Introduction to Advanced Graphing Techniques

This tutorial is a follow-up to the previous tutorial, Graphical Analysis. In this tutorial we will cover the following advanced topics:

1. Obtaining error estimates for fitting constants
2. Fitting nonlinear functions
3. Using the delta function to make a first derivative graph

1. Obtaining Error estimates for fitting constants

When fitting data to a straight line (or when fitting nonlinear data), we would like an estimate of how much error we can expect in the returned fitting constants from Graphical Analysis. This feature is built-in to Graphical Analysis; you just need to know where to look!

As a tutorial example, we will use the same data and graphs as in the previous tutorial, the completed graph for the Gas Behavior Lab data. The slope and y-intercept given for the straight line are not exact but contain some error based on how well the data represents a straight line. To see an estimate of this error for each fitting constant, double click on the displayed dialog box. The Linear Fit Options dialog box will appear as shown. You can change the displayed precision of the fitting constants, the appearance (size and font) of the text in the dialog box and show the uncertainty of each fitting constant.

For this tutorial, we will keep the displayed precision as 4 significant figures. Make sure the box labeled Show Uncertainty is checked. When done the uncertainties appear as ± values after each fitting constant.

We now interpret the Slope and Y-intercept as follows:

Slope: 0.150±0.003 mm³/°C
Y-Intercept: 40.6±0.2 mm³

It is customary to round the Slope and Y-Intercept to match the magnitude of the uncertainty. For the Slope the uncertainty begins in the 3rd decimal place, so we round the slope to the 3rd decimal place.
The same is done with the Y-Intercept except the uncertainty appears in the first decimal place. Finally, we round the uncertainty values to one significant figure, ±0.003 for the slope and ±0.2 for the Y-Intercept.

2a. Fitting nonlinear functions – Arrhenius kinetics data

In chemistry and physics, much of the data we collect does not fit a straight-line function but some other nonlinear function. Graphical Analysis is just as good at finding fitting constants for this type of data as it is with linear data. For this tutorial, we will look at some kinetics data obtained from chemistry 1B. The kinetic rate constant, $k$, depends upon the Kelvin temperature, $T$, in a non-linear fashion as shown in the graph. In order to fit this data, we need a mathematical expression that gives the correct functionality of how the rate constant depends upon temperature. In other words, $k$ can be written in function form:

$k(T) = f(T,A,B,C\ldots)$ Where $T$ is the Kelvin temperature and $A$, $B$, $C$, … are fitting coefficients that should not depend upon the x-value, in this case $T$. To use Graphical Analysis, the user MUST KNOW the mathematical form of the function that correctly models their data. For the temperature dependence of the rate constant, this function was determined empirically a long time ago by Arrhenius and has the mathematical form:

$k(T) = Ae^{-E_a/RT}$

where $A$ is a prefactor (a FITTING COEFFICIENT), $E_a$ is the activation energy for the reaction (also a FITTING COEFFICIENT), $R$ is the universal gas CONSTANT (8.315 J/mol•K) and $T$ is the Kelvin temperature. A plot of Arrhenius data collected for the iodination of acetone in chemistry 1B is given below.

The data may look straight, but don’t be fooled! This data must be fit to the Arrhenius equation. The directions given in the tutorial are for this data and the Arrhenius equation but the techniques used can be applied to any user defined function.
Step 1: Open the curve fit dialog box

Once your data is in the correct form, to fit data to a nonlinear equation, you first open the Curve Fit Dialog Box. This is found under the Analyze>Curve Fit… menu item. The dialog box that appears is shown here for the Arrhenius data:

The graph with the data you are attempting to fit should appear at the top left. Below this is a set of predefined functions you can select. The predefined functions use the capital letter constants A, B, C… as fitting coefficients. Since the Arrhenius equation is not one of the predefined functions, we will click on the Define Function… button to bring up the User Defined Function dialog box as shown below. The default entry in the dialog box is a proportional function. Replace text of this function with the Arrhenius function typed as shown in the next dialog box.

Here, A is the prefactor fitting coefficient, E is the activation energy fitting coefficient and the value of universal gas constant ($R = 8.315 \text{ J/mol}\cdot\text{K}$) is typed directly into the equation. You cannot use the
symbol $R$ since GA will interpret it as a fitting coefficient. The exp is the exponential function, and $T$ is the independent (x) variable. Click OK and return to the Curve Fit dialog box. The Arrhenius function should now be selected and appear in the list of General Equation at the bottom as shown below.

**Step 2: Do the fit to find the coefficients**
To the right you should see the function and the Coefficients, A and E listed with a starting value of 1. For the Fit Type: Automatic should be selected. Graphical Analysis will now adjust these two coefficients to give the best-fit regression line to the data set. Select the Try Fit button. Graphical Analysis will make a first attempt to find values for the two fitting coefficients. However, they will not be the best values. To find the best values the Try Fit button MUST BE REPEATEDLY SELECTED until the RMSE value reaches a minimum and does not change. This may take 3-7 iterations of the Try Fit routine. See below for the final fit to the kinetics data, 5 iterations were needed.
Step 3: Add the dialog to your graph and display the uncertainty values

As the final step, select OK and arrange the dialog box on your graph. Don’t forget to display the uncertainty values for the fitting coefficients.
We can now say the rate constant, \( k \), for the iodination of acetone fits the Arrhenius function
\[
k(T) = Ae^{-E_a/RT}
\]
with fitting coefficients of \( A = 4.7 \times 10^9 \frac{1}{Ms} \) and \( E_a = 8.04 \times 10^4 \frac{J}{mol} \). In this notation for the coefficients, the numbers in parenthesis are the ± uncertainties to assign to the last digit of the coefficient. As you can see, for the prefactor the uncertainty, \( 7 \times 10^9 \), is larger than the reported value of \( 4 \times 10^9 \). This is not uncommon with prefactors to exponential functions since a change in the prefactor can often be offset by a change in the exponential fitting coefficient, in this case \( E \). These two fitting coefficients do not act independently of each other; therefore the uncertainty in each coefficient is rather large.

**2b. Fitting other nonlinear functions – acceleration data**

In physics a simple experiment to find the acceleration due to gravity, \( a \), is have a frictionless mass drop down a vertical spark track and mark the position of the mass every 0.05 seconds or other fixed time interval. The mass position is then plotted as a function of time. Data for this type of experiment is shown below. The short name \( t \) was given to the Time data in GA.

The position, \( x \), of the falling mass as a function of time, \( t \), for constant acceleration is given by the formula:

\[
x(t) = x(0) + v(0)t + \frac{1}{2}at^2.
\]

Where \( x(0) \) is the position at time zero, \( v(0) \), is the velocity at time zero, and \( a \) is the acceleration due to gravity. In this experiment the mass was a rest at time zero so \( x(0) = 0 \) and \( v(0) = 0 \). The position function becomes

\[
x(t) = \frac{1}{2}at^2.
\]

This function has a single fitting coefficient, the acceleration due to gravity, \( a \). In GA the fitting function is shown in the User Defined Function dialog box and the fitted data is shown below. The fitted acceleration constant of \( 9.78(5) \text{ m/s}^2 \) is within the reported
uncertainty to the accepted value of 9.81 m/s².

3. Using the delta and derivative functions to make a first derivative graph

In GA the first derivative of a data set can be made by using several different functions. We will only cover the delta and derivative functions, other first derivative functions are also available but outside the scope of this tutorial. The delta and derivative functions are accessed through the Data>New Calculated Column… menu selection.

1. **delta(column)**: this function simply takes the difference between the $i^{th}$ and $(i+1)^{th}$ values in a data set. To take a first derivative of $Y$ with respect to $X$ one would enter the User Defined Function

$$\frac{\text{delta}(Y_{column})}{\text{delta}(X_{column})}$$

This would place the first derivative of $y$ with respect to $x$ in a new calculated column. Since this function uses the $(i+1)^{th}$ data point in each calculation, there will be a missing entry for the last, $i^{th}$ data point.

delta function

A new calculated column is selected and the **delta(“Position”)/delta(“Time”)** equation is entered. The graph is shown below. The derivative of position with respect to time yields an average velocity between the two positional points $(x_i,y_i)$ and $(x_{i+1},y_{i+1})$. If you fit this data to a straight line the slope will be the acceleration due to gravity, $9.8(3)$ m/s².
2. **calculus\texttt{>derivative(Ycolumn,Xcolumn)}**: This function calculates the first derivative of Y with respect to X by taking an average derivative of data pairs around the \textit{i}'\textsuperscript{th} data point. The number of data points GA uses in the average is set under the File>Settings for “File name” menu option. I would suggest the number be set to 3 to keep the first derivative as localized as possible around the \textit{i}'\textsuperscript{th} data point. **When 3 is used, the first and last derivative will be calculated incorrectly since there are not enough data points to average. These two data points should be excluded from the derivative column of data.**

derivative function

A new calculated column is selected and the **derivative(“Position”,”Time”)** equation is entered. The Calculated Column Option box and graph are shown below. If you fit this data to a straight line the slope will also be the acceleration due to gravity, $9.8(2) \ m/s^2$. Since the first and last data points are calculated incorrectly when using an average of 3 points for the derivative, they are omitted from the fit by moving the square brackets towards the middle of the data set away from the end points (see graph). Alternately, you can use the strike through feature in the edit menu to exclude the end points from consideration.
Summary
In this tutorial we looked a couple of advanced features of graphical analysis. There are many other functions in Graphical Analysis available to explore. So get out an old data set from chemistry or physics and see what new information you might be able to extract using some of the advanced features of Graphical Analysis!