Estimation of True Moments from Truncated Data

Moment analysis is a powerful tool in reactor bed analysis. Weighted moments is a technique which has been introduced to increase the accuracy of moment estimation. The supposed advantage of weighted moments is reevaluated utilizing an optimum truncation point. The resulting coefficient of variation in the moment estimates is shown to be superior to an arbitrary truncation point for all weighting factors. When an optimum truncation point is used, little advantage is observed for weighted moments.

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SCOPE

This study evaluates the influence of truncation point on the estimation of response function moments. Moment analysis is an important tool used in evaluating reaction beds, chromatographic systems, and other unsteady processes. An accurate and straightforward means of calculating moments is needed. Prior work has shown that errors in the tail of response functions leads to undesirable errors in the moments. Ostergaard and Michelsen (1969) introduced weighted moments as a means to correct this error. However, they ignored the influence of truncation point, discussed here.

CONCLUSIONS AND SIGNIFICANCE

Truncation point is shown to have an influence on the efficiency of moment estimation. This effect is great enough that the benefits claimed for weighted moments are valid only for special values of the truncation point. An optimal truncation point is defined and shown to eliminate the need for weighted moments.

INTRODUCTION

Moment analysis is a frequently used tool in the characterization of unsteady reactor processes (Ramachandran and Smith, 1978; Razavi et al., 1978; Wiedemann et al., 1978). It is especially popular in the analysis of chromatographic or reacting beds and the estimation of parameters in models describing such systems (Grubner and Underhill, 1970; Suzuki and Smith, 1971; Razavi et al., 1978). The principles of moment analysis (as well as the drawbacks) have been discussed by these authors. Basically the procedure treats the output of a system response as a distribution function. The statistical moments of the distribution are estimated from the measured response and used to build a model describing the system. Here our concern will be with the means of obtaining the best estimates for the moments.

Some of the terminology can be defined by referring to Figure 1, which represents the system response to a pulse input. The curve $f(t)$ represents the true continuous response when there are no sources of noise in the measurement. The points $g(t_i)$ represent actually measured points including noise. When the system response is a reactant concentration, measurements are typically on discrete samples rather than continuous.

At some time, data collection must be terminated and this point is shown as A_k, where k indicates that different end points may be appropriate for optimal estimation of different moments. Qualitatively the moments represent the following: 0th, mass balance, the accumulated system response; 1st, the mean time for the response to register, a measure of the rate of movement of the response through the system; 2nd, the extent of spread of the response; 3rd, the degree of asymmetry in the response; and 4th, higher-order spreading in the response.

Two major obstacles prevent the accurate determinations of statistical moments. First, the data obtained is invariably noisy; second, at some point the data must be truncated. The truncation point is usually determined by the level of noise and patience of the experimenter, frequently in an arbitrary manner. It is also possible to systematically truncate data after the collection of data is complete. The presence of noise in the tails of the distribution results in unreliable estimates for the moments. In particular, any higher order moment has significantly decreased reliability relative to any lower order moment. In practice moments higher than the second are rarely used. Even for the first and second moments, various techniques exist to correct for errors introduced by imprecise representation of the tails (Anderssen and White, 1971; Sater and Levenspiel, 1966; Kafarov et al., 1968). None of the existing corrections guarantees a best estimate or provides information on an optimal truncation point.

The method of weighted moments has recently gained in popularity (Anderssen and White, 1971; Ramachandran and Smith, 1978; Wolff et al., 1979). A critical examination of the benefits of weighted moments seems desirable at this time. In particular, what is the importance of choice of truncation point in a comparison with ordinary moments? It will be shown that the appropriate choice of truncation point increases the efficiency of ordinary moments, and further, that an optimal truncation point can be defined.

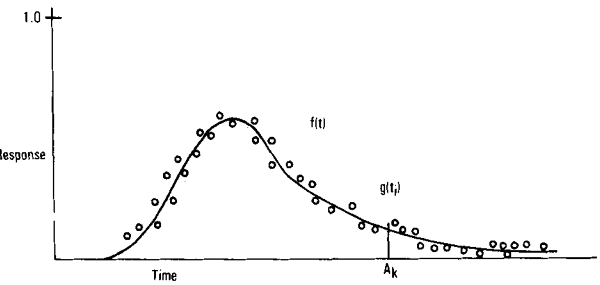

Figure 1. System response as a function of time for data including a random error component.

Moments

The true kth moment about the origin is defined as:

$$\mu_{kT} = \int_0^\infty t^k f(t)dt/\mu_0 T \qquad k > 0$$

The variable t is time and f a signal due to a pulse input, frequently the concentration of a reactant. Since this is the true moment, f is uncorrupted by noise. Without loss of generality, it can also be assumed that f is nondimensionalized so that the area under the curve is one. Alternatively this means that $\mu_{0T} \equiv 1$.

The observed moments are defined as:

$$\mu_{0E} = \int_0^{A_0} g(t)dt$$

$$\mu_{kE} = \int_0^{A_k} t^k g(t)dt/\mu_{0E}$$

where g is the measured signal including any noise, and A_k is the truncation point. Several things are worth noting about these definitions. First, μ_{0E} is not necessarily equal to one. Second, the actual calculation of the observed moments involve the approximation of the integrals by sums. Throughout this analysis it will be assumed that the error introduced in approximating the integral can be made negligible by sufficient sampling. Last, the truncation point can vary with the order of the moment.

Weighted Moments

The method of weighted moments (Ostergaard and Michelsen, 1969; Anderssen and White, 1971) utilizes the relationship of ordinary moments to the Laplace transform. The weighted moments are defined as

$$\mu_{kw}(s) = \int_0^\infty t^k e^{-st} f dt/\mu_0 w$$

with s an arbitrary parameter or transform variable with dimensions of inverse time. The integral is also the definition of the Laplace transform of $(t^k f)$. For $s = 0$, weighted moments are identical with ordinary moments. For $s > 0$ the term (e^{-st}) acts as a weight, decreasing the importance of concentrations in the tail of the curve. Further, s acts as a free variable to allow better estimation of the model parameters. A number of problems exist with this method. First, a value of s (the weighting factor) must be determined. The empirical approaches suggested to date (Anderssen and White, 1971; Wolff et al., 1979) attempt to choose s near the point where the integrand is a maximum. For output curves that are near gaussian this provides a reproducible procedure. However, as the nature of the system and its output become nongaussian the best selection criteria for s can be expected to change. Second, the procedure does not weight the signal according to the reliability of the signal but with an arbitrary weight function. This gives rise to the awkward interpretation that the leading portion of the distribution is of more significance than the trailing portion for equal concentrations. In most systems, errors are proportional to concentration or fixed, rather than dependent directly on time. Third, the method greatly increases the complexity of the relation between model parameters and experimental moments.

Weighted moments do have the advantage of insensitivity to data points in the tail of a curve. This means the contribution of an unmeasured tail can be ignored. Another advantage that has been claimed for weighted moments (Anderssen and White, 1971, Figure 2) is the possible minimization of relative error in the estimate. Implicit in this argument is the insensitivity of weighted moments to truncation point.

THEORY

Our analysis starts by assuming that the output $g(t)$ can be represented as having deterministic (f) and random (ϵ) components.

$$g(t) = f(t) + \epsilon(\sigma) \tag{1}$$

whre ϵ is the random variable and is taken normal with zero mean and variance σ^2. The variance may depend on t implicitly or f explicitly.

In the procedure described below, μ_{kE} will be used to construct an estimator of μ_{kT}. This can be done as follows. Let h_k be some constant to be determined such that:

$$\mu_{kT} = E[h_k \mu_{kE} \mu_{0E}] \tag{2}$$

The notation $E[\quad]$ and $E[\quad]^2$ is a convenient way to denote expectation with respect to the random variable. The notation $E[\quad]$ represents the mean while $E[\quad]^2$ denotes a second moment.

Standard statistical techniques (Hogg and Craig, 1965) suggest that our estimator be evaluated by examining its mean and variance (var) with respect to the random variable. If the estimator is appropriate, h_k can be chosen so that the expected value (with respect to the random variable) is the true value of the moment. However, for each truncation point a distinct value of h_k can be expected which satisfies the criterion of equating true and estimated moments. The dependence upon a truncation point introduces another parameter into the estimate. This problem is resolved by defining a best estimate as that value of the truncation point which minimizes the relative variation of the estimator. That is, the coefficient of variation (CV) is to be minimized where:

$$CV = \sqrt{\mathrm{Var}}/\mathrm{mean} \tag{3}$$

The use of CV results in an objective measure of the best estimate. If the analysis is extended to weighted moments, CV is a function of s. A plot of a variable related to CV as a function of s alone was used by Anderssen and White (1971) to show that nonzero value of s gave best estimates. First let us examine the expectation of the righthand side of Eq. 2.

$$E[h_k \mu_{kE} \mu_{0E}] = h_k E\left[\int_0^{A_k} t^k g(t)dt\right]$$
$$= h_k E\left[\int_0^{A_k} t^k f(t)dt\right] + h_k E\left[\int_0^{A_k} t^k \epsilon dt\right]$$

The last term is zero since μ has a zero mean. This leaves:

$$E[h_k \mu_{kE} \mu_{0E}] = h_k \int_0^{A_k} t^k f(t)dt \tag{4}$$

Now for the expected value to equal the true value h_k must be:

$$h_k = \int_0^\infty t^k f(t)dt \Big/ \int_0^{A_k} t^k f(t)dt$$

$$h_k = 1 + \int_{A_k}^\infty t^k f(t)dt \Big/ \int_0^{A_k} t^k f(t)dt \tag{5}$$

The h_k which has been found satisfies the requirement of giving an estimate of the true moment provided the deterministic component of the density function is known. In general this is not known although approximations such as the Gram-Charlier expansion (Ord, 1972; Johnson and Kotz, 1971) are frequently used.

The expression for h_k does suggest another form:

$$h_k = 1 + \int_{A_k}^\infty t^k f(t)dt \Big/ \int_0^{A_k} t^k g(t)dt \tag{6}$$

This also gives the correct expectation for the moments. In addition, it limits the range over which an approximation must be used for the unknown tail.

A similar analysis can be performed with weighted moments, indicated by prime. Formally it is:

$$h_k' = 1 + \int_{A_k}^\infty t^k f(t)e^{-st}dt \Big/ \int_0^{A_k} t^k f(t)e^{-st}dt \tag{7}$$

It is usually assumed the tail can be ignored due to exponential weighting giving $h_k' = 1$.

A discussion of techniques to approximate the tail is presented later. At this time our evaluation of the estimator is continued by examining its variance. The variance is:

$$\mathrm{var}[h_k \mu_{kE} \mu_{0E}] = E[h_k \mu_{kE} \mu_{0E} - E[h_k \mu_{kE} \mu_{0E}]]^2 \qquad (8)$$

For convenience Eq. 5 will be used here for a definition of h_k. The use of slightly different definitions of h_k for estimating either the moments or truncation point is a procedure that is ultimately justified by its utility.

Introducing the definitions of the moments, and the notation var for the lefthand side of Eq. 8:

$$\mathrm{var} = h_k^2 E\left[\int_0^{A_k} t^k g(t)dt - \int_0^{A_k} t^k f(t)dt\right]^2$$

$$= h_k^2 E\left[\int_0^{A_k} t^k \epsilon dt\right]^2$$

Replacing the integral by a sum

$$\mathrm{var} = h_k^2\, E[\textstyle\sum t^k \epsilon \Delta t]^2$$

The sum is for a fixed number of equally spaced points $n = A_k/\Delta t$. Consequently Δt depends on the truncation point. Proceeding by noting the variance of a sum is the sum of the variances provided the errors are independent and constant with time.

$$\mathrm{var} = h_k^2 \textstyle\sum t^{2k} (\Delta t)^2 \sigma^2 \qquad (9)$$

Analogously for weighted moments:

$$\mathrm{var} = h_k'^2 \textstyle\sum t^{2k} (\Delta t)^2 \sigma^2 e^{-2st} \qquad (10)$$

This is similar to Eq. A.10 of Anderssen and White (1971). It differs by including the term h_k', excluding a secondary weight factor (not used in their analysis) and in that the variance is still considered as a function of time.

For many experimental arrangements, σ may be assumed constant with time. If σ is not constant, the optimal truncation point will depend on the variation of the random noise variance with time.

Continuing with ordinary moments, and substituting $\Delta t = A_k/n$ and $t_i = i\Delta t$,

$$\mathrm{var} = h_k^2 \sigma^2 A_k^{2k+2} (\textstyle\sum i^{2k})/n^{2k+2} \qquad (11)$$

Returning to Eq. 4 and making similar substitutions:

$$\mathrm{mean} = h_k A_k^{k+1} [\textstyle\sum i^k f(t_i)]/n^{k+1}$$

Using Eq. 3 the CV becomes:

$$CV = \sigma \sqrt{\textstyle\sum i^{2k}} / \textstyle\sum i^k f(t_i) \qquad (12)$$

Analogously for weighted moments

$$CV = \sigma \sqrt{\textstyle\sum i^{2k} e^{-2st}} / \textstyle\sum i^k e^{-st} f(t_i) \qquad (13)$$

Two points are worth mentioning about Eqs. 12 and 13. First the CV does not depend on the correction factor h_k. This is due to h_k being a deterministic quantity. This also means that if no correction is made (i.e., $h_k = 1$), the same expression for the CV is applicable. However, the expected value of the estimator would be incorrect. Secondly the dependence of the CV on the truncation point is not explicit. Expression 12 for the ordinary moments depends implicitly on truncation point through the shape of the signal (f) which is being measured. For weighted moments the truncation point also enters into the weighting factor. But since s is arbitrary and time appears in the weight only as st, similar arguments can be made for Eq. 13. Regardless of the technique used, system input is expected to markedly affect the CV.

To examine the quantitative behavior of the CV, it will be assumed that f can be represented by a Gram-Charlier expansion. This is a common technique, especially when an explicit solution to the model is not available (Wiedemann et al., 1978; Razavi et al., 1978). Using only the first two moments in x to represent a nonreacting porous bed:

$$f = x_0 \exp[-(x_0 - M_1)^2/2M_2]/\sqrt{2\pi M_2}$$

Then the spatial moments are $M_1 = vt$, $M_2 = 2Dt$, while x_o = distance to end of bed, t time, v the flow rate, and D a dispersion coefficient. The distribution in x rather than t was chosen so that utilizing only the first two moments still results in f being a solution to the dispersion equation. In dimensionless form:

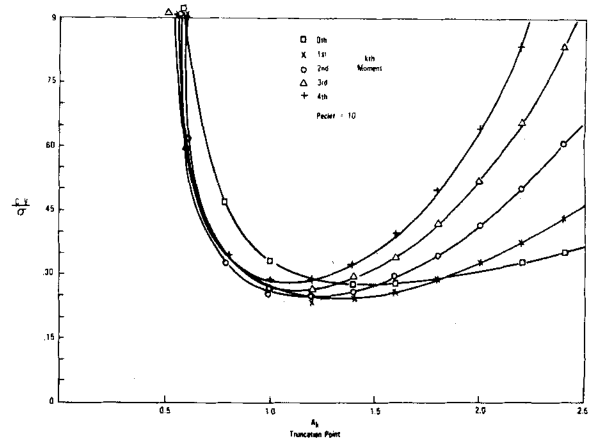

Figure 2. Influence of truncation point on the ratio of CV to σ, for a nonreacting porous bed, using unweighted moments. A_k is dimensionless.

$$f = \exp[-Pe(1 - T)^2/4T]/\sqrt{4\pi T/Pe} \qquad (14)$$

Where $Pe = vx_o/D$ is the Peclet number as used by Brenner (1962). It is the estimation of Pe or D for which the use of moment analysis is proposed. $T = vt/x_o$ is the number of void volumes eluted. Using Eq. 14 in Eq. 12, the ratio of CV to σ is shown in Figure 2 as a function of truncation point. It is readily apparent that the quality of estimation with ordinary moments is drastically affected by truncation point. Most interesting is that the minimum occurs slightly after the arrival of the peak. Also the minimum shifts to earlier times for higher moments. Anderssen and White (1971) used $A_k = 3.0$ for their comparisons. A fair comparison of ordinary moments with weighted moments must consider the effect of truncation point.

The information in Figure 2 for the second moment was then used in Eq. 13 to determine the influence of weighting factor. The CV was plotted as a function of s, using both the optimum truncation point and a value of 3.0 void volumes. Figure 3 clearly indicates that the main advantage of weighted moments disappears if a proper truncation point is used. Similar results are obtained for the other moments. While a slight minimum may appear in the weighted moments, it is not so great as to justify the extra work involved in using weighted moments.

To effectively use ordinary moments it becomes necessary to determine the truncation point for a particular data set. To evaluate the effect of model parameter on truncation point the Peclet number was varied. Figure 4 shows the result for the second mo-

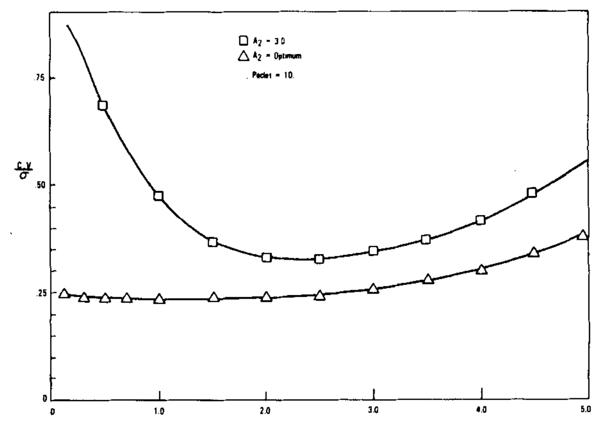

Figure 3. Influence of weighting factor, s on the ratio of CV to σ, for an optimal and suboptimal truncation point.

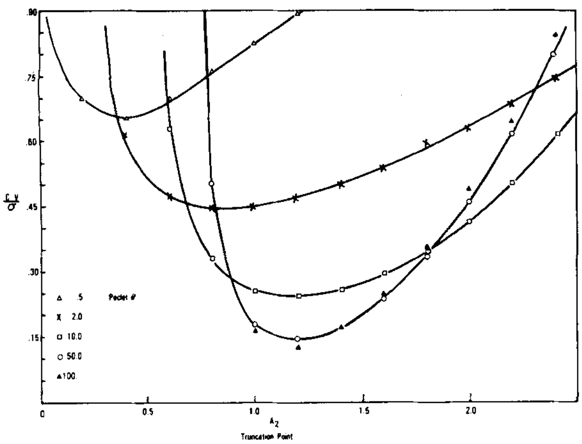

Figure 4. Influence of Peclet number on the graph of the ratio of *CV* to σ vs. truncation point.

ment truncation point. It is apparent that for small *Pe* not only does the truncation point shift to earlier times but also the accuracy of the estimator decreases. This relates to proper design of the experiment, a larger Peclet number can be obtained with a longer column. For many column studies *Pe* is at least 10 and a fixed truncation point (1.2) can be selected. Similar results hold for the other moment, Table 1.

The values given in Table 1 using Eq. 12 are a convenient reference point but are not always useful. When studying reacting solutes or when the void volume is unknown, a different procedure must be used. Equation 12 must be minimized with respect to the truncation point. Since the numerator is treated as a constant, this is equivalent to maximizing the denominator. Taking the derivative with respect to A_k and setting equal to zero gives:

$$\sum (df/dt) t_i^k (\Delta t)^{-k} [t_i / n\Delta t] = 0$$

where $t_i = i\Delta t$ and $\Delta t = A_k/n$ have been used. The term in brackets is dt/dA_k or i/n.

Multiplying by $(\Delta t)^{k+2}\, n$:

$$\sum t_i^{k+1} \frac{df}{dt} \Delta t = 0$$

The sum is approximated by an integral so that integration by parts can be used.

$$A_k^{k+1} f(A_k) - (k + 1) \int_0^{A_k} t^k f dt = 0$$

The integral is the truncated estimate of the *k*th moment. Replacing the integral by a sum:

$$A_k^{k+1} f(A_k) - (k + 1) \sum t^k f \Delta t = 0$$

or:

$$A_k^{k+1} f(A_k) - (k + 1) \mu_{kE} \mu_{0E} = 0 \qquad (15)$$

Equation 15 provides a convenient working relation. As the moments are calculated, the lefthand side of Eq. 15 can be checked for a change of sign. Table 1 compares the truncation points determined using Eqs. 15 and 12 respectively when $n = 50.0$ or 100.0 and Peclet equal to 10.0 or 100.0. A similar calculation for $n = 10$ showed a slight increase in A_k (about 0.1) using Eq. 12, while Eq. 15 only gave usable values for the first moment. For n large enough Eq. 15 is a useful relation to predict truncation point. Some care must be taken in using Eq. 15 to insure that a global maximum is obtained. Visual inspection of the data for multiple peaks will usually reveal such a case. In such cases Eq. 15 must be used to look for a second zero.

It is interesting to look at the case when truncation changes the number of data points collected. An expression analogous to Eq. 15 is obtained:

TABLE 1. OPTIMUM TRUNCATION POINTS

k	From Eq. 12	From Eq. 15
1	1.3	1.3
2	1.2	1.2
3	1.1	1.1
4	1.0	1.1

$$A_k^{k+1} f(A_k) - (k + 0.5) \mu_{kE} \mu_{0E} = 0$$

Calculations using Eq. 12 gave values similar to Table 1 but consistently larger by 0.1 when Peclet = 10. However, the above relation failed to detect a truncation point except for the first moment.

The analysis of the problem is complete except for the actual determination of the estimated moment. The correction factor (h_k) is a function of the true moments used in approximating the tail. Assume that the tail f is Gram-Charlier (Ord, 1972; Kotz and Johnson, 1971):

$$f(t) = \exp(-x^2/2)/\sqrt{2\pi}$$

where $x = (t - \mu_{1T})/\sigma_T$

$$\sigma_T^2 = \mu_{2T} - \mu_{1T}^2$$

The approximation can also be written for the first four moments. To illustrate the procedure only the first two moments will be estimated. Since f depends on both μ_{1T} and μ_{2T} then both h_1 and h_2 also depend on both μ_{1T} and μ_{2T}. As a result, two nonlinear equations in two unknowns are obtained. Rewriting Eq. 2 using Eq. 6:

$$\mu_{kT} = \mu_{kE} \mu_{0E} + \int_{A_k}^{\infty} f(t)\, t^k dt \qquad k = 1, 2 \qquad (16)$$

If the first four moments are to be estimated, four equations in four unknown are to be solved. In all cases the integration can be performed explicitly (Appendix).

DISCUSSION

A number of significant points result from the analysis presented here. Most noteworthy is the importance of truncation point on the value of statistical moments. A fair comparison of ordinary with weighted moments requires consideration of an optimal truncation point. Figure 3 indicates that weighted moments do not provide a better estimate. If improved estimates are to be obtained, greater attention needs to be paid to experimental design (Wolff et al., 1979, p. 106) and optimal truncation of data.

Equation 15 provides a tool for the determination of optimum truncation point from any system response. Further, Eq. 15 does not require the calculation of any quantities not already needed for moment estimation. Where Eq. 15 is not appropriate Eq. 12 can be used.

The analysis presented here does not delineate the best truncation scheme. A number of obvious failings exist. Foremost among the problems in the analysis is the assumption of a constant error in system response. If a solute concentration is measured spectrophotometrically with an instrument linear in transmittance, the precision of the concentration varies with the concentration (Kolthoff et al., 1969, p. 1978).

A second problem is the arbitrary choice of only a single truncation point. As mentioned earlier the leading portion of a response curve is also subject to errors. A reasonable approach would be to exclude an initial segment, thus requiring two truncation points.

Another drawback is the assumption that the response function can be expanded as a Gram-Charlier series in the region of the tail. It was chosen because of its prior use in moment analysis (Kubin, 1964; Grubner and Underhill, 1970; Razavi et al., 1978). It has the advantage of giving theoretically the correct moments (Ord, 1972; Johnson and Kotz, 1971). Further, it takes advantage of the fact that many signals appear gaussian. When higher (than second) moments are estimated and the signal has significant skew, other approximations may be needed. A generalization can be made that the truncation point is a function of the nature of the signal.

The last limitation is the assumption of fixed sampling frequency. In practice, truncation involves changing the number of data points. This could be expected to bias the results toward premature truncation. However, at this time it is not clear whether any of these problems constitute a serious limitation to the use of truncated moments. It is clear that the case for weighted moments needs to be reevaluated.

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NOTATION

A	= truncation point
D	= dispersion coefficient
f	= signal, uncorrupted by noise
g	= signal including noise
h	= correction constant applied to truncation moment
h'	= correction constant applied to weighted moment
i	= integer index of summation
k	= subscript to indicate order of moment applicable
M	= spatial moments for simple dispersion model
Pe	= Peclet number, VX_o/D
r	= random variable
s	= weighting factor and Laplace transform variable
t	= time
T	= number of pore volumes eluted from a column, dimensionless residence time
V	= interstitial velocity
X	= reduced variable = $(t - \mu_{1T})/\sigma_T$
x_o	= column length
ϵ	= magnitude of error in signal
μ_{kT}	= true kth momth of pure signal or population
μ_{kE}	= estimate of kth moment from sample data or of signal plus noise
μ_{kW}	= estimate of kth moment based on weighting procedure
σ	= standard deviation of random variable
σ_T	= standard deviation of second central moment

APPENDIX

Equation 16 is readily integrated for k equal to one and two to give:

$$\mu_{1T} = \mu_{1E}\mu_{0E} + \{\sigma\sqrt{2}\exp[-(A_1 - \mu_{1T})^2/2\sigma^2] + \mu_{1T}\sqrt{\pi}\,\mathrm{erfc}[(A_1 - \mu_{1T})/\sigma\sqrt{2}]\}4\sigma\sqrt{\pi}$$

and:

$$\mu_{2T} = \mu_{2E}\mu_{0E} + \{\sqrt{\pi}(\mu_{1T}{}^2 + \sigma^2)\mathrm{erfc}[(A_2 - \mu_1)/\sigma\sqrt{2}] + \sigma\sqrt{2}\,(\mu_{1T} + A_2)\exp[-(A_2 - \mu_{1T})^2/2\sigma^2]\}/4\sigma\sqrt{\pi}$$

where $\sigma^2 = \mu_{2T} - \mu_{1T}^2$.

This represents two nonlinear equations in μ_{1T} and μ_{2T}. Zero finding or nonlinear regression techniques can be used to find the values of μ_{1T} and μ_{2T} satisfying the above equations.

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