QUANTIFYING MEASUREMENT UNCERTAINTY IN ANALYTICAL

CHEMISTRY – A SIMPLIFIED PRACTICAL APPROACH

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Abstract - **Following a simple and practical approach can minimize the headaches of calculating the components of measurement uncertainty. Basic requirements for planning an analysis, realistically estimating the magnitude of uncertainty sources, and combining uncertainty components will be presented using examples of analytical chemistry methods.**

Keywords: cause and effect diagram; combined uncertainty; Kragten spreadsheet; measurement; quantification; uncertainty

1. Introduction

What follows is a simple and practical approach to quantify measurement uncertainty, u, based on information gathered from many helpful resources. To the novice attempting to quantify the uncertainty in a chemical analysis, the task may seem daunting and far from simple because of the multiple new terms, diagrams and calculations required. It may be tempting to just hazard a guess as to the magnitude of the uncertainty, since it is just an estimate anyway, isn't it? However, the complete approach shown here is widely applicable and can minimize the headaches of calculating measurement uncertainty. The complete approach can also lead to a more accurate analytical determination. A generalized scheme for planning the analysis and estimating and combining the uncertainty sources is followed by examples.

2. Background

### *Planning an analysis of the composition of a sample*

The comments that follow are based on the assumption that the analyst is interested in measuring one or more analytes in a sample that has been provided to the laboratory. This planning can be applied to a specific one-time analysis or to the general analysis scheme for a routine testing laboratory with minor modifications made based on the sample, analyte, and experience.

- Select a general analytical method based on the accuracy required.
- Plan the analysis so that all the information of interest can be extracted from the data to reach a valid and repeatable conclusion with a minimal expenditure of time and cost.
- Determine what constitutes a representative test sample and the number of representative test samples required.
- Write out the measurement equation for the result (*i.e.,* the equation that explicitly shows how the various measured and theoretical quantities from the experiment are combined to obtain the final result) and consider the factors that can influence variability and bias of the result. Factors that influence the variability and bias of the analytical result should be controlled to the extent that a subsequent repeat analysis of the original sample likely will yield a result that agrees within the limits of uncertainty. Apparent variability should not be controlled to the point that repeated measurements are limited to a single test sample in a short period of time, since that limitation likely will produce a result that cannot be repeated at a later date for other test samples. As stated by W. J. Youden, a chemist and recognized expert in statistical design of experiments, "Repeat measurements cannot reveal the vicissitudes of measurement making unless the operator gives the vicissitudes a chance to occur" [1]. A book by Box, Hunter and Hunter [2] is an excellent source of additional information on experimental design.
- Make measurements.
- Estimate the magnitude of each uncertainty source after all of the measurements in the analysis plan are completed,

## *Estimating the magnitude of uncertainty sources*

Determine the major sources of uncertainty that are associated with each component of the measurement equation. Focus on the largest uncertainty sources. Those sources that have a magnitude of one-third or more of the largest source should be examined in detail. Less attention should be spent estimating smaller sources. The Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" [3], hereafter referred to as the "Eurachem Guide", lists common sources and values of uncertainty in its Appendix G. It is

helpful, but not always necessary, to draw out a simple cause and effect diagram that includes each component of the measurement equation and the major sources of uncertainty for each component. For some complicated determinations it may be easier to write out first a separate diagram for each of the measurement equation components and then combine them into a final simplified diagram. Appendix D of the Eurachem Guide [3] and an article by Ellison [4] provide guidance in the construction of a cause and effect diagram. Uncertainty evaluated using statistical methods is referred to as Type A [5, 6]. All other ways of evaluating uncertainty are referred to as Type B [5, 6]. All uncertainties need to be expressed as standard deviations or standard uncertainties. Type B uncertainties are always expressed as probability distributions. The equations used to calculate the standard uncertainty for three common probability distribution models (normal, rectangular or uniform, and triangular) are shown in Figures 1 – 3. After the magnitudes of the significant components of uncertainty are calculated they are combined and multiplied by an coverage factor, *k*, to determine the expanded uncertainty.


$$\text{mean value} = (a_+ + a_-)/2$$
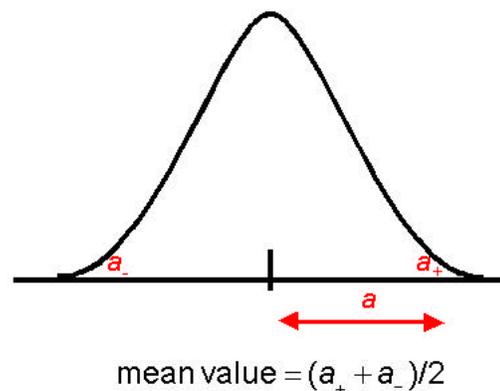
Confidence interval = 2a
Uncertainty estimate is for ± a

Standard uncertainty =

$a/1.96$ for 95 % confidence interval

$a/2.576$ for 99 % confidence interval

$a/3$ for 99.73 % confidence interval (3 standard deviations)

Use when evaluated from:
- limits of random replication
- standard deviation
- confidence interval

Figure 1. Normal distribution

$$\text{mean value} = (a_{+} + a_{-})/2$$
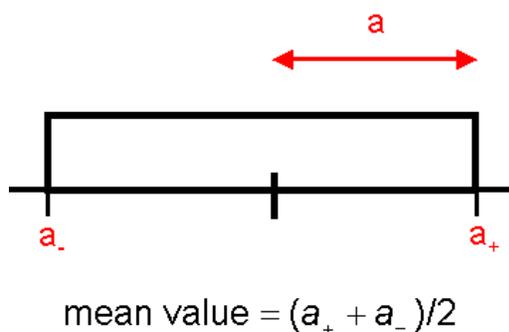
$a = (a_{+} - a_{-})/2$

Interval = 2a

Standard uncertaint $y = a/\sqrt{3}$

Default model if information is limited

Use when evaluated from:

•specification with no confidence level

•maximum range with unknown
 shape of distribution

Figure 2. Uniform distribution

$$\text{mean value} = (a_{+} + a_{-})/2$$
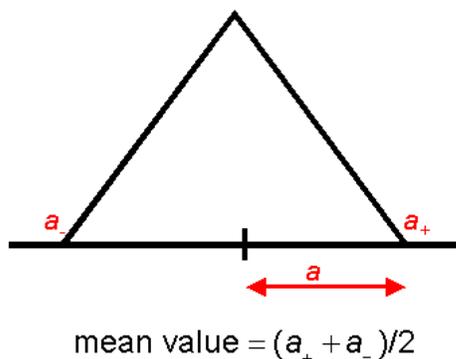
Interval = 2a

Standard uncertainty = $a/\sqrt{6}$

Use when evaluated from:

•maximum range with central tendency

•maximum range with symmetric distribution

Figure 3. Triangular distribution

Combining uncertainty components

Although uncertainty components are not errors, the individual components are combined using law of propagation of error formulas in which the combined uncertainty, u_c, is the square root of the sum of the squares (RSS) of the individual uncertainty components, each scaled to reflect its potential impact on the final result. Computing partial derivatives of the measurement equation with respect to each term in the equation using calculus is a correct, but sometimes complicated, way of obtaining the appropriate scaling factors for combining components. Calculating the relative uncertainty of the components and combining them using a simple, unscaled RSS is easier and sometimes avoids the need for explicit calculation of the scaling factors from the measurement equation. However, this method may result in calculation errors, especially if the measurement equation is not an exclusive mix of either only additions and subtractions, or only multiplications or divisions. In addition, components of the measurement equation that may have variables in common (mutually dependent) may be calculated incorrectly using a simple RSS. An alternate approach that avoids the need to explicitly compute partial derivatives and minimizes the risk of calculation errors is the calculation of the combined uncertainty using a Kragten spreadsheet. A Kragten spreadsheet (which is a tool for estimating uncertainty based on calculus) uses a numeric approximation to the scaled RSS [7] to combine uncertainty components. Kragten [7] and the Eurachem Guide [3] provide an alternative and more detailed explanation than that provided here.

Although the explanation of a Kragten spreadsheet may give the appearance that using it is complicated, it is in fact, very straightforward. In a Kragten spreadsheet the absolute magnitude of each component of the measurement equation and its absolute standard uncertainty are entered into predetermined cells of a spreadsheet. Once the template for the spreadsheet is set up, the analyst only has to enter the measurement equation, components of the measurement equation, and the corresponding standard uncertainties. With the exception of Type A uncertainties, or uncertainties of zero bias components that do not change the measurement result (as explained in the examples that follow), no relative values are added in the applications shown here.

Table 1. Generalized form of Kragten spreadsheet with four components

	1	2	3	4	5
1	Value	A	B	C	D
2	Uncertainty	a	b	c	d
3	A	A + a	A	A	A
4	B	B	B + b	B	B
5	C	C	C	C + c	C
6	D	D	D	D	D + d
7	$R = 1000*A*B*C/D$	$R_a = 1000*[A+a]*B*C/D$	$R_b = 1000*A*[B+b]*C/D$	$R_c = 1000*A*B*[C+c]/D$	$R_d = 1000*A*B*C/(D+d)$
8		$= R - R_a$	$= R - R_b$	$= R - R_c$	$= R - R_d$
9	$DIF_{sum} = DIF_a+DIF_b+DIF_c+DIF_d$	$DIF_a = (R - R_a)^2$	$DIF_b = (R - R_b)^2$	$DIF_c = (R - R_c)^2$	$DIF_d = (R - R_d)^2$
10	$SQRT(DIF_{sum})$	$= |R - R_a|/SQRT(DIFsum)$	$= |R - R_b|/SQRT(DIFsum)$	$= |R - R_c|/SQRT(DIFsum)$	$= |R - R_d|/SQRT(DIFsum)$
11	2	<-- k			
12	$k*SQRT(DIF_{sum})$	<-- $k*u_c$			
13	$100*k*u_c/R$	<-- relative unc. (%)			

The following explanation applies to Table 1 as well as any other Kragten spreadsheet. A generalized form of the Kragten spreadsheet for a four-component (A, B, C, D) measurement equation with each component having a standard uncertainty (a, b, c, d) and a coverage factor of k = 2 is shown in Table 1. The result, R, of the measurement equation is calculated. This result should agree with the determined value. The result of the measurement equation is varied once for each component (A, B, C, …) by adding the magnitude of its uncertainty (a, b, c…) to the value of the component and calculating a new result (R_a, R_b, R_c,…). For each component the difference between the result, R, and the new result (R_a, R_b, R_c, …). is squared. All of the squared differences (DIF_a, DIF_b, DIF_c, …) are summed and the square root of the sum is calculated. The value of RSS is the combined standard uncertainty. The assumptions and calculations used to estimate the most significant uncertainty components always should be re-evaluated.

Though specific to Table 1, the following explanation shows how any Kragten spreadsheet is structured. The value of each of the four components is entered in the section of the first column shaded in yellow (rows 3 – 6). The value of each of the four standard uncertainties is entered in the section of the second row shaded in green (columns 2 – 5). The spreadsheet is pre-formatted so that the entered component values also appear in row 1 above their corresponding standard uncertainties entered in row 2. Each of the rows to the right of the entered values (in column 1, rows 3 - 6) are pre-formatted to equal the contents of column 1 with the following exception. Progressing diagonally from column 2, row 3 to column 5, row 6, and shaded in blue, the component of that row and the corresponding standard uncertainty of that column are added, once for each component. The measurement equation is entered in each column of the row immediately below the entered components (row 7) so that its result is determined by the contents of the cells immediately above it (in this example, rows 3 – 6). In this example, once the spreadsheet is set up, the analyst only has to enter the measurement equation (row 7), the four components of the measurement equation (column 1, rows 3 – 6), the four corresponding standard uncertainties (columns 2 – 5, row 2), and the coverage factor, k (column 1, row 11). The original result and a new result for each component are calculated in row 7, based on the values in rows 3 - 6. Each of the differences in the result is calculated in row 8. The sum of the squares of the differences is calculated in column 1 of row 9 and each square of the differences corresponding to its entered component and standard uncertainty is calculated in the remaining columns of row 9. The combined standard uncertainty, calculated as the RSS, is shown in column 1, row 10.

This general spreadsheet has some additional features that are not in the originally conceived Kragten spreadsheet [7]. In row 10, columns 2 - 5, the magnitude of each component of the standard uncertainty, relative to the combined standard uncertainty, is calculated. The coverage factor, k, is entered in column 1, row 11. The

expanded uncertainty is calculated in column 1, row 12, and the percent relative expanded uncertainty is calculated in column 1, row 13. Other modifications based on the analyst's needs can be made. Note that it is easy to change any re-evaluated components and to see the effect of any changes on the total uncertainty. If additional components were added, the columns and rows would be expanded once for each addition.

The Kragten spreadsheet is based on the assumption that the result, R, changes linearly within the interval of $R \pm R_{(a, b, c, ...)}$. Subtracting the magnitude of the uncertainties instead of adding them serves as a check of this linearity. If the assumption of linearity is correct, the combined uncertainty does not change significantly whether the standard uncertainty is added or subtracted. Linearity should not be a problem if the interval of $R \pm R_{(a, b, c, ...)}$ is relatively small and the measurement equation is not a complicated function. Therefore, if the interval of $R \pm R_{(a, b, c, ...)}$ is relatively large (e.g., when the signal-to-noise ratio of a measurement is small), this approach to estimation of uncertainty may not be valid.

Two examples of analytical chemistry methods will be used to demonstrate the estimation and quantification of measurement uncertainty. The first is a titration example taken directly from Appendix A of the Eurachem Guide [3] and the second is a gravimetry example based on a recently completed determination at the National Institute of Standards and Technology (NIST). Keep in mind that different analysts are likely to have different experience and judgement. When provided with the same information, they may model the uncertainty of the Type B components of the measurement equation differently, and make different estimates of the total uncertainty.

The magnitude of the some of the uncertainties stated here, in the first example, are slightly different than some of those shown in the Eurachem Guide [3] because some of the values in the Eurachem Guide are the result of rounding prematurely. Rounding, especially for the most significant uncertainty sources, should be avoided (especially when using spreadsheets) until the final calculation of the total uncertainty. In both of the following examples some of the values may appear to have too many significant figures. The extra figures are carried through until the calculation of the total uncertainty to avoid confusion that could be caused by rounding prematurely.

Example 1. Titration of NaOH with KHP

In this example sodium hydroxide (NaOH) is standardized by titration against standard potassium hydrogen phthalate, KHP. The major uncertainty sources and their magnitude are determined.

Measurement equation

First the measurement equation is written as

$(1) \qquad c_{NaOH} = 1000 \cdot ((m_{KHP}) \cdot (P_{KHP})/((M_{KHP}) \cdot (V_T))$ [mol L^{-1}]

where,

c_{NaOH} = concentration of the NaOH solution [mol L^{-1}]
1000 = conversion factor [mL] to [L]
m_{KHP} = mass of the titrimetric standard KHP [g]
P_{KHP} = purity of the titrimetric standard given as a mass fraction
M_{KHP} = molecular weight of KHP [g mol^{-1}]
V_T = titration volume of NaOH solution [mL].

Cause and effect diagram

Next, a simple cause and effect diagram is drawn (Figure 4) showing the four components of the measurement equation that may contribute to the uncertainty of the result. The uncertainty of each component is evaluated and is added to the cause and effect diagram as shown in Figure 5. Since the repeatability terms for the volume, endpoint, and mass of KHP are incorporated into the repeatability of the result, they are combined into one contribution to the result as shown in Figure 6. Figure 6 shows that there are actually 5 uncertainty components: the original 4 and the measurement replication. Figures 5 and 6 are simplifications of the diagrams in the original example [3].
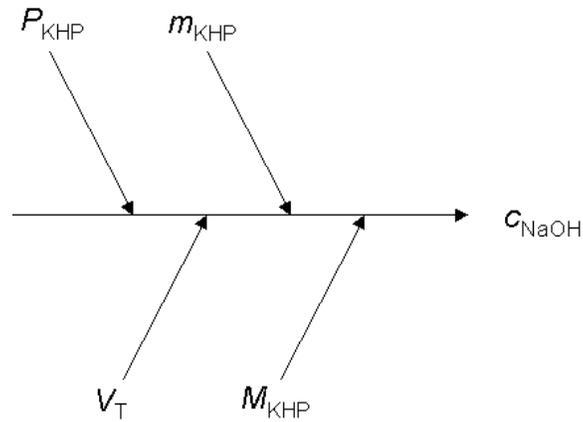
Figure 4. Simple cause and effect diagram for standardization of a NaOH solution with KHP
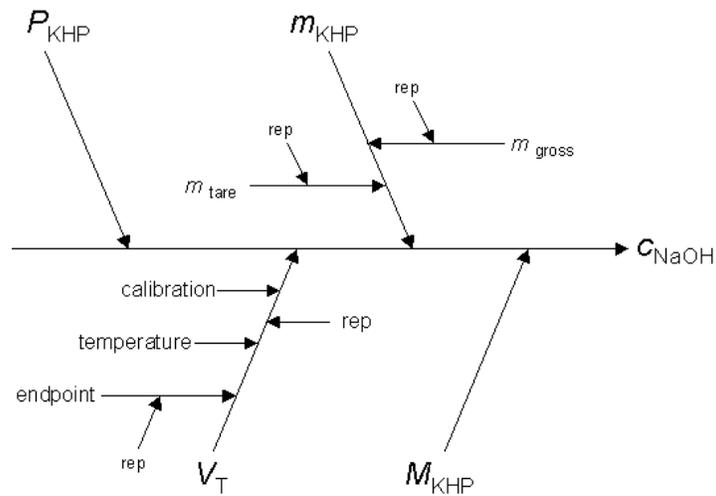

Figure 5. Detailed cause and effect diagram for standardization of a NaOH solution with KHP
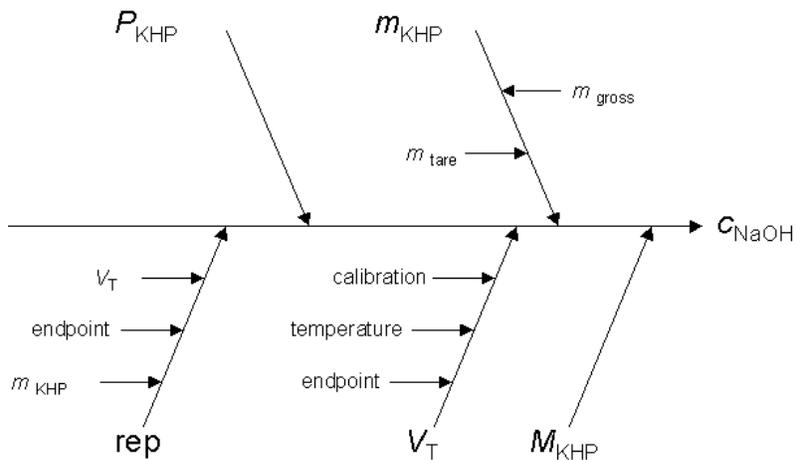

Figure 6. Detailed cause and effect diagram with repeatabilities combined for standardization of a NaOH solution with KHP

Quantification of Uncertainty

The magnitude of each of these components needs to be evaluated. Each of these components, in turn, may be the product of several uncertainty components. The amount of effort expended to estimate the magnitude of the uncertainty component should be commensurate with its relative contribution to the overall uncertainty.

Measurement replication

The most obvious and easily calculated uncertainty component is the measurement replication, which is commonly calculated as the standard deviation of the mean. In this example the replication uncertainty was calculated from a method validation study to be 0.05 %, relative. The Type A measurement replication is entered in the Kragten spreadsheet as a relative uncertainty of 0.05 % with its value in the measurement equation replication set as 1. Since this uncertainty component implicitly combines the repeatability from all of the terms in the measurement equation, it is already in the units relative to the result and does not need scaling.

Mass of the KHP

The mass of the KHP was determined as the difference of the container with KHP, and the container after the KHP was added to the sample. As shown by Figure 6, the weighing repeatability is considered separately. A Type B estimate is made for the linearity of the balance. The balance calibration certificate states that the linearity is ± 0.15 mg and recommends the use of a uniform distribution model to calculate the standard uncertainty. The balance linearity component is calculated as

$$\frac{0.15\,\text{mg}}{\sqrt{3}} = 0.0866\,\text{mg}.$$

Since the mass of KHP is calculated as the difference of two independent determinations this uncertainty needs to be summed twice as the RSS of the standard uncertainties. The standard uncertainty of the mass is calculated as

$$\sqrt{(0.0866\,\text{mg})^2 + (0.0866\,\text{mg})^2} = \sqrt{2 \cdot (0.0866\,\text{mg})^2}$$

$$= \sqrt{2} \cdot (0.0866\ \text{mg}) = 0.122\ \text{mg}.$$

Purity of the KHP

The certificate for the KHP states a purity of 1.0000 ± 0.0005 with no information on a coverage factor. By default the uniform distribution model is used to calculate the Type B standard uncertainty as

$$\frac{0.0005}{\sqrt{3}} = 0.00029.$$

Molecular weight of the KHP

The uncertainty of the molecular weight of the KHP is calculated from the International Union of Pure and Applied Chemistry (IUPAC) uncertainties of the atomic weights [8]. A uniform distribution is used, presumably by default, to calculate the standard uncertainty in this example from the Eurachem Guide. It could be argued that the uncertainties of the atomic weights have a central tendency so that a triangular or normal distribution (See Figures 1 – 3) is more appropriate. However, since the magnitude of this uncertainty component is relatively insignificant, the model used is not important here. It could also be argued that because of its small magnitude, this uncertainty source could be ignored in the final calculation. Since this source is included in the original example [3], it will be included here. However, the calculation of this source will not be repeated here. The magnitude of the standard uncertainty is 0.0038 g mol^{-1}.

Volume of the NaOH solution

As shown by Figure 6, volume repeatability is considered separately. Type B estimates are made for the calibration of the buret and temperature variability. The manufacturer states the limits of accuracy as ± 0.03 mL. In this example a triangular distribution is used because a central tendency is assumed. An argument also could be made that ± 0.03 mL is a specification that should be modeled as a uniform distribution because any buret within the specified range of ± 0.03 mL has been deemed acceptable by the manufacturer. In addition, just as with the uncertainty provided for purity, since the manufacturer has not provided further information on the uncertainty, the uniform distribution should be considered by default. Since the buret calibration is the major source of uncertainty, the calculation of the magnitude of this uncertainty should be considered carefully (The calibration bias and its uncertainty could be estimated more

accurately by measuring the mass of solution delivered by the buret, correcting for density to determine volume, and comparing the received volume value to the delivered volume value). Assuming a triangular distribution, the calibration standard uncertainty is calculated as

$$\frac{0.03\,\text{mL}}{\sqrt{6}} = 0.0122\,\text{mL}.$$

In this example the magnitude of the Type B estimate for temperature is calculated based on a temperature variation of $\pm$ 3 °C and the assumption of a normal distribution with 95 % confidence (divide by 1.96). Since the NaOH titrant is very dilute (mass fraction < 0.01 %), the expansion coefficient of water can be used. The variation in the volume is calculated by multiplying the volume delivered (18.64 mL) by the expansion coefficient for water ($2.06 \cdot 10^{-4}$ °C^{-1} at 20°C) [9] and the temperature variation ($\pm$ 3 °C) and

dividing that quantity by the factor for the normal distribution model with 95 % confidence (1.96) as

$((18.64\,\text{mL}) \cdot (2.06 \cdot 10^{-4}\,°\text{C}^{-1}) \cdot (3\,°\text{C}))/1.96$
$= 0.0059\,\text{mL}.$

The volume standard uncertainty is calculated by the RSS of the standard uncertainties of the buret calibration and the temperature variability as

$$\sqrt{(0.0122\,\text{mL})^2 + (0.0059\,\text{mL})^2} = 0.0136\,\text{mL}.$$

Combined standard uncertainty

The combined standard uncertainty is determined to be 0.000101 mol L^{-1} in Table 2 (column 1, row 11). Page 48 of the Eurachem Guide [3] shows similar calculations. In Table 2 it is obvious that the uncertainty of the volume is the major source of uncertainty. In this example the analyst should consider a more thorough investigation of this source of uncertainty.

Table 2. Kragten spreadsheet for NaOH titration

			rep	m_{KHP}	P_{KHP}	M_{KHP}	V_T
		1	2	3	4	5	6
	1	Value	1.0	0.3888	1.0	204.2212	18.64
	2	Uncertainty	0.0005	0.00013	0.00029	0.0038	0.0136
rep	3	1.0	1.0005	1.0	1.0	1.0	1.0
m_{KHP}	4	0.3888	0.3888	0.38893	0.3888	0.3888	0.3888
P_{KHP}	5	1.0	1.0	1.0	1.00029	1.0	1.0
M_{KHP}	6	204.2212	204.2212	204.2212	204.2212	204.2250	204.2212
V_T	7	18.64	18.64	18.64	18.64	18.64	18.654
c_{NaOH}	8	0.102136	0.102187	0.102171	0.102166	0.102134	0.102062
$u(y, x_i)$	9		0.000051	0.000035	0.000029	-0.000002	-0.000074
$u^2(y), u^2(y, x_i)$	10	1.021E-08	2.61E-09	1.20E-09	9E-10	4E-12	5.53E-09
$u_c(c_{NaOH})$	11	0.000101	51%	34%	29%	2%	74%

Example 2. Gravimetric determination of K mass fraction in KH$_2$PO$_4$

In this example the mass fraction of potassium, K, in potassium dihydrogen phosphate, KH$_2$PO$_4$, a fertilizer, is determined. In this method potassium is separated on an ion exchange column and is isolated as a precipitate of potassium sulfate, K$_2$SO$_4$. The bulk of the K (> 99.8 %) is

determined gravimetrically and corrections are made for residual K, precipitate contaminants, and estimated transfer losses. Since the Type A measurement replication of the result of this procedure is less than 0.01 %, relative, the uncertainties of these corrections have the potential to be a significant contribution to the overall uncertainty. The major uncertainty sources and their magnitude are determined.

Measurement Equation

First the measurement equation is written as

(2) $\quad w_K =$

$100 \cdot ((m_{\text{Total K}_2\text{SO}_4}) \cdot (2A_K/M_{\text{K}_2\text{SO}_4}))/m_{\text{Sample}}$ [%]

where,

w_K	= mass fraction of K [%]
$m_{\text{Total K}_2\text{SO}_4}$	= total mass of K_2SO_4 [g]
A_K	= atomic weight of K [g mol^{-1}]
$M_{\text{K}_2\text{SO}_4}$	= molecular weight of K_2SO_4 [g mol^{-1}]
$2A_K/M_{\text{K}_2\text{SO}_4}$	= 0.4487347 gravimetric factor [8]
m_{Sample}	= sample mass [g].

The measurement equation is further expanded by the equation for the total mass of K_2SO_4 as

(3) $\quad m_{\text{Total K}_2\text{SO}_4} = m_{\text{Grav K}_2\text{SO}_4} + m_{\text{Res K}_2\text{SO}_4} +$

$m_{\text{Loss K}_2\text{SO}_4} - m_{\text{Cont K}_2\text{SO}_4}$ [g]

where,

$m_{\text{Total K}_2\text{SO}_4}$	= total mass of K_2SO_4 [g]
$m_{\text{Grav K}_2\text{SO}_4}$	= mass gravimetric K_2SO_4 [g]
$m_{\text{Res K}_2\text{SO}_4}$	= mass residual K_2SO_4 [g]
$m_{\text{Loss K}_2\text{SO}_4}$	= mass calculated transfer loss [g]

$m_{\text{Cont K}_2\text{SO}_4}$ $\quad$ = mass K_2SO_4 contaminants [g].

The complete measurement equation, a combination of equations 2 and 3, is

(4) $\quad w_K = 100 \cdot ((m_{\text{Grav K}_2\text{SO}_4} + m_{\text{Res K}_2\text{SO}_4} +$

$m_{\text{Loss K}_2\text{SO}_4} - m_{\text{Cont K}_2\text{SO}_4}) \cdot (2A_K/M_{\text{K}_2\text{SO}_4}))/m_{\text{Sample}}$ [%].

Cause and effect diagram

Next, a simple cause and effect diagram is drawn (Figure 7) showing the six components of the measurement equation that may contribute to the uncertainty of the result. The uncertainty of each component is evaluated and is added to the cause and effect diagram as shown in Figure 8. Note that, for ease of calculations, two significant uncertainty components for the K_2SO_4 mass, m_{Grav} and m_{Temp}, are added separately. Since the repeatability terms for the sample and precipitate mass are incorporated into the repeatability of the result, they are combined into one contribution to the result as shown in Figure 9. Figure 9 shows that there are actually eight uncertainty components: five of the original six from the measurement equation (4), two components split off from the remaining one of the original six, and one component of measurement replication.
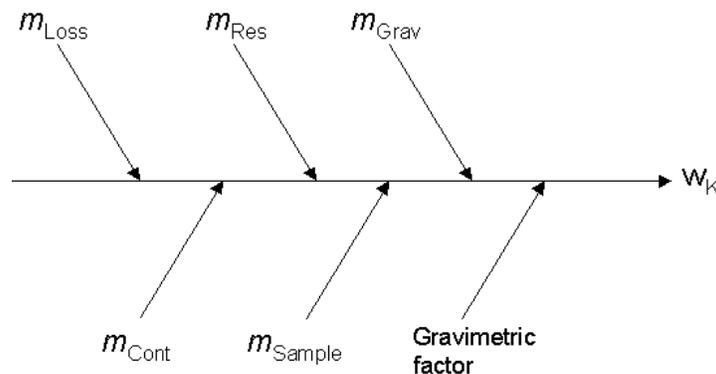

Figure 7. Simple cause and effect diagram for gravimetric determination of K in KH_2PO_4
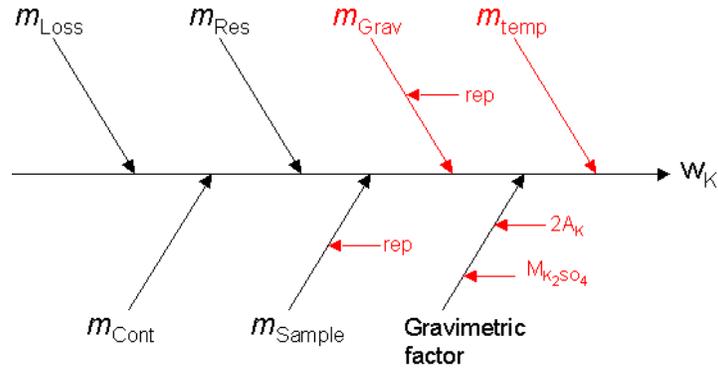
Figure 8. Detailed cause and effect diagram for gravimetric determination of K in KH_2PO_4
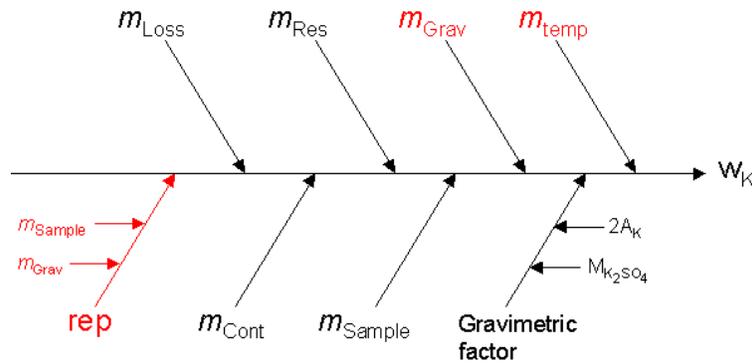

Figure 9. Detailed cause and effect diagram with repeatabilities combined for gravimetric determination of K in KH_2PO_4

Quantification of Uncertainty

The magnitude of each of these components is evaluated. A total uncertainty based on the result of an average sample is calculated. Details of the magnitude of each component, which are beyond the scope of this explanation, can be found elsewhere [10, 11].

Measurement replication

The result is based on duplicate samples of KH_2PO_4 determined in three separate runs. The mean result of each run is used to determine the overall mean so that any Type A uncertainties for the measurement of the blank, sample, and precipitate masses, which are only applicable to an individual run, are easily incorporated into the uncertainty for all three runs [10]. In this manner they do not have to be calculated and added separately to the total uncertainty. The standard deviation of the three runs is 0.00647 %, relative. The relative standard deviation of the mean of the runs (N = 3) is calculated as

$$\frac{0.00647 \text{ \%}}{\sqrt{3}} = 0.00373 \text{ \%}.$$

Mass of the sample

The mass of the sample was determined as the difference of the container with the KH_2PO_4 and the container after the KH_2PO_4 was added to the sample. As shown by Figure 9, the weighing repeatability is considered separately. A Type B estimate, based on the range of masses obtained for a standard mass weighed along with the samples, is made for the bias and resolution of the balance. The uncertainty is estimated as ± 0.030 mg and is modeled as a triangular distribution because it has a central tendency [5]. The balance uncertainty is calculated as

$$\frac{0.030 \text{ mg}}{\sqrt{6}} = 0.0122 \text{ mg}.$$

Since the KH_2PO_4 mass is calculated as the difference of two independent determinations, this

uncertainty needs to be summed twice in the same manner as used in example 1. The standard uncertainty of the mass is calculated as

$$\sqrt{2} \cdot (0.0122 \text{ mg}) = 0.0173 \text{ mg}.$$

Mass of the K_2SO_4 precipitate

The uncertainty of the K_2SO_4 precipitate mass is estimated in the same manner as that used for the sample mass so that the standard uncertainty is also 0.0173 mg.

Temperature of heating the K_2SO_4 precipitate

The temperature required to obtain a stoichiometric K_2SO_4 precipitate was determined to be 825 °C in a preliminary study. A temperature of 750 °C was used in previous work [12]. A zero bias is estimated for the 825 °C temperature selected for heating the precipitate. The relative difference of 0.0148 %, for the difference in mass at 750 °C and 825 °C determined in the preliminary study, is used as an estimate of the uncertainty of the bias of the heating temperature. This difference is modeled as a uniform uncertainty. The standard uncertainty is calculated as

$$\frac{0.0148 \text{ \%}}{\sqrt{3}} = 0.00854 \text{ \%}.$$

The result of the measurement equation is not changed by the bias of the heating temperature, however, the standard uncertainty is added to the total uncertainty. In effect, the measurement equation is multiplied by a value of 1 and the heating temperature uncertainty is calculated based on the relative standard uncertainty.

Residual K

The amount of K in solutions collected before and after the fraction separated for precipitation as K_2SO_4, and in rinses of the transfer vessels, was determined by flame atomic emission spectrometry (FAES). The standard uncertainty is estimated to be 40 %, relative, based on the range of replicate values for standards and samples. This large relative uncertainty results from measurements of K in the residual solutions near the detection limit of the FAES determination. Since the magnitude of this uncertainty is a minor component of the total uncertainty, no additional effort was made to improve this estimate. Based on an average

residual K correction of 0.0081 mg, as K_2SO_4, the standard uncertainty is calculated as

$$(0.0081 \text{ mg}) \cdot (0.4) = 0.0032 \text{ mg}.$$

K_2SO_4 precipitate contaminants

Contaminants in the K_2SO_4 precipitate were determined by inductively coupled plasma mass spectrometry (ICPMS). The standard uncertainty of the ICPMS semi-quantitative determination is estimated as 50 %, relative. Based on an average correction of 0.0196 mg, as sulfates, the standard uncertainty is calculated as

$$(0.0196 \text{ mg}) \cdot (0.5) = 0.0098 \text{ mg}.$$

Transfer losses

Several sources of bias may be present from losses in sample transfers and the ion-exchange separation. These sources were addressed in detail elsewhere [10, 13]. The maximum loss that could occur, estimated by linearly summing the individual losses, is 0.0618 %, relative. It is unlikely that a loss of this magnitude occurred. The magnitude of the correction is best modeled using the assumption that it is most likely that there is zero bias and that the probability of a bias linearly decreases to zero at the maximum relative bias of 0.0618 %. Therefore, the mean bias can be calculated [14] as having a magnitude of one-third of the maximum interval, which equals 0.0206 %. The model for this bias is shown in Figure 10. This bias has the effect of decreasing the apparent K value. The negative of this bias is added as a correction in terms of the equivalent mass of K_2SO_4 to each individual sample. The average magnitude of this correction is 0.0435 mg based on the mean relative bias of 0.0206 % for the K_2SO_4 mean mass of 0.21093 g. The standard uncertainty of this correction is calculated by dividing the magnitude of the correction by the square root of 2 [14]. The relative standard uncertainty of the transfer loss correction is calculated as

$$\frac{0.0435 \text{ mg}}{\sqrt{2}} = 0.0307 \text{ mg}.$$

Atomic weight of K and molecular weight of K_2SO_4

Since the uncertainties of the atomic and molecular weights of the K and K_2SO_4 are insignificant, relative to the combined uncertainty

(< 5 %), the magnitude their uncertainties are not estimated.

most likely bias $= 0$

maximum bias $= a$

estimated bias $= a/3$

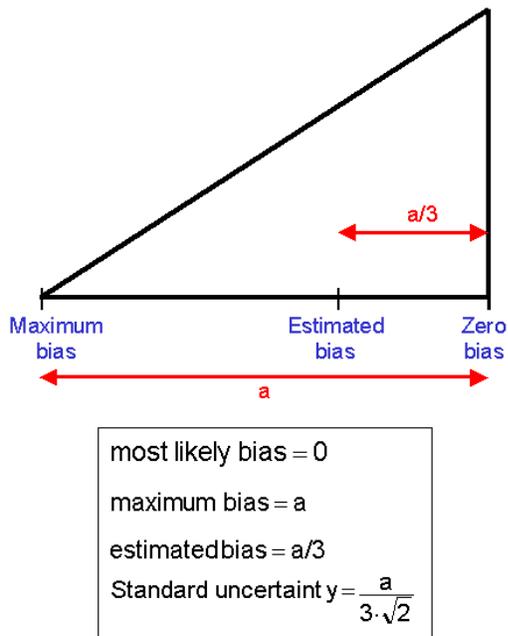Standard uncertainty $y = \dfrac{a}{3 \cdot \sqrt{2}}$

Figure 10. Deming model [14] for likely zero bias and probability of a bias linearly decreases to zero at maximum bias

Combined standard uncertainty and expanded uncertainty

The combined standard uncertainty is shown in Table 3 (column 1, row 13). The expanded uncertainty (column 1, row 15) is calculated by multiplying the combined standard uncertainty by a coverage factor of 2. The relative expanded uncertainty (column 1, row 16) is 0.041 %. Any component of the measurement equation that does not have a significant uncertainty (e.g., atomic weights) is not added as an extra row and column. However, for all calculations of the result, it is required that all of the components be part of the measurement equation. Therefore, in this example, each component of the measurement equation, except the K atomic weight and the K_2SO_4 molecular weight, are entered as a row. In addition, the measurement replication and the precipitate heating temperature are added as components with a value equal to 1, since they do not change the value of the result. In Table 3 it is obvious that the uncertainty of the transfer loss is the major source of uncertainty. It is appropriate that this source of uncertainty has been studied very thoroughly [10, 12].

Table 3. Kragten spreadsheet for w_K in KH_2PO_4

			rep	m_{Sample}	m_{Grav}	m_{Res}	m_{Loss}	m_{Cont}	m_{Temp}
			1	2	3	4	5	6	7	8
	1	Value	1.0	0.3294450	0.2109263	0.0000081	0.0000435	0.0000196	1.0
	2	Uncertainty	0.0000373	0.0000173	0.0000173	0.0000032	0.0000307	0.0000098	0.0000854
rep	3	1.0	1.0000373	1.0	1.0	1.0	1.0	1.0	1.0
m_{Sample}	4	0.3294450	0.3294450	0.3294623	0.3294450	0.3294450	0.3294450	0.3294450	0.3294450
m_{Grav}	5	0.2109263	0.2109263	0.2109263	0.2109436	0.2109263	0.2109263	0.2109263	0.2109263
m_{Res}	6	0.0000081	0.0000081	0.0000081	0.0000081	0.0000113	0.0000081	0.0000081	0.0000081
m_{Loss}	7	0.0000435	0.0000435	0.0000435	0.0000435	0.0000435	0.0000742	0.0000435	0.0000435
m_{Cont}	8	0.0000196	0.0000196	0.0000196	0.0000196	0.0000196	0.0000196	0.0000294	0.0000196
m_{Temp}	9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0000854
w_K	10	28.7345	28.7355	28.7330	28.7368	28.7349	28.7387	28.7331	28.7369
$u(y, x_i)$	11		0.001073	-0.001511	0.002359	0.000441	0.004188	-0.001337	0.002455
$u^2(y), u^2(y, x_i)$	12	3.455E-05	1.15E-06	2.28E-06	5.57E-06	1.9E-07	1.754E-05	1.79E-06	6.03E-06
$u_c(w_K)$	13	0.005878	**18%**	**26%**	**40%**	**8%**	**71%**	**23%**	**42%**
k	14	2							
$k*u$	15	0.0118		$M_{K_2SO_4}$		174.2602	g mole^{-1} [8]		
rel unc	16	0.041%		A_K		39.0983	g mole^{-1} [8]		

3. Conclusions

A generalized scheme for planning a measurement and a simple and practical approach to estimating and combining the components of measurement uncertainty have been shown. Several resources have been noted that should be consulted to help estimate and quantify measurement uncertainty. A generalized Kragten spreadsheet with useful modifications can be used as a tool to simplify the combination of uncertainty sources and minimize calculation errors. Simple and practical approaches to estimating and combining uncertainties for two analytical chemistry methods have been demonstrated.

Acknowledgements

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