International Union of
Pure and Applied Chemistry

Guidelines for the use of atomic weights

Journal:	*Pure and Applied Chemistry*
Manuscript ID	PAC-REC-16-04-01
Manuscript Type:	Recommendation
Date Submitted by the Author:	01-Apr-2016
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Keywords:	atomic weights, atomic-weight intervals, molecular weight, standard atomic weight, measurement uncertainty, uncertainty propagation
Author-Supplied Keywords:	

DE GRUYTER Pure Appl. Chem. 2016; aop

Sponsoring body: IUPAC Inorganic Chemistry Division Committee: see more details on page XXX.

IUPAC Recommendation

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Guidelines for the use of atomic weights

DOI: ..., Received ...; accepted ...

Abstract: Standard atomic weights are widely used in science, yet the uncertainties associated with these values are not well-understood. This recommendation provides guidance on the use of standard atomic weights and their uncertainties. Furthermore, methods are provided for calculating standard uncertainties of molecular weights of substances. 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; standard atomic weight; uncertainty; uncertainty propagation

1 Introduction

Atomic weights provide a practical link the SI base units kilogram and mole. For every substance, or mixture of substances, the conversion from mass to amount of substance (chemical amount (6)) and vice versa can be carried out once the molecular weight has been determined. Standard atomic weights play a key role in these calculations. These values are regularly evaluated and published by the Commission on Isotopic Abundances and Atomic Weights (CIAAW, www.ciaaw.org) of the International Union of Pure and Applied Chemistry (IUPAC). The work undertaken by CIAAW to keep the standard atomic weights up-to-date deals broadly with two aspects: appreciation of improved measurements of isotopic composition of the elements, and the improved knowledge about natural variations of the isotopic composition of the elements (5). On the advice of CIAAW, in 2009 IUPAC resolved to disseminate standard atomic weights of elements using either of two different notations (17):

1. traditional short-hand notation giving a single value followed by an expanded uncertainty between parenthesis applicable to the last quoted digit of that value, e.g., $A_r(\mathrm{Cd}) = 112.414(4)$, and
2. interval notation for elements whose isotopic composition varies appreciably in nature, e.g., $A_r(\mathrm{C}) = [12.0096, 12.0116]$ representing the interval of atomic-weight values of these elements found in "normal" materials (11).

The expanded uncertainty used in the traditional short-hand notation is to be understood so that for example for cadmium, the atomic weight of cadmium in any "normal" material is practically certain to lie inside the interval [112.410, 112.418]. While the new interval notation did emphasize the magnitude of the natural variations of atomic-weight values, for many users it was unclear how to employ the given intervals in calculations and uncertainty evaluations.

These Guidelines provide a basis for understanding the standard atomic weights and their uncertainties so that users can readily employ them in a variety of calculations. Informative examples are provided to

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illustrate the computations and to enable their implementation in practice, in software, or in quality control documents, among others. These Guidelines are accompanied by an IUPAC Technical Report (12) that provides a more in-depth treatment of the subject. The authors wish to emphasize that such calculations should always be performed with the most recent values for the (standard) atomic weights. Throughout these Guidelines the standard atomic weights of 2013 are used (9).

2 Terms and definitions

1. **atomic weight**
   relative atomic mass, $A_r(E)$
   Amount-weighted average of the atomic masses of the isotopes of an element E in a material, divided by the unified atomic mass unit (dalton).
2. **normal material**
   Material that is a reasonably possible source for an element or its compounds in commerce, for industry or science, and the material is not itself studied for some extraordinary anomaly, and its isotopic composition has not been modified significantly in a geologically brief period (11).
3. **standard atomic weight**
   CIAAW-recommended atomic weight, applicable to all normal materials.
4. **molecular weight**
   Sum of the atomic weights of elements in a substance, weighted by their stoichiometric coefficients.
5. **standard molecular weight**
   Molecular weight calculated using the standard atomic weights of its constituent elements.
   Note: Standard atomic weights are commonly used for calculating molecular weights of normal materials.
6. **reference atomic weight**
   CIAAW-recommended atomic weights applicable to materials from specific sources.
   Note: In CIAAW reports, reference atomic weights are given for elements whose standard atomic weight is given in interval notation for specific sources such as air, water, or rocks (9).
7. **delta-zero reference material**
   Reference material that is well-characterised used to establish the origin of a delta scale.

3 Standard atomic weights

Many forms of notation have been employed over the years to express standard atomic weights (1; 14). CIAAW currently employs, as mentioned previously, two notations: the single-value shorthand notation with the explicit uncertainty given in parenthesis and the two-value interval notation with no uncertainty given explicitly. Thus, an atomic weight interval is characterised by a lower limit, a, and an upper limit, b, whereas the traditional short-hand notation of the standard atomic weight provides a single value and the associated expanded uncertainty (Table 1). It is important to stress that neither of these notations alters the meaning of the quantity, and that both summarize CIAAW decision to express the standard atomic weight of an element using two values; either with an upper- and lower-bound or with the representative value and its uncertainty. 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 (17).

Standard atomic weights and their uncertainties are determined by CIAAW (17; 11). In the process leading to determinations of these standard atomic weights, all published data concerning the isotopic compositions of "normal materials" for each element are evaluated, and a value with an indication of the uncertainty, or an atomic-weight interval is established. In this process, the uncertainty is attributable to

both variations in the isotopic composition of the element in normal materials, and the uncertainty about the masses of the isotopes (17; 11).

Unless interval arithmetic is employed, the majority of scientific calculations require a single, representative value of the quantity and its uncertainty. Extracting a representative value and an indication of associated uncertainty from a standard atomic weight involves assignment of a probability distribution that explicitly or implicitly represents the state-of-knowledge of the standard atomic weight in the material(s) of interest.

The representative value may be the expected value (mathematical expectation, or mean) of that distribution, and the indication of associated uncertainty may be the corresponding standard deviation (standard uncertainty) (2). However, and most importantly, the expected value does not necessarily represent the "most-likely" value (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 may differ. Using CIAAW notations for the standard atomic weight of an imaginary element, [99, 101] or 100(1), neither would imply that a value of 100 is more likely to occur than any other value between 99 and 101. Thus, both notations tell us that the atomic weight in any normal material will be greater than or equal to 99 and will be less than or equal to 101. The distinction between the two notations serves to emphasize that for some elements (e.g., hydrogen or carbon) the atomic-weight values vary significantly in nature between materials whereas for other elements (e.g., fluorine or zinc) our knowledge about the atomic weights is limited mainly by the uncertainty about the nuclide masses and their abundances.

4 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 derivative quantities whose calculation involves such experimental data. The *Guide to the expression of uncertainty in measurement* (GUM) (2) and its supplements (3; 4) provide a harmonized 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 generally recognizes that the knowledge about this true value is imperfect or incomplete. Thus, if an isotopic composition of an element in a material has not been directly determined by measurement of the material, information about the material still may enable the assignment of a value to the isotopic composition along with an associated standard uncertainty for use in calculations. Such assessment leads to larger 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 (2), information about input quantities is modelled by means of probability distributions. The Monte Carlo methods of GUM Supplements 1 and 2 (3; 4) 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 depict the variability of the quantity in different materials in nature; 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(2), the case of a standard atomic weight can be described as follows. The probability that the value of A_r(E) for some element E lies within the interval from a to b is practically 100 %, and the probability that A_r(E) lies outside this interval is essentially zero. If there is no specific knowledge about the possible values of A_r(E) within the interval, one can only assume that it is equally probable for A_r(E) to lie anywhere within it, and therefore be described by a uniform (rectangular) distribution of possible values. This description is well-aligned with the efforts by the CIAAW to establish with great care the end points of the atomic-weight interval, or the interval given by a value with the uncertainty between parenthesis for the standard atomic weight (17; 9). The wording from the GUM clause 4.3.7 makes sufficiently clear under which conditions the rectangular distribution is a legitimate choice and

that it applies to standard atomic weights (2). 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", following Occam's razor 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.

This recommendation suggests that the standard atomic weight be interpreted probabilistically, taking as viewpoint that the only information at hand that the atomic weight is needed for a normal material. In this conformity, the user of a standard atomic weight is not required to seek a better (and probably more accurate) interpretation, taking further information into consideration. It is up to the user of the standard atomic weight to decide whether the approach in this recommendation is fit-for-purpose. The accompanying Technical Report (12) describes, and illustrates with examples, assignments of possibly non-uniform probability distributions to atomic weights that encapsulate additional information about the material (for example, about its provenance). In fact, if the interpretation given in this recommendation is deemed to be not fit-for-purpose, more information should be taken into account to reduce the uncertainty about the atomic weight.

Hence, under the conditions outlined in this recommendation all standard atomic weights are assigned the rectangular distribution representing a most simplified representation of the lack-of-knowledge (16; 17). 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 (2):

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

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

$$u(A_{\mathrm{r}}(\mathrm{E})) = \frac{b-a}{\sqrt{12}} \tag{2}$$

which is the standard deviation of the rectangular distribution.

In the short-hand notation 95.95(1), it is understood that the 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. In this example, the half-width of the interval is 0.01 and hence the standard uncertainty is $0.01/\sqrt{3} = 0.006$.[1]

This simplistic interpretation of standard atomic weights – where the midpoint of the standard atomic weight interval is taken as the value, does not reflect that the natural variations of the atomic weight are not necessarily symmetric for the most representative materials (10). The accompanying Technical Report (12) provides alternatives to the probabilistic interpretation of these Guidelines to address, among others, the fact that the distribution of values of the atomic weight may not be symmetric. 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.

5 Examples of obtaining atomic weights

Performing scientific calculations requires that, at a minimum, all input variables have an associated 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 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.

1 The GUM clause 7.2.2 recommends using this notation for a standard uncertainty with the qualification where the number in parentheses is the numerical value of (the combined standard uncertainty) u_{c} referred to the corresponding last digits of the quoted result (2). In these guidelines, the conventions of CIAAW are followed. In particular, given the description of the standard atomic weight, as in 192.217(3) for iridium, 0.003 is interpreted as an expanded uncertainty with a coverage factor of $k = \sqrt{3}$.

Table 1. Standard atomic weights of carbon and iridium and their interpretation

Variable	Standard atomic weight	Assigned probability distribution	Value	Standard uncertainty
A_r(C)	[12.0096, 12.0116]	Rectangular	(12.0096+12.0116)/2 = 12.0106	(12.0106 - 12.0096)/(2 $\sqrt{3}$) = 0.0006
A_r(Ir)	192.217(3)	Rectangular	192.217	0.003/$\sqrt{3}$=0.002

Table 2. Reference atomic weights of oxygen in different sources

Variable	Reference atomic weight	Assigned probability distribution	Value, A_r(O)	Standard uncertainty
CO in air	[15.999 28, 15.999 37]	Rectangular	(15.999 28+15.999 37)/2 = 15.999 32	(15.999 37 - 15.999 28)/(2$\sqrt{3}$) = 0.000 03
CO_2 in air	[15.999 46, 15.999 52]	Rectangular	(15.999 46+15.999 52)/2 = 15.999 49	(15.999 52 - 15.999 46)/(2 $\sqrt{3}$) = 0.000 02

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 iridium in Table 1, using equations (1) and (2).

Example 2: Reference atomic weight

There are cases when the uncertainty of a standard atomic weight is not fit for purpose. In such cases, it might be possible to reduce the uncertainty of the atomic weight if the origin of the material is known. For many elements, CIAAW provides detailed information about the atomic weights of elements in various materials (9; 7). It is important to review the appropriateness of the assigned provenance critically when using reference atomic weights. As an example, Table 2 shows the reference atomic weights of oxygen in two sources.

Example 3: Atomic weight of boron in specific samples

When the isotopic composition of the element in the 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 (9). For an element E with isotopes ^{i}E and ^{j}E in material P (where usually $i > j$, meaning that the heavier isotope appears in the numerator of the fraction defining $R(^{i}\mathrm{E}/^{j}\mathrm{E})_\mathrm{P}$:

$$\delta^{i}\mathrm{E}_{\mathrm{P,std}} = \delta(^{i/j}\mathrm{E}_{\mathrm{P,std}}) = \frac{R(^{i}\mathrm{E}/^{j}\mathrm{E})_\mathrm{P}}{R(^{i}\mathrm{E}/^{j}\mathrm{E})_\mathrm{std}} - 1 \qquad (3)$$

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, $R(^{11}\mathrm{B}/^{10}\mathrm{B})_{951} = R_{951} = 4.0436(2)_{k=2}$ (7). From here, the isotope ratio of boron in the sample P, $R(^{11}\mathrm{B}/^{10}\mathrm{B})_\mathrm{P} = R_\mathrm{P}$, can be calculated from a measured boron isotope ratio in the test material using

Table 3. Atomic weight of boron in specific samples

Source	Isotope delta, $\delta^{11}\mathrm{B}_{951}$	Value, $A_\mathrm{r}(\mathrm{B})$	Standard uncertainty, $u(A_\mathrm{r}(\mathrm{B}))$
Seawater	+39.9(1) ‰	10.817 88	0.000 07
Borax from Turkey	−4.1(4) ‰	10.811 10	0.000 09

equation (3), and then the atomic weight is obtained:

$$A_\mathrm{r}(\mathrm{B})_\mathrm{P} = \frac{1}{m_\mathrm{u}} \frac{m_\mathrm{a}(^{10}\mathrm{B}) + m_\mathrm{a}(^{11}\mathrm{B})(1+\delta^{11}\mathrm{B}_{\mathrm{P},951})R_{951}}{1+(1+\delta^{11}\mathrm{B}_{\mathrm{P},951})R_{951}} \tag{4}$$

Equation (4) is obtained by combining equation (3) with the expression below relating the atomic weight to isotope ratios:

$$A_\mathrm{r}(\mathrm{B})_\mathrm{P} = \frac{1}{m_\mathrm{u}} \frac{m_\mathrm{a}(^{10}\mathrm{B}) + m_\mathrm{a}(^{11}\mathrm{B})R_\mathrm{P}}{1+R_\mathrm{P}} \tag{5}$$

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

$$u^2(A_\mathrm{r}(\mathrm{B})_\mathrm{P}) = \Delta m_\mathrm{a}(\mathrm{B}) \frac{R_{951}^2 \cdot u^2(\delta^{11}\mathrm{B}_{\mathrm{P},951}) + (1+\delta^{11}\mathrm{B}_{\mathrm{P},951})^2 \cdot u^2(R_{951})}{(1+R_{951}(1+\delta^{11}\mathrm{B}_{\mathrm{P},951}))^4} \tag{6}$$

where $\Delta m_\mathrm{a}(\mathrm{B}) = m_\mathrm{a}(^{11}\mathrm{B}) - m_\mathrm{a}(^{10}\mathrm{B})$.

6 Molecular weights

A common application of atomic weights and standard atomic weights is the calculation of molecular weights. These play an important role in relating the SI unit for mass (kg) to the SI unit for amount of substance (mol). The conversion between these two base quantities depends on the chemical substances involved. For a single component in a material or mixture, the molecular weight M_r is conventionally calculated from the atomic weights of the elements present in the molecule and the stoichiometric coefficients as

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

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

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 (2), or the Monte Carlo method from the GUM-S1 (3). Usually the uncertainty calculation for the molecular weight will be part of a larger calculation, such as the computation of the mixture composition from a gravimetrically prepared mixture (15; 8). Whether the methods for calculating the measurement uncertainty associated with a molecular weight of these Guidelines are used, or those of the accompanying Technical Report (12), should be decided on the impact that the calculated uncertainties have in the subsequent calculations.

Applying the law of propagation of uncertainty to the expression for calculating the uncertainty of the molecular weight

$$u^2(M_\mathrm{r}) = \sum_\mathrm{E} v_\mathrm{E}^2 u^2(A_\mathrm{r}(\mathrm{E})) \tag{8}$$

where the correlation between pairs of atomic weights of elements can be neglected.

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

Variable	Standard atomic weight	Assigned probability distribution	Value	Standard uncertainty	Stoichiometric coefficient	Uncertainty contribution
$A_r(C)$	[12.0096, 12.0116]	Rectangular	12.0106	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 73]	Rectangular	15.9994	0.000 21	1	0.000 21
$M_r(C_2H_6O)$			46.0685			0.001 30

7 Examples of obtaining molecular weights

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

Example 4: Standard molecular weight of ethanol

To illustrate the use of the equations for calculating the molecular weight, the 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. As for the uncertainty, the width of these intervals is converted into standard uncertainties using expressions applicable to rectangular distributions over such intervals. The uncertainty contribution is the product of the stoichiometric 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 (2).

From the magnitudes of the uncertainty contributions (Table 4, last column), it can be seen that the largest contributor to the standard uncertainty of the molecular weight is carbon whereas the contribution of oxygen is approximately ten times smaller. The presentation of the uncertainty budget in this format facilitates the comparison of the relative importance of the different sources of uncertainty. In this case it indicates clearly that if the uncertainty associated with the molecular weight of ethanol is deemed to be too large to be fit-for-purpose, 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, and it is illustrated in the next example.

Example 5: Reference 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 smaller uncertainty than the standard atomic weight of oxygen applicable to all natural materials. To illustrate the use of CIAAW diagrams detailing the natural variations of the isotopic composition of the elements (9), consider naturally-produced ethanol whose hydrogen and oxygen comes from seawater and air, and whose carbon derives from corn. The following reference atomic weights of carbon, hydrogen, and oxygen were obtained:

$A_r(C) = [12.0107, 12.0111]$ for naturally-occurring ethanol,

$A_r(H) = [1.007\,90, 1.008\,01]$ for naturally-occurring water,

$A_r(O) = [15.999\,05, 15.999\,45]$ for continental water and air.

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

Variable	Expected value	Assigned probability distribution	Standard uncertainty	Stoichiometric coefficient	Uncertainty contribution
$A_r(C)$	12.0109	Rectangular	0.000 12	2	0.000 24
$A_r(H)$	1.007 955	Rectangular	0.000 032	6	0.000 19
$A_r(O)$	15.999 25	Rectangular	0.000 12	1	0.000 12

For these atomic weights, the following expected values are derived:

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

Table 5 shows the reference molecular weight of ethanol calculated from these reference atomic weights. One can see that the reference molecular weight of ethanol has an uncertainty that is four times smaller than that of the standard molecular weight (Table 4). If the uncertainty associated with the reference molecular weight is still deemed to be too large to be fit-for-purpose, then the atomic-weights of all elements present should be measured.

8 Monte Carlo methods

In addition to the law of propagation of uncertainty from the GUM (2), 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 molecular weights. It can be described by the following steps (3):

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. Sample an atomic-weight value for each element from above distributions;
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.

These molecular-weight values are 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 methylamine (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 atomic weight intervals, and in particular reveals that only for methylamine is the distribution of the molecular weight approximately normal (or, Gaussian) The Monte Carlo results are summarized in Table 6.

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 which results from rescaling the corresponding rectangular distributions of the standard atomic weights.

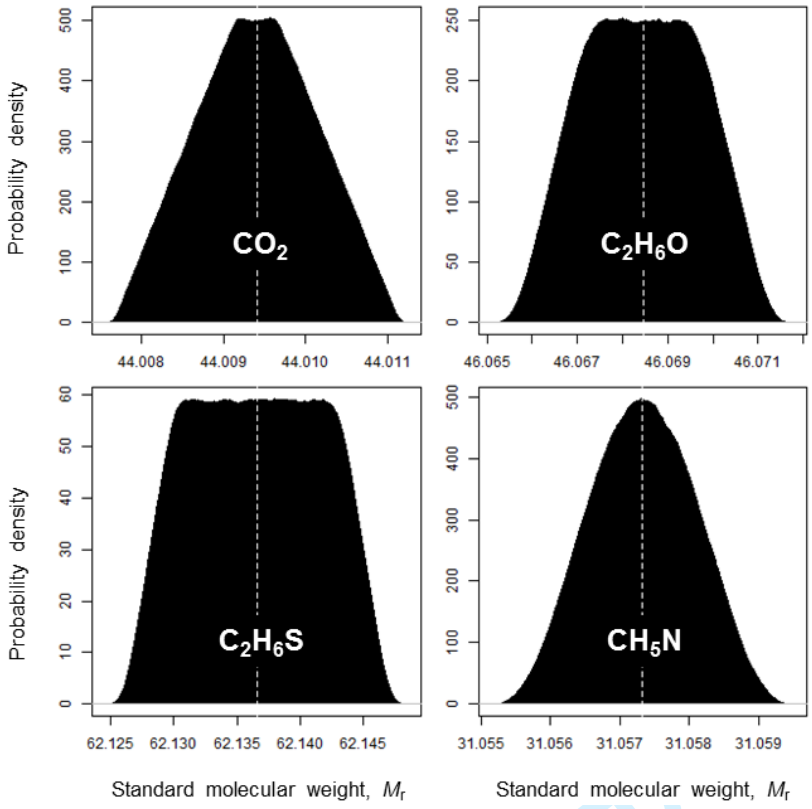

Fig. 1. Propagation by Monte Carlo simulation of the probability distributions of the standard atomic weights to calculate the probability distribution of the molecular weight of carbon dioxide, ethanol, ethanethiol, and methylamine. One million samples were used to generate the output probability distributions.

Table 6. Standard molecular weights, their standard uncertainties, lower- and upper-values of the 95 % coverage intervals, and the relative widths of these intervals for four molecules

Molecule	M_r	$u(M_r)$	$q_{0.025}(M_r)$	$q_{0.925}(M_r)$	$\Delta q/u(M_r)$
CO_2	44.0094	0.0007	44.0081	44.0108	3.77
C_2H_5OH	46.0685	0.0013	46.0662	46.0707	3.61
C_2H_5SH	62.1366	0.0051	62.1278	62.1453	3.44
CH_3NH_2	31.0573	0.0007	31.0559	31.0587	3.79

9 Combining molecular weights for components in mixtures

In chemistry, not one but several molecular weights are often required simultaneously. For example, gravimetric determination of the mass fraction of silver by the precipitation of silver chloride requires the ratio $A_r(Ag)/M_r(AgCl)$. In mixtures like air or natural gas, often there are components that have certain elements in common. The fact that such elements appear in multiple molecules gives rise to correlations in the computed molecular weights (12; 15). 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 (14):

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

Since the standard atomic weights of hydrogen and oxygen can be assumed to be uncorrelated, the following equation can be used:

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

The equality is only approximate because, differently from what happens for 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 [9, 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 (12).

Using the 2013 standard atomic weights $R = 15.8728$ with $u(R) = 0.0012$ which is significantly different from 16. In this example we considered two independent atomic weights. 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 (15).

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

$$\begin{aligned} u^2(M_{r,CH_4}) &= 1^2u^2(A_r(C)) + 4^2u^2(A_r(H)) \\ &= 1 \cdot (0.00058)^2 + 16 \cdot (0.000078)^2 = 4.3 \cdot 10^{-7} \end{aligned} \tag{11}$$

and the standard uncertainty is $u(M_{CH_4}) = 0.000\ 66$. For propane, the variance associated with the molecular weight is

$$\begin{aligned} u^2(M_{r,C_3H_8}) &= 3^2u^2(A_r(C)) + 8^2u^2(A_r(H)) \\ &= 9 \cdot (0.00058)^2 + 64 \cdot (0.000078)^2 = 3.4 \cdot 10^{-6} \end{aligned} \tag{12}$$

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

The covariance between the molecular weights of methane (CH_4) and propane (C_3H_8) can be computed using equation F.2 of the GUM (2):

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

where the summation runs over all elements in common (in this example $z = 2$, namely carbon and hydrogen) and $v_{z,\mathrm{X}}$ is the stoichiometric coefficient of element z in molecule X. For the molecular weights of methane and carbon, this implies that the summation covers carbon and hydrogen. The expression for the covariance between the molecular weights becomes

$$\begin{aligned} u(M_{\mathrm{r,CH_4}}, M_{\mathrm{r,C_3H_8}}) &= 1 \cdot 3u^2(A_\mathrm{r}(\mathrm{C})) + 4 \cdot 8u^2(A_\mathrm{r}(\mathrm{H})) \\ &= 3 \cdot (0.00058)^2 + 32 \cdot (0.000078)^2 = 1.19 \cdot 10^{-6} \end{aligned} \tag{14}$$

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

$$r(M_{\mathrm{r,CH_4}}, M_{\mathrm{r,C_3H_8}}) = \frac{u(M_{\mathrm{r,CH_4}}, M_{\mathrm{r,C_3H_8}})}{u(M_{\mathrm{r,CH_4}})u(M_{\mathrm{r,C_3H_8}})} = \frac{1.19 \cdot 10^{-6}}{0.00066 \cdot 0.00184} = 0.989 \tag{15}$$

The calculation of a correlation coefficient from a covariance is given in the equation 14 of the GUM (2).

To appreciate the significance of the correlation between the standard molecular weights of methane and propane, consider a mixture of these two gases which is prepared from pure methane ($m_{\mathrm{CH_4}} = 459.6263$ g) and pure propane ($m_{\mathrm{C_3H_8}} = 140.3737$ g) (15; 8). The amount fraction of propane in the mixture is given by

$$x_{\mathrm{C_3H_8}} = \frac{n_{\mathrm{C_3H_8}}}{n_{\mathrm{CH_4}} + n_{\mathrm{C_3H_8}}} = \frac{m_{\mathrm{C_3H_8}}/M_{\mathrm{r,C_3H_8}}}{m_{\mathrm{CH_4}}/M_{\mathrm{r,CH_4}} + m_{\mathrm{C_3H_8}}/M_{\mathrm{r,C_3H_8}}} \tag{16}$$

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

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

The expressions for the sensitivity coefficients (partial derivatives) are as follows (15):

$$\begin{aligned} \frac{\partial x_{\mathrm{C_3H_8}}}{\partial M_{\mathrm{r,CH_4}}} &= \frac{m_{\mathrm{C_3H_8}}/M_{\mathrm{r,C_3H_8}}}{(m_{\mathrm{CH_4}}/M_{\mathrm{r,CH_4}} + m_{\mathrm{C_3H_8}}/M_{\mathrm{r,C_3H_8}})^2} \cdot \frac{m_{\mathrm{CH_4}}}{M^2_{\mathrm{r,CH_4}}} \\ &= \frac{140.3737/44.0956}{(459.6263/16.0425 + 140.3737/44.0956)^2} \cdot \frac{459.6263}{16.0425^2} = 0.005610 \end{aligned} \tag{18}$$

$$\begin{aligned} \frac{\partial x_{\mathrm{C_3H_8}}}{\partial M_{\mathrm{r,C_3H_8}}} &= -\frac{m_{\mathrm{CH_4}}/M_{\mathrm{r,CH_4}}}{(m_{\mathrm{CH_4}}/M_{\mathrm{r,CH_4}} + m_{\mathrm{C_3H_8}}/M_{\mathrm{r,C_3H_8}})^2} \cdot \frac{m_{\mathrm{C_3H_8}}}{M^2_{\mathrm{r,C_3H_8}}} \\ &= -\frac{459.6263/16.0425}{(459.6263/16.0425 + 140.3737/44.0956)^2} \cdot \frac{140.3737}{44.0956^2} = -0.002041 \end{aligned} \tag{19}$$

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

$$\begin{aligned} u^2(x_{\mathrm{C_3H_8}}) = &\ 0.005610^2 \cdot 0.00066^2 + (-0.002041)^2 \cdot 0.00184^2 \\ &+ 2 \cdot 0.005610 \cdot (-0.002041) \cdot 1.19 \cdot 10^{-6} = (5.6 \cdot 10^{-7})^2 \end{aligned} \tag{20}$$

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

$$u^2(x_{\mathrm{C_3H_8}}) = 0.005610^2 \cdot 0.00066^2 + (-0.002041)^2 \cdot 0.00184^2 = (5.3 \cdot 10^{-6})^2 \tag{21}$$

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

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, for example in these few lines of R code (13):

```
H = runif(1e6, min=1.00784, max=1.00811)
C = runif(1e6, min=12.0096, max=12.0116)
M.methane = C + 4*H; M.propane = 3*C + 8*H
m.propane = 140.3737; m.methane = 459.6263
x.propane = (m.propane/M.propane) / ((m.methane/M.methane) + (m.propane/M.propane))
c(x.propane=signif(mean(x.propane),5), "u(x.propane)"=signif(sd(x.propane), 2))
```

The corresponding output is

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

For mixtures of multiple components, this pair-wise evaluation of the correlations 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-S2 (4). An example for a hydrocarbon mixture is given elsewhere (12). 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 (15) and the Monte Carlo method. Table **??** shows correlation coefficients between the standard molecular weights of five common substances.

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Acknowledgment: The following IUPAC projects contributed to this Recommendation: 2011-040-2-200 and 2013-032-1-200.

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