AUTOMATED SYSTEM FOR CALCULATING
THE UNCERTAINTY OF STANDARDS (U)

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AUTOMATED SYSTEM FOR CALCULATING THE UNCERTAINTY OF STANDARDS (U)

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ABSTRACT

Working Calibration and Test Material (WCTM) solutions are essential as standards in the surveillance of analytical methods, the calibration of equipment and methods, and the training and testing of laboratory personnel. Before the WCTM can be used it must be characterized. That is, the WCTM concentration and its associated uncertainty must be estimated. The characterization of a WCTM is a tedious process. The chemistry and subsequent statistical analysis require a significant amount of care. For a nonstatistician, the statistical analysis of a WCTM characterization can be quite difficult. In addition, the WCTM traceability and characterization must be thoroughly documented as required by DOE Order 5633.3 [1]. An automated system can easily do the statistical analysis and provide the necessary documentation.

INTRODUCTION

The quality of analytical chemistry measurements for controlling plant processes and accounting for nuclear materials is of utmost importance. Through measurement control programs, well characterized WCTM's can be used to determine and control the quality of various analytical measurements. Estimates of bias and variability can be computed for each analytical method. These estimates can be used for measurement adjustments and for computing limits of error for input/output accountability measurements, shipper/receiver differences, and inventory differences. These limits of error will include the uncertainties for both the analytical measurements and the WCTM.

REVIEW OF METHODOLOGY FOR CHARACTERIZING THE RCTM

The Reference Calibration and Test Material (RCTM) is usually a standard reference material obtained from the National Institute of Standards and Technology (NIST). The RCTM starting material is similar to the WCTM to be characterized, or it is adjusted to match the matrix of the WCTM.

The RCTM starting material may require cleaning or other preparation before the characterization of the WCTM takes place. To begin, several mass measurements are made on the RCTM starting material. The starting material is then dissolved and diluted in an appropriate acid solution. Prior to dissolving the starting material, several mass measurements are made on the solution container. After the starting material has been dissolved, several more mass measurements are made on the solution and container. The RCTM makeup concentration and its uncertainty are derived from the following statistics:

- The sample mean and sample variance associated with the estimated purity of the RCTM starting material
- An air buoyancy correction factor
- The sample mean and sample variance associated with the estimated mass of the RCTM starting material
- The sample mean and sample variance associated with the estimated mass of the solution container
- The sample mean and sample variance associated with the estimated mass of the solution and container

The RCTM solution is then transferred to several containers. The certified value of the RCTM starting material must be confirmed by laboratory analysis of the RCTM solutions. After this has been done, the RCTM solutions can be used to characterize WCTM's.

A preparation scheme for the RCTM is given in Figure 1.

![Preparation Schemes for Calibration and Test Materials](chart.png)

Figure 1. Preparation Schemes for Calibration and Test Materials
REVIEW OF METHODOLOGY FOR CHARACTERIZING THE WCTM

The methodology for characterizing the WCTM involves parallel laboratory analyses of the RCTM and WCTM solutions. A minimum of two independent analytical methods must be used in the parallel analysis of the RCTM and WCTM solutions.

The WCTM is usually obtained from plant process tanks. This solution is appropriately processed and placed in containers.

Random samples of RCTM and WCTM containers are submitted for laboratory analysis. The laboratory should analyze the containers in random order.

Using the laboratory results, the final WCTM estimated concentration and its uncertainty are derived from the following statistics:

- The estimated RCTM makeup concentration and its associated uncertainty
- The sample mean and sample variance associated with the RCTM solutions
- The sample mean and sample variance associated with the WCTM solutions

A preparation scheme for the WCTM is given in Figure 1. The methodology for characterizing a WCTM is discussed in more detail in references [2] and [3].

THE STATISTICAL ANALYSIS FOR CHARACTERIZING A WCTM

Several steps are involved in the statistical analysis of a WCTM characterization. These steps are described below.

1. Estimate the concentration of the RCTM starting material and its associated uncertainty.

2. Specify the uncertainty of the laboratory methods used to analyze the RCTM and WCTM solutions. The target uncertainty in estimating the final WCTM concentration should also be specified. This information is used to determine the number of laboratory analyses required on the RCTM and WCTM solutions.

3. Confirm the certified value of the RCTM starting material using the RCTM solutions.

4. Submit randomly chosen samples of RCTM and WCTM containers for laboratory analysis. The order in which the containers are analyzed by the laboratory should be randomized.

5. Estimate the WCTM and RCTM concentrations and their associated uncertainties based upon the laboratory analyses.

6. Test the equality of the sample variances obtained by the same analytical method for the RCTM and WCTM solutions.

7. Bias correct the estimated WCTM concentrations with respect to the ratio of the estimated RCTM starting material concentration and the estimated RCTM solution concentration.

8. Estimate the uncertainties associated with the bias corrected WCTM estimated concentrations.

9. Test the equality of the bias corrected WCTM estimated concentrations. This involves a T-test where the degrees of freedom are computed using Satterthwaite's formula.

10. The final WCTM concentration is estimated as a weighted sum of the bias corrected WCTM estimated concentrations. The weights used in this computation are functions of the estimated uncertainties associated with the bias corrected WCTM estimated concentrations.

11. Finally, the uncertainty associated with the final estimated WCTM concentration is estimated.

Needless to say, the statistical analysis for a WCTM characterization is complex. A more detailed discussion of the statistical analysis for a WCTM characterization is given in reference [2].

ADVANTAGES OF AN AUTOMATED SYSTEM

There are three major advantages to automating the calculation of the uncertainty of standards.

First, the statistical analysis is automated. The statistical analysis of the characterization process is complex and prone to errors. If done manually, the analysis needs to be done at least twice to check for errors. And even then, some errors may remain.

The second advantage is automating the documentation of the characterization process. Documenting the traceability of the WCTM and the statistical analysis is required by DOE Order 5633.3 [1]. An automated system can produce the required documentation immediately.

The third advantage is the maintenance of a database for the characterization of standards. A record of the laboratory analyses for a characterization process along with other characterization information is stored on the computer. If a characterization requires a review, the information will be available to do so. More importantly, if documentation is lost, it can be regenerated quickly.

THE DESIGN OF AN AUTOMATED SYSTEM

The automated system for calculating the uncertainty of standards is an interactive, menu-driven system. It was designed and programmed using Base SAS, SAS/AF, and SAS/FSP software products. The system runs on an IBM 3090 computer at the Savannah River Site.

Base SAS, SAS/AF, and SAS/FSP are software products developed and maintained by SAS Institute in Cary, NC. Base SAS is used for general purpose data management, report writing, and simple data analysis. SAS/FSP is used for developing interactive, full-screen data entry applications. SAS/AF is a software tool for developing interactive, menu-driven software systems. Using SAS/AF the individual capabilities of Base SAS, SAS/FSP, and other SAS software products can be integrated into a single system.

A system is designed by defining all of the tasks the system must perform. Each task is then individually programmed and becomes a menu item in the system. Figure 2 represents the
configuration of the automated system for calculating the uncertainty of standards.

![Diagram of a system design for automated system for calculating the uncertainty of standards.](image.png)

The system tasks are described below:

- The Controlled Entry task will only let the appropriate personnel into the system. This was done through the use of user ID/password validation. This task is part of the procedure that invokes the system.

- The Data Entry and Editing tasks allow the user to enter and edit characterization ID information, WCTM target standard deviation information, RCTM makeup value information, RCTM confirmation information, and RCTM/WCTM laboratory results.

- The Database Management tasks allow the user to save or browse information in the characterization database. Users will not be allowed to delete data.

- The Statistical Analysis and Reporting tasks allow the user to determine the required sample sizes for achieving the WCTM target standard deviation, to do the RCTM makeup value analysis, to do the RCTM confirmation analysis, and to determine the final WCTM concentration and uncertainty. Documentation will be printed at the printer and immediately received.

**SYSTEM MAINTENANCE**

System maintenance is an important consideration when designing software systems. Unfortunately, it is often overlooked or not given adequate consideration. Software systems that are not properly maintained have short lifetimes and are not cost effective.

The Base SAS, SAS/AF, and SAS/FSP software products are well documented in SAS Institute publications. SAS Institute has a good reputation for providing technical support in the use of all SAS products.

Through good system design, system maintenance can be easily accomplished. By breaking the system down into distinct tasks or menu items, the system becomes substantially easier to program, debug, and maintain. A programmer can update one or more menu items without affecting the other items. Additional tasks or menu items may be added with ease and without affecting the other items in any way. Thus, as the needs of the users change, the system can change to meet those needs.

**FUTURE DIRECTIONS**

Several other working standards will be integrated into this system. These include plutonium oxides and the isotopic distributions of both plutonium and uranium standards. The software will include decay corrections for the short half-lives of some isotopes.

**CONCLUSIONS**

Working Calibration and Test Materials are the cornerstones of a good laboratory measurement quality control program. An automated system can do the statistical analysis for a WCTM characterization and maintain a database of WCTM characterizations. It also provides documentation for establishing WCTM traceability and for the WCTM characterization process as required by DOE Order 5633.3 [1].

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**REFERENCES**


