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OFFICE MEMORANDUM

TO : Distribution

DATE: June 30, 1976

FROM : Dave Curtis

William E. Goode

SUBJECT : ANALYTICAL RESULTS

SYMBOL : H8-76-310

0912 Reference

Recent discussions with customers and the enclosed document from Claude Sill point out the need to discuss the radiochemical results that are generated by the H8 analytical chenistry section.

All radiochemical results reported from this laboratory include an uncertainty that reflects only the 1σ standard deviation associated with the random nature of the radioactive decay process. This value does not reflect uncertainties due to pipetting errors, weighing errors, untraced loss of material, etc. We are trying to extablish a quality control program that attempts to evaluate these potential errors. As Sill points out quantitatively estimating these errors is difficult. However, we think we have a reasonable program for Pu. Results of this quality control effort have been, and will continue to be reported in the quarterly report. These results are reported such that the users can evaluate the overall accuracy, precision and absolute detection limit for the Pu procedure. When enough data has been obtained we will publish the results in an appropriate forum.

We are guilty of generating computer output with more significant figures than is merited. The programs are being rewritten to alleviate this problem. We have assumed that the customers were aware of the proper treatment of significant figures. However, a word of caution is perhaps appropriate. All results should be rounded off to properly reflect the significance of the result as shown by the uncertainty.

There is a great deal of information to be obtained from the uncertainties reported with each result. It is a kind of figure of merit for that result. The overall uncertainty in the result cannot be better than the uncertainty associated with the counting statistics. It may be worse due to the previously mentioned problems of pipetting, weighing etc. If we assume that these latter types of errors are relatively the same for all samples (undoubtedly an incorrect assumption) or if they are small relative to the counting errors (probably a correct assumption for low level samples), then the counting statistics offer the best criteria for evaluating the relative worth of a result. It is patently wrong to calculate an unweighted mean for radiochemical results. It assumes that the uncertainties are equal which they obviously are not. For instance, given two results 1.0 ±1.0 and 0.01 ±0.001, an unweighted mean gives an average of 0.50 which gives undue consideration to the larger result which is in fact below the detection limit. Whereas a weighted average gives a mean value of 0.01 which correctly reflects

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the fact that one value is reasonably well defined and the other is not. One can ignore the necessity to weight the results when the uncertainties are small relative to the result. However, it is a fatal error if one is dealing with samples with unequal uncertainties.

The uncertainty reflects the absolute quantity of the analyte relative to the background, a function of the concentration of analyte in the sample, the sample size and the tracer recovery. Neither the magnitude of the result nor the percent tracer recovery are good criteria for evaluating the validity of a result. A result of large magnitude may only reflect large corrections due to small sample size and/or poor tracer recovery (only one of which can be controlled by the analysts). This fact will be readily apparent from the relative magnitude of the uncertainty. A low tracer recovery indicates there is a problem with the chemical procedures and it degrades the sensitivity of the procedure. However, if one accepts the basic assumption that isotopic equilibrium has been established between a tracer and the isotope to be analyzed then a low recovery does not directly degrade the result. The main source of direct uncertainty associated with low tracer recovery is the uncertainty in counting statistics due to a decreased number of counts in the tracer peak. However, this is again manifest in the reported uncertainty of the result.

Occasionally the number of counts in a sample peak will be identical to the number of counts in the background. This situation produces a zero result. The mathematics is such that this situation also generates an uncertainty of zero. This is obviously incorrect and such cases should be considered as such. The uncertainty in such cases is actually quite large since we are subtracting two values of equal magnitude to get an infinitely small value. We are trying to assess the correct way to address this problem, but as yet do not have a satisfactory solution.

There has been a lot of ^{241}Am data generated in the process of developing the procedure for this isotope. I would like to reiterate some of the points made recently by Daryl Knab in an attempt to aid you in evaluating the data. We cannot judge the value of the data for your experiment, we can only pass on to you our results with the precautions as we see them.

1. The reported percent recovery on the ^{241}Am computer data sheets should be ignored in all cases. It is an artifact of the computer program and does not reflect the real tracer recovery. If you wish to assess the recovery, look at the column marked "tracer counts" on the computer data sheet. One hundred percent recovery yields 2900 counts in 80,000 secs. Also see the earlier comments concerning

tracer recovery. A low recovery does not off-handedly mean the result is of no value.

2. The ^{241}Am procedure was often ineffective in removing other α-emitters. These emitters can interfere with the α-spectrum of ^{241}Am. If the interference is due to Pu we can quantitatively assess the interference and calculate a good ^{241}Am value. If you wish to do this we will assist in making the corrections. Corrections cannot be assessed for other α-emitters and results of these type of samples can only be considered as upper limits.

3. Another problem that has been encountered in the ^{241}Am procedure is the failure to remove macro quantities of non-radioactive materials. This degrades the resolution of the spectrum and makes it difficult or impossible to resolve the ^{241}Am peak from the ^{243}Am peak. In general we have attempted, where possible, to do the calculation by hand. Each of these values should be considered on its own merit.

DC:te

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REPORTING OF ANALYTICAL RESULTS

Analytical Chemistry Branch
Health Services Laboratory
U. S. Energy Research
and Development Administration

There is considerable confusion in the way various laboratories report their analytical results, particularly those from radiochemical measurements. Some laboratories report the standard deviation resulting from measurement of the random processes only; others report the random uncertainty after multiplication by two or three to obtain higher confidence limits. In many cases, only the statistical uncertainty of the final sample measurement is included, while other equally important random uncertainties incurred earlier in the determination are completely ignored. Some laboratories report various combinations of random plus systematic uncertainties, sometimes with no clear explanation as to what was done.

In addition to the confusion, there are other objectionable practices that are widespread. Analytical results should be reported in such a way as to convey as much information as clearly as possible. However, physical measurements should not be permitted to appear more precise and/or accurate than they really are to prevent unwarranted conclusions from being drawn from the data. For example, many laboratories report standard deviations to three or more significant figures with no more justification than "that's what the computer gives." A standard deviation is a value by which the associated measurement can be expected to vary once out of every three times. To infer that the results are sufficiently precise to permit interpretation of the standard deviation to three or four significant figures is certainly optimistic, even if the value of the standard deviation used were correct. More often, the value used is not even correct for several reasons: other important random errors have not been propagated to the final result; the population distribution is either not known or is known to be skewed; and other nonrandom (systematic) uncertainties are present and have not been included.

Another bad practice encountered frequently is the failure to ensure decimal agreement between the result and its associated uncertainty. For example, results such as 1.2 ± 0.002 or 1.234 ± 0.2 are internally inconsistent and should be clarified. Either the result is more precise than is given, as indicated by its standard deviation, and more significant figures should be retained; or the result is much less precise than indicated, and the number of significant figures should be decreased to agree with the precision indicated by the standard deviation. Lack of correspondence in the decimal places of numbers being added or subtracted frequently is responsible for implied precision and accuracy that cannot possibly be achieved. For example, suppose the annual release of

radioactivity from several facilities was 21,200,000 curies from one, 5,260 curies from another, and 1.62 curies from a third. To say that the total activity released from the site was 21,205,261.62 curies certainly implies a precision in the measurement that is both incorrect and unintended.

Analytical results obtained from this Branch will reflect the following criteria.

Every result will be expressed as a finite number with a plus-or-minus uncertainty attached. The term "not detected" will not be used because it indicates only that the substance in question was in fact not detected by whatever means employed but gives no quantitative information as to the sensitivity with which it was not detected. The human eye is a much more sensitive indicator of the size of a lump of coal than the macro scales in the coal yard. The term "detection limit" will be used only to describe quantitatively the sensitivity of the analytical procedures available and not to express the quantitative results of actual analyses. The same objections and prohibition are also true with respect to the use of other similarly quantitatively nondescriptive terms such as nil, none, trace, negligible, etc. Except in the absolute sense of the last molecule, even the term "zero" is meaningless and requires quantitative description by use of appropriate numerical values, e.g., 0.00 is certainly different in its implication than 0.

The plus-or-minus value attached to the result is the total statistical uncertainty resulting from measurement of all random processes involved, properly carried through to the final result using the fundamental law of propagation of errors, at the 68% confidence level (i.e., one standard deviation). The standard deviation will be rounded off to one significant figure, or to not more than two significant figures when the numbers involved are less than 15. For example, the number 12 has twice as many significant figures as the number 9, but an absolute uncertainty of one part in the last place produces a relative uncertainty that is not significantly different for either number. The result itself will then be rounded off so that the last significant figure retained will occur in the same decimal place as that in which the standard deviation occurs. THESE NUMBERS MUST THEN BE INTERPRETED BY THE USER WITH DUE CONSIDERATION FOR THE CONFIDENCE LIMITS DESIRED!

An estimate of all nonrandom or systematic uncertainties incurred anywhere in the measurement process, if significant compared to the random uncertainties, will be placed in parentheses after the standard deviation. This estimate is highly subjective and generally difficult or impossible to achieve with any substantial accuracy. However, the impressions of the analyst can be as important in assessing the accuracy and acceptability of the final result as the numerical data. Because the numerical data are more objective and susceptible of exact statistical interpretation,

the systematic uncertainties will be kept separate so that the precision with which the measurement was carried out can be kept clearly defined.

In the past, it has been the practice of this Branch to report analytical results at or near the detection limit somewhat indiscriminately in either of two ways. A "less than" value such as $< 6 \times 10^{-9}$ μCi/ml, corresponding to the detection limit at the 95% confidence level for the conditions used, and the net disintegration rate actually obtained together with the standard deviation of its determination, such as $2 \pm 3 \times 10^{-9}$ μCi/ml, have both been used. Although both numbers mean almost but not quite the same thing statistically, it was thought that the practical conclusions to be obtained and the intent would be clear from the way the data were presented. However, some confusion, loss of data, and additional problems have resulted. Particularly, when large numbers of radiochemical results are to be combined, such as in obtaining yearly averages, mean trends, etc., the question arises as to how to handle results reported in terms of "less than," detection limits, or negative numbers.

In all radiochemical measurements near the detection limit, the net value is obtained from the difference between a gross count and a background count, which are nearly identical in size for the same counting time and which reflect the measurement of statistically random processes. The problem is further complicated by the fact that a net reagent blank, also near zero, must also be determined in the same way as the net sample measurement and subtracted therefrom. Consequently, if the sample contains "no" activity, there is exactly the same probability of obtaining small positive net values that are in fact "zero" as in obtaining equally small negative net values that are 'zero' because of the identical statistical probability of either number being numerically larger than the other. The inclination to accept a small positive value as being real simply because it is positive, but to reject an equally small negative value because it is negative is a purely human reaction, totally unsupported by mathematical statistics when random events are being measured. Although it is completely clear and logical that there can be no such thing as a negative concentration, it is equally clear that elimination of small negative numbers representing measurements of random processes will surely give rise to a slightly positive bias in the means of a large number of measurements.

Henceforth, it will be the policy of this Branch to report the net disintegration rate (expressed as a concentration) and standard deviation actually obtained, whether or not the sign is negative. When the absolute value of the net rate can be rounded off to one significant figure occurring in a decimal place to the right of the one in which the standard deviation occurs, the value is rounded to zero. For example, 0.086 ± 0.2 is rounded upwards to 0.09 and then to 0.10 and reported as 0.1 ± 0.2; 0.04 ± 0.2 is rounded downward and reported as 0.0 ± 0.2. Net negative

numbers should then be rounded upwards to zero by the customer before publication or other release after the averages have been determined, or on each individual result if no further mathematical treatment is intended. It may be predicted with some confidence that net negative numbers larger than two or three times the standard deviation of the net will not be encountered. Much larger values would give increasing confidence that the negative values were real. Because of the physical impossibility of such a result, presence of a systematic error in the measurement is indicated that will be identified and eliminated.

Claude W. Sill

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