# Fitting Correlated Data: A Critique of the Guggenheim Method and Other Difference Techniques

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In certain data treatment procedures, like the Guggenheim method for first-order kinetics data with a background and various combination differences methods in spectroscopy, the analyzed data are obtained by taking differences of the raw data to render the resulting analysis simpler. Such methods can yield correlated data, the proper quantitative analysis of which requires correlated least squares. A formal treatment of these procedures shows that the source of the correlation is not the subtraction itself but the multiple use of data points from the raw data set in producing the differences. Typical applications of the Guggenheim method entail fitting the logarithm of the absolute differences to a straight line. Monte Carlo studies of both a constant-error and a proportional-error model for a declining exponential with a background show that neglect of weights is likely to be a greater source of imprecision than neglect of correlation. The most common form of the method of combination differences does not involve multiple use of the raw data and thus is a statistically sound procedure with no correlation problem.

## Introduction

In 1926, Guggenheim[1] suggested a method for analyzing first-order kinetics data when the desired exponential information is superimposed upon a background: Record data for a number of early times $t_i$ and then also for a set of later times displaced by a constant interval $\tau$. Then, subtract corresponding values (at $t_i$ and $t_i + \tau$) to eliminate the background and estimate the rate constant from the slope of a logarithmic plot of the absolute differences versus $t_i$. Although modern computational methods have long since rendered such graphical methods obsolete, the Guggenheim method still features in the undergraduate physical chemistry curriculum[2,3] and is even used surprisingly often in research applications (e.g., eight research citations of ref 1 in 2002).

Another area in which subtraction is used to simplify data analysis is the method of combination differences in spectroscopy.[4] This method is designed to isolate the dependences on the parameters for one level from those for other levels. Again, the transformed data yield a nearly linear plot suitable for graphical analysis. While the combination differences approach is still considered useful in confirming assignments, it is seldom utilized in quantitative research work these days. Other subtraction techniques have been applied to spectroscopic data in the teaching literature.[5,6]

There is a problem with such difference methods, however, when they are implemented quantitatively through least-squares (LS) fitting. They can lead to correlated data, which require correlated LS for proper analysis. Neglect of the correlation can have a big impact on the precision of the analysis. As one dramatic illustration of this point, in a recent study[7] of statistical errors in isothermal titration calorimetry,[8] I considered two different models for the nature of the error in the titrant volume as delivered by a motorized syringe. If the incremental volumes are considered random, the parameter standard errors actually increase with increasing number of titration steps. On the other hand, if the incremental volumes are considered to be the *differences* between two random quantities (the total delivered volume after $i - 1$ and $i$ steps), they possess correlated error. As a result of this correlation, the parameter errors become smaller and *decrease* with increasing number of titration steps. Both dependences were accounted for formally and confirmed through Monte Carlo calculations.

Although procedures for correlated LS fitting have long been known,[9−14] many workers remain unaware of both the procedures and the conditions that make them necessary. What attention has been focused on this problem has normally been in the context of multistep LS analysis — where data are first fitted to some intermediate parameters that are then subsequently fitted to the final parameters. Although the starting data are generally assumed to possess random error, the output parameters of an LS fit are almost always correlated, so the second step of such an analysis must properly be a correlated fit. By contrast, the cases reviewed above may involve correlation in the data — which are no longer "raw" but "partially cooked" through the subtraction process.

In this paper, I review the procedures for fitting correlated data and illustrate them specifically for the Guggenheim method, using Monte Carlo (MC) techniques to confirm the formal results. A key result of this study is that correlation in the data stems not from the subtraction process, as widely assumed, but from multiple use of the original data points in the transformed data set used in the fitting. As a consequence, if Guggenheim's original procedure is followed to the letter, there is no correlation problem. Also, in most cases of its application, the oft-disparaged method of combination differences is actually a statistically sound procedure. In both cases, however, a direct fitting approach of the original data is normally both easier and better than fitting the transformed data.

## Theoretical Background

**Least Squares with Correlation.** Methods for the LS fitting of data to both linear and nonlinear models are available from

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very many sources,[15−21] so I review here only enough of the formalism to establish the necessary notation. I adopt the usual assumptions of unbiased data with normally distributed error in the dependent variable ($y$) only. In the MC computations, this error is added randomly to points on the exact curve, which is consistent with the assumption that there exists such a true curve with random error superimposed.

The goal of an uncorrelated LS fit is the minimization of the sum of weighted, squared residuals ($\delta_i$, observed − calculated),

$$\mathcal{J} = \Sigma\, w_i\, \delta_i^2 \tag{1}$$

When the fitted quantities are correlated, this expression must be replaced by

$$\mathcal{J} = \boldsymbol{\delta}^{\mathbf{T}}\, \mathbf{W}\, \boldsymbol{\delta} \tag{2}$$

where the weight matrix **W** contains nonzero off-diagonal elements. (If **W** is diagonal, eq 2 reduced to eq 1, with $W_{ii} = w_i$.) Most nonlinear and all linear problems, both correlated and uncorrelated, can be solved using the "inverse Hessian" approach,[19] in which the parameter estimates $\boldsymbol{\beta}$ are iteratively improved using the equations

$$\mathbf{X}^{\mathbf{T}}\, \mathbf{W}\, \mathbf{X}\, \Delta\boldsymbol{\beta} \equiv \mathbf{A}\, \Delta\boldsymbol{\beta} = \mathbf{X}^{\mathbf{T}}\, \mathbf{W}\, \boldsymbol{\delta} \tag{3}$$

and

$$\boldsymbol{\beta}_1 = \boldsymbol{\beta}_0 + \Delta\boldsymbol{\beta} \tag{4}$$

The elements of **X** are $X_{ij} = (\partial F_i/\partial\beta_j)$, evaluated at $x_i$ using the current values $\boldsymbol{\beta}_0$ of the parameters. The fit function $F$ expresses the relations among the variables and parameters; in the common case where $y$ can be expressed as an explicit function of $x$, it can be taken as

$$F_i = y_{\mathrm{calc}}(x_i) - y_i = -\delta_i \tag{5}$$

For linear problems, convergence occurs in one cycle, for any starting values $\boldsymbol{\beta}_0$. For nonlinear models, convergence occurs eventually, provided the starting values $\boldsymbol{\beta}_0$ are sufficiently near a minimum in the $\chi^2$ surface.

The parameter variances are the diagonal elements of the variance−covariance matrix **V**, which is proportional to $\mathbf{A}^{-1}$. The latter is normally computed in solving eq 3 for $\Delta\boldsymbol{\beta}$. If the error structure of the data is known a priori (as it always is in an MC calculation in which Gaussian error of known $\sigma$ is added to the true curve), then for an uncorrelated fit, $W_{ii} = w_i = \sigma_i^{-2}$ and

$$\mathbf{V} = \mathbf{A}^{-1} \tag{6}$$

This equation remains valid in the general case, where the weight matrix **W** is the inverse of the variance−covariance matrix of the data

$$\mathbf{W} = \mathbf{V}_{\mathrm{d}}^{-1} \tag{7}$$

As already noted, correlation in the data is manifested as nonzero off-diagonal elements in $\mathbf{V}_{\mathrm{d}}$ and **W**, and it is these that mediate the correlation in the fit.

For linear fit models, both correlated and uncorrelated, the parameters are distributed normally, with variances given *exactly* by eq 6. This condition can thus be used to validate an MC code on a linear model. For nonlinear models, the parameters are not normally distributed and may not even have finite variance. However, from computational studies of a number of common nonlinear fit models,[21−24] I have arrived at a 10% "rule of thumb": If $\sigma_{\beta i} < |\beta_i|/10$, then the Gaussian assumption for the distribution of $\beta_i$ should suffice within 10% to specify its confidence limits. In the context of MC computations on a nonlinear model, it is useful to define the "exact" nonlinear $\mathbf{V} \equiv \mathbf{V}_{\mathrm{nl}}$, which is obtained from eq 6 using exactly fitting data for the model. The reason for this is that, for nonlinear models, the structure of **A** can depend on the parameters $\boldsymbol{\beta}$ and the dependent variable **y** as well as on **x**, and hence, can vary from data set to data set. By contrast, in linear fitting, **A** depends only on **x**, and thus, is known completely a priori for any data set **y** having this **x**.

From an experimental standpoint, one can never know the data error structure exactly. However, with manageable effort, it is usually possible to characterize the data error well enough to justify use of eq 6 for the parameter errors, and the $\chi^2$ test to check the fit.[18,21] This knowledge is particularly useful for cases when the number of degrees of freedom $\nu$ in the fit is small, because the relative standard deviation in $\chi^2$ is $(2/\nu)^{1/2}$, and the a posteriori (or ignorance) **V** so widely used

$$\mathbf{V}_{\mathrm{p}} = \frac{\mathcal{J}}{\nu}\mathbf{A}^{-1} \tag{8}$$

scales with $\chi^2$. Accordingly, the estimated parameter standard errors from $\mathbf{V}_{\mathrm{p}}$ have a relative uncertainty of $(2\nu)^{-1/2}$. Through eq 8, one is using the fit itself to estimate the data error. In unweighted fitting ($w_i = 1$), the estimated data variance is $s_y^2 = \mathcal{J}/\nu$; in weighted fitting where the relative but not the absolute errors of the data are known, $\mathcal{J}/\nu$ is the estimated variance for data of unit weight. It should be emphasized that if unweighted fitting is used naively on data that should be treated by weighted and/or correlated LS, eq 8 is simply wrong in its prediction of the parameter errors. The extent of its error can only be assessed through MC computations.

**Guggenheim Test Model.** Guggenheim's recommended procedure does not involve correlation, as already noted, but the variants used by many workers do. For example, data are often collected at evenly spaced time intervals, and the data set is simply displaced along the time axis for subtraction and subsequent analysis. This model permits the role of correlation to be illustrated most clearly and is the one I have used here. Specifically, I have generated and analyzed data using

$$y = b + a\, \exp(-kt) \tag{9}$$

with $b = a = k = 1$ and taking values from $t = 0$ to $t = 3$ at intervals $\Delta t \equiv t_{i+1} - t_i = 0.1$. Results are examined as a function of the time displacement, for constant $\sigma_y$ and for $\sigma_y$ proportional to $y$. (These error models roughly bracket those encountered in real data.[25])

Let **z** represent the set of differences obtained by subtracting points separated by $\ell\,\Delta t$ (i.e., $z_i = y_i - y_{i+\ell}$). If there are $n$ $y$ values, there are thus $m = (n - \ell)\mathbf{z}$ values to be fitted. **z** and **y** are related by a linear transformation

$$\mathbf{z} = \mathbf{L}\mathbf{y} \tag{10}$$

in which **L** contains $m$ rows and $n$ columns. The nonzero elements of **L** are $L_{ii} = 1$ and $L_{i,i+1} = -1$. The variance−covariance matrix $\mathbf{V}_y$ of the $y$ values is diagonal by assumption, with elements $(i,i) = \sigma_{yi}^2$. Accordingly, the variance−covariance matrix for the $z$ values is[23,26]

$$\mathbf{V}_z = \mathbf{L}\, \mathbf{V}_y\, \mathbf{L}^{\mathrm{T}} \tag{11}$$

and for the Guggenheim fit, $\mathbf{W} = \mathbf{V}_z^{-1}$.

It is easy to show that the diagonal elements of the $m \times m$ matrix $\mathbf{V}_z$ are $(\sigma_{yi}^2 + \sigma_{yi+\ell}^2)$ (i.e., the result from error propagation for subtraction of two random variates). Moreover, if $\ell \geq m$, *all off-diagonal elements in* $\mathbf{V}_z$ *are zero, and there is no correlation problem*. This condition (also stated as $\ell \geq {}^{n}/_{2}$) occurs when none of the original $y$ values is used more than once, from which it is clear that the correlation arises from such multiple use of individual data points, not from subtraction. This makes sense, because the difference of two random variates is itself a random variate, of exactly predictable variance in the case of normal variates.[23,27]

We are now in position to fit the $m$ differences $\mathbf{z}$ to an exponential without a background. However, the whole point of the Guggenheim method is to render the data in linear form through a logarithmic transformation. For this purpose, we must propagate the errors in the $z_i$ values into the corresponding errors in $u_i = \ln(z_i)$. For uncorrelated $z_i$, this is trivial: $\sigma_{ui} = \sigma_{zi}/z_i$. However, when there are nonvanishing off-diagonal elements in $\mathbf{V}_z$, the logarithmic transformation is more involved. The correct expression for this is a little-known and little-used extension[28,29] of the only slightly better known expression for propagation of error in functions of correlated variables[23]

$$\sigma_f^2 = \mathbf{g}^{\mathbf{T}}\mathbf{V}\mathbf{g} \tag{12}$$

In eq 12 $\mathbf{V}$ represents the variance−covariance matrix of a set of parameters, and the elements of $\mathbf{g}$ are the ordered partial derivatives of the function $f$ with respect to these parameters. The extension yields the variance−covariance matrix of a set of such functions (e.g., values of $f$ at different values of an independent variable)

$$\mathbf{V}_u = \mathbf{G}^{\mathbf{T}}\,\mathbf{V}_z\,\mathbf{G} \tag{13}$$

Here the "parameters" are the $m$ $z_i$ values, and the set of functions are the $m$ values $u_i = \ln(z_i)$. Accordingly, $\mathbf{G}$ is diagonal, with elements $z_i^{-1}$, and the elements of $\mathbf{V}_u$ are $\mathbf{V}_{u,ij} = \mathbf{V}_{z,ij}/(z_i\, z_j)$. Again, the diagonal elements are as expected for uncorrelated $z_i$ values.

## Results and Discussion

Calculations were carried out for the constant error model, using $\sigma_y = 0.01$, and for the proportional error model having $\sigma_{yi} = 0.01 \times y_i$. Data were fitted as a function of $\ell$ using (1) the correlated fit models for the exponential and log forms of the data, (2) models for both forms with proper weighting but neglect of the correlation (i.e., neglect of off-diagonal elements in $\mathbf{V}_z$ and $\mathbf{V}_u$), and (3) unweighted log fits. In the last of these, statistics were accumulated for both the actual errors in $k$ and for the apparent errors as returned by the a posteriori $\mathbf{V}_p$. In all cases, the MC calculations employed techniques like those described before.[21−25,30]

At the outset, Monte Carlo computations confirmed that the correlated fit algorithms were working properly (including giving the same results for both versions, exponential and log-linear). The chosen error structures make most of the computed $\sigma_k$ values much less than 0.1, so there were no significant disparities between the "exact" $\mathbf{V}_{nl}$-based estimates and the MC statistics. For example, the respective errors for $\ell = 8$ in the exponential fit of the constant-error model were 0.020738 and 0.020736, well within the Monte Carlo precision for $10^5$ data sets. For the correlated log fits, the disparities were slightly larger (e.g., 0.03037 and 0.03062 for $\ell = 12$). The larger difference in this case is attributed to the nonnormality of the data as a result of the log transformation.[30] This interpretation was supported by observation of closer agreement when $\sigma_{yi}$ was reduced by factors of 10−1000, with the greater reductions needed for small $\ell$.

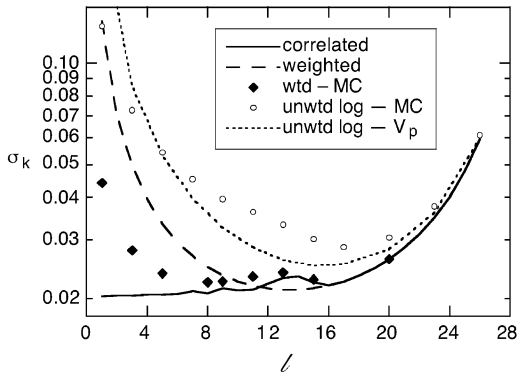


**Figure 1.** Standard error in first-order rate constant $k$ (dimensions reciprocal time) from various implementations of the Guggenheim method, for exponential data superimposed upon a background (eq 9, $a = b = k = 1$) with constant error $\sigma_y = 0.01$. The curve marked "weighted" shows the $\mathbf{V}_{nl}$-based predictions for analysis by a model that accounts for the weights but not the correlation, while the "wtd − MC" points show the actual results of analyzing the data this way. The results of analysis by unweighted log-linear fits are shown as points (MC statistics) and the dashed curve (apparent, rms values from $\mathbf{V}_p$ in the MC calculations). The MC calculations behind the last three curves involved at least $10^4$ data sets per point.

For the log fits, there is another problem: Negative differences can occur for small $\ell$, and there is no proper way to include data sets with negative $z_i$ values in the MC statistics. (They present no problem for the exponential fits.) To avoid this problem, the scale of the $y$-error was reduced by a factor of 1000 for the relevant MC computations. Where results are shown below for the stated $\sigma_y$ values of 0.01 or 1% of $y$, the log fit results have actually been obtained by using the reduced scale $\sigma_y$ values and then scaling back up for display. This procedure uses the property that the parameter standard errors scale with $\sigma_{yi}$ for a given data error structure. Of course, it also means that the plotted results for the log fits are hypothetical for small $\ell$.

Figure 1 illustrates results for the constant-error model. As expected, the correlated models give the most precise estimates of $k$ at all $\ell$, and the correlated and weighted models converge in their predictions at $\ell = 16$. Note that the first three labeled quantities in this figure apply to both the exponential and the log-linear fit models, because with proper attention to weights, these are identical (apart from the practical limitations already noted). It is also interesting that the correlated model yields for $\ell = 1$ a precision identical to that obtained when the full original data set is fitted directly to eq 9; not surprisingly, the correlated $\sigma_k$ exceeds this value for all other $\ell$. The points marked "wtd − MC" show that the practitioner who neglects the correlation but not the weights actually does much better than one might think (based on $\mathbf{V}_{nl}$) for small $\ell$, but somewhat worse in the midrange of $\ell$ that is more likely to be used in an application. In fact, the actual (MC) statistics show that the weighted model is not much worse than the correlated model in this range. On the other hand, the unweighted log-linear treatment yields much larger actual standard errors and greater disparities between the actual and the apparent values (from $\mathbf{V}_p$). Thus, in this case, neglect of weights turns out to be a bigger flaw than neglect of correlation. The significant disparities between apparent ($\mathbf{V}$-based) errors and actual (MC) for both the weighted and the unweighted log-linear treatments serves to accentuate the

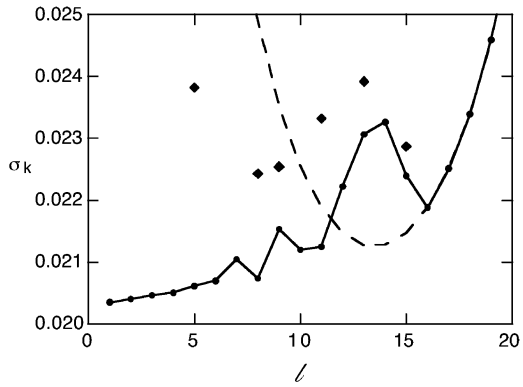


**Figure 2.** Enlargement of lower region of Figure 1, showing structure in $\sigma_k$ for correlated model. Curves and points are as identified in Figure 1.

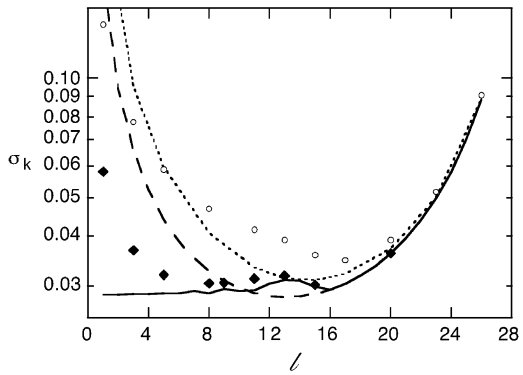


**Figure 3.** Standard error in first-order rate constant for proportional error, $\sigma_y = 0.01 \times y$. Points and curves are as identified in Figure 1.

point that the **V** matrix is meaningful only when the fit model matches the actual error structure of the data.

The apparent structure in the correlated fit results and in the weighted MC results is real, as is shown in Figure 2. This figure also shows that if one must use the Guggenheim model with data like those generated for this test model, a good choice for $\ell$ is the lowest value that avoids the correlation problem (16 in this case) and which incidentally agrees with Guggenheim's description of his procedure. The standard error in $k$ at this point is only 8% greater than the minimum value, but one must still take weights into account in a log-linear fit to realize this precision. (The weights are constant for the exponential fit in the constant-error model, because $\sigma_z^2 = 2\ \sigma_y^2$.)

Repetition of the computations behind Figure 1 for the proportional error model yields the results illustrated in Figure 3. These are qualitatively similar to those in Figure 1, but with somewhat smaller relative increase in $\sigma_k$ for the unweighted log fits. Note that for an exponential without background, the unweighted log-linear fit is statistically correct for the proportional error model in the absence of correlation (because $\sigma_u = \sigma_y/y$). However, this simple relation is lost when differences are taken, so nonconstant weights are needed in the log-linear fits for both error models.

The biases revealed in the MC computations were sometimes statistically significant for the very large ensembles of data sets processed ($\geq 10^4$) but were never significant from a practical standpoint. Thus, the main effects of neglect of weights and correlation in the Guggenheim method remain the loss of efficiency and the reporting of incorrect ($\mathbf{V}_p$- or $\mathbf{V}_{nl}$-based) parameter standard errors.

## Conclusion

The Guggenheim and other difference methods can yield data that are correlated, requiring correlated least squares for proper analysis. A formal analysis of such difference methods shows that the correlation is not a result of the subtraction but of the multiple use of the original (random) data in computing the differences. The difference between two random variates remains a random variate, with variance exactly equal to the sum of the variances of the two quantities involved in the subtraction, when the data are normal. However, the sign of the random deviation becomes important when the same variate is added to generate one difference point and subtracted to generate another. A correlated treatment of such data yields formal agreement between the predictions of the variance−covariance matrix for the fit model and the results of Monte Carlo computations on data generated to be consistent with the model. The proper accounting for correlation in this situation always leads to a reduction in the parameter errors. However, from a practical standpoint, neglect of weights is a bigger source of imprecision than neglect of correlation in typical applications of the Guggenheim method.

In spectroscopy, application of the method of combination differences to spectra containing only R and P branches does not use individual lines more than once; thus, the procedure is statistically sound and does not require correlated fitting. In fact, preliminary calculations show that the estimates of rotational and centrifugal distortional constants can be obtained with nearly identical precisions in combination difference analyses and whole-band fits.[31] However, if Q lines are present also and if certain fine splittings are neglected, it is possible to generate three different combination differences for a given ($v$,$J$) level, and these are mutually correlated. Neglect of this correlation is responsible for the reported discrepancies between **V**-based and MC estimates of standard errors in one published study.[32] Neglect of correlation is an even greater problem in the method of "successive differences," in which adjacent lines are subtracted to remove the band origin from the fit model.[5,6] The flaws in such methods have been characterized in detail elsewhere.[31]

Finally, it is worth emphasizing that the point of the present study has been the clarification of the role of correlation in difference fitting methods, not the selling of such methods. The direct fitting of the raw data to the correct linear or nonlinear relation, with weights as appropriate, is so straightforward nowadays that in few situations will such difference methods be found advantageous for quantitative analysis. The assumption of random error in the raw data is reasonable in most cases (with the notable exception of the example of isothermal titration calorimetry[7]), making correlation a nonproblem in the direct fitting approaches.

**Note Added after ASAP Posting.** This article was released ASAP on 9/6/2003 with an incorrect volume number in reference 7. The correct version was posted on 9/12/2003.

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