PNWD-3260
WTP-RPT-049, Rev. 0

Methodology for Adjusting and Normalizing Analyzed Glass Compositions

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WTP
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Report

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Completeness of Testing

This report describes the results of work and testing specified by Subtask 2 of Test Specification 24590-WTP-TSP-RT-01-002 and Test Plan TP-RPP-WTP-097. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/ Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager — Date
WTP R&T Support Project

Research and Technology Manager — Date

Summary

For the Immobilized High Level Waste (IHLW) and Immobilized Low Activity Waste (ILAW) vitrification processes of the Waste Treatment Plant (WTP), chemical analyses of process samples (e.g., slurry samples) and glass samples will be used to estimate glass compositions. Glass composition estimates will be used directly, as well as indirectly through property-composition models, to control the IHLW and ILAW processes, demonstrate compliance with applicable specifications, and report glass compositions and properties in production records. Glass composition estimates based on samples and chemical analyses of glasses made in laboratory crucible studies and melter tests may also be required.

Chemical analyses of glass samples[1] generally do not yield glass component[2] weight percent (wt%) concentrations that sum to 100 wt%. Non-detection of minor glass components can contribute to this result, but typically that is not a significant cause for total glass wt% concentrations differing significantly from 100 wt%. The primary cause is analytical imprecision in measured glass component concentrations, with percent relative standard deviations ranging from 3 - 5% to more than 100% depending on the wt% concentration of the glass component and the analytical method. Also, glass preparation or analytical biases can occur that cause biased wt% concentrations for one or more components. One or more biased component wt% concentrations can cause the total wt% concentration for a glass to differ significantly from 100 wt%. This report describes adjustment methods, such as blank and bias corrections, for some of these analytical problems.

Samples can be taken from glass or from slurries prior to melting, but in either case it is reasonable to transform analytical results to glass oxide wt%. The transformation is straightforward for glass samples. For slurries the transformation is to the glass oxide wt% expected in the product glass after melting. The impact of the melting process on particular constituents, which is well known, needs to be included in the transformation. This report assumes that such an appropriate transformation has been made on analytical results for slurries. Throughout the report the term glass sample is used, but it is intended to represent either glass or slurry samples.

Property-composition models are mathematical functions that relate glass composition to glass properties (e.g., chemical durability according to a specified leach test). Property-composition models can be used to predict glass property values for glass compositions. Mixture experiment models (Cornell 2002) are widely used as all or part of glass property-composition model forms. Mixture models require that weight fractions of glass components in the model sum to 1.0 (or wt% to 100%). Because chemical analyses of glass compositions typically will not satisfy this constraint, a normalization procedure is needed to impose this constraint on the vector of measured wt% concentrations. This report describes a normalization procedure for chemical analyses of samples. However, normalization is only appropriate after first assessing and correcting any biases in analyzed glass compositions. Generally, property-composition models are developed using target compositions that automatically sum to 100%. If instead analyzed glass compositions are used to develop models, the same adjustment and normalization steps should be performed on them as well.

A sampling event may include replicate analyses of multiple samples taken from a given container (e.g., process vessel, canister of glass, or laboratory crucible of glass). The method in this report is to normalize each individual replicate analysis of each replicate sample, after first performing data screening

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[1] The term "glass sample" is used to refer to any process sample (e.g., melter feed sample), product sample (e.g., glass shard sample), laboratory crucible sample, or melter test sample that is chemically analyzed to yield a glass composition estimate.

[2] Glass components are typically expressed as oxides (e.g., boron oxide, B_2O_3) or halogens (e.g., fluorine, F).

and bias correction steps. Property-composition models can then be applied to each individually normalized composition, yielding an individual property prediction for each replicate analysis of each replicate sample. A sampling event will thus generate replicate property predictions for the replicate chemical analyses of each of the replicate samples. Individually normalized glass compositions and resulting individual property predictions can then be used for several WTP purposes. These purposes include: (1) waste form qualification activities prior to IHLW or ILAW production, and (2) process control, monitoring, and compliance activities during IHLW or ILAW production.

Replicate chemical analyses of replicate samples from a given sampling event could potentially be grouped into one or more analytical laboratory batches, each of which includes Quality Control (QC) samples and Certified Reference Material (CRM) samples. This added sample information can be used for composition adjustment steps, such as blank correction or bias correction. Therefore, these composition adjustment steps would need to be performed for an entire laboratory batch prior to the normalization of the resulting individual glass composition vectors.

This report presents the results of initial work to develop a procedure for performing glass composition adjustments (if needed) and normalizations on analyzed glass compositions. The procedure includes the following features:

- data screening
- non-detect replacement
- blank correction
- bias detection and correction (if needed)
- normalization of analyzed (and corrected, if needed) glass compositions

This report gives specific methods and formulas for blank correction, bias correction, and normalization. Specific methods for data screening and non-detect replacement will be addressed elsewhere.

Steps of the procedure implementing these features and the corresponding equations are presented in the report. Discussions of the options considered and equation derivations are presented in Appendices. The normalization approach is based on minimizing the sum of the weighted, squared differences between the analyzed glass component concentrations (after any needed blank or bias corrections) and the normalized concentrations. Different weighting schemes were considered within this weighted least squares (WLS) normalization approach. Weights equal to the variances of the glass wt% concentrations are recommended.

The procedure requires well-established prior estimates of analytical percent relative standard deviations (%RSDs) for each detected component in blank, CRM, and unknown glass samples. It also requires well-established prior estimates of sampling %RSDs for each detected component in unknown glass samples. These prior estimates must be based on sufficient data or experience to be well determined. The sampling %RSDs will depend on the way in which samples are obtained (e.g., crucible glass samples, melter test samples, WTP melter feed samples, WTP product samples). The analytical %RSDs will depend on the analytical preparations and instruments used, nonradioactive versus radioactive environment, and other factors. It is envisioned that analytical and sampling %RSDs applicable to the WTP IHLW and ILAW vitrification plants and analytical facilities will be estimated by statistical analyses of statistically designed studies as part of the qualification activities.

The report includes a realistic example that illustrates the application of each of the steps of the adjustment and normalization procedure for analyzed glass compositions. The example illustrates how the procedure improves an analyzed glass composition by performing blank corrections, bias corrections, and normalization to adjust for analytical problems, as well as reduce the standard deviations of the blank/bias-corrected component concentrations.

The procedure for adjusting (blank and bias corrections) and normalizing analyzed glass compositions presented in this report may require fine-tuning as experience is obtained in applying it to analyzed glass compositions. For example, the procedure should be applied to chemical analyses of many crucible and melter test glasses (for both IHLW and ILAW glasses) where the target compositions are known. Such experience with the procedure may suggest modifications or enhancements that could be documented in a future revision of this report. Also, detailed procedures for screening outlying data must be developed in the future that could then be documented in a revision of this report.

Acknowledgments

This work and report were conducted to satisfy FY2001 and FY2002 scope under the Statistics Task of the Waste Treatment Plant Support Project at Battelle, Pacific Northwest Division. The work was performed in accordance with the following Waste Treatment Plant project documents:

- Technical Scoping Statement B-72
- Test Specification 24590-WTP-TSP-RT-01-002, Rev. 0
- Test Plan 24590-WTP-TP-RT-01-003, Rev. 0 (Battelle Test Plan TP-RPP-WTP-097, Rev. 0).

The work was specifically identified as Subtask 2 in the Test Plan.

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Quality Assurance

The work and results in this report were performed according to the project Quality Assurance (QA) plan (Battelle 2001) and QA manual and procedures (Battelle 2002). Most of the work was method development, so QA procedures applicable for such work were applied. Calculations associated with illustrative examples are not quality-affecting, so associated QA procedures (e.g., calculation and software control) were not applied. In summary, all QA requirements have been satisfied for the methods described in this report to be used in IHLW or ILAW quality-affecting activities.

Acronyms, Terms, and Abbreviations

ARG-1	Analytical Reference Glass-1
B_i	The wt% concentration of glass component (e.g., oxide) "i" in a quality control blank test. Typically such results would be expressed in terms of wt% elemental concentrations instead of wt% glass component concentrations. However, the latter simplifies the computations and yields the same eventual result for an adjusted and normalized glass composition.
BNI	Bechtel National, Inc.
CHG	CH2MHill Hanford Group, Inc.
CRM	Certified Reference Material
CRV	Concentrate Receipt Vessel (in the IHLW or ILAW vitrification facility)
DL	Detection Limit
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
PW	Pretreated waste
GFC	Glass former chemicals
g_{ijk}	Adjusted (blank corrected and/or bias corrected) analyzed weight percent of the i^{th} glass component for the k^{th} replicate analysis of the j^{th} glass sample
g_{ijk}^{*}	Normalized version of analyzed (blank corrected and/or bias corrected as needed) weight percent of the i^{th} glass component for the k^{th} replicate analysis of the j^{th} glass sample.
Glass sample	The term "glass sample" refers to any process sample (e.g., melter feed sample), product sample (e.g., glass shard sample), laboratory crucible sample, or melter test sample that is chemically analyzed to yield a glass composition estimate.
HLW	High Level Waste
IHLW	Immobilized High Level Waste
ILAW	Immobilized Low Activity Waste

LAW	Low Activity Waste
MFPV	Melter Feed Preparation Vessel (in the IHLW or ILAW vitrification facility)
MFV	Melter Feed Vessel (in the IHLW or ILAW vitrification facility)
NA	Not analyzed
ND	Not detected (or non-detect)
PCT	Product Consistency Test
PSWP	Products and Secondary Wastes Plan
p_{Ai}	Analytical relative standard deviation (RSD) for the wt% concentration of the i^{th} glass component in an unknown glass sample
p_{Si}	Sampling relative standard deviation (RSD) for the wt% concentration of the i^{th} glass component in an unknown glass sample
p_{Bi}	Analytical relative standard deviation (RSD) for the wt% concentration of the i^{th} glass component in a blank sample. It is more natural to express blank results and uncertainties in terms of elements rather than glass components (e.g., oxide components). However, the latter simplifies the discussion and provides the same eventual results.
p_{Ci}	Analytical relative standard deviation (RSD) for the wt% concentration of the i^{th} glass component in a certified reference material
QA	Quality Assurance
QC	Quality Control
QL	Quantitation Limit
RR7	Round Robin 7
RSD	Relative standard deviation, for example, p_{Ai} or p_{Si}
%RSD	Percent relative standard deviation
SD	Standard deviation

σ_{Ai}	Analytical standard deviation for the wt% concentration of the i^{th} glass component in an unknown glass sample
σ_{Si}	Sampling standard deviation for the wt% concentration of the i^{th} glass component in an unknown glass sample
σ_{Ci}	Combined sampling and analytical standard deviation for the wt% concentration of the i^{th} glass component in the CRM
σ_{Ti}	Standard deviation for the certified, nominal glass wt% concentration of the i^{th} glass component in the CRM
σ_{Ti*}	Standard deviation for the normalized version of the certified, nominal glass wt% concentration of the i^{th} glass component in the CRM
T_i	Certified, nominal wt% concentration of the i^{th} glass component in the CRM
T_i^*	Certified, nominal wt% concentration of the i^{th} glass component in the CRM, normalized to sum to 100 wt%.
WAPS	Waste Acceptance Product Specifications
WCP	Waste Compliance Plan
WLS	Weighted least squares
WTP	Waste Treatment Plant
wt%	Weight percent
WVDP	West Valley Demonstration Project
WVRG-6	West Valley Reference Glass-6
x_{ijk}	Analyzed weight percent of i^{th} glass component for k^{th} replicate analysis of j^{th} glass sample

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1.0 Introduction

Various process samples, chemical analyses, and measurements will be required to control Waste Treatment Plant (WTP) vitrification facilities that will produce Immobilized High Level Waste (IHLW) and Immobilized Low Activity Waste (ILAW). In addition, process and/or product samples, chemical analyses, and measurements will be required to satisfy applicable compliance requirements. For example, the Waste Acceptance Product Specifications (WAPS) describe various compliance requirements for IHLW (USDOE 1996). Also, the contract between the Department of Energy (DOE) and Bechtel National, Inc. (BNI 2001) specifies compliance requirements for ILAW, as well as additional compliance requirements for IHLW.

Although the process-product control and compliance strategies are still under development, many aspects have been determined. The current compliance strategies for the WTP are given in the Waste Compliance Plan (WCP, CHG 2001a) and the Products and Secondary Wastes Plan (PSWP, BNI 2002). Many of the compliance strategies outlined in the WCP and PSWP are statistical in nature. That is, the strategies involve quantifying and accounting for variations and uncertainties in controlling the IHLW and ILAW vitrification processes and in satisfying compliance requirements. Statistically based strategies will be developed for pre-production (that is, qualification) activities, as well as for production and acceptance activities. Strategies for environmental regulatory compliance (e.g., plant emissions, or complying with Land Disposal Restriction (LDR) and de-listing criteria) are described in the delisting/LDR data quality objectives document (BNI 2001). These strategies will also be statistically based.

Several aspects of the WTP qualification, process-product control, and compliance strategies require estimates of glass compositions and their uncertainties. During WTP qualification activities, glass composition estimates may be required for non-radioactive and radioactive glasses made in crucibles and non-radioactive glasses made in melter tests. During WTP operation, IHLW and ILAW composition estimates will be based on process (e.g., melter feed) or product (e.g., glass shard) samples, depending on the aspect of the IHLW or ILAW process-product control or compliance strategy being addressed. Glass composition estimates will be used directly, as well as indirectly through property-composition models, to implement the required qualification, process-product control, compliance, and reporting requirements for IHLW and ILAW.

Chemical analyses of glass samples generally do not yield component weight percent (wt%) concentrations that sum to 100 wt%. Not analyzing (NA) and/or not detecting (ND) some components present in glass above detection limits can contribute to this. However, this report assumes that chemical analyses are performed for all components present in a glass at detectable concentrations. Non-detection of minor glass components typically contributes little to differences from 100 wt%. The main reasons total wt% concentrations differ from 100 wt% are:

- Glass preparation or analytical biases that cause biased wt% concentrations for one or more glass components
- Imprecision in analyzed glass wt% concentrations, with percent relative standard deviations (%RSD) ranging from 3-5% to over 100%.

Biases can also occur in collecting process or product samples. For example, a problem with a melter feed sampler could result in samples that under-represent the solid fraction and over-represent the liquid fraction of melter feed. However, such sampling biases cannot be addressed by the methods described in this report, which focus on addressing biases and imprecision in analytical measurements.

Property-composition models are mathematical functions that relate glass composition to glass properties. For example, a property of considerable interest is the chemical durability of glass based on the Product Consistency Test (PCT) (ASTM 1997). Property-composition models can be used to predict glass property values for glass compositions. Mixture experiment models (Cornell 2002) are widely used as all or part of glass property-composition model forms. Mixture models require the weight fractions of glass components in the model sum to 1.0 (equivalently, wt% must sum to 100%). Because chemical analyses of glass samples typically will not satisfy this constraint, a normalization procedure is needed to impose this constraint on the measured glass composition. This report describes a normalization procedure for chemical analyses of samples associated with a particular sampling event. However, any needed adjustments to analyzed glass compositions (e.g., blank or bias corrections) must be performed before normalization. Otherwise, the normalization process could induce biases in unbiased analyzed wt% concentrations.

Discussion with personnel from the West Valley Demonstration Project (WVDP) and Defense Waste Processing Facility (DWPF) sites revealed that neither site uses mixture models for qualification, compliance, or process control criteria. Instead they use somewhat simpler regression models that do not require glass component wt%'s to sum to 100%. Therefore, a normalization step is not required or used at DWPF or WVDP. However, DWPF and WVDP do take steps to minimize the likelihood of measurement, uncertainties, sampling uncertainties, or biases causing decision errors regarding product compliance. At DWPF the total wt% of the component vector is required to be between 95% and 105%. At WVDP, the usual QC percent recovery requirement on analytical spikes is increased from the more commonly used “within 80% to 120%” to “within 90% to 110%”. The data adjustment and normalization steps in this report are more rigorous and make use of additional information. Recall that normalization is required due to the use of mixture models.

A sampling event may include replicate analyses of multiple samples taken from a given container (e.g., IHLW or ILAW process vessel, IHLW or ILAW canister of glass, laboratory crucible of glass, or drum/canister from melter testing). The method in this report is to normalize each individual replicate analysis of each replicate sample, after data screening and bias correction steps. Property-composition models can be applied to each individually normalized composition, yielding an individual property prediction for each replicate analysis of each replicate sample. A sampling event will thus generate replicate property predictions for the replicate chemical analyses of each of the replicate samples. Individually normalized glass compositions and resulting individual property predictions can then be used for several WTP purposes. These purposes include: (1) waste form qualification activities prior to IHLW or ILAW production, and (2) process control, monitoring, and (3) compliance activities during IHLW or ILAW production.

Chemical analyses of samples from a given sampling event may be grouped into one or more analytical laboratory batches that include Quality Control (QC) samples and Certified Reference Material (CRM) samples. The main QC sample of interest in this report is a blank sample. A CRM is a material that has been carefully produced in a large, homogeneous quantity and assigned a certified nominal concentration for each glass component, as well as a standard deviation for the nominal concentration of each component. The term “certified” typically means that a highly qualified and accurate reference laboratory performs replicate analyses of replicate samples of the reference material, which are then statistically summarized to yield the nominal (usually average) concentrations and standard deviations of nominal concentrations. Note that slurry CRM should be used for slurry samples and glass CRM for glass samples. The QC and CRM sample information can be used for composition adjustment steps, such as blank correction or bias correction.

This report presents the results of initial work to develop a procedure for performing any needed adjustments (blank and/or bias corrections) and normalizations on analyzed glass compositions. It does not address specific screening methods or particular non-detect replacement strategies. The remaining sections cover the following topics. Section 2 provides a general overview of the IHLW and ILAW vitrification processes, summarizes possible needs for glass composition estimates, and describes the objectives for adjusting and normalizing analyzed glass compositions. Section 3 describes the steps of the procedure for adjusting and normalizing analyzed glass compositions. Equations for implementing the steps and calculating the uncertainties of glass composition estimates are also provided in Section 3. Section 4 includes a realistic example that illustrates the application of each of the steps of the adjustment and normalization procedure for analyzed glass compositions. Section 5 provides conclusions and recommendations, and Section 6 lists cited references. The appendices provide additional details and discussion of the steps of the procedure for adjusting and normalizing analyzed glass compositions.

2.0 Justification and Objectives for a Procedure on Analyzed Glass Compositions

Section 2.1 provides a general overview of the IHLW and ILAW vitrification processes and introduces the generic terms used to refer to IHLW and ILAW process vessels and other process steps. Section 2.2 summarizes the various WTP qualification, process control, and compliance activities where estimates of glass compositions or their uncertainties will be needed. Section 2.3 describes the objectives for the procedure to: (1) adjust and normalize chemical analyses of glass samples, and (2) quantify the uncertainties in the resulting normalized compositions.

2.1 IHLW and ILAW Vitrification Processes

This report focuses on developing the steps of a procedure to adjust and normalize analyzed glass compositions. To better understand the procedure and its application, the reader should review the Section 2.2 discussion and illustration of the IHLW and ILAW vitrification processes and where glass composition estimates will be needed.

Figure 2.1 presents a generic and simplified overview of the IHLW and ILAW vitrification processes. The purpose of the figure is to illustrate the key process vessels, the glass former chemicals system, the melter, and possible sampling and measurement points.

Sampling points being considered by the WTP Project for process-product control and compliance strategies (indicated by a circled S in Figure 2.1) include: pretreated waste (PW), Concentrate Receipt Vessel (CRV), glass former chemicals (GFC), Melter Feed Preparation Vessel (MFPV), Melter Feed Vessel (MFV), and canisters of glass (subsequent to pouring from the melter and cooling). Sampling and chemical analyses are planned to verify the PW is acceptable for transfer to the vitrification facility (IHLW or ILAW). Similarly, individual GFCs may be sampled and chemically analyzed to verify their compositions before use in the vitrification facilities.

Level and/or volume measurements will be made in the CRV, MFPV, and MFV (indicated by a diamond-enclosed L in Figure 2.1). Such measurements are important for estimating compositions, and in verifying transfers to and from the MFPV, MFV, and other process vessels.

Weight measurements will be used to determine appropriate quantities of individual GFCs to add to waste feed concentrates in the MFPV. As indicated by a diamond-enclosed W in Figure 2.1, weights of individual GFCs will be determined, as well as weights of combined GFCs in the GFC Batch Makeup Hopper and the GFC Feed Hopper. Multiple weighing points provide for verifying transfers of individual and combined GFCs.

The possible sampling and measurement points in the IHLW and ILAW vitrification processes shown in Figure 2.1 are not intended to present a comprehensive list of all possible sampling or measurement points that may be used for process-product control or specification compliance. As the WTP Project progresses in developing and finalizing IHLW and ILAW process-product control and compliance strategies, sampling and measurement points may be added or deleted.

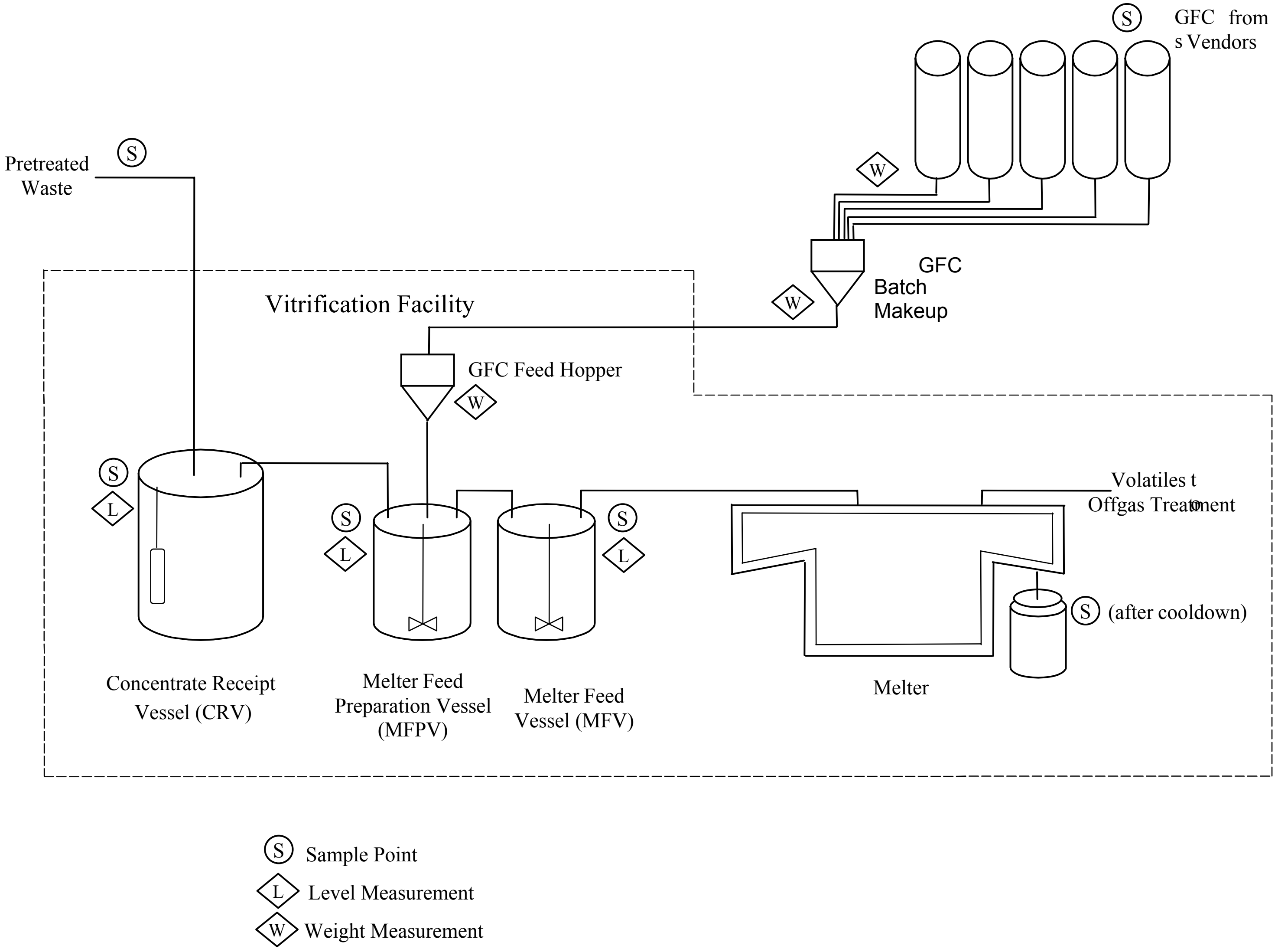

Figure 2.1. General View of the IHLW and ILAW Vitrification Processes

2.2 Justification for a Procedure on Analyzed Glass Compositions

Table 2.1 lists several IHLW and ILAW qualification, process control, and compliance activities that require or must produce glass composition estimates and their uncertainties based on chemical analyses of glass samples.[1] General descriptions of these activities are listed in Table 2.1, with WAPS or Contract specifications referenced, if appropriate.

Table 2.1. Activities Related to Possible WTP Needs for Glass Composition Estimates Based on Chemical Analyses of Samples

	Specification Number (if applicable)	
Activity Related to Glass Compositions and Composition Uncertainties	**WAPS**	**Contract**
Verify compositions of nonradioactive or radioactive crucible glasses	1.1.1	2.2.2.6.1
Verify compositions of radioactive glasses made from pretreated tank waste samples	1.1.1	2.2.2.6.1
Verify compositions of glass made from melter tests	1.1.1	2.2.2.6.1
Report chemical composition in production records	1.1.2	2.2.2.6.2
Demonstrate canistered glass is homogeneous & shard samples representative	1.1.2	2.2.2.6.2
Demonstrate that glass composition can be controlled using process samples	1.1.2	2.2.2.6.2
Quantify uncertainties in analyzing and reporting glass compositions	1.1.2	2.2.2.6.2
Report radionuclide composition in production records	1.2.2	2.2.2.7.2
Demonstrate leach test compliance using property-composition models (a)	1.3	2.2.2.17.2 2.2.2.17.3
Demonstrate compliance with dangerous waste requirements (e.g., using toxicity characteristic leaching procedure (TCLP)-composition models) (a)	1.5	1.2.2.1.5, 2.2.2.20
Report U and Pu content	1.6	NR
Demonstrate compliance with heat generation requirements (b)	3.8.2	NR
Demonstrate compliance with dose rate requirements (b)	3.9.2	2.2.2.9
Demonstrate compliance with radionuclide limits	3.14	2.2.2.8
Demonstrate compliance with waste loading requirements	NR	1.2.2.1.6, 2.2.2.2

(a) Property-composition models will be used for these and other purposes. Sufficiently accurate and precise glass composition estimates are needed for property-composition models to yield sufficiently accurate and precise property predictions.
(b) Software for calculating heat generation and dose rates will depend on estimates of glass and radionuclide composition.
NR = Not Required

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[1] The generic term "glass sample" is used to refer to any sample that leads to an estimate of glass composition (e.g., glass from laboratory crucible studies, glass from melter tests, process samples (e.g., melter feed samples from the MFPV or MFV), and IHLW or ILAW product samples).

2.3 Objectives for Glass Composition Adjustment and Normalization

Five general objectives for the treatment of analyzed glass compositions prior to reporting are described as follows. As discussed in more detail in Section 3.1, data are assumed expressed as wt% concentrations of glass components.

A. Data Screening. This objective is to screen for outlying or unacceptable analytical results. The first aspect of the objective is to decide whether any analyzed glass wt% concentrations are unacceptably different from other concentrations for the same glass component in the same sampling event. This aspect of the objective applies to glass samples and to CRM samples. The second aspect of the objective is to determine if the total wt% concentration over all of the glass components is too different from 100% for a particular CRM sample or glass sample. This determination should be made for CRM samples before any blank corrections are made and for glass samples after any blank and/or bias corrections have been made. Analyzed glass compositions with unacceptable values of total wt% concentration should be discarded.

B. Non-detect Replacement. This objective is to replace analytical concentrations reported only as being less than an associated detection limit (DL). Replacement values are needed so the normalization step can be completed. Ideally, DLs are sufficiently small so the particular replacement approach has little impact on the estimated glass composition (or property-composition model predictions based on the estimated glass composition) obtained after subsequent procedure steps are implemented. Future investigations are recommended to determine whether non-detect replacement should be performed, and if so, to demonstrate the insensitivity to non-detect replacement methods.

C. Blank Correction. This objective is to perform blank correction of CRM and glass wt% concentrations if associated QC blank results are found to be greater than the DL. Blank correction impacts the uncertainty associated with the resulting blank-corrected concentrations.

D. Bias Correction. This objective is to determine if analyzed glass wt% concentrations of CRM samples are statistically different from the corresponding certified glass wt% concentrations. If so, the same bias is assumed to impact the glass sample results, and appropriate bias correction (discussed subsequently in the report) is performed. Bias correction impacts the uncertainty associated with the resulting bias-corrected concentrations.

E. Normalization. This objective is to modify vectors of analyzed (and blank and/or bias corrected, if needed) wt % concentrations of glass components in an optimal manner so the resultant vector of wt % concentrations is minimally changed, but sums to 100%. Note the set of measured wt% concentrations for the various glass components for an analyzed sample is called a “vector” throughout the remainder of this report. The components of such a vector should sum to 100 wt%, and if not, normalization of the vector components to sum to 100 wt% is the ultimate objective.

These objectives are concerned with the status at a given point (e.g., in the IHLW or ILAW process) at a given time (that is, for a given sampling event). Estimated glass compositions and property-composition model predictions based on analyzed glass compositions at various process steps and times will be combined to address the status of the IHLW or ILAW process over a period of time. Thus, normalization and the steps that precede it need consider only the analytical results obtained at a given point and time. Observed differences within the given process step and given time (i.e., a sampling event) are due to sampling and analytical uncertainty. Differences over time or throughout the process are due to the inherent variability in the waste or it’s processing. As stated, such differences are not considered in this report. Rather they would be considered in the data analysis of glass composition estimates, or property-composition model predictions made from glass composition estimates, over a defined processing period.

3.0 Adjustment and Normalization Steps for Analyzed Glass Compositions

This section presents the statistical methods and formulas for adjusting and normalizing a vector of wt% concentrations of glass components. Typically glass components are expressed as oxides (e.g., SiO_2 and Al_2O_3) or halogens (e.g., F and Cl). In the discussions that follow, the technical details referred to are in Appendices A and B.

3.1 Data Structure and Uncertainties

For analytical determinations of glass wt% concentrations, several glass samples (which could involve replicate analyses of replicate samples at a given sampling event) will be processed together in an analytical laboratory batch along with required QC samples and CRM samples. Therefore, the same blank correction and/or bias correction (which will be based on the QC samples and/or CRM samples as described in the following discussion) will be performed on all the glass samples in the laboratory batch.

Each chemical analysis of a sample (QC blank, CRM, or glass) will generate a vector of measured concentrations. Although the analytical results may be reported initially as elemental wt% concentrations, for this work it is assumed that all results are expressed ultimately as wt% concentrations of glass components (typically oxides or halogens). Expressing analyzed compositions as glass wt% concentrations is very natural for CRM or unknown glass samples, but not for QC blank samples (which are not glasses). However, it is computationally simpler to perform all of the glass composition adjustment and normalization calculations using glass wt% concentrations (even for QC blank samples). Also, the results are the same as when blank corrections are performed using elemental wt% concentrations, and then the remaining calculations are performed using glass wt% concentrations. Appendix A discusses the conversion from elemental wt% concentrations to glass wt% concentrations.

A completely rigorous approach to normalizing a glass composition would consider the sampling and chemical analysis covariance structures for wt% concentrations of glass components. However, estimating the needed sampling and analysis covariances would require substantial experimental effort, which is unlikely to be performed for the WTP Project. Therefore normalization methods proposed here for vectors of glass component wt% concentrations use only the sampling and analysis uncertainties (i.e., standard deviations or relative standard deviations) for individual components. These standard deviations (SDs) or relative standard deviations (RSDs) will be estimated as part of future WTP Project work. Hence, for purposes of developing the methods presented in this report, the SDs and RSDs are assumed known or previously estimated. The adjustment and normalization steps in the following discussion are applied for each glass component individually with the subscript "*i*" denoting the component.

3.1.1 Data Structure for Unknown Glass Samples

From a given sampling event, assume *m* glass samples are to be analyzed with *r* replicated analyses of each. The resulting data for each glass component "*i*", $i = 1, 2, \dots, q$, are denoted x_{ijk}, $j = 1, 2, \dots, m$ and $k = 1, 2, \dots, r$. For each glass component "*i*" and general *m* and *r*, this provides the data structure:

$$\begin{array}{c} x_{i11}, x_{i12}, \ldots x_{i1r} \\ x_{i21}, x_{i22}, \ldots x_{i2r} \\ . \\ . \\ x_{im1}, x_{im2}, \ldots x_{imr} \end{array} \qquad (3.1)$$

It is assumed the x_{ijk} resulting from chemical analyses are expressed as (or converted to) glass wt% concentrations. Equation (A.1) of Appendix A addresses the conversion of elemental wt% concentrations to glass wt% concentrations.

A row in Equation (3.1) represents the r replicated analyses of glass component "i" based on the j^{th} sample ($j = 1, 2, \ldots, m$). Variation within a row is due to analytical preparation and measurement uncertainties. In this work, it is assumed the analytical relative standard deviation (RSD, denoted by p_{Ai})[1] for each glass component "i" and its analytical method is known or has been previously estimated[2]. The convention of using known RSD for each glass component is assumed throughout the discussion in this report. However, the RSD approach is not essential, and similar methodology can be applied using absolute standard deviations (SDs). In this report, analytical SDs are calculated from analytical RSDs as $\sigma_{Aijk} = p_{Ai} x_{ijk}$.

Variation between the rows in Equation (3.1) would include analytical uncertainty and also be due to differences in the replicate samples from a given sampling event (for example, due to non-homogeneity in the sampled material and/or due to variations related to the sampling device). Generally this "sampling uncertainty" would be expected to be minimal as long as well-mixed material is sampled and the sampling device introduces only minimal uncertainty.[3] This source of uncertainty will be represented for glass component "i" by the sampling standard deviation σ_{Si}. The sampling and analytical standard deviations could be estimated using production samples by performing multiple chemical analyses of multiple samples and estimating the standard deviations using variance component estimation methods. However, this work assumes such studies have been conducted with sampling and analytical uncertainties established as part of qualification activities. The sampling RSD denoted p_{Si} is assumed known for each glass component "i" and material type/sampling situation.[4] In this report, sampling SDs are calculated from sampling RSDs as $\sigma_{Sijk} = p_{Si} x_{ijk}$.

Generally, all samples for a given sampling event will be analyzed in a common analytical laboratory batch involving only a single calibration of associated instrumentation and a single set of QC samples and CRM samples. If the samples from a sampling event are split among separate analytical laboratory batches, each resulting subset would be treated as described in the subsequent composition adjustment and normalization steps.

3.1.2 Data Structure for CRM and Blank Samples

Samples of a CRM will be included in analytical batches to enable detection of biases that occur in analytical preparation and measurement. The CRM will have certified, nominal glass wt% concentrations (denoted T_i, $i = 1, 2, \ldots, q$) and standard deviations of these nominal wt% concentrations (denoted σ_{Ti}, $i = 1, 2, \ldots, q$). The glass components composing the CRM may be only a subset of the q components

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[1] Note that RSD = %RSD/100.

[2] The WTP Project has planned activities to estimate analytical uncertainties that would then be used as described in this report.

[3] It is also assumed the sampling device collects a representative (unbiased) sample of the material. The procedure discussed in this report can correct only for analytical preparation or instrument biases affecting both CRM and unknown glass samples—it cannot correct for biased glass samples.

[4] The WTP Project has planned activities to estimate sampling uncertainties for process sampling and for glass shard sampling. These glass-component sampling uncertainties would be used as described in this report, depending on whether glass compositions are being determined for process sampling or glass shard sampling. Similarly, if sampling uncertainty is an issue for glass samples from crucible studies or melter tests, glass-component sampling uncertainties would be estimated and used as described in the report.

analyzed for an unknown glass. For those components not in the CRM, the associated values T_i and σ_{Ti} are zero. The bias detection using CRM results, and potentially the resulting bias correction of the glass sample results, obviously cannot be performed for such zero CRM components. Note, however, between the CRM and unknown glass samples the major components and often many minor components1 should be the same. Hence, bias detection and correction should be possible for the major components and many minor components.

The assumption is that certified, nominal CRM wt% concentrations include values for all components in the CRM and sum to 100 wt% ($\sum_{i=1}^{q} T_i = 100$). Suppose the sum has a small difference from 100 wt% due to random analytical errors in the certified, nominal composition. Then, the nominal composition (T_1, T_2, … , T_q) can be normalized using the normalization method presented in this report. The resulting normalized, nominal composition (T_1^*, T_2^*, … , T_q^*) then has $\sum_{i=1}^{q} T_i^* = 100$, and T_i^* would be used in place of T_i in formulas in this report.

Each analytical batch is to contain u samples of the CRM, each chemically analyzed once. The CRM is assumed homogeneous with minimal sampling uncertainty, so single measurements of each of the u samples are sufficient for purposes of bias detection and correction. The u wt% concentrations for CRM component "i" are represented by c_{ij}, $j = 1, 2, \ldots, u$. The variation among measurements of component "i" from CRM samples is assumed to have a known standard deviation $\sigma_{Ci} = p_{Ci}T_i$, where p_{Ci} is the RSD for measuring the i^{th} component in the CRM. The CRM analytical results will be used for bias detection and for bias correction, if needed.

Included in the analytical batch QC samples is a blank sample (i.e., de-ionized water), so that blank corrections are possible. If blank correction is necessary for a particular glass component, it is performed on all CRM and glass sample results (for that component) in the analytical batch. The result of a blank analysis for glass component "i" is denoted B_i, with RSD denoted p_{Bi}. This RSD would be based on previous studies of replicated analyses of blanks. Then, the absolute SD for a blank result can be calculated as $\sigma_{Bi} = p_{Bi}B_i$.

3.2 Adjustment and Normalization Steps for Analyzed Glass Compositions

The specific steps of the procedure to adjust and normalize analyzed glass compositions are shown in the decision tree displayed in Figure 3.1. The top portion of this decision tree displays Steps C1 to C3 for working with analytical results on the CRM and QC samples. The bottom portion displays Steps S1 to S5 for adjusting and normalizing the analytical results on the glass sample(s). The procedure steps in Figure 3.1 are performed within each analytical batch with the exception of outlier screening, which could be performed across multiple analytical batches from the same sampling event. Except for Step S5 and parts of Steps C1 and S4, all steps work with one glass component at a time.

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[1] The "major" components should include those: (i) identified as reportable in IHLW or ILAW specifications, or (ii) having significant effects on glass properties and are included in property-composition models. CRMs usually contain several minor components in order to be more representative of waste glasses.

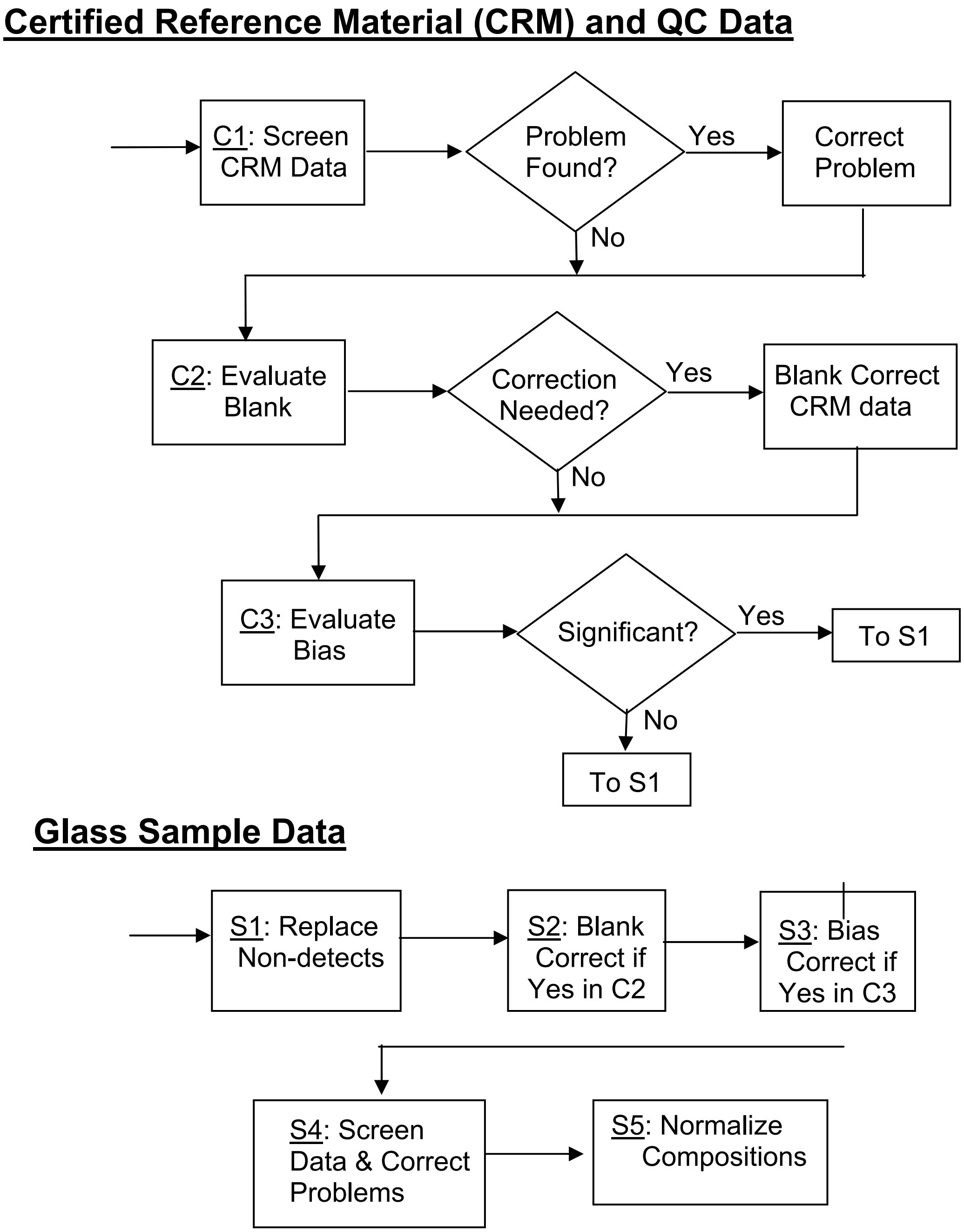

Figure 3.1. Adjustment and Normalization Steps for Analyzed Glass Compositions

The assumption is that all components present in CRM and glass samples are analyzed using one or more analytical methods. That is, no "not analyzed" (NA) results appear. However, "not detected" (ND) results may be present. If NA results are found for components that comprise more than a negligible fraction of a glass, a procedure step could be added that replaces NA results with target, nominal, or other estimated values for the unanalyzed glass components. Such a step was considered beyond the scope of the current procedure, but could be added in future work.

The remainder of this section gives a brief narrative description of the procedure steps. Specific computational steps and formulas are provided in Section 3.3. Where needed, additional discussion (including potential alternative approaches for particular steps) is given in Appendix A.

3.2.1 CRM/QC Sample Data

Note that all CRM data analysis steps described in the following material are performed within particular analytical batches.

Step C1: Screen CRM Data – This step has two objectives:

- Screen the CRM glass wt% concentrations $c_{ij}, j = 1, 2, \ldots, u$ for inappropriate outlying values. Specific methods for screening outliers are not given here because it may not be advisable for this step to be "automated" within software. Similarly, specific recommendations for replacement values for any deleted outliers are not given in this report. It is beyond the scope of the current work to develop automated outlier screening algorithms. However, possible approaches for outlier evaluation are described in Appendix A.
- Check whether the total of analyzed CRM glass wt% concentrations is within a specified amount of 100 wt%. CRM sample result vectors ($c_{1j}, c_{2j}, \ldots, c_{qj}$) with total glass component wt% concentrations too different from 100 wt% are rejected. While specific limits should be established relative to processing and compliance requirements, a ±10 wt% threshold is assumed here. Therefore, any CRM sample with glass wt% concentrations totaling less than 90% or greater than 110% is disallowed for use in subsequent steps. Should all CRM glass wt% vectors fail to meet this criteria, either bias correction cannot be completed, or the analytical batch must be re-analyzed.

Step C2: Evaluate Blank – Let DL_i denote the detection limit of the analytical method and QL_i the quantitation limit for glass component "i". Generally DL_i is a quantity, that when exceeded for a particular analyte i, the sample is considered to contain that analyte at a level greater than zero with high confidence. The QL_i, for an analyte is a level greater than which the analyte can similarly be detected, but while also meeting QC requirements on accuracy and precision (for example, percent recovery, closeness of primary/duplicate, etc.). If the blank result B_i exceeds QL_i, and under some conventions also exceeds a quantity such as 5% of an associated analyzed glass sample, the following would occur. The batch either would not be used, per QC requirements, or the results for the associated component would at a minimum be flagged for the batch.

If B_i is less than DL_i, no blank adjustment is made because no blank measured value is available, and the bias evaluation proceeds in Step C3. In cases where B_i is negative (e.g., due to background or other corrections in some measurement processes, no bias correction would be made. If B_i is greater than DL_i , it is subtracted from the mean CRM result for component "i". In addition, B_i will be subtracted in Step S2 from the glass sample results x_{ijk} for component "i" in the same analytical batch. Blank correction is done in absolute terms (i.e., by subtraction) rather than relative terms (by multiplication), because the nominal blank results are all zeros. If in fact the blank value exceeds an associated glass sample or CRM result, a negative value would result from a blank correction. In such a case, it is recommended the glass sample result be blank corrected to a zero value. In this case, additional QC evaluation is warranted and an elevated detection limit may be more appropriate for the analytical batch for the component of interest. Finally, we assume that DL_i, QL_i, and B_i are expressed as glass wt% concentrations, as discussed in the second paragraph of Section 3.1.

Step C3: Evaluate Bias – The overall mean (potentially blank-corrected) of the CRM results per glass component ($\bar{c}_i$ or $\bar{c}_i - B_i$) is statistically compared to the certified, nominal value of the CRM for that component (T_i, or T_i^* if it was necessary to normalize the T_i as discussed in Section 3.1.2). Whether or not this bias is statistically significant will determine if bias correction is to be performed in Step S3. For further discussion of "statistical significance" see text accompanying Equation (A.3) in Appendix A.

3.2.2 Glass Sample Data

Step S1: Replace Non-detects – Before a vector of glass wt% concentrations ($x_{1jk}, x_{2jk}, \ldots , x_{qjk}$) can be normalized to sum to 100 wt%, any values reported as less than the detection limit need to be replaced to avoid introducing bias in adjusting and normalizing analyzed glass compositions. Because the selection of particular replacement values is expected to have minimal impact on the normalized glass composition, a simple replacement of one-half the detection limit ($x_{ijk} = 0.5DL_i$) is recommended. Additional discussion of this topic is included in Appendix A.

Step S2: Blank Correct – If blank correction was performed in Step C2 on the CRM results from the same analytical batch, the same blank value B_i is subtracted from the glass wt% concentration for component "i" for each glass sample from the batch.

Step S3: Bias Correct – If the mean of analyzed wt% concentrations for a given CRM glass component is determined to have a statistically significant bias in Step C3, bias correction is performed for that component in all glass samples analyzed in the same analytical batch. The ratio of the CRM nominal value to the estimated bias for a given glass component is used in relative bias corrections.

Step S4: Screen Data – Before normalization proceeds, the set of $m \times r$ wt% concentrations for each glass component from the sampling event (possibly from different analytical batches) should be screened considering the same two objectives as in Step C1. These objectives are to screen for:

(i) outliers within each glass component across the sampling event
(ii) unacceptable total glass wt% concentrations across glass components within a particular sample vector.

Specific methods to screen outliers are not given in this report because it is not clear whether this step should be or will be "automated" within WTP software. Suggested approaches for outlier evaluation are described in Appendix A.

Regarding objective (i): complete analyzed glass compositions could be declared as outlying, or wt% concentrations for individual glass components could be declared as outlying. If a glass component outlier is removed, the associated vector of glass wt% concentrations for the particular replicate sample and analysis will be missing a value for use in the normalization. Therefore, a replacement value would be needed. If the extreme value is to be completely discounted as being a legitimate value, replacement by the component mean over the other samples and replications from the sampling event would be logical. If on the other hand the extreme value is thought to contain some useful information, while simply being too extreme, it could be replaced by a relatively large (or small) value. Since the outlying value that was omitted must have been either the maximum or minimum of the component wt% concentrations to which it was compared, the next largest or smallest (as appropriate) of the remaining wt% concentrations for that component could be used as a logical replacement value. In either case, the uncertainty assigned to the replaced value could be taken to be the same as the uncertainty of the value used for the replacement.

For objective (ii), recall Step C1 where CRM sample result vectors with total wt% concentrations outside the range of 90 wt% to 110 wt% were discarded. Similarly, glass sample result vectors with total wt% concentrations too different from 100 wt% are rejected. A stricter 5 wt% threshold is assumed for this portion of the procedure, because any needed blank and bias corrections already will have been made. Therefore, under these stricter constraints, any glass sample with resulting total wt% concentration less than 95 wt% or greater than 105 wt% would be disallowed for use in subsequent analyses. However, specific wt% acceptance limits should be established by the WTP Project based on what is expected to be achievable in WTP analytical facilities and relevant processing and compliance requirements.

Step S5: Normalize Compositions – For each adjusted glass composition wt% vector meeting the 95 wt% to 105 wt% criterion, normalization is performed. A weighted least squares (WLS) approach is recommended that minimizes the sum of squared differences between the un-normalized and normalized glass wt% concentrations, weighted by the variance of the un-normalized values. Two different computational approaches provide the same solution. Refer to Appendix A for a general discussion and to Appendix B for a more detailed derivation of the approaches. Uncertainty expressions for the final normalized values are provided in Section. 3.3. The derivations of the uncertainty expressions are discussed in Appendix B.

3.3 Computational Steps and Formulas for Adjusting and Normalizing Analyzed Glass Compositions

This section presents the computational steps and formulas for adjusting and normalizing analyzed glass compositions.

Step C1: Screen CRM Data – Perform the following:

- Reject outliers (See Appendix A for outlier detection discussion).
- Reject any CRM wt% concentration vector (c_{1j}, c_{2j}, … , c_{qj}) with total wt% concentration $\sum_{i=1}^{q} c_{ij}$ outside the specified acceptable range (90 wt% to 110 wt% is assumed for illustration purposes in this report).

Step C2: Evaluate Blank – If the blank value B_i for glass component "i" is less than the associated detection limit DL_i, no blank adjustment is made to either the CRM analyzed values ($c_{ij}, j = 1, 2, \ldots, u$) or the glass sample analyzed values ($x_{ijk}, j = 1, 2, \ldots, m; k = 1, 2, \ldots, r$) because no blank measured value is available. Otherwise, blank values $B_i > DL_i$ are used to make blank corrections as part of Step C3. See Step C2 of Section 3.2.1 for additional discussion.

Step C3: Evaluate Bias – For glass component "i", the CRM samples in an analytical batch have certified nominal wt% concentrations T_i, $i = 1, 2, \ldots, q$ with corresponding standard deviations σ_{T_i}, $i = 1, 2, \ldots, q$.[1] The analyzed CRM wt% concentrations are represented by c_{ij}, $i = 1, 2, \ldots, q$ and $j = 1, 2, \ldots, u$.

---

[1] If the CRM certified values T_i must be normalized as described in Section 3.1.2, then the normalized values T_i^*, $i = 1, 2, \ldots, q$ and their standard deviations σ_{T_i*}, $i = 1, 2, \ldots, q$ are used in this step (see Equations (3.13) and (3.14) for derivation of σ_{T_i*}),

Analytical SDs for CRM measurements are $\sigma_{Ci} = p_{Ci}T_i$, and for blank values B_i are $\sigma_{Bi} = p_{Bi}B_i$, where p_{Bi} and p_{Ci} are the established RSDs (e.g., during qualification activities). Note that B_i and σ_{Bi} are omitted in the following formulas if no blank correction is made. The average of the analyses of the CRM samples is

$$\bar{c}_i = \sum_{j=1}^{u} c_{ij} \; , i = 1, 2, \ldots, \mathrm{q} \, , \tag{3.2}$$

with standard deviation (sometimes referred to as *standard error*)

$$\sigma_{\bar{c}i} = \frac{\sigma_{Ci}}{\sqrt{u}} = \frac{(p_{Ci}T_i)}{\sqrt{u}} \, . \tag{3.3}$$

If outlier(s) have been removed in Step C1, the total number u of CRM analyses should be adjusted downward accordingly. Then, the chemical analyses of CRM samples for the related analytical batch have significant bias for glass component "i" if

$$\frac{\left|\bar{c}_i - B_i - T_i\right|}{\sqrt{\sigma_{\bar{c}i}^2 + \sigma_{Bi}^2 + \sigma_{Ti}^2}} > z_a \; , \tag{3.4}$$

where z_α is the 100(1-α)% percentile of the standard normal distribution. The use of z_α assumes the variances in the denominator of (3.4) are well established (see Appendix A for more discussion of this statement). Otherwise, glass component *"i"* has no statistically significant bias. In either case, proceed to Step S1.

Step S1: Replace Non-detects – Replace any glass sample wt% concentrations reported as "less than the detection limit" with one-half the detection limit, that is $x_{ijk} = 0.5 \; DL_i$. See Appendix A for discussion.

Step S2: Blank Correct – If blank correction was performed in Step C2 on the CRM results from the same analytical batch, the same blank value B_i is subtracted from each glass sample wt% concentration from the batch: $x_{ijk} - B_i, j = 1, 2, \ldots, m$ and $k = 1, 2, \ldots, r$. If no bias correction is needed according to Step C3, skip Step S3, and proceed to Step S4, using

$$g_{ijk} = x_{ijk} - B_i \tag{3.5a}$$

as the adjusted wt% concentration for the i^{th} glass component in the k^{th} chemical analysis of the j^{th} glass sample in the same analytical batch.

Step S3: Bias Correct – The blank and bias corrected wt% concentration for the i^{th} glass component in the k^{th} chemical analysis of the j^{th} glass sample is

$$g_{ijk} = (x_{ijk} - B_i)(\frac{T_i}{\bar{c}_i - B_i}) \tag{3.5b}$$

for each glass sample result from the analytical batch. The second factor in Equation (3.5b) is the bias correction factor. This factor is taken to be 1.0 for glass components that need no bias correction. Note the value B_i is omitted in Equations (3.5a) and (3.5b) if no blank correction was made in Step S2. Proceed to Step S4.

Step S4: Screen Glass Sample Data – Perform the following:

- Reject outliers (See Appendix A for outlier detection discussion).
- Reject any glass sample wt% concentration vector ($g_{1jk}, g_{2jk}, \ldots, g_{qjk}$) with total wt% concentration $\sum_{i=1}^{q} g_{ijk}$ outside the specified acceptable range (95 wt% to 105 wt% has been assumed for illustration purposes in this report).

Step S5: Normalize Compositions – After completing the previous steps for each glass component, the adjusted g_{ijk} wt% concentrations are available. The vector ($g_{1jk}, g_{2jk}, \ldots, g_{qjk}$) denotes an adjusted analyzed glass composition from the k^{th} replicate analysis of the j^{th} glass sample. The resulting normalized glass composition vector is denoted by

$$(g^*_{1jk}, g^*_{2jk}, \ldots, g^*_{qjk}), \tag{3.6}$$

where $\sum_{i=1}^{q} g^*_{ijk} = 100$. Let w_{ijk} be the variance of g_{ijk} denoted by σ^2_{gijk}. This variance expression will have one of several forms, as follows:

a) If g_{ijk} is not bias-corrected, then

$$w_{ijk} = \sigma^2_{gijk} = x^2_{ijk}(p^2_{Ai} + p^2_{Si}) + \sigma^2_{Bi} \ , \tag{3.7}$$

where p_{Ai} and p_{Si} are the analytical and sampling RSDs for the i^{th} glass component.

b) If g_{ijk} is bias-corrected, then

$$w_{ijk} = \sigma^2_{gijk} = \left[\frac{(x_{ijk} - B_i)T_i}{\bar{c}_i - B_i}\right]^2 \left[\frac{x^2_{ijk}(p^2_{Ai} + p^2_{Si}) + \sigma^2_{Bi}}{(x_{ijk} - B_i)^2} + \frac{\sigma^2_{Ti}}{T_i^2} + \frac{\sigma^2_{\bar{c}i} + \sigma^2_{Bi}}{(\bar{c}_i - B_i)^2} - \frac{2\sigma_{Bi}{}^2}{(x_{ijk} - B_i)(\bar{c}_i - B_i)}\right], \tag{3.8}$$

When no blank correction is made for glass component "*i*", Equations (3.7) and (3.8) reduce to

$$w_{ijk} = \sigma^2_{gijk} = x^2_{ijk}(p^2_{Ai} + p^2_{Si}) \tag{3.9}$$

and

$$w_{ijk} = \sigma^2_{gijk} = \left[\frac{x_{ijk}T_i}{\bar{c}_i}\right]^2 \left[p^2_{Ai} + p^2_{Si} + \frac{\sigma^2_{Ti}}{T_i^2} + \frac{\sigma^2_{\bar{c}i}}{\bar{c}_i{}^2}\right]. \tag{3.10}$$

Given the values of w_{ijk} in Equations (3.7), (3.8), (3.9), or (3.10), either of two computational approaches can be used for normalization. First, a constrained optimization routine (such as Solver in Microsoft Excel) readily gives the correctly constrained solution. Second, the following expression can be used (see derivation in Appendix B):

$$g_{ijk}^{*} = g_{ijk} + \frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}} \left[100 - \sum_{i=1}^{q} g_{ijk} \right], i = 1, 2, \ldots, q \tag{3.11}$$

If the solution in Equation (3.11) has $g_{ijk}^{*} < 0$ for some glass component(s) "*i*", the negative component(s) g_{ijk}^{*} are replaced by 0. Then, the remaining non-zero components g_{ijk}^{*} are renormalized using Equation (3.11) with only the associated values w_{ijk} as given in Equations (3.7), (3.8), (3.9), or (3.10). Thereby, the proper constrained solution (i.e., normalized glass composition) is obtained.

Equation (3.11) readily lends itself to deriving the final uncertainties to be associated with the normalized values g_{ijk}^{*}, $i=1, 2, \ldots, q$. These resulting uncertainties are

$$Var(g_{ijk}^{*}) \;=\; \sigma_{g_{ijk}^{*}}^{2} = \left(\frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}}\right)^{2} \Big[\sum_{\substack{l=1 \\ l \neq i}}^{q} Var(g_{ljk})\Big] \;+\; \left(1 - \frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}}\right)^{2} [Var(g_{ijk})],\; i = 1, 2, \ldots, q\,. \tag{3.12}$$

Standard deviations may be obtained by taking the square root of results from Equation (3.12).

When $Var(g_{ijk}) = w_{ijk}$ as used in this report, Equation (3.12) can be considerably simplified (as shown in Appendix B) to:

$$Var(g_{ijk}^{*}) \;=\; \sigma_{g_{ijk}^{*}}^{2} = w_{ijk}\Big[1 - \frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}}\Big],\quad i = 1, 2, \ldots, q \tag{3.13}$$

or

$$Var(g_{ijk}^{*}) \;=\; Var(g_{ijk})\,\Big[1 - \frac{Var(g_{ijk})}{\sum_{i=1}^{q} Var(g_{ijk})}\Big],\quad i = 1, 2, \ldots, q\,. \tag{3.14}$$

The quantity in square brackets in Equations (3.13) and (3.14) is obviously less than 1.0 for any $Var(g_{ijk}) > 0$. Hence, Equation (3.14) demonstrates the variances of the normalized values g_{ijk}^{*} are reduced with respect to the variances of the original corresponding values g_{ijk}. This result holds providing the weights w_{ijk} are understood to be the glass wt% variances. For the other choices of the weights w_{ijk} considered in Appendix B, this reduced variance result did not remain true in computational examples. That is, when using the other weighting schemes, at least one of the constituent's estimated variances were larger after normalization than they had been prior to normalization. Only the choice of w_{ijk} as $Var(g_{ijk})$ gave uniformly smaller (or the same) estimated variances after normalization.

4.0 Example Illustrating Glass Composition Adjustment and Normalization Steps

This section presents an example illustrating the results of applying the procedure described in Section 3 for adjusting and normalizing an analyzed glass composition. The example is partially based on results from Round Robin 7 (RR7) conducted by the Materials Characterization Center (Smith, Eggett, and Smith 1997). It was necessary to construct an example using modified results to illustrate several steps of the procedure.

Tables 4.1 and 4.2 contain the results of the example. Table 4.1 contains the results associated with the CRM, which is Analytical Reference Glass-1 (ARG-1). Table 4.2 displays the results associated with the "unknown" glass sample, which is West Valley Reference Glass-6 (WVRG-6). In each table, the glass components of interest (all oxides) are listed in the leftmost column. The example and contents of Tables 4.1 and 4.2 are further described in Sections 4.1 and 4.2, respectively. After a discussion of the general steps shown in the tables, an example computational summary is provided for a specific glass component.

4.1 Example Results Associated with the Blank and CRM

In Table 4.1, the second column lists the nominal CRM (ARG-1) glass wt% concentrations T_i, with the related standard deviations σ_{Ti} given in the next column. These nominal values and standard deviations for ARG-1 are listed in Smith (1993) and were obtained by Corning, Inc. in work for the Materials Characterization Center. Standard deviations listed to a fourth decimal place were obtained from associated Corning worksheets to avoid having to use rounded-off zero standard deviations that were listed in (Smith 1993). Zero values in the T_i and σ_{Ti} columns of Table 4.1 indicate the associated glass components were not present in the CRM.

Because the nominal CRM glass wt% concentrations T_i did not sum to 100, they were normalized using the WLS approach with the component variances σ_{Ti}^2 as weights.[1] The normalized wt% concentrations T_i^* are given in Table 4.1 along with the resulting standard deviations σ_{Ti}^*. Note that the standard deviations of the normalized wt% concentrations are smaller than the standard deviations of the unnormalized wt% concentrations, as discussed in Section 3 and Appendix B. For this example, the normalized T_i^* were used as the nominal values denoted as T_i in the formulas of Section 3 and Appendices A and B.

The results obtained from three analyses of CRM samples, all part of the same analytical batch of samples, are shown in the Table 4.1 columns indicated by c_{i1}, c_{i2}, and c_{i3}. The subscript "i" indexes the glass components. These results were constructed as part of this example to illustrate several aspects of the adjustment procedure. Note the zero values in these columns result from non-detects for those components not present in the CRM. Because those components are indeed not present in the CRM, it would make no sense to replace non-detects by non-zero values as might be done for samples of an unknown glass. However, for two such components, MoO_3 and SO_3, false positive values were assumed

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[1] In the Section 3 procedure to adjust and normalize analyzed glass compositions, the assumption is the nominal composition of the CRM has a total glass wt% concentration of 100 wt%. If not, it is appropriate and consistent to normalize the nominal CRM composition (assuming it is not subject to analytical biases, and does not have "not analyzed" or missing analyses of CRM components).

at greater than detection limits.[1] Note in this example these false positives have no significant impact on any of the procedure steps since they are in fact essentially removed through subsequent blank correction.

Recall the data screening (Step C1) assesses whether each analyzed CRM composition has reasonable total glass wt% (e.g., between 90 wt% and 110 wt%). Each of the three analyses in Table 4.1 passes this criterion. Step C1 also includes investigation of potential outlying values among each set of values c_{i1}, c_{i2}, and c_{i3}. No such outlying values are regarded as present in these results. Thus, the mean of the analyzed CRM results, $\bar{c}_i$, is given in the indicated column.

Blank results B_i used in Step C2 appear in the indicated column of Table 4.1. These blank values are expressed as glass wt% concentrations to simplify the process of adjusting analyzed glass compositions.[2] Zero values indicate non-detects that again are simply replaced by zero because that is the expected true value in the blank. Non-zero values occur from analysis results greater than detection limits. These values are used to blank-correct the mean CRM value, as well as the results for the corresponding components for the glass sample (Table 4.2).

When blank corrections are made, the standard deviations for the blank results are used in subsequent computations. Similarly, when bias corrections are made, subsequent calculations account for the standard deviations of CRM analyses. These standard deviations are assumed as obtained from pre-established within-laboratory analytical %RSD values, denoted 100 p_{Bi} (blank %RSD) and 100 p_{Ci} (CRM %RSD).[3] For this example, 100 p_{Ci} values appropriate for CRM analyses were selected based on glass analysis %RSD estimates in Hrma et al. (1994, Appendix A) and unpublished meeting handouts or minutes for Round Robins 2 through 6 performed by the Materials Characterization Center. The 100 p_{Bi} values were assumed to be 30% for all glass components. The %RSD values used for blank and CRM analyses are listed in subsequent columns of Table 4.1.

The estimated (and potentially blank-corrected) bias in CRM analyses is provided in the column of Table 4.1 indicated by ($\bar{c}_i$ -B_i -T_i^*). The statistical significance of this bias is evaluated as part of Step C3 in the column of Table 4.1 that refers to the associated Equation (3.4). Note that Equation (3.4) uses the SD σ_{Ti}* and the SDs obtained from the established values p_{Bi} and p_{Ci}. When the value of the statistic from Equation (3.4) is statistically significant, the relative bias correction factor is computed as in Equation (3.5b). Otherwise, no bias correction is made, and the bias correction factor is 1.0.

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[1] The Corning, Inc. report did not list results for any components not included in ARG-1. For our example, the assumption was the components with zero values were analyzed and not detected. "False positives" for MoO_3 and SO_3 were added to illustrate how the procedure deals with them. In adding the false positives, CRM, blank, and unknown glass samples were all assumed affected by false positives approximately to the same extent.

[2] Section 3 and Appendix A discuss why it is possible to work with blank results as glass wt% concentrations, rather than elemental wt% concentrations.

[3] Short-term to intermediate-term within-laboratory %RSDs are of interest. Longer-term within-laboratory and lab-to-lab uncertainties should be indirectly addressed (i.e., "removed") by the bias-assessment and bias-correction aspect of the procedure.

Table 4.1. CRM (ARG-1), Blank, and Bias Evaluation Portion of Example

Glass Comp. "*i*"	CRM Nominal (wt%) T_i	SD CRM Nominal (wt%) σ_{Ti}	Normalized CRM Nominal (wt%) T_i^*	SD Norm. CRM Nominal (wt%) σ_{Ti^*}	Blank (wt%) B_i	Blank Analytical %RSD 100 p_{Bi}	CRM Analytical %RSD 100 p_{Ci}	Analyses of CRM Samples (wt%)			Analyzed CRM Mean (wt%) $\bar{c}_i$	Estimated CRM Bias (wt%) $\bar{c}_i - B_i - T_i^*$	$\frac{\text{Bias}}{\text{SD(Bias)}}$ Eq. (3.4)	Bias Correction Factor Eq. (3.5b)
								c_{i1}	c_{i2}	c_{i3}				
Al2O3	4.73	0.022	4.7289	0.0218	0.051	30	4	5.48	5.68	5.29	5.48333	0.7035	5.436	0.8705
B2O3	8.67	0.04	8.6662	0.0390	0	30	3	8.69	9.13	8.25	8.69	0.0238	0.153	1.0000
BaO	0.088	0.001	0.0880	0.0010	0	30	5	0.107	0.092	0.085	0.09467	0.0067	2.292	0.9296
CaO	1.43	0.009	1.4298	0.0090	0.004	30	6	1.32	1.51	1.38	1.40333	-0.0305	-0.616	1.0000
CeO2	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
CoO	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
Cr2O3	0.093	0.001	0.0930	0.0010	0	30	5	0.09	0.084	0.092	0.087	-0.0060	-2.219	1.0689
Cs2O	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
CuO	0.004	0.0001	0.0040	0.0001	0	30	20	0.006	0.004	0.003	0.00433	0.0003	0.653	1.0000
Fe2O3	14.0	0.073	13.9875	0.0670	0.012	30	3	12.8	13.4	12.5	12.9	-1.0995	-4.713	1.0854
K2O	2.71	0.016	2.7094	0.0159	0	30	5	2.52	2.16	2.29	2.32333	-0.3861	-5.601	1.1662
La2O3	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
Li2O	3.21	0.015	3.2095	0.0149	0	30	4	3.11	3.24	2.98	3.11	-0.0995	-1.356	1.0000
MgO	0.86	0.005	0.8599	0.0050	0.05	30	5	0.80	0.85	0.83	0.82667	-0.0833	-2.909	1.1072
MnO2	2.31	0.012	2.3097	0.0120	0	30	5	2.31	2.44	2.13	2.29333	-0.0163	-0.243	1.0000
MoO3	0	0	0.0000	0.0000	0.003	30	30	0.004	0.002	0.002	0.00267	-0.0003	-0.330	1.0000
Na2O	11.50	0.023	11.4988	0.0228	0.20	30	4	9.68	10.22	9.97	9.95667	-1.7421	-7.297	1.1786
Nd2O3	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
NiO	1.05	0.006	1.0499	0.0060	0	30	6	0.99	1.11	0.97	1.02333	-0.0266	-0.739	1.0000
P2O5	0.22	0.011	0.2197	0.0110	0	30	20	0.20	0.15	0.13	0.16	-0.0597	-2.779	1.3733
PdO	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
Pr6O11	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
RhO2	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
RuO2	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
SO3	0	0	0.0000	0.0000	0.004	30	30	0.005	0.004	0.003	0.004	0.0000	0.000	1.0000
SiO2	47.9	0.157	47.8422	0.0809	0.11	30	5	46.5	43.8	45.1	45.1333	-2.8189	-2.159	1.0626
Sm2O3	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
SrO	0.0037	0.0002	0.0037	0.0002	0	30	30	0.004	0.003	0.003	0.0033	0.0004	-0.600	1.0000
ThO2	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
TiO2	1.15	0.007	1.1499	0.0070	0	30	3	0.92	0.95	1.02	0.96333	-0.1866	-10.311	1.1937
UO2	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
Y2O3	0	0	0.0000	0.0000	0	30	30	0	0	0	0	0.0000	0.000	1.0000
ZnO	0.02	0.0001	0.0200	0.0001	0	30	15	0.023	0.016	0.020	0.01967	-0.0003	-0.195	1.0000
ZrO2	0.13	0.005	0.1299	0.0050	0.007	30	7	0.14	0.11	0.12	0.12333	-0.0136	-1.848	1.1170
Total	100.079		100					95.69	94.955	93.168	94.606			

4.2 Example Results Associated with the Glass Sample

Table 4.2 presents the results for the blank correction, bias correction, and normalization of a single chemical analysis of WVRG-6. Note that this glass is being treated as an "unknown" composition, although the nominal composition for this glass is available (e.g., see Smith, Eggett, and Smith 1997) and listed in the final column. These nominal values are included for comparison to the final adjusted and normalized column. The contents of Table 4.2 are described further in the following paragraphs.

Chemical analysis and sampling %RSDs, assumed to be previously established values, are listed as $100\,p_{Ai}$ and $100\,p_{Si}$ in Table 4.2. The analytical %RSDs are short-term to intermediate-term within-laboratory uncertainties, obtained from the Hrma et al. (1994) and RR2 to RR6 results described in Section 4.1. Sampling %RSDs were assumed to be 5% for every glass component, although the procedure can certainly account for different sampling %RSDs for different components.

Analyzed glass wt% concentrations x_i are shown in the indicated column of Table 4.2 for a glass sample included in the same analytical batch as the CRM and blank samples (Table 4.1). Recall that if any component results had been non-detects, they would have been replaced in Step S1 by one-half the detection limit to facilitate computations. These values are all greater than associated DL's, which are not readily available for this example and are thus not listed. A listing of such DL's would generally be recommended.

Next in Table 4.2 are the blank-corrected values $x_i - B_i$ resulting from Step S2. Note the blank results from Table 4.1 are used here. The bias-corrected results g_i are obtained from Step S3 by multiplying the bias correction factor from Table 4.1. This step adjusts only those components that are associated with statistically significant biases, as determined in the Table 4.1 evaluations. Hence, bias-correction cannot be applied for any components that were not present in the CRM (ARG-1) samples.

The standard deviations σ_{g_i} are obtained from Equations (3.7), (3.8), (3.9), or (3.10) as appropriate, depending on previous blank and/or bias corrections performed for the i^{th} component. Note that prior to normalization in Step S5, a final data screening in Step S4 is completed. Each blank- and/or bias-corrected glass wt% vector is required to sum to between 95 wt% and 105 wt%[1]. The example in Table 4.2 easily meets this criterion. In addition, the screening step includes investigating the set of all glass sample vectors resulting from a sampling event for outlying results. That portion of the screening step cannot be illustrated because only one sample analysis is in the example.

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[1] The 95 to 105 wt% range was chosen merely for discussion and illustration purposes. The acceptable range should be chosen based on the capabilities and experience of particular analytical laboratories.

Table 4.2. Analyzed Glass Composition (WVRG-6) Adjustment and Normalization Portion of Example

Glass Comp. "i"	Analysis %RSD 100 p_{Ai}	Sampling %RSD 100 p_{Si}	Analyzed Glass (wt%) x_{ijk}	Blank Corrected Glass (wt%) $x_{ijk} - B_i$	Bias Corrected Glass (wt%) g_{ijk}	SD Bias Corrected Glass (wt%) $\sigma_{g_{ijk}}$	Weight for Normalization w_{ijk}	Normalized Glass (wt%) g_{ijk}^*	SD Normalized Glass (wt%) $\sigma_{g_{ijk}^*}$	Nominal Glass (wt%) (a)
Al2O3	4	5	6.93	6.879	5.988	0.4117	0.1695	5.9788	0.4087	6.02
B2O3	3	5	12.51	12.51	12.510	0.7295	0.5321	12.4806	0.7128	12.80
BaO	5	5	0.137	0.137	0.127	0.0098	0.0001	0.1273	0.0098	0.14
CaO	6	5	0.567	0.563	0.563	0.0443	0.0020	0.5629	0.0443	0.57
CeO2	10	5	0.20	0.2	0.200	0.0224	0.0005	0.2000	0.0224	0.17
CoO	20	5	0.017	0.017	0.017	0.0035	0.0000	0.0170	0.0035	0.019
Cr2O3	5	5	0.166	0.166	0.177	0.0137	0.0002	0.1774	0.0137	0.17
Cs2O	7	5	0.05	0.05	0.050	0.0043	0.0000	0.0500	0.0043	0.079
CuO	5	5	0.05	0.05	0.050	0.0035	0.0000	0.0500	0.0035	0.055
Fe2O3	3	5	11.15	11.138	12.088	0.7384	0.5452	12.0581	0.7211	11.90
K2O	5	5	4.52	4.52	5.271	0.4038	0.1630	5.2621	0.4010	5.13
La2O3	35	5	0.042	0.042	0.042	0.0148	0.0002	0.0420	0.0148	0.048
Li2O	4	5	3.54	3.54	3.540	0.2267	0.0514	3.5372	0.2262	3.68
MgO	5	5	0.85	0.8	0.886	0.0721	0.0052	0.8855	0.0721	0.92
MnO2	5	5	1.14	1.14	1.140	0.0806	0.0065	1.1396	0.0806	1.09
MoO3	10	5	0.038	0.035	0.035	0.0043	0.0000	0.0350	0.0043	0.039
Na2O	4	5	7.01	6.81	8.026	0.5624	0.3163	8.0085	0.5549	8.12
Nd2O3	6	5	0.322	0.322	0.322	0.0251	0.0006	0.3220	0.0251	0.13
NiO	6	5	0.26	0.26	0.260	0.0203	0.0004	0.2600	0.0203	0.26
P2O5	10	5	0.9	0.9	1.236	0.2080	0.0433	1.2335	0.2077	1.18
PdO	15	5	0.339	0.339	0.339	0.0536	0.0029	0.3388	0.0536	0.031
Pr6O11	15	5	0.062	0.062	0.062	0.0098	0.0001	0.0620	0.0098	0.059
RhO2	20	5	0.015	0.015	0.015	0.0031	0.0000	0.0150	0.0031	0.019
RuO2	20	5	0.029	0.029	0.029	0.0060	0.0000	0.0290	0.0060	0.033
SO3	15	5	0.25	0.246	0.246	0.0395	0.0016	0.2459	0.0395	0.26
SiO2	5	5	38.75	38.64	41.059	3.1455	9.8951	40.5120	1.2656	40.90
Sm2O3	10	5	0.064	0.064	0.064	0.0072	0.0001	0.0640	0.0072	0.060
SrO	10	5	0.025	0.025	0.025	0.0028	0.0000	0.0250	0.0028	0.024
ThO2	5	5	2.8	2.8	2.800	0.1980	0.0392	2.7978	0.1977	3.36
TiO2	3	5	0.751	0.751	0.896	0.0548	0.0030	0.8963	0.0548	0.80
UO2	5	5	1.13	1.13	1.130	0.0799	0.0064	1.1296	0.0799	0.56
Y2O3	7	5	0.04	0.04	0.040	0.0034	0.0000	0.0400	0.0034	0.042
ZnO	15	5	0.03	0.03	0.030	0.0047	0.0000	0.0300	0.0047	0.031
ZrO2	7	5	1.25	1.243	1.388	0.1461	0.0213	1.3872	0.1459	1.30
Total			95.934	95.493	100.653			100		99.999

(a) This column lists the nominal composition of the WVRG-6 glass per West Valley records. It is included for comparison to the normalized glass compositions g_{ijk}^*.

The normalization weights w_i for Step S5 are simply the squared σ_{g_i} values, that is, Var(g_i). The normalization step yields the normalized values g_i^* that indeed sum to 100 wt%. The reduced uncertainty after normalization can be observed by comparing σ_{g_i} and σ_{g_i*}. The reductions in these SDs ranged from 0% to about 2.3% on a relative basis, except for a 59% reduction in the SD for SiO_2. The σ_{g_i*} values were calculated using Equation (3.13).

A summary of specific example computations can be observed by considering the first row of each table. In Table 4.1, the Al_2O_3 CRM mean is 5.48333 wt%. In the bias computation, this CRM mean is blank corrected by subtracting off the blank value 0.051 wt%. Comparison to the normalized nominal value 4.7289 wt% then gives a bias of 0.7035 wt%. Because the Bias/SD(Bias) ratio is sufficiently large, this bias is deemed statistically significant. A bias correction factor of 0.8705 is obtained by dividing the nominal value by the bias corrected CRM mean, that is, 4.7289 / (5.48333 – 0.051).

In Table 4.2, the Al_2O_3 analyzed concentration of 6.93 wt% for the "unknown" WVRG-6 sample is similarly blank corrected to 6.879 wt% by subtraction of the blank value 0.051 wt%. This value is in turn bias corrected to 5.988 wt% by multiplying using the established 0.8705 bias correction factor. Note that propagation of the blank, CRM, and glass sample uncertainties gives the SD (associated with the 5.988 wt% adjusted values) as 0.4117 wt%. This SD value squared is the weight 0.1695 for the normalization step.

Similar computations are performed for all components with their adjusted results subsequently summing to 100.653. The weighted normalization step then forces this sum to 100. The effect of normalization on the Al_2O_3 blank and bias-corrected concentration is a reduction from 5.988 wt% to 5.9788 wt%, as shown in Table 4.2. The normalization step reduces the SD of the Al_2O_3 concentration from 0.4117 wt% to 0.4087 wt%, as similarly shown in Table 4.2.

4.3 Discussion

The adjustment and normalization procedure was very successful for the example results in Tables 4.1 and 4.2. The original chemical analysis of WVRG-6 had a total glass wt% concentration of 95.934. Blank concentrations greater than zero (assumed to be greater than DLs, which were not available) were present for nine components (Al_2O_3, CaO, …, ZrO_2) in the constructed example, as shown in Table 4.1. Corresponding blank corrections were made, as shown in Table 4.2. Statistically significant biases were detected for eleven components (Al_2O_3, BaO, …, ZrO_2) as shown in Table 4.1. The corresponding bias corrections are shown in Table 4.2. The results affected by blank corrections and bias corrections are identified by shaded table cells in Tables 4.1 and 4.2. After blank and bias corrections, the total wt% for the adjusted concentrations was 100.656. Normalization yielded the final estimate of glass composition (denoted g_i^*), with wt% concentrations totaling 100 wt%. The blank-corrected, bias-corrected, and normalized estimates of component wt% concentrations (in the third-from-the-last column of Table 4.2) compare very favorably to the nominal values (in the last column of Table 4.2).

Keep in mind the example in this section is based on RR7 results, but was partially constructed with the goal of illustrating several steps of the procedure and yielding good results. The glass adjustment and normalization procedure presented in this report needs to be applied to many "real" glass analysis examples to test its performance and make any needed modifications or enhancements.

5.0 Conclusions and Recommendations

This report presents the results of initial work to develop a procedure for reporting glass compositions based on appropriate adjustments of chemical analyses of "glass" samples. "Glass" samples could be process (e.g., melter feed) samples, product (e.g., shard) samples, laboratory crucible samples, or melter test samples). The procedure includes the following features:

- data screening
- non-detect replacement
- blank correction
- bias correction
- normalization of adjusted compositions to sum to 100 wt%.

Specific methodologies for implementing several of these steps are described in the report, with more extensive discussion and technical details given in Appendices A and B. Data screening and non-detect replacement methodologies are to be finalized elsewhere.

The normalization approach is based on minimizing the sum of the weighted, squared differences between the adjusted glass component wt% concentrations (g_{ijk}) and the normalized glass component wt% concentrations (g_{ijk}^*). Different weighting schemes are described in Appendix B. Variances were chosen as the weights because they correspond to using differences between the adjusted and normalized differences expressed in standard deviation units (as described in Appendix B). Also, using variances as weights in the normalization procedure reduces the variances (uncertainties), i.e., $\mathrm{Var}(g_{ijk}^*) < \mathrm{Var}(g_{ijk})$.

The procedure for adjusting and normalizing analyzed glass compositions makes several assumptions and has several requirements, briefly summarized and discussed as follows.

<u>CRMs, Nominal Compositions, and Standard Deviations</u>—One or more CRMs are available with composition(s) representative of the unknown glass samples that will be chemically analyzed. The CRMs must have certified (or otherwise well-established) values of the nominal component wt% concentrations and standard deviations of the nominal glass wt% concentrations. If the CRM nominal values are means (averages) over replicate samples, preparations, or chemical analyses, the standard deviations should: (i) correspond to the means (i.e., they should be *standard errors*), and (ii) be properly calculated using statistical *variance component estimation* methods to account for multiple sources of uncertainty, such as sampling, preparation, and analyses.

<u>Same Analytical Batch</u>—Blank, CRM, and unknown glass samples must be analyzed in the same analytical batch. Multiple analytical batches may be used to accommodate many samples of one or several unknown glasses, as long as blank and CRM samples are analyzed as part of each analytical batch. This process permits blank corrections and bias corrections.

<u>Replicate CRM Analyses</u>—Although not mandatory, replicate analyses of CRM samples in each analytical batch are highly encouraged. Replicate analyses of CRM samples provide for more precise assessment and correction of biases, which in turn provide for smaller uncertainties of bias-corrected and normalized versions of analyzed glass compositions.

<u>"Not Analyzed" and "Not Detected" Components</u> —All components in a glass sample that are (i.e., in the CRM glass) or may be (i.e., in the unknown glass) present at concentrations higher than detection limits must be chemically analyzed. That is, we assume no "not analyzed" glass components are present at

higher than detection limits. The procedure does account for "not detected" results being obtained for components present at concentrations below detection limits.

False Positives—If "false positive" results (glass component concentrations above detection limits for components not contained in the glass) are obtained, it is assumed that blank, CRM, and unknown glass samples are affected to the same absolute extent. In this case, the blank-correction step of the procedure adjusts for the false positives.

Prior Estimates of %RSDs—Prior estimates of chemical analysis %RSDs for each component detected in the blank[1], CRM, and unknown glass samples must be available. Prior estimates must also be available for sampling %RSDs of each component detected in unknown glass samples.[2] These prior estimates must be based on sufficient data or experience to be well determined. The sampling %RSDs will depend on the way in which samples are obtained (e.g., crucible glass samples, melter test samples, WTP process samples, WTP product samples). The analytical %RSDs will depend on the analytical preparations and instruments used, nonradioactive versus radioactive environment, and other factors. Analytical and sampling %RSDs applicable to the WTP IHLW and ILAW vitrification and analytical facilities will be estimated by statistical analyses of statistically designed studies as part of qualification activities.

Analytical %RSDs—Analytical %RSDs must account for within-laboratory preparation and chemical analysis uncertainties. Only short- to intermediate-term (i.e., up to several months) uncertainties are of interest. Long-term within-laboratory and lab-to-lab variations in results often appear as biases over time. Hence, it is assumed these variations will be removed by the bias-correction step of the procedure.

Outlier Screening—Analyzed CRM and glass samples must be screened, and outliers removed or replaced, in order not to affect the adjusted and normalized glass compositions resulting from the procedure. It was beyond the scope of this work to develop detailed, objective statistical algorithms for detecting and/or replacing outliers. However, we recommend developing such outlier detection algorithms as part of future work.

If the WTP project decides to implement all or part of the methodology discussed in this report, work will be required to address some of the preceding issues. In some cases (e.g., estimating %RSDs), this work is already planned. In other cases the work will be included in plans for related work. Also, if the WTP project adopts some or part of the methodology for using and reporting analyzed glass compositions, the methodology should be discussed or referred to in the IHLW and ILAW compliance strategy documents and qualification documents.

The procedure for adjusting (blank and bias corrections) and normalizing analyzed glass compositions presented in this report should be considered preliminary until sufficient experience is obtained in applying it to analyzed glass compositions. For example, the procedure should be applied to chemical analyses of many crucible and melter test glasses (for both IHLW and ILAW glasses) where the target compositions are known. Such experience with the procedure may suggest modifications or enhancements that could be documented in a future revision of this report.

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[1] As previously discussed, blank results and %RSDs are assumed to be expressed as (or converted to) glass wt% concentrations.

[2] CRMs are assumed to be sufficiently homogeneous that sampling %RSDs are very small, compared to analytical uncertainties, and thus can be ignored.

6.0 References

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Appendix A: Details and Discussion of Procedure Steps for Glass Composition Adjustment and Normalization

This appendix provides additional discussion (beyond that of Section 3) on various aspects of the procedure for adjusting and normalizing analyzed glass compositions.

An important assumption for this work is that every component present at detectable levels in CRM samples and glass samples is chemically analyzed. Different analytical methods (preparations or instruments) may be used for different components, but it is assumed that analysis is performed for every detectable component. In other words, "not analyzed" (NA) results do not appear for glass components at levels greater than detection limits. However, "not detected" (ND) results may appear. If NA results are observed for components that comprise more than a negligible fraction of a CRM or glass, a procedure step would have to be added that replaces NA results with target, nominal, or other estimated values for the unanalyzed glass components. Such a step was considered beyond the scope of the current procedure, but could be added in future work. Hrma et al. (1994, Appendix A) and Smith et al. (2001, Section 4.1.2) contain examples of using target and nominal values for unanalyzed glass components.

In Section 3.1, reference is made to conversion from elemental wt% to glass wt%. Glass wt% concentrations are assumed throughout this report, but in some cases conversion from elemental wt% concentrations first may be required. This conversion is done as follows for the i^{th} analyte, $i = 1, 2, \dots, q$:

$$g_i = \frac{MWC_i}{(MW_i)(CAT_i)}(e_i)\,, \qquad \text{(A.1)}$$

where g_i = glass wt% concentration of the i^{th} glass component, MWC_i = molecular weight of the i^{th} glass component (typically an oxide or halogen), MW_i = molecular weight of the i^{th} element, CAT_i = number of cations in the i^{th} glass component, and e_i = elemental wt% of the i^{th} element. Because this is a simple linear conversion, steps of the glass composition adjustment and normalization procedure could be performed in terms of: (i) glass wt% concentrations, or (ii) elemental wt% concentrations with the results converted to glass wt% concentrations. In this report, all calculations are performed in terms of glass wt% concentrations. Although glass wt% concentrations have little meaning for blank results, blank correction can still be performed in those terms simply by first converting the blank elemental wt% concentrations using Equation (A.1). Because (A.1) is a linear conversion, the results are the same.

The following paragraphs present a more complete discussion (than is provided in Sections 3.2 and 3.3) of the adjustment and normalization steps for analyzed glass compositions.

Step C1: Screen CRM Data

Deletion of outlying analytical values for the i^{th} glass component in the CRM sample (c_{ij}, $j = 1, 2, \dots, u$) should always be done only with due caution and, ideally, with identification of special causes that make the outlying values questionable. A proposed level of statistical rigor is not specified in this preliminary work, but it should be at a level appropriate to meet qualification requirements. At a minimum, if obviously disparate results are observed, some investigation of their potential special causes should be conducted. If such special causes are identified, the corresponding measurements should be omitted from the analysis. More formal statistical outlier criteria can be applied instead; see Barnett and Lewis (1984) for particular methods. For environmental data, EPA QA/G-9 (EPA 1998) provides additional guidance.

Such statistical criteria would use the established standard deviations

$$\sigma_{Ci} = p_{Ci} T_i \ , \ i = 1, \ 2, \ \dots \ , \ q \tag{A.2}$$

to identify outlying values among the u CRM results for the i^{th} glass component (i.e., the c_{ij}, $j = 1, 2, \dots, u$).

Note that deletion of any outliers reduces the number u of CRM results. The value of u should, therefore, be reduced accordingly for use in subsequent computational steps.

The other function of this screening step is to prevent the use of analyzed glass compositions that have severe measurement problems (i.e., sample preparation or chemical analysis). The "placeholder" assumption in Sections 3.2 and 3.3 is to reject any single CRM analyzed composition (c_{1j}, c_{2j}, … , c_{qj}) that has a total of unadjusted glass component wt% concentrations (i.e., $\sum_{i=1}^{q} c_{ij}$) outside the range of 90 wt% to 110 wt%. The ±10 wt% limits around 100 wt% are somewhat arbitrary. These limits should be evaluated and specified by the WTP Project relative to qualification requirements and what can be achieved in a particular analytical laboratory. Whatever limits are ultimately chosen, any analyzed composition with total wt% concentration outside the desired range is omitted from subsequent analyses.

Step C2: Evaluate Blank

Blank corrections are made on an "absolute" basis, because there are no nominal values (other than zero) for blank correction on a "relative" basis. Hence, blank results cannot be expressed as percentages or proportions of the true/nominal value.

Step C3: Evaluate Bias

Equation (3.4) gives the statistical comparison

$$\frac{\left|\bar{c}_i - B_i - T_i\right|}{\sqrt{\sigma_{\bar{c}i}^2 + \sigma_{Bi}^2 + \sigma_{Ti}^2}} > z_\alpha \tag{A.3}$$

for evaluating the bias in analyzed wt% concentrations of component "i" in the CRM. In Equation (A.3), the blank-corrected (if applicable) mean for glass component "i" of CRM results from an analytical batch ($\bar{c}_i - B_i$) is compared to the corresponding nominal value (T_i). The comparison is made relative to the uncertainties of these quantities, shown as absolute variances (squared standard deviations) in the denominator of Equation (A.3). These standard deviations are obtained from previously established RSDs as described in Section 3.3. The values Bi and σ_{Bi} in Equation (A.3) are omitted if no blank correction was made.

The RSD estimates used to obtain the variances in the denominator of Equation (A.3) may be based on relatively small amounts of data. If so, the standard-normal distribution value z_α should be replaced by the appropriate t-distribution value $t_\alpha(f)$ whose degrees of freedom f depend on the amount of data used in generating the RSD estimates. The impact of this change should be minimal, because in such cases z_α is smaller than $t_\alpha(f)$. Hence, the use of z_α could result in making some bias corrections that would not be made if $t_\alpha(f)$ were used. The particular value α, and thus z_α or t_α, should be selected relative to qualification requirements.

If outlier(s) have been removed in Step C1, the total number *u* of CRM analyses should be adjusted downward accordingly in Equation (A.3). If the inequality in Equation (A.3) does not hold, the bias is not statistically significant, and no bias correction is made. If the inequality does hold, the bias is deemed statistically significant, and glass sample analyses are bias corrected in Step S3.

Step S1: Replace Non-detects

A method for replacement of analytical non-detect (ND) results is needed so that minor biases are not introduced to glass composition estimates during the normalization step (S5). Ignoring NDs is the same as treating them as zeros. This will generally lead to underestimating the total wt% of analyzed glass component concentrations. Although this underestimate could be small, it would result in the introduction of biases during the normalization step.

Varying levels of rigor can be applied in replacing ND analytical results in statistical applications. The optimal character of various replacement strategies depends strongly on the ultimate use of the replacement values in the particular application. Options range from simple numerical replacement to maximum likelihood estimation under assumed distributions. It is expected that analyzed glass component values less than detection limits will have minimal impact on normalized glass compositions and predictions made from property-composition models.

To evaluate this assumption, a single ND result could be replaced by zero and the sequence of Steps S2 through S5 performed. Then the ND could be replaced by its detection limit instead and the sequence of Steps S2 through S5 could be performed similarly. In applications involving linear expressions, the two results obtained would clearly bound what would have been obtained from whatever the value less than the detection limit truly was. If the difference in the two results is not of practical significance, as is expected, the replacement convention is relatively unimportant. If the difference is significant, additional investigation may be warranted.

For this preliminary work, the simple replacement of NDs by one-half the detection limit is proposed. This avoids the obvious under-estimation if all NDs are replaced by zero and probable over-estimation if they are replaced by the detection limits. This approach is proposed with the expectation the normalization process and the ultimate use of the normalized glass wt % compositions will be not be impacted significantly by the replacement convention.

Step S2: Blank Correct

When CRM values are blank-corrected, the corresponding glass sample values from the same analytical batch are similarly blank-corrected. The formula in Step S3 addresses both blank corrections and bias corrections.

Step S3: Bias Correct

Relative bias correction was proposed in Equation (3.5b) as:

$$g_{ijk} = (x_{ijk} - B_i)\left(\frac{T_i}{\bar{c}_i - B_i}\right). \tag{A.4}$$

Alternatively, bias correction on an absolute basis could be considered if representative CRM glasses are available with compositions very similar to the compositions of WTP IHLW and ILAW glasses to be sampled and analyzed. Because such availability is unlikely, at least in the short term, bias correction on a relative basis is probably more useful. However, note that bias correction on an absolute basis using CRM glasses of similar compositions to glasses being analyzed would likely yield better (i.e., more accurate and/or precise) final estimates of glass composition. Also, bias correction on an absolute basis would result in somewhat simplified uncertainty expressions compared to those in Equations (3.7), (3.8), (3.9), or (3.10).

Step S4: Screen Data

At this point in the sequence of procedure steps, any required ND replacement and blank or bias corrections have been completed for the respective analytical batches that make up the sampling event. Thus, the complete set of the *m x r* component wt% concentrations in Equation (3.1) is available with any needed adjustments made. These adjusted wt% concentrations g_{ijk} for each glass component $i = 1, 2, \ldots,$ q are given by:

$$\begin{array}{c} g_{i11}, g_{i12}, \ldots g_{i1r} \\ g_{i21}, g_{i22}, \ldots g_{i2r} \\ . \\ . \\ . \\ g_{im1}, g_{im2}, \ldots g_{imr} \end{array} \qquad \text{(A.5)}$$

Prior to the subsequent normalization of each of the *m x r* replicate ($g_{1jk}, g_{2jk}, \ldots g_{qjk}$) vectors, another data screening step is recommended. This screening includes two features: (1) outlier detection among the g_{ijk} values, and (2) composition vectors ($g_{1jk}, g_{2jk}, \ldots g_{qjk}$) being unacceptable due to total wt % concentrations (i.e., $\sum_{i=1}^{q} g_{ijk}$) being too different from 100%.

As with outlier screening among the CRM results, differing levels of rigor could be applied in screening for outliers among these glass sample results. However, at this point outliers could occur at several different levels, which raises certain issues as follows:

1. Each group of *r* replicated measurements of glass component "*i*" associated with a single sample "*j*" (i.e., g_{ijk}, $k = 1, 2, \ldots, r$) could be examined for an outlying measurement from one or more of the replicate chemical analyses. However, if a value g_{ijk} is identified as outlying, a replacement value would be required prior to the normalization step, or else that whole replicate chemical analysis would be discarded.

2. The *m* sample means for glass component "*i*" (one from each group of *r* replicated analyses for each of the *m* distinct samples) could be examined for an outlying sample. If one or more glass components have outlying mean values (over the replicate analyses) for a given sample, all results from that sample would be discarded. Alternatively, if only one or two glass components had outlying means for a given sample, replacement values could be used. However, replacement values would be needed for each replicate analysis of the affected glass components, if a normalized glass composition is produced for each replicate glass analysis.

3. The entire group of $m \times r$ measurements could be screened for individual outlying measurements. Again, the issue would arise as to whether to discard any glass analysis with an outlying value for even one glass component, or to use replacement values to complete the normalization step.

An appropriate level of data scrutiny should be performed in each of these cases relative to qualification requirements.

At this step of the procedure, rejection of glass wt % vectors with total wt % concentrations outside the range of 95% and 105% has been used in this report for discussion purposes. The specific screening levels should be determined by the WTP Project relative to qualification requirements and analytical laboratory capabilities.

Step S5: Normalize Compositions

A complete discussion of normalization features is given in Appendix B.

Appendix B: Weighted Least Squares Normalization of Analyzed Glass Compositions

This appendix discusses the weighted least squares (WLS) approach for normalizing analyzed (and possibly blank corrected and bias corrected) glass compositions. It also develops closed-form equations for calculating normalized glass compositions and their uncertainties. WLS normalization is Step S5 of the procedure shown in Figure 3.1 and described in Sections 3.2 and 3.3.

WLS Normalization of Glass Compositions

In Step S4, prior to normalization, g_{ijk} denotes the adjusted (by any blank correction or bias correction necessary) wt% concentration of the i^{th} glass component of the j^{th} replicate analysis of the k^{th} sample, where $i = 1, 2, \ldots, q$; $j = 1, 2, \ldots, r$: and $k = 1, 2, \ldots, m$; and where q denotes the number of glass components, m the number of glass samples for a given sampling event, and r the number of replicate analyses per glass sample. Note that the subscripts j and k can be considered fixed throughout this entire section because the normalization is done for each of the $m \times r$ vectors individually. The j,k subscripts are nonetheless included to match the notation in other sections of this report. This section discusses normalizing an analyzed (and possibly blank corrected and or bias corrected) glass composition ($g_{1jk}, g_{2jk}, \ldots, g_{qjk}$) so the resulting vector of normalized wt% concentrations ($g_{1jk}^*, g_{2jk}^*, \ldots, g_{qjk}^*$) satisfies the constraints

$$\sum_{i=1}^{q} g_{ijk}^* = 100 \text{ and } g_{ijk}^* \geq 0 \text{ for each } i = 1,\ 2,\ \ldots,\ q \tag{B.1}$$

Many normalization schemes are possible, but the proposed general approach is based on WLS, as discussed by Deming (1964) and Mandel (1964). This approach minimizes

$$\sum_{i=1}^{q} \frac{(g_{ijk} - g_{ijk}^*)^2}{w_{ijk}}, \tag{B.2}$$

where $1/w_{ijk}$ denotes a weight corresponding to the analyzed (and possibly blank corrected or bias corrected) wt% concentration of the i^{th} glass component in the $(j,k)^{th}$ wt% concentration vector. Thus the goal is to generate the smallest possible sum-of-squares of weighted differences between the g_{ijk} and the g_{ijk}^* quantities in (B.2), while still achieving the normalization criteria in (B.1). Note that while the actual "weights" are $1/w_{ijk}$, for simplicity in the remainder of this document, the values w_{ijk} are similarly referred to as weights.

With the WLS normalization approach, larger values of w_{ijk} allow relatively larger changes in the associated wt% concentrations g_{ijk}. This can be seen by recognizing that a larger value of w_{ijk} in (B.2) will offset (or down-weight) a larger squared difference $(g_{ijk} - g_{ijk}^*)^2$. If the w_{ijk} are measures of uncertainty of the associated g_{ijk} values, then those g_{ijk} with greater uncertainties would be adjusted in the normalization by relatively larger amounts.

Derivation of Closed-Form Normalization Expressions

Disregarding for now the constraints $g_{ijk}^* \geq 0.0$ ($i = 1, 2, \ldots, q$), the solution to the constrained minimization problem given by (B.1) and (B.2) is subsequently shown to be:

$$g^*_{ijk} = g_{ijk} + \frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}} \left[100 - \sum_{i=1}^{q} g_{ijk} \right], \quad i = 1, 2, \ldots, q \tag{B.3}$$

The derivation of this result follows. To incorporate the constraint for the g_{ijk}^* summing to 100, a Lagrange multiplier is included in the minimization of

$$\sum_{i=1}^{q} \frac{(g_{ijk} - g^*_{ijk})^2}{w_{ijk}} + \lambda(100 - \sum_{i=1}^{q} g^*_{ijk}) \tag{B.4}$$

Taking partial derivatives with respect to each g_{ijk}^* and λ, and setting them equal to zero gives the system of equations

$$-\frac{2}{w_{ijk}}(g_{ijk} - g^*_{ijk}) - \lambda = 0, \; i = 1, 2, \ldots, q \tag{B.5}$$

and

$$(100 - \sum_{i=1}^{q} g^*_{ijk}) = 0 \tag{B.6}$$

Solving for g_{ijk}^* in (B.5) gives for each "*i*",

$$g^*_{ijk} = \frac{\lambda w_{ijk}}{2} + g_{ijk} \tag{B.7}$$

Replacing g_{ijk}^* in (B.6) using (B.7) gives

$$100 - \sum_{i=1}^{q} \left[\frac{\lambda w_{ijk}}{2} + g_{ijk} \right] = 0 \tag{B.8}$$

Solving (B.8) for λ gives

$$\lambda = \frac{2}{\sum_{i=1}^{q} w_{ijk}} [100 - \sum_{i=1}^{q} g_{ijk}] \tag{B.9}$$

Replacing λ in (B.4) using (B.9) gives

$$-\frac{2}{w_{ijk}}(g_{ijk} - g^*_{ijk}) - \frac{2}{\sum_{i=1}^{q} w_{ijk}} [100 - \sum_{i=1}^{q} g_{ijk}] = 0, \; i = 1, 2, \ldots, q \tag{B.10}$$

and solving this expression for g_{ijk}^* gives the solution in (B.3). Note that summing the expressions in (B.3) from 1 to *q* indeed gives the value 100.

Note for glass wt% concentrations g_{ijk} that originally sum to less than 100 wt%, the additional constraints $g_{ijk}^* \geq 0.0$ are trivially met because only increases from g_{ijk} to g_{ijk}^* result, and $g_{ijk}^* \geq g_{ijk} \geq 0.0$

for each "*i*". When wt% concentrations sum to more than 100 wt%, which requires reductions to the g_{ijk}, the solution (B.3) does have the potential that some g_{ijk}^{*} could be less than 0.0.

Linear programming methods involving constrained optimization show that if the unconstrained solution does not satisfy the constraints, then the constrained minimization solution lies on the boundary of the constraint region (see Mandel 1964 or Taha 1976). In this application, this means if a g_{ijk}^{*} is negative in (B.3), the optimum solution meeting the additional non-negative constraints is obtained by replacing the negative $g_{ijk}*$ value(s) by zero, and then re-normalizing the resulting vector using the original weights w_{ijk} for only the remaining glass components "*i*". Iterating this way until a solution is obtained with no negative values will give the optimum constrained solution.

An alternative computational approach is to use a constrained optimization routine available in several software packages. The Microsoft EXCEL Solver constrained optimization routine was used to confirm the preceding results for several test cases. The same solutions were obtained using the software as were obtained in the direct approach above, both when no negative results were obtained with the direct method, and when negative results were obtained and iteration was necessary.

Derivation of Uncertainty Expressions

A benefit of discussing the direct approach is the straightforward derivation of the resulting uncertainties of the normalized g_{ijk}^{*} values as given in the following and in Equation (3.12):

$$Var(g_{ijk}^{*}) \;=\; \sigma^2_{g_{ijk}^{*}} = \left[\frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}}\right]^2 [\sum_{\substack{l=1\\ l\neq i}}^{q} Var(g_{ljk})] \;+\; \left[1-\frac{w_{ijk}}{\sum_{i=1}^{q} w_{ijk}}\right]^2 [Var(g_{ijk})]\,,\; i = 1, 2, \ldots, q \quad \text{(B.11)}$$

This expression is obtained from (B.3) in a straightforward manner by regrouping terms with respect to the subscript "*i*" and expanding the variance expression. Because the estimated covariance structure of the various analytes will not likely be available, nor will sufficient data be obtained to provide reasonable estimates, the independence of the glass component uncertainties is assumed both in the derivation of (B.11) and in the subsequent selection of the weights w_{ijk}.

When the weights w_{ijk} are taken to be $Var(g_{ijk}.)$, (B.11) simplifies to the results in (3.13) and (3.14). To see this, replace $Var(g_{ijk})$ by w_{ijk} in (B.11), expand the squared bracket term, regroup terms, and simplify to get (3.13). Recall that expression (3.13) demonstrates the result that the variances of the normalized glass wt% concentrations are less than those of the original glass wt% concentrations, provided that the weights w_{ijk} are indeed the variances of the original glass wt% concentrations.

The variances of the g_{ijk} are as given in Equations (3.7), (3.8), (3.9), or (3.10). The derivations of the formulas given in those equations are discussed briefly in the following.

As given in (3.7), for non-bias-corrected values g_{ijk},

$$w_{ijk} = \sigma^2_{gijk} = Var(x_{ijk} - B_i) = (p_{Ai}x_{ijk})^2 + (p_{Si}x_{ijk})^2 + \sigma^2_{Bi} = x_{ijk}{}^2(p_{Ai}{}^2 + p_{Si}{}^2) + \sigma^2_{Bi}\;, \qquad \text{(B.12)}$$

where p_{Ai} and p_{Si} are the analytical and sampling RSDs for the i^{th} glass component.

If instead g_{ijk} is a bias-corrected value, then in (3.8)

$$w_{ijk} = \sigma^2_{gijk} = \left[\frac{(x_{ijk} - B_i)T_i}{\bar{c}_i - B_i}\right]^2 \left[\frac{x^2_{ijk}(p^2_{Ai} + p^2_{Si}) + \sigma^2_{Bi}}{(x_{ijk} - B_i)^2} + \frac{\sigma^2_{Ti}}{T_i^2} + \frac{\sigma^2_{\bar{c}i} + \sigma^2_{Bi}}{(\bar{c}_i - B_i)^2} - \frac{2\sigma_{Bi}{}^2}{(x_{ijk} - B_i)(\bar{c}_i - B_i)}\right]. \quad \text{(B.13)}$$

The derivation of this expression is the straightforward result of successive applications of common variance propagation expressions for ratios and products. First consider the variance propagation of the ratio,

$$w_{ijk} = \sigma^2_{gijk} = \left[\frac{(x_{ijk} - B_i)T_i}{(\bar{c}_i - B_i)}\right]^2 \left[\frac{Var[(x_{ijk} - B_i)T_i]}{[(x_{ijk} - B_i)T_i]^2} + \frac{\sigma^2_{\bar{c}i} + \sigma^2_{Bi}}{(\bar{c}_i - B_i)^2} - \frac{2Cov[(x_{ijk} - B_i)T_i, (\bar{c}_i - B_i)]}{(x_{ijk} - B_i)T_i(\bar{c}_i - B_i)}\right], \quad \text{(B.14)}$$

where

$$Cov[(x_{ijk} - B_i)T_i, (\bar{c}_i - B_i)] = T_i\sigma^2_{Bi}. \quad \text{(B.15)}$$

Next, consider the variance propagation of the product,

$$Var[(x_{ijk} - Bi)T_i] = [(x_{ijk} - Bi)T_i]^2 \left[\frac{(\sigma^2_{xijk} + \sigma^2_{Bi})}{(x_{ijk} - B_i)^2} + \frac{\sigma^2_{Ti}}{T_i^2}\right] = (x_{ijk} - B_i)^2\sigma^2_{Ti} + T_i{}^2(\sigma^2_{xijk} + \sigma^2_{Bi}). \quad \text{(B.16)}$$

Replacing σ^2_{xijk} by $x_{ijk}{}^2(p_{Ai}{}^2 + p_{Si}{}^2)$ in (B.16), then substituting (B.15) and (B.16) into (B.14) and simplifying, gives (B.13).

If no blank correction is made, (B.13) reduces to

$$w_{ijk} = \sigma^2_{gijk} = \left[\frac{x_{ijk}T_i}{\bar{c}_i}\right]^2 \left[(p^2_{Ai} + p^2_{Si}) + \frac{\sigma^2_{Ti}}{T_i^2} + \frac{\sigma^2_{\bar{c}i}}{\bar{c}_i{}^2}\right]. \quad \text{(B.17)}$$

Options Considered for Weights

The following four options were investigated for the weights w_{ijk}:

1) **w_{ijk} = 1.0 for all *i, j, k*.** Then equal weights are applied to each glass wt% concentration, and an equal shift of size

$$\frac{100 - \sum_{i=1}^{q} g_{ijk}}{q} \quad \text{(B.18)}$$

is added to each value to g_{ijk} to obtain g_{ijk}^*,

2) **$w_{ijk} = g_{ijk}$ for all *i, j, k*.** The glass wt% concentrations themselves are used as weights. This will permit the largest concentration to be changed the greatest absolute amount. In fact, for these weights, equation (B.3) reduces to

$$g_{ijk}^* = 100 \frac{g_{ijk}}{\sum_{i=1}^{q} g_{ijk}} , \tag{B.19}$$

a normalization convention that is commonly used. Note that for this weighting scheme, $g_{ijk}^* \geq 0.0$ in all cases.

3) **$w_{ijk} = \sigma_{gijk}$ for all *i, j, k*, where σ_{gijk} is the standard deviation of g_{ijk}.** The uncertainties (standard deviations) in glass wt% concentrations are used as weights, so those with greater uncertainties will be given the largest absolute adjustments in the normalization. Note that these standard deviations are expressed in absolute terms in this report, but they are obtained from relative standard deviations assumed to be known or previously estimated for each glass component.

4) **$w_{ijk} = \sigma_{gijk}^2$ for all *i, j, k*.** This option is similar to Option 3, with the variances of the glass wt% concentrations used as weights rather than the standard deviations.

Several examples were used to investigate the relative performance of the four weight conventions listed above. The performance in these examples and the associated intuitive appeal led to selecting the variances in Option 4 as the recommended weights.

Option 1 above is not at all reasonable because equal shifts for each glass component are obtained regardless of the magnitudes of the glass wt% concentrations or their uncertainties. When glass wt% concentrations sum to more than 100%, this option often leads to small wt% concentrations being adjusted to negative values.

Option 2 is not an unreasonable approach, but it ignores the uncertainties in the glass wt% concentrations.

Options 3 and 4 are similar, but Option 3 has the unappealing feature that the sum of ratios of "squared units" divided by "regular units" is minimized. Option 4 instead standardizes the differences by also using squared units in the denominator. Thus

$$\sum_{i=1}^{q} \frac{(g_{ijk} - g_{ijk}^*)^2}{w_{ijk}} = \sum_{i=1}^{q} \frac{(g_{ijk} - g_{ijk}^*)^2}{\sigma_{gijk}^2} = \sum_{i=1}^{q} \left[\frac{g_{ijk}}{\sigma_{gijk}} - \frac{g_{ijk}^*}{\sigma_{gijk}} \right]^2 = \sum_{i=1}^{q} (z_{ijk} - z_{ijk}^*)^2 , \tag{B.20}$$

so that using the variances as weights corresponds to working in terms of squared differences of "unitless" numbers of standard deviations (z_i and z_i*). This is analogous to what is typically done in WLS regression when fitting models to data. Further, using the variances as weights has the advantage of reducing the variances of the normalized glass wt% concentrations to be less than the variances of the non-normalized wt% concentrations.

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