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ESTIMATION OF GAS-CHROMATOGRAPHIC PEAK PARAMETERS IN THE PRESENCE OF BASE-LINE NOISE

by

PATRICK C. KELLY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"ESTIMATION OF GAS-CHROMATOGRAPHIC PEAK PARAMETERS
IN THE PRESENCE OF BASE-LINE NOISE"

submitted by PATRICK C. KELLY in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The precision of a measurement of a gas-chromatographic peak depends on the intensity and character of the base-line noise, the shape and size of the peak, the prior information, and the method of estimation. An estimation method is presented that approaches the highest precision capable of any method used with a given gas-chromatographic system. Unlike most other estimation methods, the method has the ability to use all the information available to estimate the peak parameters, including prior information as well as information from the chromatogram.

The base-line noise of many detectors can be statistically characterized by a power-density spectrum. In such systems, the estimation of peak parameters is most easily carried out in the frequency domain on the Fourier transform of the chromatogram. Although any mathematical model that can completely describe a peak is suitable for estimation purposes, a peak model that uses cumulants, which are related to moments, has certain mathematical advantages.

Digitization of a continuous chromatogram involves the loss of some information, but the loss can be controlled by the choice of the sampling interval, the sampling time, and the quantization interval. Essentially all the information in a chromatogram about a peak lies in a section of the chromatogram, centered about the mean of the peak, which has a length equal to eight standard deviations of the peak plus the autocorrelation width of the base-line noise.

The estimation method was verified experimentally by analyzing mixtures of hydrocarbons on a simple isothermal gas chromatograph employing a thermal conductivity detector. Standard deviations of 0.003 relative for peak area and 0.02 index units for retention index were obtained. As shown by the analysis of computer-generated peaks, these standard deviations could be reduced to 0.0005 and 0.002 if the experimental conditions were carefully controlled. A peak model with seven adjustable parameters adequately fitted moderately sized peaks of aliphatic hydrocarbons, but was inadequate for large peaks and peaks of aromatic compounds.

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PRINCIPAL SYMBOLS

A	Peak area
$\underset{\sim}{\alpha}$	Set of parameter estimates
B, $B(\underset{\sim}{\alpha})$, $B_{\underset{\sim}{x}}(\underset{\sim}{x})$	Parameter bias
C_x	Power-density spectrum of noise
c_x, c_{x_q}, c_{q_x}	Autocovariance function of noise
$\underset{\sim}{D}$, $\underset{\sim}{D}'$	Parameter dispersion matrix and correlation matrix
D^r	r'th order derivative
d	Stepping factor
E	Expectation operator
$f(t)$	Peak function
$\underset{\sim}{g}$, g^*	Vector gradient of M with respect to $\underset{\sim}{\alpha}$
h	Impulse-response function of noise-whitening filter
$\underset{\sim}{I}$, $\underset{\sim}{I}_p$, $\underset{\sim}{I}_d$	Information matrix (Fisher's)
I_{Tx}	Retention index of compound x
i	Square root of -1
K_r	r'th order cumulant
M	Logarithm of posterior p.d.f.
p	Damping factor
$p_{\underset{\sim}{\alpha}}$, $p_{\underset{\sim}{\alpha}\mid\underset{\sim}{x}}$, $p_{\underset{\sim}{x}}$, etc.	Probability-density function (p.d.f.)
$\underset{\sim}{Q}$	Sum of weighted squared deviations
S, $S(\underset{\sim}{\alpha})$	Mean-square error of parameter estimates
s	Reduced frequency in units of $1/\Delta t$
T, T_I	Interval of time over which samples of chromatogram are taken

T_c	Autocorrelation width of base-line noise
t	Time (sec)
t_0	Peak retention time
Δt	Sampling interval (sec)
V, $\underset{\sim}{V}_p$, $\underset{\sim}{V}_x$, etc.	Parameter variance
W_c	Total power of base-line noise
$W(\nu)$	Spectral (smoothing) window
$\underset{\sim}{x}$, $\underset{\sim}{x}_s$, $\underset{\sim}{x}_a$, etc.	Chromatographic data
$y(z)$	Standardized peak-shape function
z	Reduced time in units of Δt
$\underset{\sim}{\alpha}$	True values of peak parameters
$\underset{\sim}{\Delta}$, $\underset{\sim}{\Delta}_g^*$, $\underset{\sim}{\Delta}_s^*$, etc.	Parameter correction vector
$\delta(t)$	Delta function
$\underset{\sim}{\xi}$	Mean-square error efficiency of an estimator
ζ	Reduced time in units of σ
η	Reduced frequency in units of $1/\sigma$
ν	Frequency (Hz)
$\xi(z)$	Jitter error in units of Δt
σ	Peak width (standard deviation)
σ_j, σ_d	Standard deviations of jitter error and integration dead-time error
τ	Lag, argument of autocovariance function
Π	Rectangle function
Ш	Sampling function

CHAPTER 1

THEORETICAL

In gas chromatography the ultimate concern is with the peak(s) that are representations of the distribution of solute molecules in a gas. Information about a peak is obtained from a chromatogram, which ordinarily is a voltage-time representation of the peak. The information in a chromatogram, however, is corrupted by random fluctuations, which we call base-line noise, that are not directly attributable to the peak. Base-line noise adversely influences the precision of measurement of peak parameters. This thesis is concerned with the application of statistical communication theory and estimation theory to the minimization of the effects of base-line noise on the estimation of peak parameters. This study is not concerned with the source of base-line noise, but only its effect. Moreover, this study is not concerned with distortions in the observed peak caused by the detector itself or any other determinate errors that can be corrected by calibration.

The theory of estimation, and the mathematical techniques used to describe peaks and noise that are presented here have been successfully applied in many fields outside of gas chromatography: economics, communications, radar, and seismology, among others. Since these fields are outside the normal range of contact of people working in gas chromatography, this chapter attempts to provide a general, though incomplete, discussion of these methods and a brief guide to the literature. Most of the general material is described more completely in References 1 to 4. The primary purpose of this chapter, however, is to describe and explain the techniques used in Chapter 2 for the analysis of peaks obtained from an isothermal gas-chromatographic system with a thermal conductivity detector. Undoubtedly these methods are applicable to many areas of chemistry outside of gas chromatography.

In order to distinguish a peak from extraneous noise or non-peak signal components, the shape of the peak must be defined at least as accurately as the precision of the measurements warrant. For example, to define a peak as something that has area, retention time, and width is not enough; noise waveforms may have these attributes also. Since a general closed mathematical definition (or model) for the shape of a peak has not yet been developed, a model consisting of a series of terms of decreasing importance should be fruitful provided the number of significant parameters required is not impractically large. Series representations of variously shaped peaks can be developed from several basis functions: Gaussian, lognormal, Poisson, Beta, or Gamma (5). The Gram-Charlier type A series, based on the Gaussian function, has received the most attention in the literature on gas chromatography (6-9), and a special form of it (Edgeworth's form) has been chosen for study here. The third and higher coefficients of Edgeworth's form of the Gram-Charlier type A series, defined below, are called cumulants. Cumulants have been widely used for the characterization of statistical distributions. They are related to moments but they are mathematically easier to deal with and we believe they are more fundamental than moments. Although cumulants do not have direct physical significance in the same way that peak area is related to quantity of a solute, they have theoretical significance (6-9) and may provide qualitative information about a solute (9,10).

For the purposes of this study it is assumed that the essential characteristics of base-line noise can be described by the statistical distribution of ordinate values of the points on a base line. Specifically, base-line noise is assumed to be a stationary random process with a normal or Gaussian probability-density function. Since the base-line noise of most gas-chromatographic detectors results from several independent sources, the assumption of a normal probability-density function should be accurate*. When the statistical behavior of noise does not change with time, the noise is said to be stationary. The assumption that base-line noise is stationary during the elution of a peak should hold when the experimental parameters that affect the base line are not changing with time, as in isothermal gas chromatography; but it may not hold in programmed temperature gas chromatography if the intensity of the base-line noise increases as the column temperature increases. Noise with an intensity or variance that increases with increasing amplitude of the signal (as during the elution of a peak) is nonstationary and is usually difficult to treat in the presence of stationary noise. Noise that depends on the amplitude of the signal may constitute a major part of the noise of ionization detectors and detectors that measure the radioactivity of a sample, but should be negligible for thermal conductivity detectors.

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*The central-limit theorem states that subject to certain very general conditions, the sum of random variables becomes more and more normal as the number of independent random variables increases (11).

The fluctuations in measurements of peak parameters are not entirely due to base-line noise. For example, small random variations in column temperature and column inlet pressure can cause fluctuations in peak retention times and shapes without affecting the base line. In concentrating on the effects of base-line noise the approach taken here is complementary to that of Goedert and Guiochon (12). These authors have studied the effects of random variations in the experimental conditions, which are classified here as non-base-line noise, on the measurement of peak area and peak height. The total variance of peak-parameter measurements is a combination of the variance due to non-base-line noise and that due to base-line noise. The variance due to base-line noise alone can be estimated from the statistical characteristics of a section of base line, and this estimated variance used to separate the contributions of the two types of noise to the total observed variance of the parameters.

Peak retention time is commonly measured from the peak maximum, which is only a single point from the peak profile. Points on the sides of the peak, however, also contain information about retention time. If the entire peak is considered in the calculation of peak parameters, a decrease in the variance of the parameter estimates should be attainable. Noise always adds variance to a parameter estimate, in an amount that depends in part on the method of estimation or measurement. The estimation method developed in this thesis is optimal or nearly optimal in the sense that the variance of the parameter estimates approaches the ultimate minimum variance. This is achieved by using all of the information in the chromatogram, not merely the information obtainable from a few points such as the peak maximum and the peak width at the base line.

The computation required in the estimation method is sufficiently complex so that an offline digital computer is necessary. Using a computer means that the data must be digitized. Some of the information contained in a continuous signal is invariably lost on digitization. Nevertheless, interval-area samples taken at constant intervals of time (13) contain almost all the information in a chromatogram provided the sampling interval is less than a certain minimum value. Also, the information lost from quantization is negligible if the quantization interval is small relative to the intensity of base-line noise.

The notational conventions of Bracewell (1) have been followed whenever possible. One of these is that the Fourier transform of a function is capitalized. Others are the use of the convolution symbol $*$, and the letters Ш and П from the Russian alphabet, which have a pictorial similarity to the functions they represent. Three different time and frequency scales are used. Time in seconds is represented by the symbol t, and frequency in the corresponding scale (hertz) by ν. Time in peak-width units and in sampling-interval units is represented by the symbols ζ and z, and frequency in the corresponding scales is represented by η and s.

PEAK MODELS

Peak shapes can be most easily compared when peaks are reduced to unit area and unit width, and are centered at the origin. Defining the area, A , retention time, t_0 , and width, σ , as follows:

$$A = \int_{-\infty}^{\infty} f(t) \, d \, t \tag{1}$$

$$t_0 = \frac{1}{A} \int_{-\infty}^{\infty} t \, f(t) \, d \, t \tag{2}$$

$$\sigma^2 = \frac{1}{A} \int_{-\infty}^{\infty} (t-t_0)^2 \, f(t-t_0) \, d \, t \tag{3}$$

a dimensionless peak-shape function, $y(\zeta)$, can be derived from a peak on a noise-free chromatogram, $f(t)$, through the formula

$$y(\zeta) = f(t)\sigma/A \tag{4}$$

where ζ is dimensionless reduced time:

$$\zeta = (t-t_0)/\sigma \tag{5}$$

The above definitions of the retention time and width of a peak are the mean and the standard deviation. These are different from the more common definitions as the time of the maximum and the width at the base or a certain fraction of the height. The peak models discussed below are simplified when the above definition of a peak-shape function is used, and this is the primary reason why we define retention time and width as the mean and standard deviation.

With a noise model applicable to most detectors (described in the next section) the parameter estimates are best calculated on the Fourier transform of the chromatogram. Moreover, the mathematical expression for the peak-shape model defined below is simpler as a function of frequency than as a function of time. Even though the Fourier transform operator may be complicated, the advances in computer algorithms for numerical Fourier transforms make the use of the operator of little concern (14). The Fourier transform of a standardized peak shape function is

$$Y(\eta) = \int_{-\infty}^{\infty} \exp[-i2\pi\eta\zeta]\, y(\zeta)\, d\,\zeta \tag{6}$$

where i is the square root of -1, and η is frequency in a dimensionless standardized scale.

Parameters

The three parameters area, A, retention time, t_0, and peak width, σ, along with a peak-shape function, completely and uniquely describe a peak. Knowing the values of the three parameters is enough to distinguish a particular peak from any other peak only when the peak-shape function is previously known. Because of the complexity of the gas-chromatographic process and the difficulty of controlling experimental conditions, accurate prior knowledge of the peak shape function is usually not available. Therefore, in the mathematical model of a peak, parameters in addition to A, t_0, and σ are required to describe the peak-shape function. For estimation purposes, any set of parameters that can completely and uniquely describe the peak-shape function will serve. It is not necessary that the parameters have an easily interpreted physical meaning, especially if only A, t_0, and σ are required for subsequent calculations, but it is desirable. Three possible sets of parameters of a peak-shape function are samples from a previous chromatogram (15), moments (8), and cumulants.

The first, second, third, ... moments of a peak-shape function may be defined as derivatives of the Fourier transform of the peak-shape function:

$$\mu_r = (-i2\pi)^{-r} \mathrm{D}^r [Y(\eta)]_{\eta=0} \tag{7}$$

where D^r is the differential operator, $\partial^r/\partial\eta^r$, and r is equal to 1,2,3,... . In contrast, the cumulants of a peak-shape function are defined as derivatives of the logarithm of the Fourier transform of the peak-shape function:

$$K_r = (-i2\pi)^{-r} \mathrm{D}^r [\ln Y(\eta)]_{\eta=0} \tag{8}$$

The moments and cumulants defined by Equations 7 and 8 are ordinary moments and cumulants of the peak-shape function defined by Equation 4. These dimensionless numbers are referred to here as the standardized moments and cumulants of a peak. The first three standardized cumulants are equal to the first three standardized moments. But, a cumulant of a higher order, r, is a function of the lower-order moments from 1 to r. Tables of the algebraic formulas relating moments to cumulants are given in Kendall and Stuart (16). The first cumulant of a standardized peak-shape function is equal to zero, and the second is equal to one. The third and the fourth standardized cumulants are sometimes called skew and excess.

An infinite number of parameters in any one of the above sets will completely specify any physically possible peak-shape function. But an infinite set of parameters is unnecessary because in the presence of noise the peak-shape function can never be specified exactly. Therefore, if the parameters are arranged in order of decreasing significance (increasing statistical variance or decreasing information content), only the lower-order parameters up to the number that can describe the peak-shape function to a required level of significance need to be estimated. The parameters that are estimated are called the adjustable parameters, and the remaining parameters in the infinite set, which are given an *a priori* value, are called the nonadjustable parameters.

The estimation of a large number of parameters is undesirable as well as unnecessary because, as the number of parameters to be estimated increases, the peak-shape function becomes increasingly general and thus able to fit a wider range of differently shaped peaks. A model that is too general is likely to include nonpeak components such as noise or interfering peaks along with the true peak in a chromatogram. One way of introducing into the peak model the prior information needed to distinguish a true peak from noise is by limiting the number of adjustable parameters. When there is little prior information about the model required for a particular peak, a compromise must be made; the number of adjustable parameters should be enough so that the peak model can fit the peak, but not so many as to fit any nonpeak components that may be present.

In this study cumulants are chosen to be the parameters for peak-shape functions. Since moments can be calculated from cumulants, cumulants have the same theoretical interpretation as moments, but they are easier to manipulate [they are additive under convolution, (6)]. Simplicity is the only objective reason why we choose cumulants over moments. The model incorporating cumulants as parameters is chosen with the prior information that in simple ideal chromatographic systems the peak-shape function approaches the Gaussian function.

Peak Shapes

A peak-shape function can be represented by a series of terms that are functions of the cumulants of the peak-shape function by use of the general Charlier derivative-series method (5). Given the Fourier transform of some basis function, $\Phi(\eta)$, the series expansion of the Fourier transform of a peak-shape function, $Y(\eta)$, is

$$Y(\eta) = \Phi(\eta)\ \exp[\sum_{r=1}^{\infty} (K_r - \gamma_r)(-i2\pi\eta)^r/r!] \tag{9}$$

where K_r and γ_r are the r'th cumulants of the peak-shape function and the basis function. The basis function should be chosen so that only the first few cumulants of the peaks being investigated need be estimated. For example, the Poisson function might be used for moderately tailed peaks. When a Gaussian basis-function is used, Equation 9 becomes

$$Y(\eta) = \exp\left[\sum_{r=1}^{\infty} K_r(-i2\pi\eta)^r/r!\right] \tag{10}$$

because all the cumulants of a Gaussian function are zero, except for the second, which is equal to one. An equivalent form of Equation 10 can be obtained by expansion of the exponential and collection of powers of η :

$$Y(\eta) = \left[1+\sum_{r=3}^{\infty} U_r(-i2\pi\eta)^r/r!\right]\exp[(-i2\pi\eta)^2/2] \tag{11}$$

where U_3 and U_5 are equal to K_4 and K_5 , and $U_6 = K_6 + 10K_3^2$, $U_7 = K_7 + 35K_4K_3$, $U_8 = K_8 + 56K_5K_3 + 35K_4^2$, ... Equation 11 defines the Gram-Charlier type A series (GCA series), and Equation 10 defines Edgeworth's form of the GCA series (17). The most frequently used series expansion of a chromatographic peak (6-9) is the time domain version of Equation 11:

$$y(\zeta) = \left[1+\sum_{r=3}^{\infty} U_r h_r(\zeta)\right] e^{-\zeta^2/2} \tag{12}$$

where $h_r(\zeta)$ is the Tchebycheff-Hermite polynomial:

$$h_r(\zeta) = e^{\zeta^2/2} (-D)^r e^{-\zeta^2/2} \tag{13}$$

Equation 9 , carried to the sixth cumulant, is used as a model in Chapter 2.

Although the GCA series and the Edgeworth series are formally equivalent, terminating them after a finite number of terms involves different prior information about the nonadjustable parameters. Consequently, the effects of the termination on the precision and accuracy of the adjustable parameters may be different. The coefficients of the sixth and higher terms of the GCA series are functions of lower-order cumulants, whereas the coefficients of all the terms of Edgeworth's series are the cumulants themselves. Since the high-order coefficients of the GCA series contain information about lower order cumulants, neglecting a high-order coefficient would involve the loss of some information about the lower-order cumulants. For example, suppose the third cumulant of a peak-shape function were equal to one and the cumulants of higher order were equal to zero. This peak-shape function is a possible representation of an actual peak, but since the peak would be partly negative, it would be unusual. The series representation of the peak in Edgeworth's form could be terminated after the term involving the third cumulant. On the other hand, the representation of the same peak in GCA form would have to be continued at least to the sixth term because from the contribution of the third cumulant, the sixth term would be equal to ten, a value that might be significant even if the sixth cumulant were insignificant. For simplification of the effects of termination on parameter estimation, therefore, any one term of a series model of a peak-shape function should depend on only one parameter.

The coefficients of the GCA series being functions of more than one cumulant does not mean that this series should not be used for the representation of peak-shape functions. For certain peak shapes in certain types of noise, the coefficients of the GCA series, U_r, could conceivably approach insignificance faster than cumulants and would therefore be preferred to cumulants.

A NOISE MODEL

Errors in the estimates of peak parameters due to base-line noise are caused by the unpredictability of the noise. But, because all physical signals are bandlimited (18), base-line noise is never completely unpredictable. Given a point on a base line, a second point occurring some time later will likely be within a range of the first point that depends on the intensity and character of the noise and the separation of the points. By giving the most weight to points on a base line nearest a peak, a chromatographer uses this relation, sometimes unconsciously, when he examines the base line under the peak. When noise is stationary, so that its average properties do not change with time, and when the mean of the noise is zero, the randomness as well as the predictability, or nonrandomness, of noise is characterized by the autocovariance function, $c_x(\tau)$, which is the average of the product of the ordinate values, $x(t)$, of two points on a base line taken τ units of time apart (19).

$$c_x(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_{-T/2}^{T/2} x(t)\, x(t+\tau)\, d\, t \tag{14}$$

where τ is called the lag. Sometimes the terms autocovariance and autocorrelation are interchanged, but we reserve the term autocorrelation for a normalized autocovariance (see Equation 49). The autocovariance at zero lag is the variance of the noise; as the lag becomes large, the autocovariance should approach zero, indicating that points far apart are independent (covariance independent).

Power-Density Spectrum

The Fourier transform of an autocovariance function is the power-density spectrum*, $C_x(\nu)$. If x and t have dimensions of volts and seconds, C_x will have dimensions of volt squared per hertz. The power-density spectrum of noise is the variance density per unit frequency, hence the area of a power-density spectrum, which is the integral of the variance density over all frequencies, is equal to the variance or power of the noise, $c_x(0)$. White noise is noise that has a constant or flat power-density spectrum over a wide frequency range. The autocovariance function of white noise consists of a spike-like function which rapidly approaches zero on both sides of the origin.

The method for estimation of peak parameters described later requires the use of the probability-density function (p.d.f.) of the points on a base line. If the p.d.f. of the noise is normal, as assumed here, then the noise is completely characterized by its power-density spectrum. In the limit of continuous sampling so that integrals can replace summations, the joint p.d.f. of a set of points, $\underset{\sim}{x}$, on a section of base line is

$$p_{\underset{\sim}{x}}(\underset{\sim}{x}) = b \exp[-1/2 \int_{-\infty}^{\infty} \frac{|X(\nu)|^2}{C_x(\nu)} d\,\nu] \qquad (15)$$

where $X(\nu)$ is the Fourier transform of the section of base line being

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*A power-density spectrum may also be called a power spectrum or a spectral density as in Reference 3.

studied. The existence of the integral in Equation 15 requires that the power-density spectrum, $C_x(\nu)$, be greater than zero for all frequencies. This causes no difficulty in practice when the data are quantized because quantization introduces white noise with a power-density spectrum greater than zero over the range of frequency being considered. The constant, b , in Equation 15 is independent of the particular section of base line being studied; therefore its evaluation is unnecessary.

A point on a base line in the time domain is dependent on all the other points for which the autocovariance is greater than zero. The dependence may extend over a large number of points and over a wide period of time. Calculations involving stationary normal noise are considerably simplified in the frequency domain because the Fourier transform of highly interdependent base-line noise results in a set of effectively independent points, the variance of each point, $X(\nu)$, being equal to $C_x(\nu)$. If the points on the base-line were effectively independent of each other, that is, if the noise were white over the frequency range of interest, of course, there would be no need to do the calculations in the frequency domain.

The probability-density function of a section of base line, $p_{\underset{\sim}{x}}(\underset{\sim}{x})$, is used only formally in the estimation calculations; its actual value is not determined. Nevertheless, the value of $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ for a particular section of base line is proportional to the probability that the base line is caused by noise alone. For example, if the value of $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ is unusually low, the chromatogram probably contains a component that is not noise, possibly a peak. If a peak is subtracted from the base line, the value of $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ might become reasonably large, and the increase may indicate that the original chromatogram contained a peak similar to the one that was subtracted.

Power-Density Spectrum Estimation

The calculation of the integral in Equation 15 requires prior knowledge of the power-density spectrum. The definition of the autocovariance function (Equation 14) suggests that the power-density spectrum may be estimated from the Fourier transform of a section of a chromatogram that does not contain a peak (20) :

$$C_x(\nu) \simeq |X(\nu)|^2/T \quad , \qquad (16)$$

where T is the interval of time over which data is taken. The section of base line used for the estimate of the power-density spectrum could be taken some time before or after the peak being examined; all that is required is that the noise be stationary enough so that the noise near the peak will not differ greatly from the noise used to estimate the power-density spectrum. The variance of the spectral-density estimate, $C_x(\nu)$ in Equation 16, is equal to $C_x(\nu)^2$ and is independent of the amount of data used. The precision can be improved by averaging the spectrum over a small range of frequency. The averaging process resulting in $C'_x(\nu)$, called smoothing or convolution, is described by the equation:

$$C'_x(\nu) = \int_{-\infty}^{\infty} C_x(u)\, W(\nu-u)\, d\,u \qquad (17)$$

where $W(\nu)$ is a weighting function called a spectral window (20).

The convolution operation is conveniently represented by the symbol * . With this symbol, Equation 16 can be written

$$C'_x(\nu) = C_x(\nu) * W(\nu) \tag{18}$$

The variance of the smoothed spectral-density estimate, $C'_x(\nu)$, is

$$\text{variance of } C'_x(\nu) \simeq \frac{1}{T} C'_x(\nu)^2 \int_{-\infty}^{\infty} W(u)^2 \, d\, u \tag{19}$$

After convolution with $W(\nu)$, the variance of the power-density spectrum decreases with increasing amounts of data and can be made as small as desired. But, the increase in precision obtained by smoothing is at the expense of accuracy; the estimate will be biased by an amount proportional to the curvature of $C_x(\nu)$ and to the width of the spectral window. The bias can be decreased by filtering the data to give a nearly white spectrum before smoothing (21). We apply this filter to the data in the time domain to minimize end effects as discussed later in the section on sampling. In the time domain, filtering resulting in $x'(t)$ is represented by convolution

$$x'(t) = x(t) * h(t) \tag{20}$$

where $h(t)$ is the impulse-response function of the filter. Since the mean of a base line in gas chromatography is arbitrary, it has a high variance indicating that the power-density spectrum of base-line noise will be extremely high at zero frequency. To whiten this intense noise at zero frequency, the filter $h(t)$ should have zero area (Figure 1, II). The digital filter, [-1,2,-1], gives an approximately flat spectrum for the base-line noise of a thermal conductivity detector (see Chapter 2). The compromise between bias and precision that governs the choice of a spectral window is not critical when the spectrum is white. We have used a simple digital spectral window, [¼,½,¼].

Convolution in the time domain (Equation 20) corresponds to multiplication in the frequency domain; therefore, the power-density spectrum can be regained from the smoothed spectrum by multiplying the smoothed spectrum by the inverse of the absolute square of the Fourier transform of the impulse-response function of the filter. At zero frequency both the spectrum of the filtered data and the filter-transfer function, $H(0)$, are zero leaving the power-density spectrum, $C_x(0)$, undefined. Since $X(0)$, the mean of the base-line noise, has a high variance, $C_x(0)$ is usually extremely large; therefore, its reciprocal, needed in Equation 15, is defined to be zero.

Figure 1 shows the steps involved in the estimation of a power-density spectrum. First, filter the data in the time domain using a filter that will give a nearly white spectrum (Figure 1, I to III). Fourier transform and calculate the power-density spectrum using Equation 16. Smooth according to Equation 18 (Figure 1, IV to VI), and then multiply by the inverse of the square of the transfer function of the filter (Figure 1, VII and VIII). These operations are summarized by

$$C_x(\nu) = \frac{1}{T} \left[|X'(\nu)|^2 * W(\nu) \right] |H(\nu)|^{-2} \qquad (21)$$

FIGURE 1

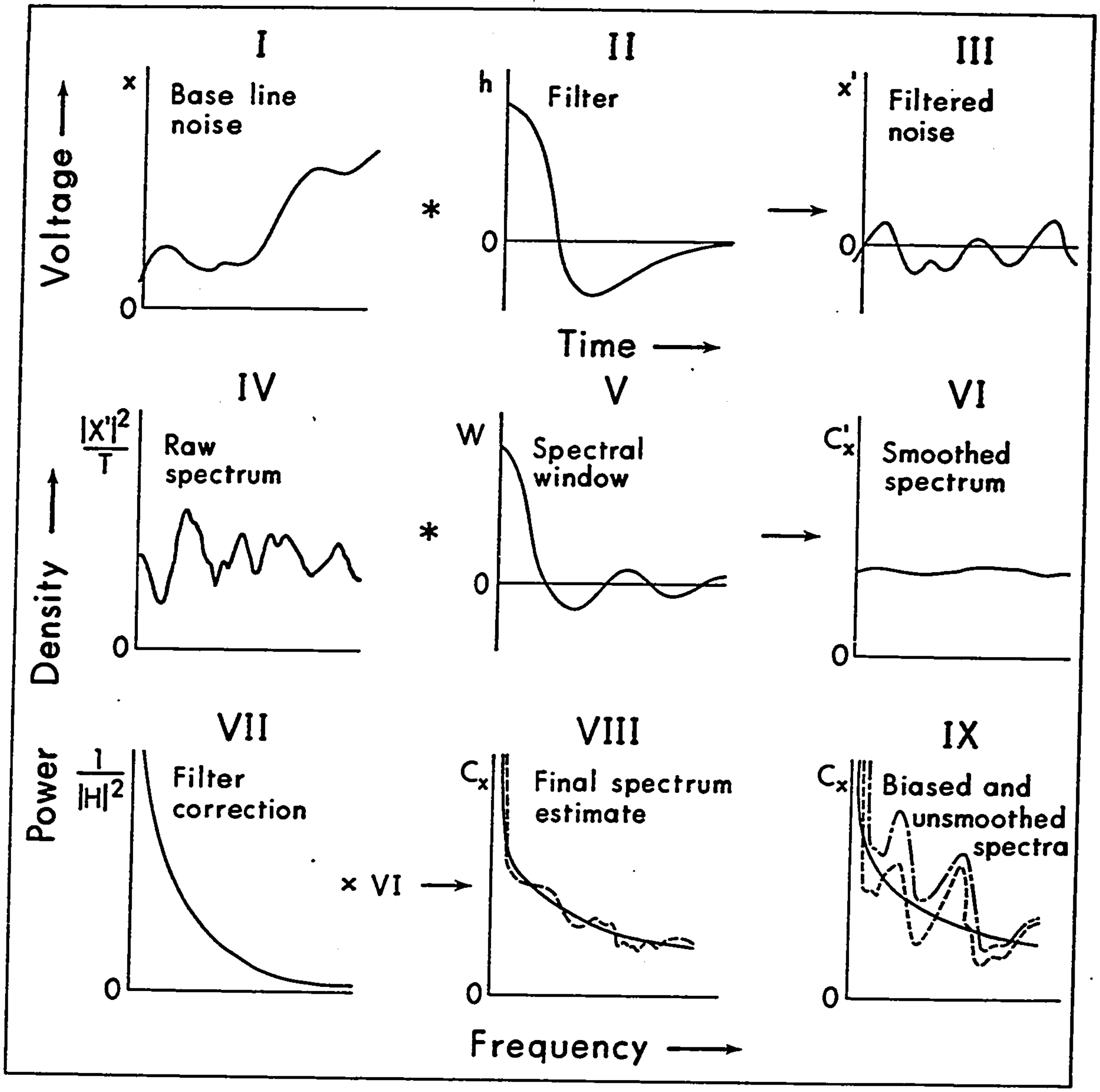
I
II
III
Voltage ⟶
x
Base line noise
0
h
Filter
0
*
→
x'
Filtered noise
0
Time ⟶
IV
V
VI
Density ⟶
|X'|²/T
Raw spectrum
0
*
W
Spectral window
0
→
C'x
Smoothed spectrum
0
VII
VIII
IX
Power
1/|H|²
Filter correction
0
× VI ⟶
Cx
Final spectrum estimate
0
Cx
Biased and unsmoothed spectra
0
Frequency ⟶

Figure 1. Estimation of power-density spectrum (schematic). I, section of base-line noise; II, impulse-response function of a whitening filter; III, filtered data resulting from the convolution of I and II; IV, power-density spectrum of the filtered data; V, a spectral window; VI, smoothed power-density spectrum obtained by convolving V with IV; VII, reciprocal of the absolute square of the impulse-response function of the filter in II. The dashed line in VIII is the final power-density spectrum of the base-line noise obtained by multiplying VI by VII. The solid curve in VIII and IX is the true power-density spectrum obtained as T approaches infinity. The upper-dashed curve in IX is the unsmoothed spectrum resulting from the multiplication of IV and VII. The lower-dashed curve in IX is the biased spectrum obtained by smoothing without whitening. Since all of the curves except I and III are symmetric about the ordinate axis, the negative parts of the curves have been omitted.

with

$$C_x(0)^{-1} = 0$$

Two useful, simple characterizations of noise are the power or variance and the autocorrelation width. The power is defined by the equation

$$W_c = \int_{-\infty}^{\infty} C_x(\nu)\, d\,\nu \tag{22}$$

and the autocorrelation width by

$$T_c = C_x(0)/W_c \tag{23}$$

One half the autocorrelation width is an indication of the separation in time between independent or uncorrelated points in the noise. For the calculation of W_c and T_c in practice, it can be assumed that $C_x(0) \simeq C_x(1/T)$.

DIGITIZATION

Converting an analog signal such as the voltage from a detector into a form that can be used by a digital computer involves two distinct processes. First, a finite number of samples are taken; second, the samples are quantized. The resulting digitized signal is a finite series of numbers each having a finite number of significant digits. The effect of these processes on the precision and accuracy of sampled data is described in detail below.

Sampling

The application of the theory presented in (1) is discussed in the following section. The information contained in a chromatogram and the information contained in a set of samples of the chromatogram can be compared when the set of samples is treated as a function of continuous time rather than discrete time. The delta function, $\delta(t)$, which is a generalized function and not a function in the usual sense, but can be treated as if it were, represents a single sample. The delta function can be defined as the limit of a Gaussian function as the standard deviation approaches zero; although it is infinitely high and infinitesimally narrow, it has unit area. Figure 2, I shows a delta function at time t' as an arrow of unit height. Multiplying a data function, $x(t)$, by $\delta(t-t')$ results in a function defined for all time that represents a sample of the data at time t' (Figure 2, II). The operation of taking samples of a function, $x'(t)$, at constant intervals of time, Δt seconds apart, is described by

$$x_s(z) = \sum_{n=-\infty}^{\infty} \delta(z-n)x(z) \qquad (24)$$

FIGURE 2

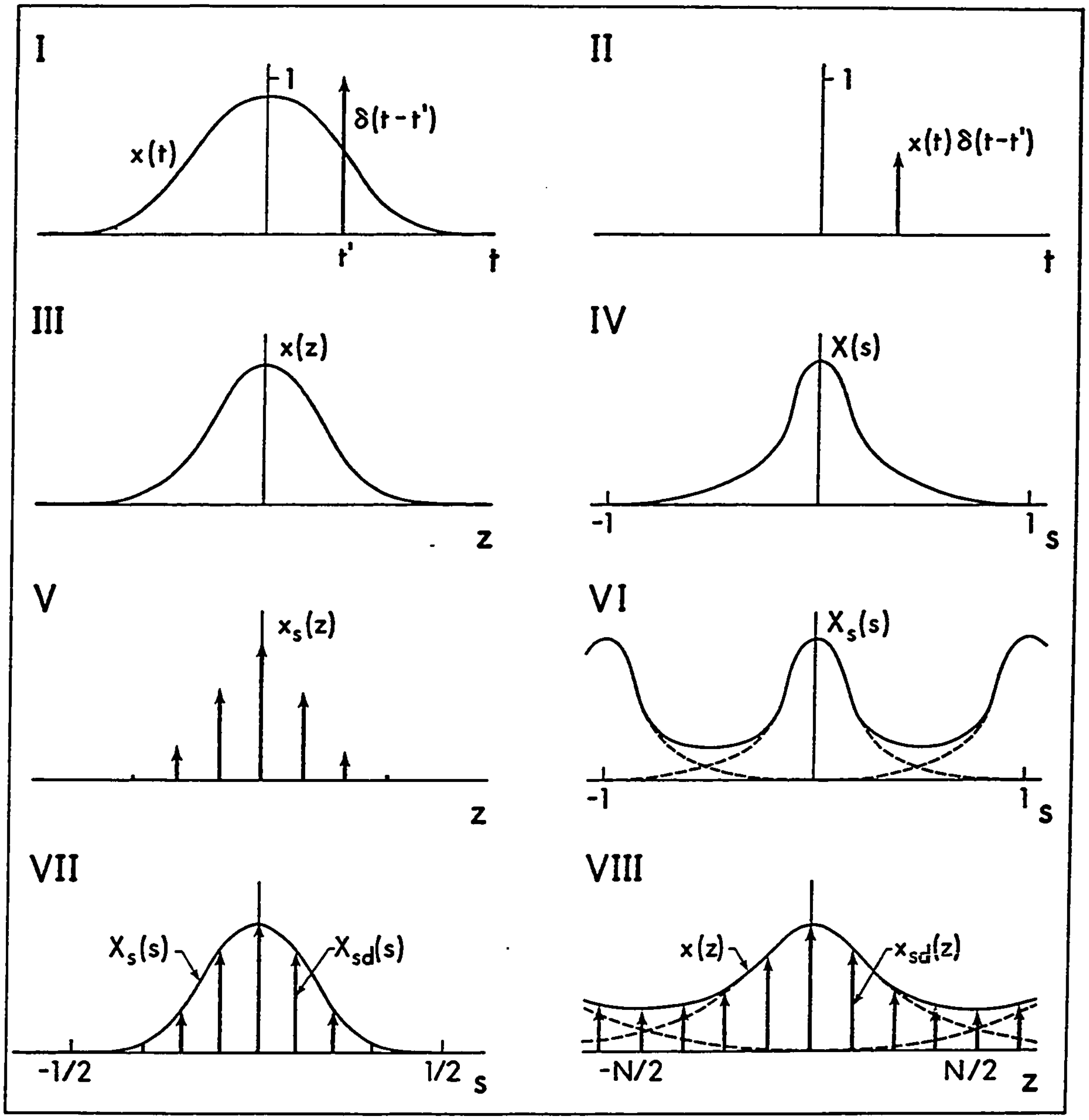
I
1
δ(t - t')
x(t)
t'
t
II
1
x(t) δ(t-t')
t
III
x(z)
z
IV
X(s)
-1
1
s
V
$x_s(z)$
z
VI
$X_s(s)$
-1
1
s
VII
$X_s(s)$
$X_{sd}(s)$
-1/2
1/2
s
VIII
x(z)
$x_{sd}(z)$
-N/2
N/2
z

Figure 2. Sampling of a chromatogram in the time and frequency domain (schematic). I, a continuous chromatogram and a delta function; II, sample of the chromatogram resulting from the multiplication of the continuous chromatogram by the delta function; III, chromatogram in reduced time; IV, Fourier transform of III; V, constant interval samples of III; VI, Fourier transform of sampled chromatogram, the dashed lines show the separate replicas of IV; VII, the Fourier transform of a sampled chromatogram that has less intense high frequency components than VI so that no overlap occurs, $X_{sd}(s)$ is the frequency sampled form of $X_s(s)$; VIII, x_{sd} is the inverse Fourier transform of the frequency sampled data X_{sd} in VII. In VIII the dashed lines are the separate replicas of the original continuous-data function in the time domain.

where

$$x(z) = x'(t)/\Delta t$$

and z is reduced time equal to $t/\Delta t$. The result of sampling the data, $x_s(z)$, is obtained by multiplication of two functions: the original data function and another consisting of a series of delta functions spaced one unit of reduced time apart. Representing the series of delta functions (the sampling function) by the symbol $Ш(z)$ in Equation 24 gives

$$x_s(z) = x(z)\, Ш(z) \tag{25}$$

where

$$Ш(z) = \sum_{n=-\infty}^{\infty} \delta(z-n) \tag{26}$$

In the frequency domain,

$$X_s(s) = X(s) * Ш(s) \tag{27}$$

where s is reduced frequency equal to $\nu\Delta t$, and $X(s)$ is the Fourier transform of the continuous data (Figure 2, IV).

Figure 2, VI shows the effect of convolution by $Ш(s)$ in the frequency domain; replicas of the Fourier transform of the original data function, $X(s)$ (Figure 2, IV), are formed at intervals of one unit of frequency. These replicas will overlap (Figure 2, VI) and interfere unless $X(s)$ is equal to zero for all frequencies greater than or equal to 1/2. If there is no overlap, $X_s(s)$ will be identical to $X(s)$ over the region where $|s|$ is less than 1/2 and the inverse Fourier transform of the central replicate will regenerate the original continuous curve. Therefore, provided the sampling interval, Δt , is small enough so that

$$X(s) = 0 \quad \text{when} \quad |s| \geq 1/2 \tag{28}$$

the samples will contain all the information in the data. In absolute units the critical sampling frequency $1/(2\Delta t)$ Hz is called the Nyquist frequency.

The Fourier transform of a function sampled in the time domain is continuous (Equation 27), whereas the Fourier transform algorithm used in a digital computer is discrete; that is, the Fourier transform is calculated at frequencies that are multiples of $1/N$ where N is the number of samples taken. ($N\Delta t$ is equal to T , the interval over which the data are sampled in the time domain.) When the fast Fourier transform algorithm (14) is used, the number of samples must usually be a power of 2 , though the number of samples available may not be an exact power of 2 . If M is a power of 2 and the number of samples available, N , is less than M , then the last $M - N$ samples can be given the value zero, and the Fourier transform will be calculated at frequencies that are multiples of $1/M$ rather than $1/N$. The case of N equal to M is discussed below, although the theory for the case of N less than M is different and more complicated, the practical consequence of sampling the Fourier transform is the same as that for N equal to M . A discrete Fourier transform of a function is equivalent to taking constant-interval samples, in the frequency domain, of the continuous Fourier transform of the function. The sampling operation in the frequency domain can be represented symbolically as multiplication by a sampling function, $N\,\text{Ш}(Ns)$ (Figure 2, VII):

$$X_{sd}(s) = X_s(s)\,N\,\text{Ш}(Ns) \tag{29}$$

The time-domain version of frequency-sampled data is the inverse Fourier transform of Equation 29:

$$X_{sd}(z) = x_s(z) * \text{Ш}(z/N) \tag{30}$$

When the sampling theory used for sampling in the time domain is applied to sampling in the frequency domain, samples of $X_s(s)$ at intervals of $1/N$ are equivalent to the continuous function, $X_s(s)$, provided the section of base line taken is large enough so that

$$x_s(z) = 0 \quad \text{when} \quad |z| \geq N/2 \tag{31}$$

Figure 2, VIII shows the overlap error resulting from an attempt to regenerate a data function when N (or T) is too small. Since a Gaussian function approaches zero only at infinity in the time domain, taking the discrete Fourier transform of a Gaussian peak will introduce an error the magnitude of which will increase as the width of the peak (σ) increases relative to the period of time over which the data are taken (T). From a table of ordinate values of a Gaussian function, the maximum error relative to the peak maximum is less than 10^{-6} when T is greater than 9.8σ. Also, since the Fourier transform of a Gaussian function is itself a Gaussian function [with a standard deviation equal to $1/(2\pi\sigma)$] and is never equal to zero for any frequency, taking samples of a Gaussian peak in the time domain will introduce an error the magnitude of which will increase as the peak width decreases relative to the sampling interval (Δt). The maximum relative error is less than 10^{-6} when the peak width is greater than $1.7\Delta t$. The combination of these time- and frequency-domain restrictions means that at least seventeen (1.7×9.8) samples of constant interval are required to specify a Gaussian peak with a relative accuracy better than 10^{-6}. The requirements of Δt and T for a peak in the presence of base-line noise are discussed below in the section on estimation theory.

The condition that a base line be zero at the ends of the section of base line over which samples are taken (Equation 31) is seldom met in practice because the variable zero control of the detector is set so that the output signal will never be negative or zero throughout the chromatographic run. Also, trends in the base line, or noise with a period greater than $T/2$, will cause at least one end of the sampled section to be significantly different from zero. Although extra parameters for the mean and the trend in a base line could be included in the peak model, it is easier to filter the data to remove these components before Fourier transforming. Including a parameter for the mean is equivalent to filtering the data with a function that has zero area, but a filter that removes any component other than the mean may destroy some of the information in the data about the peak being measured. We have found that the noise-whitening filter used in the estimation of power-density spectra [$h(t)$ in

Equation 20] is suitable for this purpose.

Interval-Area Sampling

Interval-area samples (13) are defined by

$$x_a(z) = [\int_{z-\frac{1}{2}}^{z+\frac{1}{2}} x(t)\ d\ t]\ Ш(z) \tag{32}$$

Equation 32 can be written

$$x_a(z) = [x(z) * \Pi(z)]\ Ш(z) \tag{33}$$

where integration is represented as convolution by a rectangle function, $\Pi\ (z)$, where

$$\Pi(z) = 1 \quad \text{when} \quad |z| < 1/2$$

and

$$\Pi(z) = 0 \quad \text{when} \quad |z| > 1/2 \tag{34}$$

In practice a small dead time occurs between interval-area samples while the integrator is transferring the data and being reset to zero in preparation for the next sample. If d is the relative dead time, the rectangle function in Equation 33 should be replaced by $\Pi(\frac{z+d/2}{1-d})$, but if the dead time is small compared to the sampling interval, this small correction can be ignored.

In the frequency domain, the interval-area sampled data become

$$X_a(s) = X(s)\ \frac{\sin(\pi s)}{\pi s} * \ Ш(s) \tag{35}$$

Comparing Equation 35 with the equation for instantaneous sampled data, Equation 27, interval-area sampling multiplies the Fourier transform of the original data by the Fourier transform of a rectangle function (Figure 3, I). This gives interval-area sampling an advantage over instantaneous sampling in that noise at high frequencies (s greater than 1/2) is attenuated and is less likely to cause overlap errors. The data in the useful frequency range (s less than 1/2), however, will be distorted. The determinate error in the estimates of peak parameters caused by this distortion can be calculated from the definition of cumulants (Equation 8). The resulting corrections are the well known Sheppard corrections for grouping (22); the corrections for peak area, retention time, and odd-order cumulants are zero, but the corrections for peak width and even-order cumulants can be significant. These corrections could be applied to the parameter estimates or included in the peak model, with the understanding that neglecting high-order uncorrected cumulants introduces the prior information that these cumulants have the values of the Sheppard corrections. Sheppard's corrections are exact for a peak function, but only approximate when a peak is contaminated by noise. It is better, therefore, to correct the data rather than the parameter estimates even though more computation is required. Correcting the data, however, introduces a bias into the estimate of the power-density spectrum; more is said about this below.

After filtering the Fourier transform of interval-area sampled data is

FIGURE 3

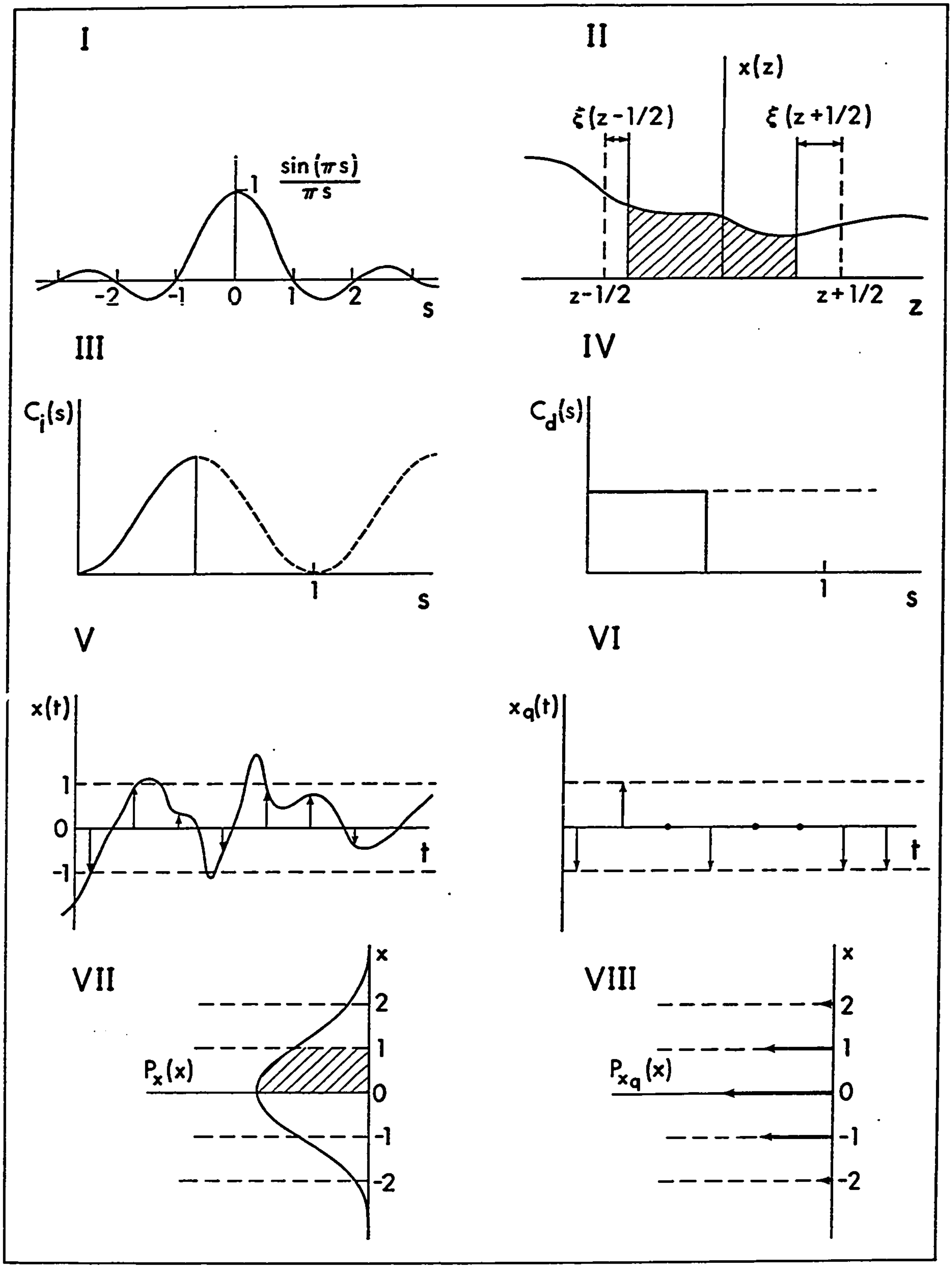
I
1
$\frac{\sin(\pi s)}{\pi s}$
-2
-1
0
1
2
s
II
x(z)
ξ(z-1/2)
ξ(z+1/2)
z-1/2
z+1/2
z
III
$C_i(s)$
1
s
IV
$C_d(s)$
1
s
V
x(t)
1
0
-1
t
VI
$x_q(t)$
t
VII
x
2
1
$P_x(x)$
0
-1
-2
VIII
x
2
1
$P_{x_q}(x)$
0
-1
-2

Figure 3. Digitization effects. I, Fourier transform of rectangle function; II, effect of jitter errors (schematic); III, power-density spectrum of jitter noise; IV, power-density spectrum of noise caused by integration dead time fluctuations; V, continuous data (schematic, with arrows representing instantaneous samples); VI, result of the quantization of the data in V (schematic); VII, probability-density function of continuous data in V (schematic); VIII, probability-density function of quantized data in VI (schematic). The lined area in II is the interval area sample resulting from jitter. With no jitter, the integration would extend to the dashed lines. The area of the lined part of VII is equal to the area of the delta function represented by an arrow from the origin in VIII.

$$X_a'(s) = X(s)\ H(s)\ \frac{\sin(\pi s)}{\pi s} \tag{36}$$

where $H(s)$ is the transfer function of the filter and where the sampling-interval and the sampling-time conditions (Equations 28 and 31) are assumed to have been met. The corrected Fourier transform of the data required for the estimation of the peak parameters is then

$$X(s) = X_a'(s)\ [H(s)\ \frac{\sin(\pi s)}{\pi s}]^{-1} \tag{37}$$

For the calculation of the integral in $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ Equation 15 we define the Fourier transform of the data at zero frequency, $X(0)$, to be zero because the reciprocal of the power density spectrum, $C_x(0)^{-1}$, is defined to be zero.

Jitter

Variation in the sampling interval is called jitter; as shown below, jitter adds noise to interval-area sampled data that increases with signal amplitude. Although we do not consider jitter noise in the noise model (because it is nonstationary), jitter always occurs to some extent in practice. We consider jitter noise here with a view to measuring it and thereby determining the limitations of the noise model. The results below are a simple extension of the theory presented in (23) to interval-area sampling. Figure 3, II illustrates that the jitter at the beginning of integration, $\xi(z-1/2)$, is the difference between the time when integration actually begins and the time when it was expected to have begun, $z - 1/2$. The effect of jitter is then as shown in the equation

$$x_{aj}(z) = [\int_{z-\frac{1}{2}+\xi(z-\frac{1}{2})}^{z+\frac{1}{2}+\xi(z+\frac{1}{2})} x(t)\, d\, t]\ Ш(z) \tag{38}$$

A Taylor series expansion of $x_{aj}(z)$ taken to the first power of the jitter gives

$$x_{aj}(z) \simeq x_a(z) + [x(z+1/2)\ \xi(z+1/2) - x(z-1/2)\ \xi(z-1/2)]\ Ш(z) \tag{39}$$

Equation 39 is an adequate approximation of Equation 38 when the standard deviation of the jitter is small compared to the sampling interval, and when $d\, x(z)/d\, z$ is small compared to $x(z)$. The slope condition holds when the Nyquist sampling condition is met and there is little signal density at frequencies near the Nyquist frequency. Jitter as defined above can be considered a continuous random process sampled at the same time as the data. It is assumed that the jitter has a normal p.d.f. with zero mean and standard deviation σ_j, and has a white power-density spectrum extending beyond the Nyquist sampling frequency so that the autocovariance function of the jitter is effectively a delta function. It is assumed, also, that the jitter, $\xi(z)$, is uncorrelated with the signal, $x(z)$. If the signal and the jitter are correlated (by mechanical vibration, for example) a more elaborate model than that used here would be required. The autocovariance function of jittered interval-area samples is then

$$c_j(z) \simeq c_{x_a}(z) + [c_x(0)+\overline{x}^2]\ \sigma_j^2\ [2\delta(z) - \delta(z+1) - \delta(z-1)] \tag{40}$$

and the power-density spectrum is

$$C_{j}(s) \simeq C_{x_a}(s) + 2(W_c+\bar{x}^2)\,\sigma_j^2\,[1-\cos(2\pi s)] \qquad (41)$$

The mean of the data, $\bar{x}$, is included in Equation 41 because in the calculation of the noise power, W_c in Equation 22, the power-density at zero frequency is given a value that is reasonable for noise with a zero mean; the actual value of $C_x(0)$ is equal to the square of the mean of the data. Equation 41 shows that jitter adds a noise component to interval-area-sampled data that has an intensity proportional to the square of the mean of the data.

Another noise source associated with sampling is caused by the variation in the integrator dead time referred to previously. Assuming that the dead time has a normal p.d.f. with a standard deviation, σ_d , that is much less than the mean dead time, and that the variation in dead time has a white power-density spectrum uncorrelated with the signal, dead-time noise adds to the base-line noise a component with a white power-density spectrum equal to $(W_c+\bar{x}^2)\sigma_d^2$. Figures 3, III and IV compare the power-density spectra of jitter and variable dead time noise.

Quantization

The second step of digitization is quantization. As shown in Figure 3, V to VIII, quantization can give a data sample a random error and a constant error both of which may be as large as one half the quantization interval. Below the theories presented in (24) and (25) are summarized and interpreted. Quantization of a random variable is equivalent to taking interval-area samples of the p.d.f.

of the noise. In a normalized scale where the data, x , are taken in units of the quantization interval, the p.d.f. of quantized noise is

$$p_{x_q}(x-1/2) = p_x(x) * \text{Ш}(x-1/2)\ \ \text{Ш}(x-1/2) \tag{42}$$

where $p_x(x)$ is the p.d.f. of the data at a specified time. A considerable simplification in the equations given below results when $p_x(x)$ in Equation 42 is shifted downward one half unit. Although shifting adds a constant error to the mean of the data, this error can be ignored since the mean is arbitrary. The joint p.d.f. of x_1 at time t , and x_2 at time $(t+\tau)$ is then

$$p_{x_q}(x_1,x_2) = p_x(x_1,x_2) * \Pi(x_1) * \Pi(x_2)\ \ \text{Ш}(x_1)\ \ \text{Ш}(x_2) \tag{43}$$

and the Fourier transform of this joint p.d.f. (along the x axis, not the usual transform along the time axis) is

$$P_{x_q}(\chi_1,\chi_2) = P_x(\chi_1,\chi_2)\ \frac{\sin(\pi\chi_1)}{\pi\chi_1}\ \frac{\sin(\pi\chi_2)}{\pi\chi_2} * \text{Ш}(\chi_1) * \text{Ш}(\chi_2) \tag{44}$$

The autocovariance function of the quantized noise can be obtained from Equation 44 with the formula

$$c_{x_q}(\tau) = \left[\frac{1}{(-i2\pi)^2}\ \frac{\partial^2 P_{x_q}(\chi_1,\chi_2)}{\partial\chi_1\ \partial\chi_2}\right]_{\chi_1=\chi_2=0} \tag{45}$$

When the data have a normal p.d.f., the Fourier transform of the joint p.d.f. of two data points is

$$P_x(\chi_1,\chi_2) = \exp\{-w[\chi_1^2+2\rho(\tau)\chi_1\chi_2+\chi_2^2]\} \tag{46}$$

where

$$w = (2\pi)^2 W_c/2 \tag{47}$$

In terms of the autocovariance function of the base-line noise (Equation 14), the variance, W_c, in Equation 46 is

$$W_c = c_x(0) \tag{48}$$

and the autocorrelation function, $\rho(\tau)$, in Equation 46 is

$$\rho(\tau) = c_x(\tau)/c_x(0) \tag{49}$$

From Equations 44, 45, and 46 the autocovariance function of quantized noise is

$$c_{x_q}(\tau) = W_c\rho(\tau) + 4\sigma^2 \sum_{n=1}^{\infty} (-1)^n \exp(-wn^2) - \frac{1}{4\pi^2} \sum_{n=-\infty}^{\infty}{}' \sum_{m=-\infty}^{\infty}{}' \frac{(-1)^{n+m}}{nm} \exp\{-w[n^2+2\rho(\tau)nm+m^2]\} \tag{50}$$

where the prime on $\sum_n{}'$ means omission of the value at $n = 0$.

Equation 50 shows that quantization adds noise to the data, and the second and third terms of the equation express the autocovariance function of the quantization noise. Using the symbol $c_q(\tau)$ for the autocovariance function of the quantization noise and using only the most significant terms in Equation 50 gives, for the indicated values of the autocorrelation function of the base-line noise, $\rho(\tau)$,

$$\begin{aligned} c_q &= 1/12 - (4W_c + 1/\pi^2)e^{-w} &&, \quad \rho(\tau) = 1 \\ &= -\,4W_c e^{-w} + (e^{-2w} - 2e^{-3w})/(2\pi^2) &&, \quad \rho(\tau) = 1/2 \\ &= -\,4W_c e^{-w} &&, \quad \rho(\tau) = 0 \\ &= -\,4W_c e^{-w} - (e^{-2w} - 2e^{-3w})/(2\pi^2) &&, \quad \rho(\tau) = -\,1/2 \\ &= -\,1/12 - (4W_c - 1/\pi^2)e^{-w} &&, \quad \rho(\tau) = -\,1 \end{aligned} \tag{51}$$

Since the derivative of $c_q(\tau)$ with respect to $\rho(\tau)$ is equal to $\pm\infty$ when $\rho(\tau)$ is equal to ± 1 , the constants $(\pm 1/12)$ in Equation 51 occur only when $\rho(\tau)$ is identically equal to ± 1 . In most practical situations $\rho(\tau)$ is identically equal to $+1$ when the lag is zero and is seldom equal to ± 1 when the lag is any other value. Therefore, $c_q(\tau)$ has a component at zero lag that is in effect a delta function. The power-density spectrum of quantization noise, consequently, has a white component that extends to infinite frequency, but when the data are sampled, only the portion between the negative and positive Nyquist frequencies is observed. (There is no overlap error because the autocovariance function, being a delta function, is not affected by sampling.) The impulsive nature of $c_{q_x}(\tau)$ arises from the assumption that the quantization interval is exactly constant; jitter in the quantization interval no doubt occurs to some extent in practice and would broaden the impulsive component. The resulting power-density spectrum would approach zero at high frequencies, but unless the sampling interval were extremely small or the jitter in the quantization interval severe, the power-density spectrum of the impulsive component should be nearly constant in the observed frequency range.

Apart from the constants ($\pm$ 1/12), the terms in Equation 51 do not vary rapidly with small changes in the value of $\rho(\tau)$; hence the equation can be used to sketch in the approximate autocovariance function of the quantization noise when the autocovariance function of the base-line noise is known. When the standard deviation of the base-line noise is small enough, the terms other than the constant 1/12 can be neglected. (If the standard deviation is one half, in units of the quantization interval, the largest of these terms is about 10^{-6}.) Therefore, under most experimental conditions the effect of quantization is to add white noise to the base-line noise. In absolute units, the power of quantization noise is $1/12\ q^2$ (volts^2), where q is the quantization interval in volts. When the p.d.f. of base-line noise is normal, the p.d.f. of quantized base-line noise will not be normal because the p.d.f. of quantization noise is rectangular. When the standard deviation of the base-line noise is several times the quantization interval, however, the effect of the rectangular p.d.f. can be ignored.

Quantization of interval-area samples occurs after the integration over the sampling interval, so the correction for the distortion caused by interval-area sampling, Equation 36, should not be applied to quantization noise. In the calculation of the integral in $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ in Equation 15, however, the same error occurring in the data, $|x(\nu)|^2$, and the power density spectrum, $C_x(\nu)$, results in the cancellation of the error. Therefore, applying the correction for interval-area sampling to quantization noise will not affect the parameter estimates, but will introduce a consistent error in the estimates of the parameter standard deviations (defined below), which depend on $C_x(\nu)$ but are independent of the data.

ESTIMATION

Information from the Data

The object of estimation is to extract a peak from a base line so that the peak can be reconstructed as it would appear were there no base-line noise. Finding the peak that caused the data reduces to estimating the parameters of the peak model when the model is given. But, because the estimates will be derived from random data, the estimates themselves will be random, and it will not be possible to state the exact values of the parameters that caused the peak in a particular chromatogram. Knowing the probability structure of the noise, however, one can give the probability that a certain range of true values caused the peak in the data.

The parameters of a peak on a base line are related to the data through the equation

$$x(t;\underset{\sim}{\alpha}) = f(t;\underset{\sim}{\alpha}) + g(t) \tag{52}$$

where $f(t;\underset{\sim}{\alpha})$ is the peak function, $g(t)$ the base-line noise, and $\underset{\sim}{\alpha}$ the set of parameters. For the purposes of this study, α_0 is the peak area, α_1 is the retention time, α_2 is the peak width, and α_3 and higher are the standardized cumulants, K_3 and higher. When a peak is not present in the chromatogram, the p.d.f. of the data, $\underset{\sim}{x}$, is given by Equation 15; therefore, when a peak is present, the p.d.f. of $\underset{\sim}{x}$, given $\underset{\sim}{\alpha}$ (the true values of the parameters), is

$$p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha}) = p_{\underset{\sim}{x}}(\underset{\sim}{x}-\underset{\sim}{f}) \tag{53}$$

by the use of Equation 52. Equation 53 holds when the peak model,

$f(t;\underset{\sim}{\alpha})$, represents the peak completely, or at least accurately enough so that any deviation of the peak model from the true peak is indistinguishable from noise.

Prior Information

The true values of the parameters, $\underset{\sim}{\alpha}$ may vary from experiment to experiment because of indeterminate variations in the experimental conditions (non-base-line noise) that may affect the parameters without having an effect on the base line. The knowledge or the lack of knowledge about the parameters for a particular experiment is best described by a p.d.f., $p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})$, called the prior p.d.f. of the parameters (26) . Assuming that the experimental conditions that affect the true values of the parameters do not vary during the elution of the peak, one can speak of the "true" values for a particular experiment. (It is assumed, also, that the true values of the parameters are practically independent of the base line.) The prior p.d.f. states the degree of belief in the hypothesis (26) that previously obtained values of the parameters still apply to the experiment under study. In other words it expresses, in concrete terms, the state of the information about the true values of the parameters before the experiment is begun. The amount of prior information can have an important effect on the accuracy and precision of the parameter estimates; precise prior information is essential for the estimation or detection of small peaks that are barely distinguishable form the base-line noise.

Often in an analytical problem the experimenter has some information, however vague, about the parameters before the experiment is begun. In gas chromatography little is usually known about the area of a peak except that the area is finite and positive (or partly negative in anomalous cases), but the retention time and peak width of a previously identified compound are often known precisely. This prior information could be either obtained directly from the accumulated results of previous experiments on the same apparatus or predicted theoretically from published data and the experimental conditions. The prior p.d.f. of the parameters obtained by either of these methods is likely to be normal or nearly normal when the number of previous experiments is large by the central-limit theorem (11) . A normal prior p.d.f. is completely characterized by its mean, $\underset{\sim}{\alpha}_p$, and its variance, $\underset{\sim}{V}_p$. Normality of the prior p.d.f. is unnecessary, but desirable because it aids the numerical determination of the most probable values of the parameters. If prior information is not available for a particular parameter, it is reasonable to assume that all values of the parameter within a physically possible range are equally probable; then the prior p.d.f. is uniform and can be represented by a rectangle function. An exact statement of the limits of the range of the parameter is not required. For the estimation method described below, it is important to know only that the true value of the parameter is well within the permitted range.

The prior information introduced by the choice of the peak model can be interpreted as giving the nonadjustable parameters certain means and zero variance. For example, in the Charlier derivative series with a Gaussian basis function, the high-order cumulants have means equal to zero.

Bayesian Estimation

From the p.d.f. of the data given the parameters (Equation 52) and the prior p.d.f. of the parameters, the p.d.f. of the parameters given the data can be obtained from the following form of Bayes' theorem (27):

$$p_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\underset{\sim}{\alpha}|\underset{\sim}{x}) = \frac{p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})\ p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha})}{p_{\underset{\sim}{x}}(\underset{\sim}{x})} \tag{54}$$

where

$$p_{\underset{\sim}{x}}(\underset{\sim}{x}) = \int_{\Omega} p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})\ p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha})\ d\,\underset{\sim}{\alpha} \tag{55}$$

The multiple integration in Equation 55 is over the parameter space Ω . Although not indicated in the notation, Equation 54 is conditional on the experiment being run in situations where the prior p.d.f. of the parameters and the previously obtained autocovariance function of the base-line noise are applicable. The p.d.f. of the parameters given the data defined by Equation 56 is called the posterior p.d.f. of the parameters (26). The posterior p.d.f. does not contain irrelevant information about the details of the base-line noise but does contain all the essential information in the data about the parameters. Being a multivariate function defined over an infinite domain, however, a posterior p.d.f. is too cumbersome for most purposes. Since numbers are easier to deal with than functions, a few characterizing numbers will simplify the interpretation of a posterior p.d.f. Below we discuss the estimation of parameter values that best describe the position or location of a posterior p.d.f.

Point Estimators

A set of operations applied to data to obtain an estimate is called an estimator. The resulting set of estimates is represented by the symbol $\utilde{a}$ to distinguish it from the set of true values, $\utilde{\alpha}$. Our goal is to find an estimator whose estimates contain all of the available information. Such an estimator we call "ideal". Since the posterior p.d.f. contains all the information about the parameters, the relative merit of an estimator will depend on how well the p.d.f. of the parameters given the estimates, $p_{\utilde{\alpha}|\utilde{a}}(\utilde{\alpha}|\utilde{a})$, "matches" the posterior p.d.f., $p_{\utilde{\alpha}|\utilde{x}}(\utilde{\alpha}|\utilde{x})$. If the two p.d.f.'s are not the same, the estimates will contain less information than the data.

When the moments of two p.d.f.'s are the same, then the p.d.f.'s themselves are the same; therefore, moments should be a valid basis for the comparison of a posterior p.d.f. with an estimator p.d.f. The first two moments are usually sufficient to characterize an estimator. It is conceivable, however, that if some estimator A were poorer than estimator B on the basis of the first two moments, estimator A might "match" the posterior p.d.f. better than estimator B on the basis of higher moments. In practical applications characteristics of an estimator other than moments may be important. Some examples of practical criteria are economics, mathematical simplicity, calculation speed, and insensitivity to changes in the probability structure of the system (in particular, nonstationarity in the autocovariance function of base-line noise). These criteria are not considered here on the grounds that once an ideal estimator is obtained, a simplification that results in a more practical estimator can be justified by comparing the moments of the practical estimator with those of the ideal estimator. Furthermore, the mathematical structure of an ideal estimator may contain clues to practical simplifications; working downward in complexity is easier than building a better estimator from a poor one.

The difference between the first moments or means of an estimator p.d.f. and a posterior p.d.f. may be called the bias. The bias for parameter α_j is

$$B_{x_j}(x) = \int_{-\infty}^{\infty} \alpha_j \, p_{\underset{\sim}{\alpha}|\underset{\sim}{a}}(\underset{\sim}{\alpha}|\underset{\sim}{a}) \; d\,\underset{\sim}{\alpha} - \int_{-\infty}^{\infty} \alpha_j \, p_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\underset{\sim}{\alpha}|\underset{\sim}{x}) \; d\,\underset{\sim}{\alpha} \qquad (56)$$

By use of the expectation operator, E_y , to represent averaging over y (that is, multiplying by the p.d.f. of variable y and integration with respect to y), Equation 56 can be written:

$$B_{x_j}(x) = \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{a}}(\alpha_j) - \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\alpha_j) \qquad (57)$$

The second moments about the means or the variances are

$$V_{\underset{\sim}{x}_j}(\underset{\sim}{x}) = \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{x}}\{[\alpha_j - \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\alpha_j)]^2\} \qquad (58)$$

and

$$V_{\underset{\sim}{a}_j}(\underset{\sim}{a}) = \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{a}}\{[\alpha_j - \mathrm{E}_{\underset{\sim}{\alpha}|\underset{\sim}{a}}(\alpha_j)]^2\} \qquad (59)$$

An ideal estimator will have zero bias, and the variance of the estimator p.d.f. will be equal to the variance of the posterior p.d.f.

Although an evaluation of the bias and the variances defined above may be difficult, it is possible to approximate them or at least make inferences about them by considering averages of the estimates over the data and the parameters. Averaging over the data for a given fixed set of values of the parameters, a conditional bias can be defined by

$$B_j(\underset{\sim}{\alpha}) = \mathrm{E}_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(a_j-\alpha_j) \tag{60}$$

The conditional bias is an average over the data of the difference between two parameter values, while the bias of an estimator defined in Equation 56 is an average over the parameters of the difference between two p.d.f.'s. In some situations using an estimator that has zero conditional bias may be desirable, but as shown in an example below, an ideal estimator may have a non-zero conditional bias. The overall bias of an estimator, averaged over both the data and the parameters, is

$$B_j = \mathrm{E}_{\underset{\sim}{x},\underset{\sim}{\alpha}}(a_j-\alpha_j) \tag{61}$$

where the joint p.d.f. of the data and the parameters required in the expectation operation, $\mathrm{E}_{\underset{\sim}{x},\underset{\sim}{\alpha}}$, is

$$p_{\underset{\sim}{x},\underset{\sim}{\alpha}}(\underset{\sim}{x},\underset{\sim}{\alpha}) = p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})\; p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha}) \tag{62}$$

The overall bias also is different from the bias of an estimator defined in Equation 56. If one is zero, the other may be nonzero, but under certain conditions discussed below, both will be zero. The conditional variance of an estimator for parameter α_j is

$$V_j(\underset{\sim}{\alpha}) = E_{\underset{\sim}{x}|\underset{\sim}{\alpha}}\{[a_j - E_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(a_j)]^2\} \tag{63}$$

and the overall variance is

$$V_j = E_{\underset{\sim}{x},\underset{\sim}{\alpha}}\{[a_j - E_{\underset{\sim}{x},\underset{\sim}{\alpha}}(a_j)]^2\} \tag{64}$$

The overall variance can be obtained experimentally by running a large number of experiments; usually, it is the only characteristic of an extimator that can be directly observed in practice. The other characteristics must be inferred from a p.d.f. that may not be directly observable when the p.d.f. is a function of the unknown true values of the parameters. When an estimator is unbiased (overall bias equal to zero), the overall variance is the variance of the estimates about the mean of the prior p.d.f. (α_p , in the case of a normal prior p.d.f. and the midpoint of the range in the case of a uniform p.d.f.). Since the overall variance is strongly influenced by the randomness of the parameters, it is more characteristic of the entire experimental system than of the estimator. Because it is less influenced by the prior p.d.f., the mean-square error, defined as the average difference between the estimated and the true values of the parameters, characterizes the estimator better than the overall variance. The conditional mean-square error is

$$S_j(\underset{\sim}{\alpha}) = E_{\underset{\sim}{x}|\underset{\sim}{\alpha}}[(a_j - \alpha_j)^2] \tag{65}$$

and the overall mean-square error is

$$S_j = E_{\underset{\sim}{x},\underset{\sim}{\alpha}}[(a_j - \alpha_j)^2] \tag{66}$$

The following equations give the relations between the mean-square errors and the biases and variances:

$$S_j(\underset{\sim}{\alpha}) = V_j(\underset{\sim}{\alpha}) + B_j(\underset{\sim}{\alpha})^2 \tag{67}$$

$$S_j = V_j - V_{p_j} + 2E_\alpha\{\alpha[B-B(\alpha)]\} \tag{68}$$

where V_{p_j} is the variance of the prior p.d.f. The conditional mean-square error is always at least as large as the conditional variance. The overall mean-square error may be larger or smaller than the overall variance; if the conditional bias is zero, it will be smaller.

An important result concerning the overall mean-square error can be derived from the posterior p.d.f. This result, called the Cramér-Rao inequality (28), states that the smallest possible value of the overall mean-square error of any estimator is greater than or equal to the diagonal of the dispersion matrix:

$$S_j \geq D_{jj} \tag{69}$$

where the dispersion matrix is the inverse of the information matrix, $\underset{\sim}{I}$,

$$\underset{\sim}{D} = \underset{\sim}{I}^{-1} \tag{70}$$

The elements of the information matrix are derivatives of the posterior p.d.f. averaged over the data and the parameters:

$$I_{jk} = -E_{\underset{\sim}{x},\underset{\sim}{\alpha}}\left[\frac{\partial^2 \ln p_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\underset{\sim}{\alpha}|\underset{\sim}{x})}{\partial \alpha_j \; \partial \alpha_k}\right] \tag{71}$$

The Cramér-Rao inequality holds provided the derivatives in Equation 71 exist and are absolutely integrable with respect to $\underset{\sim}{x}$ and $\underset{\sim}{\alpha}$. In the noise and peak models used here these conditions will not be satisfied when the prior p.d.f. of a parameter, α_r for example, is uniform because the derivative with respect to α_r will not exist at the discontinuous end points of the p.d.f. The mean square error of α_r might then be less than D_{rr}. But, if the posterior p.d.f. is concentrated well within the ends of the uniform p.d.f., then the Cramér-Rao inequality will hold approximately. An estimator that satisfies the equality in Equation 69 is said to be efficient, efficiency, ε_j, (overall mean square efficiency) being defined as the ratio of the minimum mean-square error to the actual mean-square error:

$$\varepsilon_j = D_{jj}/S_j \tag{72}$$

An efficient estimator exists only if the information matrix, defined by Equation 71, is independent of the values of the data and the parameters; this is true only when the posterior p.d.f. is normal (29).

MP Estimator

From Equation 57, the mean of the p.d.f. of an ideal estimator and the mean of the posterior p.d.f. should have the same value. Therefore, the mean of the posterior p.d.f. would be an ideal estimator in terms of bias but the mean is often difficult to calculate. Another estimator, also based on the posterior p.d.f. but more easily calculated than the mean, consists of taking the most probable values of the parameters to be the parameter estimates (MP estimator). If an efficient estimator exists, the MP estimator will be efficient and unbiased, and the p.d.f. of the MP estimator will be the same as the posterior p.d.f. Consequently, if the posterior p.d.f. is normal, then the MP estimator will be ideal in the sense that the estimates along with the information or dispersion matrix will contain everything that can be said about the parameters.

Example

To illustrate the use of an MP estimator, consider the problem of estimating the mean, α , of the retention time of a gas-chromatographic peak from n measurements (runs) $x_1, x_2, \ldots, x_n$. Runs on previous days showed that the true mean has a normal p.d.f. with mean α_p and variance V_p , and that the individual measurements are independent and have a normal p.d.f. with variance C . The posterior p.d.f. of the true mean, α , given the data, $\underset{\sim}{x}$, is

$$p_{\alpha|\underset{\sim}{x}}(\alpha|\underset{\sim}{x}) = (2\pi V')^{-1/2} \exp[-(\alpha - \frac{V_p\bar{x} + \alpha_p c/n}{V_p + c/n})^2/2V'] \qquad (73)$$

where

$$\bar{x} = \sum_{j=1}^{n} x_j/n$$

and

$$V' = \frac{C}{n}\,\frac{1}{1+C/(nV_p)}$$

The MP estimator, a, is found by equating the first derivative with respect to α of the right side of Equation 73 to zero, replacing α with a, and solving for a:

$$a = \frac{V_p\bar{x} + \alpha_p C/n}{V_p + C/n} \tag{74}$$

The MP estimator of the mean, the weighted average of the prior mean and the data mean, is not the same as the commonly used estimator, $\bar{x}$; nevertheless, a and $\bar{x}$ become approximately equal when either the number of measurements or the prior variance becomes large. The estimator p.d.f. of α, given a, is

$$p_{\alpha|a}(\alpha|a) = (2\pi V')^{-1/2}\exp[-(\alpha-a)^2/2V'] \tag{75}$$

Since $p_{\alpha|a}(\alpha|a)$ is equal to $p_{\alpha|\underset{\sim}{x}}(\alpha|\underset{\sim}{x})$ for all values of α, the MP estimator is ideal; also, since the posterior p.d.f. is normal, the MP estimator is efficient and unbiased.

The different quantities defined above that are used to characterize an estimator are listed below for the MP estimator of the mean retention time.

$$B(\alpha) = \frac{\alpha_p-\alpha}{1+nV_p/C} \tag{76}$$

$$B_{\underset{\sim}{x}}(\underset{\sim}{x}) = B = 0 \tag{77}$$

$$V(\alpha) = V' \frac{1}{1+C/(nV_p)} \tag{78}$$

$$S(\alpha) = V' \frac{1+(\alpha_p-\alpha)^2 C/(nV_p^2)}{1+C/(nV_p)} \tag{79}$$

$$V = \frac{V_p}{1+C/(nV_p)} \tag{80}$$

$$S = D = V' = \frac{C/n}{1+C/(nV_p)} \tag{81}$$

$$V_{\underset{\sim}{x}}(\underset{\sim}{x}) = V_a(a) = V' \tag{82}$$

The overall bias B and the estimator bias $B_{\underset{\sim}{x}}(\underset{\sim}{x})$ are zero, whereas the conditional bias $B(\alpha)$ is nonzero except when the true mean happens to equal the prior mean (Equation 76). But, when n or V_p are large, the conditional bias approaches zero. A nonzero conditional bias would be undesirable when the estimates of the retention times of two peaks on the same chromatogram are used to calculate a retention ratio or a retention index. Here, it would be better to use the MP estimator of the final result, utilizing prior information of the final result itself, rather than to combine the estimates of two retention times. The estimator variance, $V_a(a)$, is less than either the prior variance, V_p, or the variance of the average of the data, $\bar{x}$, which is equal to C/n. The overall variance, V, is greater than the sum of the prior variance and the variance from the data (C/n) when C/n is less than V_p; in other cases V is less than V_p (Equation 80). If the prior variance was assumed to be infinite when in fact it was finite, that is, if the prior information was ignored in the estimation, the overall variance would be equal to the sum of the prior variance and the variance from the data, $V_p + C/n$. In the statement of the estimation problem the true mean was assumed to be random; in some situations the true mean may be constant and the prior information may be random. For example, suppose the prior mean, α_p , is the average of m measurements and the prior variance, V_p , is equal to C/m . The MP estimator would in effect be the average of n plus m measurements, the m measurements being considered as prior information. The overall variance (Equation 80) correctly gives the average variance of α about α_p . But, because the prior mean could be far from the true mean in a single sequence of n runs, the overall variance is not a useful result in this case. The overall mean-square error gives the more realistic variance of the estimate about the true value of the mean.

Estimator for Nonlinear Peak Model

In the noise model described here the parameters must be linear in the peak function for the MP estimator to be efficient. Edgeworth's form of the GCA series (Equation 10) is nonlinear (except for α_0 , the peak area), and therefore the MP estimator will be inefficient and generally biased. Nevertheless, the loss in efficiency and the bias are not usually serious. The primary hypothesis of this thesis is that the MP estimates along with the dispersion matrix or the information matrix, though not ideal characterizations of a posterior p.d.f., are approximately ideal. Even when the MP estimator is poor in terms of variance and bias, it may be valuable in its own right in giving the estimates that are the most probable in the light of the data available.

The Edgeworth series is a transcendental function of the peak parameters. Hence the MP estimators for the individual parameters cannot be derived in the form of an explicit algebraic function as can the MP estimator of the mean in the example considered above (Equation 74). The estimator of each parameter depends* on the values of all the other parameters, and all the estimates must be determined simultaneously. If the prior information about a particular parameter is strong and the information from the data adds little to the total information (see below), simply assigning the value of the prior mean to the estimate of that parameter may be adequate without calculating it, that is, the parameter may be made nonadjustable. When only the first few parameters of a series peak-shape model are estimated, it is assumed that the data will contribute little to the information about the high order parameters; these parameters can thus be given a constant value and made nonadjustable. When the peak-shape function is well known, it may be necessary to estimate only the area, the retention time, and the width of the peak. Reference (15) gives an example in which the parameters of the peak-shape function are a set of samples of the peak on a previous chromatogram.

Fisher's Measure of Information

The posterior p.d.f. (Equation 54) is proportional to the product of the prior p.d.f. and the p.d.f. of the data, given the values of the parameters. Therefore, the information matrix defined by Equation 71 is the sum of two parts:

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*The dependence is mathematical rather than statistical, though the estimates may be statistically dependent also.

$$\underset{\sim}{I} = \underset{\sim}{I}_{\mathrm{p}} + \underset{\sim}{I}_{\mathrm{d}} \quad . \tag{83}$$

The prior-information matrix, $\underset{\sim}{I}_{\mathrm{p}}$, has the elements

$$I_{\mathrm{p}_{jk}} = -\mathrm{E}_{\underset{\sim}{\alpha}}\left[\frac{\partial^2 \ln p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})}{\partial\,\alpha_j\ \partial\,\alpha_k}\right] \tag{84}$$

If the vector of prior variances, $\underset{\sim}{V}_{\mathrm{p}}$, is extended to be a matrix with covariances as well as variances, then the prior-information matrix will be equal to the inverse of the covariance matrix. When one or more of the parameters has a uniform prior p.d.f. and if the MP estimates are well within the end points of the uniform p.d.f.'s, the corresponding rows and columns of the prior-information matrix can be given the value zero. The data-information matrix, $\underset{\sim}{I}_{\mathrm{d}}$, has the elements

$$I_{\mathrm{d}_{jk}} = -\mathrm{E}_{\underset{\sim}{x}}\left[\frac{\partial^2 \ln p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha})}{\partial\,\alpha_j\ \partial\,\alpha_k}\right]_{\underset{\sim}{\alpha}=\underset{\sim}{\alpha}} \tag{85}$$

In the noise model used here, Equation 85 becomes

$$I_{\mathrm{d}_{jk}} = \int_{-\infty}^{\infty} \frac{1}{C_x(s)}\,\frac{\partial\, F(s)}{\partial\,\alpha_j}\,\frac{\partial\, F^{\dagger}(s)}{\partial\,\alpha_k}\,\mathrm{d}\,s \tag{86}$$

where the dagger † means take the complex conjugate.

The diagonal elements of an information matrix are quantitative measures of the average amount of information contained in the data (including the prior data) about the parameters, or from another viewpoint, they are the worth of the parameters in terms of the information the parameters contain about a peak. Some parameters may contain information from the data already contained in other parameters. The off-diagonal elements of an information matrix express the degree of this redundancy between two parameters. Although there are other measures of information, this one, called Fisher's measure (30), arises naturally from considerations of the posterior p.d.f. and is intuitively related to the familiar usage of precision defined as the reciprocal of variance. Fisher's measure of information is not an absolute measure of precision or information, however, because the magnitude of the matrix elements I_{jj} depend on the units of the parameters. Therefore, Fisher's information measure may not be suitable for the comparison of the information content of the parameters of different peak models. The magnitudes of the diagonal elements of the information matrix are used here for the comparison of the information in the parameters of peaks with different parameter values.

An essential requirement of a series model of a peak-shape function is that the information content of a parameter in the series must decrease with increasing order of the parameter. As more and more parameters are included in a model, they should eventually contain all the information about the peak*. Edgeworth's series satisfies this requirement: in white noise the ratio of the information in parameter r to the preceeding parameter of order $(r-1)$ is equal to $2(2r-1)/r^2$ when r is greater than 3 . In general, the information matrix for any peak model is symmetric, element I_{jk} is equal to element I_{kj} ,

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*In some models, the information content of a parameter may first increase and then decrease with increasing order. The initial increase may be disregarded.

and the determinant of the information matrix is greater than zero. The off-diagonal elements of the information matrix for Edgeworth's series, because of the symmetry with respect to frequency of the derivatives in the definition of the matrix elements (Equation 85), are zero for even-odd subscript pairs except for the elements containing derivatives of the peak width, α_2 . That is, element I_{jk} is equal to zero when $j + k$ is odd except when j or k is equal to 2 .

Predicted Standard Deviations

The square root of the diagonal elements of a dispersion matrix ($\underset{\sim}{D}$, Equation 70) are estimates of the standard deviations of the parameters. These predicted standard deviations are random variables because, in the case of inefficiency, they depend on the data. The off-diagonal elements of $\underset{\sim}{D}$ are covariances. They indicate the magnitude of the statistical interdependence of errors between two parameters in the same way an autocovariance function characterizes noise. For example, if the noise were to cause parameter estimate a_j to have a certain error, then parameter a_k probably would have an error D_{jk} times the error in a_j . The degree of interdependence is more easily seen in the correlation matrix, $\underset{\sim}{D}'$, where

$$D'_{jk} = D_{jk}(D_{jj}\ D_{kk})^{-\frac{1}{2}} \qquad (87)$$

The diagonal elements of a correlation matrix are equal to 1 , and the off-diagonal elements can be neither greater than 1 nor less than -1. The Cramér-Rao inequality does not give specific information about the magnitude of individual covariances; the actual covariances may be greater or less than the corresponding element of the dispersion matrix.

A geometrical interpretation of the Cramér-Rao inequality in reference (28) uses the complete disperson matrix to make probability statements about the errors in the parameters taken as a group.

Ideally the off-diagonal elements of the correlation matrix for a peak model are all zero. In this case the estimation of the high-order parameters of a series model could be omitted without significantly affecting the estimates of low-order parameters. Neglecting a cumulant in Edgeworth's series, or giving it the value zero, when in fact it has the value K', introduces a determinate error equal to $-K'$. If lower order cumulants have a nonzero correlation with the neglected cumulant, the error can propagate downward to give the lower cumulant estimates a significant bias. On the other hand, if the estimator is inefficient, zero correlation does not necessarily rule out this kind of error. For Edgeworth's series the correlation between retention time (an odd-order parameter) and any even-order parameter is zero. Hence, neglecting even-order cumulants should not have a significant effect on the bias of the retention-time estimate.

The other off-diagonal elements of the correlation matrix for the parameters of the Edgeworth series are generally nonzero, and their magnitudes vary greatly with the values of the parameters. The values of even-even and odd-odd subscript correlations are positive and may be an high as 0.99, but decrease as the distance from the matrix diagonal increases. The values of the even-odd correlations are generally small or negative; sometimes they may be as low as -0.99.

Efficiency and Bias

For an MP estimator to be efficient, the magnitudes of the elements of the information matrix must be constant over all values of the parameters. Therefore, as the values of the elements become more nearly constant over the range of parameter values in which the posterior p.d.f. is most significant (such as ± 3 standard deviations from the maximum), the MP estimator will become more efficient. As the number of independent samples used in the estimation approaches infinity, the MP estimator becomes efficient, unbiased, and normal (31). But the number of independent samples that contain information about a peak is limited by the finite width of the peak and by the autocovariance of the noise. Nevertheless, as the amount of information (the magnitude of the diagonal elements of $\underset{\sim}{I}$) increases, the posterior p.d.f. becomes more concentrated about its maximum and the range over which the posterior p.d.f. is significant becomes smaller. Therefore, since the nonlinearity of the system that contributes to inefficiency does not increase with the values of the diagonal elements of $\underset{\sim}{I}$, the posterior p.d.f. must become more nearly constant over the significant range, and the MP estimator must become more efficient as the information increases. This argument is often stated in terms of signal-to-noise ratios (32) , but these are equivalent to the diagonal elements of the information matrix, I_d . In a situation where the MP estimator might be highly inefficient and highly biased because of insufficient information in the data and little prior information, to present the entire posterior p.d.f. would be better than to attempt to characterize it with a point estimate and an approximate variance. The amount of information about the parameters can be increased experimentally by increasing the area of the peak relative to the noise power or by decreasing the similarity of the peak to the noise waveforms. For example, a chromatogram with a noise power-density spectrum concentrated at low frequencies would give more information about narrow peaks than broad peaks of the same area because narrow peaks have more information at high frequencies, where the noise intensity is low.

Bias, since it is defined in terms of means, can result from choosing the maximum rather than the mean of the posterior p.d.f. when the posterior p.d.f. is asymmetric about its maximum. Bias in an MP estimator caused by asymmetry in the posterior p.d.f. will decrease with increasing information for the same reason that efficiency increases with more information. Nonstationary base-line noise can cause bias in the estimates of parameters as well as in the estimates of parameter standard deviations. Nonstationarity that results in changes in the magnitude of the power-density spectrum but not its mathematical form might be reduced by approximating the power-density spectrum with a simple function and estimating one or two parameters of the function along with the peak parameters. This method can be used only when the power-density spectrum does not change or changes only slightly during the elution of a peak. In the problem of estimating the mean of a set of measurements discussed above, the variance of a single measurement is assumed to be constant and known. If the variance changed from day to day, it could be estimated along with the mean. However, depending on the form of the prior p.d.f., the MP estimator of the variance may be inefficient (because the posterior p.d.f. is not normal) and may be biased (because the posterior p.d.f. is asymmetric about its maximum).

Sampling Interval and Sampling Time

In practice an important cause of both bias and inefficiency is presenting the estimator with insufficient data either in the frequency domain (sampling over too small a range of frequency) or in the time domain (sampling over too short a period of time). Consider the loss of efficiency, and also the loss of information, in the frequency domain caused by sampling the Fourier transform of data between finite Nyquist frequencies. According to Equation 87 a diagonal element of a data information matrix, $I_{\mathrm{d}_{jj}}$, is an integral of a function of frequency. This function can be called the information function of parameter α_j. The information functions are real, positive, and even functions of frequency, and they approach zero at high frequencies. The total information is the integral of a frequency function over infinite limits. Although using finite integration limits will cause loss of some information, a small loss, such as 1% of the total information, may be acceptable in practice. Given a 1% or some other acceptable information loss, integration limits $\pm s_j$ could be found so that integration of the information function between these limits would attain (100-1)% of the total information. If the integration limits are evaluated for each parameter and the largest limit (s_{I}) found, then the sampling interval Δt_{I}

equal to $1/(2s_I)$ would be the largest that could be used for the parameters to contain at least (100-1)% of the information in the data. Outside the frequency range $\pm s_I$ the data contain little information about the parameters. Since data that contain no information cannot contribute to bias, the maximum sampling interval, Δt_I, will be small enough to ensure that bias as well as information loss are within acceptable limits. Similarly, the time intervals, T_j, within which the data contain an acceptable fraction of the total information about parameter α_j can be found by use of the inverse Fourier transforms of the information functions. The inverse Fourier transform of an information function is a function of time and its integral between infinite limits is equal to the total information, $I_{d_{jj}}$. However, finding the shortest acceptable time interval, T_I, in the time domain, where information functions are oscillatory, will be more difficult than finding s_I in the frequency domain. The information functions in the time domain are symmetrical about the retention time of a peak. Therefore, data should be taken the same distance $(T_I/2)$ on each side of the mean even when the peak has a pronounced tail.

Even though the above methods for finding the maximum sampling interval and the minimum sampling time are exact and clearly defined, they may be difficult to evaluate. An approximate method for calculating the maximum sampling interval is discussed in the section on digitization. Points on a base line separated by more than one half the autocorrelation width of the noise, T_c (Equation 22), are effectively independent; therefore points more than one half the autocorrelation width plus four peak widths (standard deviations) from the retention time of a peak should contain little information about the peak. Hence, a reasonable approximation of T_I is $(8\sigma+T_c)$.

CHAPTER 2

EXPERIMENTAL

Many computer-based methods for the reduction of chromatographic data are designed for the computer rather than for the chromatographic system. Most computer methods are designed to meet the limitations of data storage, time, and cost, or to handle data from several chromatographs simultaneously. These methods have an important role in the automation of routine analyses; nevertheless, if all the information in a chromatogram is to be used to obtain the most precise measurements, a method designed for the chromatogram is required. In research applications and in some routine applications the information contained in a chromatogram about a peak may be a more important consideration than the cost of extracting the information. The *maximum posterior probability* (MP) method, described in Chapter 1, is suited to such applications because it utilizes as much of the available information as possible for the estimation of peak parameters. In this chapter the MP method is applied to the estimation of peaks obtained from an isothermal gas-chromatographic system with a thermal conductivity detector. Isolated peaks are considered primarily, though in limited circumstances the method is useful for the detection of small peaks under a larger peak.

In the MP method the most probable values of the parameters of a peak model are taken to be the estimates of the parameters of an experimentally observed peak. The probabilities of different values of the parameters are derived from a probability-density function (p.d.f.) called the *posterior* p.d.f. of the parameters. Once the posterior p.d.f. has been obtained, the determination of the values of the parameter estimates is a purely numerical problem. The mathematical details of the method used by the authors are given in the Appendix.

The posterior p.d.f. contains all the available information about the parameters of a peak. The MP estimates and the minimum mean-square errors calculated from the posterior p.d.f. together contain nearly all the available information in that they approximately specify the posterior p.d.f. The square root of the minimum mean-square errors, here called the *predicted standard deviations*, are approximate standard deviations of the parameters due to base-line noise alone. These and the *information matrix*, which provides a quantitative measure of information, are defined in the Appendix.

The posterior p.d.f. is proportional to the product of two p.d.f.'s (Equation A-1, Appendix). One is the p.d.f. of the parameters given the data, which contains the information in the experimental observations about the parameters. The other is the *prior* p.d.f. of the parameters, which contains information about the parameters available from previous experience. The p.d.f. of the parameters given the data reflects the effect of the randomness of the data on the apparent values of the parameters. The derivation of this p.d.f. requires clearly and carefully defined models for the randomness of the data, for the peak as a function of the parameters to be estimated, and for the relation between the peak model and the data (see Appendix I). These models may be called the *a priori* information about the system because they are not based on direct experimental evidence. In contrast to the *a priori* information, that contained in the prior p.d.f. of the parameters may be obtained from direct observation. In this study, prior information is unavailable, and therefore a prior p.d.f. is chosen that is the least informative of all possible p.d.f.'s. *A priori* information about a chromatographic system is obtained by a process of induction from other systems that the experimenter believes are similar to the system under study.

Since *a priori* assumptions may be incorrect for particular experiments, the results may not be valid descriptions of reality. Nevertheless, the results will be self-consistent with respect to the *a priori* information, and independent checks to confirm the reality of the models being used can be made after the experiment has been carried out.

For the purpose of obtaining all the information in a chromatogram about a peak, the mathematical form of the model for the peak is unimportant. The primary consideration is that the peak model must specify the actual peak as completely as possible. The peak model used here (Edgeworth's form of the Gram-Charlier type-A series) is based on the Gaussian function. The choice of the parameters used to indicate deviations of the peak shape from the Gaussian form also is unimportant. The shape parameters used here are *standardized cumulants*. (The word *standardized* is usually omitted.) Cumulants, though related to moments, are mathematically more simple and for this reason are preferred. The parameters are represented by the symbols

A for peak area, t_0 for retention time (mean), σ for peak width (standard deviation), and K_3 to K_6 for the cumulants.

In the model for base-line noise the average behavior of base-line noise is completely characterized by an *autocovariance function*, the Fourier transform of which is a *power-density spectrum*. It is assumed that the noise has a normal p.d.f. It is also assumed that the power-density spectrum is independent of time (*stationary*) so that the spectrum can be estimated from a section of base line without a peak. Although the estimate of the power-density spectrum may be considered prior information about the chromatographic system, the assumption that the estimate is stationary and is an accurate description of the noise during the elution of a peak is *a priori* information. Only noise that adds to the chromatographic signal is considered in the estimation of peak parameters. Multiplicative noise or noise with a variance that increases with increasing signal smplitude was studied and found to be negligible in the chromatographic system examined.

In practice, base-line noise is not the only cause of variation in the values of estimated parameters. Fluctuations in the carrier-gas flow rate and the column temperature cause variations that may be larger than those caused by base-line noise. For the purpose of testing the MP estimator a chromatographic system is required in which only base-line noise affects the estimates of the parameters. Moreover, the true values of the parameters must be known to detect bias. A system satisfying these requirements to a degree that can show the influence of the estimator itself on highly precise results may be difficult to construct. Such a system, however, can be simulated by placing peaks generated by a computer with known values of parameters onto sections of actual base-line noise. Although the simulated chromatograms can be used to test the MP estimator under the *a priori* assumptions, they cannot be used to test the applicability of the *a priori* assumptions to reality; for this, actual peaks must be analyzed.

In summary, the application of the MP method to a specific chromatographic system consists of the following steps.

1. Characterize the random part of the data. Choose a model, determine the values of the parameters of the model (here we determine the power-density spectrum), and then test the applicability of the model (for stationarity, normality, etc.).
2. State the mathematical model of the peak(s).
3. State the prior information about the parameters of the peak in the form of a p.d.f.
4. Write computer programs and test them with computer generated peaks.
5. Analyze actual chromatograms.
6. Study the results to check the applicability of the models and the adequacy of the digitization of the data in steps 1 and 5 (quantization level, sampling interval, and sampling time).

In the material that follows, presented in three separate parts, base-line noise is studied through power-density spectra, the MP estimator itself is tested through the use of computer-generated peaks on actual base-line noise, and the MP method is applied to actual chromatographic peaks. The assumptions made, and the mathematical details of the peak model and the computation method used are presented in Appendix I.

EXPERIMENTAL

Chromatograms were digitized by taking *interval-area samples* (defined in Chapter 1). An Aerograph Digital Integrator Model 471-42 operated in the manual integrate mode was used for this purpose. The interval areas were printed on paper tape and manually transferred to punched cards. The remote readout terminals were connected to an Adjustable Time Delay (Potter and Brumfield, Model CHD) through a 100-ohm resistor and a 0.02-MFD capacitor as in Figure 4.

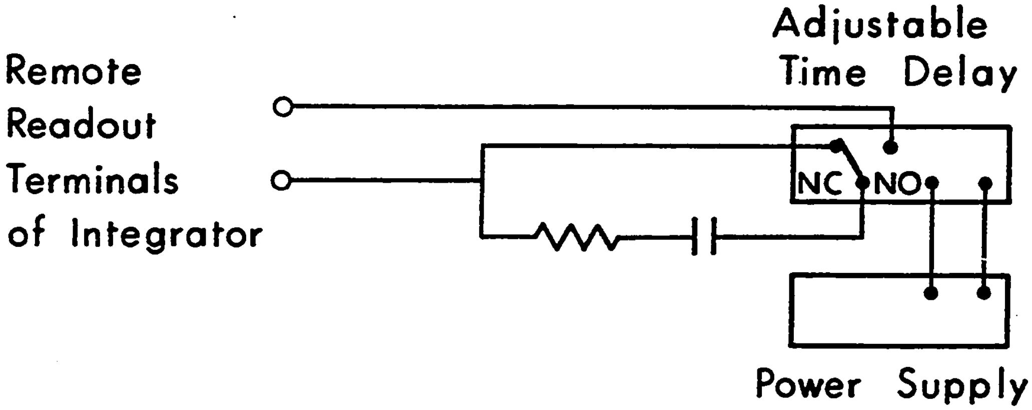

Figure 4. Schematic wiring diagram of circuit used to obtain interval-area samples of detector signal.

The capacitor limited the integration dead time to less than 60 μsec as measured with an oscilloscope. A Gow Mac Model 9999-C Power Supply provided constant voltage for the Adjustable Time Delay. The sensitivity of the integrator was specified to be 2.5×10^{-7} volt sec/count. The sampling interval was measured independently for each chromatographic run by dividing the elapsed time, as indicated by the integrator's internal clock (line-frequency synchronous), by the total number of samples taken. Drift in the sampling interval over a 14-hr period was less than 0.1% .

The thermal conductivity cell was a Gow Mac Model 9285 semi-diffusion pretzel cell with type-W tungsten filaments mounted in a TR IIB temperature-regulated case. A Gow Mac Model 9999-C Power Supply supplied bridge current. A two-diaphram pressure regulator supplied helium carrier gas at 50 psig. Sections of thermometer capillary along with a needle valve controlled the flow of helium through the sample and reference sides of the detector separately. The flows were adjusted to 40 ml/min by use of a soap-bubble flowmeter. Sample of 1 μl of liquid plus 1 μl of air were injected on-column with a Hamilton 10-μl syringe having a Chaney Adapter.

Most of the data were obtained with a 4-m, 0.31-cm i.d., copper column packed with 10% SE-30 on 60 to 80 mesh Chromosorb P. The column temperature was held at 80.10°C to within an estimated 0.05°C in a Colora water-bath thermostat. The temperature of the thermal conductivity cell was set at approximately 120°C with a variable voltage transformer rather than the internal temperature controller. The pressure drop across the column was 139 cm Hg, barometric pressure varied between 68.7 and 69.1 cm Hg, detector current was 250 ma, and the sampling interval was 1.504 ± 0.002 sec.

The following digital filter (the necessity for filtering the data is discussed in Chapter 1) was used for both minimizing the sampling end-point errors and for whitening base-line noise for estimation of power-density spectra:

$$h(z) = \delta(z) - [\delta(z-1)+\delta(z+1)]/2 \tag{88}$$

where δ represents a delta function and z represents reduced time in units of the sampling interval, Δt . The first and the last data samples were given the value zero after filtering. The filtered data were corrected for both the filtering and the distortion caused by interval-area sampling by multiplying the Fourier transform of the filtered data by $(\pi s)/[2 \sin(\pi s)]^3$, where s is reduced frequency. The corrected Fourier transform of the data at zero frequency was defined to be zero because the mean of the base-line noise, being arbitrary, causes the power-density of the noise at zero frequency to be extremely large.

POWER-DENSITY SPECTRA

Curve A in Figure 5 is an estimate of the power-density spectrum of the base-line noise for the gas-chromatographic system described above. The estimate was obtained from five base-line sections of 512 interval-area samples each. The sections were taken between chromatographic runs over a period of 14 hr. The five separate estimates of the power-density spectrum were averaged; the averaging process smooths the estimate and is equivalent to convolution with a Bartlett spectral window (34). A Hanning spectral window used for further smoothing is described by

$$W(s) = \delta(s)/2 + [\delta(s-1/N)+\delta(s+1/N)]/4 \qquad (89)$$

where N is the number of data samples. The power-density spectrum of the base-line noise after filtering (Equation 88), but before smoothing and correcting, was not flat, but decreased slightly at low frequencies. The filter did not give a completely flat spectrum, and smoothing this uncorrected spectrum caused a positive bias at low frequencies. Nevertheless, the error is not so large as the negative bias that would be introduced if the spectrum were smoothed after correcting for filtering. The *power* (total variance) of the noise was 17 μv^2 and the *autocorrelation width* 242 sec. The power of the individual sections of base line ranged from 0.4 to 55 μv^2, and the autocorrelation widths ranged from 115 to 243 sec. The variation in the power is a measure of the degree of nonstationarity in the system. The observed variation was much greater than would be expected of a stationary process. Nearly all the variation occurred

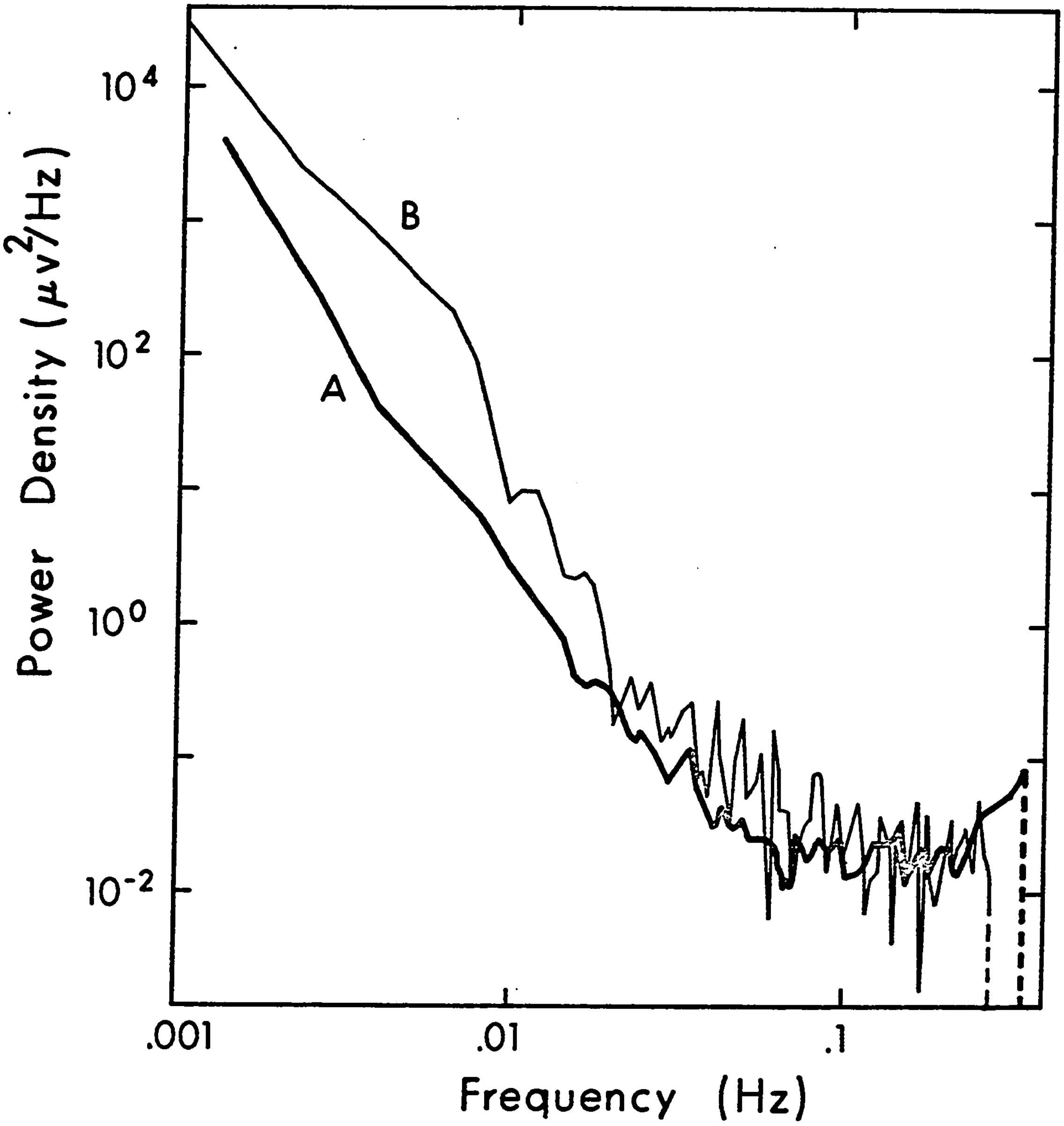

Figure 5. Power-density spectra of base-line noise from a thermal conductivity detector. The dashed lines indicate the Nyquist frequencies, which are 0.33 Hz for A and 0.28 Hz for B .

at the lowest frequencies (0.001 to 0.004 Hz). Tests with computer-generated peaks (discussed in detail below) show that these large variations in power have little effect on MP estimates of peak parameters.

Curve B in Figure 5 is the estimate of a power-density spectrum obtained for base-line noise with the automatic temperature controller of the detector in operation. The controller introduced an oscillation in the base line with an amplitude of about 10 μv peak to peak. The oscillation accounts for the slight shoulder on curve B at about 0.005 Hz, which corresponds to the cycle frequency of the controller. The power and the autocorrelation width of curve B is 110 μv^2 and 280 sec. Curve B is less smooth than curve A in Figure 5 because it was derived from only one section of 512 samples instead of five as for curve A.

The base-line noise of the gas-chromatographic system (curve A in Figure 5) is characterized by intense noise at low frequencies. Above 0.02 Hz the noise is much less intense and is essentially white. The white part of the spectrum has an average power density of 0.017 $\mu v^2/Hz$. About 25% of the white noise component is caused by quantization which is a noninstrumental source of noise. The remaining instrumental white noise has an average power-density of 0.012 $\mu v^2/Hz$; the primary sources of this noise are probably the amplifier of the integrator and the power supply of the detector. The relatively large proportion of quantization noise could be decreased by either amplifying the detector signal or reducing the quantization interval.

Interval-area sampling attenuates the noise at frequencies above the *Nyquist sampling frequency* [$1/(2\Delta t)$, where Δt is the sampling interval], but just above and less than twice the Nyquist frequency there is little attenuation (Figure 3, I). Sampling causes the power density of the noise in this region to overlap the power density just below the Nyquist frequency (Figure 3, VI). The overlap accounts for part of the upturn of spectrum A as the Nyquist frequency is approached, because the instrumental white-noise component probably extends through the region where overlap occurs. The remainder of the upturn is caused by the application of the correction for distortion due to interval-area sampling to quantization noise. Quantization noise is introduced after sampling and therefore does not require correction, but it cannot be separated from base-line noise, which does require correction.

The random variation of the sampling interval (*jitter*) was measured by taking a number of sets of noise data with the zero-offset control of the detector bridge adjusted to give average outputs ranging from 0 to 30 mv. The power density, averaged over twenty points nearest the Nyquist frequency and nearest one half of the Nyquist frequency, when plotted against the square of the signal average, gave two straight lines with little scatter. The slopes of the lines were substituted in the equation for jitter noise (Equation 41) and the equation for noise due to variation in integration dead time to give 40 μsec as the standard deviation of jitter, and 90 μsec as the standard deviation of the variation in integration dead time. The result for jitter is reasonable and probably accurate, but the result for variation in dead-time is larger than the integration dead-time itself. This violates the assumption made in the derivation of the effects of variation in integration dead time so the value 90 μsec is not an accurate estimate of the true value. A result this high could occur if the p.d.f. of the variations was non-normal, but more likely was caused by a noise source other than variation in integration dead time that also has a white power-density spectrum that increases with the amplitude of the detector signal. The noise from the integrator amplifier undoubtedly increases to some extent with increasing level of input signal. The power density of the noise at low frequencies also increased with signal level, but not so regularly and not at the same rate as at high frequencies. Further runs with a well insulated mercury cell and a voltage divider as a signal source showed conclusively that an important part of the power density of the noise at low frequencies was from the integrator amplifier (see Table VIII).

ESTIMATOR EVALUATION

The estimation method was tested by adding computer-generated peaks with known parameter values to the sections of base-line noise used for estimating the power-density spectra. Other than round-off errors in the computer-generated peaks (which were negligible) and numerical errors in the estimation process (see Appendix II), the base-line noise was the only source of error in the analysis of these simulated chromatograms. The computer-generated peaks were not interval-area sampled, hence the sections of base-line noise and the power-density spectra were not corrected for interval-area sampling. This means that the average characteristics of the base-line noise of the system being tested are slightly different from those of the experimental system. The difference is small (the correction for interval-area sampling is relatively small), however, and since the MP method is independent of the type of noise (as long as an accurate power-density spectrum is used), the results of the test will be valid for the experimental system. The retention times of the computer-generated peaks were taken from a set of pseudo-random real (nonintegral) numbers with a uniform p.d.f. The estimated parameter values were compared with the true values through the use of Student's t . Bias was considered significant when the 90% confidence interval about the observed value of Student's t did not include the value zero. The variances of the estimates were compared by use of the *efficiency*, which is the ratio of the predicted to observed variance. The predicted variance, obtained from the Cramér-Rao inequality (Equation 69), is the smallest possible variance of any estimator.

The predicted standard deviations in Figure 6 are square roots of the averages of the predicted variances for each parameter, calculated for each set of peaks. The relative standard deviation of area and the absolute standard deviations of the other parameters are approximately inversely proportional to peak area over the range 10^3 to 10^6 counts. This range would correspond to about 0.0003 to 0.3 μl of normal octane. For areas or amounts greater than this range the curves in Figure 6 should continue as straight lines. Therefore, when base-line noise is the only source of error, results as precise as desired could be obtained by increasing peak area.

Table I gives the actual performance of the MP estimator for peaks similar to normal octane. Many of the efficiencies are significantly greater than one. Theoretically the efficiency of an estimator cannot be greater than one, but an experimentally measured efficiency can be greater than one for two reasons. The first is the randomness of both the observed variance and the expected variance. The variance of the observed variance is approximately inversely proportional to the number of experimental runs. Because the peak model is nonlinear, the predicted variance of a parameter depends on the values of all the parameters and will vary as the parameter estimates vary. When the total information about the parameters is reasonably large, however, the variation of the predicted variance should be negligible in comparison with the variation or variance of the observed variance. From the ten runs furnishing the data for peak area in Figure 6, the relative standard deviation of the predicted

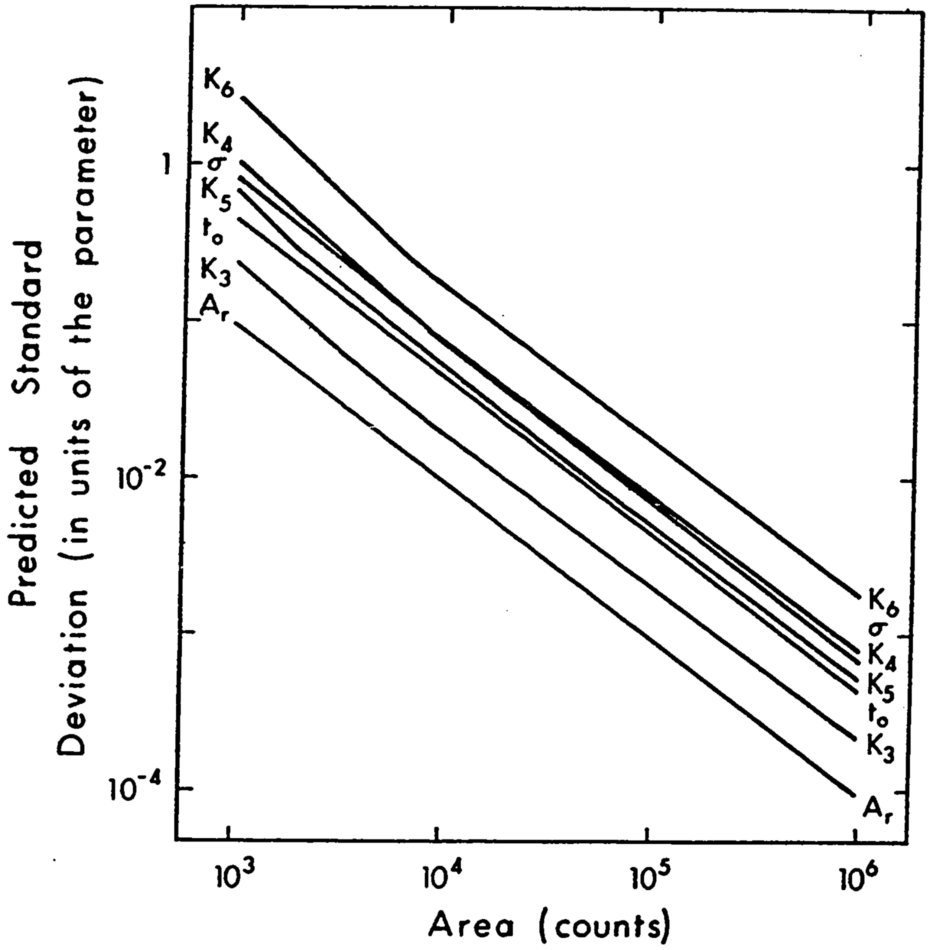

Figure 6. Variation of predicted standard deviation with peak area. Except for area, the parameters of the peaks have values similar to those of normal octane in Table IV. Area is in units of integrator counts; 10^3 units correspond to about 0.03% of a 1 μl sample. The standard deviations of area, A_r, are relative, and those of t_0 and σ are in units of the sampling interval. The power-density spectrum is that of curve A in Figure 5.

TABLE I

Effect of Peak Area on MP Estimator Performance[a]

Efficiency (ε)[b]

Area	10^3	10^4	10^5	10^6
A	4.4	1.6	2.4	1.7
t_0	5.7	2.2	3.0	4.1
σ	8.1	2.6	2.3	2.0
K_3	3.7	2.1	1.7	2.4
K_4	1.4	5.0	2.9	2.5
K_5	6.2	2.9	1.5	2.7
K_6	9.3	10.	5.8	2.8

Bias (Student's t)[c]

Area	10^3	10^4	10^5	10^6
A	-1.5	-0.1	1.2	1.0
t_0	-1.0	-0.7	0.1	0.6
σ	-1.2	0.5	1.3	1.4
K_3	-0.6	-0.2	0.2	0.8
K_4	-0.1	1.0	1.4	2.1
K_5	-0.8	0.1	0.2	0.5
K_6	1.5	1.6	2.0	2.6

[a] Ten computer generated peaks were evaluated for each area. The peak parameters are as in Figure 6.

[b] The 90% confidence interval for ε is $0.53\varepsilon_0 < \varepsilon < 2.7\varepsilon_0$, where ε_0 is the observed efficiency.

[c] The 90% confidence interval is $t \pm 1.8$.

variance was 10% at 10^3 and 0.01% at 10^6 area units. The approximate relative standard deviation for an observed variance, on the other hand, is $\sqrt{2/n}$ where n is the number or runs, or 45% for ten runs. Confidence intervals for the estimated efficiency, which is a ratio of variances, were calculated by use of Fisher's F distribution. The predicted variance in the numerator of the efficiency ratio was assumed to have an infinite number of degrees of freedom.

The second cause of an estimated efficiency greater than one is inaccuracy in the power-density spectrum. For example, if the spectrum is mutliplied by a constant, the predicted variance, and therefore the efficiency, will be proportional to the constant; the observed variance, however, will not change. The positive bias at low frequencies of the estimate of the power-density spectrum probably is the major cause of the efficiencies in Table I being greater than one. The error in the power-density spectrum should not have serious consequences; it should have little effect on bias of the parameters (except possibly for extremely broad peaks, discussed below) and merely make the predicted standard deviations slightly conservative. The efficiencies still can be used to detect trends in the performance of the MP estimator.

Effect of Peak Area

Contrary to the theoretical prediction in Chapter 1, Table I shows that as peak area and information increased, efficiency seemed to decrease and bias to increase. (The amount of information about a parameter is roughly equal to the inverse square of the predicted standard deviation.) In view of the randomness of efficiency and bias these variations may be coincidental. The steady change in bias from negative to positive, and the less pronounced decrease in efficiency with increasing area is probably the result of numerical errors in the estimation process rather than a property of the MP estimator itself. As the amount of information increases, the demand for numerical accuracy also increases. But all the data in Tables I, II, and III were obtained with approximately the same numerical accuracy in that the probability of the estimates was close to the probability of the most probable values of the parameters (same termination constant, see Appendix II). A better procedure might be to vary the termination constant with the amount of information so the numerical accuracy can increase as the information increases.

Effect of Peak Width

Again contrary to the predicted trend, Table II shows that efficiency generally seems to decrease as peak width decreases and as information increases. The cause of the disagreement with theory is probably the positive bias in the estimate of the power-density spectrum at low frequencies. As peak width increases, the information for all the parameters concentrates at low frequencies. Thus, the information matrix, and consequently the predicted variances, for wide peaks will be influenced more than for narrow peaks by the bias in the power-density spectrum. The decrease in apparent efficiency with increasing peak width is caused by a determinate error in the predicted variances; whereas for increasing peak area the decrease in apparent

TABLE II

Effect of Peak Width on MP Estimator[a]

	A_r			t_0			σ		
σ	s.d.[b] (x10^3)	ε[c]	t[d]	s.d.	ε	t	s.d.	ε	t
2.0	0.16	0.6	0.1	0.00027	0.8	1.2	0.00045	0.5	-0.2
4.0	0.72	0.3	-1.4	0.0017	1.2	-0.5	0.0034	0.6	-1.3
10.0	7.6	0.8	-0.6	0.038	0.3	0.3	0.067	1.1	-0.2
16.0	22.	0.4	-1.4	0.23	23.	-7.0	0.29	13.	-0.3
25.0	59.	3.4	-0.8	1.1	1.4	-0.3	1.7	1.9	-0.2

[a] Five runs were made for each value of σ (in units of the sampling interval). The true peak area was 10^5 integrator counts, and the true values of all the cumulants were zero. The noise used to give curve B in Figure 5 was used for a base line.

[b] Relative square root of average expected variance.

[c] The 90% confidence interval is $0.42\varepsilon_0 < \varepsilon < 5.6\varepsilon_0$.

[d] The 90% confidence interval is $t \pm 2.1$.

efficiency is caused by a determinate error in the observed variances.

As the total amount of information about a peak decreases, the posterior p.d.f. flattens and eventually more than one maximum may appear. The base-line noise may form peak-like curves, which will appear as maxima in the posterior p.d.f. and will be especially evident along the retention-time axis. Predicted variances, which depend on the curvature of the posterior p.d.f. near the absolute maximum, are accurate only when the posterior p.d.f. is normal. A posterior p.d.f. with multiple maxima is definitely not normal, and the actual variances will be greater than predicted. Therefore, as information decreases and the detection limit is approached, efficiency should decrease, though the decrease does not begin within the ranges of area and peak width in Tables I and II.

Although the bias of most of the parameters in Table I is insignificant, there seems to be a general trend of increasing bias with increasing order of the parameters, which might be expected because of the increasing nonlinearity of the high-order parameters. If the test for bias were based on the predicted rather than the observed variance, the bias of all the parameters would be significant because the efficiencies are all greater than one. In Table II the bias appears to be independent of the peak width.

Number of Data Points

The effect of the number of data points used in the estimation on bias and efficiency is shown in Table III. Evidently, the rule of thumb derived in Chapter 1 (the number of data points that

TABLE III

Effect of Number of Data Points on MP Estimator[a]

$\sigma = 2.0, \quad T_I = 169$[b]

		A_r		t_0		σ	
N	Q	ε	t	ε	t	ε	t
512	454	0.6	0.1	0.8	1.2	0.5	-1.7
100	124	0.5	-0.1	0.4	1.3	0.4	-0.2
50	57	0.3	0.0	0.4	1.3	0.3	-0.1
s.d.	=	0.00016		0.00027		0.00045	

$\sigma = 4.0, \quad T_I = 177$

512	457	0.3	-1.4	1.2	-0.5	0.6	-1.4
150	147	0.3	-1.5	0.5	1.5	0.7	-1.6
100	123	0.4	-1.7	0.5	0.2	0.6	-1.7
60	66	0.3	-1.3	0.4	0.3	0.6	-1.3
s.d.	=	0.00072		0.0017		0.0034	

$\sigma = 10.0, \quad T_I = 233$

512	457	0.8	-0.6	0.3	0.3	1.1	-0.2
200	186	1.1	0.2	0.4	0.6	1.4	0.4
100	110	0.8	-0.1	0.5	-0.2	1.2	0.2
s.d.	=	0.0076		0.038		0.067	

[a] Five runs were made for each value of N (number of data points used in the estimation). Same conditions as for Table II.

[b] $T_I = 8\sigma + T_c$, where T_c is the autocorrelation width of the noise.

cover eight peak standard deviations plus the autocorrelation width of the noise) gives an adequate number of points for the noise studied. Half that number decreases the efficiency for any of the parameters by no more than 50%. Bias seems to stay constant as the number of points decreases, but since the efficiency decreases (because the observed variance increases), the value of the bias in units of the parameters actually increases. The *sum of weighted squared deviations*, represented by the symbol Q in Table III, should theoretically be nine less than the number of points, N (see Appendix I). A constant difference between Q and N as N decreases could be explained by bias in the estimate of the power-density spectrum. The actual value of Q decreases more slowly than N in Table III, probably because of end effects arising from the chromatographic signal being nonzero near the ends of the interval over which samples were taken.

Effect of Nonstationary Noise

Nonstationarity was examined by analyzing sets of five to ten computer-generated peaks added to the lowest- and highest-power base-line sections used to obtain curve A in Figure II. The two sections were taken about six hours apart. The efficiencies were usually greater by a factor of two on the low-power noise than on the high-power noise for peak widths ranging from ten to twenty sampling-interval units, but there was no consistent difference in bias. Even though the power of the high-noise section was more than 100 times the power of the low-noise section, the values of Q were not greatly different: 520 and 420. The power of noise, therefore, is a poor indicator of the effect of the noise on parameter estimates.

Moreover, the nonstationarity encountered did not seriously affect the estimation process.

CHROMATOGRAPHIC PEAKS

In this section results obtained from actual chromatographic peaks are presented. No effort was made to optimize the performance of the chromatographic system. The column was designed only to give peaks broad enough to minimize sampling errors with the integrator-sampling system operated at the maximum practical sampling rate. Tables IV, V, and VI summarize the results of measurements of two hydrocarbon mixtures. One mixture contained about 3.6% by weight of each of normal heptance, 2,3,4-trimethylpentane, and normal octane. The other mixture contained about 4% of each of normal heptane, toluene, and normal octane. The solvent was 2-methylpentane.

TABLE IV

Means of Peak Parameters

	A_r[a]	t_0[b,c]	σ[c]	K_3	K_4	K_5	K_6
Normal heptane	1.025	262.6	3.89	0.107	0.08	0.15	0.14
Normal octane	1.016	545.9	7.24	0.067	0.04	0.23	0.03
2,3,4-trimethylpentane	.919	391.7	5.42	0.045	0.04	0.16	0.08
Toluene	.919	413.8	5.88	0.464	0.40	0.21	0.52

[a] Relative area response per gram.
Areas were normalized, divided by the weight of the component, then averaged (not relative to any particular compound).

[b] Net retention time.

[c] In units of the sampling interval.

TABLE V

Standard Deviations of Peak Parameters

	Number of Peaks		A_r (x10^3)	t_0	σ	K_3	K_4	K_5	K_6
Normal heptane	16	Obs.[d]	2.4[a]	1.4	0.035	0.010	0.032	0.036	0.12
		Pred.	0.4[b]	0.0007[c]	0.0012	0.0007	0.0024	0.0019	0.007
Normal octane	16	Obs.	3.1	2.9	0.053	0.016	0.027	0.048	0.09
		Pred.	0.6	0.0038	0.0066	0.0018	0.0064	0.0044	0.016
2,3,4-tri-methylpentane	11	Obs.	1.5	2.0	0.038	0.010	0.028	0.038	0.12
		Pred.	0.5	0.0018	0.0031	0.0012	0.0044	0.0032	0.011
Toluene	5	Obs.	2.7	2.0	0.026	0.006	0.028	0.028	0.06
		Pred.	0.4	0.0016	0.0026	0.0010	0.0021	0.0018	0.005

[a] Relative standard deviation of relative response per gram.

[b] Includes the theoretical contribution from all peaks used in normalization.

[c] Predicted standard deviation of net retention time, includes contribution from air peak

[d] Upper number is the observed standard deviation, lower number is the median of the predicted standard deviations.

TABLE VI

Correlation Between Parameter Deviations

Normal Heptane

	t_0	σ	K_3	K_4	K_5	K_6	
A	-0.1	-0.3	-0.5	0.4	-0.6	0.5	Obs.[a]
	0.0	0.9	-0.1	0.8	-0.1	0.6	Prd.
t_0		0.7	0.4	0.2	0.3	0.1	Obs.
		0.0	0.9	0.0	0.8	0.0	Prd.
σ			0.4	0.4	0.4	0.3	Obs.
			-0.1	0.95	-0.2	0.8	Prd.
K_3				-0.1	0.93	-0.2	Obs.
				-0.1	0.94	-0.1	Prd.
K_4					-0.2	0.98	Obs.
					-0.1	0.96	Prd.
K_5						-0.3	Obs.
						-0.1	Prd.

[a] In each pair of entries the upper number is the observed correlation, and the lower is the median of the predicted correlation. For 16 determinations, the 90% confidence interval for the true correlation coefficient is ± 0.44 and 0.70-0.96 when the observed correlation is zero and 0.9 .

TABLE VI (Continued)

Normal Octane

	t_0	σ	K_3	K_4	K_5	K_6	
A	0.1	0.6	-0.4	0.4	-0.1	0.0	Obs.
	0.0	0.9	-0.1	0.8	-0.3	0.7	Prd.
t_0		0.8	0.0	0.4	-0.3	0.4	Obs.
		0.0	0.9	0.0	0.7	0.0	Prd.
σ			-0.1	0.7	-0.2	0.4	Obs.
			-0.1	0.96	-0.3	0.9	Prd.
K_3				0.0	0.8	0.4	Obs.
				-0.1	0.93	-0.1	Prd.
K_4					0.0	0.8	Obs.
					-0.3	0.96	Prd.
K_5						0.2	Obs.
						-0.3	Prd.

Standard Deviations

The observed standard deviations in Table V are all greater than those predicted. The low efficiency could not have been caused by the efficiency inherent in the MP estimator because the efficiency obtained for computer-generated peaks was generally greater than one. The predicted standard deviations account for the effect of base-line noise only; the low efficiency must be the result of non-base-line noise caused by fluctuations in flow rate and pressure of the carrier gas, temperature of the detector cell and the column, etc.

The observed and predicted standard deviations for relative normalized area agreed with a factor of 3 to 6. In spite of the crude chromatographic system, the standard deviations were low by usual criteria. With an apparatus designed to control non-base-line noise, Goedert and Guiochon (12) attained a relative standard deviation of only 0.6×10^{-3} for a peak with roughly the same width but twenty times the area, in absolute units, of the normal heptane peak described in Table IV. The predicted standard deviations for relative normalized area were calculated from the predicted standard deviations of the individual area measurements*.

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*Let A_1 be the area of the component of interest and $A_2, A_3, \ldots, A_n$ be the areas of the other components. The normalized area is

$$A_1' = A_1/S \tag{90}$$

where $S = \sum_{j=1}^{n} A_j$. The square of the standard deviation of the normalized area is

$$(\Delta A_1')^2 = [(S'\Delta A_1)^2 + A_1^2 \sum_{j=2}^{n} (\Delta A_j)^2]/S^4 \tag{91}$$

where $S' = \sum_{j=2}^{n} A_j$ and ΔA_j is the standard deviation of component j. The areas are assumed to be statistically independent and this will apply when the peaks are far enough apart so the information functions for areas do not overlap in the time domain.

The observed relative standard deviations are greater for absolute area (34×10^{-3} for normal heptane) than for normalized area because of the sample-injection technique.

The observed standard deviations for retention time in Table V are about 1000 times those predicted, probably because of low-frequency fluctuations of the carrier-gas flow rate and the column temperature. Low-frequency fluctuations should not affect relative retention-time or retention-index measurements as much as absolute retention-time measurements. The mean, observed standard deviation, and predicted standard deviation for the retention index of 2,3,4-trimethylpentane were 754.61, 0.022, and 0.0019; for toluene these were 762.66, 0.026, and 0.0018. The observed standard deviations for retention index were indeed only ten times the predicted values. Precision estimates are seldom included in published retention-index data. Retention indices are usually reported to the nearest whole number and seldom to the nearest tenth (34). Precise measurements of retention indices may not be necessary because absolute retention indices are difficult to reproduce on different columns. Nevertheless, precise values are needed to compare the retention indices of different compounds on the same column and to measure the rate of change of retention index with column temperature. The highly precise estimates of retention time obtainable by the method presented here should be valuable for these purposes.

The predicted standard deviations for the retention indices reported above include the contribution from the predicted standard deviation of the retention time of the air peak*. Although the air peaks were too narrow (σ equal to 1.0 sampling-interval units) to obtain a good fit, the MP estimates of the air-peak retention times were used in the retention-index calculations. The derivative with respect to retention time of the function M, which is used to obtain the MP estimates (see Appendix II), is antisymmetric in the frequency domain, whereas the overlap error in the frequency domain

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*Let t_a, t_n, t_x, t_{n+1} be the retention times, and Δt_a, Δt_n, Δt_x, Δt_{n+1} be the standard deviations of the retention times of air, the n'th normal hydrocarbon, compound x , and the n+1'th normal hydrocarbon. The retention index of compound x is then

$$I_{Tx} = 100n + 100N/D \tag{92}$$

where

$$N = \log(t_x - t_a) - \log(t_n - t_a)$$

and

$$D = \log(t_{n+1} - t_a) - \log(t_n - t_a)$$

The square of the standard deviation of the retention index is

$$(\Delta I_{Tx})^2 \simeq \frac{100^2}{D^4} \{ (\frac{D\, \Delta t_x}{t_x - t_a})^2 + (\frac{N\, \Delta t_{n+1}}{t_{n+1} - t_a})^2 + [\frac{(N-D)\Delta t_n}{t_n - t_a}]^2 + [(\frac{D}{t_x - t_a} - \frac{N}{t_{n+1} - t_a} + \frac{N-D}{t_n - t_a})\Delta t_a]^2 \} \tag{93}$$

Equation 93 gives the minimum variance derived from the Cramér-Rao inequality (Equation 69). Equation 92 is the definition of a retention index, but the direct substitution of retention-time estimates into the defining equation does not give an MP estimator of the retention index. Similarly, the definition of peak area is unrelated to the MP estimator of area. These remarks also apply to the estimates of relative normalized area discussed in the previous footnote, that is, the estimator of normalized area based on the definition of normalized area may not be the best estimator.

caused by the peak being too narrow is symmetric and should have little effect on the retention-time estimates of the air peaks. The *error curves* (the difference between observed and fitted peak, see Appendix I) for air peaks were indeed symmetric about the retention times, showing that the error in the fit was primarily in the area and width parameters. In any case, the effect of small errors on the retention time of the air peak is negligible in the retention index of peaks far from the air peak.

Base-line noise accounted for about 10% of the observed standard deviations for the peak width and the cumulant measurements. Part of the remaining variation may be due to noise that increased with signal amplitude; this noise would cause variations in peak shape that would not affect area and retention time so much as it would the higher-order parameters.

In Table VI, the observed correlations between parameter deviations from the mean were calculated by use of the Olkin and Pratt correction for bias (35). Most of the observed correlations agree with the predicted correlations within the 90% confidence interval. The correlations between errors in retention time and peak width, however, are consistently and significantly higher than the predicted values of zero. The high correlations are caused by the strong physical relation between retention time and peak width that was not included in the peak model. If this relation were known exactly, the retention-time and peak-width parameters could be replaced with a single parameter.

Low-frequency fluctuations in the flow rate of the carrier gas with a period longer than peak retention times would introduce a proportional error into the retention times of all the peaks in a chromatogram. The high positive correlation (greater than 0.97) found between deviations of retention times for all pairs of peaks on the same chromatogram confirmed the effect of extremely low-frequency flow fluctuations. Peak-width errors were affected less strongly; the correlations between errors in the widths of peaks on the same chromatogram were greater than 0.56 for all pairs of peaks. Cumulants were unaffected; the correlations between errors in the cumulants of different peaks were near zero.

The sum of weighted squared deviations, Q, for the peaks described in Table IV exceeded the expected values by 10 to 1000 times. Part of the excess deviation is due to the nonstationarity of the noise; the values of Q varied by a factor of 10 from run to run for the same component. The two major contributions to the large values of Q are incomplete agreement of the true peak shape with the peak model (poor fit) and interfering peaks (impurities that give small peaks near the peak of the principal compound). Interfering peaks will be discussed first.

Interfering Peaks

A typical error curve for toluene (Figure 7, I) shows what appears to be a single interfering peak with a maximum 3.7σ greater than that of the principal peak. The effects of interfering peaks on MP estimation were studied by adding principal and minor pairs of computer-generated peaks with similar parameters (except for area and

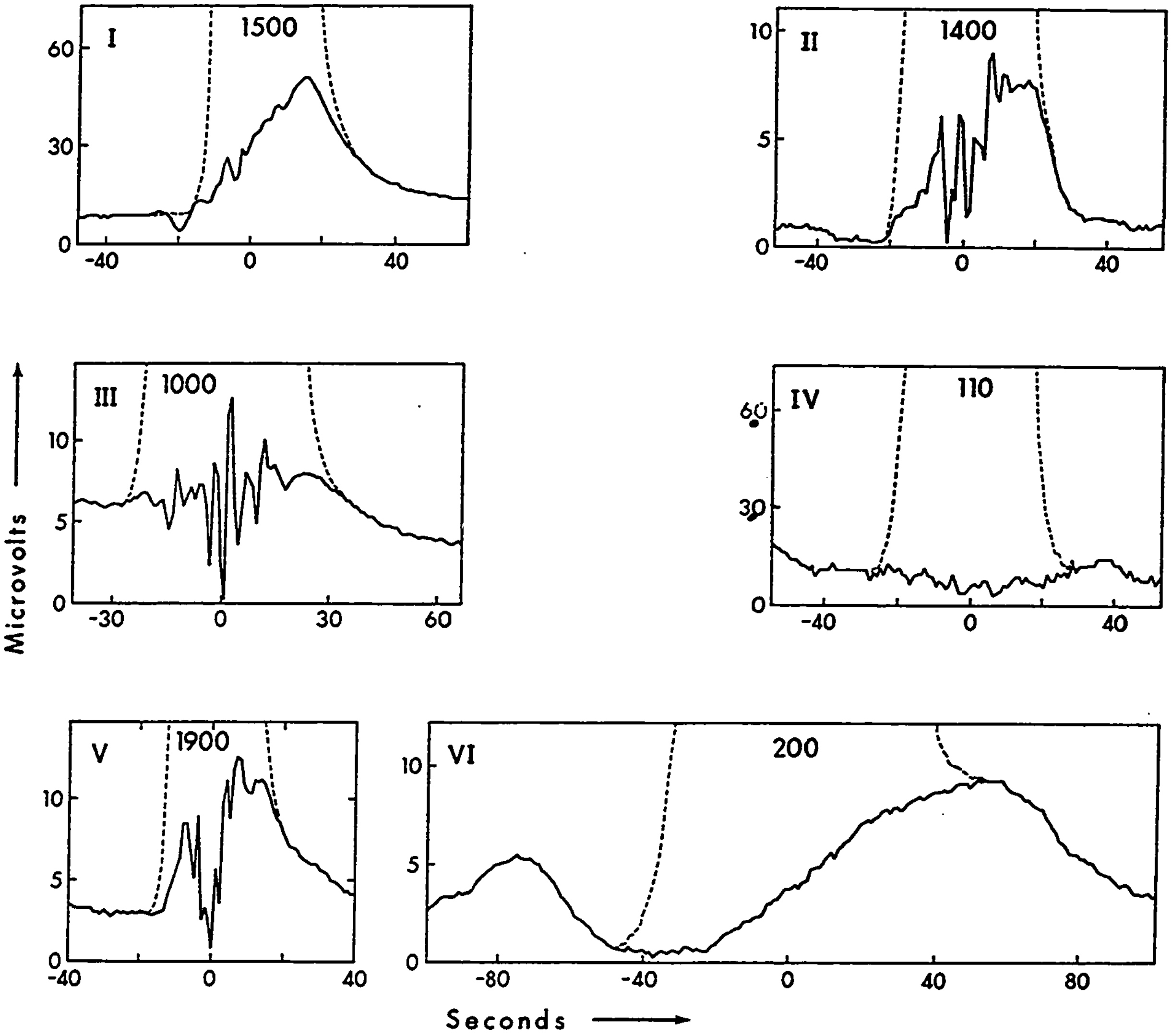

Figure 7. Error curves of chromatographic peaks. I, toluene; II, 2,3,4-trimethylpentane; III and IV, normal octane; V, normal heptane; VI, normal nonane with severe drift. The number at the top of each figure is the approximate height of the peak in microvolts. The dashed lines are the profiles of the peaks. The mean values of the parameters of the peaks in I, II, III, and V are given in Table IV.

retention time) to a section of base-line noise. Error curves similar to Figure 7, I were obtained with peaks comparable in size and shape to the toluene pair. The height of the peak on the error curve was found to be proportional to the true area of the interfering peak. Relative peak heights give the area of the interfering toluene peak, if it is a peak, as 2.7% of the area of the toluene peak. Similarly, the error curve for 2,3,4-trimethylpentane (Figure 7, II) shows an interfering peak that would be about 0.5% of the principal peak. The normal heptane peak appears to have two interfering components (Figure 7, V) of about 0.3% and 0.4% .

The effect of an interfering peak on Q can be calculated from the amount of information in the data about area (I_{11} , defined by Equation A-7 in the Appendix). The amount of information for area is the sum of weighted squared deviations of a peak with unit area from a constant zero base line. Therefore, the amount of area information for the toluene peak times the square of the area of the interfering peak should give a crude estimate of the contribution of Q of the interfering peak. The median value of Q for toluene was 4.4×10^4 , and the estimated contribution of the interfering peak is 4.0×10^4 . The values of Q obtained for computer-generated interfering peaks agreed with the estimated value within an order of magnitude. The agreement was not so good for heptane and 2,3,4-trimethylpentane, however. For these peaks the interfering peaks accounted for only 10% of the excess in the values of Q .

The detectability of interfering peaks was studied by running mixtures of 2,2,4-trimethylpentane (principal) and heptane (minor) diluted with 2,3,4-trimethylpentane. The concentration of 2,2,4-trimethylpentane was 3.6% by volume; the separation between the principal and minor components was (3.0 ± 0.4)σ (resolution 0.7 ± 0.1). The left part of Figure 8 shows the peaks as they appeared on a strip chart recorder. Where the concentration of normal heptane is 10% of that of 2,2,4-trimethylpentane, heptane appears as a slight elongation of the tail of the principal peak. Below 10% there is no visual indication of an interfering peak. With the use of error curves, however, an interfering peak is evident at 0.1% (not shown in Figure 8), and at 0.6% there is no doubt that an interfering peak is present. The use of error curves increases the detectability of an interfering peak by a factor of at least 10 in this case.

Relying on the detection of interfering peaks in the manner described above may be hazardous. If the peak model is too general, that is, if the parameters contain insufficient prior information, the peak model may fit multiple peaks as a single entity. A study of computer-generated peaks using up to the sixth cumulant in the peak model, revealed that an interfering peak could be fitted along with the principal peak (incorporated within the model) without leaving a trace of the interfering peak on the error curve. The factors influencing the incorporation of an interfering peak are the relative areas of the peaks, the difference between their retention times, and the total amount of information available about the principal peak. The information in the data about the principal peak depends on the shape and size of the peak relative to the power-density spectrum

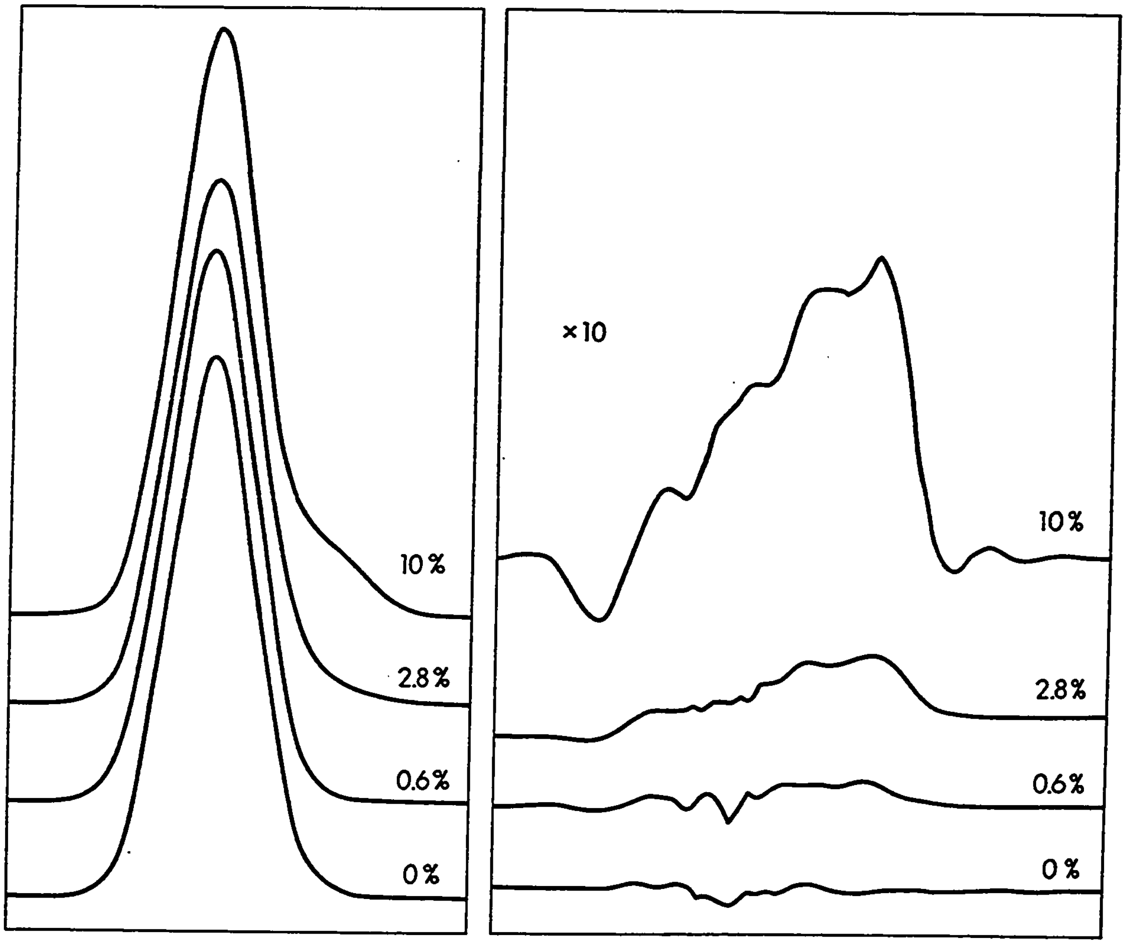

Figure 8. Detection of an interfering peak by use of chart recordings (left) and error curves (right). The percentage figures refer to the concentration of the interfering peak relative to the principal peak.

of the base-line noise. For example, the information about a peak decreases with increasing peak width. The interfering peaks in a set of computer-generated peaks were visible on the error curves when the peak widths were equal to 2 sampling-interval units, but were incorporated within the peak model and did not appear on the error curves when the peak widths were equal to 10 units. (The area of the principal peak was 10^6 integrator counts, the separation was 3σ (resolution 0.75), and the area of the minor peak was 0.1% of the area of the principal peak.) Although an error curve may not indicate an interfering peak when it is incorporated within the peak model, a peak that is incorporated will have a distinct effect on the values obtained for the cumulants. If the cumulants of the pure principal compound were known, an interfering peak could be detected by comparing the cumulants of the pure and the impure compounds. It would be just as well, though, to introduce the prior information about the pure compound directly into the peak model or into the prior p.d.f. of the cumulants.

When error curves of computer-generated peaks have the appearance of the error curve of toluene in Figure 7, I, all the parameter estimates have positive bias except area, which is slightly less than the true value. When the retention time of the interfering peak is less than that of the principal peak, giving an error curve the mirror image of Figure 7, I , the effect of the interfering peak on the even-order parameters is the same as when the retention time of the interfering peak is greater than that of the principal peak, whereas the odd-order parameters have negative bias. The values of the cumulants obtained for toluene are significantly greater than those of 2,3,4-trimethylpentane (Table IV). If the peak in the error curve for toluene were due to an interfering peak, the difference between the cumulants of toluene and 2,3,4-trimethylpentane could be attributed to the bias in the estimates of the cumulants of toluene due to the interfering peak.

Limitations of Peak Model

The above results on the detectability of interfering peaks are self-consistent and valid with respect to the *a priori* information. Nevertheless, attempts to isolate an impurity in toluene by fractional trapping were unsuccessful. The toluene did not contain an impurity with a concentration as high as 2.7% . Furthermore, error curves obtained for benzene were similar to those for toluene, and the benzene would be unlikely to have an impurity with the same relative area and retention as an impurity in toluene. The peaks on the error curves of benzene, toluene, and possibly normal heptane and 2,3,4-trimethylpentane were due to residuals that the peak model could not fit. These peaks could be fitted if the peak model were extended to include more adjustable parameters, but a better approach would be to use a different basis function. A Poisson basis function might be suitable for the peaks of the aromatic compounds studied here.

The cumulants of a Poisson function are all equal to a positive constant. Therefore, attempting to fit a Poisson peak with a Gaussian basis function and a finite number of cumulants as adjustable parameters will introduce negative bias into the nonadjustable cumulants, which are assumed to be zero. This negative bias will propagate downward to the low-order adjustable cumulants through the correlation between errors in high- and low-order cumulants. (An interfering peak, in comparison, will cause a positive bias in the low-order adjustable cumulants.) Therefore, the true values of the cumulants for toluene may be significantly greater than the values in Table IV. Even though they are biased, the difference between the estimated values of the cumulants of 2,3,4-trimethylpentane and toluene are clearly evident. The numerical differences between these peak-shape parameters show that cumulants can be used to aid identification. The visual difference between the shapes of 2,3,4-trimethylpentane and toluene on a strip-chart recorder was relatively small.

The error curves obtained for normal octane (Figure 7, III is a typical example) indicate a poor fit without a straight-forward explanation. Estimating the values of the cumulants beyond the sixth order should improve the fit. Without actually using an expanded peak model, the effect of including additional parameters was studied by examining the error curves of computer-generated peaks with nonzero values of cumulants up to the tenth order. The error curve in Figure 7, III is characterized by an envelope of high-frequency oscillations, the major component of which has a distance between nodal points of 0.5σ . The error curves obtained when the peak model was terminated at the next lower cumulant were similar to the curves in Figure 9 for K_3 to K_6 . As the order of the terminal cumulant increases, the distance between nodal points on the error curve near the retention time decreases, but only from 1.8σ for K_3 to 1.0σ for K_{10} . Hence, if the error curve of normal octane was

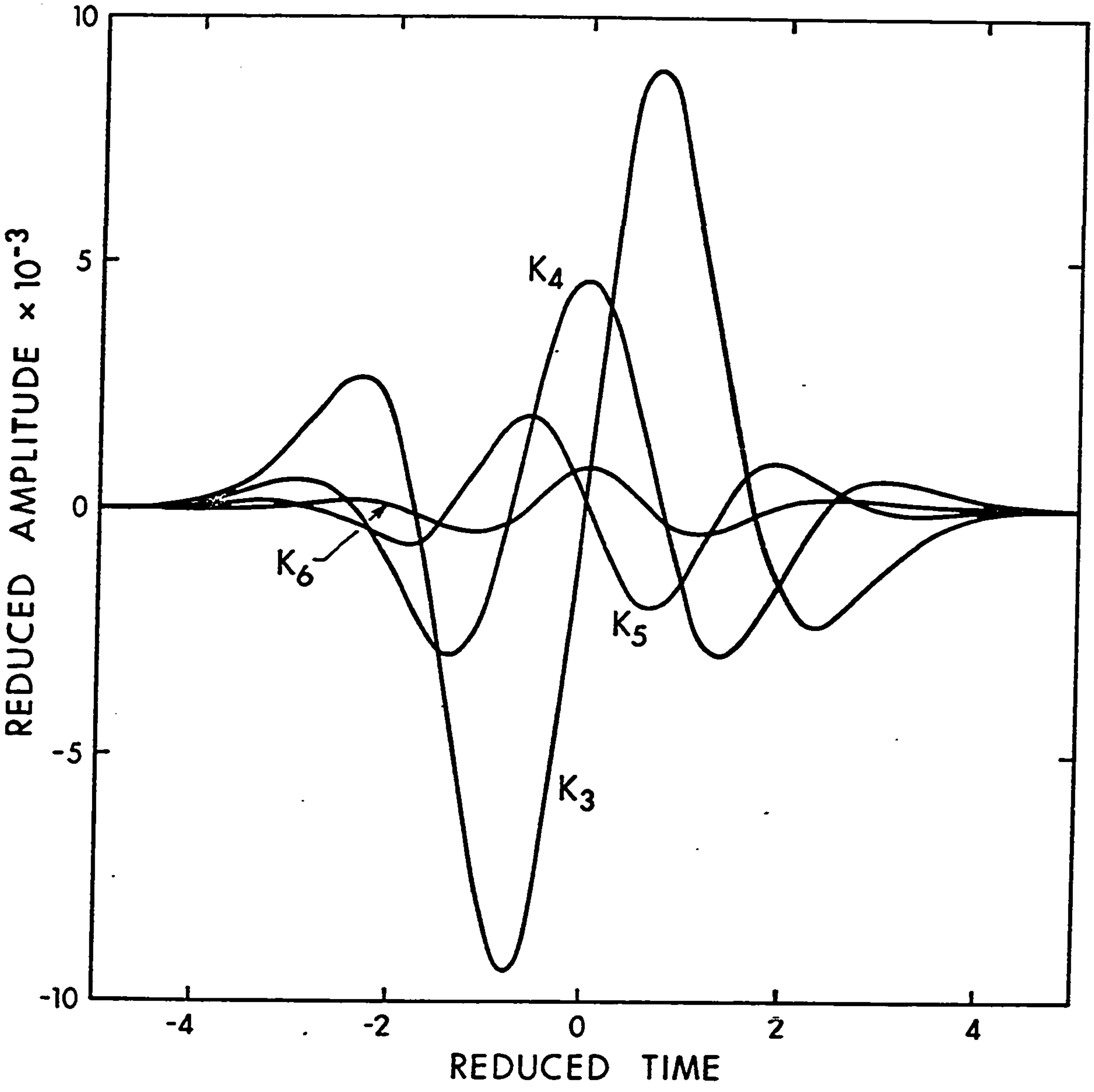

Figure 9. Additive effect of cumulants on a Gaussian peak in the time domain. Each curve is the difference between a standardized peak shape function in the form of Edgeworth's series with one non-zero cumulant and a standardized Gaussian peak shape function. The values of the standardized cumulants, K_3 to K_6, are 0.1, -0.1, 0.1, and 0.1 .

caused by use of an incomplete model, the normal octane peak would require a model with adjustable cumulants up to perhaps the twentieth order. Such high-order cumulants could not reasonably cause oscillations of the magnitude seen in Figure 7, III because of the decreasing amount of information in a cumulant, and hence the decreasing influence of a cumulant, as order increases. A number of cumulants considered as a group may be significant, however, as in the case of a Poisson peak where each cumulant is equal to the same constant. If there was a functional relation between the cumulants of a peak, the parameters of the function could be estimated rather than a large number of individual cumulants.

As peak area and information decreases, the influence of the nonadjustable cumulants decreases, and better fits can be obtained. The error curve for octane (Figure 7, IV) at one tenth the area of the peak giving the error curve in Figure 7, III indicates a perfect fit. At lower areas, however, the estimates of the cumulants are much less precise and are valueless for the purpose of comparing peak shapes.

Error curves similar to Figure 7, III were obtained when white noise with power proportional to the square of the signal amplitude was added to computer-generated peaks in a simulation of jitter noise. But to produce oscillations of the same magnitude as those in Figure 7, III the standard deviation of jitter would have to be more than ten times the value found from the study of power-density spectra. Furthermore, the major features of error curves of normal octane were reproducible from run to run; reproducibility would not be possible if the oscillations were random.

CONCLUSION

In general, if enough data points are used, if the base-line noise is reasonably stationary, and if all the nonadjustable parameters are either zero or insignificant, the MP estimates of the first seven parameters of Edgeworth's series are unbiased, and the variances of the parameters due to base-line noise are approximately the same as the predicted variances. The method is insensitive to severe low-frequency noise or drift; Figure 7, VI shows a perfect fit in the presence of an intense low-frequency oscillation caused by the temperature controller of the detector.

The most important limitation of the method is that the conditions listed in the above paragraph must be known to apply to the system under study before the estimation is carried out. All measurement methods are subject to similar *a priori* conditions, but the MP method brings these assumptions to the foreground where they can be clearly defined and tested.

One of the most worrisome assumptions is that of stationarity of the base-line noise. We found the greatest effect of nonstationarity to be in the accuracy of predicted standard deviations. If more accurate standard deviations were required, the effect of nonstationarity and the effect of errors in the measurement of power-density spectra could be reduced by approximating the power-density spectrum with a simple function of one or two parameters. These parameters could then be estimated along with the peak parameters to give an accurate estimate of the current power-density spectrum.

There is some reluctance in the literature about measuring high-order moments (8,9) because of the increasing influence of base-line noise on measurements of moments of increasing order. Using the MP method to measure cumulants (a cumulant is equal to the moment of the same order plus a combination of moments of lower orders), however, we have shown that the decrease in precision is not so rapid as to make the measurement of the sixth-order cumulant valueless. Depending on the power-density spectrum of the base-line noise, the precision may in fact increase with increasing order (in Table V for K_4 and K_5).

The MP method is extremely sensitive to the presence of small peaks near the principal peak. This sensitivity is a disadvantage in that measurements of cumulants for their own sake requires highly pure samples. Nevertheless, the ability to detect a seemingly invisible peak on the shoulder of a large peak is valuable in itself. It would be better, both for the purpose of measuring the shape of a peak and of detecting interfering peaks, to extend the peak model to include multiple peaks each with a separate set of parameters. The fitting of multiple peaks has been done using a Gaussian peak model (36) and a model based on samples of a previously run peak (15) . Greater effective resolution and lower detection limits should be attained, however, if a more complete and accurately defined peak model were used, and if the characteristics of the base-line noise were taken into consideration.

The data presented is for peaks for which there was no prior information about any of the parameters. Prior information about any one parameter will decrease the standard deviation for that parameter and any other parameter that is correlated with it. For example, consider the effect of complete prior information (zero prior standard deviation) about high-order parameters on the predicted standard deviation for the area of a normal octane peak. The relative standard deviations (x1000) are 0.82 (with K_7 and higher well known), 0.61 (with K_6 and higher well known), 0.61 (with K_5 , etc.), 0.43 (K_4), 0.42 (K_3), 0.23 (σ), 0.23 (t_0), and 0.0 (A , and all other parameters well known). The most significant parameters for area are K_6 , K_4 , and σ . This is also indicated by the high correlations between these parameters and area shown in Table VI. Prior knowledge of the shape and width of the normal octane peak would reduce the standard deviation for area by a factor of 3.5 . On the other hand, prior knowledge of the retention time would have no effect on the precision of area estimates. It must be emphasized, however, that these results are the standard deviations due to baseline noise alone predicted for an efficient estimator. Although the MP estimator is nearly efficient when the amount of information is large, it is inefficient near the detection limit where the information is small. Near the detection limit, prior information about retention time may be important for the estimation of area.

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APPENDIX I

MODELS

The posterior p.d.f. of the set of parameters, $\underset{\sim}{\alpha}$, given the data, $\underset{\sim}{x}$, is given by Bayes' theorem

$$p_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\underset{\sim}{\alpha}|\underset{\sim}{x}) = \frac{p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})\ p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha})}{p_{\underset{\sim}{x}}(\underset{\sim}{x})} \tag{A-1}$$

where $p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})$ is the prior p.d.f. of the parameters, $p_{\underset{\sim}{x}|\underset{\sim}{\alpha}}(\underset{\sim}{x}|\underset{\sim}{\alpha})$ the p.d.f. of the data given the parameters, and $p_{\underset{\sim}{x}}(\underset{\sim}{x})$ a scaling or normalizing factor. Since the maxima of a function and the maxima of the logarithm of the function occur together, finding the maximum of a posterior p.d.f. is equivalent to finding the minimum of the function

$$M(\underset{\sim}{\alpha}) = -\ln[p_{\underset{\sim}{\alpha}|\underset{\sim}{x}}(\underset{\sim}{\alpha}|\underset{\sim}{x})] + \text{constant} \tag{A-2}$$

where the constant is independent of the true values of the parameters, $\underset{\sim}{\alpha}$.

A priori information about the experimental system is embodied in the functional form of the p.d.f.'s in Equation A-1. In the chromatographic system used here, the *a priori* information consists of the following statements.

(*a*) Since there was no prior information about the parameters, the prior p.d.f. of the parameters, $p_{\underset{\sim}{\alpha}}(\underset{\sim}{\alpha})$, is assumed to be uniform for each parameter.

(*b*) The detector signal is the sum of the base-line noise and the peak function, and any noise with an amplitude that increases with increasing signal amplitude is either absent or negligible.

(*c*) The base-line noise is a stationary random process with a multivariate normal p.d.f. and a known power-density spectrum, $C_x(\nu)$.

(*d*) The peaks being studied are accurately represented by Edgeworth's form of the Gram-Charlier type-A series, and all cumulants above the sixth are equal to zero. An accurate representation means that the difference between the true peak function and the estimated peak function is indistinguishable from the base-line noise.

With this prior information the M function becomes

$$M = 1/2 \int_{-\infty}^{\infty} \frac{|X(\nu)-F(\nu)|^2}{C_x(\nu)} d\nu \qquad \text{(A-3)}$$

where $X(\nu)$ is the Fourier transform of the chromatographic data and $F(\nu)$ the Fourier transform of the peak function:

$$\begin{aligned} F(\nu) &= A(\cos\theta + i\sin\theta)\exp[-(2\pi\sigma\nu)^2/2 \\ &\quad + K_4(2\pi\sigma\nu)^4/24 - K_6(2\pi\sigma\nu)^6/720] \end{aligned} \qquad \text{(A-4)}$$

where

$$\theta = -(2\pi t_0\nu) + K_3(2\pi\sigma\nu)^3/6 - K_5(2\pi\sigma\nu)^5/120$$

ν is frequency (Hz), A is area, t_0 is retention time, σ is width, and K_3 to K_6 are standardized cumulants. The elements of the information matrix are given by Equation A-5.

$$I_{jk} = \int_{-\infty}^{\infty} \frac{1}{C_x(\nu)} \frac{\partial F(\nu)}{\partial \alpha_j} \frac{\partial F^{\dagger}(\nu)}{\partial \alpha_k} \, d\,\nu \qquad \text{(A-5)}$$

where † indicates the complex conjugate. Predicted standard deviations are defined as the square root of the diagonal elements of the inverse of the information matrix. The M function can be evaluated by use of a digital computer provided that, in the digitization of the signal from the detector, the sampling interval is small enough, and that the sampling time is long enough that the integral in Equation A-3 can be replaced by a summation over a finite frequency range.

Terminating Edgeworth's series at the sixth cumulant in Equation A-4 limits the range of peak shapes that this model can accurately represent. One of the conditions on a peak model, if it is to be a realistic representation of an actual peak, is that the absolute value of the Fourier transform of the function at all frequencies must be less than or equal to the value of the function at zero frequency (37). In the peak model defined by Equation A-4, this condition means that the value of K_4^2/K_6 must be less than 1.6. When this condition is met, a plot of the absolute value of $F(\nu)$ against frequency has a peak-like profile with a maximum at zero frequency. If K_4^2/K_6 is greater than 1.2, however, the peak will have secondary maxima. In the critical region where K_4^2/K_6 is less than 1.6 but greater than 1.2, the shape of the absolute value of $F(\nu)$ changes rapidly with small changes in either K_4 or K_6. Figure 9 shows the time-domain difference between peaks with the indicated values of individual cumulants and a Gaussian peak with cumulants that are all equal to zero. As this figure indicates, the effect of the even cumulants on the shape of a peak is symmetric about the mean, and the effect of the odd cumulants is not exactly but nearly antisymmetric.

From Equation A-3 , when the *a priori* assumptions are true, the minimum of M is the sum of a number of random variables, each of which is normal with unit variance. Twice the minimum value of M , represented by the symbol Q , has a chi-square distribution with degrees of freedom equal to the number of data points less the sum of the number of parameters being estimated (seven) and the number of degrees of freedom lost by filtering (two, when the filter described by Equation 88 is used). The mean or expected value of Q is equal to the number of degrees of freedom, and if Q is significantly greater or less than expected, the *a priori* assumptions are unlikely to be true. A graph of the error curve $[x(t)-f(t,\underset{\sim}{a})]$, where $\underset{\sim}{a}$ represents the estimated values of the set of parameters, can be used as a qualitative test of the peak-model assumption. If the peak model is correct, the error curve in the region of a peak should be indistinguishable from the base-line noise before and after the peak. The curves in Figure 9 are error curves that would be obtained if there were no base-line noise and if individual cumulant estimates were in error.

APPENDIX II

MINIMIZATION

In this study the process of finding the minimum of the M-function in Equation A-3 was started by finding crude initial estimates of the parameters. The initial estimates of the cumulants were zero. The approximate area, retention time, and width of the peak were determined by use of the definitions in Chapter 1 after subtracting a linear base line from under the peak. The end points of this base line were taken as the center of a five-point moving average when, going downward on each side of the peak, the difference between a data point and the preceeding moving average was less than a preset value. After the initial estimates were obtained, the set of data samples containing the peak was filtered, Fourier transformed, and corrected for the distortion caused by filtering and interval-area sampling. Then a parameter correction vector, $\underset{\sim}{\Delta}$, was calculated as outlined below, and the previous estimates were replaced by new ones:

$$\underset{\sim}{\alpha}_{n+1} = \underset{\sim}{\alpha}_{n} + \underset{\sim}{\Delta}(\underset{\sim}{\alpha}_{n}) \qquad \text{(A-6)}$$

This procedure was repeated until a minimum of M was reached.

As a function of two parameters at a time, M makes a surface that can be pictured as a distorted bowl. A contour of constant height on this bowl would look like an elongated and distorted ellipse. The elongation was reduced and the accuracy of the computer calculations was improved by transforming the parameters into a new coordinate system in which the amount of information about each parameter is unity (38) :

$$\alpha_j^* = \alpha_j (I_{jj})^{-1/2} \tag{A-7}$$

$$I_{jk}^* = I_{jk} (I_{jj}\ I_{kk})^{-1/2} \tag{A-8}$$

A ball released on the M-surface would begin to roll downward along the negative gradient towards the minimum. The computer method based on this idea would use the following correction vector:

$$\underset{\sim}{\Delta}_g^* = -d\ \underset{\sim}{g}^* (\underset{\sim}{\alpha}_n) \tag{A-9}$$

where

$$g_j^* = \frac{\partial M}{\partial \alpha_j} (I_{jj})^{-1/2} \tag{A-10}$$

and d is the distance of the step along the gradient. Before the process is begun, a value for d must be found. An appropriate step distance is difficult to find, however, and a different value may be needed for each new iteration. Moreover, the correction vector, $\underset{\sim}{\Delta}_g^*$, may sometimes point nearly 90° away from the minimum (Figure 10, I) . In the method of scoring for parameters (39) , both difficulties are reduced by assuming that the M-surface, at point $\underset{\sim}{\alpha}_n$, is quadratic in the form it would have if the peak model were linear. The first derivative of M (the gradient) and the assumed second derivative (the information matrix) are calculated and the minimum of the surface having these derivatives is used for the correction vector:

$$\underset{\sim}{\Delta}_s^* = -\underset{\sim}{I}^{*-1}\ \underset{\sim}{g}^* \tag{A-11}$$

Often one side of the M-surface is steeper than the other.

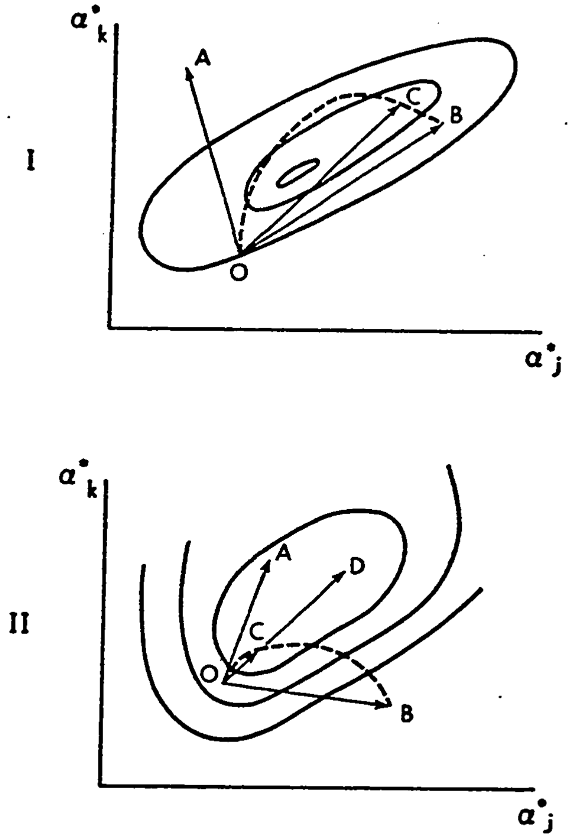

Figure 10. Visualizations of minimization surfaces:

I, effect of damping factor (schematic). The closed curves are contours of constant value of M . Line OA is in the direction of the negative gradient, $-\underset{\sim}{g}^*$, at point O; OB is the correction vector, $\underset{\sim}{\Delta}_s^*$; and OC is the damped correction vector, $\underset{\sim}{\Delta}_p^*$. The dashed line is the locus of the damped correction vector as the damping factor, p , goes from zero at point O to infinity at point B .

II, effect of step along damped correction vector. The labels are as in I . The damped correction vector, line OC , can easily be extended to point D which is closer to the minimum than point C .

If the initial estimate is on the less steep side, the correction vector, $\underset{\sim}{\Delta}_s^*$, may overshoot the minimum and arrive at a point even higher than the starting point. The reciprocal of a damping factor added to the diagonal elements of the information matrix, $\underset{\sim}{I}^*$, gives a correction vector that is between the negative gradient and $\underset{\sim}{\Delta}_s^*$ in direction and less than $\underset{\sim}{\Delta}_s^*$ in magnitude (38) (Figure 10, I):

$$\underset{\sim}{\Delta}_p^* = -(\underset{\sim}{I}^* + 1/p\ \underset{\sim}{U})^{-1}\ \underset{\sim}{g}^* \tag{A-12}$$

where $\underset{\sim}{U}$ is a unit matrix and p a positive damping factor. As the value of the damping factor approaches zero, the damped correction, $\underset{\sim}{\Delta}_p^*$, approaches the direction of the negative gradient, approaches zero in magnitude, and the slope, $\mathrm{d}\,M/\mathrm{d}\,p$, approaches the square of the length of the gradient, $|\underset{\sim}{g}^*|^2$ (40) . The best damping factor, the value that gives the lowest value of M , was found by a method similar to that used by Pitha and Jones (41). Starting with a trial value (p_1 equal to 40 or the best value from the previous iteration), a second trial value, p_2 , was tried, which was the value that gave the minimum of a quadratic function of $\ln(p+0.1)$ fitted to M_0 (the initial value for which p_0 is equal to zero), M_1 , and $\mathrm{d}\,M/\mathrm{d}\,p$ at p equal to zero. The third trial value was at the minimum of the quadratic fitted to M_0 , M_1 , and M_2 . The fourth was fitted to the lowest three previous values of M_p . In anomalous cases where the extrapolated value of p was less than zero, arbitrary values of p were tried that were fractions or multiples of the best value of p obtained so far. Further attempts after the second were stopped when p was greater than 10^5 or when the difference between the predicted minimum of M and the actual value was less than 5% of the difference between the actual value and M_0 . If an M_p that was less than M_0 could not be found after four attempts, the lowest value of p was divided by 10 until such a value could be found. Sometimes the optimal value of the damping factor was difficult to find. More than one minimum in the graph of M versus p occurred in some cases. Figure 10, I shows a minimum along the dashed line at point C and another between points C and O .

As the damping factor becomes small, the damped correction vector, $\underset{\sim}{\Delta}_p^*$, becomes small and the decrease in M also may become small. The rate of convergence was greatly imporved at little cost in computing time if a one-dimensional search was carried out for the lowest value of M along the line defined by the damped correction vector, $\underset{\sim}{\Delta}_p$, when the angle between $\underset{\sim}{g}$ and $\underset{\sim}{\Delta}_p$ was less than 50° (38) .

$$\underset{\sim}{\Delta}_d = d\,\underset{\sim}{\Delta}_p \tag{A-13}$$

where d is the length of the step. The optimal value of the stepping factor was found by a method similar to the method used to find the optimal value of the damping factor except that a quadratic function of the stepping factor itself was used for extrapolation and interpolation. Sometimes a step of 1000 times the length of the damped step could be made. Such a step could be the equivalent of many iterations using the damped step alone. The circumstances where a step along Δ_p is valuable occurs when the M-surface has a steep face that flattens out sharply, as when K_4 and K_6 are in or near the critical region (Figure 10, II).

Minimization processes can be terminated in a number of ways. One of the more common methods is to stop when the greatest change of the values of all of the parameters per iteration is less than a specified constant. The basic criterion of a minimum, however, is that the gradient $(\underset{\sim}{g})$ is zero at the minimum and the rate of change of the parameters per iteration has no relation to the gradient. The best criterion for accuracy is to stop when the length of the gradient is less than a constant. An economic criterion, as well as an accuracy criterion for termination, based on the cost of computer time, is usually necessary. One such method is to stop when the rate of decrease of M per second of computation time or per iteration is less than a given constant. Premature termination may occur with this method when the rate of change of M per iteration is low in a particular iteration due perhaps to difficulty in finding the optimal damping factor. The influence of a few poor iterations on termination can be minimized by adding fractions of the rates of decrease of M per previous iterations to the rate for the current iteration. We use the following algorithm. Starting with D_0 equal to M_0, D_n for iteration n is calculated from the formula

$$D_n = f\, D_{n-1} + M_n - M_{n-1}$$

where f is a positive constant less than one (0.1 was suitable). Then, if $|\underset{\sim}{g}^*|$ was less than a constant, k_g, or if D_n/M_n was less than a constant, k_D, the process was terminated. The value 0.0001 was suitable for both constants.

Computer programs were written in Fortran IV and run on an IBM 360-67 computer with the Fortran H compiler; 96K of storage was required. The computation time for a single peak varied from a few seconds to nearly one minute; in general, the computation time was inversely proportional to the width of the peak and increased when the fit was poor. The computation times for the computer-generated peaks, for which a good fit could always be obtained, were usually about half the time required for a real peak with similar parameter values. The median computation times for normal heptane and normal octane were 4.5 and 4.2 sec.

APPENDIX III

COMPUTER PROGRAMS

CONTENTS*

Main Programs

Subroutines

---

[*] The numbers listed after each program or subroutine are the subroutines called within that program.

Library Subroutines

21. CH201A - provides date and time of day

22. CS003A,C - provides random number from a uniform distribution

23. CS019A,B,C - provides elapsed computation time

24. CS012A - matrix inversion

Output Examples

```
C   PROGRAM M1
C   BAYESIAN ESTIMATION OF PEAK PARAMETERS
C   SINGLE PEAKS
C   PARAMETER ESTIMATES ARE LISTED IN THE ORDER: AREA,
C   RETENTION TIME,WIDTH, THEN THE THIRD TO SIXTH CUMULANTS.
C   THE PARAMETER HAVE DIMENSIONS OF THE INPUT DATA.
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGER NAME(17),IP(5),NDATE(6)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      DIMENSION DIF(512),DX(257)
      N=512
      CALL CH201A(NDATE)
      CALL SET
C
C   READ IN SET INFORMATION AND NAME.
C      CARD 1- IP(1),IP(2),IP(3),HLEVEL,FTEST
C           IP(1)(1X,I1)-OUTPUT PARAMETER
C                 =0 -MINIMUM OUTPUT
C                 =3 -MAXIMUM OUTPUT  (SEE BAYES)
C           IP(2)(I1) - STATISTICS OUTPUT PARAMETER
C                 =0 - NO OUTPUT
C                 =1 OR 2 - GRAPH OF ERROR CURVE
C                 =3 - AS FOR 2 PLUS REAL PARTS OF TRANSFORMED
C                      DATA AND ERROR CURVE (SEE BAYES ALSO)
C           IP(3)(I1)  -ANALYSIS CASES (SEE DETECT)
C                 =0 NO  PRIOR  INFORMATION
C                 =1  PRIOR  INFORMATION -SMALL PEAKS
C                 =2  PRIOR  INFORMATION -LARGE PEAKS
C           HLEVEL(F8.0)- PARAMETER FOR DPINIT
C           FTEST(F10.0) - TERMINATION PARAMETER FOR BAYES
C   END OF SET MUST BE FOLLOWED BY A BLANK CARD.
C
      READ(5,101) IP(1),IP(2),IP(3),HLEVEL,FTEST
      IF(FTEST.LT.1.0D-06) FTEST=1.0D-03
      IF(HLEVEL.LT.1.0D00) HLEVEL=5.0D00
C
C   READ IN INVERSE OF POWER-DENSITY SPECTRUM (SEE PROGRAM M4)
C
      READ(5,105) (W(J),J=1,257)
      CALL DCLPRT(257,W)
C
C   READ IN CHROMATOGRAM.
C   LAST CARD OF CHROMATOGRAM MUST BE FOLLOWED BY A BLANK CARD
C   IF LAST CARD FULL.
C
   10 CALL DATARD(CGRAM,M,IERR,NORUN)
C
C   READ IN PEAK INFORMATION
C      CARD 1- NRUN,NOP,L1,L2, NAME
C           NRUN(I2)   -CHROMATOGRAM NUMBER
C           NOP(I2)    -PEAK NUMBER
C           IP(4,5)(2I4) - SAMPLE NUMBERS BETWEEN
```

```
C              WHICH PEAK IS LOCATED
C          NAME(17A4) -NAME OF PEAK
C      CARD 2- PRIOR  MEANS  PA(I),I=1,7  (7F10.0)
C      CARD 3- PRIOR  STANDARD DEVIATIONS
C              PV(I), I=1,7 (7F10.0)
C  CARDS 2 AND 3 ARE OMITTED WHEN IP(3)=0
C  THE LAST SET OF PEAK INFORMATION MUST BE FOLLOWED
C  BY A BLANK CARD.
C
   20 READ(5,102) NRUN,NP,IP(4),IP(5),(NAME(I),I=1,17)
      IF(IP(5).EQ.0) GO TO 10
      IF(IP(1).GT.0.AND.IERR.EQ.0) WRITE(6,999)
      WRITE(6,202) NORUN,NP,IP(4),IP(5),NAME,NDATE
      GO TO 22
   21 IF(IP(3).GT.0) READ(5,104) PA,PV
      GO TO 20
   22 IF(IERR.GT.0) GO TO 21
      IF(IP(3).EQ.0) GO TO 24
      READ(5,104) PA,PV
      WRITE(6,204) PA,PV
   24 IP4=IP(4)
C
C  OBTAIN INITIAL ESTIMATES
C
      CALL DETECT(IP,HLEVEL)
      IF(IP(4).LT.0) GO TO 20
      L=IP(5)-IP(4)+1
C
C  CONDITION THE DATA
C
      CALL CONVRT(L)
C
C  OBTAIN ESTIMATES
C
      CALL BAYES(IP,FTEST,P,FSM,SEC,DIF)
      IF(IP(2).EQ.0) GO TO 20
      IF(IP(2).LT.3) GO TO 28
      DO 26 J=2,256
          I=N+2-J
          DX(J) =DSQRT(X(J)**2+X(I)**2)
   26 CONTINUE
      DX(257)=DSQRT(X(257)**2)
   28 CALL FTPEAK(A,X,DIF)
      IF(IP(2).LT.3) GO TO 50
      DO 32 J=2,257
          DIF(J)=DX(J)-DIF(J)
   32 CONTINUE
      DIF(1)=0.0D00
      DX(1)=0.0D00
C
C  PRINT OUT REAL PART OF FOURIER TRAMSFORM OF CHROMATOGRAM
C
      CALL DCLPRT(257,DX)
C
```

```
C  TABULATE REAL PART OF ERROR CURVE
C
      CALL DCLPRT(257,DIF)
C
C  PRINT OUT GRAPH OF ERROR CURVE
C
   50 CALL DIFFT(9,X)
      TEMP=10.0D00*A(3)
      IF(A(3).GT.10.0D00) TEMP=100.0D00
      IF(A(3).LT.2.5D00) TEMP=30.0D00
      KS=IDINT(A(2)-TEMP)
      KL=IDINT(A(2)+TEMP)
      IF(KS.LT.1) KS=1
      IF(KL.GT.L) KL=L
      L=KL-KS+1
      DO 30 J=1,L
          I=IP4+KS-1+J
          K=KS+J
          TEMP=CGRAM(I)
          DIF(J)=TEMP-X(K)
          X(J)=TEMP
   30 CONTINUE
      WRITE(6,998)
      CALL GRAPH(X,DIF,A,Y,W,L,300,2)
      GO TO 20
  101 FORMAT(1X,3I1,F8.0,F10.0)
  102 FORMAT(2I2,2I4,17A4)
  104 FORMAT(7F10.0)
  105 FORMAT(8D10.5)
  202 FORMAT(1H0,'  RUN  ',I2,'  PEAK  ',I2,2I6,23A4)
  204 FORMAT(1X,1P7D15.5)
  998 FORMAT(1H0)
  999 FORMAT(1H1)
      END
```

```
C  PROGRAM M2
C  BAYESIAN ESTIMATION OF PEAK PARAMETERS
C  MULTIPLE ISOLATED PEAKS FOR RETENTION INDEX MEASUREMENT
C  PRINTS OUT SUMMARY OF RUN
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      DIMENSION DIF(512),AP(5,7),SDA(5,7),T(5),SDT(5),AR(5)
     1         ,SDR(5),FS(5)
      INTEGER NAME(17),IP(5),NPT(5),NDATE(6)
      N=512
      CALL CH201A(NDATE)
      CALL SET
C
C  PROGRAM PARAMETERS SAME AS FOR PROGRAM M1, EXCEPT REAL
C  PARTS OF DATA AND ERROR CURVE NOT PRINTED FOR IP(2)=3
C
      READ(5,1000) IP(1),IP(2),IP(3),HLEVEL,FTEST
      IF(HLEVEL.LT.1.0D00) HLEVEL=5.0D00
      IF(FTEST.LT.1.0D-06) FTEST=1.0D-03
      READ(5,1001) (W(J),J=1,257)
      CALL DCLPRT(257,W)
C
   10 IOK=1
      CALL DATARD(CGRAM,M,IERR,NORUN)
C
C  READ IN PEAK INFORMATION
C    PEAK NUMBER (NP) - 1 - AIR PEAK, 2 - SOLVENT,
C    3 - NORMAL HYDROCARBON, 4 - COMPOUND WHOSE RETENTION
C    INDEX IS TO BE MEASURED, 5 - NORMAL HYDROCARBON
C    IF IP(5) FOR SOLVENT PEAK IS BLANK,
C    SOLVENT NOT ANALYZED
C
   20 READ(5,1002) NRUN,NP,IP(4),IP(5),NAME
      IF(IP(5).EQ.0) GO TO 10
      IF(IP(4).EQ.0) GO TO 41
      WRITE(6,999)
      WRITE(6,2000) NORUN,NP,IP(4),IP(5),NAME,NDATE
      GO TO 24
   22 IF(IP(3).GT.0) READ(5,1003)
      GO TO 40
   24 IF(IERR.GT.0) GO TO 22
      IF(IP(3).EQ.0) GO TO 26
      READ(5,1004) PA,PV
      WRITE(6,2002) PA,PV
   26 CALL DETECT(IP,HLEVEL)
      IF(IP(4).LT.0) GO TO 40
      L=IP(5)-IP(4)+1
      NPT(NP)=L
      CALL CONVRT(L)
      IP4=IP(4)
      CALL BAYES(IP,FTEST,P,FSM,SEC,DIF)
```

```
      IF(IP(2).LT.3) GO TO 29
      CALL FTPEAK(A,X)
      CALL DIFFT(9,X)
      KS=IDINT(A(2)-10.0D00*A(3))
      KL=IDINT(A(2)+10.0D00*A(3))
      IF(KS.LT.1) KS=1
      IF(KL.GT.L) KL=L
      L=KL-KS+1
      DO 28 J=1,L
          I=IP4+KS-1+J
          K=KS+J
          TEMP=DBLE(CGRAM(I))
          DIF(J)=TEMP-X(K)
          X(J)=TEMP
   28 CONTINUE
      CALL GRAPH(X,DIF,A,Y,W,L,300,2)
   29 IF(IP(4).LT.0) GO TO 40
      A(2)=A(2)+DFLOAT(IP4)-1.0D00
      DO 30 J=1,7
          AP(NP,J)=A(J)
          SDA(NP,J)=Y(J)
   30 CONTINUE
      T(NP)=A(2)
      SDT(NP)=V(2,2)
      FS(NP)=FSM
      IF(NP.LT.5) GO TO 20
C
C  IF ERROR OCCURS, SET SUMMARY DATA TO ZERO BUT CONTINUE TO
C    ANALYZE OTHER PEAKS
C
      GO TO 50
C
   40 IOK=-1
   41 DO 42 J=1,7
          AP(NP,J)=0.0D00
          SDA(NP,J)=0.0D00
   42 CONTINUE
      NPT(NP)=0
      SDT(NP)=0.0D00
      FS(NP)=0.0D00
      T(NP)=0.0D00
      AR(NP)=0.0D00
      SDR(NP)=0.0D00
      GO TO 20
C
C  CALCULATE SUMMARY DATA
C
   50 IF(IOK.GT.0) GO TO 60
      DO 52 J=1,5
          T(J)=0.0D00
          SDT(J)=0.0D00
          AR(J)=0.0D00
          SDR(J)=0.0D00
   52 CONTINUE
```

```
      RETI=0.0D00
      SDRET=0.0D00
      GO TO 70
   60 T0=T(1)
      SD0=SDT(1)
      DO 62 J=1,5
          IF(NPT(J).EQ.0) GO TO 61
          A(J)=SDT(J)
          T(J)=T(J)-T0
          SDT(J)=DSQRT(SDT(J)+SD0)
          AR(J)=AP(J,1)/AP(3,1)
          SDR(J)=DSQRT((SDA(J,1)/AP(J,1))**2+(SDA(3,1)/
     1                     AP(3,1))**2)*AR(J)
   61     CONTINUE
   62 CONTINUE
      SDT(1)=0.0D00
      SDR(3)=0.0D00
      XN=DLOG10(T(4)/T(3))
      XD=DLOG10(T(5)/T(3))
      RETI=1.0D02*XN/XD+7.0D02
      R1=XD/T(4)
      R2=XN/T(5)
      R3=(XN-XD)/T(3)
      SDRET=DSQRT(R1**2*A(4)+R2**2*A(5)+R3**2*A(3)
     .       +(R3+R1-R2)**2*A(1))*1.0D02/XD**2
C
   70 WRITE(6,2003) NORUN,NDATE
      NP=4
      WRITE(6,2004) NP,RETI,SDRET
      WRITE(6,2005)
      WRITE(6,2006) ((I,(AP(I,J),J=1,7),T(I),AR(I),
     1               NPT(I),I=1,5)
      WRITE(6,2007)
      WRITE(6,2008)  ((I,(SDA(I,J),J=1,7),SDT(I),SDR(I),
     1                FS(I),I=1,5)
      GO TO 10
  999 FORMAT(1H1)
 1000 FORMAT(1X,3I1,F8.0,F10.0)
 1001 FORMAT(8D10.5)
 1002 FORMAT(2I2,2I4,17A4)
 1003 FORMAT(//)
 1004 FORMAT(7F10.0)
 2000 FORMAT(1H0,'  RUN  ',I2,'  PEAK  ',I2,2I6,23A4)
 2002 FORMAT('    PRIOR  INFORMATION - MEANS AND STD. DEVS.'
 20021      /2(4X,1P3D15.5,0P4F10.6/))
 2003 FORMAT('1DATA SUMMARY   RUN NUMBER ',I2,80X,6A4)
 2004 FORMAT('0     RETENTION INDEX  PEAK NO.',I2,' =',F10.5
 20041  ,10X,'STD. DEV. =',F10.6)
 2005 FORMAT(' PEAK PARAMETERS',74X,'NET RETENTION  RELATIVE
 20051          AREA  NO. POINTS')
 2006 FORMAT('0',I3,1P3D15.5,0P4F10.6,F14.4,F14.8,I10)
 2007 FORMAT('0PARAMETER STANDARD DEVIATIONS',84X,
 70071        'SUM OF SQUARED DEV.')
 2008 FORMAT('0',I3,1P3D15.5,0P4F10.7,F14.5,F14.9,1PD14.4)
      END
```

```
C  PROGRAM M3
C  ANALYZES COMPUTER GENERATED PEAKS ADDED TO REAL BASE
C  LINE NOISE. AS MANY TRIALS AS DESIRED MAY BE RUN ON THE
C  SAME SECTION OF BASE LINE.  THE ARTIFICIAL PEAKS ARE
C  GENERATED FROM EDGEWORTH'S SERIES EXTENDED TO THE TENTH
C  CUMULANT.  BASE-LINE SECTION LIMITED TO 512 POINTS.
C  AN INTERFERING PEAK WITH THE SAME SHAPE AND WIDTH AS THE
C  PRINCIPAL PEAK CAN BE INTRODUCED.
C  THE SIMULATED CHROMATOGRAM CAN BE MULTIPLIED BY WHITE
C  NOISE TO SIMULATE JITTER.
C  ERROR CURVE OF LAST TRIAL IN SERIES IS PLOTTED
      IMPLICIT REAL*8 (A-H,O-Z)
      INTEGER IP(5),NDATE(6)
      REAL*4 CGRAM,RET,DOWN,UP,RN(512),ALPHA
      DIMENSION EX(512),AT(11),DA(7),DV(7),VM(7),VV(7),
     1          PINT(512),X2(257)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      N=512
      CALL SET
C
C  READ IN GENERAL PROGRAM PARAMETERS
C
      READ(5,1001) IP(1),IP(2),IP(3),HLEVEL,FTEST
      IF(HLEVEL.LT.1.0D00) HLEVEL=5.0D00
      IF(FTEST.LT.1.0D-06) FTEST=1.0D-03
      IF(IP(2).LT.1) IP(2)=1
      IP1=IP(1)
      IP2=IP(2)
C
C  READ IN INVERSE-POWER-DENSITY SPECTRUM
C
      READ(5,1002) (W(J),J=1,257)
      CALL DCLPRT(257,W)
C
C  READ IN BASE-LINE NOISE
C
    5 CALL DATARD(CGRAM,M,IERR,NORUN)
      IF(IERR.GT.0) STOP 1
C
C  READ IN TRUE VALUES OF PARAMETERS. (TWO CARDS)
C  RETENTION TIME, A(2), MAY BE BLANK
C
   10 READ(5,1003) (AT(I),I=1,7)
      IF(AT(1).EQ.0.0D00) GO TO 5
      READ(5,1003) (AT(I),I=8,11)
      IF(IP(3).EQ.0) GO TO 11
      READ(5,1003) (PA(I),I=1,7)
      READ(5,1003) (PV(I),I=1,7)
   11 CALL CH201A(NDATE)
      IP(1)=IP1
      IP(2)=IP2
C
C  READ IN EXPERIMENT PARAMETERS
```

```
C    NEXP = NUMBER OF TRIALS TO BE MADE
C    INITIAL = INITIAL RANDOM NUMBER FOR RETENTION TIME
C              GENERATOR. (POSITIVE INTEGER)
C    IP4, IP5 = NUMBER OF DATA POINTS LEFT AND RIGHT OF
C               RETENTION TIME TO BE USED BY ESTIMATOR
C              TOTAL NUMBER OF POINTS USED = IP4+IP5+1
C    SECMAX = IF TOTAL ELAPSED COMPUTUTATION TIME FOR THE
C             EXPERIMENT EXCEEDS SECMAX, FURTHER TRIALS WILL
C             NOT BE MADE, BUT THE SUMMARY DATA
C             WILL BE PRINTED OUT
C    DOWN, UP = RANGE OF RETENTION TIMES.
C    ALPHA = PROPORTIONALITY FACTOR FOR MULTIPLICATIVE NOISE
C            NO NOISE ADDED IF ALPHA=0.0D00.
C    Z = INITIAL NUMBER FOR NORMAL-WHITE NOISE GENERATOR
C        (MULTIPLICATIVE NOISE)
C    AS1 = AREA OF INTERFERING PEAK RELATIVE
C          TO PRINCIPAL PEAK
C    AS2 = DIFFERENCE BETWEEN RETENTION TIMES OF INTERFERING
C          AND PRINCIPAL PEAK IN UNITS OF
C          WIDTH OF PRINCIPAL PEAK
C
      READ(5,1004) NEXP,INITAL,IP4,IP5,SECMAX,DOWN,UP,ALPHA,
     1              Z,AS1,AS2
      IF(NEXP.EQ.0) NEXP=5
      IF(NEXP.GT.100) NEXP=5
      WRITE(6,999)
      WRITE(6,2000) ALPHA,Z,AS1,AS2,NDATE,(AT(I),I=1,7),
     1              NEXP,INITIAL,IP4,IP5,SECMAX,DOWN,UP
      WRITE(6,2005) (AT(I),I=8,11)
      IF(IP(3).GT.0) WRITE(6,2006) PA,PV
      CALL CS003A(INITAL)
      TIME=0.0D00
      DO 12 I=1,7
          DA(I)=0.0D00
          DV(I)=0.0D00
          VM(I)=0.0D00
          VV(I)=0.0D00
   12 CONTINUE
      FM=0.0D00
      FM2=0.0D00
      IEXP=1
C
C  GENERATE WHITE NOISE IF REQUIRED.
C
      IF(Z.LT.1.0D00) GO TO 20
      CALL RNG(N,RN,Z)
      DO 14 J=1,N
          RN(J)=ALPHA*RN(J)+1.0
   14 CONTINUE
C
C  GENERATE RETENTION TIME.
C
   20 CALL CS003C(DOWN,UP,RET,NRAND)
      AT(2)=DBLE(RET)
```

```
      PA(2)=AT(2)
      IP(4)=IDINT(AT(2))-IP4
      IF(IP(4).LT.1) IP(4)=1
      IP(5)=IDINT(AT(2))+IP5
      IF(IP(5).GT.N) IP(5)=N
      L=IP(5)-IP(4)+1
      IF((IP(1).GT.1).AND.(IEXP.GT.1)) WRITE(6,999)
C
C  GENERATE TRUE PEAK
C
      CALL FEPEAK(AT,X,EX)
      IF(X(1).LT.1.0D00) GO TO 10
      IF(IEXP.EQ.NEXP) CALL DCLPRT(257,EX)
      CALL DIFFT(9,X)
      A(1)=0.0D00
      A(2)=0.0D00
      IF(AS1.GT.0.0D00) GO TO 210
      DO 205 J=1,L
          I=IP(4)-1+J
          PINT(J)=DBLE(CGRAM(I))
  205 CONTINUE
      GO TO 225
C
C  GENERATE INTERFERING PEAK IF REQUIRED
C
  210 A(1)=AS1*AT(1)
      A(2)=AT(2)+AT(3)*AS2
      DO 215 J=3,7
          A(J)=AT(J)
  215 CONTINUE
          CALL FTPEAK(A,PINT)
      CALL DIFFT(9,PINT)
      DO 220 J=1,L
          I=IP(4)-1+J
          PINT(J)=PINT(I)+DBLE(CGRAM(I))
  220 CONTINUE
      A(2)=A(2)+1-IP(4)
  225 AT(2)=AT(2)+1-IP(4)
      WRITE(6,2001) IEXP,AT(2),RET,IP(4),IP(5),A(1),A(2)
      IF(ALPHA.GT.0.0) GO TO 235
      DO 230 J=1,L
          I=IP(4)+J-1
          TEMP=PINT(J)+X(I)
          X(J)=TEMP
          EX(J)=TEMP
  230 CONTINUE
      GO TO 250
  235 DO 240 J=1,L
          I=IP(4)+J-1
          REMP=DBLE(RN(J))
          TEMP=(PINT(J)+X(I))*REMP
          X(J)=TEMP
          EX(J)=TEMP
          PINT(J)=PINT(J)*REMP
```

```
  240 CONTINUE
C
C  OBTAIN INITIAL ESTIMATES (MODIFIED FORM OF DETECT)
C
  250 CALL DETECT(IP,HLEVEL)
      IF(IP(4).LT.0) GO TO 20
      CALL CONVRT(L)
      IF(IEXP.NE.NEXP) GO TO 255
      IP(1)=3
      IP(2)=3
  255 CALL BAYES(IP,FTEST,P,FSM,SEC,X2)
      IF(IP(4).LT.0) GO TO 32
      DO 30 I=1,7
          DA(I)=DA(I)+A(I)-AT(I)
          DV(I)=DV(I)+(A(I)-AT(I))**2
          EXP=Y(I)**2
          VM(I)=VM(I)+EXP
          VV(I)=VV(I)+EXP**2
   30 CONTINUE
      FM=FM+FSM
      FM2=FM2+FSM**2
   32 TIME=TIME+SEC
      IF(TIME.GT.SECMAX) GO TO 50
      IF(IP(4).LT.0) GO TO 20
      IF(IEXP.GE.NEXP) GO TO 50
      IF(IP(4).GT.0) IEXP=IEXP+1
      GO TO 20
C
C  PLOT ERROR CURVE FOR LAST TRIAL
C
   50 CALL FTPEAK(A,X)
      CALL DIFFT(9,X)
      KS=IDINT(A(2)-10.0D00*A(3))
      KL=IDINT(A(2)+10.0D00*A(3))
      IF(KS.LT.1) KS=1
      IF(KL.GT.L) KL=L
      L=KL-KS+1
      DO 28 J=1,L
          I=KS+J-1
          X(J)=EX(I)-X(I)
          PINT(J)=PINT(I)
          K=I+IP(4)-1
          EX(J)=X(J)-PINT(J)
   28 CONTINUE
      CALL GRAPH(EX,X,PINT,A,Y,L,250,3)
C
C  PRINT OUT SUMMARY OF EXPERIMENT
C
      IF(IEXP.LT.2) GO TO 10
      EXP=DFLOAT(IEXP)
      EXP1=DFLOAT(IEXP-1)
      DO 52 I=1,7
          DA(I)=DA(I)/EXP
          DV(I)=(DV(I)-EXP*DA(I)**2)/EXP1
```

```
         VM(I)=VM(I)/EXP
         VV(I)=(VV(I)-EXP*VM(I)**2)/EXPI
         Y(I)=DSQRT(DV(I))
         VV(I)=DSQRT(VV(I))
         IF(DV(I).GT.1.0D-20) DV(I)=VM(I)/DV(I)
         PA(I)=DSQRT(VM(I))
      IF(Y(I).GT.1.0D-20) A(I)=DA(I)*DSQRT(EXP)/Y(I)
   52 CONTINUE
      FM=FM/EXP
      FM2=(FM2-EXP*FM**2)/EXP1
      IF(FM2.GT.1.0D-20) FMS=(FM-DFLOAT(IP(5)-IP(4)-7))/
     1                          DSQRT(EXP*FM2)
      TIME=TIME/EXP
      WRITE(6,999)
      WRITE(6,2000) ALPHA,Z,AS1,AS2,NDATE,(AT(I),I=1,7),
     1              NEXP,INITIAL,IP4,IP5,SECMAX,DOWN,UP
      WRITE(6,2002) IEXP,FM,FM2,FMS,TIME
      WRITE(6,2003)
      WRITE(6,2004) ((I,DA(I),Y(I),DV(I),A(I),PA(I),VM(I),
     1               VV(I)),I=1,7)
      GO TO 10
  999 FORMAT(1H1)
 1001 FORMAT(1X,3I1,F8.0,F10.0)
 1002 FORMAT(8D10.5)
 1003 FORMAT(7F10.0)
 1004 FORMAT(2I10,2I5,3F5.0,E10.2,F10.0,E10.2,F5.0)
 2000 FORMAT(1H0,'EXPERIMENT PARAMETERS',1PE15.2,0PF15.0,
 20001       1P2D15.2,20X,6A4/
 20002         4X,1P3D15.5,0P4F10.6,I3,I8,2I4,3F6.0)
 2001 FORMAT(1X,'EXP NO.',I4,1PD22.5,0PF10.5,2I10,1PD22.5,
 20011       0PF15.5)
 2002 FORMAT(1H0,'N=',I3,2X,'SUM OF SQUARES - MEAN =',1PD15.
 20021     5,'   VARIANCE =',D15.5,'   T =',D15.5,
 20022       '  AVERAGE TIME(SEC.) =',0PF10.1)
 2003 FORMAT('0',T25,'OBSERVED',T85,'PREDICTED'/
 20031       '0',  11X,'MEAN DEV.',8X,'STD. DEV.',7X,
 20032'EFFICIENCY',7X,'STUDENTS T',15X,'STD. DEV.',13X,
20033  'VAR.STD. OF VAR.')
 2004 FORMAT(1H0,I3,1P4D17.5,7X,3D17.5)
 2005 FORMAT(49X,4F10.6)
 2006 FORMAT(' PRIOR VALUES'/4X,1P3D15.5,0P4F10.6/
 20061  'PRIOR STANDARD DEVIATIONS'/4X,1P3D15.5,0P4F10.6)
      END
```

```
C  PROGRAM M4
C  ESTIMATES POWER-DENSITY SPECTRUM
C  GIVES PUNCHED CARD OUTPUT FOR USE IN PEAK ESTIMATION
C  PROGRAMS (WITH AND WITHOUT GROUPING CORRECTION).
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM(2000)
      DIMENSION X(512),UX(512),W(512)
      N=512
      N2=256
      K=257
      FA=6.283185307179586/512.0D00
      Z=1.0D00/510.0D00
C
C READ IN ONE SET OF DATA (512 DATA POINTS).
C
    4 CALL DATARD(CGRAM,M,IERR,NRUN)
      IF(IERR.GT.0) STOP 1
C
C  FILTER WITH(-1/2,1,-1/2)
C
      X(1)=0.0D00
      L=N-1
      DO 6 J=2,L
          X(J)=DBLE(CGRAM(J)-0.5E00*(CGRAM(J-1)+CGRAM(J+1)))
    6 CONTINUE
      X(N)=0.0D00
C
C  FOURIER TRANSFORM
C
      CALL DFFT(9,X)
      DO 8 J=2,N2
          I=N+2-J
          X(J)=(X(J)**2+X(I)**2)*Z
      UX(J)=X(J)
    8 CONTINUE
      X(K)=(X(K)**2)*Z
      UX(K)=X(K)
C
C SMOOTH WITH HANNING SPECTRAL WINDOW (1/4,1/2,1/4)
C
      VAR=X(2)
      X(2)=0.75*X(2)+0.25*X(3)
      DO 10 J=3,N2
          UAR=X(J)
          X(J)=0.25D00*(VAR+X(J+1))+0.5D00*UAR
          VAR=UAR
   10 CONTINUE
      X(K)=0.5D00*(X(K)+UAR)
C
C  CORRECT FOR FILTERING AND GROUPING
C
      DO 12 J=2,K
          HC=(1.0D00-DCOS(FA*DFLOAT(J-1))**2
          X(J)=X(J)/HC
```

```
              UX(J)=UX(J)/HC
              W(J)=X(J)*(FA/(2.0D00*DSIN(FA*DFLOAT(J-1)/2.0D00))
     1                       **2)
   12 CONTINUE
      X(1)=X(2)
      UX(1)=UX(2)
      W(1)=W(2)
      WRITE(6,2000)
      CALL DCLPRT(K,UX)
      WRITE(6,2001)
      CALL DCLPRT(K,X)
      WRITE(6,2002)
      CALL DCLPRT(K,W)
      DO 20 J=2,K
      X(J)=1.0D00/X(J)
      W(J)=1.0D00/W(J)
   20 CONTINUE
      X(1)=0.0D00
      W(1)=0.0D00
C
C   PUNCH OUT DUPLICATES OF INVERSE OF NONGROUPED
C   AND GROUPED SPECTRA
C
      WRITE(7,1000) (X(J),J=1,K)
      WRITE(7,1000) (X(J),J=1,K)
      WRITE(7,1000) (W(J),J=1,K)
      WRITE(7,1000) (W(J),J=1,K)
      GO TO 4
 1000 FORMAT(8D10.5)
 2000 FORMAT('1RAW POWER-DENSITY SPECTRUM')
 2001 FORMAT('0HANNED POWER-DENSITY SPECTRUM')
 2002 FORMAT('0GROUPED AND HANNED POWER-DENSITY SPECTRUM')
      END
```

```
C  PROGRAM M5
C  DETERMINES CORRELATIONS BETWEEN ERRORS OF PARAMETERS
C  ESTIMATED BY PROGRAM M2.
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(4,16,7),B(7),S(4,7),C(7,7)
C
C  READ IN PARAMETER VALUES
C    IND = CODE NUMBER OF PEAK
C        = 1 - NORMAL HEPTANE (16 RUNS)
C        = 2 - NORMAL OCTANE (16 RUNS)
C        = 3 - 2,3,4-TRIMETHYLPENTANE (11 RUNS)
C        = 4 - TOLUENE (5 RUNS)
C  A(1) IS PEAK AREA DIVIDED BY WEIGHT OF COMPONENT.
C  A(2) IS NET RETENTION TIME.
C
      READ(5,1000) (((A(IND,I,J),J=1,7),I=1,16),IND=1,2)
      READ(5,1000) ((A(3,I,J),J=1,7),I=1,11)
      READ(5,1000) ((A(4,I,J),J=1,7),I=12,16)
C
C  NORMALIZE AREAS
C
      DO 205 I=1,11
          AREA=(A(1,I,1)+A(2,I,1)+A(3,I,1))*1.0D-05
          A(1,I,1)=A(1,I,1)/AREA
          A(2,I,1)=A(2,I,1)/AREA
          A(3,I,1)=A(3,I,1)/AREA
  205 CONTINUE
      DO 210 I=12,16
          AREA=(A(1,I,1)+A(2,I,1)+A(4,I,1))*1.0D-05
          A(1,I,1)=A(1,I,1)/AREA
          A(2,I,1)=A(2,I,1)/AREA
          A(4,I,1)=A(4,I,1)/AREA
  210 CONTINUE
      I3=1
      I4=16
      IND=0
    1 IND=IND+1
      GO TO (15,15,13,14,100),IND
   13 I4=11
      GO TO 15
   14 I3=12
      I4=16
C
C  OBTAIN MEANS
C
   15 DO 25 I=1,7
          B(I)=0.0D00
          S(IND,I)=0.0D00
          DO 20 J=1,7
               C(I,J)=0.0D00
   20     CONTINUE
   25 CONTINUE
      WRITE(6,2000) IND
```

```
      DO 35 I=I3,I4
          WRITE(6,2001) I,(A(IND,I,J),J=1,7)
          DO 30 J=1,7
               B(J)=B(J)+A(IND,I,J)
   30     CONTINUE
   35 CONTINUE
      DO 40 J=1,7
          B(J)=B(J)/DFLOAT(I4-I3+1)
   40 CONTINUE
      WRITE(6,2002)
C
C  OBTAIN COVARIANCES
C
      DO 55 I=I3,I4
          DO 50 J=1,7
               A(IND,I,J)=A(IND,I,J)-B(J)
               DO 45 K=1,J
                    C(J,K)=C(J,K)+A(IND,I,J)*A(IND,I,K)
   45          CONTINUE
   50     CONTINUE
          WRITE(6,2001) I,(A(IND,I,J),J=1,7)
   55 CONTINUE
      DO 60 J=1,7
          S(IND,J)=DSQRT(C(J,J)/DFLOAT(I4-I3))
   60 CONTINUE
      WRITE(6,2003)
      DO 70 I=I3,I4
          DO 65 J=1,7
               A(IND,I,J)=A(IND,I,J)/S(IND,J)
   65     CONTINUE
          WRITE(6,2004) I,(A(IND,I,J),J=1,7)
   70 CONTINUE
      WRITE(6,2005)
      WRITE(6,2001) IND,(B(J),J=1,7)
      WRITE(6,2006)
      WRITE(6,2001) IND,(S(IND,J),J=1,7)
      WRITE(6,2007)
C
C CALCULATE CORRELATIONS AND CORRECT FOR BIAS
C
      DO 80 I=1,7
          DO 75 J=1,I
               C(I,J)=C(I,J)/(S(IND,I)*S(IND,J)*DFLOAT(I4-I3))
                C(I,J)=C(I,J)*(1.0D00+(1.0D00-C(I,J)**2)/
     .                    (2.0D00*DFLOAT(I4-I3-3)))
   75     CONTINUE
          WRITE(6,2008) I,(C(I,J),J=1,I)
   80 CONTINUE
      GO TO 1
  100 WRITE(6,2006)
      WRITE(6,2001) (IND,(S(IND,J),J=1,7),IND=1,4)
      WRITE(6,2009)
      IND=0
  106 IND=IND+1
```

```
      GO TO (101,102,103,104,105,200),IND
  101 I1=1
      I2=2
      I3=1
      I4=16
      GO TO 110
  102 I2=3
      I4=11
      GO TO 110
  103 I1=2
      GO TO 110
  104 I1=1
      I2=4
      I3=12
      I4=16
      GO TO 110
  105 I1=2
C
C  CALCULATE CORRELATIONS OF PARAMETERS BETWEEN
C  DIFFERENT PEAKS ON SAME CHROMATOGRAM
C
  110 DO 120 I=1,7
          B(I)=0.0D00
               DO 115 J=I3,I4
               B(I)=A(I1,J,I)*A(I2,J,I)+B(I)
  115     CONTINUE
          B(I)=B(I)/DFLOAT(I4-I3)
          B(I)=B(I)*(1.0D00+(1.0D00-B(I)**2)/
     1                (2.0D00*DFLOAT(I4-I3-3)))
  120 CONTINUE
      WRITE(6,2010) I1,I2,B
      GO TO 106
  200 STOP
 1000 FORMAT(7F10.0)
 2000 FORMAT('1DATA  SET',I3,'   NORMALIZED AREA')
 2001 FORMAT('0',I4,F17.0,6F17.4)
 2002 FORMAT('0  DEVIATIONS FROM MEAN')
 2003 FORMAT('0  NORMALIZED DEVIATIONS')
 2004 FORMAT('0',I4,7F17.4)
 2005 FORMAT('0  MEANS')
 2006 FORMAT('0  STANDARD DEVIATIONS')
 2007 FORMAT('0  CORRELATIONS BETWEEN PARAMETERS OF SAME',
20071      ' PEAK')
 2008 FORMAT('0',10X,I3,7F15.4/)
 2009 FORMAT('0CORRELATIONS BETWEEN PEAKS')
 2010 FORMAT('0',2I2,7F17.4)
      END
```

```
      SUBROUTINE BAYES(IP,FTEST,P,FSM,SEC,X2)
C  ESTIMATES PEAK PARAMETERS
C   IP(1) IS OUTPUT PARAMETER
C         =0 - PRINTS FINAL ESTIMATES, 'SUM OF SQUARES',
C              DAMPING FACTOR, COMPUTATION TIME,
C              BUT NO HEADING
C         =1 - AS FOR 0, WITH HEADING
C         =2 - AS FOR 1, PLUS ESTIMATES AT EACH ITERATION
C         =3 - AS FOR 2, PLUS OUTPUT FROM DAMP AND STEP
C    FTEST = TERMINATION FACTOR
C    P = DAMPING FACTOR (RETURNED)
C    FSM = MINIMUM 'SUM OF SQUARES' (RETURNED)
C    SEC = ELAPSED COMPUTATION TIME (SECONDS)
C    X2 = WORK SPACE (257)
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      DIMENSION DISPM(7,7),RHS(7),XX(7),BB(7,7),RR(7),
     1          DIA(7),AM(7),AL(7),X2(1),C(7),CM(7)
      INTEGER IP(5),PIVOT(7)
      DATA N/512/,N2/256/,K/257/,DROP/0.1D00/
      NTIME=2500000
      CALL CS019A(NTIME)
      NIT=0
      IND=0
      IF(IP(1).GT.0) WRITE(6,1000)
      DO 2 J=2,N2
          I=N+2-J
          X2(J)=W(J)*(X(J)**2+X(I)**2)
    2 CONTINUE
    3 X2(K)=W(K)*X(K)**2
      CALL INFORM(0,FSP,X2,C)
      FSM=FSP
      DESENT=FSP
      GO TO 5
C
C  OBTAIN INFORMATION MATRIX (V) AND GRADIENT VECTOR (Y)
C
    4 CALL INFORM(1,FSP,X2,C)
C
C  INTRODUCE PRIOR INFORMATION, IF ANY, TO V AND Y
C
    5 IF(IP(3).GT.0) CALL PRIOR
      FS0=FSP
      GL=0.0D00
C
C  SCALE PARAMETER SPACE TO IMPROVE NUMERICAL PRECISION
C
      DO 6 I=1,7
          AL(I)=A(I)
          AM(I)=A(I)
          DIA(I)=1.0D00/(DSQRT(V(I,I)))
```

```
          Y(I)=Y(I)*DIA(I)
          GL=GL+Y(I)**2
    6 CONTINUE
      GS=-2.0D00*GL
      DO 9 I=1,7
          DO 7 J=1,7
               V(I,J)=V(I,J)*DIA(I)*DIA(J)
    7     CONTINUE
    9 CONTINUE
    8 CALL CS019B(KTIME)
      SEC=2.6D-5*DFLOAT(NTIME-KTIME)
      P=0.0D00
      IF(IP(1).LT.2) GO TO 10
      WRITE(6,999)
      WRITE(6,1001) NIT,(A(I),I=1,7),FSM,P,GL,SEC
C
C  CALCULATE DAMPING FACTOR
C
   10 CALL DAMP(IP,IND,P,FSP,GS,GAMMA)
      IF(IND.GE.100) GO TO 30
      Z=1.0D00+1.0D00/P
   16 DO 18 I=1,7
          V(I,I)=Z
   18 CONTINUE
      CALL CS012A(V,DISPM,RHS,XX,7,BB,RR,PIVOT)
C
C  CALCULATE CORRECTION VECTOR AND NEW ESTIMATES
C
      CL=0.0D00
      GAMMA=0.0D00
      DO 22 I=1,7
          CORR=0.0D00
          DO 20 J=1,7
               CORR=CORR+Y(J)*DISPM(I,J)
   20     CONTINUE
          GAMMA=GAMMA+ CORR*Y(I)
          CL=CL+CORR**2
          CORR=CORR*DIA(I)
          A(I)=AL(I)+CORR
          C(I)=CORR
   22 CONTINUE
      GAMMA=GAMMA/DSQRT(GL*CL)
      IF(DABS(1.0D00-GAMMA).GT.1.0D-05) GO TO 23
      GAMMA=0.0D00
      GO TO 24
   23 GAMMA=DARCOS(GAMMA)*57.295779
C
C  TEST IF NEW ESTIMATES ARE REASONABLE
C
   24 CALL TEST(IP)
      IF(IP(4).LT.0) GO TO 60
C
C
C  OBTAIN 'SUM OF SQUARES' FOR NEW ESTIMATES
```

```
C
      CALL INFORM(2,FSP,X2,C)
      IF(FSP.GE.FSM) GO TO 10
      GAMAM=GAMMA
      FSM=FSP
      DO 26 I=1,7
          AM(I)=A(I)
          CM(I)=C(I)
   26 CONTINUE
C
C  REPEAT WITH DIFFERENT VALUE OF DAMPING FACTOR
C
      GO TO 10
   30 NIT=NIT+1
C
C  STEP ALONG CORRECTION VECTOR IF NECESSARY
C
      IF(GAMAM.LT.50.0D00)  CALL STEP(IP,FSM,FSO,AL,AM,CM,
     1                                 X2,A)
      IF(IP(4).LT.0) GO TO 60
C
C  END OF ITERATION - TEST FOR CONVERGENCE
C
   32 IND=1
      FSP=FSM
      DO 34 I=1,7
          A(I)=AM(I)
   34 CONTINUE
      DESENT=DROP*DESENT+FSO-FSM
      IF(DESENT/FSM.GT.FTEST) GO TO 37
      WRITE(6,1004)
      GO TO 40
   37 IF(GL.GT.FTEST) GO TO 35
      WRITE(6,1012)
      GO TO 40
   35 IF(NIT.LT.40) GO TO 36
      IP(4)=-2
      WRITE(6,1005)
      GO TO 50
   36 IF(SEC.LT.60.0D00) GO TO 4
      IP(4)=-3
      WRITE(6,1006)
      GO TO 50
C
C  STATISTICS SECTION
C  IP(2) IS STATISTICS OUTPUT PARAMETER
C        =0 - PRINTS OUT DEGREES OF FREEDOM (NU),
C             NORMALIZED CHI**2 (D)
C        =1 - AS FOR 0, RETURNS DISPERSION MATRIX (V)
C        =2 - AS FOR 1, PRINTS SCALED GRADIENTS, SQUARE OF
C     SCALED GRADIENT LENGTH AND LENGTH, STANDARD DEVIATIONS,
C             AND RELATIVE STANDARD DEVIATIONS.  RETURNS
C             STANDARD DEVIATIONS IN Y AND
C             CORRELATION MATRIX IN V.
```

```
C        =3 - AS FOR 2, AND PRINTS OUT CORRELATION MATRIX.
C
   40 IF(IP(2).LT.1) GO TO 50
      DO 44 I=1,7
          V(I,I)=1.0D00
   44 CONTINUE
      CALL CS012A(V,DISPM,RHS,XX,7,BB,RR,PIVOT)
      DO 45 I=1,7
          XX(I)=Y(I)
          Y(I)=DSQRT(DISPM(I,I))
   45 CONTINUE
      DO 48 I=1,7
          DO 46 J=1,7
          V(I,J)=DISPM(I,J)/(Y(I)*Y(J))
   46     CONTINUE
   48 CONTINUE
      GS=0.0D00
      DO 49 I=1,7
          XX(I)=XX(I)*Y(I)*2.0D00
          Y(I)=Y(I)*DIA(I)
      IF(DABS(A(I)).GT.1.0D-5) RR(I)=Y(I)/DABS(A(I))
          GS=GS+XX(I)**2
   49 CONTINUE
      GAMMA=DSQRT(GS)
   50 CALL CS019B(KTIME)
      SEC=2.6D-05*DFLOAT(NTIME-KTIME)
      WRITE(6,1001) NIT,(A(I),I=1,7),FSM,P,GL,SEC
      IF(IP(4).LT.0) GO TO 60
      IF(IP(2).LT.2) GO TO 60
      NU=IP(5)-IP(4)-7
      DEV=1.0D01
      IF(NU.GT.10) DEV=DSQRT(2.0D00*FSM)-
     1                 DSQRT(DFLOAT(NU*2-1))
      WRITE(6,1013) XX,GAMMA,GS
      WRITE(6,1007) NU,DEV,(Y(I),I=1,7)
      WRITE(6,1008) FTEST,RR
      IF(IP(2).LT.3) GO TO 60
      WRITE(6,1009)
      WRITE(6,1010) ((V(I,J),J=1,7),I=1,7)
   60 CALL CS019C
      RETURN
```

```
 999 FORMAT(1H )
1000 FORMAT('0NIT',7X,'A1',13X,'A2',13X,'A3',10X,'A4',8X,
10001'A5',8X,'A6',8X,'A7',10X,'FSM',16X,'P',9X,'TIME')
1001 FORMAT(1X,I3,1P3D15.5,0P4F10.6,1PD15.6,D10.2,D12.2,
10011     0PF7.2)
1004 FORMAT(10X,'TERMINATED BY SLOW CONVERGENCE')
1005 FORMAT(10X,'TERMINATED BY ITERATION LIMIT')
1006 FORMAT(10X,'TERMINATED BY TIME LIMITATION')
1007 FORMAT(' ESTIMATED STANDARD DEVIATIONS',60X,'NU=',I5,
10071     5X,'D=',1PD15.5/4X,3D15.5,0P4F10.6)
1008 FORMAT(' RELATIVE STANDARD DEVIATIONS (PERCENT) ',66X,
10081      'FTEST =',F10.7/4X,2P3F15.5,4F10.6)
1009 FORMAT(' CORRELATION MATRIX')
1010 FORMAT(1H0,20X,7F10.4)
1011 FORMAT(89X,1PD15.6,D10.2)
1012 FORMAT(10X,'TERMINATED BY SMALL GRADIENT')
1013 FORMAT(' SCALED GRADIENTS'/4X,1P3D15.2,4D10.2,2D12.2)
     END
```

```
      SUBROUTINE INFORM(IP,PHI,X2,C)
C
C  IP IS OPTION PARAMETER
C      =0 - RETURNS INFORMATION MATRIX AND GRADIENT VECTOR
C           AND SUM OF SQUARED DEVIATIONS
C      =1 - RETURNS INFORMATION MATRIX AND GRADIENT ONLY
C      =2 - RETURNS SUM OF SQUARED DEVIATIONS ONLY
C  X2 = WEIGHTED ABSOLUTE SQUARE OF DATA, USED IN
C  CALCULATION OF 'SUM OF SQUARES' WHEN CONTRIBUTION FROM
C  FITTED PEAK IS NEGLIGIBLE (REAL PART OF NORMALIZED
C  PEAK IS LESS THAN EXP(-20) )
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      DIMENSION EF(7),OF(7),X2(1),C(1)
      DATA N/512/,N2/256/,M/7/,TWOPI/6.283185307179586/
      IF(IP.EQ.2) GO TO 100
      DO 4 I=1,M
         Y(I)=0.0D00
         DO 2 J=1,M
              V(I,J)=0.0D00
    2    CONTINUE
    4 CONTINUE
    6 FA=TWOPI/DFLOAT(N)
      FM=FA*(A(2)-1.0D00)
      FS=FA*A(3)
      IF(IP.NE.1) PHI=0.0D00
      DO 20 J=2,N2
         S=DFLOAT(J-1)*FS
         S2=S*S
         F=((-A(7)*S2/30.0D00+A(5))*S2/12.0D00-1.0D00)*
     1                                   S2/2.0D00
         IF(F.GT.-20.0D00) GO TO 7
         IF(IP.NE.1) PHI=PHI+X2(J)
         GO TO 18
    7    IF(F.LE.1.0D01) GO TO 8
         WRITE(6,1000) (A(IL),IL=1,7)
         GO TO 40
    8    ALPHA=DEXP(F)
         S3=S2*S
         SA=DFLOAT(J-1)*FA
         I=N+2-J
         ARG=(-A(6)*S2/20.0D00+A(4))*S3/6.0D00-DFLOAT(J-1)*
     1                                                     FM
         CF=DCOS(ARG)
         SF=DSIN(ARG)
         DPR=ALPHA*CF
         DPI=ALPHA*SF
   10    PR=X(J)-A(1)*DPR
         PI=X(I)-A(1)*DPI
         U=W(J)
         IF(IP.NE.1) PHI=PHI+U*(PR*PR+PI*PI)
```

```
       IF(IP.EQ.2) GO TO 18
       EF(2)=0.0D00
       OF(2)=-SA
       EF(3)=((-A(7)*S2/20.0D00+A(5))*S2/6.0D00-1.0D00)*
   1                                           S*SA
       OF(3)=(-A(6)*S2/12.0D00+A(4))*S2*SA/2.0D00
       EF(4)=0.0D00
       OF(4)=S3/6.0D0
       EF(5)=S2*S2/24.0D00
       OF(5)=0.0D00
       EF(6)=0.0D00
       OF(6)=-S3*S2/120.0D00
       EF(7)=-S3*S3/720.0D00
       OF(7)=0.0D00
       Y(1)=Y(1)+U*(PR*DPR+PI*DPI)
       U=U*ALPHA
       T=U*ALPHA
       V(1,1)=V(1,1)+T
       DO 12 K=2,M
            Y(K)=Y(K)+U*(PR*(EF(K)*CF-OF(K)*SF)
   .                    +PI*(OF(K)*CF+EF(K)*SF))
            V(K,K)=V(K,K)+T*(EF(K)*EF(K)+OF(K)*OF(K))
12     CONTINUE
       DO 14 K=4,M
            V(3,K)=V(3,K)+T*(EF(3)*EF(K)+OF(3)*OF(K))
14     CONTINUE
       V(1,3)=V(1,3)+T*EF(3)
       V(2,3)=V(2,3)+T*OF(2)*OF(3)
       DO 16 K=5,M,2
            IK=K-1
            V(1,K)=V(1,K)+T*EF(K)
            V(2,IK)=V(2,IK)+T*OF(2)*OF(IK)
16     CONTINUE
18 CONTINUE
20 CONTINUE
22 IF(IP.EQ.1) GO TO 28
26 PHI=2.0D00*PHI+X2(N2+1)
   IF(IP.EQ.2) GO TO 40
28 V(4,6)=-V(5,5)*4.0D00/5.0D00
   V(5,7)=-V(6,6)*5.0D00/6.0D00
   Y(1)=2.0D00*Y(1)
   V(1,1)=2.0D00*V(1,1)
   FA=2.0D00*A(1)
   FM=FA*A(1)
   DO 34 I=2,M
       Y(I)=FA*Y(I)
       V(1,I)=FA*V(1,I)
       V(I,1)=V(1,I)
       V(I,I)=FM*V(I,I)
       K=I+1
       IF(K.EQ.(M+1)) GO TO 40
       DO 32 J=K,M
            V(I,J)=FM*V(I,J)
            V(J,I)=V(I,J)
```

```
   32      CONTINUE
   34 CONTINUE
   40 RETURN
C
C  DETERMINE IF 4'TH AND 6'TH CUMULANTS ARE
C  IN CRITICAL REGION
C
  100 T=A(5)**2-1.6D00*A(7)
      IF(T.LE.0.0D00) GO TO 6
      SA=1.0D00/(TWOPI*A(3))
      IF(DABS(A(7)).GT.1.0D-10) GO TO 105
      IF(A(5).LE.1.0D-10) GO TO 6
      S=DSQRT(12.0D00/A(5))*SA
      IF(S.GT.0.6D00) GO TO 6
      GO TO 120
  105 T=DSQRT(T)
      S=(A(5)-T)*15.0D00/A(7)
      S2=(A(5)+T)*15.0D00/A(7)
      IF(S.LE.0.0D00.AND.S2.LE.0.0D00) GO TO 6
      IF(S.GT.0.0D00.AND.S2.GT.0.0D00) GO TO 110
      S=DMAX1(S,S2)
      GO TO 115
  110 S=DMIN1(S,S2)
  115 S=DSQRT(S)*SA
      IF(S.GT.0.6D00) GO TO 6
  120 S=A(5)**2/1.6D00
      C(7)=S-A(7)+C(7)
      A(7)=S
      GO TO 6
 1000 FORMAT(4X,1P3D15.5,0P4F10.6)
      END
```

```
      SUBROUTINE DAMP(IP,IND,P,FS,GS,GAMMA)
C
C  CALCULATES DAMPING FACTOR (P) FOR NEXT TRIAL
C  IF OUTPUT PARAMETER, IP(1), IS EQUAL TO 3, PRINTS OUT
C  INFORMATION ON EACH TRIAL (SEE STATEMENT NUMBER 700)
C    IND = TRIAL NUMBER
C    FS = SUM OF SQUARES FOR P
C    GS = SLOPE OF FS(P) AT P=0
C    GAMMA = ANGLE BETWEEN SCALED CORRECTION VECTOR AND
C            NEGATIVE GRADIENT (DEGREES)
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(9),B(3),X(3),F(3)
      INTEGER IP(5)
      DATA N/3/,UP/1.0D01/,DOWN/1.0D-01/,H/1.0D-01/,
     .      HL/-2.302585092994046/
      IF(IND.GT.0) GO TO 10
      PL=40.0D00
      GO TO 100
   10 IF(IND.EQ.1) GO TO 100
      FSP=FS-F0
      IF(FSP.GT.0.0D00) PBAD=P*0.95D00
      IF(FSP.GE.FSM) GO TO 20
      FSM=FSP
      PM=P
   20 GO TO (100,200,300,400,700,700),IND
C
C  FIRST TRIAL - PREVIOUS VALUE
C
  100 F0=FS
      FSM=0.0D00
      IF(PL.GT.1.0D07) PL=PL*DOWN
      PM=PL
      P=PL
      PBAD=1.0D20
      F(1)=0.0D00
      X(1)=HL
      IND=2
      GO TO 900
C
C SECOND TRIAL - MINIMUM OF QUADRATIC
C
  200 F(2)=FSP
      X(2)=DLOG(P+H)
      IF(IP(1).GT.2) WRITE(6,1000) GAMMA,FSP,P,X(2)
      B(3)=(F(2)-F(1)-H*GS*(X(2)-X(1)))/(X(2)-X(1))**2
      B(2)=H*GS-2.0D00*B(3)*HL
      B(1)=F(1)-B(2)*HL-B(3)*HL**2
      IND=3
      GO TO 500
C
C  THIRD TRIAL
C
  300 IF(P.GT.1.0D05) GO TO 700
```

```
      F(3)=FSP
      X(3)=XP
      IF(IP(1).GT.2) WRITE(6,1001) B(1),B(2),B(3),FP,IC,
     1                             GAMMA,FSP,P,XP
      IND=4
      GO TO 450
C
C  FOURTH TRIAL
C
  400 IF(P.GT.1.0D05) GO TO 700
      IF(IP(1).GT.2) WRITE(6,1001) B(1),B(2),B(3),FP,IC,
     1                             GAMMA,FSP,P,XP
C    GAMMA = ANGLE BETWEEN SCALED CORRECTION VECTOR AND
C            NEGATIVE GRADIENT (DEGREES)
      FP=F(1)
      K=1
      IF(F(2).LE.FP) GO TO 405
        FP=F(2)
        K=2
  405 IF(F(3).LE.FP) GO TO 420
      K=3
  420 F(K)=FSP
      X(K)=XP
      IND=5
  450 DO 460 J=1,N
          B(J)=F(J)
          A(J)=1.0D00
          K=J+N
          A(K)=X(J)
          K=K+N
          A(K)=X(J)**2
  460 CONTINUE
C
C  CALCULATE CONSTANTS OF QUADRATIC
C
      CALL DSIMQ(A,B,N,IC)
C
C  ANALYZE CASES AND TAKE APPROPRIATE ACTION
C
      IF(IC.GT.0) GO TO 700
  500 FP=0.0D00
      IF(B(3).GT.0.0D00) GO TO 510
      IF(B(2).GT.0.0) GO TO 505
      IC=3
  503 P=PM*UP
      XP=DLOG(P+H)
      GO TO 800
  505 IF(B(1).LE.0.0D00) GO TO 507
      IC=2
      GO TO 503
  507 IC=4
      GO TO 515
  510 XP=-B(2)*0.5D00/B(3)
      IF(XP.GT.HL) GO TO 520
```

```
      IC=5
  515 P=P*DOWN
      XP=DLOG(P+H)
      GO TO 800
  520 FP=B(1)+B(2)*XP+B(3)*XP**2
      IF(FP.LE.FSM) GO TO 525
      IC=10
      GO TO 700
  525 IF(XP.LT.20.0D00) GO TO 530
      IC=7
      GO TO 503
  530 P=DEXP(XP)-H
      IC=0
      IF(P.GT.1.0D-08) GO TO 800
      P=1.0D-08
      IC=6
C
C  PRINT OUT INFORMATION
C     B(1-3) = CONSTANTS OF QUADRATIC
C     FP = PREDICTED MINIMUM OF QUADRATIC
C     IC = ANALYSIS CASE CODE - SEE PROGRAM ITSELF
C     FSP = DIFFERENCE BETWEEN WEIGHTED 'SUM OF SQUARES'
C            AT P=0 AND AT THE CURRENT VALUE OF P
C     P = CURRENT VALUE OF DAMPING FACTOR
C     XP = LN(P+0.1)
C
  700 IF(IP(1).GT.2) WRITE(6,1001) B(1),B(2),B(3),FP,IC,
     1                              GAMMA,FSP,P,XP
      IF(FSM.LT.0.0D00) GO TO 710
      P=P*DOWN
      IND=6
      IF(P.LE.1.0D-10) GO TO 710
      GO TO 900
  710 P=PM
      PL=PM
      IND=100
      GO TO 900
  800 IF(P.LT.PBAD) GO TO 900
      P=PM*2.0D00
      IC=8
      IF(P.GE.PBAD) P=0.5D00*(PBAD+PM)
  900 RETURN
 1000 FORMAT(79X,F10.2,1PD15.6,2D10.2)
 1001 FORMAT(16X,1P3D15.2,D15.6,I3,0PF10.2,1PD15.6,2D10.2)
      END
```

```
      SUBROUTINE STEP(IP,FSM,FSL,AL,AM,CM,GX2,A)
C
C  CALCULATES OPTIMAL VALUE OF STEP (S) ALONG DAMPED
C  CORRECTION VECTOR AND RETURNS NEW VALUES OF PARAMETERS
C  IF OUTPUT PARAMETER, IP(1), EQUALS 3, INFORMATION IS
C  PRINTED OUT AT EACH TRIAL (SEE STATEMENT NUMBER 400)
C     FSM = 'SUM OF SQUARES' AT S=1
C     FSL = 'SUM OF SQUARES' AT S=0
C     AL  = PARAMETER VALUES AT S=0
C     AM  = PARAMETER VALUES AT S=1
C     CM  = CORRECTION VECTOR AT S=1
C     GX2 = WEIGHTED ABSOLUTE SQUARE OF DATA
C     A   = PARAMETER VALUES AT OPTIMAL S
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION AL(7),CM(7),GX2(1),P(3),X(3),Y(3),Q(9),AM(7),A(7)
      INTEGER IP(5)
      DATA N/7/,M/3/,UP/1.0D01/,DOWN/1.0D-01/
C
C  INITIALIZE - TRY S = 2
C
      SBAD=1.0D12
      IC=0
      XMAX=1.0D04
      P(1)=0.0D00
      X(1)=0.0D00
      PM=FSM-FSL
      P(2)=PM
      X(2)=1.0D00
      SM=1.0D00
      S=2.0D00
      IND=0
   10 IND=IND+1
      XMAX=XMAX*1.0D02
      IF(S.LT.SBAD) GO TO 12
      S=SM*2.0D00
      IC=7
      IF(S.GE.SBAD) S=0.5D00*(SBAD+SM)
C
C  CALCULATE NEW VALUES OF PARAMETERS AND 'SUM OF SQUARES'.
C  PS IS THE DIFFERENCE BETWEEN THE 'SUM OF SQUARES'
C  AT S=0 AND AT THE CURRENT VALUE OF S.
C
   12 DO 15 J=1,N
          A(J)=AL(J)+S*CM(J)
   15 CONTINUE
   16 CALL TEST(IP)
      IF(IP(4).LT.0) GO TO 405
      CALL INFORM (2,FS,GX2,Q)
      PS=FS-FSL
      IF(PS.GT.0.0D00) SBAD=S*0.95D00
   17 IF(FS.GE.FSM) GO TO 30
      FSM=FS
      PM=PS
```

```
      SM=S
      DO 20 J=1,7
          AM(J)=A(J)
   20 CONTINUE
   30 GO TO (100,200,200,200,400),IND
C
C  FIRST TRIAL, S = 2. P(1-3) AND X(1-3) ARE STORED VALUES OF
C  ATTEMPED S AND THE RESULTING PS.
C
  100 IF(IP(1).GT.2) WRITE(6,1000) PS,S
      P(3)=PS
      X(3)=S
      GO TO 300
C
C  SUBSEQUENT TRIALS
C
  200 IF(IP(1).GT.2) WRITE(6,1001) Y(1),Y(2),Y(3),PQ,IC,PS,S
      IF(DABS((PS-PQ)/PS).LE.1.0D-03) GO TO 405
C
C  REPLACE S GIVING GREATEST PS WITH CURRENT VALUE OF S
C
  208 PQ=P(1)
      K=1
      IF(P(2).LE.PQ) GO TO 210
        PQ=P(2)
        K=2
  210 IF(P(3).LE.PQ) GO TO 215
        K=3
  215 P(K)=PS
      X(K)=S
C
  300 DO 310 J=1,M
          Y(J)=P(J)
          Q(J)=1.0D00
          K=J+M
          Q(K)=X(J)
          K=K+M
          Q(K)=X(J)**2
  310 CONTINUE
C
C  CALCULATE CONSTANTS OF QUADRATIC
C
      CALL DSIMQ(Q,Y,M,IC)
C
C  ANALYZE CASES AND TAKE APPROPRIATE ACTION
C
      IF(IC.GT.0) GO TO 320
      PQ=0.0D00
      IF(DABS(Y(3)).GT.1.0D-20) GO TO 330
      IC=5
      IF(Y(2).GT.0.0D00) GO TO 320
  315 S=SM*UP
      GO TO 10
  320 S=SM*DOWN
```

```
      GO TO 10
  330 S=-0.5D00*Y(2)/Y(3)
      IF(Y(3).GT.0.0D00) GO TO 350
      IF(S.GT.SM) GO TO 340
      IC=2
      GO TO 315
  340 IC=3
      GO TO 320
  350 IF(Y(2).LT.0.0D00) GO TO 360
      IC=4
      GO TO 320
  360 IF(S.LT.XMAX) GO TO 370
      IC=6
      S=XMAX
      GO TO 10
  370 PQ=Y(1)+S*(Y(2)+S*Y(3))
      GO TO 10
C
C  PRINT OUT INFORMATION
C    Y(1-3) = CONSTANTS OF QUADRATIC
C    PQ = PREDICTED MINIMUM OF QUADRATIC
C    IC = ANALYSIS CASE CODE (SEE PROGRAM ITSELF)
C    PS = DIFFERENCE BETWEEN SUM OF SQUARES AT S=0
C         AND AT CURRENT VALUE OF S
C    S = CURRENT VALUE OF STEP FACTOR
C
  400 IF(IP(1).GT.2) WRITE(6,1001) Y(1),Y(2),Y(3),PQ,IC,PS,S
  405 RETURN
 1000 FORMAT(89X,1PD15.6,D10.2)
 1001 FORMAT(11X,1P3D20.2,D15.6,I3,D15.6,D10.2)
      END
```

```
      SUBROUTINE DSIMQ(A,B,N,KS)
C
C     SOLUTION OF SIMULTANEOUS LINEAR EQUATIONS A*X=B
C     DOUBLE PRECISION FORM OF SIMQ IN IBM SCIENTIFIC
C    SUBROUTINE PACKAGE VERSION III
C        N - NUMBER OF EQUATIONS AND VARIABLES
C        A - N BY N MATRIX OF COEFFICIENTS.
C            DESTROYED IN COMPUTATION.
C        B - VECTOR OF ORIGINAL  CONSTANTS.
C            REPLACED BY SOLUTION - X.
C        KS = 0 - NORMAL SOLUTION
C           = 1 - EQUATIONS ARE SINGULAR, SOLUTION NOT FOUND.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(1),B(1)
      TOL=0.0D00
      KS=0
      JJ=-N
      DO 65 J=1,N
      JY=J+1
      JJ=JJ+N+1
      BIGA=0.0D00
      IT=JJ-J
      DO 30 I=J,N
      IJ=IT+I
      IF(DABS(BIGA)-DABS(A(IJ))) 20,30,30
   20 BIGA=A(IJ)
      IMAX=I
   30 CONTINUE
      IF(DABS(BIGA)-TOL) 35,35,40
   35 KS=1
      GO TO 100
   40 I1=J+N*(J-2)
      IT=IMAX-J
      DO 50 K=J,N
      I1=I1+N
      I2=I1+IT
      SAVE=A(I1)
      A(I1)=A(I2)
      A(I2)=SAVE
   50 A(I1)=A(I1)/BIGA
      SAVE=B(IMAX)
      B(IMAX)=B(J)
      B(J)=SAVE/BIGA
      IF(J-N) 55,70,55
   55 IQS=N*(J-1)
```

```
    DO 65 IX=JY,N
    IXJ=IQS+IX
    IT=J-IX
    DO 60 JX=JY,N
    IXJX=N*(JX-1)+IX
    JJX=IXJX+IT
 60 A(IXJX)=A(IXJX)-(A(IXJ)*A(JJX))
 65 B(IX)=B(IX)-(B(J)*A(IXJ))
 70 NY=N-1
    IT=N*N
    DO 80 J=1,NY
    IA=IT-J
    IB=N-J
    IC=N
    DO 80 K=1,J
    B(IB)=B(IB)-A(IA)*B(IC)
    IA=IA-N
 80 IC=IC-1
100 RETURN
    END
```

```
      SUBROUTINE DETECT(IP,HLEVEL)
C
C  PROVIDES INITIAL VALUES OF PARAMETERS FOR BAYES
C  REMOVE STATEMENTS NUMBERED 1000 TO 1004
C  WHEN USED WITH PROGRAM M3.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      INTEGER IP(5)
      N=512
      M=IP(5)-IP(4)+1
C
C  TRANSFER DATA
C
 1000 L1=IP(4)
 1001 DO 1 J=1,M
 1002     I=L1-1+J
 1003     X(J)=DBLE(CGRAM(I))
 1004 CONTINUE
      L1=M+1
      DO 2 J=L1,N
          X(J)=0.0D00
    2 CONTINUE
    3 KP=IP(3)+1
      GO TO (100,200,300),KP
C
C  CASE 0  NO  PRIOR  INFORMATION
C  USES APPROXIMATE AREA, RETENTION TIME, AND WIDTH PROVIDED
C  BY DPINIT, SETS CUMULANTS TO ZERO
C
  100 CALL DPINIT(IP,HLEVEL)
      IF(IP(4).LT.0) GO TO 51
      DO 11 J=4,7
          A(J)=0.0D00
   11 CONTINUE
      GO TO 400
C
C  CASE 1  PRIOR  INFORMATION- SMALL PEAKS
C  USES PRIOR MEANS AS INITIAL ESTIMATES
C
  200 DO 21 J=1,7
          A(J)=PA(J)
   21 CONTINUE
      GO TO 32
```

```
C
C  CASE 2  PRIOR  INFORMATION- LARGE PEAKS
C  USES APPROXIMATE AREA, RETENTION TIME, AND WIDTH AND
C  PRIOR MEANS FOR THE CUMULANTS
C
  300 CALL DPINIT(IP,HLEVEL)
      IF(IP(4).LT.0) GO TO 51
      DO 31 J=4,7
          A(J)=PA(J)
   31 CONTINUE
   32 DO 33 J=1,7
          IF(PV(J).GT.0.0D00) PV(J)=1.0D00/PV(J)**2
   33 CONTINUE
C
      ENTRY TEST(IP)
C
C  SETS IP(4) TO -1 IF PARAMETER VALUES ARE UNREASONABLE
C
  400 IF(A(1).LT.0.0D00)             GO TO 42
      IF(A(2).LT.0.0D00)             GO TO 42
      IF(A(2).GT.DFLOAT(M))          GO TO 42
      IF(A(3).LE.0.5D00)             GO TO 42
      IF(A(3).GT.(DFLOAT(M)/6.0D00)) GO TO 42
      GO TO 51
   42 WRITE(6,201) (I,A(I),I=1,7)
      IP(4)=-1
      GO TO 51
C
      ENTRY PRIOR
C
C  INTRODUCES PRIOR INFORMATION
C
      DO 50 J=1,7
          Y(J)=Y(J)-(A(J)-PA(J))*PV(J)
          V(J,J)=V(J,J)+PV(J)
   50 CONTINUE
   51 RETURN
  201 FORMAT(1H0,'*****ERROR SUBROUTINE TEST-UNREASONABLE',
 2011    ' ESTIMATES'/'0',7('  A',I1,'=',1PD12.5))
      END
```

```
      SUBROUTINE SET
C
C  CALCULATES FILTER AND GROUPING CORRECTION
C  IF GROUPING CORRECTION NOT REQUIRED (FILTER CORRECTION
C  ONLY, FOR USE WITH PROGRAM M3) REPLACE STATEMENT
C  NUMBER 1000 BY:
C           HC(J)=1.0D00/(1.0D00-DCOS(2.0D00*VAR))
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      DIMENSION HC(257)
      DATA N/512/,N2/256/,K/257/,PI/3.141592653589793/
      FA=PI/512.0D00
      HC(1)=0.0D00
      DO 2 J=2,K
          VAR=FA*DFLOAT(J-1)
1000      HC(J)=VAR/(2.0D00*DSIN(VAR)**3)
    2 CONTINUE
      GO TO 10
C
      ENTRY CONVRT(L)
C
C  FILTERS DATA, FOURIER TRANSFORMS, AND APPLIES CORRECTION
C
      M=L-1
      VAR=X(1)
      X(1)=0.0D00
      DO 4 J=2,M
          FA=X(J)
          X(J)=X(J)-0.5D00*(VAR+X(J+1))
          VAR=FA
    4 CONTINUE
      X(L)=0.0D00
      CALL DFFT(9,X)
      DO 6 J=2,N2
          I=N+2-J
          X(J)=X(J)*HC(J)
          X(I)=X(I)*HC(J)
    6 CONTINUE
      X(K)=X(K)*HC(K)
   10 RETURN
      END
```

```
      SUBROUTINE DPINIT(IP,HLEVEL)
C
C  RETURNS INITIAL ESTIMATES OF A(1),A(2),A(3)
C  LEVEL, IS HEIGHT AT WHICH INTEGRATION IS TO BEGIN
C  IF ERROR OCCURS, IP(4) IS SET TO -1
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 CGRAM
      COMMON/DATA/X(512),W(257),CGRAM(2000)
      COMMON/PARM/A(7),Y(7),V(7,7),PA(7),PV(7)
      INTEGER IP(5)
      N=IP(5)-IP(4)+1
      DO 1 J=1,3
         A(J)=0.0D00
    1 CONTINUE
C
C  FIND MAXIMUM
C
      F=X(1)
      M=1
      DO 2 J=2,N
         IF(X(J).LT.F) GO TO 9
         F=X(J)
         M=J
    9 CONTINUE
    2 CONTINUE
C
C  FIND END OF LEADING AND TAILING TAIL
C
      IF((M.LT.9).OR.(M.GT.(N-9))) GO TO 8
      B2=    (X(M+1)+X(M+2)+X(M+3)+X(M+4)+X(M+5))*0.2D00
      B1=    (X(M-1)+X(M-2)+X(M-3)+X(M-4)+X(M-5))*0.2D00
      K=M+1
      L=N-6
      DO 3 J=K,L
         B2=B2+0.2D00*(X(J+5)-X(J))
         IF((X(J)-B2).LE.HLEVEL) GO TO 4
    3 CONTINUE
      GO TO 8
    4 K2=J+3
      L=M-7
      DO 5 J=1,L
         K=M-J
         B1=B1+0.2D00*(X(K-5)-X(K))
         IF((X(K)-B1).LE.HLEVEL) GO TO 6
    5 CONTINUE
      GO TO 8
```

```
C
C  CALCULATE LINEAR BASE LINE UNDER PEAK AND PARAMETERS
C
    6 K1=K-3
      SLOPE=(B2-B1)/DFLOAT(K2-K1)
      L=K2-3
      DO 7 J=K,L
         P=X(J)-SLOPE*DFLOAT(J-K1)-B1
         A(1)=A(1)+P
         D=DFLOAT(J-M)
         A(2)=A(2)+P*D
         A(3)=A(3)+P*D**2
    7 CONTINUE
      A(2)=A(2)/A(1)
      P=A(3)/A(1)-A(2)**2
      IF(P.GT.1.0D-20) A(3)=DSQRT(P)
      A(2)=A(2)+DFLOAT(M)
      GO TO 10
    8 WRITE(6,102)
      IP(4)=-1
   10 RETURN
  102 FORMAT(1H0,'***** ERROR SUBROUTINE DPINIT - ',
 1021           'PEAK WIDER THAN DATA')
      END
```

```
      SUBROUTINE FTPEAK(A,X)
C
C  GENERATES FOURIER TRANSFORM OF A PEAK  IN THE FORM OF
C  EDGEWORTH'S SERIES USING UP TO THE SIXTH CUMULANT.
C    A =  SEVEN PARAMETERS
C    X = PEAK (512 POINTS)
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(512),A(7)
      DATA N/512/,N2/256/,K/257/
      FA=6.283185307179586/512.0D00
      FS=FA*A(3)
      FM=FA*(A(2)-1.0D00)
      X(1)=A(1)
      DO 10 J=2,N2
          I=N+2-J
          S=DFLOAT(J-1)*FS
          S2=S*S
          F=((-A(7)*S2/30.0D00+A(5))*S2/12.0D00-1.0D00)
     1      *S2/2.0D00
          IF(F.GT.-20.0D00) GO TO 2
          X(J)=0.0D00
          X(I)=0.0D00
          GO TO 6
    2 IF (F .GT. 1.0D00)  GO TO 20
          ALPHA=A(1)*DEXP(F)
          ARG=(-A(6)*S2/20.0D00+A(4))*S*S2/6.0D00
     1        -DFLOAT(J-1)*FM
          X(J)=ALPHA*DCOS(ARG)
          X(I)=ALPHA*DSIN(ARG)
    6     CONTINUE
   10 CONTINUE
      X(K)=0.0D00
      IF(DABS(X(N2))+DABS(X(K-2)).GT.0.0D00) WRITE(6,1000)
      RETURN
   20 WRITE (6,1001)
      X(1) = 0.0D00
      RETURN
 1000 FORMAT(' ***** WARNING - SUBROUTINE FTPEAK - ',
 10001        'PEAK IS ALIASED')
 1001 FORMAT ( ' ***** ERROR - SUBROUTINE FTPEAK - ',
 10011        'BAD PARAMETERS')
      END
```

```
      SUBROUTINE FTPEAK(A,X,Y)
C
C  GENERATES FOURIER TRANSFORM OF A PEAK  IN THE FORM OF
C  EDGEWORTH'S SERIES USING UP TO THE SIXTH CUMULANT.
C  FOR USE WITH PROGRAM M1
C    Y =REAL PART OF PEAK FOR OUTPUT PURPOSES
C         (257 OR MORE POINTS)
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(1),X(1),Y(1)
      DATA N/512/,N2/256/,K/257/
      FA=6.283185307179586/512.0D00
      FS=FA*A(3)
      FM=FA*(A(2)-1.0D00)
      X(1)=A(1)
      Y(1)=A(1)
      DO 10 J=2,N2
         I=N+2-J
         S=DFLOAT(J-1)*FS
         S2=S*S
         F=((-A(7)*S2/30.0D00+A(5))*S2/12.0D00-1.0D00)
     1     *S2/2.0D00
         IF(F.GT.-20.0D00) GO TO 2
         X(J)=0.0D00
         X(I)=0.0D00
         Y(J)=0.0D00
         GO TO 6
    2 IF(F.GT.0.0D00) GO TO 20
         ALPHA=A(1)*DEXP(F)
         ARG=(-A(6)*S2/20.0D00+A(4))*S*S2/6.0D00
     1        -DFLOAT(J-1)*FM
         X(J)=ALPHA*DCOS(ARG)
         X(I)=ALPHA*DSIN(ARG)
         Y(J)=ALPHA
    6    CONTINUE
   10 CONTINUE
      X(K)=0.0D00
      Y(K)=0.0D00
      IF(DABS(X(N2))+DABS(X(K-2)).GT.0.0D00) WRITE(6,1000)
      GO TO 25
   20 WRITE (6,1001)
      X(1) = 0.0D00
   25 RETURN
 1000 FORMAT(' ***** WARNING - SUBROUTINE FTPEAK - ',
 10001       'PEAK IS ALIASED')
 1001 FORMAT ( ' ***** ERROR - SUBROUTINE FTPEAK - ',
 10011       'BAD PARAMETERS')
      END
```

```
      SUBROUTINE FEPEAK(A,X)
C
C  GENERATES FOURIER TRANSFORM OF A PEAK  IN THE FORM OF
C  EDGEWORTH'S SERIES USING UP TO THE TENTH CUMULANT.
C  FOR USE WITH PROGRAM M3
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(1),X(1)
      DATA N/512/,N2/256/,K/257/
      FA=6.283185307179586/512.0D00
      FS=FA*A(3)
      FM=FA*(A(2)-1.0D00)
      X(1)=A(1)
      DO 10 J=2,N2
         I=N+2-J
         S=DFLOAT(J-1)*FS
         S2=S*S
         F= ((((-A(11)*S2/90.0D00+A(9))*S2/56.0D00-A(7))
     1         *S2/30.0D00+A(5))*S2/12.0D00-1.0D00)*S2/2.0D
         IF(F.GT.-20.0D00) GO TO 2
         X(J)=0.0D00
         X(I)=0.0D00
         GO TO 6
    2 IF(F.GT.0.0D00) GO TO 20
         ALPHA=A(1)*DEXP(F)
         ARG= (((-A(10)*S2/72.0D00+A(8))*S2/42.0D00-A(6))
     1       *S2/20.0D00+A(4))*S*S2/6.0D00-DFLOAT(J-1)*FM
         X(J)=ALPHA*DCOS(ARG)
         X(I)=ALPHA*DSIN(ARG)
    6    CONTINUE
   10 CONTINUE
      X(K)=0.0D00
      IF(DABS(X(N2))+DABS(X(K-2)).GT.0.0D00) WRITE(6,1000)
      GO TO 25
   20 WRITE (6,1001)
      X(1) = 0.0D00
   25 RETURN
 1000 FORMAT(' ***** WARNING - SUBROUTINE FEPEAK - ',
 10001        'PEAK IS ALIASED')
 1001 FORMAT ( ' ***** ERROR - SUBROUTINE FEPEAK - ',
 10011         'BAD PARAMETERS')
      END
```

```
      SUBROUTINE DFFT(LOG2N,X)
C
C  FOURIER TRANSFORM OF REAL DATA IN DOUBLE PRECISION
C  X(N=2**LOG2N POINTS) IS REPLACED BY ITS COMPACT STORED
C  FOURIER TRANSFORM.  THE REAL PART FROM FREQUENCY F=0 TO
C  1/2 IS STORED AS X(J) FROM J=1 TO N/2+1.  THE IMAGINARY
C  PART FROM F=1/N TO 1/2-1/N IS STORED FROM J=N BACKWARDS
C  TO J=N/2+2.  SINCE X IS REAL, THE IMAGINARY PART OF ITS
C  TRANSFORM IS ZERO AT F=0 AND F=1/2 (IN UNITS OF THE
C  SAMPLING INTERVAL).
C  MODIFIED FROM PROGRAM OBTAINED FROM DEPT. OF PHYSICS,
C  U. OF A., EDMONTON, WRITTEN BY G. SANDE.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      INTEGER J,JN,K,KN,N,N OVER 2
      PI=3.141592653589793
      N=2**(LOG2N-1)
      CALL DRSBO(LOG2N,X)
      CALL DRSBO(LOG2N-1,X(1))
      CALL DRSBO(LOG2N-1,X(N+1))
      CALL D MR FT(LOG2N-1,X(1),X(N+1))
      N OVER 2=N/2+1
      DO 100 J=2,N OVER 2
         K=N+2-J
         JN=J+N
         KN=K+N
         XR=(X(J)+X(K))*0.5D00
         XI=(X(JN)-X(KN))*0.5D00
         YR=(X(JN)+X(KN))*0.5D00
         YI=(X(K)-X(J))*0.5D00
         ARG=PI*DFLOAT(J-1)/DFLOAT(N)
         C=DCOS(ARG)
         S=DSIN(ARG)
         T=YR*C+YI*S
         YI=YI*C-YR*S
         YR=T
         X(J)=XR+YR
         X(K)=XR-YR
         X(KN)=XI+YI
         X(JN)=YI-XI
  100 CONTINUE
      XR=X(1)+X(N+1)
      YR=X(1)-X(N+1)
      X(1)=XR
      X(N+1)=YR
      RETURN
      END
```

```
      SUBROUTINE DIFFT(LOG2N,X)
C
C  INVERSE FOURIER TRANSFORM IN DOUBLE PRECISION
C  INVERSE OF DFFT, APPLICATION OF DFFT AND DIFFT IN
C  SEQUENCE RESULTS IN THE ORIGINAL DATA.
C  MODIFIED FROM PROGRAM OBTAINED FROM DEPT. OF PHYSICS,
C  U. OF A., EDMONTON, WRITTEN BY G. SANDE.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      PI=3.141592653589793
      N=2**(LOG2N-1)
      N OVER 2=N/2+1
      N2=2*N
      FAC=1.0D00/DFLOAT(N2)
      DO 10 J=2,N
          I=N2+2-J
          X(J)=FAC*X(J)
          X(I)=-FAC*X(I)
   10 CONTINUE
      DO 100 J=2,N OVER2
          K=N+2-J
          JN=J+N
          KN=K+N
          AR=X(J)+X(K)
          AI=X(KN)-X(JN)
          BR=X(J)-X(K)
          BI=X(JN)+X(KN)
          ARG=PI*DFLOAT(J-1)/DFLOAT(N)
          C=DCOS(ARG)
          S=DSIN(ARG)
          T=BR*C+BI*S
          BI=BI*C-BR*S
          BR=T
          X(J)=AR-BI
          X(K)=AR+BI
          X(JN)=BR+AI
          X(KN)=BR-AI
  100 CONTINUE
      AR=X(1)+X(N+1)
      BR=X(1)-X(N+1)
      X(1)=FAC*AR
      X(N+1)=FAC*BR
      CALL DMRFT(LOG2N-1,X(1),X(N+1))
      CALL DRSBO(LOG2N-1,X(1))
      CALL DRSBO(LOG2N-1,X(N+1))
      CALL DRSBO(LOG2N,X)
      RETURN
      END
```

```
      SUBROUTINE D MR FT(LOG2N,X,Y)
C
C     MIXED RADIX ONE DIMENSIONAL FOURIER TRANSFORM
C     IN DOUBLE PRECISION
C  MODIFIED FROM PROGRAM OBTAINED FROM DEPT. OF PHYSICS,
C  U. OF A., EDMONTON, WRITTEN BY G. SANDE.
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1),Y(1)
      INTEGER JJ,J0,J1,J2,J3,N,M4
      REAL*8 ARG,C1,C2,C3,I0,I1,I2,I3,R0,R1,R2,R3,S1,S2,S3,
C
      INTEGER A,B,C,D,E,F,G,H,I,J,K,L,M,N,BS,CS,DS,ES,FS,GS,
     .HS,IS,JS,KS,LS,MS,AL,BL,CL,DL,EL,FL,GL,HL,IL,JL,KL,
     .LL,ML,S(13),U(13)
      EQUIVALENCE (BS,S(2)),(CS,S(3)),(DS,S(4)),(ES,S(5)),
     .(FS,S(6)),(GS,S(7)),(HS,S(8)),(IS,S(9)),(JS,S(10)),
     .(KS,S(11)),(LS,S(12)),(MS,S(13)),(AL,U(1)),(BL,U(2)),
     .(CL,U(3)),(DL,U(4)),(EL,U(5)),(FL,U(6)),(GL,U(7)),
     .(HL,U(8)),(IL,U(9)),(JL,U(10)),(KL,U(11)),
     .(LL,U(12)),(ML,U(13))
C
      N=2**LOG2N
      IF (LOG2N.LE.1) GO TO 500
      DO 400 K=2,LOG2N,2
      M=2**(LOG2N-K)
      M4=4*M
      DO 300 J=1,M
      ARG=6.283185307179586*DFLOAT(J-1)/DFLOAT(M4)
      C1=DCOS(ARG)
      S1=DSIN(ARG)
      C2=C1*C1-S1*S1
      S2=C1*S1+C1*S1
      C3=C2*C1-S2*S1
      S3=C2*S1+S2*C1
```

```
     DO 200 I=M4,N,M4
     J0=I+J-M4
     J1=J0+M
     J2=J1+M
     J3=J2+M
     R0=X(J0)+X(J2)
     R1=X(J0)-X(J2)
     I0=Y(J0)+Y(J2)
     I1=Y(J0)-Y(J2)
     R2=X(J1)+X(J3)
     R3=X(J1)-X(J3)
     I2=Y(J1)+Y(J3)
     I3=Y(J1)-Y(J3)
     X(J0)=R0+R2
     Y(J0)=I0+I2
     IF(J.EQ.1) GO TO 100
     X(J2)=(R1+I3)*C1+(I1-R3)*S1
     Y(J2)=(I1-R3)*C1-(R1+I3)*S1
     X(J1)=(R0-R2)*C2+(I0-I2)*S2
     Y(J1)=(I0-I2)*C2-(R0-R2)*S2
     X(J3)=(R1-I3)*C3+(I1+R3)*S3
     Y(J3)=(I1+R3)*C3-(R1-I3)*S3
     GO TO 200
 100 CONTINUE
     X(J2)=R1+I3
     Y(J2)=I1-R3
     X(J1)=R0-R2
     Y(J1)=I0-I2
     X(J3)=R1-I3
     Y(J3)=I1+R3
 200 CONTINUE
 300 CONTINUE
 400 CONTINUE
 500 CONTINUE
     IF (LOG2N.EQ.LOG2N/2*2) GO TO 700
     DO 600 I=1,N,2
     R0=X(I)+X(I+1)
     R1=X(I)-X(I+1)
     I0=Y(I)+Y(I+1)
     I1=Y(I)-Y(I+1)
     X(I)=R0
     Y(I)=I0
     X(I+1)=R1
     Y(I+1)=I1
 600 CONTINUE
 700 CONTINUE
     MS=N/2
     ML=N
     DO 800 K=2,12
     J=14-K
     S(J)=1
     U(J)=S(J+1)
     IF(S(J+1).GT.1) S(J)=S(J+1)/2
 800 CONTINUE
```

```
      AL=BS
      JJ=0
      DO 900 A=1,AL
      DO 900 B=A,BL,BS
      DO 900 C=B,CL,CS
      DO 900 D=C,DL,DS
      DO 900 E=D,EL,ES
      DO 900 F=E,FL,FS
      DO 900 G=F,GL,GS
      DO 900 H=G,HL,HS
      DO 900 I=H,IL,IS
      DO 900 J=I,JL,JS
      DO 900 K=J,KL,KS
      DO 900 L=K,LL,LS
      DO 900 M=L,ML,MS
      JJ=JJ+1
      IF (JJ.LE.M) GO TO 900
      T=X(JJ)
      X(JJ)=X(M)
      X(M)=T
      T=Y(JJ)
      Y(JJ)=Y(M)
      Y(M)=T
  900 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE  D RS BO(LOG2N,X)
C
C     REVERSE SUBSCRIPT BIT ORDER
C  MODIFIED FROM PROGRAM OBTAINED FROM DEPT. OF PHYSICS,
C  U. OF A., EDMONTON, WRITTEN BY G. SANDE.
C
      REAL*8 T,X
      DIMENSION X(1)
C
      INTEGER JJ
C
      INTEGER A,B,C,D,E,F,G,H,I,J,K,L,M,N,BS,CS,DS,ES,FS,GS,
     .HS,IS,JS,KS,LS,MS,AL,BL,CL,DL,EL,FL,GL,HL,IL,JL,KL,
     .LL,ML,NL,S(14),U(14)
      EQUIVALENCE (BS,S(2)),(CS,S(3)),(DS,S(4)),(ES,S(5)),
     .(FS,S(6)),(GS,S(7)),(HS,S(8)),(IS,S(9)),(JS,S(10)),
     .(KS,S(11)),(LS,S(12)),(MS,S(13)),(NS,S(14)),
     .(AL,U1)),(BL,U(2)),
     .(CL,U(3)),(DL,U(4)),(EL,U(5)),(FL,U(6)),(GL,U(7)),
     .(HL,U(8)),(IL,U(9)),(JL,U(10)),(KL,U(11)),
     .(LL,U(12)),(ML,U(13))(NL,U(14))
C
      NS=2**(LOG2N-1)
      NL=2*NS
      DO 100 K=2,13
      J=15-K
      U(J)=S(J+1)
      S(J)=1
      IF(S(J+1).GT.1) S(J)=S(J+1)/2
  100 CONTINUE
      AL=BS
      JJ=0
      DO 200 A=1,AL
      DO 200 B=A,BL,BS
      DO 200 C=B,CL,CS
      DO 200 D=C,DL,DS
      DO 200 E=D,EL,ES
      DO 200 F=E,FL,FS
      DO 200 G=F,GL,GS
      DO 200 H=G,HL,HS
      DO 200 I=H,IL,IS
      DO 200 J=I,JL,JS
      DO 200 K=J,KL,KS
      DO 200 L=K,LL,LS
      DO 200 M=L,ML,MS
      DO 200 N=M,NL,NS
      JJ=JJ+1
      IF (JJ.LE.N) GO TO 200
      T=X(JJ)
      X(JJ)=X(N)
      X(N)=T
  200 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DATARD(X,N,ERROR,NRUN)
C
C  READS IN ONE RUN OF DATA
C  CARDS, READ ACCORDING TO FORMAT STATEMENT NUMBER 101,
C  CONSIST OF AN ID NUMBER, A CARD SEQUENCE NUMBER(STARTING
C  FROM 1),AND TEN DATA NUMBERS.
C  LAST CARD OF RUN MUST BE BLANK,
C  LAST TWO CARDS OF SET MUST BE BLANK.  STOPS WHEN INITIAL
C  CARD OF RUN IS BLANK, OR WHEN RUNS ARE MIXED.
C  WHEN ERROR IN CARD SEQUENCE, SETS ERROR=4.0.
C  COUNTS THE NUMBER OF POINTS IN SET,N.
C REMOVE STATEMENT NUMBER 1000 IF PRINT OUT NOT DESIRED
C
      INTEGER ERROR
      DIMENSION X(1)
      ERROR=0
      DO 1 J=1,10
          X(J)=0.0
    1 CONTINUE
      READ(5,101) NRUN,LT, (X(I),I=1,10)
      IF(LT.EQ.0) STOP
      DO 2 I=2,10
          IF(X(I).EQ.0.0) GO TO 8
    2 CONTINUE
      WRITE(6,102) NRUN
      WRITE(6,106) LT,(X(I),I=1,10)
      DO 7 J=2,200
          L=10*J
          K=L-9
          DO 3 I=K,L
               X(I)=0.0
    3     CONTINUE
          READ(5,101) NORUN,LTI,(X(I),I=K,L)
          IF(LTI.GT.0) GO TO 10
          N=L
          GO TO 9
   10     IF(NORUN.EQ.NRUN) GO TO 4
           WRITE(6,103)
          WRITE(6,106) LT,(X(I),I=K,L)
          STOP 3
    4     IF(LTI.GT.LT) GO TO 5
          WRITE(6,104)
          ERROR=4
          WRITE(6,106) LT,(X(I),I=K,L)
          GO TO 9
    5     LT=LTI
          DO 6 I=K,L
               IF(X(I).EQ.0.0) GO TO 8
    6     CONTINUE
 1000     WRITE(6,106) LT,(X(I),I=K,L)
    7 CONTINUE
    8 N=I-1
      WRITE(6,106) LT,(X(I),I=K,N)
    9 RETURN
```

```
101 FORMAT(I2,4X,I4,10F7.0)
102 FORMAT(1H0,'RUN NUMBER  ',I6//)
103 FORMAT(1H0,10X,'ERROR SUBROUTINE DATARD - RUNS MIXED')
104 FORMAT(1H0,10X,'ERROR SUBROUTINE DATARD - ',
1041        'DATA CARD SEQUENCE')
106 FORMAT(11X,I8,10F10.0)
    END
```

```
      SUBROUTINE DCLPRT(N,X)
C
C  PRINTS OUT N DATA POINTS IN 8 COLUMNS
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      N8=N/8
      L=N8*7
      WRITE(6,100)
      DO 1 I=1,N8
         K=I+L
         WRITE(6,101) ((J,X(J)),J=I,K,N8)
    1 CONTINUE
      L=MOD(N,8)
      IF(L) 4,4,2
    2 CONTINUE
      I=N-L+1
      DO 3 J=I,N
         WRITE(6,102) J,X(J)
    3 CONTINUE
    4 RETURN
  100 FORMAT(1H0)
  101 FORMAT(8(1X,I4,1PD11.3))
  102 FORMAT(113X,I4,1PD11.3)
      END
```

```
      SUBROUTINE GRAPH (A,B,C,D,E,N,M,IC)
C
C  PLOTS FIVE VECTORS ON ONE GRAPH,
C  EACH VECTOR HAVING ITS OWN SCALE.
C        N IS THE LENGTH OF THE  VECTORS
C        M IS THE NUMBER OF LINES GRAPH EXTENDS
C          IN THE X-DIRECTION
C        IC IS THE NUMBER OF CURVES TO BE PLOTTED
C           ON THE ONE GRAPH
C  WRITTEN BY W. VANDENBORN
C
      REAL*8A,B,C,D,E
      INTEGER *2 IPT(5), IBL, IPL(110)
      DIMENSION A(1),B(1),C(1),D(1),E(1), SCALE(5), BOT(5),
     1          BP(10)
      DATA IPT/'.', '+', '*', '#', '%'/, IBL/' '/
      IF(IC.GT. 5  .OR.  IC .LT.1)  GO TO 200
      I=6
      GO TO (25,20,15,10,5) ,IC
    5 CALL PLOT(E,SCALE,BOT,I,N)
   10 CALL PLOT(D,SCALE,BOT,I,N)
   15 CALL PLOT(C,SCALE,BOT,I,N)
   20 CALL PLOT(B,SCALE,BOT,I,N)
   25 CALL PLOT(A,SCALE,BOT,I,N)
      DO 50  I=1,IC
         IM=5-IC+I
      DO 48  J=1,10
   48 BP(J) =  BOT(IM) + J*SCALE(IM)
      WRITE (6,1001)  IPT(I),BOT(IM),  BP
 1001 FORMAT (3X,A1,1P11E10.2,/)
   50 CONTINUE
      WRITE(6,1003)
 1003 FORMAT (8X,'.I.........I.........I.........I.....I',
10031        '..I.........I.........I.........I.........I',
10032        '.........I.........I..........')
      ISKIP =N/M+1
      IX=0
```

```
      DO 100  J=1,N,ISKIP
      I=6
      DO 55 II=1,110
   55 IPL(II) =IBL
      GO TO (80,75,70,65,60),IC
   60 I=I-1
      IPL(INT((SNGL(E(J))-BOT(I))/SCALE(I)*10.0+1.5))=IPT(5)
   65 I=I-1
      IPL(INT((SNGL(D(J))-BOT(I))/SCALE(I)*10.0+1.5))=IPT(4)
   70 I=I-1
      IPL(INT((SNGL(C(J))-BOT(I))/SCALE(I)*10.0+1.5))=IPT(3)
   75 I=I-1
      IPL(INT((SNGL(B(J))-BOT(I))/SCALE(I)*10.0+1.5))=IPT(2)
   80 I=I-1
      IPL(INT((SNGL(A(J))-BOT(I))/SCALE(I)*10.0+1.5))=IPT(1)
      IX =IX+1
      IF (IX .EQ. 5)  GO TO 90
      WRITE(6,1004)   IPL
 1004 FORMAT (  8X,'.',110A1, '.')
      GO TO 100
   90 WRITE (6,1006)  IPL,J
 1006 FORMAT (  8X,'-',  110A1,  '-', I4)
      IX=0
  100 CONTINUE
      WRITE(6,1003)
  150 RETURN
  200 WRITE (6,1005)
 1005 FORMAT (' IMPROPER USE OF GRAPH- ',
10051         'NUMBER OF CURVES IS INVALID')
      GO TO 150
      END
```

```
      SUBROUTINE PLOT  (X, SCALE,BOT,I,N)
C
C  PROVIDES SCALES FOR EACH CURVE IN GRAPH SUBROUTINE
C  WRITTEN BY W. VANDENBORN
C
      REAL *8 YMAX ,YMIN, X
      DIMENSION  X(1),SCALE(5),BOT(5)
      I=I-1
      YMIN=X(1)
      YMAX=X(1)
      DO 5  J=2,N
         IF(YMIN .GT. X(J))  YMIN=X(J)
         IF(YMAX .LT. X(J))  YMAX=X(J)
    5 CONTINUE
      YMA =SNGL(YMAX)
      YMI = SNGL(YMIN)
      SCALE(I)=     (YMA-YMI)/10.0
      B=10.**(INT(ALOG10(SCALE(I))))
      SCALE(I) = FLOAT(INT(SCALE(I)/(B*2.0) +1.0))
      SCALE(I) = 2.0*B*SCALE(I)
      IF(SCALE(I).GT.(YMA-YMI)) SCALE(I)=SCALE(I)/10.0
      IF(5.0*SCALE(I).GT.(YMA-YMI)) SCALE(I)=SCALE(I)/2.0
      IF(YMI.LT.0.0) GO TO 10
      BOT(I)=SCALE(I)*FLOAT(INT(YMI/SCALE(I)))
      GO TO 100
   10 BOT(I)=SCALE(I)*FLOAT(INT(YMI/SCALE(I))-1)
  100 RETURN
      END
```

```
      SUBROUTINE RNG(N,R,Z)
C
C    GENERATES N PSEUDO-RANDOM VARIABLES R FROM A NORMAL
C    DISTRIBUTION WITH ZERO MEAN AND UNIT VARIANCE.  N MUST
C    BE EVEN.  R IS COMPUTED FROM TWO VARIABLES TAKEN FROM A
C    UNIFORM DISTRIBUTION (0,1) USING THE METHOD OF BOX AND
C    MULLER, ANN. OF MATH.STAT., 12, (1958), P.610.
C    THE UNIFORM DISTRIBUTION IS GENERATED BY A SHUFFLED
C    MULTIPLICATIVE CONGRUENTIAL METHOD.
C    MACLAREN AND MARSAGLIA,J. OF THE ASS.FOR COMP. MACH.,
C    12, (1958), P. 83
C    Z IS INITIAL INTEGER OF THE UNIFORM DISTRIBUTION
C    (DOUBLE PRECISION)
C
      DIMENSION R(1),U(100)
      REAL G,F,Z*8
      INTEGER K,L,J,N
C
C    GENERATE THE NUMBERS FROM A UNIFORM DISTRIBUTION
C
      DO 10 J=1,100
         Z=DMOD(101.0*Z+1.0,100000000.0)
         U(J)=SNGL(Z)
   10 CONTINUE
      DO 20 J=1,N
         Z=DMOD(101.0*Z+1.0,100000000.0)
         K=IDINT(Z)
         L=MOD(K,100000)/1000+1
         R(J)=U(L)*1.0E-8
         U(L)=SNGL(Z)
   20 CONTINUE
C
C    COMPUTE THE NUMBERS FROM A NORMAL DISTRIBUTION
C
      DO 30 J=1,N,2
         G=6.2831853*R(J+1)
         F=SQRT(-2.0*ALOG(R(J)))
         R(J)=F*COS(G)
         R(J+1)=F*SIN(G)
   30 CONTINUE
      RETURN
      END
```

Typical Output of Program M2

```
DATA SUMMARY   RUN NUMBER  7

     RETENTION INDEX  PEAK NO. 4 = 754.65297           STD. DEV. =  0.001958
PEAK PARAMETERS

  1    4.19213D 04    5.33063D 01    1.00533D 00  0.350386  0.372427  0.449763  0.399918
  2    0.C            0.0            0.0          0.0       0.0       0.0       0.0
  3    1.18128D 05    3.15672D 02    3.88473D 00  0.099761  0.113912  0.123398  0.272634
  4    1.C6575D 05    4.43918D 02    5.38417D 00  0.034763  0.027131  0.120223 -0.000076
  5    1.13714D 05    5.96748D 02    7.17766D 00  0.073506  0.010538  0.260558  0.000069

               NET RETENTION  RELATIVE AREA  NO. POINTS
                     0.0        0.35488102       140
                                                   0
                  262.3662      1.00000000       216
                  390.6118      0.90558292       226
                  543.4421      0.96263730       226
```

```
PARAMETER STANDARD DEVIATIONS

 1     3.69420D 00     9.75642D-05     1.82706D-04 0.0005378 0.0017476 0.0017465 0.0065136
 2     0.0             0.0             0.0         0.0       0.0       0.0       0.0
 3     2.80916D 01     6.96449D-04     1.22600D-03 0.0007013 0.0024976 0.0019282 0.0070443
 4     5.19294D 01     1.79294D-03     3.07221D-03 0.0011959 0.0041654 0.0030605 0.0106940
 5     9.62464D 01     3.95494D-03     6.85650D-03 0.0018934 0.0068928 0.0047577 0.0170796

                NET RETENTION  RELATIVE AREA    SUM OF SQUARED DEV.

                   0.0          0.000090001      6.0335D 04
                   0.0          0.000000000      0.0
                   0.00070      0.0              9.2048D 03
                   0.00180      0.000489518      7.3240D 03
                   0.00396      0.000846313      2.7085D 04
```

Typical Output of Program M3

```
EXPERIMENT PARAMETERS          0.0                               0.       0.0               0.0
        1.00000D 04    1.96075D 02    7.25000D 00  0.060000  0.030000  0.250000  0.000700
N=   5  SUM OF SQUARES - MEAN =     4.96533D 02   VARIANCE = 9.57141D-01    T =    -3.41326
    5  853067 500 500    60.  100.  400.
AVERAGE TIME(SEC.) =          4.5


                         OBSERVED
       ----------------------------------------------------------------------------------------
                MEAN DEV.              STD. DEV.             EFFICIENCY             STUDENTS T

       1       1.41184D 01            1.51264D 02            3.83066D 00            2.08706D-01
       ----------------------------------------------------------------------------------------
       2      -6.76990D-05            2.29379D-04            2.83339D 01           -6.58519D-01
       ----------------------------------------------------------------------------------------
       3       2.93458D-04            1.20405D-03            2.57778D 00            5.26416D-01

       4       1.31874D-05            1.05786D-04            2.09260D 01            2.78752D-01
       ----------------------------------------------------------------------------------------
       5       4.21291D-04            9.81443D-04            2.78528D 00            9.60076D-01
       ----------------------------------------------------------------------------------------
       6       2.76859D-05            4.42338D-04            5.96702D 00            1.39955D-01

       7       1.22774D-03            2.16011D-03            2.83604D 00            1.27091D 00
```

TABLE VII

Values of Parameters Used in Program M5 to Obtain the Data for Tables IV, V, and VI

A'	t_0 (net)	σ	K_1	K_2	K_3	K_4	Peak Code Run Number
35432.	261.928	3.8753	.1101	.0611	.1824	.0596	1 1
34184.	262.767	3.8880	.1024	.0632	.1351	.0632	1 3
32172.	262.938	3.8718	.1063	.0314	.1504	.0046	1 5
32960.	262.366	3.8847	.0998	.1139	.1234	.2726	1 7
32797.	260.663	3.8492	.1018	.0738	.1333	.1223	1 9
33099.	263.410	3.9044	.0956	.1140	.0940	.2643	111
34605.	261.016	3.8750	.1010	.1367	.1293	.3636	112
33654.	263.887	3.8929	.1272	.0566	.1957	.0003	113
32522.	264.236	3.9187	.1145	.1114	.1492	.2582	114
33826.	264.489	3.9276	.1210	.1314	.1821	.3208	115
34603.	264.335	3.9044	.1170	.0587	.1996	.0011	116
34671.	261.681	3.8749	.1126	.0576	.1623	.0526	1 2
35733.	262.772	3.9824	.1138	.0868	.1914	.1735	1 4
33936.	262.492	3.8764	.0895	.0860	.0885	.1580	1 6
31299.	259.714	3.8215	.1070	.0561	.1400	.0601	1 8
34089.	262.736	3.8763	.0971	.0441	.1073	.0035	110
33792.	543.562	7.2374	.0781	.0191	.3038	.0002	2 1
32666.	545.484	7.2757	.0709	.0321	.2432	.0006	2 3
30635.	545.544	7.2384	.0786	.0256	.2518	.0004	2 5
31086.	543.442	7.1777	.0735	.0105	.2606	.0001	2 7
31299.	540.790	7.1685	.0518	.0260	.1896	.0004	2 9
31382.	546.508	7.2633	.0383	.0478	.1433	.0015	211
32894.	541.673	7.1638	.0722	.0140	.2540	.0005	212
32135.	547.817	7.2696	.0554	.0333	.1571	.0007	213
30869.	548.375	7.2655	.0748	.0312	.2029	.0006	214
32315.	548.877	7.3292	.0906	.1194	.2646	.3506	215
32999.	548.364	7.2654	.0857	.0302	.2592	.0006	216

TABLE VII (Continued)

A'	t_0 (net)	σ	K_1	K_2	K_3	K_4	Peak Code Run Number
33254.	543.115	7.2700	.0756	.0564	.2756	.0021	2 2
34457.	545.253	7.3098	.0510	.0711	.2423	.0033	2 4
32285.	544.161	7.2319	.0671	.0652	.2297	.1260	2 6
29736.	538.858	7.1506	.0778	.0340	.2620	.0007	2 8
32732.	546.014	7.2866	.0366	.0552	.1505	.0020	210
30578.	390.249	5.4097	.0457	.0112	.1737	-.0013	3 1
29441.	391.564	5.4183	.0346	.0045	.1322	.0110	3 3
27705.	391.707	5.4045	.0433	.0174	.1420	.0373	3 5
28293.	390.612	5.3842	.0348	.0271	.1202	-.0001	3 7
28281.	388.316	5.3571	.0525	.0157	.1971	.0002	3 9
28417.	392.464	5.4222	.0447	.0442	.1560	.1114	311
29855.	388.865	5.3769	.0409	.0224	.1667	.0003	312
29175.	393.208	5.4614	.0505	.0827	.1551	.2801	313
28049.	393.628	5.4428	.0695	.0455	.2404	.1598	314
29295.	393.964	5.4699	.0366	.0546	.1227	.0019	315
29937.	393.664	5.4694	.0400	.0882	.1138	.2987	316
30098.	413.459	5.9033	.4703	.4110	.2408	.5399	4 2
30820.	415.058	5.8877	.4569	.3722	.1818	.4656	4 4
29263.	414.538	5.9000	.4647	.4294	.2299	.5989	4 6
27039.	410.405	5.8397	.4713	.4213	.2272	.5560	4 8
29420.	415.506	5.8952	.4595	.3691	.1822	.4505	410

TABLE VIII

Parameters of Power-Density Spectra

Used to Determine the Intensity of Jitter[a]

With Thermal Conductivity Detector as Source

Mean (mv)	W_c (μv^2)	T_c (sec)	$C_{1/4}$[b] (μv^2/Hz)	$C_{1/2}$[b] (μv^2/Hz)
0.008	94	241	0.011	0.021
0.084	18	234	0.020	0.015
4.1	230	243	0.27	0.13
8.5	330	244	0.90	1.05
30.1	4100	242	9.9	12.7
With Mercury Cell as Source				
5.1	1800	242	4.3	2.4
12.0	83	240	15.	19.
16.8	64000	241	24.	33.
27.0	89000	176	79.	114.
33.7	53000	240	113.	178.

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[a] Graphs of the power-density spectra of both sources show that the spectra were roughly proportional to the signal mean at low frequencies. (This is indicated also by the increase of power with increasing mean.) Jitter and dead-time variations account for only a small fraction of the increase at low frequencies. Therefore, the increase at low frequencies, which is where the noise is most intense, must be due to the integrator.

[b] Power density at 1/2 and 1/4 in reduced frequency units.