TECHNICAL NOTE

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The uncertainty of atomic mass fractions in a molecule

Abstract The mass fraction of a certain atom species in a molecule is needed for the calculation of the result of some chemical analyses. Common examples are gravimetric determinations (e.g., the sulfur concentration in a sample that can be obtained from the mass of precipitated barium sulfate). A similar problem is encountered when a reference solution of an ion is prepared by dissolution of a salt. This paper presents how the uncertainty of the mass fraction is calculated from the uncertainties of the atomic weights as published by IUPAC. The value is needed for the determination of the combined standard uncertainty of the analysis. Some calculated examples illustrate the mathematical considerations presented in the paper.

Keywords Measurement uncertainty · Atomic mass fraction · Atomic weights · Atomic weight uncertainty · Gravimetric analysis

Introduction

Measurement uncertainty is a topic of growing interest, and more and more analysts agree that it is an integral part of the result as found in the laboratory. Estimated uncertainties are mandatory for analyses performed in agreement with the norm *ISO 17025* [1]. A Guide describes how the measurement uncertainty of chemical analyses is to be determined and explains the underlying concepts of the approach [2]. The Guide also presents a number of practical examples. It becomes clear that the uncertainty of molecular weights plays a role in the uncertainty determination of titrations although the respective contribution is negligibly low compared to the uncertainties of the necessary volumetric operations (see examples A2 and A3 in ref. [2]).

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The uncertainty of a molecular weight is obviously a function of the atomic weight uncertainties of all elements involved. The same is also true for the mass fraction of a certain element in a molecule or a chemical compound. For some analytical tasks the uncertainty of a mass fraction needs to be known but unfortunately this problem is not discussed in the Guide [2] or elsewhere.

Imagine the classical sulfate determination by gravimetry (i.e., by precipitation with barium ion). The insoluble barium sulfate is obtained in pure form by filtration and washing, and afterwards its amount is determined by drying and weighing. The sulfate content in the sample is calculated by:

$$c_{SO_4} = \frac{w_{BaSO_4} \cdot f_{SO_4}}{w_{Sample}} \tag{1}$$

where c_{SO_4} is the concentration of sulfate in the sample, w_{BaSO_4} is the weighed mass of barium sulfate, f_{SO_4} is the stoichiometric factor, and w_{Sample} is the weighed mass of sample.

The stoichiometric factor is the ratio m_{SO_4}/m_{BaSO_4} (i.e., the sulfate mass fraction in the salt, where m is the atomic or molecular weight, respectively). In this case, f=96.0626/233.3896=0.4116. According to the Guide the uncertainty of the sulfate concentration, $u(c_{SO_4})$, is calculated from the uncertainties of all three factors in Eq. 1[2]:

$$u(c_{SO_4}) = c_{SO_4} \sqrt{\left(\frac{u(w_{BaSO_4})}{w_{BaSO_4}}\right)^2 + \left(\frac{u(w_{Sample})}{w_{Sample}}\right)^2 + \left(\frac{u(f_{SO_4})}{f_{SO_4}}\right)^2} \tag{2}$$

For this calculation it is necessary to know the uncertainties of both weighing operations and of the stoichiometric factor or mass fraction. Weighing is potentially the task with the lowest uncertainty of all operations in the analytical laboratory if the object to be weighed is not problematic (not volatile, hygroscopic, or electrically charged) [3]. In many cases mass determinations can be performed with a typical uncertainty in the 10^{-5} to 10^{-4} range. What about the uncertainty of the stoichiometric factor?

A similar problem occurs when, for example, a solution of a salt AB is prepared in order to obtain a reference

for ion A^+ with a specified concentration, which is then used for the comparison with the sample solution by means of signal intensities (chromatographic peak sizes, optical emission intensities, etc.).

The uncertainty of the stoichiometric factor is expressed in a mathematical form that results from the general rules of uncertainty calculation (see Eq. 9 below). It is based on the uncertainties of the atomic weights involved, a topic not without problems as discussed later. However, this paper is not dedicated to the pitfalls of atomic weight uncertainties. Its aim is to present the formula for the calculation of the uncertainty of the stoichiometric factor in order to facilitate the determination of the uncertainty budgets of certain analyses.

Derivation of the uncertainty formula for atomic mass fractions

Imagine a molecule or salt M which is composed of atoms A, B, and C (the letters are general symbols of the elements and B does not mean boron, etc.). The number of atoms in the formula is indicated with a, b, and c, that is, the molecular formula is $A_aB_bC_c$. The stoichiometric factor or mass fraction f_A for element A is:

$$f_A = \frac{a \cdot m_A}{a \cdot m_A + b \cdot m_B + c \cdot m_C} = \frac{a \cdot m_A}{m_M} \quad (3)$$

where $a,b,c \equiv x$ is the number of atoms of element X in the formula, m_X is the atomic weight of element X, and m_M is the formula weight of molecule M (note: the correct abbreviation of the atomic weight of element E is $A_r(E)$ [4]; m_A is a simplification.)

In order to simplify the derivation we introduce $A=am_A$, $B=bm_B$, $\Gamma=cm_C$, and $M=m_M$; therefore,

$$f_A = \frac{A}{M} = \frac{A}{A + B + \Gamma} \quad (4)$$

The combined standard uncertainty of the mass fraction, $u_c(f_A)$, is found by partial derivation [5]:

$$u_c(f_A) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial f_A}{\partial \Xi_i} \right)^2 \cdot u^2(\Xi_i)} \quad (5)$$

where Ξ is a mass xm_X, and $u(\Xi)$ is the x-fold standard uncertainty of the atomic weight of element X, that is, $u(\Xi)=xu(m_X)$.

The partial derivatives of Eq. 4 for the molecule $A_aB_bC_c$ are:

$$\frac{\partial f_A}{\partial A} = \frac{A + B + \Gamma}{(A + B + \Gamma)^2} - \frac{A}{A + B + \Gamma} = \frac{M - A}{M^2} \quad (6a)$$

$$\frac{\partial f_A}{\partial B} = \frac{A}{(A + B + \Gamma)^2} = \frac{A}{M^2} \quad (6b)$$

$$\frac{\partial f_A}{\partial \Gamma} = \frac{A}{(A + B + \Gamma)^2} = \frac{A}{M^2} \quad (6c)$$

These three elements combine to give:

$$u_c(f_A) = \frac{1}{M^2} \sqrt{(M - A)^2 \cdot u^2(A) + A^2 \left[u^2(B) + u^2(\Gamma) \right]} \quad (7)$$

The back-transformation with $M=m_M$, $A=am_A$, $u(A)=a(u_A)$ and so on gives:

$$u_c(f_A) = \frac{1}{m_M^2} \sqrt{\begin{array}{l} (m_M - a \cdot m_A)^2 \cdot a^2 u^2(m_A) \\ + a^2 \cdot m_A^2 \left[b^2 \cdot u^2(m_B) + c^2 \cdot u^2(m_C) \right] \end{array}} \quad (8a)$$

$$u_c(f_A) = \frac{a}{m_M^2} \sqrt{\begin{array}{l} (m_M - a \cdot m_A)^2 \cdot u^2(m_A) \\ + m_A^2 \left[b^2 \cdot u^2(m_B) + c^2 \cdot u^2(m_C) \right] \end{array}} \quad (8b)$$

The general equation for a compound $A_aB_bC_c...N_n$ is:

$$u_c(f_A) = \frac{a}{m_M^2} \sqrt{\begin{array}{l} (m_M - a \cdot m_A)^2 \cdot u^2(m_A) \\ + m_A^2 \sum_{x=b, X=B}^{n, N} (x^2 \cdot u^2(m_X)) \end{array}} \quad (9)$$

The uncertainty of atomic weights

The atomic weights of all elements m_X and their uncertainties have recently been published bi-annually by IUPAC [4]. Many of these uncertainties represent a $\pm 3s$ (3 standard deviations) or even a $\pm 6s$ range [6]. However, the probability distribution of an atomic weight within this range is poorly known for most elements and the Guide recommends that these data are treated as rectangular distributions [2] although a triangular distribution can be a reasonable alternative. A rectangular distribution is always used when the "true" distribution is unknown and only the highest and lowest possible values are known. In order to obtain a standard uncertainty $u(m_X)$ from a rectangular distribution it is necessary to divide the number (strictly speaking, half the range) by $\sqrt{3}$ [5].

Problems associated with atomic weight data (including the question whether the terms "mass" or "weight" should be used) have been discussed by De Bièvre and Peiser [7]. In addition it must not be forgotten that the uncertainty of many atomic weights does not stem from the method of measurement but from the isotopic composition which is not constant for many elements. It can depend markedly on the geographic origin of the material or on its history (e.g., a water sample can be obtained from rain, ground water, fossil ice, etc.) [8]. The IUPAC table includes some hints regarding this problem [4]. There is always the possibility that the compound used by the chemist differs in composition from that used for the atomic weight determination. Nevertheless, it can be assumed that the IUPAC data are the best available to the broad scientific community.

The IUPAC table presents the data in the form of, for example, for antimony: $m_{Sb}=121.76(1)$. The number in brackets represents the uncertainty of the last digit (i.e., $m_{Sb}=121.76\pm0.01$). The standard uncertainty $u(m_{Sb})$ is therefore $0.01/\sqrt{3}=0.0058$. The relative standard uncertainty $u_{rel}(m_{Sb})$ is $0.0058/122=4.7\times10^{-5}$ (or 47 ppm).

Examples

Uncertainty of the mass fraction of Na in Na₂SO₄

IUPAC atomic weights m_X with uncertainties and standard uncertainties $u(m_X)$:

m_{Na}=22.98977±2×10⁻⁵, $u(m_{Na})$=1.15×10⁻⁵, $u_{rel}(m_{Na})$=0.5×10⁻⁶
m_S=32.065±5×10⁻³, $u(m_S)$=2.89×10⁻³, $u_{rel}(m_S)$=90×10⁻⁶
m_O=15.9994±3×10⁻⁴, $u(m_O)$=1.73×10⁻⁴, $u_{rel}(m_O)$=11×10⁻⁶

The relative uncertainties vary over three orders of magnitude.

$M_{Na_2SO_4}$

=142.04, f_{Na}=0.324

$$u_c(f_{Na}) = \frac{2}{142^2}\sqrt{\begin{array}{l}(142-2\times23)^2(1.15\times10^{-5})^2\\ +23^2\left[1^2(2.89\times10^{-3})+4^2(1.73\times10^{-4})^2\right]\end{array}}$$

$u_c(f_{Na})$=6.8×10⁻⁶=21×10⁻⁶ relative uncertainty

For molecules composed of two elements A_aB_b the absolute uncertainties of both atom fractions are identical. For example, for KF:

m_K=39.0983±1×10⁻⁴, $u(m_K)$=0.58×10⁻⁴
m_F=18.9984032±5×10⁻⁷, $u(m_F)$=2.9×10⁻⁷
M_{KF}=58.1, f_K=0.67, f_F=0.33
$u_c(f_K)$=0.33×10⁻⁶
$u_c(f_F)$=0.33×10⁻⁶

This is also true for compounds such as Al_2O_3 with $u_c(f_{Al})$=$u_c(f_O)$=2.7×10⁻⁶ (because m_{Al}=26.981538±2×10⁻⁶, $u(m_{Al})$=1.15×10⁻⁶, and m_O=15.9994±3×10⁻⁴, $u(m_O)$=1.73×10⁻⁴); or for SiF_4 with $u_c(f_{Si})$=$u_c(f_F)$=1.2×10⁻⁶ (because m_{Si}=28.0855±3×10⁻⁴, $u(m_{Si})$=1.73×10⁻⁴, and m_F=18.9984032±5×10⁻⁷, $u(m_F)$=2.89×10⁻⁷).

If the uncertainty of the mass fraction of a composed ion or part of the molecule needs to be known, it is necessary to calculate the mass uncertainty $u_c(m)$ of the ion (or part) in accordance with the Guide [2]. For a species $A_aB_bC_c... N_n$, $u_c(m)$ is:

$$u_c(m_X) = \sqrt{\sum_{x=a,X=A}^{n,N}(x \cdot u(m_X))^2} \qquad (10)$$

As an example, the mass uncertainty of the ion SO_4^{2-} is:

$$u_c(m_{SO_4}) = \sqrt{(1\times2.89\times10^{-3})^2 + (4\times1.73\times10^{-4})^2}$$
$$= 3.0\times10^{-3}$$

The uncertainty of the mass fraction of SO_4^{2-} in Na_2SO_4 is then calculated with Eq. 9 and gives $u_c(f_{SO_4})$ =6.8×10⁻⁶ or 10×10⁻⁶ relative uncertainty.

For cases such as Na_2SO_4 it is possible to use the rule mentioned above: in molecules composed from two species (which can be atoms or groups of atoms) the absolute uncertainties of both parts are identical. Therefore, if $u_c(f_{Na})$=6.8×10⁻⁶ it must be the same for the ion SO_4^{2-}. The relative uncertainties are different, of course.

To come back to the example of sulfate in barium sulfate, the easiest way to calculate $u_c(m_{SO_4})$ is to calculate $u_c(m_{Ba})$. With m_{Ba}=137.327±7×10⁻³, $u(m_{Ba})$=4.04×10⁻³, and the data given above for sulfur and oxygen we obtain: $u_c(f_{Ba})$= $u_c(f_{SO_4})$ =1.03×10⁻⁵. If we are interested in the concentration of sulfur in wheat flour, determined gravimetrically as barium sulfate, an uncertainty budget could look as follows (weighing uncertainties calculated in accordance with ref. [3]):

w_{Sample} 49.32 g of wheat flour, $u_{rel}(w_{Sample})$=3.3×10⁻⁵
w_{BaSO_4} 453.18 mg $BaSO_4$, $u_{rel}(w_{BaSO_4})$=6.4×10⁻⁵
f_S 0.137, $u(f_S)$=1.09×10⁻⁵, $u_{rel}(f_S)$=8.0×10⁻⁵
c_S (0.453 g×0.137)/49.3 g=1.3×10⁻³ g S/g flour

The analogy to Eq. 2 is:

$$u(c_S)_{rel} = \sqrt{u_{rel}^2(w_{BaSO_4}) + u_{rel}^2(w_{Sample}) + u_{rel}^2(f_S)}$$
$$= \sqrt{(6.4\times10^{-5})^2 + (3.3\times10^{-5})^2 + (8.0\times10^{-5})^2}$$
$$= 1.1\times10^{-4}$$

with the following uncertainty contributions: w_{Sample}≈5%, w_{BaSO_4} ≈10%, f_S≈55%.

The uncertainty value of 1.1×10⁻⁴ is probably the lowest possible limit. What needs to be considered in addition is the uncertainty of the stoichiometry, the purity of the precipitate, the solubility product of barium sulfate (i.e., the completeness of the precipitation), and the sample preparation if more steps than just the weighing of the flour sample are necessary. In addition, the Avogadro constant has an uncertainty (i.e., the link between the mass of an atom or a molecule and the SI unit kilogram).

Conclusion

The uncertainty of the stoichiometric factor, that is, of the mass fraction of element A in a molecule or salt M, can be a contribution to the combined standard uncertainty of an analytical procedure that is not to be neglected. It should appear in the uncertainty budget in cases where the procedure itself can be performed with high precision and accuracy such as gravimetric analyses. The equation for the combined standard uncertainty $u_c(f_A)$ of the stoichiometric factor f_A is repeated here as the essence of this paper:

$$u_c(f_A) = \frac{a}{m_M^2}\sqrt{\begin{array}{l}(m_M - a\cdot m_A)^2\cdot u^2(m_A)\\ +m_A^2\sum_{x=b,X=B}^{n,N}(x^2\cdot u^2(m_X))\end{array}}$$

where a=number of atoms of element A in the formula of molecule M, m_M=formula weight of molecule M, u=standard uncertainty, m_A=atomic weight of element A, x= number of atoms of element X in the formula, and m_X= atomic weight of element X.

778

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