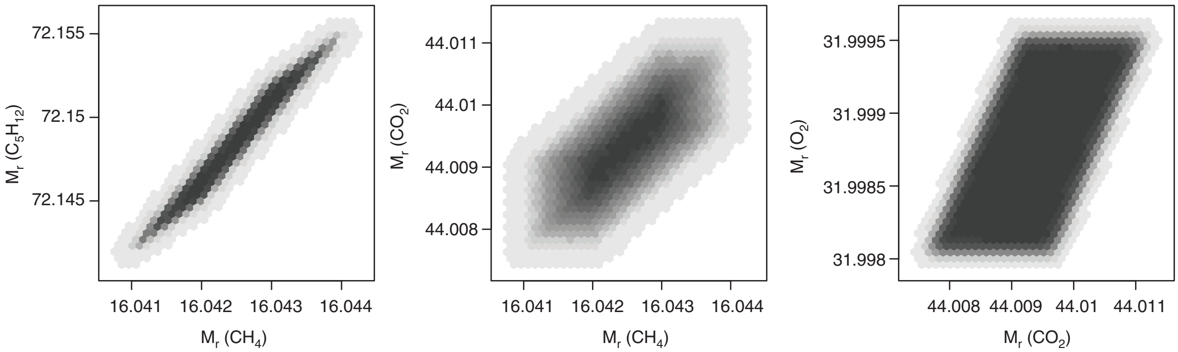

Fig. 7: Bivariate joint probability densities for the relative molecular masses of pairs of selected molecules depicted using hexagon bin smoothing [80]: the darker the shade of gray, the higher the density. The corresponding correlation coefficients are: 0.984 between methane and pentane; 0.707 between methane and carbon dioxide; and 0.595 between carbon dioxide and oxygen.

assumption that the random variables that model the uncertainty of the atomic weights of the different elements are uncorrelated.

The entries of the $N_c \times N_c$ correlation matrix $\boldsymbol{R}(\boldsymbol{M})$ corresponding to the covariance matrix are the correlation coefficients between pairs of relative molecular masses of components in the mixture. These coefficients describe the linear association between the relative molecular masses of the components, and are computed as $R_{ij}(\boldsymbol{M}) = U_{ij}(\boldsymbol{M}) / \sqrt{U_{ii}(\boldsymbol{M})U_{jj}(\boldsymbol{M})}$ for $i, j = 1, \ldots, N_c$. Table 3 shows $\boldsymbol{R}(\boldsymbol{M})$ for the relative molecular masses of the $N_c = 8$ principal components of a typical natural gas, and Fig. 7 illustrates three bivariate margins of the joint, multivariate distribution of these relative molecular masses, computed under the assumption that the random variables modeling the atomic weights of H, C, N, and O are independent and have uniform (or, rectangular) distributions on the ranges of their standard atomic weight intervals.

8 Conclusions

The assignment of probability distributions to the values between the endpoints of the intervals that represent the standard atomic weights of the elements in “normal” materials, is consistent with the definition of standard atomic weights that the CIAAW has adopted. It is also a necessary step to use such intervals in subsequent calculations, for example of relative molecular masses and of chemical compositions expressed in terms of amounts-of-substance.

Such probability distributions generally do not aim to describe the natural abundances of the atomic weights in “normal” materials. Instead, they convey what is known about the dispersion of the atomic

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weights, either in all "normal" materials generally, or in specific materials. To this extent, these distributions characterize both the knowledge about the natural variability and the measurement uncertainty, and may be used in uncertainty propagation exercises.

If the knowledge in hand is no greater than what a standard atomic weight – for example [12.0096, 12.0116] for carbon – already expresses, then a rectangular distribution should be used by default. The corresponding evaluation of uncertainty may be conservative (that is, it may be larger than it could be if more information were used), yet it serves the very general purpose of characterizing uncertainty for uncertainty calculations that do not require the utmost precision in the values of the atomic weights.

If specific information is available about the isotopic composition of the material of interest (say, because its provenance is known, or because its isotopic composition was determined experimentally), then the uncertainty associated with the corresponding value of the atomic weight may be substantially smaller than what the rectangular distribution on the standard atomic weight interval implies.

For example, we have shown that the atomic weight of boron in materials derived from its principal commercial sources is appreciably less variable than what its standard atomic weight suggests. We have also shown that the rectangular distribution generally will not be the best summary of the dispersion of the atomic weight values for materials from such sources, and we provided a procedure to characterize the associated uncertainty in such cases. Lithium provides an even more striking illustration of the role that *a priori* knowledge about the provenance of a material may have on the atomic weight of a particular element in that material, as illustrated (in §3) by the case of ground water in West Valley Creek in Pennsylvania (USA).

In some cases, a probability density from a particular parametric family of densities (for example, a scaled and shifted beta distribution, or a mixture of Gaussian distributions, among many other possibilities) may be adequate succinctly to describe the available knowledge. The usual indications of location and spread (for example, means and standard deviations) of these distributions may also be used in estimates of quantities that are functions of atomic weights, and in the characterization of the associated uncertainties when applying the conventional law of propagation of uncertainty from the GUM.

The evaluation of the uncertainty associated with relative molecular masses of compounds depends on the preliminary evaluation of uncertainties for the participating elements. In the case of mixtures, that evaluation needs to take into account the correlations caused by the presence of the same elements in different components of the mixture, which we illustrated in an example involving natural gas. However, even in the case of compounds as simple as carbon dioxide or ammonium nitrate, taking into account the provenance of the elements in the compounds, or the possibly different fractionation processes that different atoms of the same element may have undergone until they are finally conjoined in the compound of interest, can be influential in the evaluation of uncertainty for the relative molecular mass of the selected compound.

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