CONF-9007106--82

WSRC-MS--90-67

DE91 005665

MEASUREMENT CONTROL AT AN SRS ANALYTICAL LABORATORY (U)

by

Gary P. Wills

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

A paper proposed for presentation and publication at the
INMM Annual Conference
Los Angeles, CA
July 11-18, 1990

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MS9006050

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

JAN 04 1991

ys

MEASUREMENT CONTROL AT AN SRS ANALYTICAL LABORATORY (U)

Gary P. Wills
Westinghouse Savannah River Company
Savannah River Site

Aiken, South Carolina 29808

ABSTRACT

The measurement control program includes control of the analytical procedures, analyst training and qualification, and mass and balance control. A DEC 11/750 minicomputer and an interfaced Hewlett Packard 9836 desktop computer control these functions. The training and qualification program requires the analyst to analyze known and "blind" standards. Statistical tests for precision and bias are used to determine the analyst's qualification. An analyst must be qualified before he/she is permitted to use an analytical procedure for production samples. The qualified analyst must verify the operation of the measurement system prior to analyzing production samples. Balances must be tested and check-weighed and the analytical procedure must be verified by analyzing a "blind" standard. The data from the analysis is entered to the laboratory computer where it is determined to "pass" or "fail". The analyst is notified immediately by the laboratory computer if the standard, chemical or mass, has passed. The results of the chemical standard are transferred to a Hewlett Packard computer where the data are evaluated routinely. The evaluation determines the bias and the uncertainty of each analytical procedure as used by the analysts. These parameters are applied to the sample results to bias correct the results and calculate the measurement uncertainty.

INTRODUCTION

The measurement control program at a Savannah River Site analytical laboratory was instituted to provide reliable results for production samples, to give assurances of the operability of the measurement systems, and to meet the requirements of DOE Order 5633.3 for the control of nuclear material. The measurement control system includes the analytical measurement control program, the analyst training and qualification program, and the mass and balance control program.

These programs were designed into the laboratory computer system software before the laboratory was occupied. The laboratory data system is based on a DEC 11/750 computer and an interfaced Hewlett Packard 9836C desk top computer. The measurement control program includes analyses for accountability, process control, and production specification. The measurement control program covers 62 analytical methods analyzing 82 properties. In a typical week, approximately 350 chemical standards are analyzed.

ANALYTICAL METHODS CONTROL

The Analytical methods control program verifies the measurement system use to perform an analysis. The program includes all analytical methods. The analytical methods are used

for accountability, process control, and product specification measurements. The program verifies the reagents, the instruments, and the analyst. The analyst must be qualified on the analytical method to analyze samples using the method. The verification program uses "blind" standards, which we call verification standards. The analyst must successfully analyze verification standards prior to analyzing samples on an analytical method. Analytical methods must be verified once per shift prior to performing the analysis. Each analyst verifies the method prior to analyzing samples.

STANDARDS

Analytical method will have from one to six verification standards depending on the range of the properties being measured. An analytical method, which covers a wide range of property concentrations, will have four to six different concentrations for the verification standards. Analytical methods, which are analyzing a limited range of concentrations will only have one or two verification standards. Standard vials are prepared by aliquoting the required aliquot size into the vials. By aliquoting the standards to small vials, the stock bottle of the standard can be protected from evaporation from continuous opening, cross-contamination from other standards, and control over the standards can be maintained by limiting the analysis of a standard aliquot to one run. The laboratory computer randomly assigns a verification standard aliquot to one run. The laboratory computer randomly assigns a verification standard to sequential standard ID numbers, which are logged into the laboratory computer. The verification standard aliquots are labeled with the assigned standard ID numbers.

VERIFICATION

To verify an analytical method, the analyst chooses a verification standard. The analyst analyzes the standard and enters the data into the laboratory computer. The computer calculates the results and determines whether or not the standard passes. The analyst is promptly notified if the verification standard "passed" or "failed". If the standard passes, the analyst can proceed with the analyses of samples on that method. If the standard fails, the analyst can attempt another verification standard. If it passes, he must pass a third verification standard to run samples; if not, he must troubleshoot the method (see Figure 1).

When two failures occur on a method, the analyst must troubleshoot to find the problem. When the problem is corrected, the supervisor must give approval for the analyst to again attempt to verify the analytical method. Until approval is granted by the supervisor, the laboratory computer will not allow the analyst to process another verification standard. The

Successful analysis of a verification standard automatically updates the analyst's qualification record for the analytical method.

Figure 1. Analytical Method Verification Scheme

STATISTICS

The verification standard results are transferred automatically from the laboratory computer to the HP9836C computer. The verification standard results for an analytical method are routinely evaluated to determine the most appropriate statistical model to use in estimating the bias correction and the precision of the analytical measurement. The analyses data are modeled depending on the concentration range of the analysis done using either a "Multi-level" or a "Single-level" evaluation.

An analytical method which covers a large analysis range is evaluated using the "Multi-level" evaluation. This evaluation chooses the best fit of nine different models for the standard deviation.

Multi-level Standard Deviation Models

1. $s = \text{constant}$
2. $s = a + bK$
3. $s = a + bK + cK^2$
4. $\ln(s) = a + bK$
5. $\ln(s) = a + bK + cK^2$
6. $s = a + b \ln(K)$
7. $s = a + b \ln(K) + c (\ln(K))^2$
8. $\ln(s) = a + b \ln(K)$
9. $\ln(s) = a + b \ln(K) + c (\ln(K))^2$

The standard deviation equation is used to weigh the verification results. The bias equation is modeled using the best fit of a linear or a quadratic model.

Multi-level Bias Models

1. $\text{Result} = a + bK$
2. $\text{Result} = a + bK + cK^2$

The corrected result is determined using the following equations for the model chosen:

1. Linear: $\text{Corrected result} = \frac{(R-a)}{b}$
2. Quadratic: $\text{Corrected result} = \frac{-b + \sqrt{b^2 - 4c(a-R)}}{2c}$

The precision in the "Multi-level" evaluation is a propagated error of the bias corrected result and the level variability.

For analytical methods measuring samples covering narrow ranges a "Single-level" evaluation is used. In this evaluation an absolute bias or a relative bias model is used. The model chosen is decided by the data transformation done. The data transforms are

Absolute: $\text{result} - \text{known}$

Relative: $(\text{result} - \text{known})/\text{known}$.

These transformations produce the following Single-level precisions equations

Absolute: $\sqrt{s^2 + \frac{s^2}{N}}$

Relative: $\frac{\text{Result}}{(1 + \text{bias})} \sqrt{s^2 + \frac{s^2}{N}}$

where $s = \text{standard deviation}$
 $N = \text{number of data}$

and the bias correction equations of

Absolute: $\text{Corrected result} = \text{Result} - \text{bias}$

Relative: $\text{Corrected result} = \frac{\text{Result}}{(1 + \text{bias})}$

In both types of evaluations, the system automatically checks several criteria that are necessary to use the above mathematical relationships in statistical inference. We use the Von Neuman test for autocorrelation, the runs test for independence, and the goodness-of-fit test for normality.

The parameters determined for the bias correction and the precision are transferred from the HP9836C computer to the laboratory computer. The laboratory computer applies the parameters to a sample result to calculate the bias-corrected result and estimate the precision of the corrected result. The laboratory computer applies the parameters to a sample result. The laboratory computer provides the random and the systematic error estimates for each sample result to the Accountability computer.

ANALYST TRAINING AND QUALIFICATION

The analyst training and qualification program provides an objective means of determining if an analyst is capable of doing a particular analysis. In the training program, the trainee gets instruction from a chemist or a qualified analyst in the techniques of the analytical procedure and the operation of the instrument. The training program uses standards whose values are known. These standards are called training standards or bench standards. The trainer demonstrates the techniques of the analysis by analyzing a training (bench) standard on the analytical method. The trainee performs the required techniques for the trainer by analyzing a training standard. When the trainer is confident the trainee understands the analysis and the operation of the instrument, the trainee will continue to analyze training standards. The results of the training standards are entered into the laboratory computer. The computer notifies the trainee how well he did on the training standards by comparing the result against the qualified analyst's performance on the method.

When the trainee gains confidence with the method and is getting acceptable results, he gets approval from his supervisor to formally qualify on the analytical method. To qualify on an analytical method, the trainee will analyze verification standards, which the analyst will designate as qualification standards. The number of qualification standards required depends on the type of samples the method is used for. Accountability and product specification analyses require nine qualification standards to be analyzed. Process control analyses require four standards to be analyzed. The trainee runs the standards over a two-to three-day period. The results of the qualification standards are entered into the laboratory data system. When the trainee has completed the qualification standards, his supervisor determines whether he is qualified by calling up his qualification standards for the analytical method on the laboratory computer. The laboratory computer performs statistical tests for the significance of bias and precision. The laboratory computer performs statistical tests for the significance of bias and precision. The equations used to perform these tests are given in Figure 2.

Bias:
$$t = \frac{1}{\sqrt{N}} \sum_{i=1}^N \frac{R_{ci} - K}{s}$$

Precision:
$$F = \frac{1}{N} \sum_{i=1}^N \left(\frac{R_{ci} - K}{s} \right)^2$$

R_{ci} = corrected result
 K = known value
 s = method standard deviation
 N = number of standards analyzed
 $t < T(1-\alpha/2) \text{ dF}=4 \text{ or } 9, \alpha=.01 \text{ or } .10$
 $F < F(4 \text{ or } 9, 200)$

Figure 2. Qualification Equations

The trainee's bias and precision must not be statistically significant as compared to that of the qualified analysts in the laboratory to qualify on the method. If the trainee has a significant bias and/or precision, the supervisor is advised not to qualify the trainee. The trainee's supervisor has the final decision on whether to qualify the analyst. The analyst's qualification is good for one year. Disqualification on an analytical method is automatic if a verification standard is not passed in the one year period or by recommendation and/or concurrence of laboratory supervision.

MASS AND BALANCE QUALITY CONTROL

The mass and balance program controls the use of the balances throughout the laboratory. This program consists of the calibration and certification of balances, the daily balance verification, and the calibration of mass standards.

The balances are calibrated and certified prior to being put into service and thereafter on a one year basis. The balances are checked using the balance certification software developed at the Savannah River Site [1]. This software runs on an Epson HX-20 computer. The computer determines if the balance has significant bias, linearity, sensitivity, or corner loading problems. The printout from the computer is filed for a history of the balance calibration and the date of the certification is kept

in the laboratory computer database for recall of the next certification. A balance that fails a certification test is evaluated to determine if it will affect the measurements made by that balance. A balance whose certification is out of date is not used for any measurements.

Besides the balance certification program, we have a daily balance verification program. In this program, a user of a balance must verify the operation of the balance before doing any measurements. Each balance has a uniquely identified test weight assigned to it. At least once per shift the balance is to be used, the test weight is measured on the balance. The reading with the ID of the test weight and the ID of the balance are entered into the laboratory computer. The laboratory computer determines whether the measurement meets the uncertainty of the system and notifies the analyst. The database stores the mass readings of the test weight and determines the uncertainty range that the test weight must be within. The uncertainty range includes the balance uncertainty, the test weight uncertainty, and the rounding error for the balance. If the test weight is outside the range, the analyst must determine the cause and correct before using the balance for any sample measurements.

The primary mass standards used in the laboratory are calibrated once per year by the Standards Metrology Laboratory onsite to provide traceability to the National Institute of Standards and Technology (NIST). The primary mass standards are used to calibrate the test weights used in the program. The weight calibration software[1] developed for use with the Epson HX-20 computer at SRS is used to perform the weight calibration. The test weights used are inexpensive to purchase or can be fabricated from a suitable material. Therefore, they are disposable if they become contaminated. The calibration of test weights is performed annually. The date of the calibration is entered into the laboratory computer for recall of the next calibration.

CONCLUSION

The measurement control program has helped towards meeting the DOE requirements for measurement control. The program has provided our analysts with confidence in their measurements through the analytical control program. The programs have provided us with proof that our measurement systems are performing properly and providing accurate results. The measurement control program provides the error estimates associated with each sample result. With this program, the amount of data generated daily requires a computer to collect and evaluate the data.

ACKNOWLEDGMENTS

The author wishes to acknowledge Idaho Falls Analytical laboratory for the contribution of the data evaluation software used in this measurement control program.

The information contained in this article was developed during the course of work done under contract No. DE-AC09-89SR 18035 with the U.S. Department of Energy.

REFERENCES

1. S. L. Maxwell, III, and J. P. Clark. "A Portable, Automated, Inexpensive Mass and Balance Calibration System". *Proceedings of the INMM 28th Annual Meeting, Los Angeles, California, July 12-15, (1987).*

END

DATE FILMED

02 / 04 / 91