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ARTICLE

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Error Propagation Made Easy—Or at Least Easier

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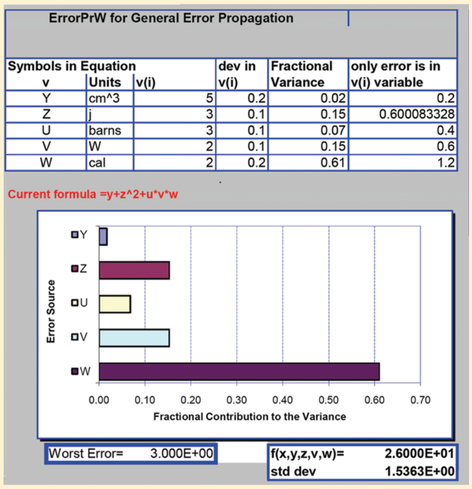
Supporting Information

ABSTRACT: Complex error propagation is reduced to formula and data entry into a Mathcad worksheet or an Excel spreadsheet. The Mathcad routine uses both symbolic calculus analysis and Monte Carlo methods to propagate errors in a formula of up to four variables. Graphical output is used to clarify the contributions to the final error of each of the individual variables as well as illustrate how well the results conform to the normal distribution. The Excel routine allows direct entry of the formula and evaluates the error by numerical approximation of the necessary partial derivatives. Students find the routines much more user friendly and informative than traditional error propagation techniques.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Problem Solving/Decision Making, Computational Chemistry, Mathematics/Symbolic Mathematics



Error analysis and error propagation are important areas in chemical curricula. The teaching of these is generally done in analytical or physical chemistry laboratories. From the student's standpoint, error propagation is generally one of the most boring and tedious subjects encountered. This *Journal* has had numerous articles on the subject of error propagation. These have ranged from the classical physical chemistry laboratory manual approaches[1−3] to application of Monte Carlo methods to improve visualization. A spreadsheet approach has been described that simplified the analysis.[4] More recently, versatile Excel routines have been made available.[5]

In the late 1980s, we introduced a powerful spreadsheet method that required that the student only type in the equation, the values of the parameters, and their uncertainties, and the macro would output the result, its uncertainty, and the contributions of the different quantities to the final uncertainty. The macro was written in the now defunct Quattro Pro, but we have written an improved version in Excel. Students find this approach easier than traditional methods, and it provides more insight into the contributions of the various errors. In addition, given the power of modern symbolic math packages such as Mathcad, there is no longer any reason for students to struggle through the error prone derivatives of the classical method. We have written a general purpose Mathcad worksheet where all one does is enter the equation of up to four variables, the parameter values, and their uncertainties. The function evaluation, the uncertainty, and the relative contributions to the error are then displayed.

Monte Carlo methods are powerful ways of carrying out error propagation and evaluations of the reliability of different data analysis methods.[6−11] We show Monte Carlo methods as well as Mathcad and Excel routines for simple error propagation. These methods help in visualizing the error propagation and the contribution of different error sources. These approaches are simpler, easier, and pedagogically more useful than traditional methods.

CALCULUS-BASED APPROACH

The traditional calculus-based approach expands the function in a first-order Taylor series, deletes the higher-order terms, and calculates the standard deviation assuming the errors in the measured quantities are uncorrelated. If y is a function of n variables, v_1 to v_n, $y = f(v_1, v_2, ..., v_n)$ with standard deviations in the variables given by σ_1, ..., σ_n, the standard deviation in y, σ_y, is

$$\sigma_y{}^2 = \sum_{j=1}^{n} \left(\frac{\partial f}{\partial v_j}\right)^2 \sigma_j{}^2 \qquad (1)$$

where σ_y^2 is the variance in y. Each summation term is the contribution to the total variance. Although direct application of eq 1 has been recommended,[3] a simpler strategy is generally used for a complex formula. The error propagation expression for the

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$$f(w,x) := \frac{w}{\ln(x)}$$

1) Fill in your function. If you use fewer variables, leave it out on the right hand side.

Variables	Uncertainties
$w := 10$	$\sigma w := 1$
$x := 10$	$\sigma x := 1$

2) Fill in the variable values and their standard deviations in the green region. Unused variables can be ignored.

$$\mathrm{Error}(w,\sigma w,x,\sigma x) := \sqrt{\left(\frac{d}{dw}f(w,x)\right)^2\cdot\sigma w^2 + \left(\frac{d}{dx}f(w,x)\right)^2\cdot\sigma x^2}$$

Error propagation

$$\mathrm{Error\_f} := \mathrm{Error}(w,\sigma w,x,\sigma x) \qquad \mathrm{FracError\_f} := \frac{\mathrm{Error\_f}}{f(w,x)}\cdot 100$$

Function	$f(w,x) = 4.343$	3) Read the symbolic error propagation results.
Std Dev f	$\mathrm{Error\_f} = 0.473$	
Fractional Error %	$\mathrm{FracError\_f} = 10.902$	

Figure 1. Mathcad worksheet for doing error propagation on a two-variable function of *w* and *x*. Error_f is the standard deviation of the function.

common basic arithmetic operation (e.g., addition, subtraction, multiplication, powers, logs, exponential, etc.) is derived and then applied to more manageable pieces. For example, consider the expression

$$y = f(x,y,z) = \frac{x^2 \ln(y)}{z^3} \tag{2}$$

One would calculate separately the errors in x^2 and $\ln(y)$ using the basic formula, then calculate the error in the product of these two quantities. Finally, after calculating the uncertainty in z^3, one would calculate the error of the quotient from the errors in the numerator and denominator. While less cumbersome than evaluating eq 1 directly, it can lead to gross errors as can be seen in this *Journal*[3] and in the following equation

$$y = f(x) = \frac{x^2}{1 + x^2} \tag{3}$$

For $x = 10$, $\sigma = 1$ by the divide-and-conquer method we get 0.99 ± 0.28, whereas the correct answer from eq 1 is 0.990 ± 0.002 or over 2 orders of magnitude difference in the error estimation. Divide-and-conquer fails because it assumes that the numerator and denominator errors are uncorrelated, but they are highly correlated because the same x is used in both. In the limit of a very large x, there is no error in y regardless of errors in x because we are just evaluating x/x! Other examples have been given in the literature.[1] In such cases, only eq 1 is viable.

With modern symbolic math software packages such as Mathcad, there is no longer any reason to fear the exact approach. Without bothering to look at the analytical derivatives one merely types the expression of eq 1 symbolically in terms of the variables used to define y and evaluates it directly. A two-variable Mathcad example is shown Figure 1. After defining the equation, the variable values and their standard deviations, the uncertainty calculation of f takes one line and the solution is read directly. We supply students with a version that handles from one to four variables. It also employs Monte Carlo methods, described later, for visualizing the results

■ MONTE CARLO METHODS

Monte Carlo methods for error propagation are versatile and simple.[12] One takes the defining equation and generates a single set of noisy variables where each variable is from a distribution that conforms to the mean and statistical distribution assumed for the data, typically Gaussian noise, and calculates the function. This provides one "experimental" value. The process is then repeated a number of times to provide a large number of "experimentally" derived results. The mean and standard deviation of this collection of experiments provides the mean and uncertainty for the function if the data had the assigned mean and standard deviation.

A number of Monte Carlo applications have been reported in this *Journal*. For example, a detailed evaluation of the optimum method for fitting binding constants was described.[7] Error estimation and visualization of the interactions between different fitting parameters for the IR spectra of DCl, visible spectra of I_2, and the van Demeter equation have been shown.[8] Using Monte Carlo methods Tellinghuisen has analyzed the best way to discriminate first- and second-order kinetic data,[9] and to demonstrate critical factors in linear fitting.[10] The idea was originally formulated by Stanislaw Ulam in 1946 at Los Alamos National Laboratory while he considered how to calculate the odds of winning at solitaire. It was formulated for the computer age by John von Neumann in 1947. The methodology was named by N. Metroplis: "It was at this time that I suggested the obvious name for the statistical methods—a suggestion not unrelated to the fact that Stan had an uncle who would borrow money from relatives because he 'just had to go to Monte Carlo'."[13]

The power and simplicity of Monte Carlo methods are revealed by the statement in the classic book on numerical methods by Press et al., "*Offered the choice between mastery of a five-foot shelf of analytical statistics books and middling ability at performing statistical Monte Carlo simulations, we would surely choose to have the latter skill*" (p 691).[14] While quoted earlier,[12] it is worth repeating. Monte Carlo methods are even used in a charming book for analyzing a series of entertaining statistical problems, including some that have no closed form solution.[15]

The simplicity of a Monte Carlo method is shown in Figure 2 where we show the error propagation for x/y case using Mathcad. Both x and y are assigned means of 2 and standard deviations of 0.3. The Monte Carlo method using 10^6 experiments gives 1.02 ± 0.23, whereas classical error propagation gives 1.00 ± 0.21, which from the standpoint of error analysis are identical. For comparison, the distribution of quotient values along with the

Monte Carlo error calculation for 2 variables

Define function and set up parameters

$f(x,y) := \frac{x}{y}$

$x := 2$ $\quad \sigma x := 0.3$ Variable values and their uncertainties

$y := 2$ $\quad \sigma y := 0.3$

Monte Carlo Calculation

trials := 1000000 1000000 trials ("experiments") is a good compromise between signal to noise ratio and computation time

j := 0.. trials − 1

xvec := rnorm(trials , x, σx)

yvec := rnorm(trials , y , σy)

Generate a vector of all individual calculations f(xvec1,yvec1), f(xvec2,yvec2) ..etc.

$Fmonte := \overrightarrow{f(xvec, yvec)}$ Calculate the vector of trial results. Vectorizing the calculation greatly speeds it up

Results

mean(Fmonte) = 1.024 Mean of fs

stdev(Fmonte) = 0.227 Standard deviation of f

Figure 2. Mathcad worksheet for doing a two-variable Monte Carlo error propagation for $f(x,y) = x/y$.

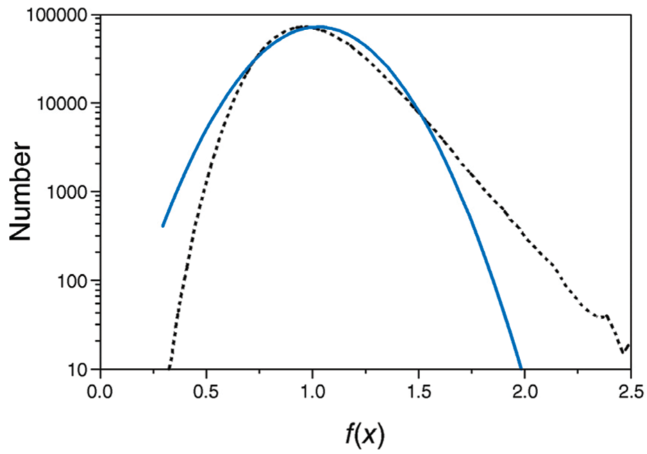

Figure 3. Distribution for Monte Carlo (dashed line) results for x/y with $x = y = 2$ and $\sigma_x = \sigma_y = 0.3$ and for a normal distribution (solid line) with the same mean and standard deviation.

normal distribution having the same mean and standard deviation are shown in Figure 3. The distribution of x/y is interesting. Even though the original data are perfectly normal, the resultant distribution of quotients is significantly skewed, which accounts for the small difference between Monte Carlo and classical error. Smaller standard deviations give a more nearly Gaussian distribution. This is a useful reminder that the data that we generate in the laboratory, which is frequently a result of many different error sources, are probably rarely Gaussian even though we like to assume so. In spite of the deviations from Gaussian, the Monte Carlo and classical error propagation mean and standard deviation agree well although the Monte Carlo result is more accurate if the input data are truly Gaussian.

As with the analytical calculus code, the Mathcad routine is simple. After the function definition and the inputs, the error propagation takes only five lines of Mathcad as shown for the x/y example in Figure 2. Similar results are easily generated in routines in packages such as Maple, Mathematica, Matlab, and Basic. For languages without a Gaussian noise generator, there are simple algorithms for generating Gaussian noise (p 289).[14] If the data are not truly Gaussian, Monte Carlo methods work using the distribution function for the noise (e.g., Poisson).

As an aside all analytical derivatives, numerical approximations to them, and double sided numerical derivatives such as we use here fail at a minimum or maximum of the function. The analytical and precise numerical approximations also fail at inflection points. In these cases, only Monte Carlo methods work.

NUMERICAL METHODS

The above methods are not cures. Not everyone has access to a symbolic math program, but virtually everyone has access to Excel. Our Excel spreadsheet method uses eq 1 with double-sided numerical derivatives,

$$\left(\frac{\partial f}{\partial v_j}\right) \cong \frac{f(v_1, v_2, \ldots, v_j + \Delta v_j, \ldots, v_n) - f(v_1, v_2, \ldots, v_j - \Delta v_j, \ldots, v_n)}{2\Delta v_j} \tag{4}$$

where all the variables in the first term are held fixed at their measured values except for v_j, which is altered to $v_j \pm \Delta v_j$. In the limit of $\Delta v_j \to 0$, this becomes the analytical derivative. Using small Δv_j allows an approximation of the required derivatives in eq 1. What should we use for the Δv_j? A reasonable value is σ_j. Even if the value is not small enough to provide an accurate analytical derivative, it is actually better because the length scale of the measurement is σ_j and using this for Δv_j provides a more accurate estimate of the rate of change of function over the real range of the uncertainty. Making this substitution

$$\sigma_y^2 = \sum_{j=1}^{n} \left[\frac{f(v_1, v_2, \ldots, v_j + \sigma_j, \ldots, v_n) - f(v_1, v_2, \ldots, v_j - \sigma_j, \ldots, v_n)}{2\sigma_j}\right]^2 \sigma_j^2 \tag{5a}$$

$$\sigma_y^2 = \sum_{j=1}^{n} \left[\frac{f(v_1, v_2, \ldots, v_j + \sigma_j, \ldots, v_n) - f(v_1, v_2, \ldots, v_j - \sigma_j, \ldots, v_n)}{2}\right]^2 \tag{5b}$$

Thus, evaluating the uncertainty in y requires only evaluating the differences between the best estimate of the function and the value at the best value with each of the variables in turn increased by one standard deviation and summing the squares of these differences. This algorithm readily lends itself to automation in a spreadsheet.

We have implemented this algorithm in Excel with convenient input and protection macros. Figure 4 is an example of error analysis in Excel, using a sample function of five variables. In this case, $f(y,z,u,v,w) = y + z^2 + uvw$. There are entry cells for each variable and their corresponding uncertainties. The equation is entered through an input Excel cell which opens on pressing CTRL E. One enters the formulae in Excel format as shown in Figure 4. This spreadsheet works similarly to the unimplemented method described in ref 4 and provides simple data entry and improved numeric accuracy. The calculated value for the function, its standard deviation, and an error budget are displayed. Also, the worst-case error is computed assuming that all the errors are fully correlated. The error budget is the factional contribution of each variable to the variance.

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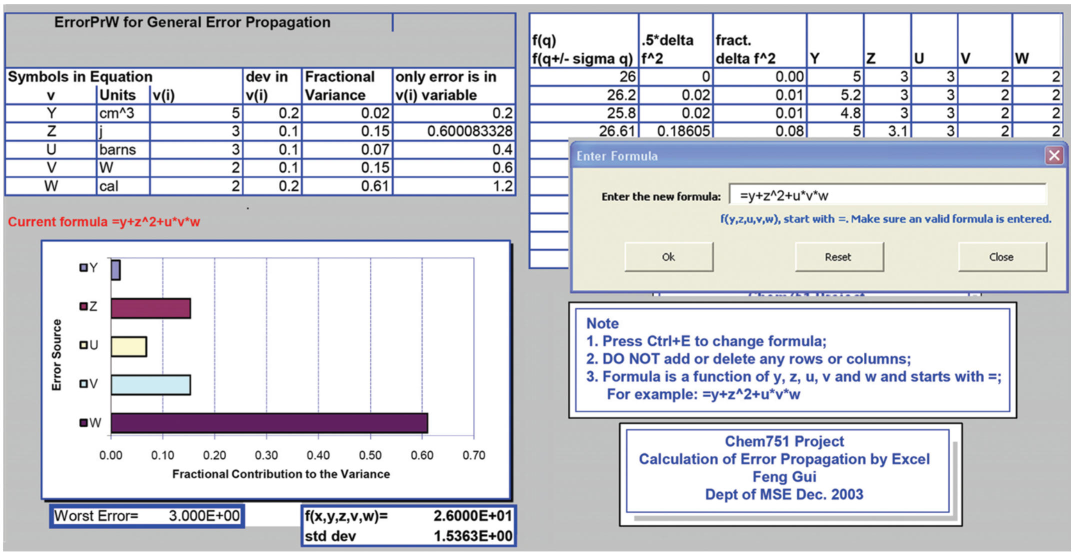

Figure 4. The critical elements of the Excel error propagation worksheet. Ctrl E has been pressed to bring up the New Formula window where the function of Y, Z, U, V and W is entered. The cells on the upper right are values used in the calculation. The units are placeholders for the writer's benefit but have no function.

Also shown are the errors in the final result if each variable in turn were the sole source of the final uncertainty. This information provides insight into the errors. Because the standard deviation is the square root of the sum of the variance from each component, it does not require much difference in one variable's standard deviation relative to the others for it to dominate the final uncertainty. This is one of the most useful features of an error analysis. It answers the question as to which variable to focus on to improve the uncertainty of the final derived number. In the example given, the standard deviation in y would have to be 6 times larger or 1.2 before its contribution to the error would equal that of w. Further even if there were no errors in any of the variables except the dominant w, the error would only be 1.2 rather than the 1.5 if all errors are present, which again shows that the other variables are minor contributors to the overall uncertainty. In short, for this experiment, improvements should be focused on improving w. The five-variable version should meet all needs. Even for equations with more variables, the number that contributes significantly to the error should never exceed this value and one can ignore the others. If in doubt as to the major error sources, the spreadsheet can be used with different subsets of the variables to determine which variables to use.

MORE COMPLEX PROBLEMS

We conclude by pointing out an example where the calculus-based method is inappropriate and spreadsheet or Monte Carlo methods are required. Consider a two-wavelength absorption measurement to determine the concentrations of two absorbing species in a mixture. If the spectra overlap extensively, there may be no wavelength where only one absorbs and it is necessary to solve the two linear equations relating absorbances, A, molar extinction coefficients, ε, and concentrations of the two species C_1 and C_2

$$A_1 = \varepsilon_{11}C_1 + \varepsilon_{12}C_2 \tag{6a}$$

$$A_2 = \varepsilon_{21}C_1 + \varepsilon_{22}C_2 \tag{6b}$$

where A_1 and A_2 are the absorbances at each of the two wavelengths. On ε, the first subscript denotes the wavelength and the second denotes the species. If the only uncertainties are in A, this is a standard error propagation problem easily solved by matrix methods, or if one is willing to work, just solve the equations in closed form and use a symbolic math program to propagate the errors, which is a somewhat messy but doable exercise. However, if one wants to handle errors in both A and ε, there is no closed form solution. The numerical derivatives method and eq 5 would work where the function would be the two solutions of the linear equations. One would have a total of six variables, the four ε and the two A, but the approach would be exactly the same. In actuality, the Monte Carlo method would be simpler and our preferred method.

CORRELATED ERRORS

Both the symbolic and Monte Carlo methods described above treat the uncertainties in the parameters as uncorrelated, that is, the magnitude and direction of the error measured on each parameter is not influenced by the errors on the other parameters. Generally, if each parameter is measured independently, this is true. However, there are important cases where this assumption fails. A classic example is when the desired quantity is a function of the slope and intercept of a linear fit.[16] These are correlated since a change in slope can be compensated by a change in intercept. In his excellent book, de Levie has discussed this problem in depth and provides an Excel routine that can be used to determine the correlation and calculate correct uncertainties.[5] Both of our routines do not handle correlated errors. However, it is straightforward to write a Monte Carlo routine that would start with noisy data around the expected function and compute the necessary results. Because the noise is on the original data and carried through all the calculations, correlations, if present, are taken into account. In our opinion, Monte Carlo methods are the most reliable approach and, with modern computers, the simplest and fastest.

CONCLUSIONS

The advanced technology of modern computers and symbolic software make the previous complex and tedious calculations of errors unnecessary for detailed error analysis. This analysis can be performed in programs in spreadsheets such as Excel or in a symbolic math packages such as Mathcad. The results are useful for designing improvements in the experiment to reduce uncertainties in the evaluated function. Monte Carlo methods are also useful for visualizing the effect of uncertainties on the distribution.

The five-variable Excel worksheet error propagation and the four-variable analytical Mathcad spreadsheet including a Monte Carlo estimate of the errors are available as Supporting Information

ASSOCIATED CONTENT

Supporting Information

The five-variable Excel worksheet error propagation and the four-variable analytical Mathcad spreadsheet including a Monte Carlo estimate of the errors. This material is available via the Internet at http://pubs.acs.org.

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