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IUPAC Technical Report

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Interpretation and use of standard atomic weights (IUPAC Technical Report)

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Abstract: Many calculations for science or trade require the evaluation and propagation of measurement uncertainty. Although relative atomic masses (standard atomic weights) of elements in normal terrestrial materials and chemicals are widely used in science, the uncertainties associated with these values are not well understood. In this technical report, guidelines for the use of standard atomic weights are given. This use involves the derivation of a value and a standard uncertainty from a standard atomic weight, which is explained in accordance with the requirements of the Guide to the Expression of Uncertainty in Measurement. Both the use of standard atomic weights with the law of propagation of uncertainty and the Monte Carlo method are described. Furthermore, methods are provided for calculating uncertainties of relative molecular masses of substances and their mixtures. Methods are also outlined to compute material-specific atomic weights whose associated uncertainty may be smaller than the uncertainty associated with the standard atomic weights.

Keywords: Atomic weights; atomic-weight intervals; molecular weight; relative atomic mass; relative molecular mass; standard atomic weight; uncertainty; uncertainty propagation.

CONTENTS

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1 Introduction

Relative atomic masses (also known as atomic weights) provide a practical link between the base units kilogram and mole in the SI, the International System of units. For every substance or mixture of substances, the conversion between mass and amount of substance (also known as chemical amount) can be carried out once the relative molecular mass (also known as molecular weight) has been determined. In this paper, the terminology used in the reports on the standard atomic weights as published by the Commission on Isotopic Abundances and Atomic Weights (CIAAW, www.ciaaw.org) of the International Union of Pure and Applied Chemistry (IUPAC) is used for the benefit of the reader who uses this Technical Report to interpret those reports when using atomic weight data in scientific and metrological calculations.

The standard atomic weights play a key role in these calculations. Their values are regularly evaluated and published by the CIAAW. The work undertaken by the CIAAW to keep the standard atomic weights up-to-date deals broadly with two aspects: the appreciation of improved measurements of isotopic composition of the elements, and the improved knowledge about natural variations of the isotopic composition of the elements in materials [1]. In 2009, the CIAAW resolved to disseminate standard atomic weights of elements using either of two different notations [2]:

(1) parenthetic notation giving a single value followed by an expanded uncertainty between parentheses applicable to the last quoted digit of that value, e.g., $A_r(\mathrm{Cd}) = 112.414(4)$, and
(2) interval notation, e.g., $A_r(\mathrm{C}) = [12.0096, 12.0116]$, representing the interval of atomic-weight values of these elements found in normal terrestrial materials [3].

Until 2009, the CIAAW only used the parenthetic notation, with the expanded uncertainty meant to cover the natural variability of isotopic compositions of normal materials, as well as the uncertainty surrounding the determination of these compositions [4]. Starting from 2009 [2], the CIAAW embarked on systematic evaluations of variations in the isotopic composition of selected elements, and, for those elements whose variations in isotopic composition dominate the uncertainty associated with their atomic weights, it adopted the interval notation. At the time of writing this Technical Report, the process of introducing the interval notation for elements whose isotopic composition varies appreciably in nature was not complete. In 2009 [2], this notation was introduced for the following ten elements: hydrogen, lithium, boron, carbon, nitrogen, oxygen, silicon, sulfur, chlorine, and thallium. In 2011 [5], the standard atomic weights of bromine and magnesium were also given in interval notation. There are, however, elements with the parenthetic notation whose isotopic composition varies appreciably in nature [6].

The expanded uncertainty used in the parenthetic notation is to be understood so that, for example, the atomic weight of cadmium in any normal material is practically certain to lie inside the interval [112.410, 112.418]. Likewise, the atomic weight of carbon in any terrestrial material is practically certain to lie inside the interval [12.0096, 12.0116]. The interval notation does not provide any information about the best value of the standard atomic weight, other than that it lies within the atomic-weight interval. While the interval notation was conceived to emphasize that natural variation in isotopic composition is the dominant component in the uncertainty of the atomic weight values of the elements for which it has been adopted, for many users it is unclear how to employ the given intervals in calculations and uncertainty evaluations. At the same time, it aimed to de-emphasise the centre of the interval as being the best estimate of the standard atomic weight [2]. For example, the midpoint of the interval for lithium [6.938, 6.997] would be a rather exceptional value for the atomic weight of lithium in any normal material: in fact, most normal, natural materials will have lithium whose atomic weight is close to the left endpoint of the interval, and only compounds artificially depleted in $^{6}\mathrm{Li}$ that have been leaked into the environment account for the right endpoint of the interval.

This Technical Report provides a basis for understanding the standard atomic weights and their uncertainties so that users can readily employ them in a variety of calculations. The guidance provided is aimed at users for which a simple interpretation of the standard atomic weights suffices, as the application does not warrant a more sophisticated treatment, as given in [7]. The contents of this Technical Report are in agreement with these more advanced treatments. In most instances, the guidance is directed at users who are satisfied with a simple probabilistic interpretation of the standard atomic weights, which provides a single value and uncertainty for an element in any normal material. This kind of uncertainty evaluation is described in the Guide to the expression of uncertainty in measurement (GUM) [8] as "type B evaluation of standard uncertainty", and involves the assignment of an appropriate probability density function to the information at hand. The value and uncertainty obtained by this uncertainty evaluation can then be used in an uncertainty evaluation as described in the GUM [8]. Similarly, using the probability density function assigned to the standard atomic weight, it can also be used in the Monte Carlo methods from GUM Supplements 1 and 2 [9, 10]. The computations are illustrated by informative examples to facilitate their implementation in practice, in software, or in quality control documents, among other applications.

This Technical Report aims to help users of the standard atomic weights propagate the associated uncertainties in cases (which are the most common in practice) where these uncertainties make but minor contributions to the uncertainties of the quantities of primary interest, for example in conversions of mass concentrations into amount concentrations, and in the computation of amount fractions in the gravimetric preparation of synthetic mixtures [11]. For more demanding applications, where the uncertainties of atomic weights make a substantial contribution to the overall measurement uncertainty, a more advanced treatment is warranted, which is provided in another IUPAC Technical Report [7] that provides a more in-depth treatment of the subject. The guidance discusses how, based on the information provided by the CIAAW, representative atomic weights can be derived for materials or groups of materials, including the evaluation of measurement uncertainty. It also illustrates the use of these representative atomic weights in a variety of applications.

The authors wish to emphasise that any calculations involving atomic weights, and standard atomic weights in particular, should always be performed with the most recent values for the (standard) atomic weights.[1] Throughout this Technical Report, the standard atomic weights of 2013 [6] are used.

2 Notational conventions

The following notational conventions [7] have been adopted, which are generally consistent with the guidance provided in the IUPAC *Green Book* [12]. 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 [13] provides little guidance on the notational aspects of isotope ratios. The choices outlined herein have been formed after consultation with the IUPAC Interdivisional Committee on Terminology, Nomenclature and Symbols (ICTNS). When parentheses and subscripts are both used to qualify the quantity, as is often done to express the results of isotope measurements, the super- and subscripts are placed immediately after the quantity symbol to which it refers (as is customary in other well-known cases, such as $t_{1/2}(^{235}\mathrm{U})$ to denote the half-life of uranium-235).

- $A_{\mathrm{r,P}}(\mathrm{E})$ denotes the relative atomic mass (also known as atomic weight) of element E in material P. For example, $A_{\mathrm{r,SEAWATER}}(\mathrm{B})$ denotes the atomic weight of boron in seawater.
- $A_{\mathrm{r}}(\mathrm{E})$ denotes the atomic weight of an element or isotope E disregarding the provenance of the element, effectively averaged over all "normal materials". For example, $A_{\mathrm{r}}(\mathrm{H}) = [1.007\,84, 1.008\,11]$, and $A_{\mathrm{r}}(\mathrm{Mo}) = 95.95(1)$ [6]. When E designates an isotope, $A_{\mathrm{r}}(\mathrm{E})$ is invariant across all materials. For example, $A_{\mathrm{r}}(^{16}\mathrm{O}) = 15.994\,914\,619\,60(17)$ [14, Table A].
- $M_{\mathrm{r,P}}(\mathrm{S})$ denotes the relative molecular mass (also known as molecular weight) of substance S as it occurs in material P. The subscript P generally may be any string that denotes the relevant material.
- $M_{\mathrm{r}}(\mathrm{S})$ denotes the relative molecular weight of substance S disregarding the provenance of the material containing the substance.

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[1] Available at www.ciaaw.org.

- $x_\mathrm{P}(\mathrm{S})$ denotes the amount fraction of substance S in material P, where S may be a molecule, element, or isotope.
- $w_\mathrm{P}(\mathrm{S})$ denotes the mass fraction of substance S in material P, where S may be a molecule, element, or isotope.
- $N_\mathrm{P}(\mathrm{S})$ denotes the number of elementary entities S in material P.
- $R_\mathrm{P}(^{i}\mathrm{E}/^{j}\mathrm{E})$ denotes the isotope-number ratio (also called isotope ratio) for isotopes $^{i}\mathrm{E}$ and $^{j}\mathrm{E}$ in material P: that is, $N_\mathrm{P}(^{i}\mathrm{E})/N_\mathrm{P}(^{j}\mathrm{E})$.
- The delta value $\delta_{\mathrm{STD,P}}(^{i}\mathrm{E}/^{j}\mathrm{E})$ 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: $\delta_{\mathrm{STD,P}}(^{i}\mathrm{E}/^{j}\mathrm{E}) = R_\mathrm{P}(^{i}\mathrm{E}/^{j}\mathrm{E})/R_\mathrm{STD}(^{i}\mathrm{E}/^{j}\mathrm{E}) - 1$.

Note that, in the notation that we adopt, the first (or only) subscript affecting the Greek letter δ designates the isotopic standard or reference. For example, $\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B}/^{10}\mathrm{B}) = +39.5$ ‰ means that the isotope ratio $R_\mathrm{SEAWATER}(^{11}\mathrm{B}/^{10}\mathrm{B})$ 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, $\delta_{\mathrm{SRM951,SEAWATER}}(^{11}\mathrm{B})$.

3 Terms and definitions

1 relative atomic mass

atomic weight, $A_\mathrm{r}(\mathrm{E})$

Ratio of the average mass of atoms of an element to the unified atomic mass unit [12, p. 47].

Note: While atomic mass is a property of an individual atom (which can be of any one of the isotopes of the element E), the atomic weight (relative atomic mass) refers to the amount-fraction weighted average mass of allatoms of element E in a sample divided by the atomic mass unit.

2 normal material

All substances, except (1) those subjected to substantial deliberate, undisclosed, or inadvertent artificial isotopic modification, (2) extraterrestrial materials, and (3) isotopically anomalous specimens, such as natural nuclear reactor products from Oklo (Gabon) or other unique occurrences [15].

3 standard atomic weight

Recommended values of relative atomic masses of the elements revised biennially by the CIAAW and applicable to elements in any normal material with a high level of confidence.

4 relative molecular mass

molecular weight

Ratio of the mass of molecules of a substance to the unified atomic mass unit [16, p. 1283].

Note: When referring to a heterogeneous mixture of molecules, such as polymers, the term "molecular weight" becomes ambiguous and one has to specify the type of averaging employed. This gives rise to quantities such as number-average molecular weight, weight-average molecular weight, or z-average molecular weight [17].

5 standard molecular weight

Molecular weight calculated using the standard atomic weights of its constituent elements.

6 representative atomic weight

Relative atomic mass of an element in a well-characterised material, or group of materials, corresponding to a typical isotopic composition of the element in nature.

Note: In CIAAW reports, representative atomic weights are provided for elements whose standard atomic weight is given in interval notation [6]. For example, the representative atomic weight of oxygen in seawater is $A_{\mathrm{r,SEAWATER}}(\mathrm{O})$ = [15.999 300 3, 15.999 307 2].

7 representative relative molecular mass

representative molecular weight

Relative molecular mass (molecular weight) of a substance or mixture of substances in a class of materials whose range of compositions and range of isotopic compositions is well-characterised, corresponding to a typical material within that class.

4 Standard atomic weights

Many forms of notation have been employed over the years to express standard atomic weights [18, 19]. The CIAAW currently employs two notations: the single-value parenthetic notation, with the explicit expanded uncertainty given in parenthesis, and the two-value interval notation, with no uncertainty given explicitly [2]. The atomic-weight interval is characterised by a lower limit, a, and an upper limit, b, whereas the parenthetic notation of the standard atomic weight provides a single value and the associated expanded uncertainty (see Table 1).

It is important to stress that neither of these notations alters the meaning of the quantity, and that both summarise the CIAAW decision to express the standard atomic weight of an element using two values – either with an upper and lower bound or with the single representative value and its uncertainty. The two notations do, however, provide different information about the quantity; the interval notation provides the end points of the coverage interval, thereby leaving open what the "best" value is [2], whereas the parenthetic notation provides the "best" value and the half-width of the interval [4]. For both notations, the assurance is given that the atomic-weight values of elements in normal materials are expected to lie between the end-points of the interval given explicitly, or within the interval corresponding to the representative value plus/minus the quoted uncertainty (unless indicated otherwise with the footnotes accompanying the standard atomic weights) [6, Table 1].

Standard atomic weights and their uncertainties are determined by the CIAAW [2]. In the process leading to determinations of these standard atomic weights, all published data concerning the isotopic compositions of "normal materials" for each element [20, 21] are evaluated, and a value with an indication of the uncertainty, or an atomic-weight interval is established [22]. In this process, the uncertainty is attributable to (1) variations in the isotopic composition of the element in normal materials, (2) the uncertainty about the isotopic composition, and (3) the uncertainty about the masses of the isotopes [2]. In principle, the user can take the standard atomic weights as provided the CIAAW, without further consideration of what gave rise to the uncertainty reflected in the data. However, these considerations become relevant if the uncertainty of the standard atomic weight, at the discretion of the user, is deemed to be too large for the case at hand. If that is the case, a representative atomic weight should be obtained instead (see example 5 and [7]).

Unless interval arithmetic is employed (see, for a discussion, [7]), the majority of scientific calculations require a single, representative value of the quantity and its associated uncertainty. Extracting an appropriate single "best value" and a corresponding indication of associated uncertainty from a standard atomic weight involves assignment of a probability distribution that explicitly or implicitly represents the state-of-knowledge about the standard atomic weight in the material(s) of interest [8, 9].

The best value of the atomic weight may be the mean (mathematical expectation, or expected value) of that distribution, and the indication of associated uncertainty may be the corresponding standard deviation (standard uncertainty) [8]. However, and most importantly, the expected value does not necessarily represent the "most-likely" value, or mode, of that probability distribution, which is the value where the corresponding probability density function achieves a maximum. In general, the mode and the expected value of a probability distribution differ.

In the table of standard atomic weights of 2007, the standard atomic weight of oxygen is listed as $A_r(\mathrm{O}) = 15.9994(3)$ [4], which should be interpreted as having an atomic weight with value 15.9994 and an expanded uncertainty of 0.0003. The GUM [8, clause 7.2.2] recommends using the parenthetic notation, such as $A_r(\mathrm{Ir}) = 192.217(3)$, to express standard uncertainty; the number in parentheses is the numerical value of the standard uncertainty referred to the corresponding last digit(s) of the quoted value. In these guidelines however, the conventions of the CIAAW are followed, which is consistent with the explanation in the *Green Book* [12, section 8.3].

As of 2009 [2], the standard atomic weight of oxygen has been stated as $A_r(\mathrm{O}) = [15.999\,03, 15.999\,77]$. In this notation, both the estimate and uncertainty depend on the probability distribution assigned to the standard atomic-weight interval as part of the type B evaluation of standard uncertainty. The distinction between the two notations serves to emphasise, that for some elements (e.g., hydrogen or oxygen), the atomic-weight values vary significantly in nature between materials (and these variations are well documented by the CIAAW), whereas for other elements our knowledge about the atomic weights is limited mainly by the uncertainty about the nuclide masses (e.g., tantalum or lanthanum) as adopted by the CIAAW or by their isotopic compositions (e.g., platinum).

5 Probabilistic interpretation of standard atomic weights

The concept of measurement uncertainty applies not only to quantities whose values are determined experimentally, but also to all derived quantities whose calculation involves experimental data. The GUM [8] and its supplements [9, 10] provide a harmonised basis for evaluating measurement uncertainty. The concept of "measurement uncertainty" conveys the notion that a margin of doubt about the true value of a quantity remains after measurement and the recognition that the knowledge about this true value is imperfect or incomplete. If an isotopic composition of an element in a material has not been directly determined by measurement, information about the material may still enable the assignment of a value to the isotopic composition along with an associated standard uncertainty for use in calculations. Such assessment leads to greater uncertainties than in situations in which accurate isotopic composition data are at hand.

Application of the law of propagation of uncertainty to obtain the standard uncertainty of an output quantity (such as a molecular weight) requires values and standard uncertainties for the input quantities (such as atomic weights). In the GUM [8], information about input quantities is modelled by means of probability distributions. The Monte Carlo methods of GUM Supplements 1 and 2 [9, 10] use the probability distributions assigned to the input quantities to produce a sample from the probability distribution of the output quantity. Usually, such probability distributions do not aim to depict the variability of the quantity values in different materials; rather, these distributions encapsulate the lack of knowledge about the true value of the quantity.

In the wording of clause 4.3.7 of the GUM [8], the case of a standard atomic weight can be interpreted as follows. The probability that the value of $A_r(\mathrm{E})$ for some element E lies within the interval from a to b is practically 100 %, and the probability that $A_r(\mathrm{E})$ lies outside this interval is practically zero. If there is no specific knowledge about the possible values of $A_r(\mathrm{E})$ within the interval, one can only assume that it is equally probable for values of $A_r(\mathrm{E})$ to lie anywhere within it, and therefore be described by a uniform (rectangular) distribution of all possible values. This description is well-aligned with the efforts by the CIAAW to establish with great care the endpoints of the atomic-weight interval, or the interval given by a value with the uncertainty between parenthesis for the standard atomic weight [2, 6]. Clause 4.3.7 in the GUM [8] explains why the rectangular distribution is an appropriate representation for the uncertainty associated with the standard atomic weights when there is no specific knowledge about the isotopic composition of the material of interest. In fact, the use of standard atomic weight implicitly conveys ignorance about the specific provenance or isotopic composition of the material. Because standard atomic weights are “equally applicable to all normal materials”, one can assume that it is equally probable for atomic-weight values to lie anywhere within the quoted interval, thereby giving no preference to any particular material. When specific knowledge is available about the isotopic composition of the material, the use of other distributions may be more appropriate [7]. For example, someone who knows, even without measuring it, that the atomic weight of the lithium in a spodumene from the Black Hills of South Dakota, in the United States, will be far to the left of the midpoint of the standard atomic weight of lithium, should assign a distribution to it other than the rectangular distribution. Likewise, the standard atomic weight interval and its midpoint is not a good choice when one is interested in the atomic weight of argon in air.

This Technical Report recommends interpreting the standard atomic weight probabilistically under the assumption that the only information to hand is what the corresponding interval conveys[2]. In this conformity, the user of a standard atomic weight is not required to seek a better (a more accurate) interpretation by taking further information into consideration. The rectangular distribution assigns the same probability density to all values within the standard atomic weight, thus giving no preference to any value in particular for the standard atomic weight. It is up to the user of the standard atomic weight to decide whether the approach is acceptable in view of the use of the atomic weight in a calculation or measurement. The approach described in this paper is aimed at those applications of atomic weights where the standard atomic weights suffice, and their uncertainties play a minor role in the application in which they are used.

Under the conditions outlined, all standard atomic weights are assigned the rectangular distribution representing a most simplified representation of the state-of-knowledge about them [2, 4]. If $A_\mathrm{r}(\mathrm{E})$ is expressed using the interval notation $[a, b]$, then a and b will be the endpoints of the rectangular distribution. The value of the atomic weight is then given by [8]:

$$A_\mathrm{r}(\mathrm{E}) = \frac{a+b}{2} \tag{1}$$

which is the mean of the rectangular distribution, and with associated standard uncertainty

$$u(A_\mathrm{r}(\mathrm{E})) = \frac{b-a}{2\sqrt{3}} \tag{2}$$

which is the standard deviation of the rectangular distribution.

In the parenthetic notation $A_\mathrm{r}(\mathrm{Mo}) = 95.95(1)$ [6], it is understood that the estimate of the true value is 95.95 and the number in parentheses is the value of the half-width of the interval referred to the corresponding last digit of the quoted value [2, 4]. In this example, the half-width of the interval is 0.01 and hence the standard uncertainty is $0.01/\sqrt{3} = 0.006$.

This simplistic interpretation of standard atomic weights, where the midpoint of the standard atomic weight interval is taken as the recommended estimate of the true value, does not imply that the natural variations of the atomic weight are necessarily symmetric for most normal materials [23] (lithium and argon, for example). The approach serves solely the purpose of ensuring that the uncertainty about the atomic weight is evaluated in accordance with the GUM [8] and its supplements [9, 10], and is duly propagated when used.

6 Examples of obtaining atomic weights

Performing calculations involving the atomic weights requires that, at a minimum, they should be assigned a single representative numerical value (for example, the mean or mathematical expectation of the probability distribution associated with the input) along with the associated standard uncertainty, and ideally that their

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[2] This recommendation was endorsed by the CIAAW in 2015 (*Chem. Intl.* 2015, 37(5–6), p. 26, https://doi.org/10.1515/ci-2015-0512).

associated uncertainties be represented by fully specified probability distributions. In this section, examples are given of how to obtain such representative values from the standard atomic weights.

Example 1: Standard atomic weight

Standard atomic weights are used for normal materials disregarding any specific knowledge about their origin or isotopic composition. To illustrate the use of standard atomic weights, example calculations are given for carbon and molybdenum in Table 1, using equations (1) and (2). The value for the atomic weight of carbon is calculated as (12.0096 + 12.0116)/2 = 12.0106 and the standard uncertainty as $(12.0116-12.0096)/(2\sqrt{3})=0.0006$. For molybdenum, the value of the standard atomic weight is 95.95 and the standard uncertainty is computed as $0.01/\sqrt{3}=0.006$.

From Eq. 2 it follows that the ratio of the full range of the rectangular distribution and the standard uncertainty is $1/\sqrt{12}$. In the parenthetic notation employed by the CIAAW, the number in parenthesis denotes the expanded uncertainty, i.e., the half-width of the rectangular distribution. Hence, the conversion factor is $1/\sqrt{3}$ (recalling that $\sqrt{12}=2\sqrt{3}$).

Table 1: Standard atomic weights of carbon and molybdenum and their interpretation.

Variable	Standard atomic weight	Assigned probability distribution	Value	Standard uncertainty
$A_r(\mathrm{C})$	[12.0096, 12.0116]	Rectangular distribution	12.0106	0.0006
$A_r(\mathrm{Mo})$	95.95(1)	Rectangular distribution	95.95	0.006

Example 2: Representative atomic weight

There are cases when the uncertainty of a standard atomic weight is too large in the sense that this uncertainty component becomes dominant in the calculation in which the standard atomic weight were used. In such cases, it may be possible to reduce the uncertainty of the atomic weight if the origin of the material is known. An atomic weight that is appropriate for a particular material, or group of materials, is called a representative atomic weight. For many elements, the CIAAW provides detailed information about the atomic weights of elements in various materials [6, 24]. It is important to review critically the appropriateness of the assigned provenance when using representative atomic weights. As an example, Table 2 shows the representative atomic weights of oxygen in two sources. The calculations are analogous to those shown in example 1 for the standard atomic weight of carbon.

The representative atomic weight for oxygen in atmospheric CO is calculated as (15.999 28 + 15.999 37)/2 = 15.999 32 and its standard uncertainty as $(15.999\,37-15.999\,28)/(2\sqrt{3})=0.000\,03$. Likewise, the representative atomic weight for oxygen in atmospheric CO_2 is calculated as (15.999 46 + 15.999 52)/2 = 15.999 49 and its standard uncertainty as $(15.999\,52-15.999\,46)/(2\sqrt{3})=0.000\,02$.

Table 2: Representative atomic weights of oxygen in two different sources and their interpretation.

Source	Representative atomic weight of oxygen	Assigned probability distribution	Value	Standard uncertainty
CO in air	[15.999 28, 15.999 37]	Rectangular distribution	15.999 32	0.000 03
CO_2 in air	[15.999 46, 15.999 52]	Rectangular distribution	15.999 49	0.000 02

Table 3: Representative atomic weights of boron in two materials from specific sources.

Source, P	Isotope delta, $\delta_{\mathrm{SRM951,\,P}}(^{11}B)$	Atomic-weight value, $A_{\mathrm{r,P}}(\mathrm{B})$	Standard uncertainty, $u(A_{\mathrm{r,P}}(\mathrm{B}))$
Seawater	39.9(1) ‰	10.817 88	0.000 07
Borax from Turkey	−4.1(4) ‰	10.811 10	0.000 09

Example 3: Atomic weight of boron in specific samples

When the isotopic composition of an element in a specific material is known, the atomic weight can be calculated directly from this information. Isotopic reference materials fall into this category of materials. Often, isotopic composition is measured relative to a standard and is expressed as an isotope delta value [6]. For an element E with isotopes ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$ in material P, isotope delta against the standard (STD) is given as follows:

$$\delta_{\mathrm{STD,P}}\left({}^{i}\mathrm{E}\right) = \frac{R_{\mathrm{P}}\left({}^{i}\mathrm{E}/{}^{j}\mathrm{E}\right)}{R_{\mathrm{STD}}\left({}^{i}\mathrm{E}/{}^{j}\mathrm{E}\right)} - 1 \tag{3}$$

where $R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})$ denotes the isotope amount ratio, $n({}^{i}\mathrm{E})/n({}^{j}\mathrm{E})$. For boron, most isotope delta measurements are performed against NIST SRM 951 boric acid standard, which has isotope ratio of boron, $R_{\mathrm{SRM951}}({}^{11}\mathrm{B}/{}^{10}\mathrm{B}) = R_{\mathrm{SRM951}} = 4.0436(33)$, where the stated uncertainty is an expanded uncertainty with a coverage factor $k = 2$ [25]. From here, the delta value of boron in the sample P relative to NIST SRM 951 can be calculated from a measured boron isotope ratio in the material P, $R_{\mathrm{P}}({}^{11}\mathrm{B}/{}^{10}\mathrm{B}) = R_{\mathrm{P}}$, using equation (3), and then the atomic weight is obtained:

$$A_{\mathrm{r,P}}(\mathrm{B}) = \frac{A_{\mathrm{r}}\left({}^{10}\mathrm{B}\right) + A_{\mathrm{r}}({}^{11}\mathrm{B})\left(1 + \delta_{\mathrm{SRM951,P}}({}^{11}\mathrm{B})\right)R_{\mathrm{SRM951}}}{1 + \left(1 + \delta_{\mathrm{SRM951,P}}({}^{11}\mathrm{B})\right)R_{\mathrm{SRM951}}} \tag{4}$$

Here $A_{\mathrm{r}}(\mathrm{E})$ denotes the atomic weight of nuclide E [12, section 2.5]. Equation (4) is obtained by combining equation (3) with the expression below relating the atomic weight to isotope ratios:

$$A_{\mathrm{r,P}}(\mathrm{B}) = \frac{A_{\mathrm{r}}\left({}^{10}\mathrm{B}\right) + A_{\mathrm{r}}({}^{11}\mathrm{B})R_{\mathrm{P}}}{1 + R_{\mathrm{P}}} \tag{5}$$

The uncertainty of $A_{\mathrm{r,P}}(\mathrm{B})$ can be propagated from the standard uncertainties of the isotope delta value and that of the delta-zero standard. Assuming that the uncertainties arising from imperfect knowledge about the nuclide atomic weights are negligible,

$$u^2\left(A_{\mathrm{r,P}}(\mathrm{B})\right) = \Delta A_r^2(\mathrm{B}) \cdot \frac{R^2_{\mathrm{SRM951}} \cdot u^2\left(\delta_{\mathrm{SRM951,P}}({}^{11}\mathrm{B})\right) + \left(1 + \delta_{\mathrm{SRM951,P}}({}^{11}\mathrm{B})\right)^2 \cdot u^2(R_{\mathrm{SRM951}})}{\left(1 + R_{\mathrm{SRM951}}\left(1 + \delta_{\mathrm{SRM951,P}}({}^{11}\mathrm{B})\right)\right)^4} \tag{6}$$

where $\Delta A_{\mathrm{r}}(\mathrm{B}) = A_{\mathrm{r}}({}^{11}\mathrm{B}) - A_{\mathrm{r}}({}^{10}\mathrm{B})$. The atomic weights of the isotopes are $A_{\mathrm{r}}({}^{10}\mathrm{B}) = 10.012\,937\,1(3)$ and $A_{\mathrm{r}}({}^{11}\mathrm{B}) = 11.009\,305\,5(4)$ [26] (see Table 3).

7 Molecular weights

A common application of atomic weights is the calculation of molecular weights. These play an important role in relating the SI unit of mass (kilogram) to the SI unit of amount of substance (mole). The conversion between these two base units depends on the chemical substances involved. For a single component in a material or mixture, the molecular weight M_{r} is calculated from the atomic weights of the elements present in the molecule and the coefficients representing the atomic composition (ν_{E}) as

$$M_{\mathrm{r}} = \sum_{\mathrm{E}} \nu_{\mathrm{E}} A_{\mathrm{r}}(\mathrm{E}) \tag{7}$$

where $A_{\mathrm{r}}(\mathrm{E})$ denotes the atomic weight of element E and ν_{E} the atomic composition coefficient of element E in the molecular formula. The summation runs over all elements E present in the molecule. For example, ethanol (C_2H_6O) is composed of carbon, hydrogen, and oxygen with atomic composition coefficients 2, 6, and 1, respectively.

When calculating a standard molecular weight, that is a molecular weight calculated from the standard atomic weights, it is always appropriate to sum over the different elements. On the other hand, greater care should be exercised when using representative atomic weights. In that case, it can be necessary to treat occurrences of one element in the molecule differently. In an example demonstrating the calculation of the representative molecular weight of ammonium nitrate [7], NH_4NO_3, the two nitrogen atoms should be treated differently, because their isotopic composition is different. Thus, the molecular weight should be calculated as $M_r(NH_4NO_3) = A_r(N(NH_4)) + 4A_r(H) + A_r(N(NO_3)) + 3A_r(O)$, where $A_r(N(NH_4))$ denotes the representative atomic weight of nitrogen in ammonium and $A_r(N(NO_3))$ that of the nitrogen in nitrate.

Just as in the case of atomic weights, the measurement uncertainty associated with the molecular weight of a molecule can be evaluated using the law of propagation of uncertainty from the GUM [8] or the Monte Carlo method from the GUM Supplement 1 (GUM-S1) [9]. Applying the law of propagation of uncertainty to the expression for calculating the molecular weight, Eq. 7, yields the following:

$$u^2(M_r) = \sum_{E} \nu_E^2 u^2(A_r(E)) \tag{8}$$

where the correlation between pairs of atomic weights of elements is neglected.

Usually the uncertainty calculation for the molecular weight will be part of a larger calculation, such as the computation of the composition of a gravimetrically prepared mixture of gases [11, 27]. Whether the methods for calculating the measurement uncertainty associated with a molecular weight of this Technical Report are used, or those of the accompanying Technical Report with more advanced approaches [7], depends on the impact that the calculated uncertainties of the molecular weights have in the subsequent calculations.

8 Examples of obtaining molecular weights

In this section, illustrative examples are given for the computation of standard and representative molecular weights of ethanol.

Example 4: Standard molecular weight of ethanol

To illustrate the use of the equations for calculating the molecular weight, the standard molecular weight of ethanol (C_2H_5OH or C_2H_6O) is calculated as shown in Table 4.

The expected values of the standard atomic weights are taken as the midpoints of the corresponding standard-atomic-weight intervals (see also equation (1)). As for the uncertainty, the widths of these intervals are converted into standard uncertainties using expressions applicable to rectangular distributions over such intervals (see equation (2)). The uncertainty contribution is the product of the atomic composition coefficient (sensitivity coefficient) and the standard uncertainty. These are squared, summed, and then the square root is taken to compute the standard uncertainty associated with the molecular weight [8].

From the magnitudes of the uncertainty contributions (Table 4, last column), it can be seen that the uncertainty of $A_r(C)$ constitutes the largest contribution ($u[A_r(C)] = 0.001\,15$) whereas the uncertainty contribution of $A_r(O)$ is six times smaller in size ($u[A_r(O)] = 0.000\,22$). Since the individual uncertainty contributions are squared before adding and taking the square root to derive the uncertainty of the molecular weight, $A_r(O)$ contributes only 2.5 % to the sum in quadrature, whereas $A_r(C)$ contributes 83.5 %, with the remaining contribution of 14.0 % originating from $A_r(H)$. The presentation of the uncertainty budget in this format

Table 4: Uncertainty budget for the standard molecular weight of ethanol.

Variable	Standard atomic weight	Probability distribution	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
$A_r(C)$	[12.0096, 12.0116]	Rectangular	12.010 60	0.000 58	2	0.001 15
$A_r(H)$	[1.007 84, 1.008 11]	Rectangular	1.007 975	0.000 078	6	0.000 47
$A_r(O)$	[15.999 03, 15.999 77]	Rectangular	15.999 40	0.000 22	1	0.000 22
$M_r(C_2H_6O)$			46.068 45			0.001 26

facilitates the comparison of the relative importance of the different sources of uncertainty. In this case, it implies that if the uncertainty associated with the standard molecular weight of ethanol is deemed to be too large, then one has to find a more precise value for the atomic weight of carbon. This can be achieved, for example, if the source of the ethanol is known, as illustrated in the next example.

Example 5: Representative molecular weight of ethanol

There are situations in science and technology where the uncertainties associated with the standard atomic weights are prohibitively large. In such situations, it might be possible to reduce the uncertainty associated with the atomic weights by considering the origin of the material at hand. For example, the atomic weight of the oxygen in air or seawater is known with considerably smaller uncertainty than the standard atomic weight of oxygen applicable to normal terrestrial materials. Such information is disseminated by the CIAAW. To illustrate the use of the CIAAW diagrams detailing the natural variations of the isotopic composition of the elements [6], consider naturally-occurring ethanol, whose hydrogen and oxygen comes from seawater and air, and whose carbon derives from corn. The following representative atomic weights of carbon, hydrogen, and oxygen were obtained:

- $A_r(\mathrm{C}) = [12.0107, 12.0111]$ for naturally-occurring ethanol,
- $A_r(\mathrm{H}) = [1.007\,90, 1.008\,01]$ for naturally-occurring water,
- $A_r(\mathrm{O}) = [15.999\,05, 15.999\,45]$ for continental water and air.

From these atomic-weight intervals, the following values are derived (see also equation (1)):

- $A_r(\mathrm{C}) = (12.0111 + 12.0107)/2 = 12.0109$,
- $A_r(\mathrm{H}) = (1.008\,01 + 1.007\,90)/2 = 1.007\,955$,
- $A_r(\mathrm{O}) = (15.999\,45 + 15.999\,05)/2 = 15.999\,25$.

The corresponding standard uncertainties are computed using the same atomic-weight intervals and Eq. (2). The standard uncertainties thus obtained are shown in Table 5. The same Table shows the representative molecular weight of ethanol calculated from these representative atomic weights. One can see that the representative molecular weight of ethanol has an uncertainty that is approximately four times smaller than that of the standard molecular weight (see Table 4). If the uncertainty associated with the representative molecular weight is still deemed to be too large, then the atomic weights of all elements present should be measured, which is usually done by measuring the isotopic composition of the elements in the material.

Table 5: Uncertainty budget for the representative molecular weight of natural ethanol.

Variable	Value	Probability distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
$A_r(\mathrm{C})$	12.0109	Rectangular	0.000 12	2	0.000 23
$A_r(\mathrm{H})$	1.007 955	Rectangular	0.000 032	6	0.000 19
$A_r(\mathrm{O})$	15.999 25	Rectangular	0.000 12	1	0.000 12
$M_r(\mathrm{C_2H_6O})$			46.068 78		0.000 32

9 Monte Carlo methods

In addition to the law of propagation of uncertainty from the GUM [8], the Monte Carlo method of the GUM-S1 may also be used to propagate the uncertainty associated with the standard atomic weights in the calculation of, e.g., molecular weights. It can be described by the following steps:

(1) Assign a rectangular probability distribution to each of the standard atomic weights to be used for the calculation of the molecular weight of the molecule of interest;

(2) Draw a random sample of an atomic-weight value for each element from the distributions in step 1;
(3) Compute the molecular weight using the values obtained in step 2;
(4) Repeat steps 2 and 3 as many times as necessary to get a sufficiently large number of values for the molecular weight (typically, 10^5 or 10^6 times).

GUM-S1 [9] gives guidance on the required number of repeats for steps 2 and 3. These molecular-weight values represent a sample from the probability distribution of the molecular weight and they can be used to compute the value, standard uncertainty, and coverage interval, or they may be used directly in subsequent Monte Carlo sampling. To illustrate the process, the standard molecular weight is calculated for carbon dioxide (CO_2), ethanol (C_2H_6O), ethanethiol (C_2H_6S), and methanamine (CH_3NH_2).

Figure 1 shows the results obtained by application of the Monte Carlo method of the GUM-S1 when rectangular distributions are assigned to the standard atomic weight intervals. The irregular structure of the probability distributions is caused by the finite sample size of the Monte Carlo method. For CO_2, for example, the output probability distribution is trapezoidal. Furthermore, it reveals that only for methanamine is the resulting distribution of the standard molecular weight bell-shaped. Moreover, none of the molecular weight distributions are approximately normal (or Gaussian). The Monte Carlo results are summarized in Table 6.

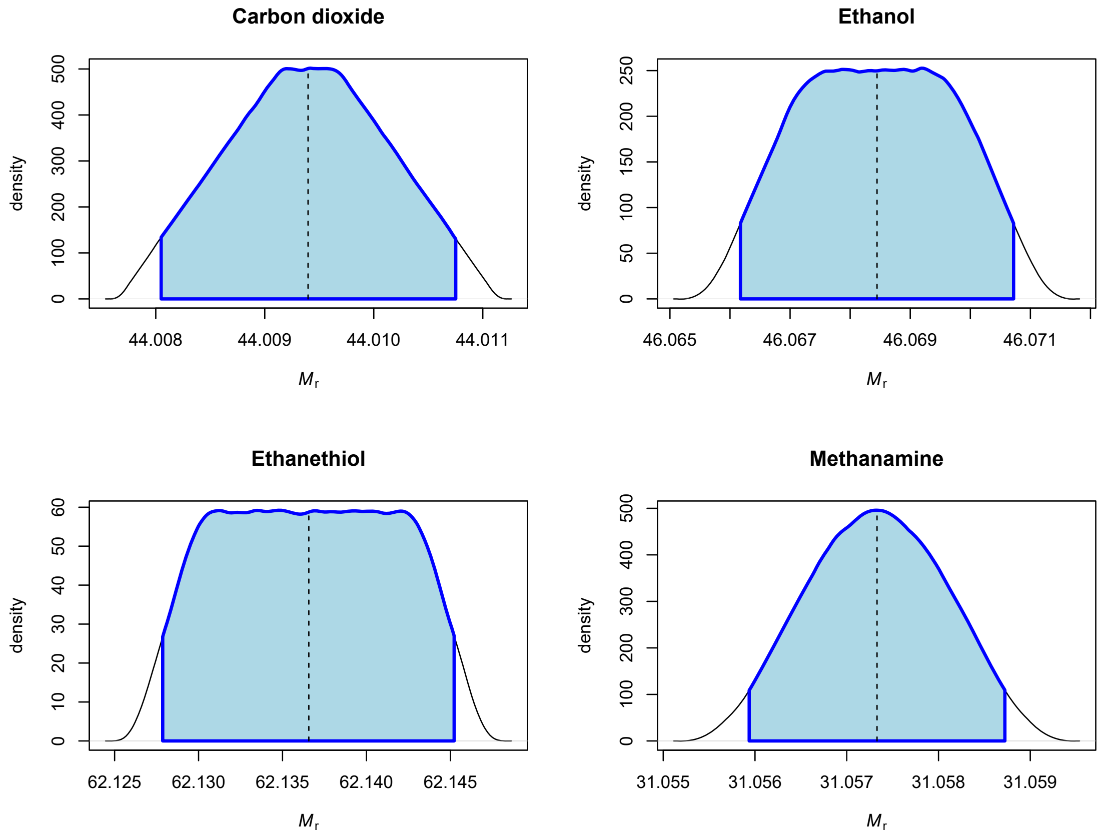

Figure 1: Propagation of the probability distributions of the standard atomic weights to calculate the probability distribution of the standard molecular weight of carbon dioxide, ethanol, ethanethiol, and methanamine using the Monte Carlo method from GUM-S1. The shaded area indicates the symmetric 95 % probability coverage interval. The dotted vertical line indicates the location of the mean. The waviness of the curves is an artefact attributable to the relatively small numbers (10^6) of sample values of the molecular weights that the probability density estimates are based on.

Table 6: Standard molecular weights (mean value, $\bar{M}_r$), their standard uncertainties, $u(\bar{M}_r)$, the values of the lower- ($q_{0.025}(\bar{M}_r)$) and upper quantiles ($q_{0.975}(\bar{M}_r)$) of the symmetric 95 % probability coverage intervals, and the widths of these intervals expressed as the multiple of standard uncertainties, $\Delta q/u(\bar{M}_r) = (q_{0.975}(\bar{M}_r) - q_{0.025}(\bar{M}_r))/u(\bar{M}_r)$.

Molecule	$\bar{M}_r$	$u(\bar{M}_r)$	$q_{0.025}(\bar{M}_r)$	$q_{0.975}(\bar{M}_r)$	$\Delta q/u(\bar{M}_r)$
CO_2	44.0094	0.0007	44.0081	44.0108	3.77
C_2H_6O	46.0685	0.0013	46.0662	46.0707	3.61
C_2H_6S	62.1366	0.0051	62.1278	62.1453	3.44
CH_5N	31.0573	0.0007	31.0559	31.0587	3.79

The last column in Table 6 gives the width of a 95 % coverage interval as a multiple of the corresponding standard uncertainty. If the output probability distribution were Gaussian, then the value of width of the coverage interval, expressed as a multiple of standard uncertainties $\Delta q/u(\overline{M_r})$ would be $2 \times 1.96 = 3.92$. For all four molecules, the coverage interval is narrower than would be obtained if the output probability distribution were assumed to be Gaussian. This should not come as a surprise, because in all cases the starting point is a rectangular distribution to model the standard atomic weights of the elements. Combining a few rectangular distributions does not usually lead to an output probability density function that is (approximately) normal [28]. The differences between the GUM-S1 coverage intervals and those based on the mean and standard uncertainty computed from the law of propagation of uncertainty become more pronounced as the coverage probability increases.

For homoatomic molecules such as O_2, P_4, S_8, or C_{60}, the probability distribution of the standard molecular weight is rectangular, resulting from rescaling the corresponding rectangular distributions of the standard atomic weights.

10 Combining molecular weights for components in mixtures

In chemistry, not one but several molecular weights are often required for a single calculation. For example, gravimetric determination of the mass fraction of silver by the precipitation of silver chloride requires the ratio $A_r(\mathrm{Ag})/M_r(\mathrm{AgCl})$. In mixtures such as air or natural gas, often there are components that have several elements in common. The fact that such elements appear in multiple molecules gives rise to correlations in the computed molecular weights [7, 11]. In applications where the uncertainty associated with the molecular weight matters, such correlations may matter too.

Example 6: Ratio of the standard atomic weights of oxygen and hydrogen

Atomic weights often are used in the form of ratios. An important historic example of this was the ratio of the standard atomic weights of oxygen and hydrogen, once thought to be exactly sixteen [19]:

$$R = \frac{A_r(\mathrm{O})}{A_r(\mathrm{H})} \tag{9}$$

Assuming that the correlation between the standard atomic weights of hydrogen and oxygen is negligible, the following equation can be used:

$$\frac{u^2(R)}{R^2} \approx \frac{u^2(A_r(\mathrm{O}))}{A_r^2(\mathrm{O})} + \frac{u^2(A_r(\mathrm{H}))}{A_r^2(\mathrm{H})} \tag{10}$$

The calculation is only approximate because, in contrast to molecular weights, which are linear combinations of atomic weights, the evaluation produced by the law of propagation of uncertainty provides only an approximation to the uncertainty associated with a ratio, as well as for other non-linear measurement functions [8, clause 5.1.6].

The correlation between the atomic weights is a complex issue. On a deeper level, for example, it is known that the natural variations of the atomic weight of hydrogen and oxygen track each other. However, if such details become relevant, one would not use standard atomic weights in the calculations, but rather take the available data and construct a more sophisticated measurement model [7].

Using the 2013 standard atomic weights we obtain $R = 15.8728$ with standard uncertainty $u(R) = 0.0012$ which is significantly different from 16. In this example we considered atomic weights of two separate elements. Next we will consider a more complex situation in which the two components share a common element.

Example 7: Composition of a mixture of methane and propane

The molecular weight of simple molecules is rarely the ultimate quantity of interest; more often than not it is a part of a much larger calculation, aiming, for example, at the calculation of a mixture composition. In this vein, let us consider a mixture of pure methane and pure propane, which can be viewed as a simplified model of a synthetic natural gas [11]. The full model would have to include also the amount fractions of the impurities in the methane and propane used for preparing the gas mixture, and hence, also the molecular weights of these impurities [27].

The uncertainties of the standard molecular weights of methane and propane are calculated as before. For methane, the variance associated with the standard molecular weight is

$$\begin{aligned} u^2(M_\mathrm{r}(\mathrm{CH_4})) &= 1^2 \cdot u^2(A_\mathrm{r}(\mathrm{C})) + 4^2 \cdot u^2(A_\mathrm{r}(\mathrm{H})) \\ &= 1 \cdot (0.000\,58)^2 + 16 \cdot (0.000\,078)^2 = 4.3 \times 10^{-7} \end{aligned} \tag{11}$$

and the standard uncertainty is $u(M_\mathrm{r}(\mathrm{CH_4})) = 0.000\,66$. The standard uncertainties for the standard atomic weights of carbon and hydrogen are taken from Table 4. For propane, the variance associated with its standard molecular weight is

$$\begin{aligned} u^2(M_\mathrm{r}(\mathrm{C_3H_8})) &= 3^2 \cdot u^2(A_\mathrm{r}(\mathrm{C})) + 8^2 \cdot u^2(A_\mathrm{r}(\mathrm{H})) \\ &= 9 \cdot (0.000\,58)^2 + 64 \cdot (0.000\,078)^2 = 3.4 \times 10^{-6} \end{aligned} \tag{12}$$

and the standard uncertainty is $u(M_\mathrm{r}(\mathrm{C_3H_8})) = 0.001\,84$.

The covariance between the standard molecular weights of methane ($\mathrm{CH_4}$) and propane ($\mathrm{C_3H_8}$) can be computed using equation F.2 of the GUM [8]:

$$u(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8})) = \sum_{z=\mathrm{C,H}} \nu_z(\mathrm{CH_4}) \cdot \nu_z(\mathrm{C_3H_8}) \cdot u^2(A_\mathrm{r}(z)) \tag{13}$$

where the summation runs over all elements in common (in this example, over carbon and hydrogen) and $\nu_z(\mathrm{X})$ is the atomic composition coefficient of element z in molecule X. For the molecular weights of methane and propane, this implies that the summation covers carbon and hydrogen. The expression for the covariance between the molecular weights becomes

$$\begin{aligned} u(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8})) &= 1 \cdot 3 \cdot u^2(A_\mathrm{r}(\mathrm{C})) + 4 \cdot 8 \cdot u^2(A_\mathrm{r}(\mathrm{H})) \\ &= 3 \cdot (0.000\,58)^2 + 32 \cdot (0.000\,078)^2 = 1.195 \times 10^{-6} \end{aligned} \tag{14}$$

The covariance between the molecular weights of methane and propane may seem a small number, but the value of the correlation coefficient, $r(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8}))$, reveals strong correlation between the two molecular weights:

$$r(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8})) = \frac{u(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8}))}{u(M_\mathrm{r}(\mathrm{CH_4})) \cdot u(M_\mathrm{r}(\mathrm{C_3H_8}))} = \frac{1.19 \times 10^{-6}}{0.000\,66 \cdot 0.001\,84} = 0.989 \tag{15}$$

The calculation of a correlation coefficient from a covariance is given in equation (14) of the GUM [8]. To appreciate the significance of the correlation between the standard molecular weights of methane and propane, consider a mixture of these two gases that is prepared from pure methane, ($m(\mathrm{CH_4}) = 459.6263$ g), and pure propane, ($m(\mathrm{C_3H_8}) = 140.3737$ g) [11, 27]. The amount fraction of propane in the mixture is given by

$$x(\mathrm{C_3H_8}) = \frac{n(\mathrm{C_3H_8})}{n(\mathrm{CH_4}) + n(\mathrm{C_3H_8})} = \frac{m(\mathrm{C_3H_8})/M_\mathrm{r}(\mathrm{C_3H_8})}{m(\mathrm{CH_4})/M_\mathrm{r}(\mathrm{CH_4}) + m(\mathrm{C_3H_8})/M_\mathrm{r}(\mathrm{C_3H_8})} \tag{16}$$

If we consider the masses of the parent gases to be free from uncertainty, just as their compositions, the squared standard uncertainty of $x(\mathrm{C_3H_8})$ can be expressed as

$$\begin{aligned} u^2(x(\mathrm{C_3H_8})) = {} & \left(\frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{CH_4})}\right)^2 u^2(M_\mathrm{r}(\mathrm{CH_4})) + \left(\frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{C_3H_8})}\right)^2 u^2(M_\mathrm{r}(\mathrm{C_3H_8})) \\ & + 2\left(\frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{CH_4})}\right)\left(\frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{C_3H_8})}\right) u(M_\mathrm{r}(\mathrm{CH_4}), M_\mathrm{r}(\mathrm{C_3H_8})) \end{aligned} \tag{17}$$

The expressions for the sensitivity coefficients (partial derivatives) are as follows [11]:

$$\begin{aligned} \frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{CH_4})} &= \frac{m(\mathrm{C_3H_8})/M_\mathrm{r}(\mathrm{C_3H_8})}{(m(\mathrm{CH_4})/M_\mathrm{r}(\mathrm{CH_4}) + m(\mathrm{C_3H_8})/M_\mathrm{r}(\mathrm{C_3H_8}))^2} \cdot \frac{m(\mathrm{CH_4})}{M_\mathrm{r}^2(\mathrm{CH_4})} \\ &= \frac{140.3737/44.0956}{(459.6263/16.0425 + 140.3737/44.0956)^2} \cdot \frac{459.6263}{16.0425^2} = 0.005\,610 \end{aligned} \tag{18}$$

$$\begin{aligned} \frac{\partial x(\mathrm{C_3H_8})}{\partial M_\mathrm{r}(\mathrm{C_3H_8})} &= -\frac{m(\mathrm{CH_4})/M_\mathrm{r}(\mathrm{CH_4})}{(m(\mathrm{CH_4})/M_\mathrm{r}(\mathrm{CH_4}) + m(\mathrm{C_3H_8})/M_\mathrm{r}(\mathrm{C_3H_8}))^2} \cdot \frac{m(\mathrm{C_3H_8})}{M_\mathrm{r}^2(\mathrm{C_3H_8})} \\ &= -\frac{459.6263/16.0425}{(459.6263/16.0425 + 140.3737/44.0956)^2} \cdot \frac{140.3737}{44.0956^2} = -0.002\,041 \end{aligned} \tag{19}$$

The amount fraction propane in the mixture is $x(\mathrm{C_3H_8}) = 0.100\,00$ and the associated variance is:

$$\begin{aligned} u^2(x(\mathrm{C_3H_8})) = {} & 0.005\,610^2 \cdot 0.000\,66^2 + (-0.002\,041)^2 \cdot 0.001\,184^2 \\ & + 2 \cdot 0.005\,610 \cdot (-0.002\,041) \cdot 1.195 \times 10^{-6} = \left(5.61 \times 10^{-7}\right)^2 \end{aligned} \tag{20}$$

By comparison, neglecting the covariance between the standard molecular weights of $\mathrm{CH_4}$ and $\mathrm{C_3H_8}$ yields the following variance of $x(\mathrm{C_3H_8})$:

$$u^2(x(\mathrm{C_3H_8})) = 0.005\,610^2 \cdot 0.000\,66^2 + (-0.002\,041)^2 \cdot 0.001\,84^2 = \left(5.3 \times 10^{-6}\right)^2 \tag{21}$$

The difference in the computed standard uncertainties is significant; ignoring the covariance between the molecular weights results in a ten-fold greater uncertainty.

The Monte Carlo method of the GUM-S1 can take correlations into account to reproduce the results above with much greater ease. The following lines of R code [29] reproduce the result obtained with equation (20):

```
H = runif (1e6, min = 1.00784, max = 1.00811)
C = runif (1e6, min = 12.0096, max = 12.0116)
M.CH4 = 1*C + 4*H
M.C3H8 = 3*C + 8*H
m.CH4 = 459.6263
m.C3H8 = 140.3737
n.CH4 = m.CH4/M.CH4
n.C3H8 = m.C3H8/M.C3H8
x.C3H8 = n.C3H8/(n.CH4 + n.C3H8)
c('x.C3H8' = mean(x.C3H8), 'u(x.C3H8)' = sd(x.C3H8))
```

The corresponding output is

```
x.C3H8     u(x.C3H8)
1.0e-01     5.6e-07
```

For mixtures of multiple components, the pairwise evaluation of the correlations as in equations (20) and (21) is too cumbersome. Instead, the model for calculating the set of molecular weights can be viewed as a multivariate measurement model, and the measurement uncertainty can be evaluated using the methods of GUM Supplement 2 [10]. An example for a hydrocarbon mixture is given elsewhere [7]. It has been demonstrated how to use this approach in computing the composition of a mixture on a molar basis using the law of propagation of uncertainty [11] and the Monte Carlo method. Table 7 shows correlation coefficients between the standard molecular weights of five common substances. The correlation coefficients are widely different, yet for the saturated alkanes, these correlation coefficients can be close to $r = 1$ (for example, for ethane and propane). For the alkenes (molecular formula C_nH_{2n}), the correlation coefficient between two molecular weights is exactly $r = 1$.

Table 7: Correlation coefficients between the standard molecular weights of common substances.

Molecule	H_2O	CO_2	NO_2	CH_4	SO_2
H_2O	1	0.481	0.700	0.280	0.070
CO_2		1	0.516	0.707	0.052
NO_2			1	0	0.075
CH_4				1	0
SO_2					1

11 Conclusions

We have shown how the information provided by the IUPAC Commission on Isotopic Abundances and Atomic Weights about the standard atomic weights should be used to derive values and standard uncertainties for the standard atomic weights. According to the simplest interpretation, standard atomic weights expressed using the parenthetic notation should be treated in the same way as those standard atomic weights that are expressed as intervals. This interpretation is based on modelling the standard atomic weight using the rectangular distribution, and computing from this distribution a value and standard uncertainty. This interpretation is especially appropriate when the uncertainties thus obtained are not dominant in the measurement or calculation in which the standard atomic weights are used. Otherwise, a more sophisticated approach, often involving the derivation of representative atomic weights for a specified material or group of materials, is recommended [7].

Molecular weights are often calculated as part of a larger calculation. In this larger calculation, the law of propagation of uncertainty from the GUM [8] or the Monte Carlo method from GUM-S1 [9] may be used to propagate measurement uncertainty. We have shown, using both approaches, how the uncertainty about the standard atomic weights can be taken into account and duly propagated as well.

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