PNNL-11002
UC-810
Project Technical Information

Demonstrating Compliance with WAPS 1.3 in the Hanford Waste Vitrification Plant Process

M.F. Bryan
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March 1996

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
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SUMMARY

The high-level waste (HLW) vitrification plant at the Hanford Site was being designed to immobilize transuranic and high-level radioactive waste in borosilicate glass. This document describes the statistical procedure to be used in verifying compliance with requirements imposed by Section 1.3 of the Waste Acceptance Product Specifications (WAPS, USDOE 1993). WAPS 1.3 is a specification for "product consistency," as measured by the Product Consistency Test (PCT, Jantzen 1992b), for each of three elements: lithium, sodium, and boron.

Properties of a process batch and the resulting glass are largely determined by the composition of the feed material. Empirical models are being developed to estimate some property values, including PCT results, from data on feed composition. These models will be used in conjunction with measurements of feed composition to control the HLW vitrification process and product.

Due to various uncertainties inherent in the HLW vitrification process, data, and models, the procedure used to verify WAPS 1.3 compliance must be statistical in nature. WAPS 1.3 does not prescribe any specific statistical approach, but it does provide some guidance on the characteristics of the statistical procedure. The interpretation of WAPS 1.3 in the context of the Hanford HLW vitrification process is discussed in some detail. The approach recommended for checking WAPS 1.3 compliance has both "during" and "after" aspects. Specifically, each process batch will be checked for compliance individually during production, and, after all batches in a waste type have been processed, compliance of the entire population of batches in this waste type will be verified.

Each process batch will be checked for compliance with WAPS 1.3 using a confidence interval on the mean PCT result for each element. Details of constructing these confidence intervals, including proper estimation of uncertainty, are given.

Compliance with WAPS 1.3 for all batches in a given waste type will be verified by using tolerance intervals for the population of PCT results (for each element) in this waste

type. During production, a "running" tolerance interval (one based on the current batch and all previous batches in the same waste type) will be used to ensure that process batches are similar enough that final, post-production verification of WAPS 1.3 compliance will be possible. This post-production verification of WAPS 1.3 compliance will also be achieved using tolerance interval methodology. Details of constructing these tolerance intervals, including proper estimation of uncertainty, are given.

Also discussed are related earlier work and some issues (removal of nuisance uncertainties; the role of normality) that should be revisited when more data and information are available on the final HLW vitrification process. Appendixes furnish technical terminology, notation, derivations, and computer code for calculating statistical multipliers and associated statistical characteristics.

GLOSSARY

Acceptable--A batch or composition for which all applicable requirements will be met (with some degree of statistical confidence, as discussed in the body of the document).

Analytical uncertainty--Uncertainty among analytical results from the same sample. This is a composite form of uncertainty, made up of *variability* induced during sample preparation and the inherent *error* of the measurement process itself.

Batch--A discrete quantity of material (waste, frit, recycle, or a combination of the three) to be processed by the Hanford high-level waste (HLW) vitrification plant.

Batch-to-batch variability--Heterogeneity between *batches* made from the same *waste type*.

Bias--Consistent departures of measured or estimated quantities from the true value (see also *error*).

Components of covariance--*Covariance matrices* representing hierarchical levels of uncertainty for multivariate data.

Components of variance--*Variances* representing hierarchical levels of uncertainty in univariate data.

Composition--The proportions of each chemical species in a batch of material to be processed by the HLW vitrification plant; usually expressed as mass fractions of nine major oxides (SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, Al_2O_3, ZrO_2) and a catchall tenth category, "Others." In some cases, individual species normally included in "Others" may be segregated.

Composition uncertainty--Uncertainty in measured or estimated quantities stemming from *variability* in material and/or sampling and analytical *error*.

Compositional data--A type of multivariate data in which the numerical values in each datum are the proportions (or percentages) of the individual components of the material or characteristic being represented by the datum. From their nature as proportions (percentages), these numerical values must lie between 0 and 1 (0 and 100%), inclusive, and they must sum to 1 (100%).

Confidence--A measure of the long-run performance of a statistical procedure, expressed as the probability that the procedure produces the advertised result. For example, the procedure for producing a 95% confidence interval for the mean of a population has a 95% chance of producing an interval that traps the mean. Note that *confidence* pertains to the procedure and not to any particular result.

Confidence interval--A type of statistical interval designed to trap, with specified *confidence*, a single fixed true value, such as the mean of a random variable.

Correlation--A standardized *covariance* which must lie between -1 and 1, *correlation* is computed by dividing the covariance between two random variables by the product of the standard deviations of the two variables.

Correlation matrix--A standardized representation of the interrelationships between individual quantities that make up a multivariate datum, the *correlation matrix* is a symmetric matrix with 1's on the diagonal and the pairwise *correlations* in the off-diagonal positions.

Covariance--A measure of the tendency of two random quantities to vary together, *covariance* is defined as the *expected value* of the product of the deviations of the two random quantities from their respective means, i.e., Covariance(X,Y) = $E(X - \mu_X)(Y - \mu_Y)$. Positive covariance indicates that the two quantities tend to increase or decrease together. Negative covariance indicates that one quantity tends to increase while the other decreases (or vice versa). Covariance can be estimated from a sample of n pairs (X_i,Y_i), i = 1, ..., n, with the formula

$$Cov(X, Y) = \frac{1}{n-1}\sum_{i=1}^{n}(X_i-\bar{X})(Y_i-\bar{Y})$$

Covariance components--See *components of covariance.*

Covariance matrix--A representation of the uncertainties and interrelationships between individual quantities that make up a multivariate datum, the *covariance matrix* is a symmetric matrix with the variances of the individual quantities on the diagonal and the pairwise *covariances* in the off-diagonal positions.

Direct constraints--Requirements and constraints on HLW material (feed composition, melt, and glass) that pertain directly to measured quantities (e.g., oxide mass fractions) or to known functions of these measured quantities.

$E(\cdot)$--See *expected value.*

Error--The random deviation of a measured or estimated quantity from the true value, related to the imperfection of the sampling or analytical procedure.

Expectation--See *expected value.*

Expected value--The average value of a random quantity; in general, given a function, h(X), of a random variable X, the *expected value* (or *expectation*) of h(X) is defined as

$$E(h(X)) \equiv \int_{-\infty}^{\infty} h(x)\, dF(x) = \int_{-\infty}^{\infty} h(x)\, f(x)\, dx\,.$$

Feed--A generic term used to refer to any material being processed in the HLW vitrification plant, upstream of the melter itself (see also *melt*).

Long-term variability--Heterogeneity in material over waste types.

Mean--A statistical measure of the average or central tendency of a random quantity; the *mean*, μ, of a random variable X is simply the *expected value* of X, i.e., $\mu = E(X)$. The mean can be estimated from a sample, X_i, i = 1, ..., n, with the formula

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$$

Melt--Material being processed by the HLW vitrification plant in the melter or before it has cooled and solidified into glass. Before reaching the melter, this material will be referred to as *feed.*

Model uncertainty--Uncertainty in an estimated property value stemming from imperfection of the model used to relate feed composition to the property.

Modelled properties--Properties of feed, melt, or glass for which statistical models are being developed to relate feed composition to the property values.

Moments--The *expected values* of powers of a random variable, X. The first moment, $E(X)$, is the *mean*, μ. *Central moments* are expected values of powers of the difference between X and its mean; the second central moment, $E(X-\mu)^2$, is the *variance.*

Multiple-batch requirement or constraint--A requirement or constraint imposed over a set of batches to be processed by the HLW vitrification plant; e.g., a property for which the requirement is imposed on an entire *waste type*, rather than on the individual batches constituting the waste type. See also *single-batch requirement or constraint.*

Nuisance uncertainty--An uncertainty that may be quantified and removed from a statistical procedure in order to increase the efficiency of the procedure.

Prediction interval--A type of statistical interval designed to trap, with specified *confidence*, a single random true value, such as a new observation of a random variable.

Relative standard deviation--The ratio of the standard deviation to the mean; estimated by $S/\overline{X}$.

S--See *standard deviation.*

S^2--See *variance.*

Sampling uncertainty--See *within-batch uncertainty.*

Single-batch requirement or constraint--A requirement or constraint imposed on each individual batch to be processed by the HLW vitrification plant, with no reference to the characteristics of preceding or succeeding batches. See also *multiple-batch requirement or constraint.*

Standard deviation--Defined as the square root of the *variance*, the *standard deviation* is a measure of uncertainty on the same scale as the original quantity. Roughly, the standard deviation is the average distance of an observed value from the mean.

Tolerance interval--A statistical procedure designed to trap, with specified *confidence*, a specified proportion of the distribution of a random variable. The proportion of the distribution to be trapped is termed the *content* of the tolerance interval. For example, a 95%/99% tolerance interval traps 99% of the distribution with 95% confidence.

Uncertainty--A general term used to refer to any of several measures of the random behavior of some quantity; for example, see *composition uncertainty*, *model uncertainty*, *variability*, and *error.*

Variability--Uncertainty related to heterogeneity in material under examination; for example, see *batch-to-batch variability.*

Variance--A statistical measure of the random behavior of some quantity, *variance* is defined as the *expected value* of the squared deviation of a random variable, X, from its mean, μ, i.e., Variance(X) = $E(X - \mu)^2$. Variance can be estimated from a sample, X_i, i = 1, ..., n, with the formula

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n}(X_i-\bar{X})^2$$

Variance components--See *components of variance.*

Variance-covariance matrix--See *covariance matrix.*

WAPS properties and requirements--Properties of and requirements on glass produced by the HLW vitrification plant, as detailed in the *Waste Acceptance Product Specifications* (WAPS, USDOE 1993). These properties and requirements are related to the performance of the glass in the repository.

Waste type--A relatively homogeneous stream of waste to be processed by the HLW vitrification plant. Several to many *batches* will be made from a single waste stream.

Within-batch uncertainty--Uncertainty among samples from the same process batch; this is a composite form of uncertainty, made up of *variability* (heterogeneity) in the process batch and the inherent *error* of the sampling process itself.

$\overline{X}$--See *mean.*

ACRONYMS

ANOVA--Analysis of variance

CVS--Composition Variability Study

DWPF--Defense Waste Processing Facility

EA--Environmental Assessment

HLW--High-Level Waste

IID--Independent and identically distributed

LTL--Lower tolerance limit

MEM--Measurement Error Model

PCT--Product Consistency Test

PVTD--Pacific Northwest Laboratory (PNL) Vitrification Technology Development

PPMD--Process/Product Model Development

RSD--Relative standard deviation

UCL--Upper confidence limit

UTL--Upper tolerance limit

WAPS--Waste Acceptance Product Specifications

WCP--Waste Form Compliance Plan

WQR--Waste Form Qualification Report

WVDP--West Valley Demonstration Project

CONTENTS

SUMMARY iii

GLOSSARY v

ACRONYMS x

1.0 INTRODUCTION 1

2.0 STATISTICAL INTERVALS AND HYPOTHESIS TESTING 4

2.1 CONFIDENCE AND TOLERANCE INTERVALS 5

2.2 APPLICATION OF STATISTICAL INTERVALS TO ACCEPTANCE TESTING 7

3.0 THE WAPS 1.3 SPECIFICATION 9

4.0 VERIFYING COMPLIANCE WITH THE WAPS 1.3 SPECIFICATION 14

4.1 GENERAL PROCEDURE FOR CHECKING WAPS 1.3 COMPLIANCE ... 16

4.2 VERIFYING WAPS 1.3 COMPLIANCE FOR A SINGLE PROCESS BATCH 19

4.3 VERIFYING WAPS 1.3 COMPLIANCE OVER AN ENTIRE WASTE TYPE 20

4.4 APPLYING WAPS 1.3 TO INTERMEDIATE BATCHES 21

4.5 THE BEST CONFIDENCE/CONTENT APPROACH 22

5.0 RELATED WORK AND ISSUES 25

6.0 REFERENCES 28

APPENDIX A - STATISTICAL BACKGROUND A.1

A.1 DISTRIBUTION AND DENSITY FUNCTIONS A.2

A.2 MEAN AND VARIANCE A.4

A.3 MULTIVARIATE DATA, COVARIANCE, AND CORRELATION A.5

A.4 ESTIMATING POPULATION PARAMETERS WITH SAMPLE STATISTICS A.9

A.5 PROPERTY MODEL NOTATION A.12

A.6 REFERENCES A.13

APPENDIX B - RELATIONSHIP OF STATISTICAL MULTIPLIERS FOR ONE-SIDED TOLERANCE LIMITS TO THE NONCENTRAL t-DISTRIBUTION B.1

B.1 STATISTICAL THEORY B.1

B.2 TOLERANCE INTERVALS AND TOLERANCE LIMITS B.3

B.3 CALCULATING $k_{n,v,\gamma,p}$ B.4

B.4 BEST TOLERANCE LIMITS B.7

B.5 REFERENCES B.8

APPENDIX C - CALCULATING CONFIDENCE AND CONTENT FOR BEST TOLERANCE LIMITS C.1

APPENDIX D - ESTIMATING AND MANIPULATING UNCERTAINTIES D.1

D.1 THE MODEL FOR COMPOSITION UNCERTAINTY IN HLW VITRIFICATION DATA D.2

D.2 THE BATCH MEAN AND ASSOCIATED UNCERTAINTIES D.3

D.3 THE MULTIPLE-BATCH MEAN AND ASSOCIATED UNCERTAINTIES . D.5

D.4 ESTIMATING VARIANCE COMPONENTS D.8

D.5 PROPAGATING UNCERTAINTIES D.13

D.6 COMBINING UNCERTAINTIES D.15

D.7 UPDATING UNCERTAINTIES D.17

D.8 REFERENCES D.19

1.0 INTRODUCTION

The high-level waste (HLW) vitrification plant at the Hanford Site was being designed to immobilize transuranic and high-level radioactive waste in borosilicate glass. Each batch of plant feed material must meet certain requirements related to plant performance, and the resulting glass must meet requirements imposed by the Waste Acceptance Product Specifications (WAPS, USDOE 1993). Similar vitrification operations will be performed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. DWPF has developed a Product Composition Control System for controlling feed composition and for checking and documenting product quality (Postles and Brown 1991, WSRC 1993). The *HWVP Project Waste Form Qualification Program Plan* (Randklev 1993) calls for the development of a product composition control-type system to perform these functions for the Hanford HLW vitrification plant.

The objectives of the Process/Product Model Development (PPMD) cost account of the Pacific Northwest Laboratory Vitrification Technology Development (PVTD) Project include developing and testing methods and algorithms for the Hanford HLW vitrification process/product control system. Various aspects of these methods and algorithms are discussed by Bryan and Piepel (1993), Bryan and Piepel (1994), and Bryan, Piepel, and Simpson (1994). Due to uncertainties in the data and models to be used in controlling HLW vitrification operations and product quality, these methods and algorithms must be statistical in nature. For each process batch, the algorithms will: 1) choose a target feed composition, 2) estimate the actual feed composition by reconciling various process measurements, 3) use the estimated feed composition to estimate, check, and document various batch and product characteristics, and 4) recommend remediation strategies for process batches that do not meet requirements.

Attributes[a] of a process batch and the resulting glass are largely determined by the composition of the feed material. In addition, remediation options are limited once material reaches the melter. Therefore, the relationships between "upstream" feed composition and "downstream" batch and glass properties will be exploited to ensure acceptable batch and glass properties and to perform any required remediation *before* material enters the melter.

Development of empirical models relating feed composition to important batch and glass properties is one objective of the ongoing Composition Variability Study (CVS; Hrma, Piepel, et al. 1992, 1994). The Hanford HLW process/product control system will use these models to estimate batch and glass properties as functions of feed composition.[b]

Two general types of uncertainty are important in HLW vitrification process/product control: *composition uncertainty*[c] and *model uncertainty*. Composition uncertainty is the uncertainty inherent in estimates of feed composition. This type of uncertainty may stem from heterogeneity in material, imperfection of measurement processes, or both. Composition uncertainty must be taken into account when estimating and checking any batch or glass attribute. Three components of composition uncertainty will play a role in estimating and checking batch and glass attributes:

(a) Established usage reserves the word *property* for characteristics of the melt and glass (which will usually be estimated via models based on feed composition), but requirements and constraints will also be imposed on feed composition (oxide mass fractions and functions thereof). To avoid confusion, the word attribute is used here to refer to any characteristic of HLW vitrification material (feed, melt, and glass).

(b) The general forms of the CVS models are discussed in Section A.5. As noted there, several of the CVS models actually predict functions of property values, rather than the raw property values. For example, the models used to demonstrate WAPS 1.3 compliance predict the natural logarithm of the relevant properties.

(c) Composition uncertainty might also be called *data uncertainty*, since it exists to some degree in virtually any process used to collect data. However, the main type of data to be used in HLW vitrification process/product control will be compositional data, so the more specific term is used here. This term should be understood to include uncertainties in other types of data (e.g., tank level measurements) employed in HLW vitrification process/product control.

- Batch-to-batch variability -- Heterogeneity between process batches made from the same waste type and frit. This type of heterogeneity might also be called between-batch variability or within-waste type variability.

- Within-batch uncertainty -- A combination of heterogeneity within a single process batch and any imperfections in the sampling process. This type of uncertainty might also be called sampling uncertainty.

- Analytical uncertainty -- A combination of heterogeneity within a sample, variability induced during sample preparation, and any imperfections in the analytical process.

Model uncertainty derives from the use of empirical models to calculate batch and glass properties. This uncertainty must be taken into account when estimating and checking modelled properties. Estimating this type of uncertainty is another objective of the CVS and therefore is not discussed in this document.

The main focus of this document is checking and demonstrating compliance of glass produced by the HLW vitrification process with the WAPS 1.3 specification. Some methods and issues dealt with in this document are similar to those treated in two documents developed for the West Valley Demonstration Project (WVDP): Anderson, Eggett, and Piepel (1992), and Eggett and Piepel (1991). The major topics covered by this document are

- types of statistical intervals and their use in demonstrating compliance with specifications (Section 2);

- interpretation of the WAPS 1.3 specification (Section 3);

- methods for checking and documenting compliance with WAPS 1.3 (Section 4); and

- related work and issues (Section 5).

Appendix A presents the statistical background and notation used in this document. Appendix B establishes the relationship between the noncentral t-distribution and statistical multipliers required for constructing tolerance limits. Appendix C contains a computer program that calculates best tolerance limits and related statistical characteristics. Appendix D discusses estimating and manipulating components of uncertainty for the HLW vitrification process.

2.0 STATISTICAL INTERVALS AND HYPOTHESIS TESTING

The HLW vitrification process/product control system will use statistical tests to verify compliance with various requirements. The statistical tests to be used by this system are intimately linked with statistical *intervals*. In this section, two types of statistical intervals are discussed, as are the general principles underlying the applicability of each interval type to the requirements imposed on HLW vitrification material.

A statistical interval is, roughly, a range of values in which an unknown true value is believed (or expected) to lie. The interval is defined by a lower bound (or limit), an upper bound, or both. A *two-sided* statistical interval has both a lower bound and an upper bound. A *lower one-sided* interval has only a lower bound, and no statement is made about an upper bound, while an *upper one-sided* interval has only an upper bound, and no statement is made about a lower bound. The bounds themselves are often referred to as two-sided or one-sided. The specifications imposed by WAPS 1.3 on HLW vitrification material are such that only upper one-sided intervals are required. Since an upper one-sided interval is characterized by the associated upper bound, much of the discussion below refers directly to the upper bound.

Associated with each type of interval discussed here is a quantity known as the statistical *confidence*. Confidence is a measure of the success rate of the procedure by which a statistical interval is constructed, i.e., how often the procedure produces an interval that actually traps the true value. Confidence is expressed as either a probability (between zero and one) or a percentage. For example, the procedure to produce a 95% confidence bound has a 95% chance of producing a bound that traps the unknown true value. Technically, the confidence actually rests in the *procedure* used to construct the bound or interval, *not* in the bound or interval itself. Confidence refers to the long-run performance of the procedure, not the performance of any particular calculated interval. As used in HLW vitrification process/product control, confidence controls the probability of concluding that a particular requirement or specification is met when in fact it is violated.

2.1 CONFIDENCE AND TOLERANCE INTERVALS

A *confidence interval*[a] is designed to trap a single fixed true value (most often a population parameter) with specified confidence. For example, a 95% confidence interval for the mean of a population is designed to trap the mean of the population with 95% confidence. An upper confidence limit (UCL) is of the form:

$$UCL \equiv \bar{y} + t_{\nu,\gamma} s/\sqrt{n}\,, \tag{1}$$

where $\bar{y}$ denotes the sample mean, s denotes the sample standard deviation, n denotes the sample size (number of observations) upon which the estimated mean is based, ν denotes the degrees of freedom[b] associated with the estimated standard deviation, γ denotes the confidence associated with the UCL, and $t_{\nu,\gamma}$ denotes the 100γ-th percentile of the central t-distribution.[c] This $t_{\nu,\gamma}$ is an example of a *statistical multiplier*. Such multipliers appear in many statistical calculations and are chosen to reflect and/or compensate for uncertainties in estimated quantities that appear in the calculation.

A *tolerance interval* is designed to capture, with specified confidence, a predefined proportion of the statistical distribution associated with some population.[d] For example, consider testing whether a given proportion of process batches have attribute values below a maximum allowable value. In this application, individual batch attribute values are thought of

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(a) This name, though endowed on the procedure by its creator, is unfortunate, in that it results in a confusing dual usage of the word "confidence." As stated above, some level of statistical confidence is associated with each type of statistical interval discussed here. The distinctions among the interval types lies in the nature of the unknown quantities they are designed to trap.

(b) If the standard deviation s is estimated from a random sample of size n from a normal population with a single source of variation, $\nu = n-1$.

(c) More information on statistical concepts and notation appears in Appendix A.

(d) A tolerance interval can also be thought of as a confidence interval for lower and/or upper percentiles of the underlying statistical distribution, but this interpretation is not discussed further here.

as arising at random from an underlying population (the population of all batches that could have been made from this waste type). A tolerance interval can be used to check whether the desired proportion of this underlying population does fall below the maximum allowable value.

The proportion of the population to be captured is termed the *content* of the tolerance interval. Two percentages (or probabilities) are usually used to specify a tolerance interval -- the first percentage specifies the confidence associated with the tolerance interval; the second specifies the content of the tolerance interval. For example, a 95%/99% tolerance interval is one designed to capture 99% of the underlying population with 95% confidence.

An upper tolerance limit (UTL) is of the form:

$$UTL = \bar{y} + k_{n,\nu,\gamma,p}\, s, \tag{2}$$

where ν denotes the degrees of freedom associated with the estimated standard deviation (s), γ and p denote the confidence and content (respectively) associated with the UTL, and $k_{n,\nu,\gamma,p}$ is the statistical multiplier required to construct the tolerance limit.[a]

The simple forms of Equations (1) and (2) (and the statistical multipliers therein) rest on the assumption that the sample mean ($\bar{y}$) and standard deviation (s) are derived from the same data set, one assumed to be adequately modelled as a simple random sample of size n from a normal population subject to a single source of uncertainty.[b] Several complications will arise in applying these methods to HLW vitrification process/product control.

Data collected as part of HLW vitrification process/product control will be subject to several sources of uncertainty (e.g., batch-to-batch, within-batch, analytical, and model uncertainties). As discussed in Section 4 and Appendix D, these sources of uncertainty and the associated degrees of freedom must be properly combined to estimate the standard

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(a) The value of $k_{n,\nu,\gamma,p}$ can be obtained from the noncentral t-distribution; this relationship is detailed in Appendix B.

(b) This simple case of estimating the population mean and uncertainty (standard deviation) is treated in Appendix A.

deviation (s) and degrees of freedom (ν) used to construct the UCL and/or UTL. Also, the UCL and UTL are affected by the sample size (n) associated with the particular mean ($\bar{y}$) under consideration. In the case of data subject to several sources of uncertainty, the simple relationship between the degrees of freedom associated with the uncertainty estimate and the sample size associated with the mean (i.e., $\nu = n-1$) may break down. This relationship may also break down when uncertainty estimation takes advantage of data not used in estimating the mean.[a] This issue is addressed in Appendix D.

Although compositional data cannot be strictly normally distributed, statistical theory suggests that functions of such data (such as the CVS models used to predict various melt/glass properties) should be more closely approximated by normal distributions than are the underlying compositions, and that, *a fortiori*, means of such functions should be even more closely approximated by normal distributions. Preliminary Monte Carlo investigations bear out the suggestion that statistical methods based on the assumption of normality will perform quite well in HLW vitrification process/product control. When data become available for the HLW vitrification process, this issue should be revisited.

2.2 APPLICATION OF STATISTICAL INTERVALS TO ACCEPTANCE TESTING

Given the inevitable uncertainties in process measurements, models, and other elements of the HLW vitrification process/product control system, statistical acceptance testing must be used to verify compliance of HLW vitrification material with requirements or specifications. Confidence and tolerance intervals (and the associated bounds or limits) can be used in acceptance testing, as follows. Suppose that an attribute, Y, of a population (e.g., a single process batch, or a group of batches from a single waste type) is required to be less than some maximum acceptable value, U, and that n measurements or observations, y_i, $i = 1, ...,n$, are available from this population. From these data, $\bar{y}$ and s can be used to construct either the UCL for the mean or the UTL for some proportion of the distribution of

(a) This would be the case if, for example, uncertainty estimates used for statistical inference on the current process batch took into account data on previous batches or on vitrification operations at another site (e.g., the DWPF at Savannah River).

Y. If the UCL or UTL is less than U, the population is deemed acceptable; otherwise, the population is deemed unacceptable.

The choice between using the UCL or the UTL in the acceptance test depends on the form of the specification and on knowledge or assumptions about the uncertainties associated with the data. The UCL is appropriate if there is a single, fixed true value of Y in the population and all (or most) of the uncertainty in the observed values is extrinsic (i.e., induced in the sampling and analysis process). The UTL is appropriate if there is intrinsic variability in Y, i.e., if the true value of Y varies in the population.

3.0 THE WAPS 1.3 SPECIFICATION

The WAPS 1.3 specification that appears in USDOE (1993) is:[a]

"1.3 SPECIFICATION FOR PRODUCT CONSISTENCY

The producer shall demonstrate control of waste form production by comparing, either directly or indirectly, production samples to the Environmental Assessment (EA) benchmark glass [2]. The producer shall describe the method for demonstrating compliance in the WCP and shall provide verification in the Production Records. The producer shall demonstrate the ability to comply with the specification in the WQR.

1.3.1 Acceptance Criterion

The consistency of the waste form shall be demonstrated using the Product Consistency Test (PCT) [3]. For acceptance, the mean concentrations of lithium, sodium and boron in the leachate, after normalizing for the concentrations in the glass, shall each be less that those of the benchmark glass described in the Environmental Assessment for selection of the DWPF waste form [4]. The measured or projected mean PCT results for lithium, sodium and boron shall be provided in the Production Records. The producer shall define the statistical significance of the reported data in the WQR. One acceptable method of demonstrating that the acceptance criterion is met, would be to ensure that the mean PCT results for each waste type are at least two standard deviations below the mean PCT results of the EA glass.

1.3.2 Method of Compliance

The capability of the waste form to meet this specification shall be derived from production glass samples and/or process control information.

Production Records shall contain data derived from production samples, or process control information used for verification, separately or in combination. When using process control information to project PCT results, the producer shall demonstrate in the WQR that the method used will provide information equivalent to the testing of samples of actual production glass."

(a) In the quoted text, WCP refers to the Waste Form Compliance Plan; WQR refers to the Waste Form Qualification Report; and References [2], [3], and [4] are USDOE (1982), Jantzen (1992b), and Jantzen (1992a), respectively.

The Product Consistency Test (PCT, Jantzen 1992b) measures the quantities of elements leached from ground glass in deionized water. WAPS 1.3 requires that "the mean concentrations of lithium, sodium and boron in the leachate ... shall each be less than those of the" Environmental Assessment (EA) benchmark glass, described in Jantzen (1992a). Note that WAPS 1.3 does not explicitly state upper limits on PCT results. Limits based on PCT testing of the EA glass by the Savannah River Technology Center (WSRC 1993) appear in Table 1.

The HLW process/product control strategy will treat lithium, sodium, and boron separately; i.e., WAPS 1.3 will be interpreted as establishing three separate requirements on HLW vitrification material. In addition, it is envisioned that these limits will be applied to lithium, sodium, and boron PCT releases as calculated both from models for quenched glass and from models for canister centerline cooled glass. Therefore, WAPS 1.3 requirements will be applied to six glass properties.

Table 1. WAPS 1.3 Requirements for Lithium, Sodium, and Boron

Property	Maximum Allowable Value[a]
PCT for Li	4.8 g/m^2
PCT for Na	6.6 g/m^2
PCT for B	8.2 g/m^2

(a) WAPS does not explicitly specify limits. These limits are based on PCT testing of the EA glass by the Savannah River Technology Center (WSRC 1993).

WAPS 1.3 allows either direct or indirect comparison with the EA benchmark glass, using information from "production glass samples and/or process control information."[(a)] The HLW process/product control system will employ an indirect method of comparison (via empirical models developed from the CVS database), using process control information (feed composition), for demonstrating compliance with WAPS 1.3. This implies that the statistical comparisons must take into account both composition uncertainty and model uncertainty.

The current version of WAPS 1.3 gives an example of "one acceptable method" of demonstrating compliance: "ensur[ing] that the mean PCT results for each waste type are at least two standard deviations below the mean PCT results of the EA glass." The basis and justification for this suggested method are questionable (as discussed below), but the method itself and consideration of its shortcomings give some guidance useful in developing a compliance strategy based on sound statistical principles. For example, the suggested method implies that the "mean PCT results" to be used in demonstrating compliance are means *taken over a given waste type.* On the other hand, the standard deviation to be used in the suggested method could reasonably be interpreted either as the standard deviation associated with the underlying data (resulting in a compliance strategy based on tolerance intervals) or as the standard deviation *of the mean* (resulting in a compliance strategy based on confidence intervals). In addition, data from the HLW vitrification process are subject to several sources of uncertainty. The suggested method gives no guidance on which sources of uncertainty should be included in the standard deviation. There are other ambiguities in the suggested method and other parts of the current WAPS 1.3 specification. These ambiguities must be examined and resolved in order to develop a well-founded compliance strategy.

Examining the motivation for the suggested method may provide some guidance for formulating a compliance strategy. Perhaps the suggestion is based on the fact that the two-sided interval $\mu \pm 2\sigma = (\mu-2\sigma, \mu+2\sigma)$ contains just over 95% of a normal distribution with

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(a) WAPS 1.3 also requires demonstration of the equivalence of a method based on process control information (e.g., feed composition) to one based on testing of samples of actual production glass. Model validation and verification performed as part of the CVS work will serve to meet this requirement.

(true) mean μ and (true) variance σ^2. This suggests that the authors of the current WAPS 1.3 specification had 95% in mind for some characteristic of the statistical procedure. However, there are at least two problems with this motivation (and with the suggested method itself):

- The true mean and standard deviation of each glass property will be unknown and must be estimated with the data-based quantities, $\overline{y}$ and s. The interval $\overline{y} \pm 2s = (\overline{y}-2s, \overline{y}+2s)$ is the data-based analogue of $\mu \pm 2\sigma$. This data-based interval resembles a two-sided tolerance interval, with $k_{n,\nu,\gamma,p}$ replaced by the constant 2. The confidence and content of such an interval are functions of the sample size; for small samples, at least one of these two characteristics will be quite low.[a] A well-founded compliance strategy should establish some minimum confidence and content for all sample sizes, which requires retaining control of the statistical multiplier used to construct the interval.

- Since WAPS 1.3 implies a maximum allowable value, but *not* a minimum value, for each property, two-sided intervals like $(\overline{y}-2s, \overline{y}+2s)$ are inappropriate. As discussed in Section 2, an upper one-sided interval (or the associated upper limit) is appropriate in this situation.

Finally, the statement that "the producer shall define the statistical significance of the reported data" is confusing -- "statistical significance" is usually associated with a decision or result based on a statistical procedure, *not* with the data used in the procedure. (A given set of data can usually be used in several different statistical procedures to address several different questions, so the "significance" of data is not uniquely defined.) The "significance" of a statistical result is (roughly) a measure of the quality of the result. Even this rather loose definition of "statistical significance" leads to problems interpreting WAPS 1.3. The current text requires only reporting of the statistical significance; therefore, simply reporting a decision and the associated significance level would satisfy this portion of the specification, *even if the significance level indicates that the decision is unsupported by the data.* A better approach to controlling the quality of the statistical result is to control the quality of the

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(a) It should also be noted that using a fixed statistical multiplier (e.g., 2) effectively penalizes large samples -- either the confidence or the content (or both) associated with a fixed statistical multiplier is greater for large samples than for small samples. Therefore, using a fixed statistical multiplier in acceptance testing essentially requires higher confidence and/or content for larger sample sizes.

statistical procedure, by requiring demonstration of compliance at some minimum confidence level (e.g., 95%).

A well-founded statistical approach to demonstrating compliance with WAPS 1.3 must address all the issues discussed above. The Hanford HLW vitrification process/product control system will demonstrate with at least 95% confidence that lithium, sodium, and boron releases are below the corresponding maximum allowable values. The PCT releases will be calculated from measured feed composition, using the CVS models. Compliance will be demonstrated in two ways: 1) for each individual process batch, and 2) over all batches in a waste type. For each process batch, 95% UCLs will be used to compare the calculated releases to the maximum allowable values. For all batches in a given waste type, 95%/95% UTLs will be used to compare the calculated releases to the maximum allowable values. The details of constructing these UCLs and UTLs, including proper estimation of the associated uncertainties, are given in Section 4 and Appendix D.

4.0 VERIFYING COMPLIANCE WITH THE WAPS 1.3 SPECIFICATION

The HLW vitrification process/product control system will employ a dual strategy for verifying compliance with the WAPS 1.3 specification. Compliance will be verified for each process batch individually (the single-batch approach), and it will be verified over all process batches in a given waste type (the multiple-batch approach). This dual strategy for checking WAPS 1.3 requirements adds conservatism and allows checking of WAPS 1.3 properties both during and after processing of a waste type. The general mechanics of these two types of compliance checks are similar; the similarities are discussed in Section 4.1. The specifics of the single-batch approach are discussed in Section 4.2, and the specifics of the multiple-batch approach are discussed in Section 4.3. Applying the multiple-batch check for each process batch (in addition to its application after processing of all batches in a waste type) is discussed in Section 4.4. Best tolerance limits and associated statistical characteristics are discussed in Section 4.5. Technical details and justifications for much of what appears in Section 4 are given in Appendix D.

As discussed in Section 3, each type of compliance check will be applied separately to six different PCT releases (PCT release for lithium, sodium, and boron, using CVS models for both quenched glass and canister centerline cooled glass). In order to simplify the discussion below, reference is made only to a single type of PCT release; it should be understood that this discussion applies to each of the six different types of PCT release.

As noted in Section 1, the CVS PCT models actually predict the natural logarithm of PCT [ln(PCT)], rather than raw PCT values. This presents no difficulty for the WAPS 1.3 compliance strategy. The means, uncertainties, confidence limits, and tolerance limits will be estimated for ln(PCT). Once the UCLs and UTLs have been produced, either 1) the UCLs and UTLs will be compared to the natural logarithm of the maximum allowable values, or 2) the UCLs and UTLs will be transformed to the original PCT scale (by exponentiation) before comparison with the maximum allowable values. This minor complication is ignored below. References to PCT values (units, etc.) estimated from CVS models should be understood to be ln(PCT) values (units, etc.).

The model and underlying assumptions to be used for HLW vitrification process/product control are as follows. Y_{ijk} represents the (natural logarithm of) PCT value estimated from the k-th analysis of the j-th sample from the i-th batch. Y_{ijk} is subject to model uncertainty and to three sources of composition uncertainty (batch-to-batch variability, within-batch uncertainty, and analytical uncertainty). Model uncertainty will be estimated separately and then combined with composition uncertainty, as discussed in Sections 4.2, 4.3, D.5, and D.6. Composition uncertainty (and its components) will be estimated using the following model:

$$Y_{ijk} = \mu + \beta_i + \omega_{ij} + \alpha_{ijk} , \qquad (3)$$

where $\beta_i \sim (0,\sigma_\beta^2)$, $\omega_{ij} \sim (0,\sigma_\omega^2)$, $\alpha_{ijk} \sim (0,\sigma_\alpha^2)$, and all the random variables are uncorrelated. In this model, σ_β^2 represents batch-to-batch variability, σ_ω^2 represents within-batch uncertainty, and σ_α^2 represents analytical uncertainty.[a] In addition, b denotes the number of batches in a single waste type, w_i denotes the number of samples taken from the i-th batch,[b] and a_{ij} denotes the number of analyses performed on the j-th sample from the i-th batch. If $w_i = w$ for all i, and $a_{ij} = a$ for all i and j, the data are said to be *balanced*. Otherwise, the data are said to be *unbalanced*. The discussion below focuses on the case of balanced data; extensions to unbalanced data are discussed in Appendix D. General statistical concepts and notation are covered in Appendix A.

(a) The β_i, ω_{ij}, and α_{ijk} are known as *random effects*. The quantities σ_β^2, σ_ω^2, and σ_α^2 (and estimates of these quantities) are known as *variance components* (or *components of variance*).

(b) It may seem more intuitive to use s_i for the number of samples taken from the i-th batch. However, the letter s (and subscripted versions thereof) is reserved in this document for denoting a standard deviation. Therefore, w_i is used to denote the number of samples within a batch.

4.1 GENERAL PROCEDURE FOR CHECKING WAPS 1.3 COMPLIANCE

For both the single-batch approach and the multiple-batch approach, the general procedure for checking compliance with the WAPS 1.3 requirement consists of six steps:

1) Estimate the mean PCT release.

2) Estimate (univariate) composition uncertainty.

3) Combine estimated composition uncertainty with any prior information.

4) Estimate model uncertainty.

5) Combine composition and model uncertainties and estimate the associated strength of belief (degrees of freedom).

6) Use the mean PCT value and the combined uncertainty estimate to carry out the statistical test, e.g., by constructing either the UCL or the UTL and comparing it to the specified limit.

The specific forms of the means and uncertainties depend upon the type of compliance check (single-batch or multiple-batch). These forms and other specific aspects of the statistical procedures are discussed in Sections 4.2, 4.3, D.2, and D.3. The more general aspects of each of these steps are discussed below.

Two types of means are of interest in HLW vitrification process/product control: 1) the batch mean, for checking WAPS 1.3 compliance on a single-batch basis, and 2) the multiple-batch mean, for checking WAPS 1.3 compliance on a multiple-batch basis. Since PCT results will be predicted from composition data using CVS models, two methods are available for calculating these means: 1) by using the CVS model to predict mean PCT from the mean of the observed compositions (the "estimate-transform" method), and 2) by using the CVS model to predict a PCT result for each observed composition and then calculating the mean of these predicted PCT results (the "transform-estimate" method). In the latter method, the problem is first transformed from multivariate composition space into univariate property (PCT) space, and estimation takes place in the univariate space.

At this time, there is no compelling reason to favor one method over the other. (In fact, for a first-order PCT model, the two methods should yield identical results.) Since the notation attending the "transform-estimate" method is somewhat simpler (in that it avoids the complexities of multivariate data), and since the transformation from multivariate composition space to univariate property space is used below in uncertainty estimation, the "transform-estimate" method is assumed here. Note however that batch mean compositions are required in propagation of model uncertainty (as described in Sections 4.2 and 4.3). These mean compositions are not routinely computed in the "transform-estimate" method.

Since inference is to be carried out for both batch mean PCT and multiple-batch mean PCT, an uncertainty estimate is required for each of these means. Just as for estimating the means, there are two options for calculating these uncertainty estimates: 1) perform (multivariate) uncertainty estimation in composition space and then propagate these results into univariate property (PCT) units (the "estimate-transform" method), and 2) transform multivariate compositions into univariate PCT results (using a CVS model) and then perform univariate uncertainty estimation (the "transform-estimate" method). Again, there is at this time no compelling reason to choose between these two options. The relative statistical optimality properties are unknown. Another basis for choosing between the two is the relative computational burden. Roughly, the "transform-estimate" method is likely to be more efficient unless the number of the number of properties to be examined is much greater than the number of oxides in each composition.[a] Since the number of properties involved in HLW vitrification process/product control is roughly equal to the number of oxides in each composition, the "transform-estimate" method is assumed here.

(a) The "estimate-transform" method requires calculating multivariate uncertainties for compositions. The "transform-estimate" method requires calculating univariate uncertainties for each property. The number of quantities in a multivariate uncertainty estimate (covariance matrix) increases as the square of the number of elements in the data vector (e.g., the number of oxides in each composition). Therefore, the "transform-estimate" probably enjoys a computational advantage unless the number of properties is much larger than the number of oxides in each composition.

For HLW vitrification process/product control, composition uncertainties will be estimated from an accumulating database of results for the current waste type. It is anticipated that ANOVA estimation methods (Section D.4) will be employed to yield estimates of variance components. If necessary, these variance components will be combined to yield estimates of the contribution of composition uncertainty to overall uncertainty in batch and multiple-batch means. The strength of belief in these combined estimates of uncertainty will be quantified by the associated degrees of freedom, calculated using the Satterthwaite approximation (Section D.6).

It may be necessary or advantageous to combine uncertainty estimates derived directly from HLW vitrification data with information on composition uncertainty derived from other sources (e.g., from DWPF or WVDP operations). If the external information is not in a form suitable for the type of uncertainty estimation used for HLW vitrification data (i.e., ANOVA estimation), it will be necessary to employ some method of updating the external sources of information with the information contained in HLW vitrification data. This topic is addressed in Section D.7.

CVS will provide estimated model uncertainties in the form of a covariance matrix for the estimated parameters of each model. These multivariate uncertainty estimates must be propagated through the CVS model to provide a univariate estimate of the contribution of model uncertainty to overall uncertainty in the predicted PCT result. Propagating multivariate uncertainties is covered in Section D.5.

Finally, composition and model uncertainties (in PCT units) must be combined to yield an overall estimate of uncertainty. The strength of belief in this overall uncertainty estimate will be quantified by the associated degrees of freedom, calculated using the Satterthwaite approximation (Section D.6). This overall uncertainty estimate will be used to construct statistical limits and to conduct the compliance checks, as described in Sections 4.2 and 4.3.

4.2 VERIFYING WAPS 1.3 COMPLIANCE FOR A SINGLE PROCESS BATCH

Verifying compliance with the WAPS 1.3 maximum allowable PCT release for a single process batch is an example of checking a single-batch requirement for a modelled property. The procedure assumes that most or all of the uncertainty in feed composition for a single process batch is the result of nuisance uncertainties (i.e., random errors in the sampling and analytical processes). In this case, a single fixed true feed composition, and therefore a single fixed true PCT release (for each element), exist for each process batch. As discussed in Section 2, when inference is required for a single fixed true quantity, an UCL for this quantity (PCT release) is appropriate. A modified version of Equation (1) of Section 2.1 will be used to calculate this UCL:

$$UCL = \overline{Y}_{i\cdot\cdot} + t_{\nu,0.95}\, s_{cs}/\sqrt{w}\ , \qquad (4)$$

where $\overline{Y}_{i\cdot\cdot}$ is the batch mean (defined and discussed in Section D.2), s_{cs} is an estimate of combined uncertainty in the within-sample means upon which the batch mean is based, w is the number of samples taken from the i-th batch, $t_{\nu,0.95}$ is the 95-th percentile of the central t-distribution with ν degrees of freedom, and ν represents the degrees of freedom associated with the estimate of combined uncertainty in the within-sample means.

Calculation of s_{cs} and ν is outlined in Section 4.1, and the technical details and procedures are discussed in Appendix D. Briefly, the combined uncertainty estimate will include any available prior information and analytical, within-batch, and model uncertainties.[a] The analytical and within-batch uncertainties (and the appropriate combination thereof) will be estimated (as discussed in Section D.4) from a database of PCT results for all batches processed using the same sampling and analysis procedures.[b] Model

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(a) It is possible, and may be desirable, to eliminate nuisance uncertainties from the statistical comparison. Elimination of nuisance uncertainties and the effects on the precision and confidence of the procedure are discussed in Section 5.

(b) In order to maintain consistency with the procedure used to estimate uncertainty associated with multiple-batch means, this database may be restricted to include only batches from the same waste type as the current batch.

uncertainty will be calculated by propagating the batch mean composition through the CVS model (Section D.5). The Satterthwaite approximation (Section D.6) will be used to estimate ν. If uncertainty information is available from processes other than the Hanford HLW vitrification process (e.g., DWPF or WVDP), the methods of Section D.7 will be used to combine this information with that available from the Hanford HLW vitrification process.

4.3 VERIFYING WAPS 1.3 COMPLIANCE OVER AN ENTIRE WASTE TYPE

Verifying compliance with the WAPS 1.3 maximum allowable PCT release over a group of process batches (e.g., over an entire waste type) is an example of checking a multiple-batch requirement for a modelled property. The procedure assumes that much of the uncertainty in feed composition between batches derives from true variability in the process (as opposed to the nuisance uncertainties introduced by random errors in the sampling and analytical processes). In this case, the quantity of interest (true PCT release in each process batch) is a random variable, and interest lies in demonstrating with high confidence that a large proportion of the population (i.e., of the statistical distribution associated with this random variable) falls below the maximum allowable value. As discussed in Section 2, when inference is required for a proportion of a population, an UTL for the random quantity (PCT release) is appropriate. A modified version of Equation (2) of Section 2.1 will be used to calculate this UTL:

$$UTL = \bar{Y}_{..} + k_{b,\nu,0.95,0.95}\, s_{cb}, \tag{5}$$

where $\bar{Y}_{..}$ is the multiple-batch mean (defined and discussed in Section D.3), s_{cb} is an estimate of combined uncertainty in the batch means upon which the multiple-batch mean is based, $k_{b,\nu,0.95,0.95}$ is the statistical multiplier required for construction of 95%/95% tolerance limit, b is the number of batches processed to date from the current waste type, and ν represents the degrees of freedom associated with the estimate of combined uncertainty in the batch means.

Calculation of s_{cb} and ν is outlined in Section 4.1, and the technical details and procedures are discussed in Appendix D. Briefly, the combined uncertainty estimate will

include composition uncertainties,[a] model uncertainty, and any available prior information. The composition uncertainties will be estimated (as discussed in Section D.4) from a database of PCT results for all batches processed to date from the current waste type.[b] Model uncertainty will be calculated by propagating each batch mean composition through the CVS model (Section D.5) and calculating an average model uncertainty for this group of process batches.[c] The Satterthwaite approximation (Section D.6) will be used to estimate ν. If uncertainty information is available from processes other than the Hanford HLW vitrification process (e.g., DWPF or WVDP), the methods of Section D.7 will be used to combine this information with that available from the Hanford HLW vitrification process.

4.4 APPLYING WAPS 1.3 TO INTERMEDIATE BATCHES

True feed composition will vary somewhat among batches in the same waste type, and therefore true PCT values will also vary. This variability (σ_β^2) must be controlled in order to preclude its growing large enough to weaken the ability to statistically demonstrate compliance over the entire waste type. Therefore, the multiple-batch WAPS 1.3 compliance check will be applied to each intermediate batch in a given waste type, as well as after processing of all batches in the waste type. Specifically, a running UTL will be calculated

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(a) The proper estimate of composition uncertainty to be used in constructing an UTL for batch means may require more investigation. The estimate recommended in Sections D.3 and D.4 includes analytical and sampling uncertainties, which, in this context, could be considered nuisance uncertainties. As discussed in Section 5, it is possible, and may be desirable, to eliminate nuisance uncertainties from the statistical comparison.

(b) In order to maintain consistency with the procedure used to estimate uncertainty associated with batch means, this database may be restricted to include only batches subject to the same sampling and analytical procedures as the current batch.

(c) An alternative would be to calculate the model uncertainty associated with the mean feed composition over all the process batches in the current group. This alternative was rejected because model uncertainty is a function of batch composition. Under the model given in Equation (3), the true batch compositions vary. Therefore, both the true PCT results and the model uncertainties associated with the calculated PCT results also vary.

for each batch, as follows. A record will be kept of the calculated PCT value, the estimated model uncertainty, and the feed composition for each process batch in the waste type. The calculated values for the current batch will be temporarily added to the database and used to compute a running mean and standard deviation for this property to date; these running estimates will be used to construct an UTL and to carry out a WAPS 1.3 compliance test as if the current batch were the last batch in the waste type. If compliance is verified, the current batch will be deemed acceptable with respect to this requirement. If the batch is deemed acceptable with respect to all other attributes as well, the data for this batch will be added permanently to the database for this waste type.

This procedure runs a slight risk that a few aberrant batches at the beginning of processing of a waste type might skew the results for the rest of the waste type. If this appears to be a problem in testing of the HLW vitrification process/product control system or during plant operations, there are several possible solutions. Stricter requirements might be imposed on the first batches in a waste type, process monitoring algorithms might be designed to scrutinize these batches, and/or a prior estimate of uncertainty might be included in the estimation of overall uncertainty. For example, it is anticipated that data from the DWPF at the Savannah River Site will be used to supply initial uncertainty estimates.

4.5 THE BEST CONFIDENCE/CONTENT APPROACH

The WAPS 1.3 compliance strategy to be used by the HLW vitrification process/product control system will require demonstration of compliance at the 95% confidence level, both for single-batch and multiple-batch testing. Multiple-batch testing will employ UTLs; the content associated with the UTLs used to demonstrate compliance with WAPS 1.3 will be set at 95%.[a] However, it may be possible to demonstrate compliance at

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(a) The statistical multiplier ($k_{n,v,\gamma,p}$) used to construct a 95%/95% UTL is greater than 2 unless the degrees of freedom associated with the estimated standard deviation exceed 65. It is expected that, in many cases, the degrees of freedom associated with the estimated standard deviation will be less than 65, so the requirement of 95% confidence and 95% content will be more conservative than the method suggested in the WAPS 1.3 specification.

a higher confidence and/or content level. If so, the higher confidence/content should also be reported. This is called the *best confidence/content approach*; and the associated tolerance intervals and limits are called *best tolerance intervals and limits*. Methods for implementing this approach are discussed below.

Both UCLs and UTLs are of the form[a]

$$\textit{Upper statistical limit} = \bar{y} + cs, \tag{6}$$

where for an UCL

$$c = \frac{t_{\nu,\gamma}}{\sqrt{n}} \tag{7}$$

and for an UTL

$$c = k_{n,\nu,\gamma,p}. \tag{8}$$

Once $\bar{y}$, s, and the associated degrees of freedom and sample size are known, the maximum allowable value of c can be calculated:

$$c_{max} = \frac{U - \bar{y}}{s}, \tag{9}$$

where U represents the maximum allowable PCT value (from Table 1). For an UCL, the confidence (γ_{max}) corresponding to c_{max} will be calculated and reported. For an UTL, the situation is somewhat more complicated, since either confidence (γ) or content (p) (or both) could be increased to yield c_{max}. The HLW vitrification process/product control system will calculate three quantities:

(a) For simplicity of presentation, the simple case (mean and standard deviation estimated from the same data, a simple random sample of size n from a population with a single source of variation, so that $\nu = n-1$) is assumed. More complicated cases are discussed in Sections 4.2 and 4.3 and Appendix D.

- γ_{max}, the highest confidence level corresponding to the nominal (95%) content; i.e., γ_{max} such that the $100\gamma_{max}$%/95% UTL is equal to U;

- p_{max}, the highest content corresponding to the nominal (95%) confidence level; i.e., p_{max} such that the 95%/$100p_{max}$% UTL is equal to U; and

- π_{max}, the confidence and content such that: 1) confidence and content are equal, and 2) the corresponding UTL is equal to U; i.e., π_{max} such that the $100\pi_{max}$%$100\pi_{max}$% UTL is equal to U.

Methods for calculating these quantities are discussed in Appendix B. A computer program for calculating these quantities appears in Appendix C.

5.0 RELATED WORK AND ISSUES

Several issues related to demonstrating WAPS 1.3 compliance may need to be revisited when more is known about the Hanford HLW vitrification process. These issues are discussed in various sections of this document. For ease of reference, these issues are recapitulated below. In addition, several topics related to demonstrating compliance with WAPS 1.3 in the WVDP are discussed by Anderson, Eggett, and Piepel (1992) and Eggett and Piepel (1991). Some of the issues discussed in those two documents are not relevant to the Hanford HLW vitrification process (e.g., the WAPS 1.3 specification has been changed since that work was done), but other issues deserve comment here.

More attention may need to be given to the types of uncertainty included in standard deviation estimates used to demonstrate compliance with WAPS 1.3. Some of the main types of uncertainty relevant to HLW vitrification process/product control (e.g., within-batch uncertainty and analytical uncertainty) include uncertainties that are induced by the sampling and measurement processes. When present, these nuisance uncertainties can inflate estimated uncertainties and can decrease the precision of statistical comparisons. As mentioned in Section 4, it may be possible to isolate and remove nuisance uncertainties from some statistical comparisons. Methods for removing nuisance uncertainties are presented by Eggett and Piepel (1991), Hahn (1982), Jaech (1984), Mee (1984), and Mulrow et al. (1988). Currently, removal of nuisance uncertainties is not recommended for HLW vitrification process/product control, for a variety of reasons:

- Obtaining estimates of nuisance uncertainties could significantly expand the required sampling and analytical data and/or effort. The availability of such data and the feasibility of this expanded effort are not yet known.

- Preliminary investigations by Eggett and Piepel (1991) indicate that "subtracting the estimable sources of nuisance uncertainty ... had minimal effect on the size of the tolerance intervals." Thus, the potential benefit of removing nuisance uncertainties may not outweigh the increased costs.

- Removing nuisance uncertainties can adversely affect the performance of the statistical procedures. Jaech (1984) demonstrates that the actual confidence and content of a 95%/95% tolerance interval can be less than the nominal values if

nuisance uncertainties are removed. The decrease in actual confidence and content can be considerable if nuisance uncertainties are large (relative to true process variability). Unfortunately, this is precisely the case in which it would seem most desirable to remove nuisance uncertainties. Procedures exist for evaluating and correcting the perturbations of confidence and content, but these procedures require information or assumptions that may not be available or tenable for the HLW vitrification process.

- Other methods are available for controlling nuisance uncertainties. For example, if analytical uncertainty is found to be large, consideration should be given to improving the measurement process. Also, increasing the number of samples taken from a process batch and the number of analyses run on each sample decreases the contribution of σ_ω^2 and σ_α^2 to uncertainty in the batch mean [see Equations (D.14) and (D.16)].

Although removal of nuisance uncertainties is not currently recommended, this issue should be revisited when more information is available on the HLW vitrification process or if testing of the process/product control system indicates that increased precision will be required to demonstrate WAPS 1.3 compliance.

Anderson, Eggett, and Piepel (1992) and Eggett and Piepel (1991) present numerical results concerning the ability to demonstrate WAPS 1.3 compliance under various allocations of sampling effort, assumptions about the underlying uncertainties, and forms of the statistical procedure. The data used in these investigations, and therefore the conclusions drawn, were specific to WVDP, but investigations of this type might be beneficial when adequate information is available about the Hanford HLW vitrification process.

The confidence and tolerance intervals discussed here are based on the assumption that the underlying data follow a normal (Gaussian) distribution. This assumption should be evaluated as actual process data become available. In many cases, normal-based methods are adequate for other underlying distributions. However, this should not be assumed without investigating the empirical data distribution. Procedures exist for statistical intervals for other types of data distributions and for nonparametric (distribution-free) tolerance intervals (Hahn and Meeker 1991). Nonparametric intervals require much larger sample sizes than do normal-based intervals.

Under the model used here to estimate property values and uncertainties [Equation (3) and the assumptions pertaining thereto], true property values are assumed to be independent across batches in the same waste type. It is possible that true property values may be correlated or may show trends across batches in the same waste type. If this appears to be the case in actual HLW vitrification data, the statistical methods recommended in this document must be modified.

Two methods for calculating mean property values and related uncertainties are discussed in Section 4.1. The "transform-estimate" method seems to be the more efficient of these two methods for HLW vitrification process/product control. In this method, CVS models will be used to transform individual measurements of feed composition to estimated property values, and univariate estimation of means and uncertainties will be employed separately for each property. In the alternate method, multivariate uncertainties would be estimated for feed composition, and these multivariate uncertainties would be transformed (propagated) to univariate uncertainties for each property. The relative efficiency and optimality of these two methods should be re-examined if the design and requirements of the HLW vitrification process are modified.

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APPENDIX A

STATISTICAL BACKGROUND

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STATISTICAL BACKGROUND

For precision and brevity in much of the body of this document, it is necessary to employ some statistical terminology and notation. This appendix introduces the required terminology and notation. Full exposition and explanation of this material is beyond the scope of this appendix, but can be found in most texts on probability and mathematical statistics (e.g., Lindgren 1976). This document also uses the concepts and notation of linear algebra, vectors, and matrices. Some of these concepts and notation are defined below; fuller coverage of this material can be found in books on linear algebra (e.g, Searle 1982).

Statistics is the art and science of making decisions in the face of uncertainty. Accordingly, a major task of statistics is the modelling and characterization of uncertainty. The most common statistical method of modelling uncertainty employs the concept of a *random variable.* Intuitively, a random variable is a quantity that cannot be measured exactly (either because its value is not fixed or because the measurement process is imperfect). Therefore, the behavior of a random variable is described in terms of the probability that the true value of the random variable exists in some set of possible values. Random variables are often denoted by capital letters, e.g., X, while individual values or realizations of a random variable are often denoted by lower case letters, with a subscript to indicate which observation is being represented. For example, n observations of the random variable X might be denoted x_1, x_2, ..., x_n, or, equivalently, x_i, i = 1, ..., n. A group of n observations may also be represented by a vector, $\underline{x}$.

Two basic types of random variables exist. A *discrete random variable* is one for which the number of possible values is finite or countably infinite. In many cases, discrete random variables are counts of the number of occurrences of certain events. For example, the number of defective items produced by a manufacturing process can range from zero to the number of items produced. A *continuous random variable* is one for which the number of

possible values is uncountably infinite. In many cases, continuous random variables take on values in an interval of possible values. For example, the value of many measured characteristics (length, weight, concentration, viscosity) must lie between some more or less well known lower and upper bounds, but, at least theoretically, the individual measurements may take on any value in the interval. Although many of the concepts discussed below apply to both discrete and continuous random variables, most of the quantities involved in HLW vitrification process/product control are best modelled by continuous random variables; therefore, this presentation focuses on continuous random variables.

A.1 DISTRIBUTION AND DENSITY FUNCTIONS

Two mathematical functions are useful in describing the behavior of a (continuous) random variable: the *distribution* (or distribution function), and the *density* (or density function). To each random variable X, there corresponds a distribution function, $F(x) \equiv \Pr\{X \leq x\}$,[a] the probability that the random variable X is less than or equal to the fixed value x. As a function, F(x) is monotonic and nondecreasing. Since for each fixed x, F(x) is a probability, F(x) must lie in the interval [0,1].

The density function, f(x), exists for most of the common statistical distributions. When it exists, the density function is simply the first derivative of the distribution function, i.e., $f(x) = F'(x)$. The density function characterizes the local behavior of the random variable. By its nature, $f(x) \geq 0$ for all x, and

$$\int_{-\infty}^{\infty} f(x)dx = 1. \qquad \text{(A.1)}$$

In order to achieve this unit integral, a density function incorporates a normalizing constant (usually a function of the parameters of the distribution, which are discussed below).

Many families of random variables (and the corresponding distributions and densities) have been found useful in statistical applications. For example, the most commonly

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(a) The symbol "≡" should be read as "is defined to be equal to."

encountered family of statistical distributions is the family of *normal* (or Gaussian) distributions. The density function for a normally-distributed random variable X is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2} \qquad \text{(A.2)}$$

(μ and σ^2 are the parameters of the normal distribution and are discussed further below).

Another important family of random variables is the gamma family. The density function for a random variable X that follows a gamma distribution is

$$f(x) = \frac{1}{\Gamma(\alpha)\beta^\alpha} x^{\alpha-1} e^{-x/\beta} I_{(0,\infty)}(x) \; . \qquad \text{(A.3)}$$

where α and β are the parameters of the gamma distribution (discussed below) and $I_{(0,\infty)}(x)$ is zero if $x \leq 0$ and one otherwise (indicating that a gamma random variable takes on only positive values).

The members of a family of random variables are distinguished by the values of the associated *parameters*. The parameters of a random variable appear in the density function and are often denoted by lower-case Greek letters. For example, the parameters of the normal density given above are μ and σ^2, while the parameters of the gamma density given above are α and β. Often, the dependence of the behavior of a random variable on the associated parameters is shown by a slight modification of notation: for example, the density of a random variable following a normal distribution with parameters μ and σ^2 may be denoted $f(x|\mu,\sigma^2)$, and the density of a gamma distribution with parameters α and β may be denoted $f(x|\alpha,\beta)$.

A common statistical shorthand for the phrase "the random variable X follows a normal distribution with parameters μ and σ^2" is "$X \sim N(\mu,\sigma^2)$." The shorthand for "the random variable X follows a gamma distribution with parameters α and β" is "$X \sim \Gamma(\alpha,\beta)$."

An important special case of the gamma distribution is the chi-square distribution. This distribution has a single parameter, f, known as the *degrees of freedom*. A chi-square

distribution with f degrees of freedom [$\chi^2(f)$] is simply a gamma distribution with parameters f/2 and 2, i.e., the $\Gamma(f/2,2)$ distribution.

A.2 MEAN AND VARIANCE

The *expectation* of a function, h(X), of the random variable X is defined as:

$$E(h(X)) \equiv \int_{-\infty}^{\infty} h(x)\,dF(x) = \int_{-\infty}^{\infty} h(x)f(x)\,dx \tag{A.4}$$

(the last expression makes sense only if the density function exists). Several such functions are important enough to warrant specific names. The *mean* of a random variable X is defined as:

$$\mu_X \equiv E(X) \equiv \int_{-\infty}^{\infty} x\ dF(x). \tag{A.5}$$

The mean of a random variable is a measure of the central value (or central tendency) of the random variable. The most common measures of dispersion about this central value are the *variance*:

$$\sigma_X^2 \equiv E(X-\mu_X)^2 \equiv \int_{-\infty}^{\infty} (x-\mu_X)^2\ dF(x) \tag{A.6}$$

and the closely related *standard deviation*:

$$\sigma_X \equiv \sqrt{\sigma_X^2}\ . \tag{A.7}$$

(When the meaning is clear from context, the subscripts on μ_X, σ_X^2, and σ_x may be omitted.) Due to the simple relationship between variance and standard deviation, much of the discussion (though not, of course, the equations) in this appendix could be framed in terms of either quantity, and shifts between variance and standard deviation go unremarked henceforth.

The mean and variance are examples of *moments* of a distribution. Moments are simply expectations of powers of the random variable (often centered by subtracting the

mean). The moments of a distribution convey information on the location and shape of the distribution and hence on the behavior of the random variable. The first moment of a distribution is the mean and, as mentioned above, is a measure of the central value (location) of the distribution. The second (central) moment is the variance and hence is a measure of the spread (scale) of the distribution. The third moment measures the skewness of the distribution, and the fourth moment measures kurtosis (how "heavy-tailed" and peaked the distribution is).

The moments of a distribution are not usually the parameters of the distribution. The exception is the normal distribution, for which the parameters μ and σ^2 are indeed the mean and variance, respectively. The mean and variance of many distributions are simple functions of the parameters. For example, the mean and variance of a $\Gamma(\alpha,\beta)$ distribution are $\alpha\beta$ and $\alpha\beta^2$, respectively; the mean and variance of a chi-square distribution with f degrees of freedom are f and 2f, respectively.

In some cases, it is useful to specify only the mean and variance of a random variable, without ascribing to it a distributional form (such as normal or gamma). In this case, an adaptation of the shorthand above is employed -- "$X \sim (\mu,\sigma^2)$" means that X is a random variable with mean μ and variance σ^2.

A.3 MULTIVARIATE DATA, COVARIANCE, AND CORRELATION

The discussion of random variables above concentrated on the *univariate* situation, i.e., the modelling of a single quantity (even though many measurements or observations of that quantity may be available). However, in many situations, the *simultaneous* behavior of several different quantities is of interest. This is the *multivariate* situation. The obvious example here is the composition of a vitrification process batch. For use in melt/glass property models, batch composition is usually expressed as mass fractions (proportions or percentages) of nine individual oxides (SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, Al_2O_3, ZrO_2) and a catchall tenth category, "Others." Since these mass fractions must sum to one, they are obviously not independent of one another; hence their simultaneous behavior is of interest.

In multivariate statistics, subscripts are used to distinguish between different random variables. For example, the 10 components of a vitrification process batch can be denoted by X_1, X_2, ..., X_{10}. Individual observations of a single random variable are usually indicated by a second subscript; for example, x_{ij} is the j-th observation of the i-th random variable.

Most of the standard univariate distributions and densities have multivariate generalizations. When modelling several random variables simultaneously, *joint distributions* and *joint densities*, which are functions that model the simultaneous probabilistic behavior of the variables, must be considered. In addition, when examining the effects of one variable on another, *conditional distributions* and *conditional densities*, which model the probabilistic behavior of one or more variables given the values of other variables, become important. The notation can get quite complex, so, rather than attempting a general treatment, notation is introduced below only as necessary.

In multivariate statistics, the tendency of several quantities to vary together ("co-vary") is of interest. The statistical *covariance* between two random variables X_i and X_j is defined as:

$$\sigma_{ij} \equiv E(X_i-\mu_i)(X_j-\mu_j) \ , \qquad \text{(A.8)}$$

where the expectation is taken with respect to the joint distribution of X_i and X_j (i.e., this is a double integral). Whereas the variance of a random variable must be nonnegative (by definition), the covariance between two random variables can be positive, negative, or zero. Positive covariance indicates that the two variables tend to vary together; i.e., if one is large (relative to its mean), the other tends also to be large, and if one is small, the other tends to be small. (The repetitive use of the word "tend" is necessitated by the probabilistic nature of the behavior of random variables.) Negative covariance indicates that the two variables tend to vary "in opposite directions;" i.e., if one is large (relative to its mean), the other tends to be

small (relative to its mean), and vice versa. Zero covariance indicates that the behavior of one variable does not affect the behavior of the other.[a]

Covariances are not scale-invariant, and their magnitudes are affected by the variances of the random variables involved. These characteristics complicate interpretation and comparison of covariances. Statistical *correlation* is essentially a standardized, unitless covariance. The correlation between X_i and X_j is defined as:

$$\rho_{ij} \equiv \frac{\sigma_{ij}}{\sqrt{\sigma_i^2 \sigma_j^2}} . \qquad \text{(A.9)}$$

Correlations must lie in the interval [-1,1]. Interpretation of the sign of a correlation is similar to that for a covariance. In addition, the closer the correlation is to 1 (or -1), the nearer the relationship between the two variables is to perfect linearity. The correlation between two random variables is zero if and only if the covariance between these two variables is zero. Two variables that have zero correlation (covariance) are said to be *uncorrelated*; if the correlation (covariance) is non-zero, the two variables are said to be *correlated*. Correlated observations are not independent.

Matrix notation is quite useful in multivariate statistics. In this document, matrices are denoted by upper case letters (e.g., Σ or S), and symbols for vectors are underlined (e.g., $\underline{\mu}$). The *random vector*, $\underline{X}$, is a vector of random variables, X_i, i = 1, ..., p. The associated *mean vector* (the vector of means of the individual random variables) is denoted by $\underline{\mu}$. A convenient method for summarizing the variances and pairwise covariances of the elements of the random vector $\underline{X}$ is the *variance-covariance matrix* (for brevity, called the *covariance matrix* below):

(a) This is not strictly true. Statistical covariance is actually a measure of *linear* covariance, so a strongly curved relation between two random variables is not necessarily reflected in the standard definition of covariance. It is in fact possible to construct two random variables with zero covariance, even though one is an exact function of the other.

$$\Sigma \equiv \begin{bmatrix} \sigma_1^2 & \sigma_{12} & \sigma_{13} & \cdots & \sigma_{1p} \\ \sigma_{21} & \sigma_2^2 & \sigma_{23} & \cdots & \sigma_{2p} \\ \sigma_{31} & \sigma_{32} & \sigma_3^2 & \cdots & \sigma_{3p} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \sigma_{p1} & \sigma_{p2} & \sigma_{p3} & \cdots & \sigma_p^2 \end{bmatrix}. \qquad \text{(A.10)}$$

The covariance matrix contains the variances of the individual random variables in the diagonal positions and the pairwise covariances in the off-diagonal positions. As a consequence of the definition of covariance, the covariance matrix is symmetric (i.e., $\sigma_{ij} = \sigma_{ji}$). If the underlying random vector has p elements, the covariance matrix has p rows and p columns; i.e., its dimension is $p \times p$.

Correlations can also be represented in matrix form; the *correlation matrix* is defined as:

$$P \equiv \begin{bmatrix} 1 & \rho_{12} & \rho_{13} & \cdots & \rho_{1p} \\ \rho_{21} & 1 & \rho_{23} & \cdots & \rho_{2p} \\ \rho_{31} & \rho_{32} & 1 & \cdots & \rho_{3p} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \rho_{p1} & \rho_{p2} & \rho_{p3} & \cdots & 1 \end{bmatrix}. \qquad \text{(A.11)}$$

The diagonal elements of a correlation matrix are always one (since, by definition, the correlation of a random variable with itself is one); the pairwise correlations appear in the off-diagonal positions. Like the covariance matrix, the correlation matrix is symmetric ($\rho_{ij} = \rho_{ji}$).

Multivariate generalizations of many common statistical distributions exist. The notation used to specify the (joint) distribution associated with a random vector $\underline{X}$ parallels that used for a univariate random variable. For example, "$\underline{X} \sim MVN(\underline{\mu},\Sigma)$" indicates that the random vector $\underline{X}$ follows a multivariate normal distribution with parameters $\underline{\mu}$ and Σ. "$\underline{X} \sim (\underline{\mu},\Sigma)$" indicates that $\underline{X}$ follows a (multivariate) distribution with mean vector $\underline{\mu}$ and covariance matrix Σ.

A.4 ESTIMATING POPULATION PARAMETERS WITH SAMPLE STATISTICS

Up to this point, various statistical distributions, parameters, and other theoretical constructs used to model the behavior of random variables have been defined and discussed. In much of statistics, such models for some *population* (real or abstract) of items are postulated or hypothesized, and information is collected about a *sample* drawn from this population. The objectives of this activity include checking the models, estimating parameters, and drawing inferences about the population, based on the sample. Estimation often involves calculating sample analogues to population parameters, moments, and other characteristics. Some of these estimation procedures, and the associated notation, are discussed below.

The usual assumption about a sample is that it is drawn *at random* from the underlying population. The technical definition of a *random sample* is somewhat involved, but essentially a random sample is one in which each item in the population has an equal chance of being selected. A related concept is that of *independent and identically distributed (IID) observations.* Given a sample of size n, x_i, i = 1, ..., n, the assumption might be that each x_i is a realization of a single random variable X, or, equivalently, that the distribution of X_i is the same for all i. This is the concept of identically distributed observations. The concept of independence is essentially that the value of X_i is unaffected by the values of any of the other X_j's ($j \neq i$). The statistical shorthand used to describe this situation is "X_i, i = 1, ..., n ~ IID D($\underline{p}$)," where D is the assumed distribution and $\underline{p}$ is the vector of parameters of D. One link between random sampling and IID observations is this: if D($\underline{p}$) is the statistical distribution for a given population, and X_i, i = 1, ..., n, is a random sample from the population, then X_i, i = 1, ..., n ~ IID D($\underline{p}$).

Assume that a random sample of size n is available from a population with mean μ and variance σ^2; i.e., X_i, i = 1, ..., n, ~ IID (μ,σ^2). The sample-based estimate of the *population mean*, μ, is the *sample mean*:

$$\bar{x} \equiv \frac{1}{n}\sum_{i=1}^{n} x_i \,. \qquad \text{(A.12)}$$

The sample-based estimate of the *population variance*, σ^2, is the *sample variance*:

$$s_x^2 \equiv \frac{1}{n-1}\sum_{i=1}^{n}\left(x_i-\bar{x}\right)^2 . \qquad \text{(A.13)}$$

The sample-based estimate of the *population standard deviation*, σ, is the *sample standard deviation*:

$$s_x \equiv \sqrt{s_x^2} . \qquad \text{(A.14)}$$

The sample mean, $\overline{X}$, is a point estimator of the population mean, μ. In many situations, both a point estimate of the population mean and some idea of the quality of this estimate are required. To address this issue, it must be recognized that the sample mean is a random variable, since it is a function of the random variables X_i, i = 1, ..., n. Therefore, the sample mean has an associated mean and variance. It can be shown that the sample mean is unbiased, i.e., that $E(\overline{X}) = \mu$, so the question of the quality of the sample mean as an estimator of the population mean comes down to the uncertainty in the sample mean. This uncertainty is measured by the standard deviation (or the variance) of $\overline{X}$. In a wide range of cases, the standard deviation of $\overline{X}$ is well estimated by

$$s_{\bar{X}} = \frac{s_X}{\sqrt{n}} . \qquad \text{(A.15)}$$

This quantity, also known the *standard error*[a] of the mean, is used to construct confidence intervals for the population mean.

The preceding discussion of the standard error of the mean is important to inference for the population mean, but it also serves to illustrate that statistical estimators, such as the sample mean, variance, and standard deviation, are random variables and thus have associated

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(a) The term "standard error" is often used to refer to the standard deviation *of an estimator*, as opposed to the standard deviation associated with individual observations.

uncertainty. This uncertainty must be quantified in order to judge the quality of the estimators and to draw inferences about true (population) values. The HLW vitrification process/product control algorithms must deal with uncertainties in statistical estimators, as well as with uncertainties in data.

In the multivariate case, each observation is a vector (rather than a single number). For example, if interest focuses on p characteristics of each item and n items are examined, the data comprise n vectors, each of length p. Denote the observed value for the j-th characteristic of the i-th item as x_{ij}, where j = 1, ..., p, and i = 1, ..., n, and assume that the observations are IID. The sample-based estimate of the *population covariance* between characteristics j and k, σ_{jk}, is the *sample covariance*:

$$\hat{\sigma}_{jk} \equiv s_{jk} \equiv \frac{1}{n-1}\sum_{i=1}^{n}\left(x_{ij}-\bar{x}_j\right)\left(x_{ik}-\bar{x}_k\right) . \qquad \text{(A.16)}$$

where $\bar{x}_j$ and $\bar{x}_k$ are the sample means of the j-th and k-th characteristics, respectively. The sample-based estimate of the *population covariance matrix*, Σ, is the *sample covariance matrix*:

$$S \equiv \begin{bmatrix} s_1^2 & s_{12} & s_{13} & \cdots & s_{1p} \\ s_{21} & s_2^2 & s_{23} & \cdots & s_{2p} \\ s_{31} & s_{32} & s_3^2 & \cdots & s_{3p} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ s_{p1} & s_{p2} & s_{p3} & \cdots & s_p^2 \end{bmatrix} = \frac{1}{n-1}\sum_{i=1}^{n}\left(\underline{x}_i-\underline{\bar{x}}\right)\left(\underline{x}_i-\underline{\bar{x}}\right)^T , \qquad \text{(A.17)}$$

where $\underline{x}_i$ is the i-th observation (a column vector containing the observed values of the p characteristics for the i-th item), $\underline{\bar{x}}$ is the column vector containing the sample means for the p characteristics, and the superscript "T" indicates vector transpose. Since there are p characteristics, the sample covariance matrix is a p × p matrix, and, like the population covariance matrix, it is symmetric. The elements of the sample covariance matrix may be computed individually [using the formula for single sample covariances given in Equation

(A.16)], or the whole matrix may be computed using the vector formula given in Equation (A.17). These methods are equivalent (unless there are missing data).

The sample-based estimate of the *population correlation* between characteristics i and j, ρ_{ij}, is the *sample correlation*:

$$\hat{\rho}_{ij} \equiv r_{ij} \equiv \frac{s_{ij}}{\sqrt{s_i^2 s_j^2}} \tag{A.18}$$

The sample-based estimate of the *population correlation matrix*, P, is the p × p symmetric *sample correlation matrix*:

$$R \equiv \begin{bmatrix} 1 & r_{12} & r_{13} & \cdots & r_{1p} \\ r_{21} & 1 & r_{23} & \cdots & r_{2p} \\ r_{31} & r_{32} & 1 & \cdots & r_{3p} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ r_{p1} & r_{p2} & r_{p3} & \cdots & 1 \end{bmatrix}. \tag{A.19}$$

A.5 PROPERTY MODEL NOTATION

Several property models being developed by CVS are *second-order mixture models*, the general form of which is

$$\phi_k = \sum_{i=1}^{10} b_{ik} x_i + \sum_{i=1}^{9} \sum_{j>i}^{10} b_{ijk} x_i x_j \,, \tag{A.20}$$

where ϕ_k is the k-th melt/glass property (or, in some cases, a simple mathematical transformation thereof), x_i and x_j are the mass fractions of the i-th and j-th oxides, and b_{ik} and b_{ijk} are the coefficients of the relation between the oxide mass fractions and ϕ_k (to be estimated from the CVS database). The oxide mass fractions used in a mixture model must sum to one, that is,

$$\sum_{i=1}^{10} x_i = 1 . \tag{A.21}$$

Some of the models developed by CVS are *first-order*, meaning that, for some properties (k), $b_{ijk} = 0$ for all i and j. The form of a first-order model is

$$\phi_k = \sum_{i=1}^{10} b_{ik} x_i . \tag{A.22}$$

Both the first-order model and the second-order model can be written in the form:

$$\phi_k = \underline{x}^T \underline{b}_k , \tag{A.23}$$

where $\underline{x}$ is the vector containing the oxide mass fractions (and cross-products thereof, if the model is second-order), and $\underline{b}_k$ is the vector of estimated coefficients relating these composition data to the k-th property. Such models are linear in the estimated coefficients, $\underline{b}_k$. First-order models are also linear in the data, $\underline{x}$.

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APPENDIX B

RELATIONSHIP OF STATISTICAL MULTIPLIERS FOR ONE-SIDED TOLERANCE LIMITS TO THE NONCENTRAL t-DISTRIBUTION

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RELATIONSHIP OF STATISTICAL MULTIPLIERS FOR ONE-SIDED TOLERANCE LIMITS TO THE NONCENTRAL t-DISTRIBUTION

This appendix treats the statistical theory and relationships underlying tolerance limits, tolerance intervals, statistical multipliers, confidence, and content. Specifically, the relationship of statistical multipliers to the noncentral t-distribution is developed and used to characterize best tolerance limits.

B.1 STATISTICAL THEORY

Let Z be a standard normal random variable; i.e., $Z \sim N(0,1)$.[a] In addition, let Y be a chi-square random variable with ν degrees of freedom; i.e., $Y \sim \chi^2(\nu)$. Assume that Z and Y are independent. Then the random variable $T_{\nu,\delta}$, defined as

$$T_{\nu,\delta} \equiv \frac{Z+\delta}{\sqrt{Y/\nu}}, \tag{B.1}$$

follows a *noncentral t-distribution with* ν *degrees of freedom and noncentrality parameter* δ (Johnson and Kotz 1970, Chapter 31);[b] i.e.,

$$T_{\nu,\delta} \sim T(\nu,\delta). \tag{B.2}$$

Assume that a random sample of n observations is taken from a normal distribution with mean μ and variance σ^2; i.e., X_i, $i = 1,...,n, \sim$ IID $N(\mu,\sigma^2)$. Define the sample mean, $\overline{X}$,

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(a) For definitions of the various terms and symbols used in this appendix, see Appendix A or the Glossary and list of Acronyms at the beginning of this document.

(b) This is, in fact, the definition of a noncentral t-distribution given by Johnson and Kotz (1970, p. 201). Readers of Johnson and Kotz should note that those authors use the symbol χ_p to represent the square root of a $\chi^2(p)$ random variable.

$$\bar{X} \equiv \frac{1}{n}\sum_{i=1}^{n} X_i \,, \tag{B.3}$$

the sample variance, S^2,

$$S^2 \equiv \frac{1}{n-1}\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2 \,, \tag{B.4}$$

and the sample standard deviation, S,

$$S \equiv \sqrt{S^2} \,. \tag{B.5}$$

It is known that

$$\bar{X} \sim N\left(\mu, \frac{\sigma^2}{n}\right) \tag{B.6}$$

(Lindgren 1976, p. 332). This implies that

$$\frac{\bar{X}-\mu}{\sqrt{\sigma^2/n}} = \frac{\bar{X}-\mu}{\sigma/\sqrt{n}} \sim N(0,1) \,. \tag{B.7}$$

Also, by Theorem 4 of Lindgren (1976, p. 334),[(a)]

$$\frac{(n-1)S^2}{\sigma^2} \sim \chi^2(n-1) \,, \tag{B.8}$$

In addition, $\bar{X}$ and S^2 are independent random variables (Lindgren 1976, p. 334, Corollary to Theorem 3), which implies that the quantities defined in Expressions (B.7) and (B.8) are independent. Therefore,

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(a) Lindgren's (1976) theorem is stated slightly differently, since Lindgren uses n, rather than n-1, in the definition of the sample variance.

$$\frac{\left[(\bar{X}-\mu)/\sqrt{\sigma^2/n}\right]+\delta}{\sqrt{\left[(n-1)\,S^2/\sigma^2\right]/(n-1)}} \sim T(\nu,\delta)\,, \qquad \text{(B.9)}$$

where $\nu \equiv n-1$. Algebraic rearrangement of the left side of Expression (B.9) yields

$$\frac{(\bar{X}-\mu)+\left(\delta\sigma/\sqrt{n}\right)}{S/\sqrt{n}} \sim T(\nu,\delta)\,. \qquad \text{(B.10)}$$

B.2 TOLERANCE INTERVALS AND TOLERANCE LIMITS

A statistical interval designed to capture a specified proportion of the distribution of a random variable with some specified probability is known as a *tolerance interval.* The proportion captured is known as the *content* of the tolerance interval; the probability with which the capture occurs is known as the *confidence* associated with the tolerance interval. A tolerance interval designed to capture 100p% of the distribution with 100γ% confidence is known as a 100γ%/100p% tolerance interval.[a] For example, a 95%/90% tolerance interval is designed to capture 90% of the population with 95% confidence.

A tolerance interval is delimited by a *lower tolerance limit* (LTL) and an *upper tolerance limit* (UTL); i.e., the interval is of the form (LTL,UTL). If the tolerance interval is designed to capture the central portion of the distribution, both limits are finite. In this case, the tolerance interval and the corresponding tolerance limits are termed *two-sided.* Two-sided tolerance intervals and limits are not considered further here.

A *one-sided* tolerance interval seeks to capture either the lower or the upper portion of the distribution. In the former case, the interval is of the form (-∞,UTL); in the latter case, the interval is of the form (LTL,∞). A one-sided tolerance interval is therefore characterized

---

(a) The naming scheme used here is "confidence/content." Some references reverse the order of these parameters.

by its finite endpoint, the associated tolerance limit; hence, the remainder of this discussion is framed in terms of tolerance limits (rather than tolerance intervals). Since an upper tolerance limit for the random variable X is also a lower tolerance limit for -X, the same statistical theory governs both types of one-sided tolerance limits. Therefore, this discussion considers only construction and characteristics of an upper tolerance limit.

A one-sided upper tolerance limit is of the form

$$UTL \equiv \bar{X} + k_{n,\nu,\gamma,p} S, \tag{B.11}$$

where $k_{n,\nu,\gamma,p}$ is a constant that depends on the assumed distribution of the data, the amount of information available on $\bar{X}$ and S^2 (reflected by n and ν, respectively), and the specified confidence (γ) and content (p). Calculation of $k_{n,\nu,\gamma,p}$ for a one-sided UTL under the assumption that the data follow a normal distribution[a] is discussed in the next section.

B.3 CALCULATING $k_{n,\nu,\gamma,p}$

In order to construct a one-sided UTL of content p and confidence γ, $k_{n,\nu,\gamma,p}$ must be chosen so that the following condition is satisfied:[b]

$$1-\gamma = Pr\{\bar{X}+k_{n,\nu,\gamma,p} S \leq \mu + z_p \sigma\}, \tag{B.12}$$

where z_p is the p-th quantile of the standard normal distribution. This condition can be manipulated algebraically as follows:

(a) That is, $\bar{X}$ and S^2 are derived from a set of n observations, X_i, i = 1,...,n, ~ IID $N(\mu,\sigma^2)$. More complicated cases, in which the underlying data are subject to several sources of variation or in which $\bar{X}$ and S^2 are based on different data, are discussed at the end of Section B.3 and in Sections D.2 and D.3.

(b) The calculations below pertain to what is known as a β-*content tolerance interval*, i.e., one which contains at least $100\beta\%$ of the underlying distribution (with the specified confidence). There also exist β-*expectation tolerance intervals*, which contain $100\beta\%$ of the underlying distribution in the long run (sometimes more, sometimes less). This type of tolerance interval is not considered further here.

$$1-\gamma = Pr\{\bar{X}+k_{n,\nu,\gamma,p}S \le \mu+z_p\sigma\}$$

$$= Pr\{\frac{(\bar{X}-\mu)-z_p\sigma}{S} \le -k_{n,\nu,\gamma,p}\} = Pr\{\frac{(\bar{X}-\mu)+(-z_p\sigma)}{S/\sqrt{n}} \le -k_{n,\nu,\gamma,p}\sqrt{n}\}. \qquad \text{(B.13)}$$

From Expression (B.10),

$$\frac{(\bar{X}-\mu)+(-z_p\sigma)}{S/\sqrt{n}} \sim T\left(\nu, -z_p\sqrt{n}\right). \qquad \text{(B.14)}$$

Therefore, $k_{n,\nu,\gamma,p}$ must be chosen so that

$$1-\gamma = Pr\{T_{\nu,-\delta} \le -k_{n,\nu,\gamma,p}\sqrt{n}\}, \qquad \text{(B.15)}$$

where

$$\delta \equiv z_p\sqrt{n}. \qquad \text{(B.16)}$$

Equation (B.15) implies

$$-k_{n,\nu,\gamma,p}\sqrt{n} = t_{\nu,1-\gamma,-\delta}, \qquad \text{(B.17)}$$

where $t_{\nu,1-\gamma,-\delta}$ is the 100(1-γ)-th percentile of the noncentral t-distribution with ν degrees of freedom and noncentrality parameter -δ.[(a)] Therefore,

$$k_{n,\nu,\gamma,p} = -\frac{t_{\nu,1-\gamma,-\delta}}{\sqrt{n}}. \qquad \text{(B.18)}$$

(a) Notation in the main result of this section [Equation (B.20)] is simplified by the use of -δ, rather than δ, as the noncentrality parameter at this point in the development.

will ensure that the UTL has the required confidence and content. Using the fact that

$$Pr\{T_{\nu,\delta} \leq t\} = 1 - Pr\{T_{\nu,-\delta} \leq -t\} \tag{B.19}$$

(Owen 1968, p. 465), the notation given in Equation (B.18) can be simplified:

$$k_{n,\nu,\gamma,p} = \frac{t_{\nu,\gamma,\delta}}{\sqrt{n}}. \tag{B.20}$$

Equation (B.20) demonstrates that the statistical multiplier, $k_{n,\nu,\gamma,p}$, required to produce a $100\gamma\%/100p\%$ UTL can be obtained from the 100γ-th percentile of a noncentral t-distribution. The content of the UTL affects the statistical multiplier through the noncentrality parameter, δ [see Equation (B.16)]. Two facts used in the discussion of best tolerance limits are: 1) to any fixed value of k, there corresponds an infinite number of combinations of γ and p such that $k_{n,\nu,\gamma,p} = k$, and 2) confidence and content are antagonistic, in the sense that if either is increased, the other must be decreased in order to maintain the same statistical multiplier.

In the development above, the assumption that $\overline{X}$ and S^2 were taken from the same data was made for ease of presentation. As long as $\overline{X}$ and S^2 are independent, S^2 is an estimate of the variance of the data from which $\overline{X}$ is drawn, and n is the number of (independent) observations contributing to $\overline{X}$, the same argument works. Therefore, S^2 might be drawn from prior information or from a combination of prior and current information. The only difficulty is that, in either of these cases, ν is not necessarily equal to n-1. In any case, ν remains a parameter of the noncentral t-distribution, and n enters through its relationship to δ [Equation (B.16)] and as the denominator in the final calculation of $k_{n,\nu,\gamma,p}$ [Equation (B.20)].

Note that if each X_i is affected by several sources of variation, the definition of n is not simple. In this case, a reasonable estimate of n is the number of observations at the highest level of the variance hierarchy. See Sections D.2 and D.3 for more discussion of this issue.

B.4 BEST TOLERANCE LIMITS

To demonstrate WAPS 1.3 compliance for a waste type, a 95%/95% UTL will be compared with the maximum allowable value, U, and compliance will be considered demonstrated if UTL $\leq$ U. It may be possible to demonstrate compliance at higher confidence and/or content levels. The highest values of confidence and content at which compliance can be demonstrated (i.e., for which UTL $\leq$ U) are called the *best confidence and content*, and the associated tolerance limit is called the *best tolerance limit.*

Let k_{max} be the maximum statistical multiplier for which UTL $\leq$ U. The statistical multiplier is maximized if UTL = U, which implies

$$k_{max} = \frac{U - \bar{x}}{s}. \qquad \text{(B.21)}$$

The best tolerance limit is one that employs a statistical multiplier equal to k_{max}, and any combination of confidence (γ) and content (p) such that $k_{n,\nu,\gamma,p} = k_{max}$ can be called "best." As mentioned in Section B.3, the number of such combinations is infinite. The HLW vitrification process/product control system will calculate three quantities:

- γ_{max}, the highest confidence level corresponding to the nominal (95%) content; i.e., γ_{max} such that the $100\gamma_{max}$%/95% UTL is equal to U;
- p_{max}, the highest content corresponding to the nominal (95%) confidence level; i.e., p_{max} such that the 95%/$100p_{max}$% UTL is equal to U; and
- π_{max}, the confidence and content such that: 1) confidence and content are equal, and 2) the corresponding UTL is equal to U; i.e., π_{max} such that the $100\pi_{max}$%$100\pi_{max}$% UTL is equal to U.

If mathematical functions for calculating probabilities and percentage points of the noncentral t-distribution are available, the relationship of $k_{n,\nu,\gamma,p}$ to this distribution can be used to calculate γ_{max}, p_{max}, and π_{max}. A computer program for calculating these quantities appears in Appendix C. This program calculates γ_{max} directly, using a function that computes probabilities of the noncentral t-distribution. The program uses a bisection search to obtain

p_{max} and π_{max}; this search exploits the (monotonic) antagonism of γ and p for a fixed value of k (see Section B.3).

B.5 REFERENCES

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Lindgren, B.W. 1976. Statistical Theory, third edition. MacMillan Publishing Co., Inc., New York.

Owen, D.B. 1968. "A Survey of Properties and Applications of the Noncentral t-Distribution," Technometrics 10(3):445-478.

APPENDIX C

CALCULATING CONFIDENCE AND CONTENT FOR BEST TOLERANCE LIMITS

APPENDIX C

CALCULATING CONFIDENCE AND CONTENT FOR BEST TOLERANCE LIMITS

This appendix presents a computer program for calculating confidence and content associated with best tolerance limits, as defined in Section B.4 of Appendix B. The program is designed for use with the statistical software package SAS® (SAS Institute Inc. 1990).[a] The code contains a large amount of internal documentation and therefore should be self-explanatory. This code will serve as a logical template for implementing the best tolerance interval approach in the high-level waste vitrification process/product control system. SAS® provides functions for calculating noncentral t probabilities (PROBT) and percentage points (TINV). Implementing the best tolerance interval approach in the high-level waste vitrification process/product control system will require implementation of similar functions or access to a library of mathematical/statistical routines that contains such functions. It may be possible to avoid implementing a TINV-like function by modifying the logic contained in the SAS® code.

REFERENCES

SAS Institute Inc. 1990. SAS® Language: Reference, Version 6, first edition. SAS Institute Inc., Cary, North Carolina.

(a) SAS® is a registered trademark of the SAS Institute Inc., Cary, North Carolina. This registered trademark is used to identify products and services of the SAS Institute Inc.

```
/*
```

CONFIDENCE AND CONTENT CALCULATIONS
FOR ONE-SIDED TOLERANCE LIMITS

Given a nominal confidence level (CONFID), a nominal content (CONTENT), and K0, the distance, expressed in standard deviation (S) units, from the sample mean (XBAR) to the specified upper bound (U) on the quantile of interest, this program finds

* G_MAX, the highest confidence such that:
  1) the upper tolerance limit is equal to U, and
  2) content = CONTENT, the nominal content.

* P_MAX, the highest content such that:
  1) the upper tolerance limit is equal to U, and
  2) confidence = CONFID, the nominal confidence level.

* G_EQ_P, the highest confidence and content such that:
  1) the upper tolerance limit is equal to U, and
  2) the associated confidence and content are equal.

The calculations done in this program take advantage of the relationship between the statistical multiplier for constructing a tolerance interval (K) and the noncentral t-distribution:

$$k = t(g, n-1, d(p)) / sqrt(n)$$

where:

* t(g,n-1,d(p)) is the g-th quantile of the noncentral t distribution with n-1 degrees of freedom and noncentrality parameter d(p),

* g is the confidence associated with the tolerance interval,

* p is the content associated with the tolerance interval,

* d(p) = z(p) sqrt(n), and

* z(p) is the p-th quantile of the standard normal distribution.

Two functions are useful in these calculations:

```
g = probt( t0, n-1, d);
k = tinv(  g,  n-1, d);
```

PROBT returns F(t0) = Pr(T <= t0), the distribution function of the noncentral t, and is therefore useful in calculating confidence. TINV returns the g-th quantile of the noncentral t and is therefore useful in calculating k values. For example,

given confidence (g), content (p), and sample size (n), the code for calculating the corresponding k value is

```
dp = probit( p) * sqrt( n);
df = n - 1;
k  = tinv( g, df, dp) / sqrt( n);
```

As n increases, k(g,n-1,d(p)) converges to z(p) for all g (see Owen, D.B., 1968, "A Survey of Properties and Applications of the Noncentral t-Distribution," Technometrics 10(3):445-478, p. 448). For large p (e.g., p >= 0.5), this convergence seems to be monotonic decreasing; for small p, the convergence seems to be monotonic increasing; and for intermediate, k seems to decrease to a minimum, then increase monotonically to z(p).

To find G_MAX, P_MAX, and G_EQ_P, the distance in standard deviation (S) units between the specified upper bound (U) and the sample mean (XBAR) is required. This distance, K0, is the statistical multiplier k such that the upper tolerance limit (UTL) is equal to U, i.e., U = UTL, where UTL = XBAR + (k * S). Given U, XBAR, and S, K0 is defined by the formula

```
k0 = ( u - xbar ) / s;
```

Calculating the highest confidence corresponding to a given k, n, and p is quite simple:

```
dp = probit( p) * sqrt( n);
df = n - 1;
t0 = k * sqrt( n);
g  = probt( t0, n-1, dp);
```

This routine, with k = K0 and p = nominal content, is used to find G_MAX.

Calculating P_MAX, the highest content corresponding to K0 and the nominal confidence level, CONFID, is somewhat more difficult, since content is an argument of both functions. A bound-and-bisect routine is used here. To understand the method, it must be remembered that confidence and content are antagonistic, in the sense that, for a fixed K0 and N, higher confidence is realized at the expense of lower content, and vice versa. G_MAX (the highest confidence corresponding to the nominal content) is used as a starting point. The content corresponding to G_MAX, p(G_MAX) serves as one of the bounds for P_MAX. If G_MAX > CONFID, p(G_MAX) is a lower bound for P_MAX, and an upper bound is obtained by increasing p until g(p) is less than CONFID. If G_MAX < CONFID, p(G_MAX) is an upper bound for P_MAX, and a lower bound is obtained by decreasing p until g(p) is greater than CONFID. Bisection on p is then used until g(p) = CONFID.

```
     Calculating highest content and confidence for K0 such that
content = confidence is also complicated by the fact that
content appears as an argument in both functions.  The
approach here uses a bound-and-bisect routine on the statistical
multiplier, k(cc), where cc represents the (equal) confidence and
content.  First, k(0.75), the statistical multiplier for a
75%/75% tolerance interval (75% confidence, 75% content) is
calculated.  If k(0.75) < K0, 0.75 is a lower bound and an upper
bound is obtained by increasing cc until k(cc) > K0.  If
k(0.75) > K0, 0.75 is an upper bound and a lower bound is
obtained by decreasing cc until k(cc) < K0.  Bisection on cc is
then used until k(cc) = K0.
*/

title 'Tolerance Interval Confidence and Content Calculations';

%let epsilon = 0.000001;

%macro calc_g;                          /*  Calculate g( k, n, p),     */
  dp = probit( p) * sqrt( n);           /*  the confidence in a        */
  df = n - 1;                           /*  tolerance interval based   */
  t0 = k * sqrt( n);                    /*  on k, sample size n, and   */
  g  = probt( t0, df, dp);              /*  content p.                 */
%mend;

%macro calc_k;                          /*  Calculate k( g, n, p),     */
  dp = probit( p) * sqrt( n);           /*  the statistical multiplier */
  df = n - 1;                           /*  for a tolerance interval   */
  k  = tinv(g,df,dp)/sqrt(n);           /*  with confidence g, sample  */
%mend;                                  /*  size n, and content p.     */

data first;
/*
     The calculations below require the quantities CONFID,
CONTENT, N, and K0.  These quantities are directly specified
(see the DO loops below), but could be read in from another data
set (via SET), from a disk file (via INFILE and INPUT), or from
text lines included here (via INPUT and CARDS).

     K0 is the distance from the sample mean (XBAR) to the
specified upper bound for the desired quantile (U), expressed
in standard deviation (S) units.  Therefore, the input data
could include U, XBAR, and S in lieu of K0.  The lines below
illustrate the process:

  keep xbar s n u confid content g_eq_p p_max g_max;

  confid  = 0.95;
  content = 0.95;
```

```
  xbar = 10;
  s    =  3;
  n    = 25;
  u    = 20;

  k0 = ( u - xbar) / s;
*/
  keep n confid content k0 g_eq_p p_max g_max;

  do n = 3, 10, 25;
    do confid = 0.75, 0.90, 0.95, 0.99;
      do content = 0.75, 0.90, 0.95, 0.99;
        do k0 = 0.25, 0.50, 1, 2, 3, 4, 5;

          k = k0;              /*  Calculate G_MAX, the highest  */
          p = content;         /*  confidence level consistent   */
          %calc_g;             /*  with K0 and nominal content.  */
          g_max = g;

/*
     Calculate P_MAX, the highest content consistent with
K0 and the nominal confidence, CONFID (i.e, such that the
corresponding UTL is equal to U).  This is done with a
bound-and-bisect routine based on g, the confidence
associated with a candidate p.

THE BOUNDING ROUTINE FOR P_MAX:

     Remember that p and g are antagonistic, in the sense that
each is a monotonically decreasing function of the other.
Therefore, the bounding routine begins by examining G_MAX
(for which the associated p equals the nominal content, i.e.,
p(G_MAX) = CONTENT).  If G_MAX > CONFID, then CONTENT is a
lower bound for P_MAX, and an upper bound is sought by
bisecting toward p = 1.  If G_MAX < CONFID, then CONTENT is
an upper bound for P_MAX, and a lower bound is sought by
bisecting toward p = 0.
*/
          if ( g_max > confid) then do;  /*  Need upper bound  */
            pl = content;                /*  for P_MAX, so     */
            pu = pl;                     /*  bisect toward 1.  */
            do until ( g < confid);
              p = ( 1.0 + pu ) * 0.5;
              %calc_g;
              pu = p;
*             put 'Bisecting up:  '  pl pu g;
              end;
            end;
```

```
          else do;                          /*  Need a lower bound    */
            pu = content;                   /*  for P_MAX, so bisect  */
            pl = pu;                        /*  toward 0.             */
            do until ( g > confid);
              p = pl * 0.5;
              %calc_g;
              pl = p;
*             put 'Bisecting down:  ' pl  pu g;
              end;
            end;

*         put 'Got bounds:  ' pl pu g;
/*
THE BISECTION ROUTINE FOR P_MAX:

     The bisection routine is straightforward:  calculate p
halfway between PL and PU, calculate g(p), and choose new bounds
based on the relationship of g(p) to CONFID.  Continue until g(p)
is sufficiently close to CONFID.
*/
          do until ( abs( g - confid) < &epsilon);
            p = ( pl + pu ) * 0.5;
            %calc_g;
            if ( g < confid)
              then pu = p;
              else pl = p;
            end;

          p_max = p;

/*
     Calculate G_EQ_P_, the highest confidence and content such
that confidence = content and the upper tolerance limit is equal
to U.  This is done with a bound-and-bisect routine based on the
statistical multiplier, k(cc), where cc represents the (equal)
confidence and content.  (The code actually manipulates p, rather
than a variable named cc, and sets g = p before every call to
CALC_K.)

THE BOUNDING ROUTINE FOR G_EQ_P:

     First, k(0.75), the statistical multiplier for a 75%/75%
tolerance interval (75% confidence, 75% content) is calculated.
If k(0.75) < K0, 0.75 is a lower bound and an upper bound is
obtained by increasing cc until k(cc) > K0.  If k(0.75) > K0,
0.75 is an upper bound and a lower bound is obtained by
decreasing cc until k(cc) < K0.
*/
          p = 0.75;
          g = p;
          %calc_k;
```

```
          if ( k < k0) then do;          /*  Need an upper bound  */
            ccl = p;                     /*  for CC, so bisect    */
            ccu = p;                     /*  toward 1.            */
            do until ( k > k0);
              p = ( 1.0 + ccu ) * 0.5;
              g = p;
              %calc_k;
              ccu = p;
              end;
            end;

          else do;                       /*  Need a lower bound   */
            ccu = p;                     /*  for CC, so bisect    */
            ccl = p;                     /*  toward 0.            */
            do until ( k < k0);
              p = ccl * 0.5;
              g = p;
              %calc_k;
              ccl = p;
              end;
            end;
/*

THE BISECTION ROUTINE FOR G_EQ_P:

     The bisection routine is straightforward:  calculate p
halfway between CCL and CCU, set g = p, calculate k(p), and
choose new bounds based on the relationship of k(p) to K0.
Continue until k(p) is sufficiently close to K0.
*/
          do until ( abs( k - k0) < &epsilon);
            p = ( ccl + ccu ) * 0.5;
            g = p;
            %calc_k;
            if ( k < k0)
              then ccl = p;
              else ccu = p;
            end;

          g_eq_p = p;
          output;
          end;
        end;
      end;
    end;
run;

proc print noobs uniform;
  var n confid content k0 g_max p_max g_eq_p;
run;
```

APPENDIX D

ESTIMATING AND MANIPULATING UNCERTAINTIES

APPENDIX D

ESTIMATING AND MANIPULATING UNCERTAINTIES

Data from the high-level waste (HLW) vitrification process will be multivariate (e.g., feed compositions) and will be subject to several sources of uncertainty. Requirements and specifications imposed on HLW vitrification material apply to univariate attributes, many of which will be calculated from (multivariate) feed compositions using empirical models developed as part of the Composition Variability Study (CVS; Hrma, Piepel, et al. 1994). Therefore, proper inference in HLW vitrification process/product control requires

- estimating univariate and multivariate uncertainties and components thereof (e.g., variances, variance components, covariance matrices, covariance components);
- propagating multivariate uncertainties to yield univariate uncertainties;
- combining univariate uncertainties to yield an estimate of overall uncertainty in an estimated attribute value, and assigning a measure of strength of belief to this overall uncertainty estimate; and
- updating existing uncertainty estimates to reflect both prior and current information.

These topics are discussed in the following sections. This appendix supplies the technical details that do not appear in Section 4. Expanded treatments of these subjects appear in Bryan and Piepel (1994), Bryan, Piepel, and Simpson (1994), and Searle, Casella, and McCulloch (1992). Basic statistical concepts and notation are covered in Appendix A.

D.1 THE MODEL FOR COMPOSITION UNCERTAINTY IN HLW VITRIFICATION DATA

Let Y_{ijk} represent the value of some attribute estimated from the k-th analysis of the j-th sample from the i-th batch of HLW vitrification process material.[(a)] Y_{ijk} is subject to model uncertainty and to three sources of composition uncertainty (batch-to-batch variability, within-batch uncertainty, and analytical uncertainty). Model uncertainty will be estimated separately and then combined with composition uncertainty (see Sections D.5 and D.6). Composition uncertainty (and its components) will be estimated using the following model:

$$Y_{ijk} = \mu + \beta_i + \omega_{ij} + \alpha_{ijk} \ , \qquad (D.1)$$

where $\beta_i \sim (0,\sigma_\beta^2)$, $\omega_{ij} \sim (0,\sigma_\omega^2)$, $\alpha_{ijk} \sim (0,\sigma_\alpha^2)$, and all the random variables are uncorrelated. In this model, σ_β^2 represents batch-to-batch variability, σ_ω^2 represents within-batch uncertainty, and σ_α^2 represents analytical uncertainty. The β_i, ω_{ij}, and α_{ijk} are known as *random effects*. The quantities σ_β^2, σ_ω^2, and σ_α^2 (and estimates of these quantities) are known as *variance components* (or *components of variance*).

The number of batches in a single waste type is denoted by b, the number of samples taken from the i-th batch is denoted by w_i,[(b)] and the number of analyses performed on the j-th sample from the i-th batch is denoted by a_{ij}. If $w_i = w$ for all i, and $a_{ij} = a$ for all i and j, the data are said to be *balanced*. Otherwise, the data are said to be *unbalanced*.

(a) Waste to be processed by the HLW vitrification plant will be classified into waste types. However, all requirements apply *within* a single waste type; no inferences are required across waste types. For this reason, the model and methods discussed here should be applied separately to each waste type. Therefore, the notation is simplified by not accounting for waste type.

(b) It may seem more intuitive to use s_i for the number of samples taken from the i-th batch. However, the letter s (and subscripted versions thereof) is reserved in this document for denoting a standard deviation. Therefore, w_i is used to denote the number of samples within a batch.

Several of the equations and methods discussed below rely on the *within-sample mean*, $\overline{Y}_{ij\cdot}$. The within-sample mean is the mean over the a_{ij} analyses performed on the j-th sample from the i-th batch:

$$\overline{Y}_{ij\cdot} \equiv \frac{1}{a_{ij}} \sum_{k=1}^{a_{ij}} Y_{ijk} \,. \qquad (D.2)$$

D.2 THE BATCH MEAN AND ASSOCIATED UNCERTAINTIES

Under the model given in Equation (D.1), the true attribute value for the i-th batch is $\mu + \beta_i$. To check a single-batch requirement on this attribute, $\mu + \beta_i$ will be estimated with the *batch mean.*[(a)] In general, the i-th batch mean is

$$\overline{Y}_{i\cdot\cdot} \equiv \frac{1}{w_i} \sum_{j=1}^{w_i} \overline{Y}_{ij\cdot} = \frac{1}{w_i} \sum_{j=1}^{w_i} \left[\frac{1}{a_{ij}} \sum_{k=1}^{a_{ij}} Y_{ijk} \right]; \qquad (D.3)$$

that is, the batch mean is a mean of w_i within-sample means from the i-th batch. By substituting for Y_{ijk} from Equation (D.1) and simplifying, it can be shown that

$$\overline{Y}_{i\cdot\cdot} = \mu + \beta_i + \frac{1}{w_i} \sum_{j=1}^{w_i} \omega_{ij} + \frac{1}{w_i} \sum_{j=1}^{w_i} \left[\frac{1}{a_{ij}} \sum_{k=1}^{a_{ij}} \alpha_{ijk} \right]. \qquad (D.4)$$

For balanced data, these expressions simplify as follows:

(a) Since the batch effect is assumed to be random rather than fixed, an argument can be made that the best estimator for the quantity $\mu + \beta_i$ is *not* the batch mean value, but a "shrunken" version of this value. Searle et al. (1992, Chapter 7, esp. pp. 258-260) discuss this problem. The preliminary Feed Test Algorithm (Bryan and Piepel 1994) ignores this complication. If testing of the HLW vitrification process/product control algorithms with the Plant Simulation Code indicates problems, this issue should be re-examined.

$$\overline{Y}_{i\cdot\cdot} \equiv \frac{1}{wa}\sum_{j=1}^{w}\sum_{k=1}^{a} Y_{ijk} = \mu + \beta_i + \frac{1}{w}\sum_{j=1}^{w}\omega_{ij} + \frac{1}{wa}\sum_{j=1}^{w}\sum_{k=1}^{a}\alpha_{ijk} . \qquad (D.5)$$

Since the target of inference for a single-batch requirement is $\mu + \beta_i$ (the true attribute value in the i-th batch), inference should be conditional on (i.e., taking as fixed) the true value of β_i. Thus, for testing a single-batch requirement, the estimate of composition uncertainty in the batch mean must account for uncertainties due to ω_{ij} and α_{ijk} (the within-batch and analytical uncertainties, respectively), but uncertainty in β_i (the batch-to-batch uncertainty) is irrelevant.

Since the batch mean is a mean of within-sample means, each within-sample mean can be viewed as an observation contributing to the batch mean. In other words, the population underlying the batch mean is the population of within-sample means, $\overline{Y}_{ij\cdot}$. Therefore, the uncertainty in the within-sample means is important in making inferences about the batch mean. In general, the (conditional) composition uncertainty associated with the j-th within-sample mean from the i-th batch is

$$Var\left(\overline{Y}_{ij\cdot} \mid \beta_i\right) = \sigma_\omega^2 + \frac{\sigma_\alpha^2}{a_{ij}} . \qquad (D.6)$$

For balanced data, this composition uncertainty is

$$Var\left(\overline{Y}_{ij\cdot} \mid \beta_i\right) = \sigma_\omega^2 + \frac{\sigma_\alpha^2}{a} . \qquad (D.7)$$

In general, the (conditional) composition uncertainty in the i-th batch mean is

$$Var\left(\overline{Y}_{i\cdot\cdot} \mid \beta_i\right) = \frac{\sigma_\omega^2}{w_i} + \frac{\sigma_\alpha^2}{w_i \overline{a}_i} , \qquad (D.8)$$

where

$$\overline{a}_i \equiv \left(\frac{1}{w_i} \sum_{j=1}^{w_i} \frac{1}{a_{ij}} \right)^{-1} . \qquad (D.9)$$

For balanced data, the (conditional) composition uncertainty in the i-th batch mean is

$$Var(\overline{Y}_{i..} \mid \beta_i) = \frac{\sigma_\omega^2}{w} + \frac{\sigma_\alpha^2}{wa} . \qquad (D.10)$$

Estimating these uncertainties is discussed in Section D.4.

Recognizing the batch mean as a mean of within-sample means assists in identifying the proper sample size to be associated with the batch mean when constructing confidence and/or tolerance limits. For example, in the balanced case, the number of individual Y_{ijk} involved in calculating the batch mean is wa, but this is *not* the proper sample size for statistical inference. The proper sample size is equal to the number of within-sample means involved in constructing the batch mean. This sample size is w, in the balanced case, or w_i, in the unbalanced case.

Model uncertainty must also be accounted for by the statistical inference procedure. Estimating model uncertainty is discussed in Section D.5. Combining model and composition uncertainties is discussed in Section D.6.

D.3 THE MULTIPLE-BATCH MEAN AND ASSOCIATED UNCERTAINTIES

The target of inference for a multiple-batch requirement is a percentile of the distribution of batch means. Under the model given in Equation (D.1) and the assumptions pertaining thereto, the true batch means, $\mu + \beta_i$, follow a distribution with mean μ and variance σ_β^2. Therefore, estimates of μ and σ_β^2 are required for statistical inference.

The procedure for checking multiple-batch requirements will use the *multiple-batch mean*, $\overline{Y}_{...}$, as an estimate of μ. The multiple-batch mean is defined as

$$\bar{Y}_{...} \equiv \frac{1}{b}\sum_{i=1}^{b} \bar{Y}_{i..} = \frac{1}{b}\sum_{i=1}^{b}\left[\frac{1}{w_i}\sum_{j=1}^{w_i} \bar{Y}_{ij.}\right]. \qquad (D.11)$$

The multiple-batch mean is a mean of the b individual batch means. By substituting for Y_{ijk} from Equation (D.1) and simplifying, it can be shown that

$$\bar{Y}_{...} = \mu + \frac{1}{b}\sum_{i=1}^{b} \beta_i + \frac{1}{b}\sum_{i=1}^{b}\left[\frac{1}{w_i}\sum_{j=1}^{w_i}\left(\omega_{ij} + \frac{1}{a_{ij}}\sum_{k=1}^{a_{ij}} \alpha_{ijk}\right)\right]. \qquad (D.12)$$

For balanced data, these expressions simplify as follows:

$$\bar{Y}_{...} = \frac{1}{bwa}\sum_{i=1}^{b}\sum_{j=1}^{w}\sum_{k=1}^{a} Y_{ijk}$$

$$= \mu + \frac{1}{b}\sum_{i=1}^{b} \beta_i + \frac{1}{bw}\sum_{i=1}^{b}\sum_{j=1}^{w} \omega_{ij} + \frac{1}{bwa}\sum_{i=1}^{b}\sum_{j=1}^{w}\sum_{k=1}^{a} \alpha_{ijk}\,. \qquad (D.13)$$

As stated above, the statistical procedure for checking multiple-batch requirements requires an estimate of σ_β^2. Estimating σ_β^2 is discussed in Section D.4. It is instructive to consider the uncertainty in the empirical batch means. In general, the composition uncertainty in the i-th batch mean is

$$Var(\bar{Y}_{i..}) = \sigma_\beta^2 + \frac{\sigma_\omega^2}{w_i} + \frac{\sigma_\alpha^2}{w_i \bar{a}_i}\,, \qquad (D.14)$$

where

$$\bar{a}_i \equiv \left(\frac{1}{w_i}\sum_{j=1}^{w_i} \frac{1}{a_{ij}}\right)^{-1}. \qquad (D.15)$$

For balanced data, the composition uncertainty in the i-th batch mean is

$$Var(\overline{Y}_{i..}) = \sigma_\beta^2 + \frac{\sigma_\omega^2}{w} + \frac{\sigma_\alpha^2}{wa} . \qquad (D.16)$$

Thus, the empirical batch means, $\overline{Y}_{i..}$, have a larger variance than do the true batch means, $\mu + \beta_i$. This variance can also be estimated using the methods discussed in Section D.4.

The proper estimate of composition variability to be used in the inferential procedure may require more investigation. This issue is related to the issue of removal of nuisance uncertainties, which is discussed in Section 5. The WAPS 1.3 compliance strategy to be used by the HLW vitrification process/product control system will employ an estimate of the variance that appears in Equation (D.16). This uncertainty is larger than σ_β^2 alone; hence, inference based on this uncertainty is conservative relative to inference based on an estimate of σ_β^2. If testing of the WAPS 1.3 compliance strategy (e.g., using the Plant Simulation Code, as discussed by Bryan and Piepel 1993) indicates that this conservatism is likely to hinder verification of WAPS 1.3 compliance, this issue should be revisited.

Recognizing the multiple-batch mean as a mean of individual batch means assists in identifying the proper sample size to be associated with the multiple-batch mean when constructing confidence and/or tolerance limits. For example, in the balanced case, the number of individual Y_{ijk} involved in calculating the multiple-batch mean is bwa, but this is *not* the proper sample size for statistical inference. The proper sample size is equal to the number of batch means involved in constructing the multiple-batch mean, b.

Model uncertainty must also be accounted for by the statistical inference procedure. Estimating model uncertainty is discussed in Section D.5. Combining model and composition uncertainties is discussed in Section D.6.

D.4 ESTIMATING VARIANCE COMPONENTS

The model given in Equation (D.1) is an example of a *two-way nested random model.* The term "nested" is applied because the random effects are hierarchical; for example, uncertainty exists among analyses within a single sample, among samples within a single batch, and among batches within a waste type. Each observed, measured, or estimated attribute value includes uncertainty introduced at each level of this hierarchy. The uncertainty at each level in this hierarchy can be represented by a variance. These hierarchical representations of uncertainty are the variance components.

Methods for estimating variance components are discussed in great detail by Searle et al. (1992). The discussion below focuses on general principles, applicability to HLW vitrification process/product control, and special features of the HLW vitrification process.

Assume that the data available for estimating variance components are balanced. As in Section D.1, the number of batches is denoted by b, the number of samples taken from each batch is denoted by w, and the number of analyses run on each sample is denoted by a. The total number of observations is then bwa. These data may be analyzed with the analysis of variance (ANOVA)[(a)], as in Table D.1. The estimates of the individual variance components are

$$\hat{\sigma}_\beta^2 = \frac{MSB-MSW}{wa}, \quad \hat{\sigma}_\omega^2 = \frac{MSW-MSA}{a}, \quad \hat{\sigma}_\alpha^2 = MSA, \qquad (D.17)$$

where the symbols used above are defined in Table 1. These ANOVA-based estimators are derived by setting the sample-based mean squares MSA, MSW, and MSB equal to their

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(a) The analysis of variance, or ANOVA, is a well-known and widely-used statistical procedure. ANOVA is discussed in most books on basic applied statistics (e.g., Snedecor and Cochran 1980); Graybill (1976) and Searle (1971) present extensive theoretical treatments of ANOVA.

TABLE D.1. Analysis of Variance Table for the Two-Way Nested Random Model, $Y_{ijk} = \mu + \beta_i + \omega_{ij} + \alpha_{ijk}$

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Expected Mean Square
Batch-to-Batch	b-1	$SSB \equiv wa\sum_{i=1}^{b}\left(\bar{Y}_{i..} - \bar{Y}_{...}\right)^2$	MSB ≡ SSB / (b-1)	$wa\sigma_\beta^2 + a\sigma_\omega^2 + \sigma_\alpha^2$
Within-Batch	b(w-1)	$SSW \equiv a\sum_{i=1}^{b}\sum_{j=1}^{w}\left(\bar{Y}_{ij.} - \bar{Y}_{i..}\right)^2$	MSW ≡ SSW / b(w-1)	$a\sigma_\omega^2 + \sigma_\alpha^2$
Analytical	bw(a-1)	$SSA \equiv \sum_{i=1}^{b}\sum_{j=1}^{w}\sum_{k=1}^{a}\left(Y_{ijk} - \bar{Y}_{ij.}\right)^2$	MSA ≡ SSA / bw(a-1)	σ_α^2
Total	bwa-1	$SST \equiv \sum_{i=1}^{b}\sum_{j=1}^{w}\sum_{k=1}^{a}\left(Y_{ijk} - \bar{Y}_{...}\right)^2$		

expectations (the "Expected Mean Squares" of Table 1) and solving for σ_α^2, σ_ω^2, and σ_β^2.[a] The degrees of freedom associated with the estimates of σ_ω^2 and σ_β^2 can be calculated from the Satterthwaite approximation (Section D.6).

Once these estimates of variance components have been calculated, they can be used to estimate composition uncertainties (and the associated degrees of freedom) for within-sample means and batch means [Equations (D.6), (D.7), (D.14), and (D.16)]. Note that the required variances are linear functions of the variance components, and that the variance component estimators given in Equation (D.17) are linear functions of the mean squares. Therefore, for balanced data, the required variances can be estimated with linear functions of the mean squares (skipping the intermediate estimation of variance components). Such a simplification of the estimation process should be used when available, since a single-step Satterthwaite approximation to the associated degrees of freedom will be more accurate than a two-step approximation. In fact, for balanced data, the estimated variances collapse to simple functions of the mean squares in Table 1:

$$\hat{V}(\overline{Y}_{ij\cdot} \mid \beta_i) = \frac{MSW}{a}, \qquad \hat{V}(\overline{Y}_{i\cdot\cdot}) = \frac{MSB}{wa}. \tag{D.18}$$

The degrees of freedom associated with these estimated variances are simply those associated with the corresponding mean squares, b(w-1) and b-1, respectively.

The estimators of variance components given in Equation (D.17) belong to the class of *ANOVA estimators*.[b] Searle et al. (1992) discuss other methods for estimating variance

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(a) The *method of moments* is a technique for deriving statistical estimators in which sample-based quantities are set equal to their expectations and the resulting equations are solved for the parameters in terms of the sample-based quantities (Lindgren 1976). Thus, the ANOVA-based estimators discussed here are examples of *method of moments estimators*.

(b) This document follows the convention of Searle et al. (1992) in applying the term "ANOVA estimators" to any estimators derived by applying the method of moments to quantities involved in an ANOVA. In some cases (e.g., when the data are not balanced), different types of ANOVA may be legitimately applied to the same data. Different method of moments may result from these different ANOVAs. Therefore, ANOVA estimators are not necessarily unique.

components, including maximum likelihood estimation, restricted maximum likelihood estimation, and Bayes procedures. Complete enumeration and elucidation of the wide variety of techniques for variance component.estimation are beyond the scope of this document. The choice of estimation technique must depend on the structure of the available data and the assumptions about the process that are considered realistic at the time. Therefore, this choice should be made when data become available, as part of the data analysis process. Some considerations in the choice of specific technique are discussed below.

It is common to assume that random effects in a linear model follow a normal distribution. In fact, some distributional assumption is required for several of the variance component estimation techniques mentioned above (e.g., maximum likelihood and Bayes procedures). The ANOVA estimators are exceptions -- they are derived simply by equating mean squares to their expected values and therefore depend only on the moments of the underlying distribution(s).

The assumption of balanced data greatly simplifies the form of the ANOVA estimators. In fact, with balanced data, several methods for variance component estimation yield estimates identical or closely related to the ANOVA estimates. Unfortunately, this is not the case if the data are unbalanced; in fact, for unbalanced data, several reasonable types of ANOVA estimators exist. Other estimation techniques yield unique estimators, but these techniques are iterative in nature and can impose a significant computational burden. If imbalance in the available data is not too large, the ANOVA estimators of Equation (D.17) (possibly modified to account for the imbalance) should provide reasonable approximations to the variance components.

ANOVA estimates of variance components can be negative. This is troubling, since the true values of variance components, by their nature as variances, must be nonnegative. Searle et al. (1992, pp. 129-131) discuss various options for dealing with this problem. One is simply to set a negative estimate to zero (thereby concluding that the related random effect contributes no uncertainty to the observed value); a second is to use one of the methods that guarantee nonnegative estimates (e.g., maximum likelihood and Bayes procedures).

Estimating multivariate composition uncertainties may be required as part of HLW vitrification process/product control. Like univariate uncertainties, multivariate uncertainties may derive from various sources, so methods for estimating components of multivariate uncertainties may be required. Just as for univariate variance components, the importance of multivariate components of uncertainty lies in their crucial role in estimating uncertainty in values (e.g., means) calculated from a set of observations, $\underline{X}_{ijk}$.

The model given in Equation (D.1) can be generalized to apply to the multivariate situation, e.g., to vectors of measured feed composition:

$$\underline{X}_{ijk} = \underline{\mu} + \underline{\beta}_i + \underline{\omega}_{ij} + \underline{\alpha}_{ijk}, \qquad (D.19)$$

where $\underline{X}_{ijk}$ is the vector of individual oxide mass fractions (X_{ijkl}, l = 1, ..., 10), and $\underline{\beta}_i$, $\underline{\omega}_{ij}$, and $\underline{\alpha}_{ijk}$ are vectors of random effects. In this multivariate generalization of Equation (D.1), it is assumed that $\underline{\beta}_i \sim (\underline{0},\Sigma_\beta)$, $\underline{\omega}_{ij} \sim (\underline{0},\Sigma_\omega)$, $\underline{\alpha}_{ijk} \sim (\underline{0},\Sigma_\alpha)$, and the random vectors $\underline{\beta}_i$, $\underline{\omega}_{ij}$ and $\underline{\alpha}_{ijk}$ are uncorrelated. In analogy to the univariate case, the covariance matrices Σ_β, Σ_ω, and Σ_α are known as *covariance components* (or *components of covariance*).

Searle et al. (1992) discuss estimation of covariance components. The method to be used in HLW vitrification process/product control is based on the methods for univariate variance component estimation discussed above and on the well-known formula for the variance of a sum of two random variables (see, for example, Lindgren 1976, p. 137):

$$Var(X_i+X_j) = Var(X_i) + Var(X_j) + 2\,Cov(X_i,X_j), \qquad (D.20)$$

from which is easily derived:

$$Cov(X_i,X_j) = \frac{1}{2}\{Var(X_i+X_j) - [Var(X_i) + Var(X_j)]\}. \qquad (D.21)$$

To obtain estimates of the components of covariance between X_i and X_j, the three univariate variance components (σ_β^2, σ_ω^2, σ_α^2) will be estimated for each of X_i, X_j, and the sum, $X_i + X_j$, and the above formula will be applied. Performing this estimation for each pair (i,j), j > i,

"fills in" the upper half of each of the matrices of covariance components; the lower half of each matrix is derived from the symmetricity of covariance matrices.

D.5 PROPAGATING UNCERTAINTIES

Many of the batch and glass attributes that must be estimated and checked as part of HLW vitrification process/product control will be calculated as functions of more than one uncertain quantity (e.g., oxide mass fractions, other process measurements, empirical model coefficients). In order to check compliance of these attributes with process and product specifications, the total (univariate) uncertainty associated with each attribute must be estimated. Therefore, a procedure for combining multivariate uncertainties (e.g., covariance matrices, covariance components) to yield univariate uncertainties is required.

For HLW process/product control, the multivariate uncertain quantities fall into two categories: 1) composition and other process measurements, and 2) empirical model coefficients. As discussed in Section 4.1, composition uncertainty and components thereof will be estimated by using the CVS models to convert individual measurements of feed composition to property values (e.g., PCT results), and then performing univariate variance component estimation for these results (using the methods discussed in Section D.4). However, future developments and investigations may indicate that efficiency could be increased by estimating (multivariate) covariance components for composition and propagating these covariance components into property (PCT) units. If this is the case, the methods discussed in this section can be used to estimate the contribution of composition uncertainty (and the components thereof) to uncertainty in property values. In any case, the methods discussed here will be used to estimate the contribution of model uncertainty to uncertainty in property values.

The procedure described below is one form of *error propagation* (or *propagation of error*). This procedure can be used to estimate uncertainty for a wide variety of functions of multivariate uncertain quantities.

The basis for the error propagation method to be used in HLW vitrification process/product control is as follows. Let y represent the characteristic of interest, and assume that $y = f(\underline{z})$, where $\underline{z}$ is a random vector with mean $\underline{\mu}_z$ and covariance matrix Σ_z. Then, using a Taylor series expansion about $\underline{\mu}_z$ to approximate $f(\underline{z})$, an approximation to the variance of y, σ_y^2, can be derived:

$$\sigma_y^2 \approx \underline{d}_z^T \Sigma_z \underline{d}_z \,, \qquad (D.22)$$

where $\underline{d}_z$ is the gradient of f (i.e., the vector of partial derivatives with respect to $\underline{z}$), evaluated at the observed value of $\underline{z}$.

The uncertainty associated with a modelled batch or glass property (y) derives from two distinct sources: 1) uncertainty associated with the estimated coefficients ($\underline{b}$) of the empirical model, and 2) uncertainty associated with the estimated composition ($\underline{x}$).[(a)] Model uncertainty will be represented by the covariance matrix, Σ_b, for the vector of estimated model coefficients (which will be obtained from CVS, Hrma, Piepel, et al. 1994). For simplicity of presentation, it is assumed here that a single covariance matrix representing composition uncertainty, Σ_x, is available. The case of several covariance components for feed composition is discussed at the end of this section.

The general method of error propagation discussed above can be applied to the case in which the random vector $\underline{z}$ consists of two distinct subvectors, e.g., the case in which $y = f(\underline{x},\underline{b})$. Denote the gradients of $f(\underline{x},\underline{b})$ with respect to $\underline{x}$ and $\underline{b}$ by $\underline{d}_x$ and $\underline{d}_b$, respectively. If $\underline{x}$ and $\underline{b}$ are uncorrelated random vectors (a reasonable assumption unless $\underline{x}$ is part of the data used to estimate $\underline{b}$), the approximate variance of y divides neatly into two parts, one attributable to composition uncertainty, the other attributable to model uncertainty:

$$\sigma_y^2 \approx \underline{d}_x^T \Sigma_x \underline{d}_x + \underline{d}_b^T \Sigma_b \underline{d}_b \,. \qquad (D.23)$$

(a) If the property model is second-order, the vector $\underline{x}$ contains not only the individual mass fractions, but also some cross-products.

For the special case where the function $f(\underline{x},\underline{b})$ is linear in both the data, $\underline{x}$, and the estimated coefficients, $\underline{b}$, this formula takes on an even simpler form. For this case, $y = \underline{x}^T\underline{b}$, $\underline{d}_x = \underline{b}$, $\underline{d}_b = \underline{x}$, and

$$\sigma_y^2 \approx \underline{b}^T\Sigma_x\underline{b} + \underline{x}^T\Sigma_b\underline{x} \,. \qquad (D.24)$$

The HLW vitrification process/product control system will estimate the two types of uncertainty (composition uncertainty and model uncertainty) separately. The method of Section D.6 will be used to combine these two types of uncertainty and to assign degrees of freedom to the resulting estimate of overall uncertainty.

As currently envisioned, HLW vitrification process/product control will use error propagation only to estimate model uncertainty. However, if the decision is made later to estimate and propagate (multivariate) covariance components for composition, the error propagation methods discussed in this section can be used to estimate the contribution of composition uncertainty (and the components thereof) to uncertainty in property values. The composition covariance components can be propagated separately. Using the method of Section D.6, the resulting univariate variance components can be combined with the estimated model uncertainty to form a univariate estimate of overall uncertainty in property units and to assign an associated number of degrees of freedom.

D.6 COMBINING UNCERTAINTIES

When observed data are subject to more than one source of uncertainty, proper estimation of the uncertainty in a function (e.g., the mean) of these observations requires combining variance components. In addition, estimating variance components often requires combining mean squares, and the HLW process/product control algorithms must combine model uncertainty with composition uncertainty. In many cases (including all so far identified for HLW vitrification process/product control), the required combination of mean squares or variance components is a weighted sum, where the weights are related to the distribution of sampling effort (e.g., the number of samples per batch and the number of

analyses per sample) or strength of belief in the individual variance components. In general, such weighted sums take the form:

$$s_c^2 = \sum_{j=1}^{p} c_j s_j^2 , \qquad (D.25)$$

where s_c^2 is the required combination of the individual variance components, s_j^2, with weights c_j.

Some measure of the quality of s_c^2 must be available in order to use this estimate to draw inferences. The quality of a variance estimate is often quantified by the associated degrees of freedom. The weighted sum above incorporates several variance estimates, each with an associate number of degrees of freedom, f_j. What number of degrees of freedom should be associated with the combined variance estimate, s_c^2? HLW process/product control will use the answer given by Satterthwaite (1946); the degrees of freedom to be associated with s_c^2 is

$$f_c = \frac{\left(\sum_{j=1}^{p} c_j s_j^2\right)^2}{\sum_{j=1}^{p} \frac{\left(c_j s_j^2\right)^2}{f_j}} = \frac{\left(s_c^2\right)^2}{\sum_{j=1}^{p} \frac{\left(c_j s_j^2\right)^2}{f_j}} . \qquad (D.26)$$

Satterthwaite's approximation, as the above formula is known, was derived under the assumption of normality. Caution should be exercised in applying this formula when some of the c_j are negative (which is often the case when estimating variance components). Methods and additional requirements in this case are discussed by Gaylor and Hopper (1969), who show that the approximation is adequate when the component (or the sum of the several components) being subtracted is relatively small.

D.7 UPDATING UNCERTAINTIES

In some cases, an uncertainty estimate may be available from a source external to the actual Hanford HLW vitrification process data. For example, an uncertainty estimate may be available from operations at other sites (e.g., DWPF, WVDP) or from simulations of the HLW vitrification process. It may be desirable to combine this external uncertainty estimate with data from the Hanford HLW vitrification process. Combining an external uncertainty estimate with current data is here referred to as updating the uncertainty estimate.

If the external uncertainty estimate can be expressed as a variance, s^2, with an associated number of degrees of freedom, f, the method described in Section D.6 can be used to combine this information with variance estimates derived using the methods of Sections D.4 and D.5. However, if the external uncertainty estimate appears in some other form, another method of combining this estimate with Hanford HLW vitrification process data must be employed. For example, the external uncertainty estimate may appear as an estimated variance, s^2, with an associated standard deviation, e.[a] This section describes two methods for combining such an external uncertainty estimate with HLW vitrification process data.

The first method is an adaptation of the method in Section D.6. This method relies on the properties of the chi-square distribution to calculate a number of degrees of freedom associated with s^2. If s^2 is estimated from a random sample of size n from a normal distribution, the associated random variable S^2 follows (a multiple of) a chi-square distribution with f = n-1 degrees of freedom (Lindgren 1976, p. 334, Theorem 4). Since the mean and variance of a chi-square distribution are f and 2f, respectively, the relative standard deviation (RSD) of S^2 is

$$RSD(S^2) \equiv \frac{\sqrt{Var(S^2)}}{E(S^2)} = \sqrt{\frac{2}{f}} \quad . \qquad (D.27)$$

Therefore,

(a) This e is a measure of the uncertainty in s^2, i.e., an "uncertainty of the uncertainty."

$$f = \frac{2}{\left[RSD(s^2)\right]^2} \approx \frac{2(s^2)^2}{e^2} . \qquad (D.28)$$

This approximate f can be used with s^2 and the method of Section D.6 to combine the external uncertainty estimate with uncertainty estimates derived from HLW vitrification process data.

To update an uncertainty estimate, prior information must be combined with information contained in a current data set. Combining prior and current information is one application of the branch of statistics known as *Bayesian statistics*. The second method of updating an external uncertainty estimate utilizes a Bayesian approach. Assume that n current observations, X_i, i = 1, ..., n, are available, where the X_i are a random sample from a normal distribution with mean zero and variance σ^2. As above, assume that both a prior estimate of σ^2, denoted s^2, and a prior estimate of the standard deviation of σ^2, denoted e, are available. Define

$$\gamma \equiv \frac{(s^2)^2}{e^2} + 2 = \frac{s^4}{e^2} + 2 \qquad (D.29)$$

$$\delta \equiv s^2 \left(\frac{s^4}{e^2} + 1 \right). \qquad (D.30)$$

Based on these definitions, an updated estimate of σ^2 (one incorporating both the data and the prior information) can be constructed from one possible Bayes estimator:

$$s_u^2 = \frac{\delta_u}{\gamma_u - 1} , \qquad (D.31)$$

where

$$\delta_u = \delta + \frac{1}{2}\sum_{i=1}^{n} x_i^2 , \qquad (D.32)$$

and

$$\gamma_u = \gamma + \frac{n}{2} \qquad (D.33)$$

(in each case, the subscript "u" is used to denote an updated estimate). In addition, an updated estimate of the standard deviation of σ^2 can be constructed:

$$e_u = \frac{\delta_u}{(\gamma_u - 1)\sqrt{\gamma_u - 2}} = \frac{s_u^2}{\sqrt{\gamma_u - 2}} . \qquad (D.34)$$

More discussion of this Bayesian updating method, including derivation of the updated estimators in Equations (D.31) and (D.34), appears in Section 9 and the Appendix of Bryan, Piepel, and Simpson (1994). A multivariate version of this updating scheme appears in Anderson (1984, p. 272).

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