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AN IMPROVED METHOD FOR STATISTICAL ANALYSIS OF RAW ACCELERATOR MASS SPECTROMETRY DATA

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ABSTRACT

Hierarchical statistical analysis is an appropriate method for statistical treatment of raw accelerator mass spectrometry (AMS) data. Using Monte Carlo simulations we show that this method yields more accurate estimates of isotope ratios and analytical uncertainty than the generally used propagation of errors approach. The hierarchical analysis is also useful in design of experiments because it can be used to identify sources of variability.

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Introduction

Radioisotope data can be obtained with an accelerator mass spectrometer in a variety of ways, depending on the accelerator system and its control scheme. For example, relatively long periods of radioisotope counting may be interspersed with stable isotope beam measurements, the radioisotope and stable isotope may be monitored simultaneously, the system may cycle rapidly between samples and a standard, and so on. However, in nearly all cases the measurements take the form of intervals of radioisotope counting on a sample, interspersed with other measurements. Frequently, a group of counting episodes on one sample will be separated from other similar groups on the same sample by time spent counting on other samples, standards, or blanks.

This method of performing measurements differs significantly from some more conventional methods of radioisotope analysis. In such methods a sample may be put in a detector and counted continuously until a sufficient total of counts is recorded. This simple approach cannot be used in most AMS analyses because it is necessary to use one system to monitor more than one parameter (e.g., radioisotope counts and stable isotope beam current) and because accelerator systems are more complex, requiring frequent periods of adjustment and tuning. The complexity can also result in long-term "drift" of the system components (e.g., terminal voltage or magnet fields); this is one reason for repeating intervals of sample measurement at widely separated times.

The methods for statistical interpretation (i.e., calculation of the analytical mean value and uncertainty) of raw data from the "continuous counting" method of analysis are derived from the known statistics of Poisson processes [1]. However, the in general more intricate analytical sequence commonly used in AMS complicates the statistical interpretation.

The statistical method commonly used in AMS data interpretation has no formal name, but we will refer to it as the propagation of errors (POE) approach. In this approach a mean radioisotope/stable isotope ratio is calculated for each individual interval of isotope measurement (hereafter referred to as a "cycle") and the uncertainty associated with that mean is calculated by dividing the mean value by the square root of the number of counts measured. A number of individual cycles are then combined to give group statistics (we will refer to one combined group of cycles as a "sequence"). The sequence mean is computed from the average of the cycle means, with individual cycles weighted by their associated uncertainties. Two uncertainties are computed for the sequence. The "internal" uncertainty is obtained from the Poisson model for the individual cycle uncertainties and the "external" uncertainty from the standard deviation of the cycle means. In order to get a conservative estimate, the larger of these two uncertainties is reported. This approach to the statistical analysis of raw data is referred to in references [2] through [4].

Although the POE method as described above is relatively straight forward, the validity of its results is limited by certain requirements. In order for the cycle uncertainty estimate to be unbiased, the mean number of counts according to parent distribution (i.e., the average number of counts which would be obtained from that sample over many cycles) must be used. However, this theoretical value is in fact not available and the actual number of counts registered during each cycle must be substituted for it. This substitution may result in a biased estimate for both the mean and uncertainty. The biased estimate is then propagated by incorporation in the "internal" and "external" sequence uncertainty estimates. If the cycle uncertainty estimate is severely biased even the larger of the internal or external sequence estimates may still not be conservative.

This potential for biasing may be avoided by the use of a more appropriate statistical method. The method we propose is a classical statistical technique known as hierarchical (or nested) statistical analysis [6,7,8]. This method has the advantage that it not only avoids the substitution of experimental quantities for population characteristics, it is also specifically designed to deal with estimation of variances in systems composed of "nested" samples and subsamples, such as the AMS cycles and sequences. In the sections below we will describe the principles of hierarchical analysis and then compare its validity with that of the POE approach by means of Monte Carlo simulations of AMS runs.

Hierarchical Statistical Analysis

Our application of the hierarchical statistical analysis method presupposes that the sources of variability in AMS analyses can be broken down into two catagories: (1) random variation in the number of atoms entering the detector, assumed to be a time-independent Poisson process and (2) fluctuations in the status of the accelerator system. Different fluctuations in the accelerator status may operate on different time scales and thus may cause independent variations in the analysis at different levels in the hierarchy. It is the existence of these fluctuations which is the motivation for repeating analyses at different times, rather than simply running a large number of cycles sequentially.

The levels in the analytical hierarchy are denoted by k, referring to individual cycles, j, referring to sequences of cycles, and i, referring to series of sequences. A "tree" diagram illustrating how the hierarchies are combined is shown in Figure 1. Given the assumptions above regarding sources of variability, R_{ijk}, the measured isotope ratio, is given by:

$$R_{ijk} = \mu + \alpha_i + \beta_{ij} + \epsilon_{ijk} \qquad (1)$$

where μ is the actual mean value and α_i, β_{ij}, and ϵ_{ijk} are independent random sources of error at the series, sequence, and cycle levels, respectively. These also incorporate the Poisson counting errors.

Given a set of raw AMS data arranged into hierarchies the analysis for the balanced case ($J_i = J$, $K_{ij} = K$ over all i and j; see Figure 1 for notation) is described below.

Step 1

For each fixed (i,j) find the mean, $\bar{R}_{ij.}$, over the k-index. Then form the sums of squares of deviations from the means, $\sum_{k=1}^{K} (R_{ijk} - \bar{R}_{ij.})^2$, and sum these over all i and j. This quantity, approximately scaled by the degrees of freedom, IJ (K-1), yields an estimate of σ_ϵ^2.

Step 2

For each fixed i, find the mean $\bar{R}_{i..}$, of the $\bar{R}_{ij.}$ values by averaging over j. Then form the sums of squares of deviations from the means, $\sum_{j=1}^{J} (\bar{R}_{ij.} - \bar{R}_{i..})^2$ and sum these over i. This quantity, scaled, yields an estimate of $\sigma_\epsilon^2 + K \sigma_\beta^2$.

Step 3

Find the mean $\bar{R}_{...}$ of the $\bar{R}_{i..}$ values and the sum of squares of deviations from the mean, $\sum_{i=1}^{I} (\bar{R}_{i..} - \bar{R}_{...}^2)$. This quantity, scaled, yields an estimate of $\sigma_\epsilon^2 + K \sigma_\beta^2 + JK\sigma_\alpha^2$.

Note that as one moves up the "tree", the calculations are done in a similar and consistent manner. The scale factors, and computing formulae for both the balanced and unbalanced case are given in references [5] through [7] and specific applications to AMS data reduction are given in [8].

The variance estimates obtained by this procedure at the various levels (cycles, sequences, and series) are also useful for experimental design purposes. For example, if σ_α^2, (i.e., the variance at the cycle level) is very small in comparison to σ_β^2 and σ_ϵ^2 this would indicate little variation between series. For a given number of measurements it would then be better to run very few (perhaps only 1) series. In effect the number of measurements or calculations should be large at that level where the variance is large.

Monte Carlo Simulations

The propagation of errors and hierarchical statistical analysis equations are only methods for estimating the true variances (and means) of the analytical data. The true statistical parameters would be obtained by calculating the mean and variance of essentially an infinite number of analyses on the same sample. In practice, one would use a large number of repeated analyses of counts generated by the same procedure. Actual repitition of a sufficient number of AMS analyses is not practical, but instead Monte Carlo simulations can be used to evaluate the procedures.

We used a Monte Carlo procedure that generated Poisson counts with a specified mean rate. The counts were produced in individual cycles, which were organized into sequences and series. Each cycle, sequence, and series had additional variability added through the factors α_i, β_{ij}, and ϵ_{ijk} in

equation (1). These factors were generated as independent normal random variables with zero mean and specified variance. As discussed above, the mean and variance calculated from such data can be considered true statistics only as the number of analyses approaches infinity. However, for practical purposes, an excellent estimate of the true parameters can be obtained with a limited data set. In this case, sensitivity runs showed that increasing the number of Monte Carlo simulations past 500 did not change the parameter estimates, and thus 500 repititions were used to calculate all the results below.

The results are presented as "true" and "estimated" standard deviations according to the two models. The "true" value is the standard deviation of the 500 mean isotope ratios. The estimated value is the mean of the 500 individual standard deviation estimates. Means estimates were similarly treated. The Monte Carlo simulations were repeated for various count rates in order to illustrate the dependence on the counting rate.

Figure 2 shows the results of the simulations in terms of the standard deviation as a function of the counting rate. In these trials $\sigma_\alpha^2 = \sigma_\beta^2 = \sigma_\epsilon^2 = 0.02$ and there were two cycles in each sequence, two sequences in each series, and only one series in each analysis.

One result which is immediately apparent from Figure 2 is that the POE procedure produces a biased estimate of the standard deviation. The estimated standard deviations are uniformly less than the "true" values. This is predictable and is due to the fact that the estimated standard deviations have a large variability which is not accounted for in the internal/external calculation. In contrast to the POE procedure, the hierarchical method is shown to produce good estimates of the "true" standard deviation. For both procedures the estimated means (not shown on

Figure 2) were fairly close to the input values, although the POE procedure did slightly underestimate the true mean for low counting rates.

Another important result of the Monte Carlo simulations is that the "true" standard variation from the hierarchical method is significantly smaller than the "true" POE standard deviation. This demonstrates that the hierarchical analysis provides a better estimator for the experimental value; in other words, on the average the hierarchical method will provide estimates closer to the true isotope ratio than will the POE method. The superiority of the hierarchical method is due to the more consistent analysis of variability.

In addition to the simulations illustrated in Figure 2, additional runs were made to examine the effects of unbalanced hierarchy "trees", correlation of the counting rate with the beam current, and background counts. These are not presented in this paper, but confirm the results discussed above. They may be found in ref [8], which also contains a more detailed description of how the hierarchical method can be applied to AMS data.

Conclusions

To date, virtually all AMS raw data have been reduced by means of some variant on the POE approach. Thus one result of this study, that means estimated by POE are not significantly biased, is reassuring. However, the finding that the standard deviations are underestimated is troublesome and shows that an improved method of statistical analysis is needed. Hierarchical statistical analysis is the logical alternative. The superiority of the hierarchical approach is demonstrated by the smaller "true" standard deviations resulting from analysis of the Monte Carlo data.

Even if the POE approach did produce conservative estimates of the analytical uncertainty, the hierarchical method would still have a significant advantage. The procedure of selecting the larger of the internal/external uncertainty pair is an arbitrary method of dealing with systematic data. In contrast, the hierarchical method analyzes the sources of variation in the measurement in a consistent and organized fashion. The components of variation determined at each level in the hierarchy can thus be combined to yield a meaningful estimate of the over-all analytical uncertainty. Uncertainty estimates from the hierarchical method therefore merit a higher degree of confidence than those from the POE approach.

Finally, the ability of the hierarchical method to break down the sources of variability makes it very useful to the AMS analyst. For example, our preliminary analysis of Rochester ^{36}Cl raw data indicates that the largest variability is at the cycle-to-cycle level. This, in turn, shows that the major source of uncertainty is due to the Poisson counting statistics and short-term drift rather than long-term machine drift. Using this information, the analytical efficiency can be maximized by collecting relatively few sequences composed of many cycles. The identification of high variability at the sequence level (indicating short-term machine drift) would have dictated the opposite strategy: collection of many sequences composed of few cycles.

In summary, the hierarchical statistical method of raw data analysis possesses significant advantages over the propagation of errors approach in terms of both statistical validity and practical experimental concerns. It therefore warrants serious consideration for adoption in routine AMS analysis.

Acknowledgements

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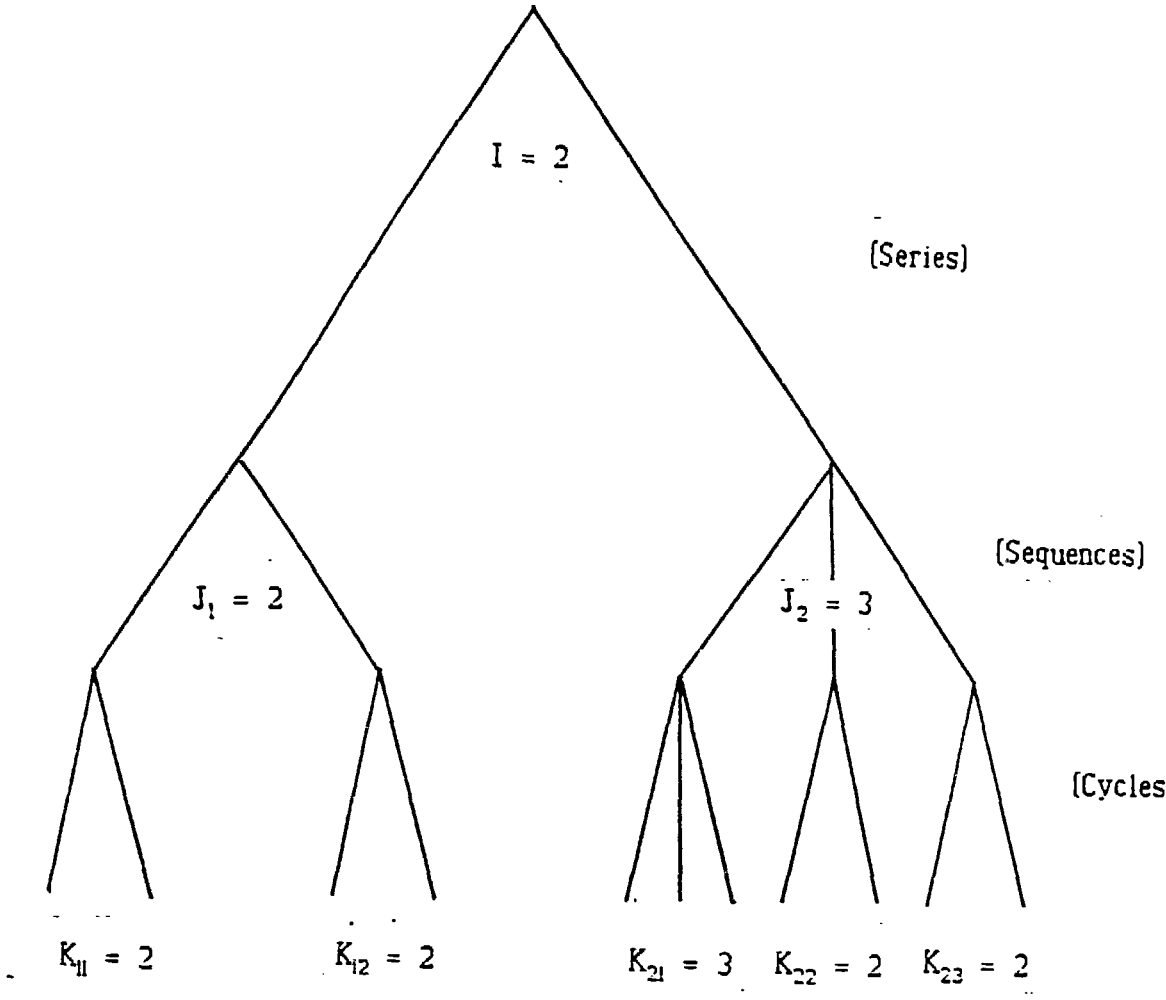
FIGURE CAPTIONS

Figure 1. "Tree" diagram illustrating how cycles are combined into sequences and sequences into series.

Figure 2. Variation of standard deviations (each calculated from 500 Monte Carlo simulations) with Monte Carlo count rates. 1 = "true" POE standard deviation (i.e., the standard deviation of the 500 POE means); P = POE estimate (i.e., the mean of the 500 individual POE standard deviation estimates); 2 = "true" hierarchical standard deviation; and, N = estimated hierarchical standard deviation.

Figure 1

Schematic Diagram for Measurements



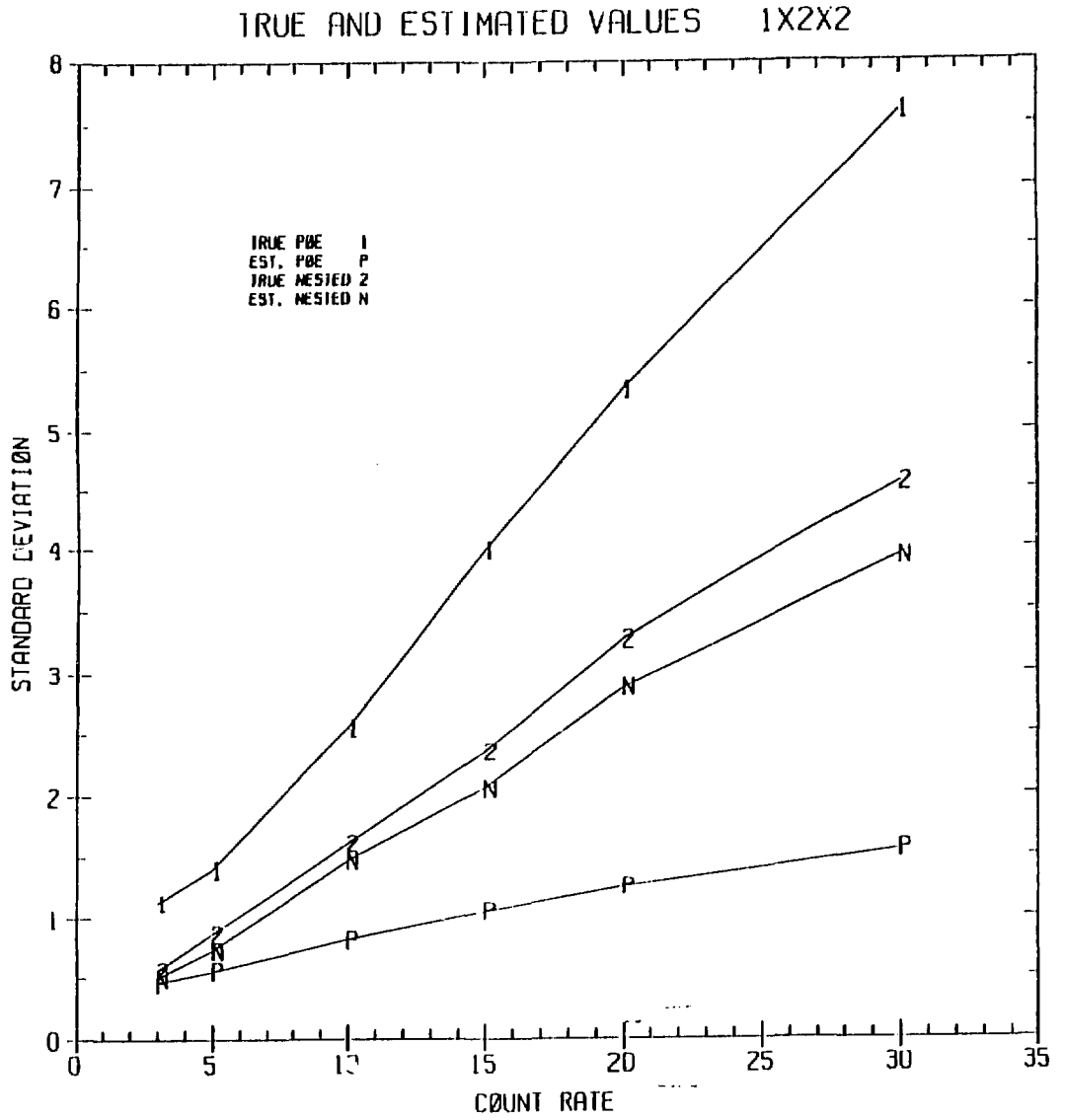

TRUE AND ESTIMATED VALUES 1X2X2
TRUE PØE I
EST. PØE P
TRUE NESTED 2
EST. NESTED N
STANDARD DEVIATIØN
CØUNT RATE
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
30
35

Fig 2