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MCC

Materials Characterization Center

Fabrication and Characterization of MCC Approved Testing Material—ATM-WV/205 Glass

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August 1988

Prepared for the U.S. Department of Energy
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FABRICATION AND CHARACTERIZATION
OF MCC APPROVED TESTING MATERIAL
ATM-WV/205 GLASS

G. D. Maupin
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J. L. Daniel

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Pacific Northwest Laboratory
Richland, Washington 99352

PREFACE

This report, prepared by the Materials Characterization Center (MCC), is one in a series of PNL-5577 reports on nuclear waste glass Approved Testing Materials (ATMs). The suffix number indicates the specific ATM described. Additional reports will be added to the series as the corresponding glass ATMs are produced. See the most recent issue of PNL-4955, Approved Reference and Testing Materials for Use in Nuclear Waste Management Research and Development Programs, for a summary of existing ATMs.

The series currently planned includes the following reports:

<u>Report No.</u>	<u>Subject Glass</u>
PNL-5577-1	ATM-1
PNL-5577-2,3,4	ATM-2, ATM-3, ATM-4
PNL-5577-5	ATM-5
PNL-5577-6	ATM-6
PNL-5577-8	ATM-8
PNL-5577-9	ATM-9
PNL-5577-10	ATM-10
PNL-5577-11	ATM-11
PNL-5577-12	ATM-12
PNL-5577-18	ATM-18
PNL-5577-WV/205	ATM-WV/205

SUMMARY

The Materials Characterization Center (MCC) ATM-WV/205 glass represents a reference commercial high-level waste form similar to that which will be produced by the West Valley Nuclear Services Co., Inc., West Valley, New York. The target composition and acceptable range of composition were defined by the sponsor, West Valley Nuclear Services.

The ATM-WV/205 glass was produced in accordance with PNL's QA Manual for License-Related Programs, MCC technical procedures, and MCC QA Plan that were in effect during the course of this work. The method and procedure to be used in the fabrication and characterization of the ATM-WV/205 glass were specified in two run plans for glass preparation and a characterization plan.

A base glass, or frit, was produced from oxide and carbonate powders. Dopants (Ce, Mo, Nd, Zr) representing the radioactive elements that would be present in a real waste glass were added to the frit as a nitrate solution dopant. Additional alumina and silica were also added. The doped frit was then melted and crushed to obtain a uniform fused-glass powder of the required composition. The fused-glass powder was then blended with 0.18 wt% graphite and melted at 1150°C for 1 h. This final melt adjusted the oxidation state of the glass. All of the ATM-WV/205 glass was produced in the form of bars 1.9 x 1.9 x 10 cm nominal size, and 96 g nominal mass. A total of 20 bars of ATM-WV/205 glass weighing 1929 g was produced. The production bars were characterized to determine the mean composition, oxidation state, and microstructure of the ATM-WV/205 product. Table A summarizes the characterization results.

The ATM-WV/205 glass meets all specifications. The elemental composition and oxidation state of the glass are within the sponsor's specifications. Visually, the ATM-WV/205 glass bars appear uniformly glassy and generally without exterior features. Microscopic examination and x-ray diffraction revealed low (about 0.5 wt%) concentrations of 3- μ m iron chrome spinel crystals and 1- μ m ruthenium inclusions scattered randomly throughout the glassy matrix. Closed porosity, with pores ranging in diameter from 20 to 135 μ m, was observed in all samples.

TABLE A. Summary of ATM-WV/205 Characterization Results

Composition:

<u>Oxide</u>	<u>Target wt%</u>	<u>Sample Mean wt%</u>	<u>Sample Std. Dev.</u>	<u>Acceptable</u>
Al ₂ O ₃	6.50	6.54	0.0474	YES
B ₂ O ₃	9.51	9.34	0.0688	YES
BaO	0.05	0.052	0.0018	YES
CaO	0.58	0.61	0.0399	YES
CeO ₂	0.35	0.307	0.0065	YES
Cr ₂ O ₃	0.30	0.262	0.0085	YES
Cs ₂ O	0.07	0.070	0.0024	YES
Fe ₂ O ₃	11.60	11.68	0.3053	YES
K ₂ O	3.42	3.59	0.2159	YES
La ₂ O ₃	0.03	0.019	0.0015	YES
Li ₂ O	2.89	2.90	0.0145	YES
MgO	1.24	1.19	0.0150	YES
MnO ₂	1.25	1.25	0.0335	YES
MoO ₃	0.002	0.0021	0.0002	YES
Na ₂ O	10.44	10.26	0.0990	YES
Nd ₂ O ₃	0.18	0.18	0.0038	YES
NiO	0.32	0.31	0.0124	YES
P ₂ O ₅	2.39	2.39	0.0377	YES
RhO ₂	0.01	0.011	0.0007	YES
RuO ₂	0.07	0.074	0.0035	YES
SiO ₂	46.13	48.0	1.6621	YES
SO ₃	0.27	0.23	0.0086	YES
SrO	0.03	0.027	0.0006	YES
TiO ₂	0.93	0.86	0.0302	YES
Y ₂ O ₃	0.02	0.019	0.0004	YES
ZrO ₂	1.43	1.41	0.0246	YES
Total	100.01	101.6		

Oxidation State:

Target Fe²⁺/Fe³⁺ of 0.10
 Observed mean of 0.084
 Acceptable: YES

Microstructure:

3 μm Fe, Cr, Mn, Ni spinel crystals
 1 μm Ru inclusions
 Closed porosity, 20-135 μm diameter
 Acceptable: YES

Devitrification:

~0.5 wt% spinel
 Trace amounts of Ru metal
 Acceptable: YES

Bulk Density:

2.65 g/cm³
 Acceptable: YES

CONCLUSION:

ATM-WV/205 is an acceptable reference material.

As of August 1987, approximately 1800 g of ATM-WV/205 was available for distribution.

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1.0 INTRODUCTION

A major responsibility of the Materials Characterization Center (MCC) is to arrange for the formulation, acquisition, and distribution of reference materials. These reference materials aid in the testing of nuclear waste forms and provide data used for evaluation of repository systems. The purpose of this document is to provide the details of the fabrication and characterization of one of those reference materials, ATM-WV/205 glass. ATM-WV/205 was produced by the MCC at the Pacific Northwest Laboratory (PNL), Richland, Washington, which is operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute.

ATM-WV/205 is a nonradioactive glass and represents a reference commercial high-level waste form similar to that which will be produced by the West Valley Nuclear Services Co., Inc., West Valley, New York. ATM-WV/205 is a borosilicate glass incorporating the nonradioactive elements that comprise nominal West Valley commercial waste; Ce, Mo, Nd, and Zr were also added to represent the radioactive elements that would be present in real waste glass. The ATM-WV/205 glass was produced at the request, and to the specifications of West Valley Nuclear Services. The ATM-WV/205 glass is a nonradioactive analog of radioactive MCC Approved Test Material, ATM-10. The method and procedure to be used in the fabrication and characterization of the ATM-WV/205 glass were specified in two run plans for glass preparation and a characterization plan. The ATM-WV/205 glass was produced and characterized in accordance with PNL's QA Manual for License-Related Programs, MCC technical procedures, and MCC QA Plan that were in effect during the course of the work. Quality Assurance verification included six surveillances, three audits by West Valley Demonstration Project staff, and two internal audits.

2.0 SYNOPSIS

A general overview of the ATM-WV/205 fabrication and characterization work is given in this section. A more detailed account is given in Section 3.0 (Fabrication) and Section 4.0 (Characterization).

A base glass, or frit, was produced from oxide and carbonate powders. The dopant elements Ce, Mo, Nd, and Zr (representing radioactive counterparts) were added to the frit as a nitrate-solution dopant. Additional silica and alumina powder were also added to achieve the revised target composition requested by the sponsor. The doped frit was heated to 550°C to remove water and decompose the nitrates. All of the frit was then melted at 1150°C for 1 h to incorporate the dopants, silica, and alumina into the glass. The doped glass was crushed and sieved to less than 150 μm and then blended to ensure homogeneity.

A small test run, representing the final fabrication steps, was then conducted. A portion (300 g) of the doped glass was combined with 0.18 wt% graphite and melted at 1150°C for 1 h. The graphite powder served to reduce the oxidation state of the melt. Three glass bars were produced from this test melt. The glass bars were analyzed for chemical composition and oxidation state. Based on specifications and statistical criteria of the sponsor, the test bars were found acceptable.

The remaining doped glass powder was treated in the same manner as that used in the test melt. All of the ATM-WV-205 glass was produced in the form of bars with 1.9 x 1.9 x 10 cm nominal size and 96 g nominal mass. A total of 20 bars of ATM-10 glass, weighing 1929 g, was produced. The production bars were characterized to determine the mean composition, oxidation state, and microstructure of the ATM-WV/205 product. Table 2.1 summarizes the characterization results.

Energy-dispersive x-ray fluorescence (EDXRF) analysis was performed on 19 of the bars. Inductively coupled plasma atomic emission spectroscopy (ICP) and wavelength-dispersive x-ray fluorescence (WDXRF) analysis were performed in duplicate on powder samples taken from six of the bars. As shown in Table 2.1, the observed mean ATM-WV/205 glass composition meets the sponsor's specification for each element and for uniformity of composition.

TABLE 2.1. Summary of ATM-WV/205 Characterization Results

Composition:

<u>Oxide</u>	<u>Target wt%</u>	<u>Sample Mean wt%</u>	<u>Sample Std. Dev.</u>	<u>Acceptable</u>
Al ₂ O ₃	6.50	6.54	0.0474	YES
B ₂ O ₃	9.51	9.34	0.0688	YES
BaO	0.05	0.052	0.0018	YES
CaO	0.58	0.61	0.0399	YES
CeO ₂	0.35	0.307	0.0065	YES
Cr ₂ O ₃	0.30	0.262	0.0085	YES
Cs ₂ O	0.07	0.070	0.0024	YES
Fe ₂ O ₃	11.60	11.68	0.3053	YES
K ₂ O	3.42	3.59	0.2159	YES
La ₂ O ₃	0.03	0.019	0.0015	YES
Li ₂ O	2.89	2.90	0.0145	YES
MgO	1.24	1.19	0.0150	YES
MnO ₂	1.25	1.25	0.0335	YES
MoO ₃	0.002	0.0021	0.0002	YES
Na ₂ O	10.44	10.26	0.0990	YES
Nd ₂ O ₃	0.18	0.18	0.0038	YES
NiO	0.32	0.31	0.0124	YES
P ₂ O ₅	2.39	2.39	0.0377	YES
RhO ₂	0.01	0.011	0.0007	YES
RuO ₂	0.07	0.074	0.0035	YES
SiO ₂	46.13	48.0	1.6621	YES
SO ₃	0.27	0.23	0.0086	YES
SrO	0.03	0.027	0.0006	YES
TiO ₂	0.93	0.86	0.0302	YES
Y ₂ O ₃	0.02	0.019	0.0004	YES
ZrO ₂	1.43	1.41	0.0246	YES
Total	100.01	101.6		

Oxidation State:

Target Fe²⁺/Fe³⁺ of 0.10
 Observed mean of 0.084
 Acceptable: YES

Microstructure:

3 μm Fe, Cr, Mn, Ni spinel crystals
 1 μm Ru inclusions
 Closed porosity, 20-135 μm diameter
 Acceptable: YES

Devitrification:

~0.5 wt% spinel
 Trace amounts of Ru metal
 Acceptable: YES

Bulk Density:

2.65 g/cm³
 Acceptable: YES

CONCLUSION:

ATM-WV/205 is an acceptable
 reference material.

The oxidation state of the ATM-WV/205 glass, as exhibited by the ratio of ferrous to ferric ($\text{Fe}^{2+}/\text{Fe}^{3+}$) ions in the glass, was determined for single samples taken from six different bars. The measured ratios ranged from 0.072 to 0.098 with a mean of 0.084. All the $\text{Fe}^{2+}/\text{Fe}^{3+}$ analyses were well within the specified range of 0.02 to 0.18.

The exteriors of all the ATM-WV/205 bars were uniform and glossy in appearance. A slight metallic sheen was observed on most bars. No indications of macroscopic phase separation or surface porosity were observed. Subsequent fracturing and cutting of seven bars revealed, by visual inspection, a small number of voids or bubbles less than 0.5 mm in diameter.

Cross sections of three bars were mounted and polished using standard metallography techniques. These samples were observed by reflected and transmitted light microscopy. Individual cubic features, measuring approximately 3 μm on an edge, were observed scattered throughout all samples. Closed porosity, with pores ranging in diameter from 20 to 135 μm , was observed in all microscopy samples.

Fractured surfaces of three bars were observed by scanning electron microscopy (SEM). Observed pore diameters ranged from 60 to 125 μm . Cubic second phase features, similar to those observed by optical microscopy, were identified by energy-dispersive x-ray spectroscopy (EDXS) as regions of high Cr, Fe, Mn and Ni concentrations. The morphology and composition of these cubic features are typical of spinel crystals often found in simulated nuclear waste glasses. A few ~1- μm -diameter ruthenium inclusions were also observed. The individual samples appeared to be of uniform composition and structure.

X-ray diffraction (XRD) analysis was conducted on powder samples taken from six bars. X-ray diffraction patterns typical of crystalline spinel-type materials were observed. A single small peak, with a location corresponding to the main peak for ruthenium metal, was also observed. These observations indicated that ATM-WV/205 glass contains very little (about 0.5 wt% in the case of spinel) crystalline material.

Water immersion bulk-density determinations were performed on sections taken from six bars. The sample densities ranged from 2.647 to 2.654; the overall mean density was 2.649 g/cm³.

The ATM-WV/205 meets all specifications. It is considered suitable for use as a reference material. As of August 1987, approximately 1800 g of ATM-WV/205 was available for distribution.

3.0 FABRICATION

The fabrication of ATM-WV/205 began on May 19, 1986, and was completed March 11, 1987. The procedures and methods used in fabrication were described in two run plans. Supporting analytical data are retained in the PNL Records Center. The ATM-WV/205 glass was produced in accordance with MCC technical procedures.

3.1 STARTING MATERIALS

The ATM-WV/205 glass was produced from the reagent-grade chemicals listed in Table 3.1. Further description of the starting chemical is presented in Appendix A.

3.2 INITIAL TEST BATCH

An initial 500-g test batch was produced from the compounds listed in Table 3.1. For this initial batch, the quantity of compound to be added was calculated based on theoretical compound/oxide conversion factors. The theoretical factors are listed in Table 3.1. These factors assume ideal stoichiometry and negligible volatility of the target elements. The main purpose of this initial test batch was to determine if empirical factors were needed.

The indicated quantities of compounds were combined using a V-blender with intensifier bar for 4 h. The mixed powder was melted in air at 1150°C for 1 h using a 500-mL platinum crucible and a Deltech^(a) furnace, model DT-31-RS. Temperature was monitored using a calibrated Type "S" thermocouple and an Omega (model 650) digital thermometer. The molten glass was poured onto a stainless steel plate. After cooling, all of the resulting glass was crushed and sieved to less than 150 μ m using an Angstrom mill with tungsten-carbide grinding chamber and an 8-in. Newark sieve (USA standard sieve series number 100).

(a) Use of manufacturers' names does not imply PNL endorsement.

TABLE 3.1. Worksheet for Undoped Preliminary Test Batch

Oxide	Target wt%	Compound Used	Theoretical Compound:Oxide Factor	Quantity of Compound Used, g ^(a)
Al ₂ O ₃	2.95	Al ₂ O ₃	1.000	14.75
B ₂ O ₃	10.40	H ₃ BO ₃	1.776	92.35
BaO	0.05	BaCO ₃	1.287	0.32
CaO	0.63	CaCO ₃	1.785	5.62
CeO ₂	0.07	CeO ₂	1.000	0.35
Cr ₂ O ₃	0.32	Cr ₂ O ₃	1.000	1.60
Cs ₂ O	0.08	Cs ₂ CO ₃	1.156	0.46
Fe ₂ O ₃	12.69	Fe ₂ O ₃	1.000	63.45
K ₂ O	3.74	K ₂ CO ₃	1.467	27.43
La ₂ O ₃	0.03	La ₂ O ₃	1.000	39.07
Li ₂ O	3.16	Li ₂ CO ₃	2.473	39.07
MgO	1.36	MgO	1.000	6.80
MnO ₂	1.37	MnO ₂	1.000	6.85
Na ₂ O	11.42	Na ₂ CO ₃	1.710	96.12 ^(b)
Nd ₂ O ₃	0.19	Nd ₂ O ₃	1.000	0.95
NiO	0.35	NiO	1.000	1.75
P ₂ O ₅	2.62	(NH ₄) ₂ HPO ₄	1.861	24.38
RhO ₂	0.01	Rh ₂ O ₃	0.941	0.05
RuO ₂	0.08	RuO ₂	1.000	0.40
SO ₃	0.23	Na ₂ SO ₄	1.774	2.03
SiO ₂	46.88	SiO ₂	1.000	234.40
SrO	0.03	SrCO ₃	1.425	0.21
TiO ₂	1.02	TiO ₂	1.000	5.10
Y ₂ O ₃	0.02	Y ₂ O ₃	1.000	0.10
ZrO ₂	<u>0.30</u>	ZrO ₂	1.000	<u>1.50</u>
	100.00			626.19

(a) Quantity of compound per 500 g glass = (500) x (oxide wt%/100) x (compound:oxide factor).

(b) Quantity adjusted to account for Na₂O contribution from Na₂SO₄.

Three powder samples were randomly selected and submitted for ICP (by two separate laboratories) and EDXRF analyses. Table 3.2 lists the analytical results from the initial test batch. With the exception of Al_2O_3 , the analyses agree with the intended target composition. Based on these findings, the theoretical conversion factors were deemed appropriate for all but Al_2O_3 . Although the source of the extra Al_2O_3 was not identified, an empirical factor (0.8912) was assigned to Al_2O_3 .

3.3 ACTUAL FRIT FABRICATION

The quantities of the compounds listed in Table 3.3 were combined and melted as described for the initial batch. Fourteen separate melts of about 425 g each were required. During four of these melts, molten glass was foamed out of the crucible. Approximately 500 g of the glass were lost because of the foaming. The molten glass was quenched onto a steel plate. After cooling, this glass was crushed and sieved to less than 150 μm . The resulting 5.5 kg of frit were mixed in a V-blender for 1 h to ensure homogeneity.

Four analytical samples were selected at random and submitted for ICP and EDXRF analyses. The samples were run in duplicate. The results are listed in Tables 3.4 and 3.5. Notice in Table 3.4 that the ICP and EDXRF analyses complement each other. The EDXRF analysis was required for the low-concentration, higher-atomic-number elements. The ICP analysis was required for the lower-atomic-number elements (Al, B, Li, Mg, Na) and for Nd. For those elements that were analyzed by both techniques, the data generally agree. In the cases of Zr and Fe, however, the numbers differ. A problem was identified with the ICP fusions. Zirconium phosphate forms a precipitate in the KOH solutions. This reaction resulted in very erratic Zr ICP values depending on when and how the fusions were run. The differences in Fe values were not resolved. For the purpose of statistical analysis, EDXRF values are used in preference to the ICP values.

A statistical test was performed to ensure that the observed mean frit composition met the sponsor's specifications. As shown in Table 3.5, the statistical test indicated that the frit composition was acceptable. The

TABLE 3.2. Chemical Analysis of ATM-WV/205 Preliminary Test Batch by Inductively-Coupled Plasma Spectroscopy (ICP) and Energy-Dispersive X-Ray Fluorescence (EDXRF)

Oxide	Target wt%	ICP Data(a), wt%			ICP Data(b), wt%			EDXRF Data, wt%			Mean, wt%	Dev. from Target, %	Allow. Dev., %	Adjust Factor
		P1	P2	P3	P1	P2	P3	P1	P2	P3				
Al ₂ O ₃	2.95	3.32	3.30	3.32	3.25	3.24	3.27	3.04	3.25	3.14	3.24	9.7	5	Yes(c)
B ₂ O ₃	10.40	10.60	10.50	10.70	10.40	10.35	10.40				10.49	0.9	5	No
BaO	0.05	0.06	0.06	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	11.1	40	No
CaO	0.63	0.66	0.68	0.67	0.73	0.76	0.74	0.70	0.70	0.71	0.71	12.0	20	No
CeO ₂	0.07				0.08	0.08	0.08	0.10	0.10	0.10	0.09	28.6	50	No
Cr ₂ O ₃	0.32	0.30	0.29	0.30	0.29	0.30	0.32	0.31	0.31	0.31	0.30	-5.2	20	No
Cs ₂ O	0.08							0.09	0.09	0.09	0.09	12.5	30	No
Fe ₂ O ₃	12.69	12.30	12.20	12.30	12.30	12.20	12.30	13.52	13.52	13.54	12.69	-0.0	7	No
K ₂ O	3.74	3.75	3.68	3.71	4.13	4.29	4.16	3.78	3.78	3.83	3.90	4.3	10	No
La ₂ O ₃	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	7.4	50	No
Li ₂ O	3.16	3.31	3.28	3.33	3.05	3.04	3.01				3.17	0.3	5	No
MgO	1.36	1.28	1.28	1.30	1.33	1.35	1.34				1.31	-3.4	15	No
MnO ₂	1.37	1.39	1.38	1.38	1.39	1.38	1.40				1.39	1.2	15	No
Na ₂ O	11.42	11.30	11.40	11.40	11.00	10.90	10.80				11.13	-2.5	10	No
Nd ₂ O ₃	0.19	0.15	0.15	0.15	0.21	0.21	0.21				0.18	-5.3	26	No
NiO	0.35	0.35	0.35	0.35	0.34	0.34	0.34	0.38	0.37	0.37	0.35	1.3	15	No
P ₂ O ₅	2.62				1.95	2.29	2.31	2.58	2.57	2.51	2.37	-9.6	20	No
RhO ₂	0.01							0.02	0.01	0.01	0.01	33.3	75	No
RuO ₂	0.08							0.09	0.09	0.09	0.09	12.5	50	No
SO ₃	0.23							0.25	0.27	0.24	0.25	10.1	50	No
SiO ₂	46.88	47.30	47.20	47.20	44.25	43.60	44.25	47.26	47.51	47.41	46.22	-1.4	5	No
SrO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.0	67	No
TiO ₂	1.02	1.00	0.96	0.99	1.00	0.99	0.99	0.95	0.96	0.96	0.98	-4.1	15	No
Y ₂ O ₃	0.02							0.02	0.02	0.02	0.02	0.0	75	No
ZrO ₂	0.30	0.24	0.24	0.25	0.26	0.20	0.27	0.30	0.29	0.30	0.26	-13.0	30	No
	100.00										99.36			

(a) ICP data from 325 Building Analytical Laboratory.

(b) ICP data from 3720 Building Analytical Laboratory.

(c) An empirical factor of 0.8912 assigned to Al₂O₃.

TABLE 3.3. Worksheet for ATM-WV/205 Frit Fabrication

Oxide	Target wt%	Compound Used	Theoretical Compound:Oxide Factor	Quantity of Compound Used, g ^(a)
Al ₂ O ₃	2.95	Al ₂ O ₃	0.891 ^(b)	157.74
B ₂ O ₃	10.40	H ₃ BO ₃	1.776	1108.20
BaO	0.05	BaCO ₃	1.287	3.86
CaO	0.63	CaCO ₃	1.785	67.47
CeO ₂	0.07	CeO ₂	1.000	4.20
Cr ₂ O ₃	0.32	Cr ₂ O ₃	1.000	19.20
Cs ₂ O	0.08	Cs ₂ CO ₃	1.156	5.55
Fe ₂ O ₃	12.69	Fe ₂ O ₃	1.000	761.40
K ₂ O	3.74	K ₂ CO ₃	1.467	329.19
La ₂ O ₃	0.03	La ₂ O ₃	1.000	1.80
Li ₂ O	3.16	Li ₂ CO ₃	2.473	468.90
MgO	1.36	MgO	1.000	81.60
MnO ₂	1.37	MnO ₂	1.000	82.20
Na ₂ O	11.42	Na ₂ CO ₃	1.710	1153.40 ^(c)
Nd ₂ O ₃	0.19	Nd ₂ O ₃	1.000	11.40
NiO	0.35	NiO	1.000	21.00
P ₂ O ₅	2.62	(NH ₄) ₂ HPO ₄	1.861	292.55
RhO ₂	0.01	Rh ₂ O ₃	0.941	0.56
RuO ₂	0.08	RuO ₂	1.000	4.80
SO ₃	0.23	Na ₂ SO ₄	1.774	24.48
SiO ₂	46.88	SiO ₂	1.000	2812.80
SrO	0.03	SrCO ₃	1.425	2.57
TiO ₂	1.02	TiO ₂	1.000	61.20
Y ₂ O ₃	0.02	Y ₂ O ₃	1.000	1.20
ZrO ₂	0.30	ZrO ₂	1.000	18.00
	100.00			7495.28

(a) Quantity of compound per 6000 g glass = (6000) x (oxide wt%/100) x (compound:oxide factor).

(b) An empirical factor was used for Al₂O₃; all other factors were theoretical.

(c) Quantity adjusted to account for Na₂O contribution from Na₂SO₄.

TABLE 3.4. Analysis of Predoped ATM-WV/205 Frit by Inductively Coupled Plasma Spectroscopy (ICP) and Energy Dispersive X-Ray Fluorescence (EDXRF).

ATM-10 Oxide	ICP Data, wt%								EDXRF Data, wt%							
	[<-----{1st Run}----->]				[<-----{2nd Run}----->]				[<-----{1st Run}----->]				[<-----{2nd Run}----->]			
	-M1A	-M1B	-M1C	-M1D	-M1A	-M1B	-M1C	-M1D	-M1E	-M1F	-M1G	-M1H	-M1E	-M1F	-M1G	-M1H
Al ₂ O ₃	2.85	2.89	2.86	2.88	2.92	2.93	2.93	2.84	2.51	2.61	2.99	2.80	2.44	2.95	3.00	2.72
B ₂ O ₃	10.00	10.10	10.00	10.00	10.10	10.20	10.30	10.10								
BaO	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.054	0.055	0.054	0.055	0.056	0.057	0.057	0.057
CaO	0.65	0.65	0.64	0.65	0.65	0.64	0.65	0.65	0.638	0.677	0.694	0.662	0.659	0.659	0.700	0.642
CeO ₂									0.098	0.101	0.098	0.105	0.100	0.099	0.100	0.098
Cr ₂ O ₃	0.29	0.29	0.29	0.29	0.29	0.30	0.30	0.30	0.292	0.299	0.296	0.302	0.305	0.294	0.296	0.292
Cs ₂ O									0.082	0.083	0.082	0.082	0.084	0.082	0.083	0.082
Fe ₂ O ₃	12.10	12.10	12.10	12.10	12.10	12.10	12.30	12.10	13.01	13.02	13.11	13.14	13.10	13.02	13.18	13.14
K ₂ O	3.31	3.27	3.14	3.14	3.56	3.59	3.63	3.73	3.62	3.57	3.61	3.64	3.67	3.64	3.67	3.59
La ₂ O ₃			0.02	0.02	0.03	0.03	0.02	0.03	0.031	0.030	0.029	0.029	0.029	0.031	0.032	0.031
Li ₂ O	3.22	3.22	3.21	3.23	3.33	3.25	3.29	3.24								
MgO	1.25	1.26	1.25	1.26	1.26	1.27	1.28	1.27								
MnO ₂	1.34	1.35	1.35	1.35	1.35	1.35	1.37	1.35								
Na ₂ O	11.30	11.20	11.10	11.10	11.10	11.10	11.10	11.10								
Nd ₂ O ₃ ^(a)	0.18	0.18	0.18	0.18	0.19	0.19	0.18	0.19								
NiO	0.32	0.33	0.33	0.33	0.34	0.34	0.36	0.34	0.356	0.354	0.359	0.360	0.357	0.357	0.360	0.362
P ₂ O ₅									2.37	2.40	2.47	2.42	2.28	2.26	2.36	2.22
RhO ₂									0.013	0.013	0.013	0.012	0.013	0.012	0.012	0.012
RuO ₂									0.095	0.095	0.093	0.093	0.095	0.092	0.096	0.094
SO ₃									0.225	0.207	0.257	0.250	0.230	0.272	0.265	0.215
SiO ₂	47.10	47.70	47.60	47.70	46.90	47.30	48.10	47.30	47.56	46.96	46.68	46.98	46.85	45.93	46.83	46.72
SrO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.029
TiO ₂	0.95	0.96	0.97	0.97	0.95	0.95	0.97	0.95	0.939	0.934	0.922	0.952	0.936	0.921	0.954	0.917
Y ₂ O ₃									0.022	0.021	0.022	0.021	0.022	0.022	0.021	0.021
ZrO ₂	0.22	0.19	0.17	0.22					0.296	0.296	0.297	0.296	0.297	0.296	0.296	0.294
Total	95.16	95.77	95.29	95.50	95.15	95.62	96.86	95.57	72.23	71.76	72.10	72.22	71.55	71.02	72.34	71.54

(a) Special preparation of fusion sample (based on ASTM Method C-146) used to increase ICP sensitivity for Nd.

TABLE 2-1. Observed and Target Mean and Range Data for 20 Elements by Fluorescence
Data and Statistical Test for Predoped ATM-WV/205 Frit

Oxide	Target wt%	Observed Mean, wt%	Method	Target Minimum, wt%	Lower 95% Conf. Int., wt%	Upper 95% Conf. Int., wt%	Target Maximum, wt%	Acceptable Range
Al ₂ O ₃	2.95	2.89	(ICP)	2.80	2.857	2.918	3.10	Yes
B ₂ O ₃	10.40	10.10	(ICP)	9.88	10.011	10.189	10.92	Yes
BaO	0.05	0.056	(XRF)	0.03	0.055	0.057	0.07	Yes
CaO	0.63	0.666	(XRF)	0.50	0.648	0.685	0.76	Yes
CeO ₂	0.07	0.100	(XRF)	0.04	0.098	0.102	0.11	Yes
Cr ₂ O ₃	0.32	0.297	(XRF)	0.26	0.293	0.301	0.38	Yes
Cs ₂ O	0.08	0.083	(XRF)	0.06	0.082	0.083	0.10	Yes
Fe ₂ O ₃	12.69	13.091	(XRF)	11.80	13.037	13.145	13.58	Yes
K ₂ O	3.74	3.625	(XRF)	3.37	3.595	3.655	4.11	Yes
La ₂ O ₃	0.03	0.030	(XRF)	0.02	0.029	0.031	0.05	Yes
Li ₂ O	3.16	3.25	(ICP)	3.00	3.214	3.283	3.32	Yes
MgO	1.36	1.263	(XRF)	1.16	1.254	1.271	1.56	Yes
MnO ₂	1.37	1.35	(ICP)	1.16	1.344	1.358	1.58	Yes
Na ₂ O	11.42	11.14	(ICP)	10.28	11.075	11.200	12.56	Yes
Nd ₂ O ₃	0.19	0.18	(ICP)	0.14	0.179	0.188	0.24	Yes
NiO	0.35	0.358	(XRF)	0.30	0.356	0.360	0.40	Yes
P ₂ O ₅	2.62	2.348	(XRF)	2.10	2.276	2.420	3.14	Yes
RhO ₂	0.01	0.012	(XRF)	0.003	0.012	0.013	0.02	Yes
RuO ₂	0.08	0.094	(XRF)	0.04	0.093	0.095	0.12	Yes
SO ₃	0.23	0.240	(XRF)	0.12	0.220	0.260	0.35	Yes
SiO ₂	46.88	46.81	(XRF)	44.54	46.438	47.188	49.22	Yes
SrO	0.03	0.028	(XRF)	0.01	0.028	0.028	0.05	Yes
TiO ₂	1.02	0.935	(XRF)	0.87	0.923	0.946	1.17	Yes
Y ₂ O ₃	0.02	0.021	(XRF)	0.01	0.021	0.022	0.04	Yes
ZrO ₂	0.30	0.296	(XRF)	0.21	0.295	0.297	0.39	Yes
Total =	100.00	99.27						

"actual batch" fabrication resulted in 5.5 kg of powdered glass, or frit. Only 2.4 kg of this frit was used in the production of ATM-WV/205 glass. The other 2.9 kg was used for production of another approved test material (ATM-10).

3.4 DOPANT SOLUTIONS

The dopants (Ce, Mo, Nd, Zr) were prepared as separate nitrate solutions. The cerium dopant was made by dissolving 52.98 g cerium nitrate hexahydrate in 1 M nitric acid and diluting to 250 mL. Ammonium molybdate (0.163 g), dissolved and diluted to 50 mL in 0.05 M nitric acid, was used as the molybdenum dopant. The neodymium dopant was prepared by dissolving 0.06 g of the oxide in 10 mL 8 M nitric and then diluting to 50 mL with deionized water. Zirconium nitrate hydrate (189.2 g) was dissolved and made up to 500 mL volume using 0.5 M nitric acid. The resulting zirconium colloidal suspension was then filtered using Whatman Number 42 paper. Samples were prepared from each of the dopant solutions and submitted for analysis.

3.5 DOPANT, SILICA, AND ALUMINA ADDITIONS TO FRIT

Following production of the frit, West Valley Nuclear Services requested the target composition be changed to a higher Al_2O_3 concentration while holding SiO_2 unchanged. This new target composition is shown as "Revised ATM-WV/205" in Table 3.6. To effect this change, 101.12 g Al_2O_3 and 71.37 g SiO_2 were combined with 2436.8 g frit using the V-blender for 1 h.

The results of the ICP analysis for the dopant solutions are shown in Table 3.7. The indicated masses of the dopants were combined and diluted to 650 mL using deionized water in a 4-L stainless steel beaker. The 2609.3 g of modified frit was then added to the beaker and mixed using a stainless steel spatula, resulting in about 1 liter of frit-dopant-additional oxides slurry.

3.6 DRYING AND DENITRATING OF THE DOPED FRIT

Approximately half of the slurry (~500 mL) was transferred to a 2-L stainless steel beaker. The beaker was then heated to 200°C using a Hoskins pot furnace. The slurry was stirred intermittently during the 2 h of drying at

TABLE 3.6. Revised ATM-WV/205 Target Composition

Oxide	Initial (Run Plan 4/4/86)		Revised (Charac. Plan 9/86)	
	Conc. wt%	Allowable Deviation, wt%	Conc. wt%	Allowable Deviation, wt%
Al ₂ O ₃	2.90	5	6.50	10
B ₂ O ₃	10.24	5	9.51	5
BaO	0.05	40	0.05	40
CaO	0.62	20	0.58	20
CeO ₂	0.38	50	0.35	50
Cr ₂ O ₃	0.32	20	0.30	20
Cs ₂ O	0.08	30	0.07	30
Fe ₂ O ₃	12.50	7	11.60	7
K ₂ O	3.68	10	3.42	10
La ₂ O ₃	0.03	50	0.03	50
Li ₂ O	3.11	5	2.89	5
MgO	1.34	15	1.24	15
MnO ₂	1.35	15	1.25	15
MoO ₃	0.002	75	0.002	75
Na ₂ O	11.62	10	10.44	10
Nd ₂ O ₃	0.19	26	0.18	26
NiO	0.34	15	0.32	15
P ₂ O ₅	2.58	20	2.39	20
RhO ₂	0.01	75	0.01	75
RuO ₂	0.08	50	0.07	50
SO ₃	0.23	50	0.27	65
SiO ₂	46.13	5	46.13	10
SrO	0.03	67	0.03	67
TiO ₂	1.00	15	0.93	15
Y ₂ O ₃	0.02	75	0.02	75
ZrO ₂	1.54	30	1.43	30
Total	100.00		100.01	
Fe ²⁺ /Fe ³⁺	0.10	±0.08	0.10	±0.08

TABLE 3.7. Dopants Added to ATM-WV/205 Frit

<u>Dopant</u>	<u>Elemental Anal. Conc., (a) mg/g</u>	<u>Amount of Dopant Added to 2607 g of Modified Frit, g</u>
Cerium	55.5	99.8
Molybdenum	1.74	9.01
Neodymium	9.95	11.99
Zirconium	64.4	350.02

(a) Analysis by ICP.

this temperature. After 2 h, the doped frit appeared relatively dry and the temperature was increased to 550°C. Additional water and nitrate fumes were liberated during the 2 h at 550°C. After a total drying time of 4 h, the dried-denitrated powder was removed. The other half of the frit-dopant slurry was treated in the same manner.

3.7 MELTING OF THE DOPED FRIT

A Deltech "DT-31-RS" furnace, located in an open-faced hood, was used to melt the doped frit. Temperature was monitored using a calibrated Type "S" thermocouple and an Omega (model 650) digital thermometer. A 500-mL platinum crucible was used to melt 500 g of frit at one time. The doped frit was added to the crucible in three additions of 150 to 200 g each. About 15 min were required between additions to avoid foaming over. After the final addition, each ~500-g melt was held ~1 h at ~1150°C and then poured onto a stainless steel plate to cool. Five melts were required to process all of the doped frit. Approximately 150 g of glass were lost due to foaming.

The doped glass appeared very glossy and homogeneous. There were no signs of macroscopic phase separation. The doped glass was crushed and sieved to 150 μ m, and the powder was mixed for 30 min in the V-blender. A total of 2475 g of powdered doped glass was recovered from the blender.

3.8 OXIDATION TEST MELT

The purpose of the oxidation test melt was to determine how much graphite should be added to the final glass melt.^(a) The graphite acts as a reductant and was used to achieve the desired $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.10 ± 0.08 . A glass similar to the intended ATM-WV/205 was produced from the chemicals listed in Table 3.8. This oxidation test glass was crushed and sieved to 150 μm . Half of the oxidation test glass was then combined with 0.20 wt% graphite. The glass/graphite was melted in a 250-mL Denver Fire Clay (DFC) crucible for 1 h and then quenched on a stainless steel plate. Subsequent testing indicated that the redox test glass treated with 0.20 wt% graphite resulted in an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.11. Based on this test, it was decided to use 0.18 wt% graphite in the actual test melt described in Section 3.9.

3.9 TEST MELT

The purpose of the test melt was to demonstrate whether the final ATM-WV/205 production glass would meet the sponsor's specifications and be a suitable reference material. The procedure used for producing the test melt was to be identical to the procedure used for the actual production glass. The test melt was performed in an open-faced hood using the Deltech furnace described in Section 3.7. A Thermolyne 2000 furnace, monitored with a calibrated Type K thermocouple, an Omega (model 650) thermometer, and a Kipp Zonnen strip chart recorder, was used for the annealing of the glass bars.

Three hundred grams of the doped glass described in Section 3.7 were combined with 0.541 g of powdered graphite. The resulting 0.18 wt% graphite was predicted to yield an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.10 based on the oxidation test melt described in Section 3.8. Approximately 125 g of the graphite spiked glass were placed in a 250-mL DFC crucible. The crucible was then placed in the Deltech furnace at 1150°C. Twenty minutes later, another 35 g of glass were

(a) The amount of graphite needed cannot be simply calculated based on stoichiometry because much of the graphite reacts with air rather than with the glass. Therefore, this empirical approach, based on experience under similar conditions, was required.

TABLE 3.8. Worksheet for Oxidation Test Glass

Oxide	Target wt%	Compound Used	Amount (a) Used, g
Al ₂ O ₃	6.50	Al ₂ O ₃	39.00
B ₂ O ₃	9.51	H ₃ BO ₄	101.36
BaO	0.05	BaCO ₃	0.39
CaO	0.58	CaCO ₃	6.21
CeO ₂	0.35	CeO ₂	2.10
Cr ₂ O ₃	0.30	Cr ₂ O ₃	1.80
Cs ₂ O	0.07	Cs ₂ CO ₃	0.49
Fe ₂ O ₃	11.60	Fe ₂ O ₃	69.60
K ₂ O	3.42	K ₂ CO ₃	30.11
La ₂ O ₃	0.03	La ₂ O ₃	0.18
Li ₂ O	2.89	Li ₂ CO ₃	42.88
MgO	1.24	MgO	7.44
MnO ₂	1.25	MnO ₂	7.50
MoO ₃	0.002	MoO ₃	0.012
Na ₂ O	10.44	Na ₂ CO ₃ (b)	83.56
Nd ₂ O ₃	0.18	Nd ₂ O ₃	1.08
NiO	0.32	NiO	1.92
P ₂ O ₅	2.39	Na ₄ P ₂ O ₇ *10H ₂ O	45.06
RhO ₂	0.01	Rh ₂ O ₃	0.05
RuO ₂	0.07	RuO ₂	0.42
SO ₃	0.27	Na ₂ SO ₄	2.87
SiO ₂	46.13	SiO ₂	276.78
SrO	0.03	SrCO ₃	0.26
TiO ₂	0.93	TiO ₂	5.58
Y ₂ O ₃	0.02	Y ₂ O ₃	0.12
ZrO ₂	1.43	ZrO ₂	8.58
Total	100.01		735.26

(a) To make 600 g of glass.

(b) Additional Na₂O from Na₄P₂O₇*10H₂O and Na₂SO₄.

added to the crucible. Three more additions of roughly 48 g each were added at 20-min intervals. The test melt was held for 30 min at 1150°C and then stirred with a 6-mm-diameter Inconel® rod. The melt looked uniform and no foam-overs occurred.

After a total of 1 h at 1150°C, the first glass bar was poured. The molten glass was poured into a preheated (~360°C) stainless steel bar mold and allowed to cool to a dull-red heat. During this time, the crucible was returned to the Deltech furnace at 1150°C; also an indentation, or "dimple," was made in the end of the glass bar where pouring had begun. The resulting 1.9 x 1.9 x 10 cm, 90-g bar was then transferred to the preheated (500°C) Thermolyne 2000 furnace for annealing.

Two more glass bars were poured and placed in the Thermolyne furnace. The three bars were annealed for 2 h at 500°C. The Thermolyne furnace was then turned off, and the bars were allowed to cool undisturbed. The cooling behavior of the Thermolyne 2000 furnace is illustrated in Figure 3.1. As expected, the cooling rate is not linear with time. However, the average cooling rate of the Thermolyne furnace between 500°C and 200°C was 100°C/h.

After the three bars had cooled to less than 50°C, they were removed from the Thermolyne furnace. The bars looked very glassy and homogeneous. A slight metallic sheen was observed on the bars. No indication of surface porosity or macroscopic phase separation was observed. The first bar poured, bar 1, was sectioned using a Buehler Isomet low-speed diamond saw with deionized-water coolant. Three cross sections ~6 mm thick were taken, one from each end and one from the center of the bar. The sections were individually crushed using a tungsten-carbide disk mill. Portions of these powders were submitted for ICP, EDXRF, WDXRF, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ analyses. In addition, each end and the center of the second bar were subjected to nondestructive EDXRF analysis.

The analytical results from the test melt are shown in Tables 3.9 and 3.10. A statistical test was performed to determine if the observed mean composition met the sponsor's specifications. As shown in Table 3.10, the analyzed composition of the test melt meets the revised ATM-WV/205 specifications.

FIGURE 3.1. Observed Cooling Rate of Thermolyne 2000 Furnace Used for Annealing ATM-WV/205 Glass Bars. Average cooling rate between 500°C and 200°C was 100°C/h.

3.10 FABRICATION OF ATM-WV/205 PRODUCTION BARS

Production of the ATM-WV/205 glass bars essentially duplicated the procedure used for the test melt (Section 3.9). The remaining 2162.0 g of doped glass was combined with 3.90 g of graphite (0.18 wt%) using the V-blender for 1 h. The glass-graphite mixture was then melted in DFC crucibles as described in Section 3.8. A total of seven melt cycles, over 2 days, was required to process all of the glass. Typically, three glass bars, measuring nominally 1.9 x 1.9 x 10 cm and weighing 96 g, were produced from each melt cycle. Each bar was "dimpled" as described in Section 2.9. Two identical Thermolyne 2000 furnaces were used to anneal the glass bars at 500°C for 2 to 6.3 h. A total of 20 full bars weighing a total of 1929 g was produced. Two partial bars of 40 g each were also produced but are not included as ATM-WV/205 production bars. An estimated 140 g of glass were trapped in the two DFC crucibles that were used.

TABLE 2.0 ANALYSIS OF ATM MM/305 T-1 M-14 By Inductively Coupled Plasma Spectroscopy (ICP), Energy-Dispersive X-Ray Fluorescence (EDXRF), Wavelength-Dispersive X-Ray Fluorescence (WDXRF), and Spectrophotometric Determination of Reduced and Total Iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$)

Oxide	Target wt%	ICP Data, wt%						EDXRF Data, wt%					
		TM1a	TM2a	TM3a	TM1b	TM2b	TM3b	TM1a	TM2a	TM3a	TM1b	TM2b	TM2b
Al_2O_3	6.50	6.50	6.58	6.52	6.44	6.45	6.50						
B_2O_3	9.51	9.57	9.36	9.36	9.50	9.40	9.50						
BaO	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.047	0.048	0.052	0.049	0.050	0.050
CaO	0.58	0.63	0.67	0.83	0.65	0.91	0.66	0.680	0.652	0.646	0.658	0.596	0.637
CeO ₂	0.35	0.30	0.32	0.31	0.32	0.31	0.31	0.348	0.353	0.364	0.295	0.297	0.301
Cr_2O_3	0.30	0.28	0.29	0.28	0.28	0.29	0.29	0.259	0.255	0.258	0.256	0.265	0.254
Cs_2O	0.07							0.071	0.074	0.075	0.074	0.075	0.074
Fe_2O_3	11.60	11.3	11.4	11.4	11.4	11.4	11.4	12.4	12.3	12.4	12.4	12.4	12.3
K_2O	3.42	1.96	3.21	2.90	2.89	2.14	2.27	3.24	3.19	3.31	3.11	3.16	3.20
La_2O_3	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.019	0.026	0.022	0.019	0.020	0.022
Li_2O	2.89	2.86	2.83	2.85	2.86	2.83	2.86						
MgO	1.24	1.24	1.26	1.26	1.25	1.28	1.23						
MnO_2	1.25	1.27	1.27	1.27	1.27	1.27	1.28	1.39	1.38	1.40	1.34	1.32	1.32
MoO_3	0.002	0.003	0.003	0.003	0.003	0.003	0.003						
Na_2O	10.44	10.2	10.8	11.0	10.3	11.4	10.8						
Nd_2O_3	0.18	0.18	0.18	0.18	0.17	0.19	0.18						
NiO	0.32	0.41	0.44	0.38	0.42	0.44	0.37	0.345	0.337	0.345	0.322	0.331	0.325
P_2O_5	2.39	2.41	2.41	2.50	2.45	2.40	2.38						
RfO_2	0.01							0.010	0.010	0.009	0.009	0.010	0.010
RuO_2	0.07							0.073	0.070	0.068	0.067	0.071	0.068
SiO_2	46.13	47.4	46.5	46.4	46.8	46.5	46.9	46.9	46.6	47.1	47.1	47.9	45.1
SrO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.026	0.027	0.026	0.025	0.024	0.025
TiO_2	0.93	0.90	0.90	0.92	0.90	0.90	0.91	0.918	0.891	0.884	0.909	0.858	0.879
Y_2O_3	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.019	0.020	0.019	0.018	0.018	0.018
ZrO_2	1.43	1.51	1.56	1.59	1.47	1.62	1.59	1.47	1.48	1.48	1.32	1.52	1.45
SO_3 (WDXRF Data)	0.27	0.20	0.20	0.19	0.20	0.20	0.19						
$\text{Fe}^{2+}/\text{Fe}^{3+}$	0.10	0.08	0.08	0.08									

TABLE 3.10. Combined Analytical Data and Statistical Test for ATM-WV/205 Test Melt

Oxide	Target wt%	Observed Mean, wt%	Method	Target Minimum, wt%	Lower 95% Conf. Int., wt%	Upper 95% Conf. Int., wt%	Target Maximum, wt%	Acceptable Range
Al ₂ O ₃	6.50	6.493	(ICP)	5.85	6.437	6.550	7.15	YES
B ₂ O ₃	9.51	9.444	(ICP)	9.03	9.351	9.537	9.99	YES
BaO	0.05	0.049	(EDXRF)	0.03	0.048	0.051	0.07	YES
CaO	0.58	0.635	(EDXRF)	0.46	0.611	0.660	0.70	YES
CeO ₂	0.38	0.293	(EDXRF)	0.19	0.286	0.300	0.57	YES
Cr ₂ O ₃	0.30	0.255	(EOXRF)	0.24	0.250	0.260	0.36	YES
Cs ₂ O	0.07	0.074	(EOXRF)	0.05	0.072	0.075	0.09	YES
Fe ₂ O ₃ (a)	11.60	11.380	(ICP)	10.79	11.345	11.414	12.41	YES
K ₂ O	3.42	3.184	(EOXRF)	3.08	3.123	3.245	3.76	YES
La ₂ O ₃	0.03	0.020	(EDXRF)	0.015	0.018	0.023	0.05	YES
Li ₂ O	2.89	2.843	(ICP)	2.75	2.826	2.859	3.03	YES
MgO	1.24	1.251	(ICP)	1.05	1.233	1.270	1.43	YES
MnO ₂	1.25	1.353	(EOXRF)	1.06	1.322	1.383	1.44	YES
MoO ₃	0.002	0.003	(ICP)	0.001	0.003	0.003	0.004	YES
Na ₂ O	10.44	10.781	(EDXRF)	9.40	10.302	11.261	11.48	YES
Nd ₂ O ₃	0.18	0.180	(ICP)	0.13	0.176	0.184	0.23	YES
NiO	0.32	0.334	(EDXRF)	0.27	0.324	0.344	0.37	YES
P ₂ O ₅ (b)	2.39	2.421	(ICP)	1.91	2.378	2.465	2.87	YES
RhO ₂	0.01	0.010	(EDXRF)	0.003	0.009	0.010	0.02	YES
RuO ₂	0.07	0.070	(EDXRF)	0.04	0.067	0.072	0.11	YES
SiO ₂	46.13	46.959	(EOXRF)	41.52	45.947	47.970	50.74	YES
SO ₃ (b)	0.27	0.194	(WDXRF)	0.09	0.191	0.198	0.45	YES
SrO	0.02	0.026	(EOXRF)	0.01	0.024	0.027	0.04	YES
TiO ₂	0.93	0.877	(EOXRF)	0.79	0.855	0.898	1.07	YES
Y ₂ O ₃	0.02	0.019	(EOXRF)	0.01	0.018	0.020	0.04	YES
ZrO ₂	1.43	1.453	(EOXRF)	1.00	1.381	1.525	1.86	YES
Total	100.01	100.51						
Fe ²⁺ /Fe ³⁺	0.10	0.084		0.02	N/A	N/A	0.18	YES

(a) EDXRF for Fe₂O₃ in this glass consistently resulted in high values relative to ICP, Fe²⁺/Fe³⁺ total iron, and atomic absorption. We chose to use ICP values for Fe₂O₃.

(b) High Zr concentration in this glass resulted in interferences that prevented analysis for P₂O₅ and SO₃ by EDXRF.

The 20 ATM-WV/205 production bars were removed from the annealing ovens. The first glass bar poured was labeled ATM-WV/205-1, the second bar poured ATM-WV/205-2, and so on. All the bars appeared very uniform and glassy. A slight metallic sheen was observed on most bars. No indications of phase separation or surface porosity were observed.

4.0 CHARACTERIZATION

The characterization of ATM-WV/205 began on May 21, 1987, and was completed July 31, 1987. The procedures and methods used for characterization of the ATM-WV/205 production bars were described in a characterization plan. Supporting analytical data are retained in the PNL Records Center. The ATM-WV/205 glass was characterized under the guidance of the MCC's Quality Assurance Plan.

The purpose of characterizing the ATM-WV/205 material was to 1) determine if the ATM-WV/205 production bars meet the specifications, and 2) determine if the glass bars are suitable for use as a nuclear waste reference material. The specifications are shown in Table 3.6 and are focused on the chemical composition and oxidation state of the glass. Other physical properties, such as the homogeneity, microstructure, and devitrification of the glass, are also important. As a nuclear waste reference material, the physical properties of the ATM-WV/205 glass should be similar to the anticipated properties of the actual West Valley nuclear waste form.

The observed mean composition and oxidation state of the ATM-WV/205 glass meet the specifications. Within the limits of analytical precision and sampling, the ATM-WV/205 glass is acceptably uniform. Except for small (3 μm), dispersed Fe, Cr, Mn, and Ni spinel crystals and ruthenium inclusions (1 μm), which are typical of waste glasses, there were no indications of phase separation on the μm scale. Closed porosity ranging in diameter from 20 to 135 μm was found randomly distributed throughout the interior of all observed samples.

The ATM-WV/205 production glass meets the specifications and is appropriate as a nuclear waste glass reference material. The remainder of this report is devoted to discussion of the individual analyses and statistical evaluation.

4.1 SAMPLING OF ATM-WV/205

Table 4.1 shows the sampling and analytical scheme that was used. A summary of the statistical design basis is given in Appendix B. The three main objectives were as follows:

- Obtain maximum information regarding overall glass composition and homogeneity with a reasonable expenditure of resources.
- Use closely related samples for several independent analytical methods. This procedure minimizes preparation variability and optimizes correlation of data.
- Sample as broadly as possible over the production lot to improve estimates of bar-to-bar variability.

Nondestructive EDXRF was performed at one location on 19 of the bars. ICP and WDXRF analysis were performed in duplicate on powder samples taken from six bars. X-ray diffraction and $\text{Fe}^{2+}/\text{Fe}^{3+}$ determinations were performed on the powders taken from the six bars. Solid portions of the six sampled bars were also used for density measurements. Scanning electron microscopy and optical microscopy were performed on samples taken from three bars.

4.2 CHEMICAL ANALYSIS

Three separate techniques were required to determine the elemental composition of ATM-WV/205 glass. Nineteen bars were subjected to EDXRF analysis at one location on each bar using a Kevex Model 0810A spectrometer with Ti, Zr, Ag, and Gd x-ray tube sources. A United States Geological Survey (USGS) AGV-1 sample was used as a reference standard. Corrections for matrix absorptions, enhancement, and interference were applied. The results are shown in Tables 4.2a and 4.2b.

Aqueous solutions prepared from powder samples taken from six ATM-WV/205 glass bars were analyzed by ICP. All glass powders were prepared and run in duplicate. Two types of fusions ($\text{NaOH}/\text{Na}_2\text{O}_2$ molten flux in a Zr crucible and KOH/KNO_3 molten flux in a Ni crucible) were used to dissolve the glass powders. The resulting salt fusions were dissolved in water, acidified, and then analyzed using a Jarrell-Ash Mark 8 ICP spectrophotometer. The ICP results are listed in Table 4.3.

TABLE 4.1. Sampling of the ATM-WV/205 Production Bars for Characterization

ATM-WV/205 Bar#	Bar Weight, g	Sampling Location ^(a)	Chemical Analysis			Microscopy		Density
			EPXRF	ICP & WDXRF ^(b)	Fe ²⁺ /Fe ³⁺	Optical & SEM	XRD	
1	97.1	middle	Yes					
2	102.0	end 1	Yes					
3	102.3	end 2	Yes	Yes	Yes	Yes	Yes	Yes
4	98.9	end 1	Yes	Yes	Yes		Yes	Yes
5	96.8	middle	Yes					
6	102.2	end 2	Yes					
7	89.4	middle	Yes					
8	88.8	end 1	Yes					
9	92.8	middle	Yes	Yes	Yes	Yes	Yes	Yes
10	88.2	end 2	Yes					
11	91.0	end 2	Yes					
12	96.6	end 1	Yes					
13	96.7	end 1	Yes					
14	97.5	middle	Yes	Yes	Yes		Yes	Yes
15	99.9	middle	Yes					
16	96.4(c)	N/A						
17	99.4	end 2	Yes					
18	95.6	end 2	Yes	Yes	Yes		Yes	Yes
19	98.7	middle	Yes					
20	98.9	end 1	Yes	Yes	Yes	Yes	Yes	Yes
Total	1929.2							

(a) "End 1" indicates end of bar where pouring began (marked by "dimple").

(b) ICP and WDXRF performed on duplicate powder samples; all other analyses were single samples.

(c) ATM-WV/205 bar 16 was consumed in a MCC Round Robin Test.

TABLE 4.2a. Energy-Dispersive X-Ray Fluorescence Analysis (EDXRF)
of ATM-WV/205 Production Bars 1 through 10

Oxide	Composition by Production Bar No., wt%									
	1	2	3	4	5	6	7	8	9	10
Al ₂ O ₃										
B ₂ O ₃										
BaO	0.054	0.052	0.056	0.048	0.055	0.052	0.052	0.052	0.053	0.054
CaO	0.606	0.632	0.649	0.592	0.548	0.632	0.588	0.562	0.630	0.634
CeO ₂	0.310	0.305	0.319	0.296	0.313	0.303	0.305	0.308	0.313	0.317
Cr ₂ O ₃	0.259	0.259	0.272	0.272	0.253	0.263	0.262	0.262	0.259	0.265
Cs ₂ O	0.070	0.069	0.073	0.066	0.072	0.069	0.068	0.071	0.070	0.072
Fe ₂ O ₃	11.67	11.44	11.92	12.14	11.57	11.61	11.39	11.35	12.02	11.88
K ₂ O	3.60	3.54	3.63	3.70	3.46	3.60	3.45	3.38	3.61	3.90
La ₂ O ₃	0.020	0.017	0.020	0.018	0.017	0.017	0.017	0.019	0.021	0.019
Li ₂ O										
MgO										
MnO ₂	1.25	1.22	1.28	1.30	1.26	1.24	1.21	1.22	1.27	1.26
MoO ₃										
Na ₂ O										
Nd ₂ O ₃										
NiO	0.325	0.305	0.327	0.339	0.308	0.317	0.303	0.298	0.327	0.328
P ₂ O ₅										
RhO ₂	0.011	0.010	0.012	0.011	0.011	0.012	0.011	0.010	0.012	0.011
RuO ₂	0.074	0.068	0.080	0.069	0.074	0.081	0.073	0.072	0.077	0.073
SiO ₂	48.3	48.8	50.1	47.1	46.2	48.1	47.3	46.9	47.9	50.9
SO ₃										
SrO	0.027	0.027	0.028	0.027	0.027	0.027	0.027	0.026	0.027	0.026
TiO ₂	0.876	0.842	0.891	0.886	0.836	0.861	0.861	0.819	0.904	0.903
Y ₂ O ₃	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.018	0.019	0.018
ZrO ₂	1.42	1.42	1.43	1.43	1.41	1.42	1.40	1.39	1.42	1.34

TABLE 4.2b. Energy-Dispersive X-Ray Fluorescence Analysis (EDXRF) of ATM-WV/205 Production Bars 11 through 20^(a)

Oxide	Composition by Production Bar No., wt%								
	11	12	13	14	15	17	18	19	20
Al ₂ O ₃									
B ₂ O ₃									
BaO	0.051	0.052	0.054	0.054	0.051	0.052	0.051	0.051	0.050
CaO	0.582	0.581	0.569	0.656	0.509	0.659	0.634	0.624	0.610
CeO ₂	0.307	0.312	0.322	0.314	0.305	0.307	0.306	0.305	0.301
Cr ₂ O ₃	0.248	0.269	0.263	0.267	0.256	0.262	0.279	0.246	0.273
Cs ₂ O	0.069	0.070	0.703	0.071	0.065	0.069	0.071	0.070	0.065
Fe ₂ O ₃	11.35	11.58	11.44	11.59	11.11	11.91	12.28	11.84	11.87
K ₂ O	3.65	3.63	3.36	3.58	2.99	3.70	3.99	3.72	3.78
La ₂ O ₃	0.017	0.019	0.020	0.019	0.019	0.021	0.016	0.20	0.018
Li ₂ O									
MgO									
MnO ₂	1.21	1.22	1.21	1.25	1.18	1.28	1.31	1.25	1.28
MoO ₃									
Na ₂ O									
Nd ₂ O ₃									
NiO	0.305	0.313	0.318	0.323	0.293	0.326	0.333	0.316	0.319
P ₂ O ₅									
RhO ₂	0.011	0.011	0.010	0.011	0.010	0.010	0.011	0.010	0.010
RuO ₂	0.074	0.075	0.078	0.076	0.071	0.074	0.075	0.070	0.071
SiO ₂	48.1	47.9	46.4	48.8	43.2	48.8	49.8	48.6	47.9
SO ₃									
SrO	0.028	0.026	0.028	0.027	0.027	0.027	0.028	0.027	0.027
TiO ₂	0.814	0.868	0.829	0.848	0.809	0.901	0.883	0.863	0.848
Y ₂ O ₃	0.019	0.018	0.019	0.019	0.020	0.019	0.019	0.019	0.019
ZrO ₂	1.42	1.36	1.42	1.42	1.42	1.43	1.43	1.43	1.41

(a) ATM-WV/205 bar 16 was not analyzed.

TABLE 4.3. Inductively Coupled Plasma Spectroscopy (ICP) of ATM-WV/205 Production Bars (duplicate samples).

Oxide	Composition by Production Bar No., wt%											
	3a	3b	4a	4b	9a	9b	14a	14b	18a	18b	20a	20b
Al ₂ O ₃	6.58	6.51	6.42	6.63	6.59	6.57	6.54	6.40	6.57	6.65	6.51	6.54
B ₂ O ₃	9.44	9.35	9.15	9.44	9.29	9.33	9.38	9.13	9.37	9.47	9.34	9.47
BaO	0.051	0.050	0.050	0.052	0.051	0.050	0.051	0.051	0.051	0.053	0.050	0.050
CaO	0.69	0.52	0.52	0.60	0.65	0.53	0.68	0.52	0.64	0.59	0.52	0.51
CeO ₂	0.29	0.27	0.28	0.24	0.30	0.27	0.30	0.28	0.29	0.24	0.27	0.25
Cr ₂ O ₃	0.29	0.30	0.29	0.29	0.28	0.29	0.29	0.29	0.29	0.29	0.29	0.3
Cs ₂ O												
Fe ₂ O ₃	11.2	11.2	11.0	11.4	11.1	11.2	11.2	11.2	11.1	11.3	11.2	11.2
K ₂ O	3.3	4.3	4.7	3.2	3.8	3.2	3.8	3.8	3.6	3.2	3.4	3.3
La ₂ O ₃	0.026	0.029	0.033	0.020	0.029	0.025	0.029	0.028	0.029	0.017	0.025	0.023
Li ₂ O	2.95	2.89	2.87	2.91	2.90	2.90	2.94	2.88	2.93	2.83	2.89	2.92
MgO	1.22	1.19	1.19	1.16	1.22	1.17	1.23	1.18	1.22	1.16	1.18	1.17
MnO ₂	1.29	1.27	1.26	1.30	1.28	1.25	1.29	1.27	1.28	1.30	1.27	1.28
MoO ₃ (a)	0.002		0.002		0.002		0.002		0.002		0.002	
Na ₂ O	10.5	10.2	10.1	10.1	10.1	10.3	10.6	10.2	10.4	10.1	10.1	10.4
Nd ₂ O ₃ (a)	0.182		0.182		0.174		0.176		0.183		0.182	
NiO	0.41	0.36	0.36	0.35	0.36	0.36	0.37	0.56	0.37	0.35	0.36	0.37
P ₂ O ₅	2.5	2.5	2.4	2.4	2.4	2.4	2.3	2.4	2.4	2.3	2.4	2.4
RhO ₂												
RuO ₂												
SiO ₂	47.3	46.4	45.8	46.6	46.7	46.5	46.6	45.6	46.7	47.0	44.0	44.5
SO ₃												
SrO	0.29	0.28	0.027	0.029	0.028	0.027	0.028	0.028	0.029	0.029	0.27	0.027
TiO ₂	0.91	0.90	0.88	0.93	0.91	0.89	0.92	0.89	0.91	0.92	0.89	0.90
Y ₂ O ₃	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO ₂												

(a) Special preparation of fusion sample, based on ASTM Method C-146, used to increase ICP sensitivity.

In order to determine sulfur concentrations in the ATM-WV/205 glass, powder samples taken from six of the bars were analyzed in duplicate by WDXRF. A Diano model 8560 XRF system (using a Cr x-ray tube, Pentaerythritol dispersion crystal, and counting at 75.76 degrees two theta) was used for this purpose. National Bureau of Standards (NBS) 1411 glass was used as a standard; the results listed in Table 4.4 were corrected to this standard.

TABLE 4.4. Wavelength-Dispersive X-Ray Fluorescence Analysis (WDXRF) of ATM-WV/205 Production Bars (duplicate samples) for SO₃

Oxide	Composition by Production Bar No., wt%											
	3a	3b	4a	4b	9a	9b	14a	14b	18a	18b	20a	20b
SO ₃	0.26	0.23	0.24	0.23	0.23	0.22	0.23	0.23	0.24	0.22	0.23	0.21

4.3 STATISTICAL ANALYSIS OF CHEMICAL COMPOSITION

This section presents the confidence intervals and tolerance intervals that were computed from the analytical results presented in Tables 4.2, 4.3, and 4.4. The confidence intervals demonstrate that the overall mean wt% oxide of every element is within the specified allowable deviation from the intended (or target) value as defined in Table 3.6. The tolerance intervals provide a predicted range of possible compositions for individual samples (or specimens) from this lot of ATM-WV/205 glass.

For each element in the ATM-WV/205 glass, the analytical results were used to construct a 95% confidence interval for the overall true mean wt% oxide in the ATM-WV/205 production bars. The determination and justification of the statistical estimation methods that were used to construct the confidence intervals are discussed in Appendix C.

The sample averages, standard deviations, and 95% confidence intervals are displayed in Table 4.5. For example, we are 95% confident that the unknown true mean Al_2O_3 concentration for the entire lot of ATM-WV/205 glass is between 6.493 and 6.592 wt%. Table 4.5 also displays the target concentration and the allowable deviation range for each component as specified by the sponsor.^(a) The confidence intervals, target values, and allowable deviation ranges were used to evaluate the acceptability of the composition of the ATM-WV/205 production bars by answering the three questions listed at the bottom of Table 4.5 for each element. These questions represent the acceptance criteria as specified by the sponsor. The answers to these questions are displayed in the last three columns of the table. Note from the last three columns of Table 4.5 that only nine of the elements have confidence intervals that include their target values; the target values for the remaining components are outside of the confidence intervals. When a target value is outside the confidence interval, the difference between the target value and the sample average is statistically significant, which implies that the unknown true mean is probably not equal to the target value. However, the confidence intervals for all components are inside the corresponding allowable error ranges. This indicates

(a) See Table 3.6 for revised composition.

TABLE 4.5. Comparison of 95% Confidence Intervals with Acceptable Error Ranges of Elements in ATM-WV/205 Glass

Oxide	Target wt%	Observed Sample(a)							Allowable Error Range			Question(b)		
		Method	Average wt%	Std. Dev.	95% Confidence Interval		1	2				3		
Al ₂ O ₃	6.50	ICP	6.5423	0.04737	6.493	to	6.592	5.85	to	7.15	YES	YES	YES	
B ₂ O ₃	9.51	ICP	9.3425	0.06878	9.270	to	9.415	9.03	to	9.99	NO	YES	YES	
BaO	0.05	EDXRF	0.0521	0.00180	0.051	to	0.053	0.03	to	0.07	NO	YES	YES	
CaO	0.58	EDXRF	0.6052	0.03991	0.586	to	0.624	0.46	to	0.70	NO	YES	YES	
CeD ₂	0.35	EDXRF	0.3067	0.00649	0.303	to	0.310	0.19	to	0.57	NO	YES	YES	
Cr ₂ O ₃	0.30	EDXRF	0.2622	0.00852	0.258	to	0.266	0.24	to	0.36	NO	YES	YES	
Cs ₂ O	0.07	EDXRF	0.0696	0.00238	0.068	to	0.071	0.05	to	0.09	YES	YES	YES	
Fe ₂ D ₃	11.60	EDXRF	11.6822	0.30526	11.535	to	11.829	10.79	to	12.41	YES	YES	YES	
K ₂ O	3.42	EDXRF	3.5929	0.21593	3.489	to	3.697	3.08	to	3.76	NO	YES	YES	
La ₂ D ₃	0.03	EDXRF	0.0186	0.00149	0.018	to	0.019	0.02	to	0.05	NO	YES	YES	
Li ₂ O	2.89	ICP	2.8988	0.01448	2.884	to	2.914	2.75	to	3.03	YES	YES	YES	
MgO	1.24	ICP	1.1880	0.01503	1.172	to	1.204	1.05	to	1.43	NO	YES	YES	
MnO ₂	1.25	EDXRF	1.2455	0.03353	1.229	to	1.262	1.06	to	1.44	YES	YES	YES	
MoO ₃	0.002	ICP	0.0021	0.00018	0.0019	to	0.0023	0.001	to	0.004	YES	YES	YES	
Na ₂ O	10.44	ICP	10.2558	0.09895	10.152	to	10.360	9.40	to	11.48	NO	YES	YES	
Nd ₂ D ₃	0.18	ICP	0.1800	0.00382	0.176	to	0.184	0.13	to	0.23	YES	YES	YES	
NiO	0.32	EDXRF	0.3164	0.01238	0.310	to	0.322	0.27	to	0.37	YES	YES	YES	
P ₂ O ₅	2.39	ICP	2.3901	0.03774	2.350	to	2.429	1.91	to	2.87	YES	YES	YES	
RhO ₂	0.01	EDXRF	0.0107	0.00074	0.010	to	0.011	0.003	to	0.02	NO	YES	YES	
RuO ₂	0.07	EDXRF	0.0735	0.00353	0.071	to	0.075	0.04	to	0.11	NO	YES	YES	
SiO ₂	46.13	EDXRF	47.9550	1.66213	47.154	to	48.756	41.52	to	50.74	NO	YES	YES	
SO ₃	0.27	WDXRF	0.2308	0.00861	0.222	to	0.240	0.09	to	0.45	NO	YES	YES	
SrO	0.03	EDXRF	0.0271	0.00055	0.027	to	0.027	0.01	to	0.04	NO	YES	YES	
TiO ₂	0.93	EDXRF	0.8600	0.03019	0.845	to	0.875	0.79	to	1.07	NO	YES	YES	
Y ₂ O ₃	0.02	EDXRF	0.0187	0.00036	0.019	to	0.019	0.01	to	0.04	NO	YES	YES	
ZrO ₂	1.43	EDXRF	1.4105	0.02464	1.399	to	1.422	1.00	to	1.86	NO	YES	YES	

(a) Number of displayed figures are for statistical purposes and are not an indication of precision.

(b) Question 1: Is the target wt% inside the confidence interval?

Question 2: Is the confidence interval half-width less than the allowable error?

Question 3: Is the confidence interval inside the allowable error range?

that the unknown true mean concentration for each element is acceptably close to the target value. Because each confidence interval is inside the corresponding allowable deviation range, the width of the confidence interval (the precision of the estimate of the unknown mean) is acceptable for every element.

It is important to note that the validity of the confidence intervals displayed in Table 4.5 depends upon a number of factors. Every attempt was made to randomly sample the material from the ATM-WV/205 production bar glass and then to randomize the order of the analyses of the samples. Therefore, the standard deviation estimates include the effects of both chemical inhomogeneity within this batch of glass and analytical imprecision. However, if any biases were present in the analytical laboratories, they cannot be evaluated from the ATM-WV/205 characterization data. Therefore, if the sample averages and confidence intervals are to be interpreted as representing the probable mean composition of the ATM-WV/205 glass, it must be strictly assumed that the analytical laboratories produce unbiased results; otherwise, the validity of the confidence intervals and the conclusion about the composition of the ATM-WV/205 glass are compromised.

As discussed above, the confidence intervals displayed in Table 4.5 are for the overall mean concentrations of the oxides. However, the confidence intervals do not provide an indication of the range of compositions of individual samples (or specimens) of glass from this batch. Therefore, tolerance intervals were constructed for this purpose. The method used is discussed in Appendix C.

Table 4.6 displays 75/75, 90/90, 95/90, and 95/95 tolerance intervals for each element. For example, consider the 95/90 tolerance interval for Al_2O_3 . We can be 95% confident that 90% of the individual samples (or specimens) obtained from this lot of glass will have Al_2O_3 concentrations between 6.340 and 6.745 wt%. As with the confidence intervals, the widths of the tolerance intervals are multiples of the sample standard deviations, which include the effects of both chemical inhomogeneity and analytical imprecision. Therefore, the interpretation of the tolerance intervals is in the context of single samples that are each analyzed in exactly the same manner as the samples in this characterization study. For some elements, especially those with low

TABLE 4.6. Tolerance Intervals for ATM-WV/205 Components

	Tolerance Interval, wt%							
	75/75		90/90		95/90		95/95	
Al ₂ O ₃	6.456	6.629	6.377	6.708	6.340	6.745	6.302	6.783
B ₂ O ₃	9.217	9.468	9.102	9.583	9.048	9.637	8.993	9.692
BaO	0.050	0.055	0.048	0.056	0.048	0.056	0.047	0.057
CaO	0.551	0.659	0.519	0.692	0.512	0.698	0.494	0.716
CeO ₂	0.298	0.316	0.293	0.321	0.292	0.322	0.289	0.325
Cr ₂ O ₃	0.251	0.274	0.244	0.281	0.242	0.282	0.238	0.286
Cs ₂ O	0.066	0.073	0.064	0.075	0.064	0.075	0.063	0.076
Fe ₂ O ₃	11.269	12.096	11.019	12.345	10.969	12.396	10.832	12.532
K ₂ O	3.300	3.885	3.124	4.062	3.088	4.098	2.992	4.194
La ₂ O ₃	0.017	0.021	0.015	0.022	0.015	0.022	0.014	0.023
Li ₂ O	2.872	2.925	2.848	2.949	2.837	2.961	2.825	2.972
MgO	1.161	1.215	1.135	1.240	1.124	1.252	1.112	1.264
MnO ₂	1.200	1.291	1.173	1.318	1.167	1.324	1.152	1.339
MoO ₃	0.0018	0.0025	0.0015	0.0027	0.0014	0.0029	0.0012	0.0030
Na ₂ O	10.075	10.436	9.910	10.602	9.833	10.679	9.753	10.758
Nd ₂ O ₃	0.173	0.187	0.167	0.193	0.164	0.196	0.161	0.199
NiO	0.300	0.333	0.289	0.343	0.287	0.345	0.282	0.351
P ₂ O ₅	2.321	2.459	2.258	2.522	2.229	2.551	2.198	2.582
RhO ₂	0.010	0.012	0.009	0.012	0.009	0.012	0.009	0.013
RuO ₂	0.069	0.078	0.066	0.081	0.065	0.082	0.064	0.083
SiO ₂	45.703	50.207	44.345	51.565	44.071	51.839	43.328	52.582
SO ₃	0.215	0.247	0.201	0.261	0.194	0.268	0.187	0.275
SrO	0.026	0.028	0.026	0.029	0.026	0.028	0.026	0.029
TiO ₂	0.819	0.901	0.794	0.926	0.789	0.931	0.776	0.944
Y ₂ O ₃	0.018	0.019	0.018	0.019	0.018	0.020	0.018	0.020
ZrO ₂	1.377	1.444	1.357	1.464	1.353	1.468	1.342	1.479

concentrations, the analytical imprecision may be the dominant contributor to the sample standard deviation. In such cases, the widths of the tolerance intervals are largely due to analytical error, rather than chemical inhomogeneity. Also, as with the confidence intervals, the validity of the tolerance intervals displayed in Table 4.6 depends on the validity of the assumption that the analytical laboratories produce unbiased results.

We conclude that the observed mean composition of the ATM-WV/205 production bars meets the client's stated requirements. Within the limits of analytical precision and sampling, the probable variation between ATM-WV/205 bars is also acceptable.

4.4 OXIDATION STATE

The oxidation states, as exhibited by the ratio of ferrous to ferric ions in the glass ($\text{Fe}^{2+}/\text{Fe}^{3+}$), of powder samples taken from six ATM-WV/205 production bars were determined. A solution-chemistry, spectrophotometric technique using 1,10-phenanthroline to determine reduced and total iron in glass (Jones, Janheski, and Goldman 1981) was used. The results are shown in Table 4.7. Notice that all six analyses well within the client's specification of 0.10 ± 0.08 . The mean value is 0.084.

TABLE 4.7. Oxidation State of ATM-WV/205 Glass as Determined by Spectrophotometry for Total and Reduced Iron

<u>ATM-WV/205</u>	<u>$\text{Fe}^{2+}/\text{Fe}^{3+}$</u>
Bar 3	0.080
Bar 4	0.089
Bar 9	0.080
Bar 14	0.084
Bar 18	0.098
Bar 20	0.072
Target =	0.10 (± 0.080)
Sample Mean =	0.084
Sample Std. Dev. =	0.0089

4.5 MICROSCOPY

Optical microscopy and SEM were used to investigate the microstructure of the ATM-WV/205 glass. Optical microscopy was performed on polished cross sections taken from three different bars. A low-magnification micrograph of a typical portion of bar is shown in Figure 4.1. Notice the voids that range in size from 20 to 135 μm . It is apparent that these voids are generally isolated and randomly distributed throughout the interior of the bars. Based on the micrographs taken from the three bars, the voids are calculated to occupy about 0.2% of the sample matrix.^(a) The voids are shown in greater detail in Figure 4.2. The bright regions seen in Figures 4.2 and 4.3 are cubic features found throughout all the viewed samples.

Fractured samples taken from three bars were observed by SEM. As shown in Figure 4.4, voids were apparent in these samples as well. Higher magnification revealed the cubic features observed by optical microscopy (compare Figures 4.3 and 4.5). EDXS taken from these cubic features indicated the regions to be concentrated in Fe, Cr, Mn, and Ni. The morphology and composition of the cubic features are characteristic of spinel crystals often found in simulated nuclear waste glasses (Chick et al. 1980). A few bright, 1- μm regions were identified by EDXS as ruthenium inclusions. As shown in Figure 4.6, EDXS taken from 100,000- μm^2 matrix regions and 10- μm^2 regions appeared identical. This similarity suggests that the glass matrix is homogeneous on a μm scale. In Figure 4.7 EDXS spectra of cubic crystals and a ruthenium inclusion are shown.

Observation by SEM and optical microscopy indicated that the ATM-WV/205 glass is generally uniform in microstructure.

4.6 X-RAY DIFFRACTION

X-ray diffraction analysis was performed on powder samples taken from six glass bars. A Philips XRG 3100 x-ray generator (copper target) and APD 3620 automated powder diffractometer were used. The recorded XRD patterns were very similar for all six samples. Slow scan techniques (~ 0.06 degrees two-theta/min) detected XRD patterns indicative of spinel crystalline material (see

(a) See Appendix D for calculations of closed-porosity volume fraction.

FIGURE 4.1. Photograph (transmitted light) of Cross Section of ATM-WV/205 Bar 9. The closed porosity, ranging in diameter from 20 to 135 μm , is estimated to be 0.2 vol% of the glass matrix. The "swirl" patterns are regions of high and low spinel concentration.

FIGURE 4.2. Photomicrograph of Cross Section of ATM-WV/205 Bar 9. Dark regions are pores or voids ranging from 20 to 135 μm in diameter. Bright dots are Fe, Cr, Mn, and Ni cubic spinel crystals, which are about 3 μm across.

FIGURE 4.3. Photomicrograph of Cross Section of ATM-WV/205 Bar 9 Showing Spinel Crystals in Detail

FIGURE 4.4. Fractured Sample of ATM-WV/205 Bar 20 as Seen by SEM. Notice the pores ranging from 65 to 125 μm in diameter. The square indicates the $\sim 100,000 \mu\text{m}^2$ area, region 1, which was analyzed by EDXS (see Figure 4.6).

FIGURE 4.5. Fractured Sample of ATM-WV/205 Bar 20 by SEM. The white angular features are cubic crystals identified by EDXS (see Figure 4.7) as being enriched in Fe, Cr, Mn, and Ni. The morphology and composition of these crystals are typical of spinel crystals often found in nuclear waste glasses. The two white, round features are ~1- μm -diameter Ru inclusions. The ~10- μm^2 matrix region 2, which was used for EDXS analysis (see Figure 4.6), is also indicated.

Figure 4.8). An additional single small peak, with location corresponding to the main peak for ruthenium metal, was also observed.

Subsequent tests were made using the same ATM-WV/205 powder samples spiked with 0.25, 0.50, and 1.0 wt% magnetite (Fe_3O_4 having a spinel crystal structure). The spiked samples were run under operating conditions identical to those used for the original ATM-WV/205 glasses. As seen in Figure 4.9, the integrated peak areas of the samples and standards were plotted versus added spinel. Using this "analysis by dilution" technique (Klug and Alexander 1974), it was concluded the samples contain about 0.5 wt% spinel. This conclusion implies that most of the Cr_2O_3 in ATM-WV/205 glass is in the spinel crystalline form.^(a)

(a) ATM-WV/205 spinel crystals contain about 50 mol% Cr_2O_3 (see Figure 4.7). At 0.5 wt% spinel, this would account for most of the 0.26 wt% Cr_2O_3 in ATM-WV/205.

FIGURE 4.6. Energy-Dispersive X-Ray Spectra (EDXS) Collected from Fractured Sample of ATM-WV/205 Bar 20 (see Figures 4.4 and 4.5 for regions). The similarity between EDXS from areas 1 and 2 indicates homogeneity of the glass matrix on the μm scale.

FIGURE 4.7. Energy-Dispersive X-Ray Spectra (EDXS) of Cubic Crystals and Ruthenium Inclusion Observed on a Fractured Surface of ATM-WV/205 Bar 20 (see Figure 4.5).

FIGURE 4.8. X-Ray Diffraction Pattern from ATM-WV/205 Bar 20 (Cu K α Radiation). Standard patterns for spinel and ruthenium metal are also presented for comparison.

FIGURE 4.9. "Analysis by Dilution" Method Used to Determine wt% Spinel in ATM-WV-205 Glass. The slope of the integrated peak intensity vs. wt% spinel was determined from ATM-WV/205 glass spiked with known amounts of spinel. The "Y" intercept is assumed to be 0. This implies that ATM-WV/205 glass contains about 0.5 wt% spinel (Klug and Alexander 1974).

4.7 DENSITY DETERMINATION

The bulk densities of solid samples taken from six glass bars were determined by a water immersion technique similar to that described in MCC-12 Test Method: "Determining Density Changes in Actinide-Doped Waste Forms." Table 4.8 shows the ATM-WV/205 density results. The mean bulk density for the six samples was 2.649 g/cm³. Only small differences (<0.2% relative) in bulk density were observed in the six samples. Values ranged from 2.647 to 2.654 g/cm³.

TABLE 4.8. Bulk Density Determination of ATM-WV/205 Glass by Water Immersion Technique

ATM-WV/205 Sample	Measurement No.			Individual Sample	
	1	2	3	Mean	Std. Dev.
Bar 3	2.6474	2.6475	2.6474	2.6474	0.00007
Bar 4	2.6478	2.6480	2.6479	2.6479	0.00011
Bar 9	2.6487	2.6488	2.6484	2.6486	0.00022
Bar 14	2.6479	2.6482	2.6477	2.6479	0.00022
Bar 18	2.6539	2.6541	2.6537	2.6539	0.00021
Bar 20	2.6506	2.6509	2.6507	2.6507	0.00015

Overall Sample

Mean = 2.649 g/cm³
Std. Dev. = 0.0083

5.0 REFERENCES

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- Klug, H. P., and L. E. Alexander. 1974. X-Ray Diffraction Procedures. Wiley Interscience Publication, New York, pp. 53-54.
- Jones, D. R., IV, W. C. Janheski, and D. S. Goldman. 1981. "Spectrophotometric Determination of Reduced and Total Iron in Glass with 1,10-Phenanthroline." Analytical Chemistry 53:923.

APPENDIX A

BASE CHEMICALS USED TO PRODUCE ATM-WV/205

APPENDIX A

BASE CHEMICALS USED TO PRODUCE ATM-WV/205

The following represents an inventory of the base chemicals that were ordered for ATM-10 glass fabrication and received at PNL on 12/16/85. All chemicals were supplied by Alfa Products (Morton Thiokol, Inc.).

Formula Received	Qty Cont.	Net Received	Lot Number(s)	
Al ₂ O ₃	250 g	750 g	042382	Aluminum oxide or low-surface area - -100 +352 mesh
H ₃ BO ₃	500 g	3 kg	021583	Orthoboric acid (ACS)
BaCO ₃	25 g	50 g	594068A	Barium carbonate - Grade 1
CaCO ₃	100 g	500 g	030883	Calcium carbonate (ACS)
CeO ₂	250 g	250 g	061085	Cesium (IV) oxide 99.9% (REO)
Cr ₂ O ₃	100 g	100 g	021785	Chromium (III) oxide 99%
Cs ₂ CO ₃	25 g	25 g	093085	Cesium carbonate 99.9% (metal base)
Fe ₂ O ₃	1 kg	2 kg	030785	Iron (III) oxide 99.9%
K ₂ CO ₃	1 kg	1 kg	072385	Potassium carbonate anhydrous
La ₂ O ₃	250 g	250 g	041985	Lanthanum oxide 99.9% (REO)
Li ₂ CO ₃	2 kg	2 kg	052285	Lithium carbonate 99%
MgO	100 g	200 g	090385	Magnesium oxide 99.5%
MnO ₂	1 kg	1 kg	120384	Manganese IV oxide 99.9+%
Na ₂ CO ₃	500 g	2.5 kg	100855	Sodium carbonate anhydrous primary standard (ACS)
Nd ₂ O ₃	50 g	150 g	031185	Neodymium oxide 99.9% (REO)
NiO	100 g	100 g	100284	Nickel (II) oxide 99%
(NH ₄) ₂ HPO ₄	500 g	500 g	021285	Ammonium hydrogen phosphate (ACS)
Rh ₂ O ₃	2 g	6 g	071984	Rhodium (III) oxide anhydrous 81.05% Rh
RuO ₂	10 g	20 g	012285	Ruthenium (IV) oxide 99.9% 75.5% REO
Na ₂ SO ₄	500 g	500 g	011384	Sodium sulfate anhydrous (ACS)
SiO ₂	10 kg	10 kg	052085	Silicic (IV) oxide 99.5%
SrCO ₃	250 g	250 g	081485	Strontium carbonate reagent
TiO ₂	250 g	250 g	032885	Titanium (IV) oxide 99.8% (metal base)
Y ₂ O ₃	50 g	50 g	022785	Yttrium oxide 99.9% (REO)
ZrO ₂	500 g	500 g	032885	Zirconium oxide 99+%

From stock on hand (used to produce dopants).

(NH₄)₂ MO₄ Baker Analyzed Reagent Lot #25638.

CeNO₃ • 6H₂O Allied Chemical Lot #B117T0195

ZrO(NO₃)₂ • n H₂O Fisher Lot#772890.

APPENDIX B

STATISTICAL DESIGN FOR SAMPLING OF ATM-WV/205 PRODUCTION BARS FOR CHARACTERIZATION

Date: September 1, 1986

To: JL Daniel

From: WM Bowen *WM Bowen*

Subject: Basis for Developing Sampling Plans for Characterization
of ATM-10 and ATM-WV/205

It is desirable to determine sampling plans for characterization of the ATM-10 and ATM-WV/205 glasses that will yield maximum information, subject to a limitation on funding. An example is presented in this memo that illustrates one possible approach to development of a sampling plan. The approach used in the example is based upon a three-stage sampling scheme that involves concepts from both finite population sampling and sampling from conceptual infinite populations. Estimation of the overall mean of a property and the variance of the estimator would involve a mix of techniques from both areas of statistical methodology. Thus, the usual hand calculation formulas for a mean and standard deviation from a simple random sample could not be used; to do so could lead to invalid and misleading conclusions about the true mean of a property and the homogeneity over the entire batch of each glass.

The sampling plan, presented below, is an illustrative example of developing a sampling plan for characterization of the ATM-10 glass. However, the same logic would apply to developing a plan for the ATM-WV/205 glass. In this example, it is assumed that the final melting, pouring, and cooling of the ATM-10 glass bars will occur on three days at the rate of ten bars per day. Since apriori estimates of the day-to-day, bar-to-bar, and section within bar variability of the properties are not available, it is not possible to use statistical formulas to determine a sampling plan that minimizes the variance of the estimator of the overall mean, subject to a fixed cost. However, the following considerations were used as guidelines in determining a sampling plan.

Since production is assumed to be spread over three days, it is very desirable to examine at least one bar from each day's production. Also, there may be bar-to-bar variations in composition, so that examining more than one bar from each day's production is desirable. There may be compositional variations within a bar (over the length of the bar), so that examining samples from more than one location on each bar would be informative. There are also other considerations; for example, "settling" within each bar may cause the composition in the lower portion of the bar to differ from that in the upper portion.

With the above considerations in mind, it is desirable to determine a sampling scheme, based upon a maximum of six samples per property, that maximizes the information on both the overall true mean of each property and the homogeneity of each property over the entire batch of material. If two bars are sampled from each day's production, then only one location within each bar can be sampled. It has been hypothesized that the maximum compositional variations within a bar would be observed by comparing a sample from the middle of the bar with one from either end. However, since only one glass sample is to be taken from each of two bars on a given day, it is desirable to include a sample from the end of one bar and the middle of the other within each day's production.

Assuming a total of six samples, the following sampling scheme is proposed. Randomly select two bars from the ten produced each day and randomly determine which bar should be sampled from an end and which bar should be sampled from the middle. Take a sample of glass from the selected location on each bar and prepare it for the various analyses. For each sample, it is recommended that a "slice" of glass be cut that represents the full height and width of the bar, and then this slice should be crushed and thoroughly blended; the purpose of this is to blend over any differences in composition due to settling.

For each property, this results in a three-stage sampling scheme, with stratified sampling of bars (i.e., the days are strata and the bars within each day are the primary sampling units). The sampling was carried out by using the SAMPLE command of the MINITAB statistical software package on the VAX 11/780 computer system at PNL. The bars within each day were represented by the integers 1 through 10, and the two locations on each bar (middle and end) were represented by the integers 1 and 2.

FIRST STAGE OF SAMPLING: All days (strata) are in the sample, and two of the ten bars were randomly selected from each strata.

SECOND STAGE OF SAMPLING: A random determination was made of which bar would be sampled from the end and which would be sampled from the middle. It should be noted that this second stage is not a truly random sampling of the many possible locations on a bar, but it is intended to obtain data that represent the hypothesized extremes in property variations, subject to the six sample limitation.

Implementation of the first two stages of sampling resulted in the plan tabulated below.

Day 1	Day 2	Day 3
Bar 2 - Middle	Bar 4 - Middle	Bar 3 - End
Bar 8 - End	Bar 7 - End	Bar 9 - Middle

THIRD STAGE OF SAMPLING: For a given type of analysis, either one or two replicate values for each property will result. This is assumed to be a random sample of size one or two from the conceptual population of all possible repeated analyses of the sample for a particular property.

The XRF analyses might be performed by using whole bars rather than samples from each bar. If so, a different sample of six bars will be analyzed. The procedure described above was repeated, by sampling from the eight bars each day that are not already in the above sample. The results are displayed below.

Day 1	Day 2	Day 3
Bar 1 - Middle	Bar 1 - End	Bar 7 - End
Bar 5 - End	Bar 8 - Middle	Bar 10 - Middle

The data from this sampling plan could be used to compute 1) an estimate of the overall true mean of each quantitative property, 2) an estimate of the variance of the estimator of the mean, 3) a 95% confidence interval for the overall true mean, 4) an estimate of the total variability of the property about the mean (homogeneity), 5) an estimate of the variance component for day-to-day variability, and 6) a composite estimate of the variance due to the combined effects of bar-to-bar, location within bar, and analytical error variability (for properties with a single analytical value per sample). For properties with more than one analytical value per sample, item 6 can be partitioned into 6A) a composite estimate of the variance due to the effects of bar-to-bar and location within bar variability, and 6B) an estimate of the variance due to analytical error.

It must be emphasized that the above example assumes that 30 bars of ATM-10 glass will be produced at the rate of 10 bars per day; however, the actual production might take more days or fewer days. Also, the number of bars produced might vary from day to day. Therefore, it is not possible to specify exactly how the sampling should be done until the production has been completed. At that time, sampling plans can be developed for each glass. The actual sampling techniques that will be used might differ from those illustrated above. The choice of sampling techniques will depend upon factors such as the actual rate of production and the analytical techniques to be used.

APPENDIX C

STATISTICAL ANALYSIS FOR THE ATM-WV/205 CHARACTERIZATION

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STATISTICAL ANALYSIS FOR THE ATM-WV/205 CHARACTERIZATION

Compositional analysis of the ATM-WV/205 glass product was performed as outlined in the formal characterization plan. The analytical methods included x-ray fluorescence (XRF) and inductively coupled plasma atomic emission spectroscopy (ICP). The details of the sampling, specimen preparation, and compositional analysis are described in the formal ATM-WV/205 characterization report. Therefore, only those details are repeated here that are necessary to support the discussion of the statistical analysis of the data. All computations referred to in the following discussions were performed by the Statistical Analysis System (SAS) software package on the PNL VAX computer system.

Without presenting formulas and computational details, this report describes the procedures used and results obtained during the statistical analysis of the ATM-WV/205 compositional data. The primary objective, as outlined in the formal characterization plan, was to 1) estimate the unknown true mean wt% oxide of each component over this entire batch of ATM-WV/205 glass product, 2) construct a 95% confidence interval (CI) for the true batch mean of each component, and 3) use these CI values to determine whether the batch mean wt% oxide of each component satisfies the specified criteria for being acceptably close to the target wt%. Also, tolerance intervals were constructed to indicate the expected range of composition of individual samples (or specimens) taken from this batch of ATM-WV/205 glass.

JUSTIFICATION OF ESTIMATION METHODS

Before constructing the confidence intervals, it was necessary to determine how the sample average and its variance would be estimated for each component. The appropriate estimation formula for each component depends on how the sampling, preparation, and analysis were performed. The sampling and compositional analysis protocol, described in the formal characterization plan, yielded adequate data to test whether compositional differences among positions

(or locations) within a bar contribute to the overall compositional variability within the batch. For the XRF data and the ICP results for Nd, this test was carried out by performing a one-way analysis of variance, where position was treated as the "main effect factor" and the bar-to-bar variability "within each position" was treated as the experimental error variance. This approach was chosen because only one position (an end or middle section) was analyzed on each bar; that is, there were no sampled bars where more than one location was analyzed. The analysis of variance for the ICP data (except for the Nd results) was based on a more elaborate model, which is further discussed below.

The analysis of variance results indicated that only Si (from the XRF analysis) and Nd (from the ICP analysis) have significant position effects. However, when 26 elements are separately tested, observing two with significant differences is not alarming. In fact, this would be expected as a manifestation of the random error in the data. Because only one position was sampled from each bar, the variability among the bar averages will include this position effect; however, because there were no groups of elements with significant differences, no special estimation methods were applied to the data for Si and Nd.

Therefore, for the purpose of computing the sample average and its variance, the position was ignored. The XRF data for each component and the ICP data for Nd were treated as a simple random sample of specimens drawn from the batch. In other words, for these components, the analysis of variance results justify the use of the usual hand calculation formulas for a sample average and sample standard deviation for a simple random sample. These formulas are preprogrammed on most hand calculators and are presented in the MCC "Guidelines for Accuracy and Precision of Test Data."

For the ICP analysis, the bars and position (location) on each bar were randomly selected. However, the ground material from each sampled specimen was split into two samples for ICP analysis. For each sample of material, analyses based on both Na and K fusions were performed. Thus, concentration values of Al, B, Li, and Mg were reported for both the Na and K fusions. Na concentration values were reported for the K fusion. Nd concentrations were reported for the K fusion, but only one Nd value was reported for each bar.

The ICP results for Al, B, Li and Mg were used with analysis of variance methods to test for 1) the position effect discussed above and 2) any systematic (nonrandom) differences between the Na and K fusion results. Without presenting equations and statistical notation, the logic underlying the analysis of the ICP data is as follows. An analysis of variance model was hypothesized that includes terms that account for the variation due to positions, bars "within positions," and duplicate samples of the material from each bar/position combination. Since both Na and K fusion results are present for each material sample, fusion was treated as a factor that is "crossed" with the other factors (positions, bars, and samples) in the model. Therefore, terms were added to the model that account for the fusion effect, and the interaction effects of fusion with position, bars, and samples.

An analysis of variance was then performed, based on this model, to determine which factors contribute significantly to the overall variability in the data for each component. None of these components had a significant position effect. In addition, Al, B, and Mg had no significant fusion effect. However, Li did have a significant fusion effect, but for each sample split, the Li concentrations from the two fusions are viewed as two nonindependent estimates of the concentration, and it is logical to average them. Therefore, the data for Al, B, Li, and Mg were reduced by averaging the two fusion results for each material sample.

Then, because position can be ignored, the variability in the data for Al, B, Li, Mg, and Na can be characterized by an analysis of variance model that includes only the effects of bars and the duplicate (or split) samples within bars. Thus, a one-way random effects analysis of variance could have been performed to estimate the variance of the overall average. However, since the number of samples per bar is the same for each bar, an equivalent but simpler method is to average the results within each bar, and then treat the six bar averages as a simple random sample. That is, the six bar averages were substituted into the usual formulas for computing a sample average and sample standard deviation.

Because there was a significant fusion effect for Li, averaging the two fusions leaves the question of correctly estimating the variance of the overall

average. Because a result from each fusion is present for each sample (or split), the Na and K fusion results are "paired" and are correlated. Also, the results for the two splits within a bar are correlated. Therefore, the variance of the overall sample average must be computed by taking this covariance structure into account. This can be done explicitly by application of analysis of variance techniques. However, because the number of splits and fusions is the same for all bars, a simpler but equivalent approach is to average the two fusion results for each sample (or split), average the two split averages, and then proceed with the computation of a sample average and standard deviation using the approach previously discussed. That is, the correct approach for combining the Li results reduces to computing an average for each of the six bars and then treating the six bar averages as a simple random sample.

COMPUTATION OF CONFIDENCE INTERVALS

With the simplified data structure assumption, as indicated by the analysis of variance results, computation of the sample averages, sample standard deviations, and 95% confidence intervals was straightforward. The XRF results for each component were treated as a simple random sample of size $n = 19$. The ICP results for each component were averaged within each bar, and the six bar averages for each component were then treated as a simple random sample of size $n=6$. The formula used to compute the 95% confidence limits is

$$\text{Ave} \pm \frac{\text{SD} \cdot t(n-1, 0.975)}{\text{sq. root of } n}$$

where Ave is the sample average, SD is the sample standard deviation, and $t(n-1, 0.975)$ is obtained from a table of the Student's t-distribution with $n-1$ degrees of freedom. For the XRF data, $t(18, 0.975) = 2.101$. For the ICP data, $t(5, 0.975) = 2.571$. The resulting 95% confidence intervals are displayed in Table 4.5 in the main body of the characterization report.

For each component, the confidence interval gives a range that probably includes the unknown true mean wt% oxide for this batch of glass (we are 95%

confident that it does). The comparison of the confidence intervals with the specified allowable error ranges is discussed in conjunction with Table 4.5 in the main body of the characterization report.

It is important to note that the validity of the confidence intervals displayed in Table 4.5 depends upon a number of factors. Every attempt was made to randomly sample the material from this batch of glass and then to randomize the order of the compositional analyses of the samples. Therefore, the standard deviation estimates, and thus the confidence interval widths, include the effects of both compositional inhomogeneity within this batch of glass and analytical imprecision. However, if any biases were present in the analytical laboratories, they cannot be evaluated or accounted for by any type of statistical analysis of the ATM-WV/205 characterization data. Therefore, if the sample averages and confidence intervals are to be interpreted as representing the probable mean composition of the ATM-WV/205 glass, it must be strictly assumed that the analytical laboratories produce unbiased results. If this assumption is not true, then the validity of the confidence intervals and the conclusions about the mean composition of the ATM-WV/205 glass are compromised.

TOLERANCE INTERVALS

As discussed above, the confidence intervals displayed in Table 4.5 in the main body of the characterization report are for the overall mean wt% oxide of the components. However, these confidence intervals do not provide an indication of the range of compositions of individual samples (or specimens) of glass that might be obtained from this batch (for example, in distributing portions of the material for testing purposes). Therefore, tolerance intervals were constructed for this purpose.

For a simple random sample of size n , tolerance intervals are computed from the formula

$$\text{Ave} \pm \text{SD} \cdot K(n, P, Q)$$

where Ave is the sample average and SD is the sample standard deviation. The quantity $K(n,P,Q)$ can be computed directly from a formula given by Bowen and Bennett^(a) for specified values of n , P , and Q . Natrella (1966) provides tables of $K(n,P,Q)$ for some selected values of P and Q .

The interval computed from the above formula is referred to as a 100P/100Q tolerance interval. For specified P and Q , we can be 100P% confident that 100Q% of the single values in the population (in this case single samples from this batch of ATM-WV/205 glass) will be inside the tolerance interval. The following values of $K(n,P,Q)$ were used to compute the tolerance intervals that are displayed in Table 4.6 in the main body of the characterization report.

n	$K(n,0.75,0.75)$	$K(n,0.90,0.90)$	$K(n,0.95,0.90)$	$K(n,0.95,0.95)$
6	1.825	3.494	4.275	5.079
19	1.355	2.172	2.337	2.784

Table 4.6 in the main body of the report displays 75/75, 90/90, 95/90, and 95/95 tolerance intervals for each component. For example, consider the 95/90 tolerance interval for Al₂O₃. We can be 95% confident that 90% of the individual samples (or specimens) obtained from this batch of glass will have wt% Al₂O₃ between 6.340 and 6.745.

As with the confidence intervals, the widths of the tolerance intervals are multiples of the sample standard deviations, which include the effects of both compositional inhomogeneity and analytical imprecision. Therefore, the interpretation of the tolerance intervals is in the context of single samples that are each analyzed in exactly the same manner as the samples in this characterization study. For example, the XRF data are based on a single analysis of a single material sample from each bar. Thus, the tolerance intervals for these components are for a single analysis of a single sample. However, the ICP data for Al, B, Li, and Mg are from analyses based on two

(a) Bowen, W. M., and C. A. Bennett. 1987. Statistical Methods for Nuclear Material Management, National Technical Information Services, Springfield, Virginia (in press), available as NUREG/CR-4604 or PNL-5849, Pacific Northwest Laboratory, Richland, Washington.

fusions for each of two duplicate samples from each bar, and the SD value used in the above equation was computed from the bar averages. Thus, the tolerance intervals for these components are for the average of K and Na fusion analyses performed on duplicate splits of a single sample (i.e., four analytical results are averaged for each material sample).

For some components, especially those with low concentrations, the analytical imprecision may be the dominant contributor to the sample standard deviation. In such cases, the widths of the tolerance intervals would be largely due to analytical error, rather than compositional inhomogeneity. Also, as with the confidence intervals, the validity of the tolerance intervals displayed in Table 4.6 depends on the validity of the assumption that the analytical laboratories produce unbiased results.

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Natrella, M. G. 1966. Experimental Statistics, National Bureau of Standards Handbook 91, Second Printing, U.S. Government Printing Office, Washington, D.C.

APPENDIX D

CALCULATION OF CLOSED-POROSITY VOLUME FRACTION IN ATM-WV/205 BAR 9 GLASS MATRIX

APPENDIX D

CALCULATION OF CLOSED POROSITY VOLUME FRACTION IN ATM-WV/205 BAR 9 GLASS MATRIX

Seven $\sim 4 \times 10^6 \mu\text{m}^2$ areas of a cross section from ATM-WV/205 Bar 9 were observed at $\sim 50\times$ using reflected light microscopy.^(a) The following is a list of the voids that were observed.

<u>Area</u>	<u>Diameter(s), μm</u>	<u>Total Area of Voids, μm^2</u>
1	45, 50, 65, 70,	1.1×10^4
2	100,	7.9×10^3
3	75	4.4×10^3
4	35	9.6×10^2
5	35, 50	2.9×10^3
6	55, 65, 125	1.8×10^4
7	65, 85	9.0×10^3
TOTAL		5.4×10^4

$$\frac{\text{Total Void Area}}{\text{Total Area Considered}} \times 100 = \text{vol\% of Voids}^{(b)}$$

$$\frac{5.4 \times 10^4}{2.8 \times 10^7} \times 100 = 0.20 \text{ vol\%}$$

(a) Additional observations made at 100, 250, and 500X indicated few voids smaller than $35 \mu\text{m}$ dia.

(b) See Underwood, E. E., A. R. Colcord, and R. C. Waugh. 1966. "Quantitative Relationships for Random Microstructures" in Ceramic Microstructures--Their Analysis, Significance, and Production, eds. R. M. Fulrath and J. A. Pask, Proceedings of the Third International Materials Symposium held at the University of California, Berkeley, June 13-16, 1966. Robert E. Krieger Publishing Company, Huntington, New York.

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