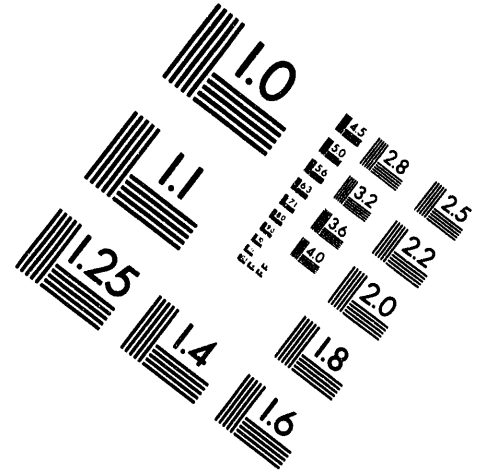
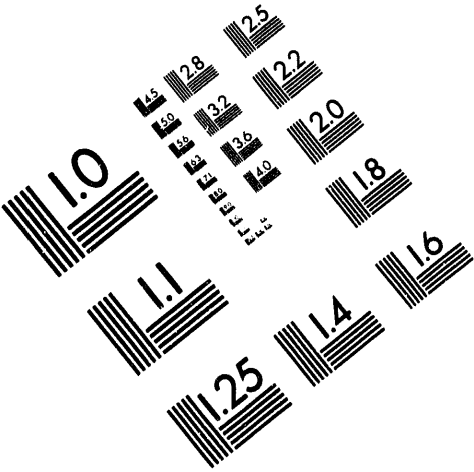




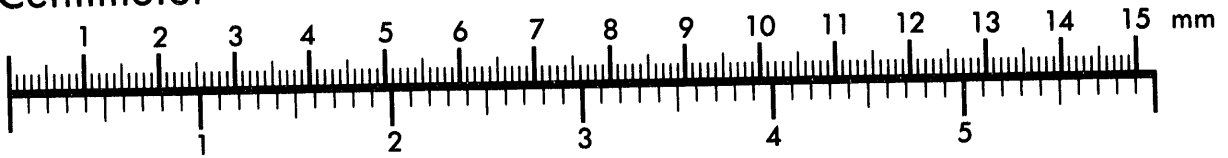
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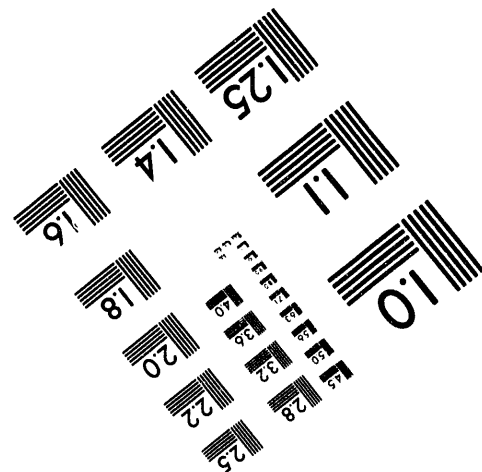
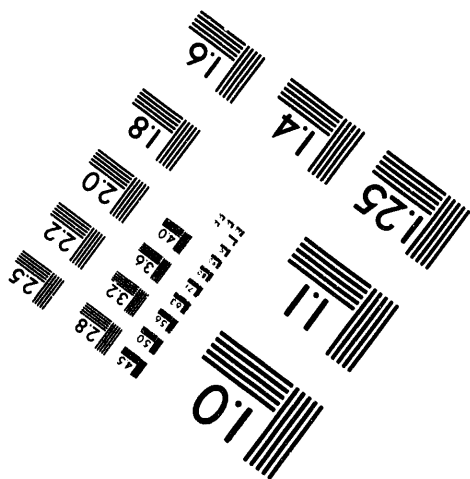
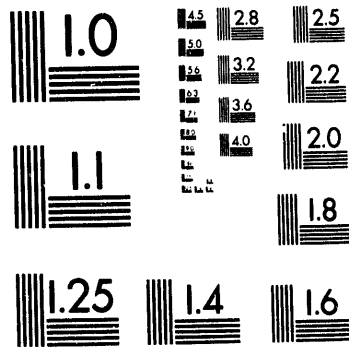
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WHAT EVERY RADIOCHEMIST SHOULD KNOW ABOUT STATISTICS

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April 1994

Presented at the
Methods and Applications of Radioanalytical
Chemistry III Conference
April 10-16, 1994
Kailua-Kona, Hawaii

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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WHAT EVERY RADIOCHEMIST SHOULD KNOW ABOUT STATISTICS¹

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Radionuclide decay and measurement with appropriate counting instruments is one of the few physical processes for which exact mathematical/probabilistic models are available. To be of quality commensurate with physics and electronics knowledge reflected in counting instruments and experiments, statistical analysis should be based on these exact models. Historically, analysis suggested in radiochemistry text books mostly reflects asymptotic large count Gaussian models, for low count situations the exact models are distinctly non-Gaussian.

This paper discusses statistical procedures associated with display and analysis of radionuclide counting data and procedures that derive from exact mathematical/probabilistic models. Both asymptotic and low count situations are considered and, for the latter, the attractiveness of fixed-count-random-time procedures is discussed.

The fundamental statistical facts of radionuclide counting are that information is proportional to counts and that uncertainty is proportional to the square root of counts. The discussion includes the practical problems associated with the assessment of uncertainty in the presence of background and estimated corrections and when the decay from radionuclides of interest must be separated from that of competing radionuclides using energy and/or half-life characteristics.

¹ The writing of this paper was funded by the United States Department of Energy under contract DE-AC06-76RLO 1830

WHAT EVERY RADIOCHEMIST SHOULD KNOW ABOUT STATISTICS¹

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Abstract

Radionuclide decay and measurement with appropriate counting instruments is one of the few physical processes for which exact mathematical/probabilistic models are available. This paper discusses statistical procedures associated with display and analysis of radionuclide counting data that derive from these exact models. For low count situations the attractiveness of fixed-count-random-time procedures is discussed.

INTRODUCTION

Radionuclide decay and measurement with appropriate counting instruments is one of the few physical processes for which exact mathematical/probabilistic models are available. To be of quality commensurate with physics and electronics knowledge reflected in counting instruments and experiments, statistical analysis should be based on these exact models. Statistical ideas and analysis suggested in radiochemistry text books (e.g. Friedlander, Kennedy and Miller, 1964 and Siegbahn 1964) mostly reflects asymptotic large count Gaussian models. For low count situations the exact models are distinctly non-Gaussian.

The use of statistics in radiochemistry can be considered at a variety of levels--elementary as in radiochemical texts, intermediate as in radiochemistry and instrumentation journals, and advanced as in mathematical statistics texts and journals. This paper discusses several issues at a level

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of detail that is critical for recovery of anything like the total information available or potentially available in radiochemical experiments. Each issue could be considered at a much deeper level. At times that is important especially for sophisticated selective analysis situations where a professional data analyst should be consulted. The level here reflects the title of the paper, "What EVERY radiochemist should know about statistics".

Specifically the paper discusses the five issues, information and uncertainty, short lived sources, few counts and random time analysis, background estimation, and multi-nuclide deconvolution by computer algorithms.

INFORMATION AND UNCERTAINTY

The most fundamental statistical facts for interpretation of radiochemical data are:

- 1) the information content of counting data is roughly proportional to the total number of counts; and
- 2) the uncertainty in information content is roughly proportional to the square root of the total number of counts.

For simple situations involving a few gross counts the above (sans "roughly") is the entire story. For more complicated situations where total counts are binned by energy and time and possibly by other decay characteristics precise characterization of information and uncertainty is more complicated.

The information roll of total count is often confused with counting rate. Increasing the counting rate increases the information content only because in fixed time the total count is increased. Thus other considerations being equal good radiochemical experimentation should maximize the number of counts from decays of interest.

The question then is how long should the counting time be in order to estimate N , or equivalently, λN precisely. The answer can be phrased in terms of the knowledge about the background and the initial signal to noise ratio. With $\hat{\beta}$ an unbiased estimate of β the minimum variance unbiased estimate for N at time t is,

$$\hat{N} = [Z(t) - \hat{\beta}t] / [\gamma(1 - e^{-\lambda t})]. \quad (1)$$

Here the denominator is the probability that an arbitrary atom decays and is recorded during the first t time units of the experiment. For the estimate (1) the relative variance can be expressed as

$$\text{Var}(\hat{N}/N) = v^{-1}[(1 - e^{-\lambda t})^{-1} - \gamma + (\lambda t / s.n)(1 - e^{-\lambda t})^{-2}] + K^2(\lambda t / s.n)^2(1 - e^{-\lambda t})^{-2}. \quad (2)$$

In equation (2)

$$v = E(\gamma N), \quad s.n = \gamma \lambda N / \beta, \quad \text{and} \quad K^2 = \text{Var}(\hat{\beta} / \beta),$$

are the expected number of activation produce decays that would be recorded as counts in infinite time, the initial signal to noise ratio, and the relative variance of the background estimate, respectively.

The form of the relative variance equation (2) clearly illustrates what is necessary for precise estimation:

1. the expected number of decays that are recorded as counts must be large;
2. the initial signal to noise ratio must not be too small;

3. the ratio of the relative standard deviation of the background estimate must be small relative to the signal to noise ratio; and
4. the time of the experiment must be intermediate, not too short and not too long.

These are qualitative rules of thumb. A more quantitative statement results from appropriate graphical display of the relative variance (2) or its square root, the standard deviation, as a function of the defining parameters. From equation (2) the relative standard deviation of the estimate can be thought of as a function of counting time expressed in half life units once the four parameters ν , γ , s.n and K are fixed. Figure 3 displays a systematic set of relative standard deviation values thought of as functions of time expressed in half life units. Specifically Figures 3A, 3B, 3C, and 3D each display a family of curves defined by varying one of the parameters and holding the other three fixed. The common central curve that is displayed as the bold curve in each plot is defined by the parameter values,

$$\nu N = 2000, \text{ s.n} = 4/1, \gamma = 50\% \text{ and } K = 3\%.$$

All of the curves are convex up with most minima somewhere between one and four half lives. Each family of curves has a message. The A family of expected total count curves shows that with other defining characteristics constant the larger the expected total count from decays the shorter the optimum counting time. The B family of signal to noise ratio curves shows that as the signal to noise ratio increases the optimum counting time increases. With a weak signal the optimum counting time is less than one half life. The C family of percent efficiency curves shows that efficiency is of

little importance once its effect on expected total count has been considered. As a second order effect higher efficiency implies more precise estimation. The D family of background precision percent two sigma curves shows that with a poor background estimate, the optimum counting time is shorter.

FEW COUNTS AND RANDOM TIME ANALYSIS

For low level counting where swamping out the electronics is not a consideration the exact time of each count can be recorded along with detailed characteristics of the decay process. These exact times allow the option of either fixed count or fixed time analysis; i.e., a number of counts n recorded in time t can be treated as either

1. the fixed time $t=T$ to record n random events or
2. the random time t to record a fixed number of events $n=N$.

The latter is attractive for low level counting since the distribution of random time is continuous and allows easy exact statistical analysis. While random time analysis may not be feasible in a production radiochemistry environment with large through put on a predetermined schedule, it does guarantee a specified relative precision in a gross count rate estimate.

For long half life relative to the counting time so that the expected count rate say ρ does not diminish the two counting procedures are easily compared. For fixed time analysis the random number n of counts has a poisson distribution with parameter ρT ; and for fixed count analysis the multiple of random time $2\rho t$ has a chi-square distribution with $2N$ degrees of freedom. The latter is the generalization of the waiting time between successive counts that has a negative exponential distribution; i.e., up to scaling a chi-square

distribution with 2 degrees of freedom. The minimum variance unbiased estimates of the counting rate $\rho=N/T$ based on random count n and on random time t are

$$r_n = n/T \text{ and } r_t = (N-1)/t, \quad (3)$$

respectively. The variances of these estimates can be expressed as

$$\text{Var}(r_n) = N/T^2 \text{ and } \text{Var}(r_t) = [N^2/(N-2)]/T^2. \quad (4)$$

Existence of the unbiased random time estimate r_t demands at least two counts and for finite variance at least three counts. Of course estimates based on such a small number will not be very precise. However, as indicated above for any number of events random time analysis admits an exact confidence interval statement on the unknown counting rate ρ . Such a $100(1-\alpha)\%$ confidence interval for ρ can be expressed as multiples of the unbiased random time estimate r_t . Specifically, the confidence interval is Lr_t to Ur_t where

$$L = \chi^2(2N, \alpha/2)/(2N-2) \text{ and } U = \chi^2(2N, 1-\alpha/2)/(2N-2). \quad (5)$$

Here, $\chi^2(k, q)$ is the 100 qth percentile point on the chi-square distribution with k degrees of freedom. Multipliers are listed in Table 1 for a selected set of fixed counts N .

Table 1 Count Rate 95% Confidence Interval Multipliers

<u>N</u>	<u>L</u>	<u>U</u>	<u>N</u>	<u>L</u>	<u>U</u>
2	0.242	5.572	25	0.674	1.488
3	0.309	3.612	50	0.757	1.322
5	0.406	2.560	100	0.822	1.217
7	0.469	2.177	400	0.907	1.103
10	0.533	1.898	1000	0.940	1.064

BACKGROUND ESTIMATION

Appropriateness of the background estimate in radiochemical analysis is a statistical issue. Two questions need to be answered before the adequacy can be ascertained. First, is background level constant in the sense that the only variability in background counting rate is induced by the poisson character of background events or does background level actually vary? An example of such variability is the background level in a specified position in a counting tomb. That level may be influenced by the character of the samples in adjacent positions and hence may change each time the tomb is loaded.

The second question is how many times will the current background be used? For example, is a background count sandwiched in between each pair of radiochemical assays or is a single background taken in the morning and possibly checked later in the day. If so, some sort of interpolation might be used for all intermediate assays.

The importance of these questions depends upon the signal to noise ratio. If the ratio is large background to academic and if it is small appropriate background treatment is critical.

To answer the first question concerning whether the background is constant over time background counts must be taken periodically. If there is concern over certain times of day (e.g. if electrical loads change significantly in the vicinity of the counting room) backgrounds should be checked during those time periods. Standard statistical procedures are available to assess whether the variability among background estimates suggest real change in background level. For fixed time background analysis suppose that c_1, c_2, \dots, c_k are k background counts with the same live time. The chi-square goodness of fit statistic

$$\chi^2_{k-1} = \sum_{i=1}^k (x_i - \bar{x})^2 / \bar{x} \quad (6)$$

which has approximately a chi-square distribution with $k-1$ degrees of freedom is a familiar procedure for assessing variability. In reality a number of procedure are available to determine whether k poisson counts suggest a common underline counting rate (i.e. Cox and Lewis 1966, Haight 1967). Fixed count analysis is particularly attractive for establishing the constancy or not of background because of the rich statistical methodology that is immediately available. Suppose that k background analyses have been done on a fixed count basis and t_1, \dots, t_k , are the k random times to record N counts. Since $2\rho t_i$ has a chi-square distribution with $2N$ degrees of freedom the quantities $t_1/N, \dots, t_k/N$ can be thought of as variance estimates for samples of size $2N+1$ from a gaussian distribution with variance $1/\rho$. Further, since the square roots can be thought of as standard deviation estimates all based on $2N$ degrees of freedom, the methodology of S control charts for standard deviations developed by Shewart (1931) and championed by Edward Deming as a

portion of the early foundation for today's Total Quality Management technology is applicable. Figure 4 presents a simple illustration of the S chart methodology based on 100 standard deviation estimates all with ten degrees of freedom. These were constructed using the above approach from 100 simulated random times to record five background counts. The first thirty standard deviations were pooled to estimate the initial standard deviation used to construct the S-chart center and limit lines. The last seventy standard deviation estimates were plotted sequentially over time. The background of two counts per unit time was augmented with a positive drift in background starting at position 65,. The drift shows up dramatically even though the lower control limit is not reached.

As long as the background level does not vary long term averaging provides precise background estimates. If background varies appropriate investigation may uncover classes of radiochemical experimentation with background varying between classes but constant within each class. Now the above background averaging applies within each class. A more difficult problem is when background is variable within a given counting system so that the appropriate background for each analysis must be determined in a narrow time window surrounding that analysis. Whether this time window is a day or a half a day or much briefer determines how well that background should be established.

When the background estimate is used several times its precision becomes more important. For example if an average background is determined each day and is used all that day the quality of analyses will tend to be blocked on days reflecting the quality of that days background estimate. Nicholson (1966) suggests a simple rule for background estimate precision that is based

on the premise that adequacy should be assessed at very low signal to noise ratio. Suppose that the same background estimate is to be used for M samples and that each sample is counted for t time units, then the background estimate should be based on s time units of counting where s is not less than $tM^{1/2}$.

MULTI-NUCLIDE DECONVOLUTION BY COMPUTER ALGORITHM

From a calculational and also a statistical stand point there are basically two approaches to resolving energy spectra into component parts associated with specific radionuclides. The energy resolution of the counting system determines the approach. For low resolution with energy peak widths proportional to the square root of energy (i.e. the NaI situation) background corrected multi-component spectra can be resolved by least squares type procedures that fit linear combinations of known standards. The statistical issues are discussed in most applied statistics text books. Pasternack (1962) and Pasternack and Liuzzi (1971) are particularly good discussions of the statistical issues couched in a radiochemistry frame work. For the high resolution near uniform width peaks (i.e. the present generation of detectors beginning with the GE (Li) situation) individual peaks can be resolved by a peak searching procedure performed on gross spectra. The procedure involves two stages. The first stage, possibly iterative, determines a broad relatively smooth base line structure, locates energy peaks on top of the base line, calculates the area under the peaks and determines the uncertainty of the area estimate. The second stage fits library spectra to locations (peak energy) and areas (peak decay rate). The sophistication in the peak searching process depends upon the application. For routine analysis when only the dominate peaks are of interest software provided by instrument vendors is

probably adequate. For complex situations where all, or most, peaks above background must be resolved, and where some peaks are close together so that small ones reside on shoulders of larger ones, individual experimenters have their favorite approach often based on their own software development efforts. From a statistical standpoint peak searching is potentially fraught with complexities and pit falls. A general recommendation would be that if the resolution is to be pushed to its limit output from a black box calculation should not be accepted without diagnostic checks. A good approach is graphical comparisons of explained and unexplained structure at each step of the peak searching process.

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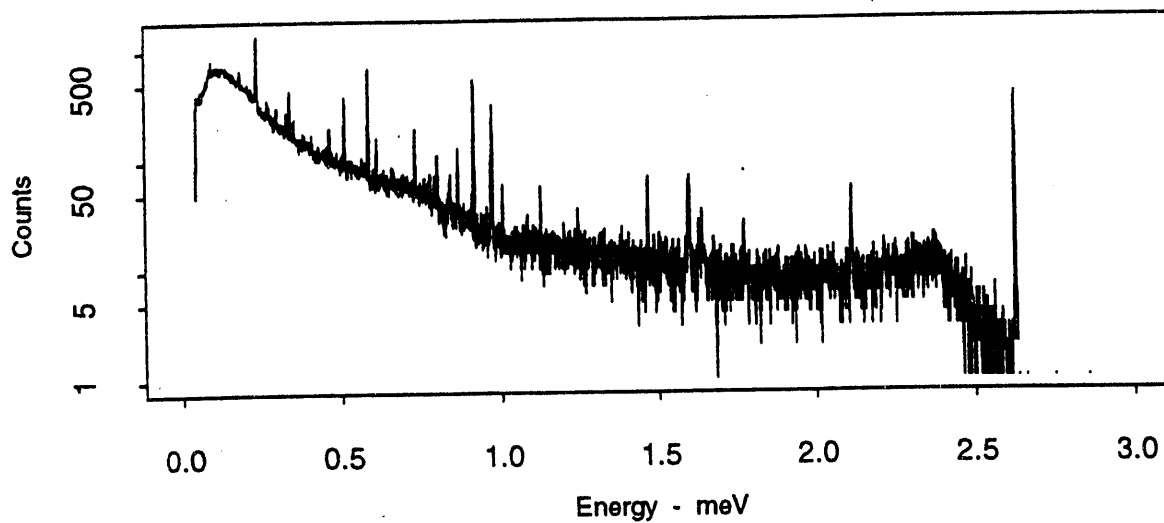
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A. LOGARITHMIC COUNT SCALE



B. SQUARE ROOT $4C+1$ SCALE

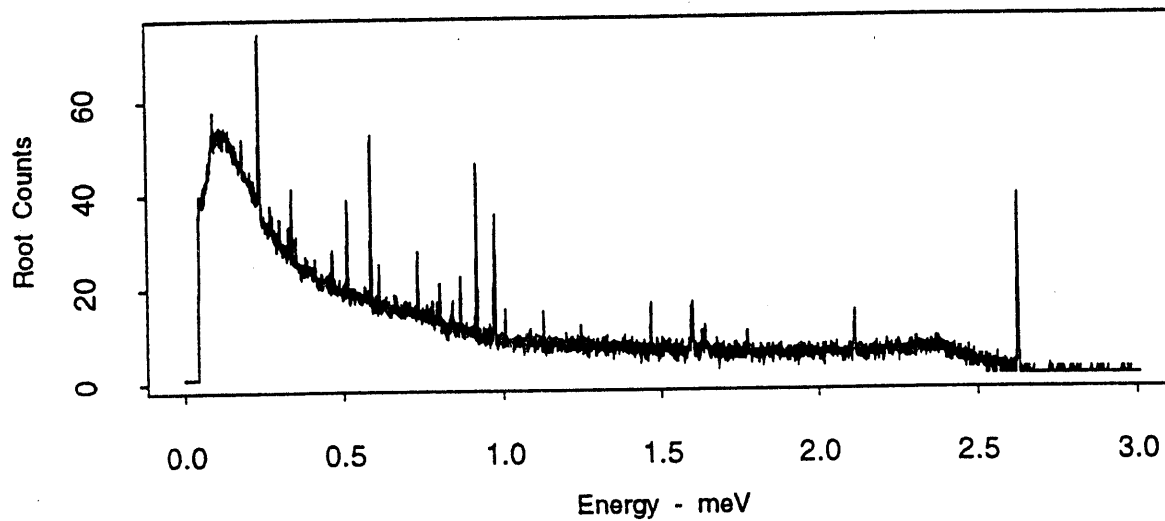
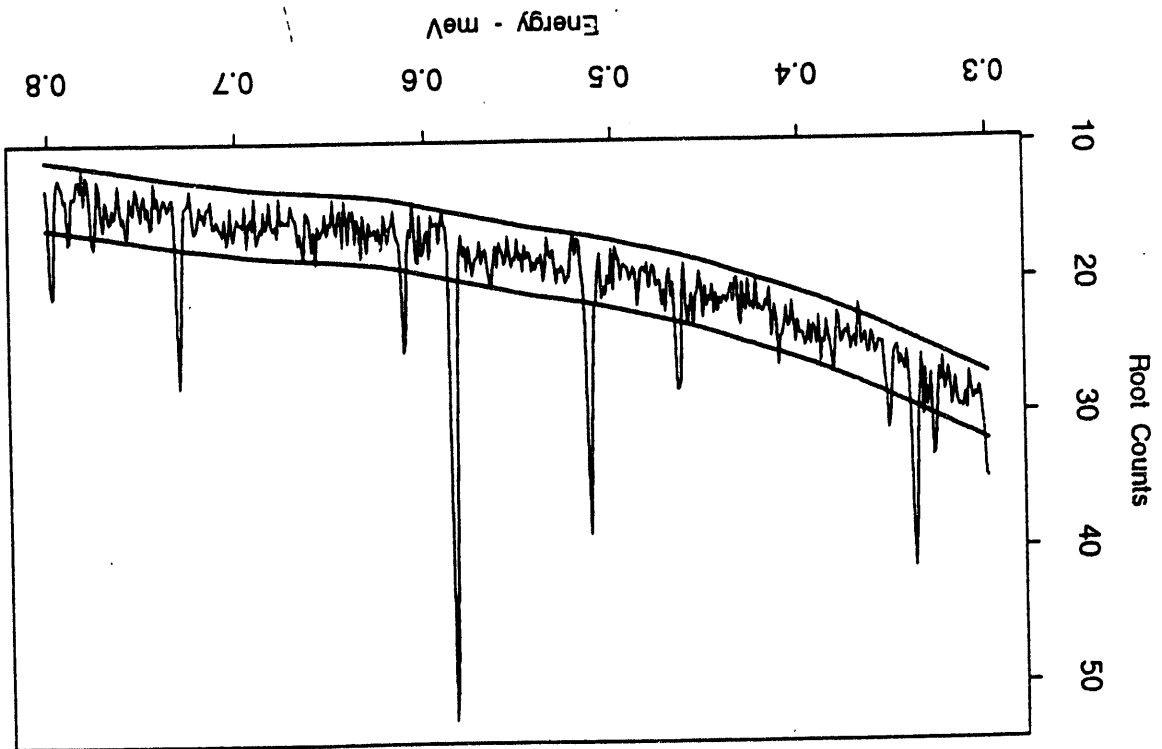


Figure 1. Gamma ray spectrum displayed as scaled counts versus energy. A. is the familiar log (count) scale and B. is a variance stabilization square root $4 * \text{count} + 1$ scale.

Figure 2. The 0.3 meV - 0.8 meV energy window of the gamma-ray spectral display of Fig 1B. The parallel curves define a 5 unit high random background band centered on a robust smooth that ignores real peaks



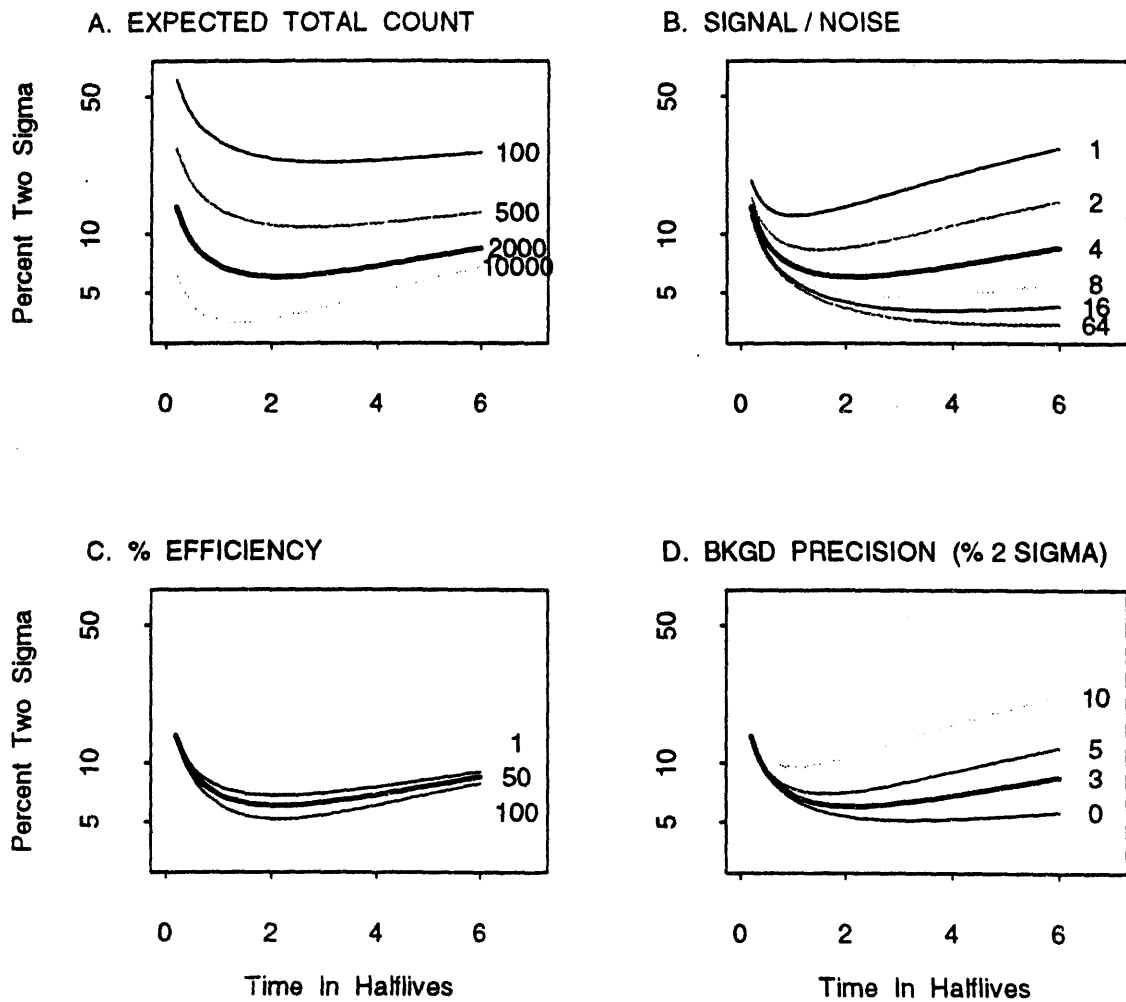


Figure 3. Precision of the estimate \hat{N} versus counting time and the four parameters, expected total count, signal/noise, efficiency and background knowledge. Each family of curves varies one parameter with others fixed at the common parameter set indicated by the bolder curve.

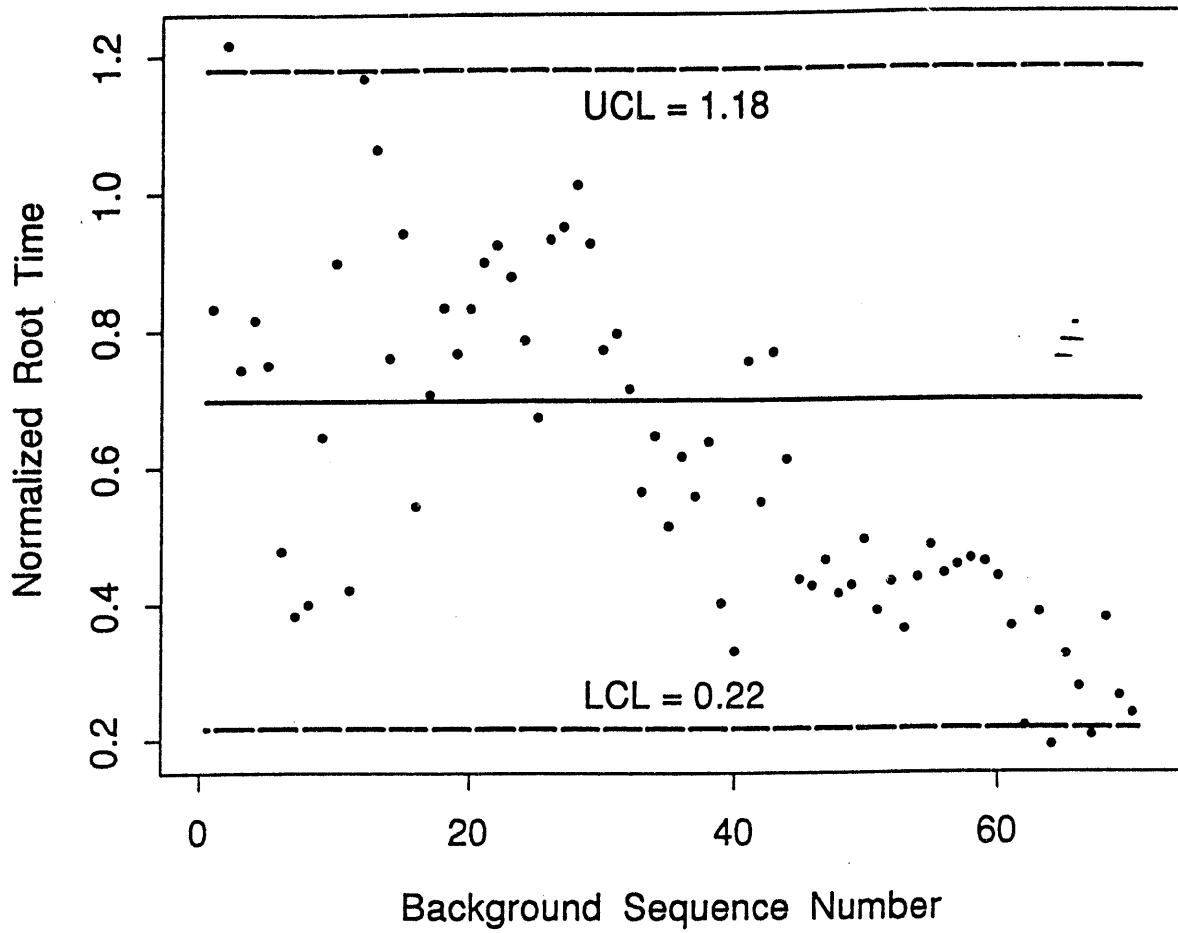


Figure 4. Application of S-chart control to background monitoring based on random times to record ten background counts.

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