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Optimal Parameters for the Measurement of the Half-Width of a Gaussian Peak

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Abstract

The problem of estimating the half-width of a Gaussian peak arises in several areas of chromatographic analysis as well as in nuclear magnetic resonance. In this paper we contrast two techniques for reducing digital data to obtain the half-width. The first is numerical integration and the second is that of curve fitting. In the numerical integration technique we find the optimal truncation parameter such that the bias and variance balance one another, while for curve fitting one needs to specify how many data points to be included in the curve fit. Our investigation shows that the two methods give about the same precision but we nevertheless recommend the curve fitting approach because it is less sensitive to the parameters used in reducing the data.

INTRODUCTION

There are many techniques in chemistry and physics in which useful information can be expressed in terms of the moments of an experimentally measured peak. For example, resolution in chromatography is generally expressed in terms of the moments of two peaks (*1–3*). There are many additional uses suggested for experimentally determined moments in the context of chromatography (*4, 5*). The diffusion constant in isoelectric focusing both in the equilibrium regime (*6*), and in the transient regime have been estimated in terms of variances of Gaussian peaks (*7, 8*). Areas or moments are sometimes used in the analysis of data in ultracentrifugation (*9*). The determination of spectral moments plays a central role in the interpretation of NMR experiments (*10–14*). Together with these studies there have been several investigations, mainly by simulation, of the effects of noise on the calculation of moments from data (*15–18*). In addition there has been a recent experimental study, in the context of NMR, by Hendrickson and Tabbey (*19*). Of particular interest in this context is the problem of how to optimize parameters in the estimation technique so as to minimize the effects of digitization error, truncation error, and degradation due to noise. In this paper we consider these factors in the estimation of the zeroth and second moments of a Gaussian peak with additive noise. Two estimation techniques will be considered, the first being that of numerical integration of the data and the second being that of curve fitting to the Gaussian form, followed by the calculation of moments of the resulting peak. In the use of both of these techniques the experimenter needs to know how much of the data should be retained to minimize resulting errors. In addition, it is sometimes desirable to have an estimate of the error.

In what follows we will assume that the recorded signal representing a single isolated Gaussian peak is of the form

$$S(x) = Me^{-x^2/(2h^2)} + \varepsilon(x), \qquad -\infty < x < \infty \tag{1}$$

where M is the maximum amplitude of the noise-free signal and $\varepsilon(x)$ is the noise term. We have also assumed that baseline drift is negligible. The zeroth through second unnormalized moments of the noise-free signal are

$$\mu_0 = Mh\sqrt{2\pi}, \qquad \mu_1 = 0, \qquad \mu_2 = Mh^3\sqrt{2\pi} \tag{2}$$

and the half-width of the peak is

$$W_{1/2} = 2\sqrt{\ln 4h} = 2.355h \tag{3}$$

We will make the further assumption that the data are available only at a set of uniformly spaced points which we write

$$x_i = (i + \theta)\Delta L, \qquad i = 0, \pm 1, \pm 2, \ldots . \tag{4}$$

where the spacing is ΔL, and $\theta\Delta L$ is the abscissa of the observed maximum of the noise-free signal. Therefore θ satisfies $-½ < \theta < ½$. The noise term at the x_i will be written as $\varepsilon(x_i) = \varepsilon_i$. These random variables will be assumed to have the properties

$$\langle \varepsilon_i \rangle \quad 0, \quad \langle \varepsilon_i \varepsilon_j \rangle = \begin{matrix} 0, & i \neq j \\ \sigma^2, & i = j \end{matrix} \tag{5}$$

The signal-to-noise ratio, S/N, will then be M/σ.

NUMERICAL INTEGRATION

In the numerical integration method the rth moment will be estimated by

$$\hat{\mu}_r = \sum_{i=-n}^{n} (i\Delta L)^r S_i \Delta L \tag{6}$$

where $S_i = S(x_i)$. Three sources of error are represented in this formula. Digitization error is represented by the parameter θ and ΔL (with a continuously recorded signal, these are both equal to zero), and the truncation error is represented by having the limits set at $\pm n$ (when $n = \infty$ this error is equal to zero). The noise error is that due to the summation over the ε_i. The sum represents a discrete approximation to an integral where the limits of integration are $\pm X$ where $X = n\Delta L$.

We will write the expression for $\hat{\mu}_r$ as

$$\hat{\mu}_r = \mu_r + \Delta\mu_r + \eta_r \tag{7}$$

where μ_r is the true rth moment, $\Delta\mu_r(n, \theta, \Delta L)$ is the combination of digitization and truncation errors, and $\eta_r(n, \Delta L)$ is the random error. The relevant statistical properties of η_r are a direct consequence of Eq. (5), and are easily seen to be

$$\langle \eta_r \rangle = 0, \qquad \langle \eta_r^2 \rangle = \sigma^2(\Delta L)^{2r+2} \sum_{i=-n}^{n} i^{2r} \tag{8}$$

The advantage of the representation in Eq. (7) is that the two components of error are additive so that we can determine them separately. Equation (5) contains the properties of the random error that will be needed. If we set $\alpha = \Delta L/h = 2.355\Delta L/W_{1/2}$, which is a dimensionless measure of the integration interval, then in the absence of noise we have the estimate

$$\hat{\mu}_r = M \sum_{i=-n}^{n} i^r(\Delta L)^{r+1} \exp\left[-(i+\theta)^2\alpha^2/2\right] \tag{9}$$

in which we have used the assumption that $\langle \varepsilon_i \rangle = 0$. Let us consider the case $r = 0$ first. We can write $\hat{\mu}_0$ as

$$\hat{\mu}_0 = M\Delta L\left\{ \sum_{i=-\infty}^{\infty} e^{-(i+\theta)^2\alpha^2/2} - \sum_{i=n+1}^{\infty} \left[e^{-(i+\theta)^2\alpha^2/2} + e^{-(i-\theta)^2\alpha^2/2}\right]\right\} \tag{10}$$

The first sum on the right-hand side of this expression can be rewritten by means of a Poisson transformation (*15*) as

$$\sum_{i=-\infty}^{\infty} e^{-(i+\theta)^2\alpha^2/2} = \frac{\sqrt{2\pi}}{\alpha}\left\{ 1+2\sum_{j=1}^{\infty} e^{-2\pi^2 j^2/\alpha^2} \cos(2\pi j\theta)\right\} \qquad (11)$$

We next observe that in any sensible experiment the data points will generally be spaced more closely than $W_{1/2}/2$ which implies that $\alpha < 1$. When this condition holds, the infinite series on the right-hand side of Eq. (11) will be negligible, the largest term being of the order of 10^{-9}. Thus, to an excellent approximation, we can express $\hat{\mu}_0$ as

$$\hat{\mu}_0 = Mh\sqrt{2\pi} - M\Delta L \sum_{i=n+1}^{\infty} [e^{-(i+\theta)^2\alpha^2/2} + e^{-(i-\theta)^2\alpha^2/2}] \qquad (12)$$

or, using the notation in Eq. (7),

$$\Delta\mu_0 = - M\Delta L \sum_{i=n+1}^{\infty} [e^{-(i+\theta)^2\alpha^2/2} + e^{-(i+\theta)^2\alpha^2/2}] \qquad (13)$$

since $\mu_0 = Mh\sqrt{2\pi}$. Similarly we find

$$\Delta\mu_2 = - M(\Delta L)^3 \sum_{i=n+1}^{\infty} i^2[e^{-(i+\theta)^2\alpha^2/2} + e^{-(i-\theta)^2\alpha^2/2}] \qquad (14)$$

In order to give numerical estimates of the tradeoff between truncation and random error, we need a function that contains both factors. For even moments it is convenient to use the relative standard deviations

$$R_j = \langle (\hat{\mu}_j - \mu_j)^2 \rangle^{1/2}/\mu_j, \qquad j = 0, 2 \qquad (15)$$

If we adopt the notation

$$u_i = \exp[-(i+\theta)^2\alpha^2/2] + \exp[-(i-\theta)^2\alpha^2/2] \qquad (16)$$

then we find that R_0 and R_2 can be expressed as

$$R_0 = \frac{\alpha}{\sqrt{2\pi}}\left[\left(\sum_{i=n+1}^{\infty} u_i\right)^2 + (2n+1)\left(\frac{N}{S}\right)^2\right]^{1/2}$$

$$R_2 = \frac{\alpha^3}{\sqrt{2\pi}}\left[\left(\sum_{i=n+1}^{\infty} i^2 - u_i\right)^2 + \left(\sum_{i=-n}^{n} i^4\right)\left(\frac{N}{S}\right)^2\right]^{1/2} \qquad (17)$$

As one would expect, the contribution from the truncation errors decreases with increasing n, while the contribution due to a finite S/N increases as the noise amplitude increases. If one wants to estimate the half-width, or equivalently, the parameter h, one starts from the estimate

$$\hat{h}^2 = \hat{\mu}_2/\hat{\mu}_0 \tag{18}$$

which is exact when there are no errors. When these errors are present, we can write the estimate in the form

$$\hat{h}^2 = (\mu_2 + \delta\mu_2)/(\mu_0 + \delta\mu_0) \tag{19}$$

where $\delta\mu_2$ and $\delta\mu_0$ represent all errors. Notice that the errors in the numerator and denominator are not independent of one another. On the assumption that $\delta\mu_0/\mu_0$ is small, we can expand the denominator and find that to lowest order

$$\frac{\hat{h} - h}{h} = \frac{1}{2}\left(\frac{\delta\mu_2}{\mu_2} - \frac{\delta\mu_0}{\mu_0}\right) \tag{20}$$

which implies the formula

$$R_h = \frac{\langle(\hat{h} - h)^2\rangle^{1/2}}{h} = \frac{\alpha}{\sqrt{8\pi}}\left[\left(\sum_{i=n+1}^{\infty}(\alpha^2 i^2 - 1)u_i\right)^2 + \left(\frac{N}{S}\right)^2 \sum_{i=-n}^{n}(\alpha^2 i^2 - 1)^2\right]^{1/2} \tag{21}$$

It should be noted that the same value of n has been used in the estimates of μ_0 and μ_2 in the present treatment.

Figure 1 shows a schematic representation of the Gaussian peak together with the various quantities used to characterize the estimation procedures. In practice one would choose a maximum abscissa of integration, X, then set n to be the least integer greater than $X/\Delta L$. Figure 2 shows curves of R_0, R_2, and R_h plotted as functions of X/h. We found that the variation of these values with changes in θ tended to be much smaller than that with respect to X/h so that the curves shown are for $\theta = 0$ here and in the remaining figures. As one would expect, there is a minimum in each of these curves where the truncation and noise errors are at their optimal compromise values. Several conclusions can be drawn from the curves in Fig. 1. The first is that the minimum in each of the curves occurs at approximately $X/h = 2.25$ or equivalently, when the interval of integration, $2X$, is approximately twice the half-width. Although the curves in Fig. 2 are for the specific values $\alpha = 0.2$

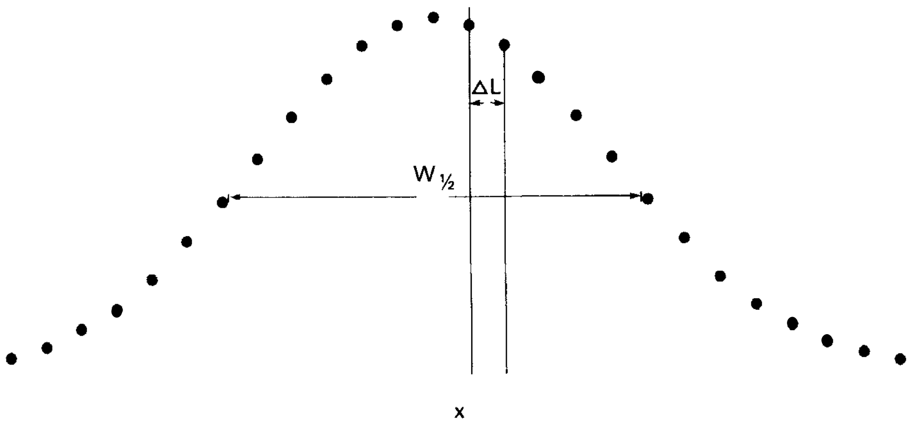

FIG. 1. Schematic diagram of an isolated Gaussian peak with the definition of the sampling interval ΔL and the half-width $W_{1/2}$. Since a sampling point occurs at $x = 0$ in this figure, the offset parameter θ is equal to zero.

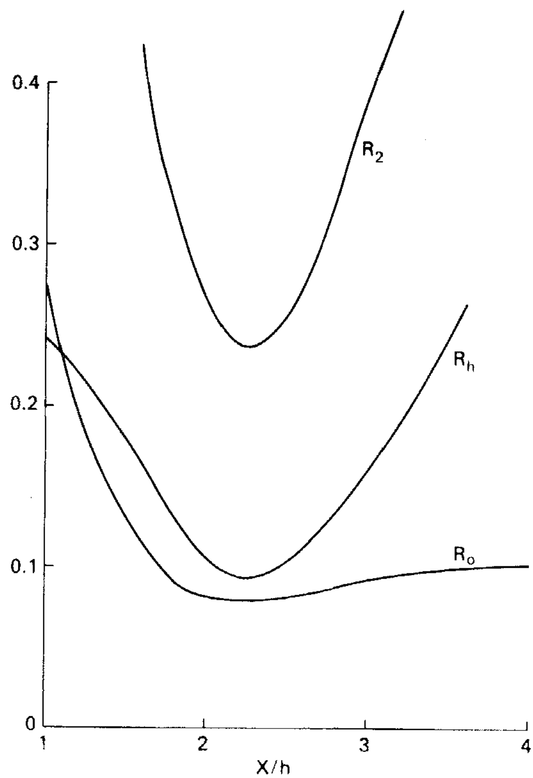

FIG. 2. Curves of the relative rms errors, R_0, R_2, and R_h plotted as a function of X/h for moments estimated by numerical integration. These curves are for $\alpha = 0.2$, $S/N = 5$, $\theta = 0$.

and $S/N = 5$, the location of the minima do not seem to depend strongly on α for $S/N > 5$ so that our result can be used as a rule of thumb. For example, when $S/N = 5$ or 10, the minima of the curves occurred at values ranging between 2.2 and 2.8 for values of α between 0.05 and 0.30. Although the positions of the minima tended to be insensitive to variations in α or S/N, the sensitivity to deviations from the minima increased markedly with α. One expects also that estimates of higher moments than $\hat{\mu}_0$ will be less accurate, hence it is somewhat surprising that the minimum value of R_h is so close to that of R_0. However, R_h is clearly more sensitive to deviations from the minimizing value of X/h than is R_0. The effects of digitization are illustrated in Fig. 3 which shows the error parameters R_0, R_2, and R_h plotted as functions of α ($=\Delta L/h = 2.36\Delta L/W_{1/2}$) for X/h at the minimizing value.

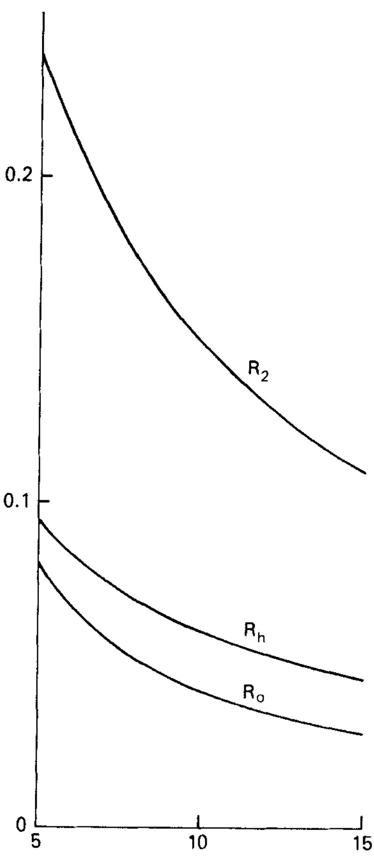

FIG. 3. Curves of R_0, R_2, and R_h plotted as a function of S/N for moments estimated by numerical integration for $\alpha = 0.2$ and $\theta = 0$.

The parameter R_h exceeds 10% only for $\alpha > 0.25$ or equivalently when there are fewer than 10 digital points covering the half-width.

CURVE FITTING

An alternative procedure for estimating moments is to use the data to estimate parameters of the peak and then calculate the resulting moments from the formula so obtained. This option is only available when, as in the present case, the functional form of the peak is known. However, the use of curve fitting is attractive for several reasons. The foremost of these is that in the absence of noise the procedure should, in principle, lead to an exact result so that the truncation problem does not arise provided that the number of available points exceeds the number of parameters to be estimated. A second advantage is that there are several good nonlinear curve fitting routines available. A final point is that when the baseline of the curve is not constant, one needs to eliminate the effect by some form of curve fitting in any case as in the recent paper by Dietrich and Gerhards (*21*). The possibility of curve fitting raises the question as to its potential in comparison to numerical integration as discussed in the last section.

To examine this question we have developed the relevant theory for curve fitting by unweighted least squares. Specifically, we will assume that one wants to fit a curve

$$\hat{S}(x) = \hat{M} \exp\left(- \frac{x^2}{2\hat{h}^2} \right) \tag{22}$$

where $\hat{M}$ and $\hat{h}$ are constants to be estimated by a least squares technique. That is to say, we minimize the following sum of squares:

$$F_n(\hat{M}, \hat{h}) = \sum_{i=-n}^{n} (\hat{S}(i\Delta l) - S(i\Delta L))^2 \tag{23}$$

where we have neglected digitization error. When the signal-to-noise ratio is sufficiently large we can linearize the differences appearing in this last summation, allowing us to calculate the criteria R_0, R_2, and R_h for this technique. In the Appendix we give a more detailed derivation of R_0. Results of the calculation are

$$R_0 = \left(\frac{N}{S} \right) \left\{ 2 \sum_{i=-n}^{n} ((i\alpha)^2 - 1)^2 \exp\left[-(i\alpha)^2\right]/\Delta_n \right\}^{1/2}$$

$$R_2 = \left(\frac{N}{S}\right)\left\{2\sum_{i=-n}^{n}((i\alpha)^2 - 3)^2 \exp\left[-(i\alpha)^2\right]/\Delta_n\right\}^{1/2} \qquad (24)$$

$$R_h = \left(\frac{N}{S}\right)\left\{2\sum_{i=-n}^{n} \exp\left[-(i\alpha)^2\right]/\Delta_n\right\}^{1/2}$$

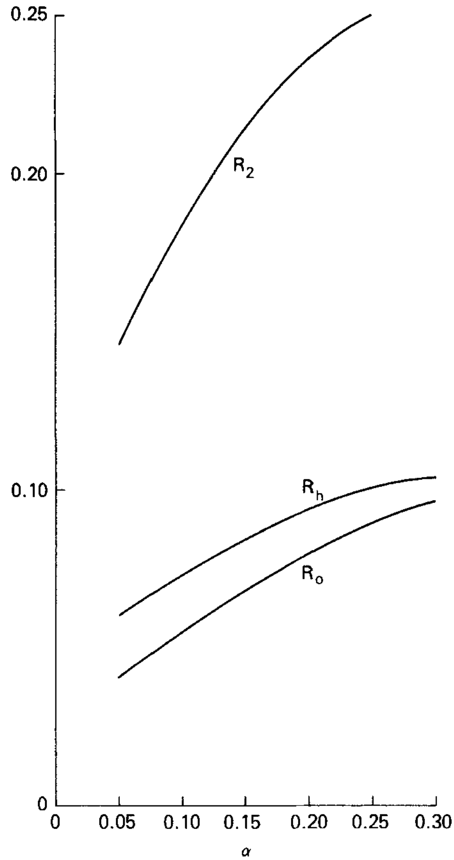

FIG. 4. Curves of R_0, R_2, and R_h plotted as a function of the normalized data interval α for moments estimated by numerical integration. The curves are for $S/N = 5$.

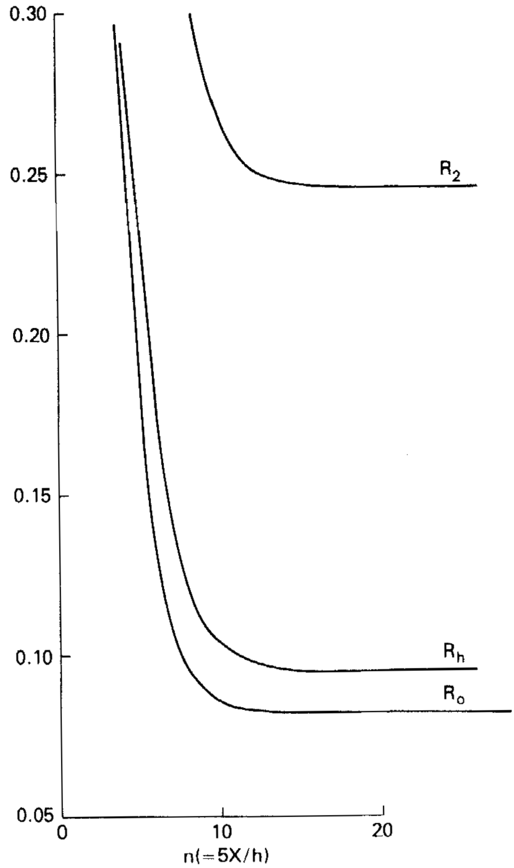

FIG. 5. Curves of R_0, R_2, and R_h plotted as a function of n, half the number of data points, for moments estimated by the curve fit method. In this figure $\alpha = 0.2$ so that the dimensionless truncation parameter X/h is given by $n(\Delta L/h) = 0.2n$, or $n = 5X/h$. These curves are for $S/N = 5$ and $\theta = 0$.

where

$$\Delta_n = \alpha^4 \sum_{i=-n}^{n} \sum_{j=-n}^{n} (i^2 - j^2)^2 \exp[-(i^2 + j^2)\alpha^2] \tag{25}$$

As we have already mentioned, there is no explicit truncation error, and whenever there are at least two data points, M and h can be found exactly in the absence of noise contamination. Figure 5 shows curves of R_0, R_2, and R_h as functions of n for $S/N = 5$ and $\alpha = 0.2$. Comparison of these curves with those in Fig. 2 shows there is a qualitative difference between the two cases in that the present curves strictly decrease to a constant value. Furthermore, the constant value is reached at approximately the optimal truncation point for numerical integration, i.e., the interval over which data are used should be at least twice the half-width. In contrast to numerical integration, however, the taking of additional points does not degrade the precision of any estimate, although taking too few points does impose a large penalty as seen in the figure. The curves in Fig. 5 are given for $S/N = 5$; it is trivial to find the effect of changing S/N since the R's are proportional to N/S. Figure 6 shows the asymptotic values of the R's plotted as a function of α. The curves are qualitatively similar to those shown in Fig. 4 and the actual values are themselves quite close. Table 1 contains a more detailed comparison of

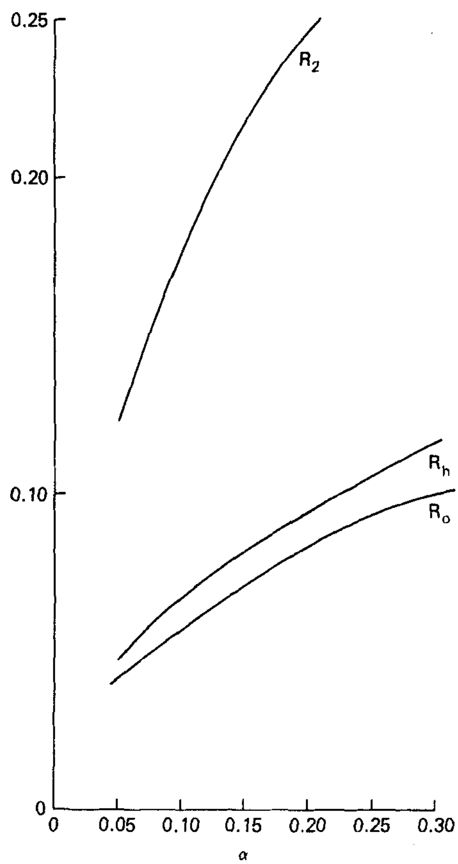

FIG. 6. Curves of R_0, R_2, and R_h plotted as a function of α for moments estimated by the curve fit method. The curves are drawn for $S/N = 5$.

TABLE 1

Comparison between Values of R_0, R_2, and R_h Calculated for Estimation by Numerical Integration (NI) and Curve Fitting (CF)

α	S/N	R_0 (NI)	R_0 (CF)	R_2 (NI)	R_2 (CF)	R_h (NI)	R_h (CF)
0.1	5	0.058	0.080	0.187	0.217	0.075	0.072
	10	0.030	0.040	0.115	0.109	0.047	0.036
0.2	5	0.081	0.082	0.235	0.247	0.093	0.095
	10	0.042	0.041	0.149	0.123	0.061	0.048

results obtained using the two methods. The differences are small and tend to favor the method of curve fitting for $S/N = 10$ while they favor numerical integration at the lower value of S/N, although the differences are minute.

DISCUSSION

While the differences indicated in Table 1 are operationally insignificant, we would nevertheless favor the use of curve fitting over that of numerical integration. This preference is based on the greater sensitivity of numerical integration to the choice of truncation parameter. We have also used a fairly simple approach to curve fitting. It is quite possible that a more sophisticated approach to curve fitting, e.g., using splines and/or smoothing the data, would lead to greater precision in the estimation of moments. Furthermore, the use of curve fitting allows the possibility of removing baseline effects when these are significant, although it is probable that the use of more parameters would degrade precision over that reported in the present paper. We have not discussed estimation of peak position; however, this could also be analyzed in the present framework at the expense of introducing one more parameter. We expect that the results would be similar to those obtained for the even moments. Another important assumption that has been made is that moments have been estimated from an isolated peak. The presence of nearby peaks will surely play an important role in determining the precision of estimates and in the choice of estimator to be used. We have not considered effects of smoothing, either intentional or through instrumental inertia, on precision. It is possible that such smoothing might work in either direction, either increasing or degrading the precision of estimates, as shown in a recent study of the estimation of peak position in the measurement of chemical shifts (*22*).

APPENDIX: DERIVATION OF R_0 FOR LEAST SQUARES CURVE-FITTING

For simplicity we derive the expression for R_0 only, derivation of the remaining error criteria being quite similar. Assume that the least squares estimates of M and h are $\hat{M}$ and $\hat{h}$, respectively. Further, let $\hat{M}$ and $\hat{h}$ be expressed as

$$\hat{M} = M + \delta M, \qquad \hat{h} = h + \delta h \tag{A1}$$

Then the normalized estimate of the zeroth moment is, to lowest order,

$$\frac{\hat{\mu}_0 - \mu_0}{\mu_0} = \frac{\delta M}{M} + \frac{\delta h}{h} \tag{A2}$$

where a term $\delta M \delta h/(Mh)$ has been neglected in comparison to the terms retained. We must therefore find expressions for δM and δh from the defining equations. For this purpose we return to Eq. (23), together with the representation of Eq. (1), for $S(x)$. The basic assumption in this treatment is that the estimates, $\hat{M}$ and $\hat{h}$, are sufficiently good that the difference $\hat{S}(x) - S(x)$ that appears in Eq. (23) can be represented in the form

$$\hat{S}(x) - S(x) \sim \frac{\partial S}{\partial M}\delta M + \frac{\partial S}{\partial h}\delta h - \varepsilon(x) \tag{A3}$$

so that higher order terms have been neglected. The two equations that determine $\hat{M}$ and $\hat{h}$ are

$$\begin{aligned} \frac{\partial F_n}{\partial \hat{M}} &= 2\sum_{i=-n}^{n} (\hat{S}(i\Delta L) - S(i\Delta L)) \frac{\partial \hat{S}}{\partial \hat{M}}\Bigg|_{\substack{x=i\Delta L \\ \hat{M},\hat{h}=M,h}} = 0 \\ \frac{\partial F_n}{\partial \hat{h}} &= 2\sum_{i=-n}^{n} (\hat{S}(i\Delta L) - S(i\Delta L)) \frac{\partial \hat{S}}{\partial \hat{h}}\Bigg|_{\substack{x=i\Delta L \\ \hat{M},\hat{h}=M,h}} = 0 \end{aligned} \tag{A4}$$

If we introduce the linear approximation in Eq. (A3) into this last equation, together with the notation

$$\left.\frac{\partial \hat{S}}{\partial \hat{M}}\right|_{\substack{\hat{M},\hat{h}=M,h \\ x=i\Delta L}} = \frac{\partial S_i}{\partial M}; \qquad \left.\frac{\partial \hat{S}}{\partial \hat{h}}\right|_{\substack{\hat{M},\hat{h}=M,h \\ x=i\Delta L}} = \frac{\partial S_i}{\partial h}; \tag{A5}$$

$$A = \sum_{i=-n}^{n}\left(\frac{\partial S_i}{\partial M}\right)^2, \qquad B = \sum_{i=-n}^{n}\left(\frac{\partial S_i}{\partial M}\right)\left(\frac{\partial S_i}{\partial h}\right), \qquad C = \sum_{i=-n}^{n}\left(\frac{\partial S_i}{\partial h}\right)^2$$

then δM and δh are the solutions to the set of equations

$$A\delta M + B\delta h = \sum_i \varepsilon_i \frac{\partial S_i}{\partial M}$$

$$B\delta M + C\delta h = \sum_i \varepsilon_i \frac{\partial S_i}{\partial h} \tag{A6}$$

From this it follows that

$$\delta M = \frac{1}{\Delta}\sum_i \varepsilon_i \left(C\frac{\partial S_i}{\partial M} - B\frac{\partial S_i}{\partial h}\right)$$

$$\delta h = \frac{1}{\Delta}\sum_i \varepsilon_i \left(A\frac{\partial S_i}{\partial h} - B\frac{\partial S_i}{\partial M}\right) \tag{A7}$$

where $\Delta = AC - B^2$. In consequence of $\langle \varepsilon_i \rangle = 0$, we find

$$\langle \delta m \rangle = \langle \delta h \rangle = 0 \tag{A8}$$

so that $\langle \mu_0 \rangle = \mu_0$ in this order of approximation. It is also easy to verify that, using Eq. (A7),

$$\langle \delta M^2 \rangle = \sigma^2 C/\Delta, \qquad \langle \delta h^2 \rangle = \sigma^2 A/\Delta, \qquad \langle \delta M \delta h \rangle = -\sigma^2 B/\Delta \tag{A9}$$

Equation (A2) implies that

$$R_0 = \frac{\langle \delta M^2 \rangle}{M^2} + 2\frac{\langle \delta M \delta h \rangle}{Mh} + \frac{\langle \delta h^2 \rangle}{h^2} \tag{A10}$$

On substituting Eq. (A9) into this last equation, together with the definition of A, B, and C in Eq. (A5) we find

$$R_0 = \frac{\sigma}{\Delta^{1/2}} \left\{ \sum_i \left(\frac{1}{M} \frac{\partial S_i}{\partial M} - \frac{1}{h} \frac{\partial S_i}{\partial h} \right)^2 \right\}^{1/2} \tag{A11}$$

where

$$\Delta = \frac{1}{2} \sum_i \sum_{i'} \left(\frac{\partial S_i}{\partial M} \frac{\partial S_{i'}}{\partial h} - \frac{\partial S_i}{\partial h} \frac{\partial S_{i'}}{\partial M} \right)^2 \tag{A12}$$

When the derivatives

$$\frac{\partial S}{\partial M} = \exp\left(-\frac{x^2}{2h^2} \right), \qquad \frac{\partial S}{\partial h} = \frac{Mx^2}{h^3} \exp\left(-\frac{x^2}{2h^2} \right) \tag{A13}$$

are used to evaluate Eqs. (11) and (12), the result is that given in Eq. (24) of the text.

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