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Coefficient of contribution to the combined standard uncertainty

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Abstract
The International Organization for Standardization (ISO) *Guide to the Expression of Uncertainty in Measurement* (GUM) describes a generic procedure for determining an estimate for the value of the measurand and its associated combined standard uncertainty from the estimates and their associated standard uncertainties for various input quantities. A user of the ISO-GUM who is interested in understanding, managing or improving the measurement procedure needs the details, usually expressed as an uncertainty budget, on how the estimate for the value of the measurand and its associated combined standard uncertainty were calculated. In particular, a user may be interested in quantifying the degrees of contribution to the combined standard uncertainty from its components. When the measurement equation is a linear function of uncorrelated input variables, the contribution from a component is usually quantified by the product of the component of uncertainty and its sensitivity coefficient. This paper introduces a coefficient of contribution that is suitable for both uncorrelated and correlated input variables. The proposed coefficient of contribution is useful for a variety of measurement equations. Correlations between input variables can significantly alter the relative importance of the contributions to the combined standard uncertainty from its components.

1. Introduction

The *Guide to the Expression of Uncertainty in Measurement* (GUM) [1] published by the International Organization for Standardization (ISO), referred to as the ISO-GUM here, recommends a generic procedure for determining an estimate y for the value Y of the measurand and its associated combined standard uncertainty $u(y)$ from the estimates $x_1, \ldots, x_n$ for the input quantities $X_1, \ldots, X_n$ and their associated standard uncertainties $u(x_1), \ldots, u(x_n)$ when the measurement equation $Y = f(X_1, \ldots, X_n)$ is specified. In the measurement equation $Y = f(X_1, \ldots, X_n)$, the symbols $X_1, \ldots, X_n$ and Y are used for variables having state-of-knowledge probability distributions about the input quantities $X_1, \ldots, X_n$ and the value Y of the measurand [1, section 4.1.6, 2]. The estimate y is determined by substituting the estimates $x_1, \ldots, x_n$ for $X_1, \ldots, X_n$ in $Y = f(X_1, \ldots, X_n)$. Thus

$$y = f(x_1, \ldots, x_n). \tag{1}$$

The measurement equation $Y = f(X_1, \ldots, X_n)$ is approximated by a first-order (linear) Taylor series about the input estimates $x_1, \ldots, x_n$ to obtain the approximation

$$Y \approx Y_{\text{linear}} = y + \sum_i c_i (X_i - x_i), \tag{2}$$

where $c_1, \ldots, c_n$ are, respectively, partial derivatives of Y with respect to $X_1, \ldots, X_n$ evaluated at $x_1, \ldots, x_n$. The partial derivatives $c_1, \ldots, c_n$ are interpreted as the sensitivity coefficients associated with the input quantities $X_1, \ldots, X_n$, respectively. If we regard x_i and $u(x_i)$ as the expected value and standard deviation of a state-of-knowledge distribution for X_i, the variance of Y_{linear} gives the following expression for

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propagating the uncertainties $u(x_1), \ldots, u(x_n)$:

$$u^2(y) = \sum_i \sum_j c_i c_j u(x_i) u(x_j) r(x_i, x_j), \qquad (3)$$

where $r(x_i, x_j)$ is the coefficient of correlation (also called the correlation coefficient) between X_i and X_j for $i, j = 1, \ldots, n$. The double sum in (3) consists of n^2 terms. Equation (3) is often expressed as

$$u^2(y) = \sum_i c_i^2 u^2(x_i) + 2 \sum_{i<j} c_i c_j u(x_i) u(x_j) r(x_i, x_j). \qquad (4)$$

When $X_1, \ldots, X_n$ are mutually uncorrelated, i.e. $r(x_i, x_j) = 0$ for $i \neq j$, equation (4) reduces to

$$u^2(y) = \sum_i c_i^2 u^2(x_i). \qquad (5)$$

A user of the ISO-GUM who is interested in understanding, managing or improving the measurement procedure needs the details, usually expressed as an uncertainty budget, on how y and $u(y)$ were calculated. In particular, a user may be interested in quantifying the degrees of contribution to the combined standard uncertainty $u(y)$ from each of the components $u(x_1), \ldots, u(x_n)$. We use the term *coefficient of contribution* for a measure of the contribution to $u(y)$ from a component $u(x_i)$, for $i = 1, \ldots, n$.

Using the ISO-GUM as the basis, the European co-operation for Accreditation has published the document *Expression of the Uncertainty of Measurement in Calibration*, referred to as EA-4/02. When the input variables $X_1, \ldots, X_n$ are mutually uncorrelated, EA-4/02 [3, equation (4.2), p 10] uses the product $u_i(y) = c_i \cdot u(x_i)$ as the contribution to the standard uncertainty $u(y)$ from $u(x_i)$, where c_i is the sensitivity coefficient associated with X_i. The EA-4/02 tabulates $u_i(y)$ in the uncertainty budget.

A joint Eurachem/CITAC Working Group has published a guide based on the ISO-GUM for *Quantifying Uncertainty in Analytical Measurement* [4], referred to as the Eurachem-Guide. When the input variables $X_1, \ldots, X_n$ are mutually uncorrelated, the Eurachem-Guide also uses the expression[5] $u_i(y)$ as the contribution to $u(y)$ from $u(x_i)$. The Eurachem-Guide displays the bar-charts of $u_i(y)$ for $i = 1, \ldots, n$. This paper describes a coefficient of contribution that is suitable for both uncorrelated and correlated input variables $X_1, \ldots, X_n$ originally proposed in Kessel [5].

In section 2, the coefficient of contribution for uncorrelated input variables is discussed. In section 3, we introduce a more general expression for the coefficient of contribution which is useful for both uncorrelated and correlated input variables. In section 4, the coefficients of contribution for measurement equations involving sums and products of input variables are discussed. Subsequently, in section 5 there is an example of correlated input quantities. The coefficients of contribution to the molar mass of lead (Pb) are calculated from the molar masses of its isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, and their amount fractions, which are correlated. A summary appears in section 6. The symbols used in this paper agree with the ISO-GUM [1] and the NIST Technical Note 1297 [6]. A list is provided in appendix A.

[5] The Eurachem-Guide uses the symbol $u(y, x_i)$ for $u_i(y)$ and defines it as $\sqrt{c_i^2 \cdot u^2(x_i)}$. Following the ISO-GUM, we use the symbol $u(y, x_i)$ for the covariance between state-of-knowledge distributions for Y and X_i.

2. Coefficient of contribution for uncorrelated input variables

When the input variables $X_1, \ldots, X_n$ are mutually uncorrelated, EA-4/02 uses the following expression as the contribution to uncertainty $u(y)$ from $u(x_i)$:

$$u_i(y) = c_i \cdot u(x_i), \qquad (6)$$

for $i = 1, \ldots, n$. The uncertainty contribution, $u_i(y)$, has the same units of measurement as the value Y of the measurand. A particular input quantity X_j may be used for evaluating a number of measurands and its uncertainty contribution may be different for different measurands. For intercomparison of the contributions of X_j with different measurands, it is desirable to express the coefficient of contribution on a scale relative to the combined standard uncertainty. Therefore, we propose the following expression as the coefficient of contribution for uncorrelated input variables:

$$h(y, x_i) = \left[\frac{u_i(y)}{u(y)}\right]^2 = \left[\frac{c_i \cdot u(x_i)}{u(y)}\right]^2. \qquad (7)$$

We may abbreviate $h(y, x_i)$ as $h_i(y)$. The coefficient of contribution, $h(y, x_i)$, expresses $u_i^2(y)$ on a dimensionless scale. It follows, from equation (5), that the values of $h(y, x_i)$ are fractions of one and they add up to one. Thus $h(y, x_i)$ may be expressed as a percentage. Expression (7) is a special case of a more general expression for the coefficient of contribution discussed in section 3.

When the input variables $X_1, \ldots, X_n$ are mutually uncorrelated, the coefficient of correlation, $R(Y, X_i)$, between the state-of-knowledge probability distributions[6] for Y and X_i is

$$r(y, x_i) = \frac{u_i(y)}{u(y)} = \frac{c_i \cdot u(x_i)}{u(y)} \qquad (8)$$

(appendix B). So $h(y, x_i) = r^2(y, x_i)$. In words, the coefficient of contribution, $h(y, x_i)$, for uncorrelated input variables is equal to the square of the coefficient of correlation, $r^2(y, x_i)$, between Y and X_i. Thus, the coefficient of contribution, $h(y, x_i)$, proposed in equation (7) has a well-understood statistical interpretation.

The coefficients of contribution are a useful part of an uncertainty budget. For example, they are useful in the Procedure for Uncertainty Management (PUMA) described in the ISO Technical Specification ISO/TS 14253-2 [7]. PUMA is used to iteratively determine a more accurate uncertainty budget for the combined standard uncertainty. At each stage, the contribution of each component to the combined uncertainty is computed. Thus, the uncertainty budget identifies the dominant components of the combined uncertainty.

2.1. Illustrative example

Consider the following example from EA-4/02 [3, section S2] on calibration of a mass of nominal value 10 kg. This example

[6] In the ISO-GUM, the state-of-knowledge probability distribution for Y is the distribution of Y_{linear} in equation (2).

Table 1. Uncertainty budget including the coefficients of contribution is given.

Quantity	Value x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $u_i(y)$	Coefficient of contribution $h(y, x_i)$
m_S	10 000.0050 g	22.5×10^{-3} g	1.0	22.5×10^{-3} g	59.6%
δm_D	0.0 g	8.66×10^{-3} g	1.0	8.66×10^{-3} g	8.8%
δ_m	0.0200 g	14.2×10^{-3} g	1.0	14.2×10^{-3} g	23.7%
δm_C	0.0 g	5.77×10^{-3} g	1.0	5.77×10^{-3} g	3.9%
δ_B	0.0 g	5.77×10^{-3} g	1.0	5.77×10^{-3} g	3.9%
m_X	10 000.0250 g	29.1×10^{-3} g	—	—	—

illustrates the calculation of the coefficients of contribution for uncorrelated input variables. The measurement equation is

$$m_X = m_S + \delta m_D + \delta_m + \delta m_C + \delta_B, \tag{9}$$

where m_X is the mass of the unknown artefact, m_S is the conventional mass of the reference standard, δm_D is the change in value of the standard since last calibration, δ_m is the observed difference in mass between artefact and standard, δm_C is the correction for eccentricity and magnetic effects and δ_B is the correction for air buoyancy.

Table 1 concatenates the coefficients of contribution $h(y, x_i)$ to the uncertainty budget given in EA-4/02.

The coefficients of contribution $h(y, x_i)$ indicate the degrees of contribution to the combined standard uncertainty from its components. For example, the uncertainty associated with the reference standard contributes 59.6% to the combined uncertainty. The coefficients of contribution can be directly added. Thus the coefficient of contribution from the two components, conventional mass and its change in value, related to the reference standard is 68.4%. Thus, more than two-thirds of the combined uncertainty comes from the reference standard itself.

3. A more general expression for the coefficient of contribution

When the input variables $X_1, \ldots, X_n$ are correlated, the coefficient of correlation, $R(Y, X_i)$, between Y and X_i denoted by $r(y, x_i)$ is

$$r(y, x_i) = \sum_j \left[\frac{c_j u(x_j)}{u(y)}\right][r(x_i, x_j)], \tag{10}$$

where $r(x_i, x_j)$ is the coefficient of correlation between X_i and X_j for $i, j = 1, \ldots, n$ (appendix B). For such cases, Kessel [5] proposed the following coefficient of contribution:

$$h(y, x_i) = \left[\frac{c_i u(x_i)}{u(y)}\right][r(y, x_i)]. \tag{11}$$

The coefficients of contribution $h(y, x_i)$ are dimensionless numbers, some of which may be negative. However, the values of $h(y, x_i)$ add up to one (appendix C). So the coefficients of contribution $h(y, x_i)$ defined in equation (11) may be expressed as a percentage.

In the special case where $X_1, \ldots, X_n$ are uncorrelated, i.e. $r(x_i, x_j) = 0$ for $i \neq j$, the coefficient of correlation $r(y, x_i)$ of equation (10) reduces to equation (8) and the coefficient of contribution $h(y, x_i)$ of equation (11) reduces to equation (7) (appendix B). Thus, the coefficient of contribution for uncorrelated input variables (equation (7)) is a special case of the more general coefficient of contribution $h(y, x_i)$ defined in equation (11).

4. Measurement equations involving sums and products of variables

Many measurement equations in chemical and physical metrology can be expressed in one of the following four forms: additive equation,

$$Y = \sum_i a_i X_i, \tag{12}$$

multiplicative equation,

$$Y = \prod_i X_i^{a_i}, \tag{13}$$

additive equation of products,

$$Y = \sum_i a_i \left(\prod_{ij} W_{ij}^{b_{ij}}\right), \tag{14}$$

and multiplicative equation of sums,

$$Y = \prod_i \left(\sum_{ij} b_{ij} W_{ij}\right)^{a_i}. \tag{15}$$

Here a_i and b_{ij} are specified constants for $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, m_i$. In the special case where $n = 2$, and $m_1 = m_2 = 2$, and a_i and b_{ij} are all equal to one, these equations reduce to $Y = X_1 + X_2$, $Y = X_1 \times X_2$, $Y = (W_{11} \times W_{12}) + (W_{21} \times W_{22})$ and $Y = (W_{11} + W_{12}) \times (W_{21} + W_{22})$, respectively. The last two equations may be expressed, respectively, as $Y = X_1 + X_2$, where $X_1 = (W_{11} \times W_{12})$ and $X_2 = (W_{21} \times W_{22})$ and $Y = X_1 \times X_2$, where $X_1 = (W_{11} + W_{12})$ and $X_2 = (W_{21} + W_{22})$. The estimates and standard uncertainties for W_{ij} are denoted by w_{ij} and $u(w_{ij})$, respectively. They are identified with the expected value and (approximate) standard deviation of W_{ij}. The coefficients of contribution for the measurement equations from (12) to (15) are discussed below.

4.1. Additive equation

The measurement equation (12) is linear and of the form of equation (2), where

$$y = \sum_i a_i x_i \tag{16}$$

and $c_i = a_i$ for $i = 1, 2, \ldots, n$. The standard uncertainty $u(y)$ associated with the estimate y of equation (16) is the positive square root of $u^2(y)$, where

$$u^2(y) = \sum_i \sum_j a_i a_j u(x_i) u(x_j) r(x_i, x_j). \tag{17}$$

So the coefficients of contribution $h(y, x_i)$ determined from equations (10) and (11) are

$$h(y, x_i) = \left[\frac{a_i u(x_i)}{u(y)}\right] [r(y, x_i)], \tag{18}$$

where

$$r(y, x_i) = \sum_j \left[\frac{a_j u(x_j)}{u(y)}\right] [r(x_i, x_j)], \tag{19}$$

for $i = 1, 2, \ldots, n$. When $X_1, \ldots, X_n$ are uncorrelated, the coefficient of correlation $r(y, x_i)$ in equation (19) reduces to

$$r(y, x_i) = \left[\frac{a_i u(x_i)}{u(y)}\right] \tag{20}$$

and the coefficient of contribution $h(y, x_i)$ in equation (18) reduces to

$$h(y, x_i) = \left[\frac{a_i u(x_i)}{u(y)}\right]^2. \tag{21}$$

4.2. Multiplicative equation

The measurement equation (13) can be approximated by a linear equation of the form (2), where

$$y = \prod_i x_i^{a_i} \tag{22}$$

and $c_i = (a_i \times y)/x_i$ for $i = 1, 2, \ldots, n$. The standard uncertainty $u(y)$ associated with y of equation (22) is obtained from the expression (3) by substituting $c_i = (a_i \times y)/x_i$. Thus,

$$u_\mathrm{r}^2(y) = \sum_i \sum_j a_i a_j u_\mathrm{r}(x_i) u_\mathrm{r}(x_j) r(x_i, x_j), \tag{23}$$

where $u_\mathrm{r}(x_i) = u(x_i)/|x_i|$ and $u_\mathrm{r}(y) = u(y)/|y|$ are the relative standard uncertainties associated with x_i and y, respectively, and $u(y) = |y| \times u_\mathrm{r}(y)$. The coefficients of contribution $h(y, x_i)$ determined from equations (10) and (11) are

$$h(y, x_i) = \left[\frac{a_i u(x_i)/x_i}{u(y)/y}\right] [r(y, x_i)] = \left[\frac{a_i u_\mathrm{r}(x_i)}{u_\mathrm{r}(y)}\right] [r(y, x_i)], \tag{24}$$

where

$$r(y, x_i) = \sum_j \left[\frac{a_j u(x_j)/x_j}{u(y)/y}\right] [r(x_i, x_j)] = \sum_j \left[\frac{a_j u_\mathrm{r}(x_j)}{u_\mathrm{r}(y)}\right] [r(x_i, x_j)], \tag{25}$$

for $i = 1, 2, \ldots, n$. When $X_1, \ldots, X_n$ are uncorrelated, $h(y, x_i)$ in equation (24) reduces to

$$h(y, x_i) = \left[\frac{a_i u_\mathrm{r}(x_i)}{u_\mathrm{r}(y)}\right]^2. \tag{26}$$

4.3. Additive equation of products

The measurement equation (14) can be expressed as two sets of hierarchical equations: equation (12) and the set of n equations represented by

$$X_i = \prod_{ij} W_{ij}^{b_{ij}}, \tag{27}$$

for $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, m_i$. The coefficients of contribution $h(y, x_i)$ for equation (12) are defined in equation (18). The coefficients of contribution $h(x_i, w_{ij})$ for n equations represented by (27) can be determined from equations such as (24) and (25) by replacing x_i with w_{ij}, a_i with b_{ij} and y with x_i. Then $\sum_j h(x_i, w_{ij}) = 1$, where $j = 1, 2, \ldots, m_i$ for each $i = 1, 2, \ldots, n$. The coefficients of contribution $h(y, w_{ij})$ for the measurement equation (14) can be defined as

$$h(y, w_{ij}) = h(y, x_i) \times h(x_i, w_{ij}) \tag{28}$$

for $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, m_i$. Since $\sum_j h(x_i, w_{ij}) = 1$, we have $\sum_i \sum_j h(y, w_{ij}) = \sum_i h(y, x_i) \sum_j h(x_i, w_{ij}) = \sum_i h(y, x_i) = 1$.

4.4. Multiplicative equation of sums

The measurement equation (15) can be expressed as two sets of hierarchical equations: equation (13) and the set of n equations represented by

$$X_i = \sum_{ij} b_{ij} W_{ij}, \tag{29}$$

for $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, m_i$. The coefficients of contribution $h(y, x_i)$ for equation (13) are defined in equation (24). The coefficients of contribution $h(x_i, w_{ij})$ for the n equation represented by (29) can be determined from equations such as (18) and (19) by replacing x_i with w_{ij}, a_i with b_{ij} and y with x_i. Then equation (28) can be used to determine the coefficients of contribution $h(y, w_{ij})$ for the measurement equation (15).

5. Coefficients of contribution in determining the molar mass of lead

The following example illustrates the calculation of the coefficients of contribution for correlated input variables from a measurement equation that is the sum of the products of input variables. The *isotopic composition* of lead varies in nature and this fact is used in many scientific applications such as source allocation and isotope fingerprinting. Suppose the measurand is the *molar mass* of lead (M_{Pb}) consisting of the following four isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The molar mass M_{Pb} is defined by the following equation:

$$M_{\mathrm{Pb}} = M_{204\mathrm{Pb}} \times f_{204\mathrm{Pb}} + M_{206\mathrm{Pb}} \times f_{206\mathrm{Pb}} + M_{207\mathrm{Pb}} \times f_{207\mathrm{Pb}} + M_{208\mathrm{Pb}} \times f_{208\mathrm{Pb}}, \tag{30}$$

where $M_{204\mathrm{Pb}}$, $M_{206\mathrm{Pb}}$, $M_{207\mathrm{Pb}}$ and $M_{208\mathrm{Pb}}$ are the molar masses and $f_{204\mathrm{Pb}}$, $f_{206\mathrm{Pb}}$, $f_{207\mathrm{Pb}}$ and $f_{208\mathrm{Pb}}$ are the corresponding *amount fractions* (also called abundance) of the four isotopes in the sample. The molar masses $M_{204\mathrm{Pb}}$, $M_{206\mathrm{Pb}}$, $M_{207\mathrm{Pb}}$ and $M_{208\mathrm{Pb}}$ are obtained from reference tables. The amount fractions $f_{204\mathrm{Pb}}$, $f_{206\mathrm{Pb}}$, $f_{207\mathrm{Pb}}$ and $f_{208\mathrm{Pb}}$ are determined from mass spectrometry. The amount fractions add up

Table 2. The values, standard uncertainties and relative standard uncertainties for the molar masses from reference [8] are given.

Quantity	Value M_i	Standard uncertainty $u(M_i)$	Relative standard uncertainty $u_r(M_i)$
$M_{204\mathrm{Pb}}$	203.973 0436	1.3×10^{-6}	6.4×10^{-9}
$M_{206\mathrm{Pb}}$	205.974 4653	1.3×10^{-6}	6.3×10^{-9}
$M_{207\mathrm{Pb}}$	206.975 8969	1.3×10^{-6}	6.3×10^{-9}
$M_{208\mathrm{Pb}}$	207.976 6521	1.3×10^{-6}	6.3×10^{-9}

Table 3. The values, standard uncertainties and relative standard uncertainties for the amount fractions (appendix D) are given.

Quantity	Value f_i	Standard uncertainty $u(f_i)$	Relative standard uncertainty $u_r(f_i)$
$f_{204\mathrm{Pb}}$	0.013 389 034	60.355×10^{-6}	4.5×10^{-3}
$f_{206\mathrm{Pb}}$	0.249 848 56	309.84×10^{-6}	1.2×10^{-3}
$f_{207\mathrm{Pb}}$	0.214 569 19	458.56×10^{-6}	2.1×10^{-3}
$f_{208\mathrm{Pb}}$	0.522 193 21	369.10×10^{-6}	7.1×10^{-4}

Table 4. Correlation coefficients between the amount fractions (appendix D) are given.

$r(f_i, f_j)$	$f_{204\mathrm{Pb}}$	$f_{206\mathrm{Pb}}$	$f_{207\mathrm{Pb}}$	$f_{208\mathrm{Pb}}$
$f_{204\mathrm{Pb}}$	1	0.309 9065	−0.204 0958	−0.170 1139
$f_{206\mathrm{Pb}}$	0.309 9065	1	−0.612 2649	−0.1294786
$f_{207\mathrm{Pb}}$	−0.204 0958	−0.612 2649	1	−0.695 0289
$f_{208\mathrm{Pb}}$	−0.170 1139	−0.129 4786	−0.695 0289	1

to one. For illustration, we will use equation (30) as the measurement equation consisting of eight input variables $M_{204\mathrm{Pb}}, M_{206\mathrm{Pb}}, M_{207\mathrm{Pb}}, M_{208\mathrm{Pb}}, f_{204\mathrm{Pb}}, f_{206\mathrm{Pb}}, f_{207\mathrm{Pb}}$ and $f_{208\mathrm{Pb}}$. This measurement equation is in the form of equation (14). For brevity we condense the subscripts and write the measurement equation (30) as

$$Y = M_1 \times f_1 + M_2 \times f_2 + M_3 \times f_3 + M_4 \times f_4, \quad (31)$$

where $Y \equiv M_{\mathrm{Pb}}, M_1 \equiv M_{204\mathrm{Pb}}, f_1 \equiv f_{204\mathrm{Pb}}, M_2 \equiv M_{206\mathrm{Pb}}, f_2 \equiv f_{206\mathrm{Pb}}, M_3 \equiv M_{207\mathrm{Pb}}, f_3 \equiv f_{207\mathrm{Pb}}, M_4 \equiv M_{208\mathrm{Pb}}, f_4 \equiv f_{208\mathrm{Pb}}$. The values, standard uncertainties and relative standard uncertainties for the molar masses, M_1, M_2, M_3 and M_4, and the amount fractions, f_1, f_2, f_3 and f_4, are given in tables 2 and 3, respectively. Since the sum of the amounts of fraction $f_1 + f_2 + f_3 + f_4$ is one, they are mutually correlated. The correlation coefficients between the amount fractions are given in table 4.

The molar masses and the amount fractions are not correlated. Therefore, it follows from equation (23) that the square of the relative standard uncertainty associated with the product $M_i \times f_i$ is equal to the sum of the squares of the relative standard uncertainties associated with M_i and f_i for $i = 1, 2, 3, 4$. The relative standard uncertainties associated with the isotope molar masses, M_i, are of the order of ten to the power minus nine and the relative standard uncertainties associated with the amount fractions, f_i, are of the order of ten to the power minus three or four. Therefore, the relative standard uncertainties associated with the products $M_i \times f_i$ are practically equal to the relative standard uncertainties associated with the amount fractions f_i for $i = 1, 2, 3, 4$. So we may regard the molar masses M_1, M_2, M_3 and M_4 in the measurement equation (31) as constants. Thus, the uncertainty in the molar mass $Y(\equiv M_{\mathrm{Pb}})$ arises almost entirely from the uncertainties associated with the amount fractions f_1, f_2, f_3 and f_4. Therefore the correlation coefficients, $r(y, f_i)$, between the molar mass Y and the amount fractions are determined from equation (19) and the corresponding coefficients of contribution, $h(y, f_i)$, are determined from equation (18). The computed values of $r(y, f_i)$ and $h(y, f_i)$ are given in table 5.

In table 5, the combined uncertainty $u(y)$ for the molar mass $Y(\equiv M_{\mathrm{Pb}})$ is two orders of magnitude smaller than each of its components $u_i(y)$. The reason is that five of the six correlation coefficients $r(f_i, f_j)$ between the amount fractions are negative and the sensitivity coefficients, which are the isotope molar masses M_i, are positive. This highlights the importance of correlations between the input variables. The coefficients of contribution $h(y, f_i)$ add up 100% as expected, but they have very large positive and negative values. This is a discomforting consequence of using the measurement equation (31) based on the amount fractions.

An alternative approach to evaluate the molar mass of lead is to use the following measurement equation based on the isotope ratios:

$$Y = \frac{R_1 \times M_1 + R_2 \times M_2 + R_3 \times M_3 + M_4}{R_1 + R_2 + R_3 + 1}, \quad (32)$$

where $Y \equiv M_{\mathrm{Pb}}, M_1 \equiv M_{204\mathrm{Pb}}, R_1 \equiv R_{204/208}, M_2 \equiv M_{206\mathrm{Pb}}, R_2 \equiv R_{206/208}, M_3 \equiv M_{207\mathrm{Pb}}, R_3 \equiv R_{207/208}, M_4 \equiv M_{208\mathrm{Pb}}$. The values of isotope ratios, their associated uncertainties and correlation coefficients are given in appendix D. As before, the uncertainties associated with the molar masses M_1, M_2, M_3 and M_4 are negligible so they may be regarded as constants.

Table 6 displays the calculated results together with correlation coefficients and coefficients of contribution for the isotope ratios. The values for the molar mass $Y(\equiv M_{\mathrm{Pb}})$ and its associated standard uncertainty $u(y)$ displayed in tables 5 and 6 differ in the last digit due to numerical rounding errors. The coefficients of contribution for the isotope ratios are positive. In this sense, it is a more pleasing approach than the earlier one based on the amount fractions.

6. Summary

The coefficient of contribution associated with a component of uncertainty is a measure of its relative contribution to the combined standard uncertainty determined according to the ISO-GUM. The coefficients of contribution are useful in understanding, managing and improving the measurement procedure. A good measure of the contribution of a component of uncertainty should have the following attributes: it should be dimensionless, one should be able to directly add the contributions and the sum of all contributions must be 100%. We described a measure for the coefficient of contribution which has these attributes. The proposed coefficient of contribution is suitable for both correlated and uncorrelated input variables and is useful for a variety of measurement equations. When the input variables are uncorrelated, the coefficients of contribution are all positive. When the input

Table 5. Correlation coefficients (between the molar mass and the amount fractions) and the corresponding coefficients of contribution are given.

Quantity	Value f_i	Standard uncertainty $u(f_i)$	Uncertainty contribution $u_i(y)$	Correlation coefficient $r(y, f_i)$	Coefficient of contribution $h(y, f_i)$
$f_{204\text{Pb}}$	0.013 3890	60.4×10^{-6}	$0.012\ \text{g mol}^{-1}$	−0.572 9004	−1185.6%
$f_{206\text{Pb}}$	0.249 849	310×10^{-6}	$0.064\ \text{g mol}^{-1}$	−0.698 6272	−7494.8%
$f_{207\text{Pb}}$	0.214 569	459×10^{-6}	$0.095\ \text{g mol}^{-1}$	−0.049 1241	−783.7%
$f_{208\text{Pb}}$	0.522 193	369×10^{-6}	$0.077\ \text{g mol}^{-1}$	0.741 1781	9564.1%
M_{Pb}	$207.208\,072\ \text{g mol}^{-1}$	—	$0.000\,595\ \text{g mol}^{-1}$	—	—

Table 6. Correlation coefficients (between the molar mass and the isotope ratios) and the corresponding coefficients of contribution are given.

Quantity	Value R_i	Standard uncertainty $u(R_i)$	Uncertainty contribution $u_i(y)$	Correlation coefficient $r(y, R_i)$	Coefficient of contribution $h(y, R_i)$
$R_{204/208}$	0.025 64	0.000 12	$-0.000\,20\ \text{g mol}^{-1}$	−0.66	22.6%
$R_{206/208}$	0.478 46	0.000 72	$-0.000\,46\ \text{g mol}^{-1}$	−0.92	72.1%
$R_{207/208}$	0.410 9	0.001 1	$-0.000\,13\ \text{g mol}^{-1}$	−0.24	5.3%
M_{Pb}	$207.208\,073\ \text{g mol}^{-1}$	—	$0.000\,594\ \text{g mol}^{-1}$	—	—

variables are correlated, the coefficients of contribution may be positive or negative but they add up to 100%. The coefficients of contribution are insightful for both correlated and uncorrelated input variables.

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Disclaimer

Certain software is identified in this paper. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the software is necessarily the best available for the purpose.

Appendix A. A list of the symbols used in this paper

Y	Value of the measurand; variable representing the state of knowledge
y	Result of measurement (estimate) for Y
$u(y)$	Standard uncertainty associated with y
$u_r(y)$	Relative standard uncertainty $u(y)/\lvert y\rvert$
Y_{linear}	First order (linear) Taylor series approximation for Y
X_i	Input quantity; variable representing the state of knowledge
x_i	Estimate for X_i
$u(x_i)$	Standard uncertainty associated with x_i
$u_r(x_i)$	Relative standard uncertainty $u(x_i)/\lvert x_i\rvert$
c_i	Sensitivity coefficient associated with X_i
$u_i(y)$	Uncertainty contribution $c_i \cdot u(x_i)$
$u(x_i, x_j)$	Covariance between X_i and X_j
$r(x_i, x_j)$	Correlation coefficient between X_i and X_j
$u(y, x_i)$	Covariance between Y and X_i
$r(y, x_i)$	Correlation coefficient between Y and X_i
$r(y_k, y_l)$	Correlation coefficient between Y_k and Y_l
$h(y, x_i)$	Coefficient of contribution from $u(x_i)$ to $u(y)$

Appendix B. The coefficients of correlation between Y_{linear} and X_i

The covariance, $C(Y_{\text{linear}}, X_i)$, between Y_{linear} in equation (2) and X_i, denoted by $u(y, x_i)$, is

$$u(y, x_i) = C(Y_{\text{linear}}, X_i) = \sum_j c_j C(X_i, X_j) = \sum_j c_j u(x_i, x_j) = \sum_j c_j u(x_i) u(x_j) r(x_i, x_j). \tag{33}$$

That is, covariance $u(y, x_i)$ is

$$u(y, x_i) = u(x_i) \sum_j c_j u(x_j) r(x_i, x_j) \tag{34}$$

and variances of X_i and Y_{linear} are $u^2(x_i)$ and $u^2(y)$, respectively. So the coefficient of correlation, $R(Y_{\text{linear}}, X_i)$, between Y_{linear} and X_i, denoted by $r(y, x_i)$, is

$$r(y, x_i) = R(Y_{\text{linear}}, X_i) = \frac{u(x_i) \sum_j c_j u(x_j) r(x_i, x_j)}{u(x_i) u(y)} = \sum_j \left[\frac{c_j u(x_j)}{u(y)}\right] r(x_i, x_j). \tag{35}$$

The coefficient of correlation $r(y, x_i)$ may be negative depending on the coefficients of correlation $r(x_i, x_j)$ and sensitivity coefficients $c_1, \ldots, c_n$. When $X_1, \ldots, X_n$ are uncorrelated, i.e. $r(x_i, x_j) = 0$ for $i \neq j$, equation (35) reduces to

$$r(y, x_i) = R(Y_{\text{linear}}, X_i) = \left[\frac{c_i u(x_i)}{u(y)}\right]. \quad (36)$$

Appendix C. The coefficients of contribution $h(y, x_i)$ add up to one

Dividing both sides of equation (3) by $u^2(y)$, we have

$$\sum_i \left[\frac{c_i u(x_i)}{u(y)} \left(\sum_j \frac{c_j u(x_j) r(x_i, x_j)}{u(y)}\right)\right] = 1. \quad (37)$$

The inner sum in equation (37) is $r(y, x_i)$. Therefore,

$$\sum_i \left[\frac{c_i u(x_i)}{u(y)} r(y, x_i)\right] = 1. \quad (38)$$

The summands in (38) are $h(y, x_i)$ (see equation (11)); so $\sum_i h(y, x_i) = 1$.

Appendix D. Values, uncertainties and correlation coefficients for isotope ratios

Suppose m output quantities Y_j, for $j = 1, \ldots, m$, are evaluated from n input quantities X_i for $i = 1, \ldots, n$ through the following measurement equations:

$$Y_j = f_j(X_1, \ldots, X_n), \quad (39)$$

for $j = 1, \ldots, m$. Then the correlation coefficient between Y_k and Y_l, denoted by $r(y_k, y_l)$, based on linear approximations of the measurement equations (39) is

$$r(y_k, y_l) = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{u_i(y_k)}{u(y_k)} \cdot \frac{u_j(y_l)}{u(y_l)} \cdot r(x_i, x_j), \quad (40)$$

for $k, l = 1, \ldots, m$ [1, section H.2.3].

The amount fractions are calculated from the isotope ratios R_i as follows:

$$f_i = \frac{R_i}{\sum_j R_j}, \quad (41)$$

where $f_1 \equiv f_{204\text{Pb}}$, $f_2 \equiv f_{206\text{Pb}}$, $f_3 \equiv f_{207\text{Pb}}$, and $f_4 \equiv f_{208\text{Pb}}$, $R_1 \equiv R_{204/208}$, $R_2 \equiv R_{206/208}$, $R_3 \equiv R_{207/208}$ and $R_4 \equiv R_{208/208} \equiv 1$. The isotope ratios R_i are determined by mass spectrometry [9]. The values of the isotope ratios, their associated uncertainties and correlation coefficients used in this paper are given in tables 7 and 8.

The correlation coefficients between the amount fractions displayed in table 4 were computed from expressions such as equation (40) using the software [11].

Table 7. Isotope ratios R_i determined from mass spectrometry [10].

Quantity	Value	Standard uncertainty	Relative standard uncertainty
$R_{204/208}$	0.025 64	0.000 12	4.7×10^{-3}
$R_{206/208}$	0.478 46	0.000 72	1.5×10^{-3}
$R_{207/208}$	0.410 9	0.001 1	2.7×10^{-3}

Table 8. Correlation coefficients between the isotope ratios arising from common correction factors are given.

Correlation coefficients	$R_{204/208}$	$R_{206/208}$	$R_{207/208}$
$R_{204/208}$	1	0.41	0.01
$R_{206/208}$	0.41	1	0.01
$R_{207/208}$	0.01	0.01	1

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