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MCC

Materials Characterization Center

Fabrication and Characterization of MCC Approved Testing Material—ATM-10 Glass

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April 1988

**Prepared for the U.S. Department of Energy
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FABRICATION AND CHARACTERIZATION
OF MCC APPROVED TESTING MATERIAL
ATM-10 GLASS

G. D. Maupin
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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-10 glass represents a reference commercial high-level waste form similar to that which will be produced by the West Valley Nuclear Service Co. Inc., West Valley, New York. The target composition and acceptable range of composition were defined by the sponsor, West Valley Nuclear Service.

The ATM-10 glass was produced in accordance with the Pacific Northwest Laboratory (PNL) QA Manual for License-Related Programs, MCC technical procedures, and MCC QA Plan that were in effect during the course of the work. The method and procedure to be used in the fabrication and characterization of the ATM-10 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. The radioactive elements (Am, Np, Pu, Tc, Th, U) were added to the frit as a nitrate solution dopant. The doped frit was then subjected to a series of chemical additions, melts, and crushings to obtain a uniform fused-glass powder of the required composition. The fused-glass powder was then blended with 0.08 wt% graphite and melted at 1150°C for 1 h. This final melt adjusted the oxidation state of the glass. All of the ATM-10 glass was produced in the form of bars 1.9 x 1.9 x 10 cm nominal size, and 93 g nominal mass. A total of 15 bars of ATM-10 glass weighing 1394 g was produced. The production bars were characterized to determine the mean composition, oxidation state, and microstructure of the ATM-10 product. Table A summarizes the characterization results.

The ATM-10 glass meets all specifications. The elemental composition and oxidation state of the glass are within the specifications of the client. Visually, the ATM-10 glass bars appear uniformly glassy and generally without exterior features. Microscopic examination revealed low (less than 2 wt%) concentrations of 3- μ m iron-chrome (suspected spinel) crystals and ~0.5- μ m ruthenium inclusions scattered randomly throughout the glassy matrix. Closed porosity, with pores ranging in diameter from 5 to 250 μ m, was observed in all samples.

TABLE A. Summary of ATM-10 Characterization Results

Composition:

Oxide	Target wt%	Sample Mean wt%	Sample Std. Dev.	Acceptable
Al ₂ O ₃	6.50	6.65	0.0209	Yes
AmO ₂	0.0068	0.0064	0.000073	Yes
B ₂ O ₃	9.26	9.17	0.082	Yes
BaO	0.05	0.045	0.00131	Yes
CaO	0.56	0.60	0.0354	Yes
CeO ₂	0.07	0.072	0.00127	Yes
Cr ₂ O ₃	0.29	0.253	0.0107	Yes
CsO ₂	0.07	0.062	0.0015	Yes
Fe ₂ O ₃	11.31	11.5	0.2065	Yes
K ₂ O	3.33	3.34	0.125	Yes
La ₂ O ₃	0.03	0.025	0.0020	Yes
Li ₂ O	2.82	2.88	0.0281	Yes
MgO	1.21	1.15	0.0296	Yes
MnO ₂	1.22	1.29	0.0219	Yes
Na ₂ O	10.17	10.5	0.150	Yes
Nd ₂ O ₃	0.17	0.168	0.0023	Yes
NiO	0.32	0.296	0.0135	Yes
NpO ₂	0.0208	0.021	0.00041	Yes
P ₂ O ₅	2.33	2.34	0.258	Yes
PuO ₂	0.0085	0.0081	0.000527	Yes
RhO ₂	0.01	0.012	0.0018	Yes
RuO ₂	0.07	0.061	0.0108	Yes
SO ₃	0.27	0.31	0.090	Yes
SiO ₂	44.9	45.8	2.391	Yes
SrO	0.03	0.025	0.00096	Yes
Tc ₂ O ₇	0.003	0.0031	0.000083	Yes
ThO ₂	3.34	3.29	0.0336	Yes
TiO ₂	0.91	0.858	0.0245	Yes
UO ₂	0.52	0.527	0.0171	Yes
Y ₂ O ₃	0.02	0.017	0.00082	Yes
ZrO ₂	0.27	0.247	0.00513	Yes
Total	100.09	101.5		

Oxidation State:

Target $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.10
 Ave $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.12 ($\pm 20\%$)
 Acceptable: Yes

Microstructure:

3 μm Fe, Cr, Mn, Ni crystals (spinel)
 0.5 μm Ru inclusions
 Closed porosity, 5-250 μm diameter
 Acceptable: Yes

Devitrification:

No crystalline material detectable by XRD
 (less than 2 wt% spinel)
 Acceptable: Yes

Bulk Density:

2.707 g/cm³ ($\pm 0.07\%$)
 Acceptable: Yes

CONCLUSION:

ATM-10 is an acceptable reference material.

Specimens of ATM-10 glass have been provided to PNL, Lawrence Livermore National Laboratory (LLNL), and Savannah River Laboratory (SRL) for use in their test programs. As of March 1987, approximately 650 g of ATM-10 were available for distribution.

ACKNOWLEDGMENT OF CONTRIBUTIONS TO ATM-10

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1.0 INTRODUCTION

The objective of the Materials Characterization Center (MCC) is to assist the U.S. Department of Energy (DOE) projects responsible for nuclear waste form production, transportation, and disposal. A major responsibility of the 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, Approved Testing Material-10 (ATM-10) glass. ATM-10 was produced by the MCC at the Pacific Northwest Laboratory (PNL) in Richland, Washington, which is operated for the DOE by Battelle Memorial Institute.

ATM-10 glass represents a reference commercial high-level waste form similar to that which will be produced by the West Valley Nuclear Service Co. Inc., West Valley, New York. ATM-10 is a borosilicate glass incorporating elements (although not necessarily the actual isotopes) which comprise nominal West Valley commercial waste. The ATM-10 glass was produced at the request of, and to the specifications of, West Valley Nuclear Service. The method and procedure used in the fabrication and characterization of the ATM-10 glass were specified in two run plans for glass preparation and a characterization plan. The ATM-10 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, four audits by West Valley Demonstration Project staff, and two internal audits.

2.0 SYNOPSIS

A general overview of the ATM-10 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 radioactive elements (Am, Np, Pu, Tc, Th, U) were added to the frit as a nitrate-solution dopant. 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 in order to incorporate the dopants 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 (350 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 first test melt. The glass bars were analyzed for chemical composition and oxidation state.

Based on the analytical results from the first test melt, and in order to meet West Valley's request to change the target composition to include more silica and alumina, a second test melt was performed. Additional silica and alumina powders were blended with 330 g of doped glass powder. In order to compensate for volatility losses observed in the first test melt, more technetium was added as a nitrate solution. The blended material was then dried, melted, crushed, and sieved. Because the first test melt experienced excessive reduction, only 0.08 wt% graphite was added to this material prior to the final melt. The resulting bars were analyzed and found acceptable.

The remaining doped glass powder was treated in the same manner as that used in the second test melt. All of the ATM-10 glass was produced in the form of bars with 1.9 x 1.9 x 10 cm nominal size and 93 g nominal mass. A total of 15 bars of ATM-10 glass, weighing 1394 g, was produced.^(a) The production

(a) The 15 production bars do not include test bars.

bars were characterized to determine the mean composition, oxidation state, and microstructure of the ATM-10 product. Table 2.1 summarizes the characterization results.

Energy dispersive x-ray fluorescence (EDXRF) analysis was performed on all 15 bars. Inductively coupled plasma atomic emission spectroscopy (ICP) analysis was performed in duplicate on powder samples taken from six of the bars. As shown in Table 2.1, the observed mean ATM-10 glass composition meets the sponsor's specification for each element and for uniformity of composition.

The oxidation state of the ATM-10 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 0.11 to 0.14, with a mean of 0.12. All the $\text{Fe}^{2+}/\text{Fe}^{3+}$ analyses were well within the specified range of 0.02 to 0.18.

The external surfaces of the ATM-10 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 smaller 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-light microscopy and autoradiography. Individual cubic features, measuring approximately 3 μm on an edge, were observed scattered throughout all samples. In some regions the cubic features were grouped together, forming clusters. Closed porosity, with pores ranging in diameter from 5 to 250 μm , was observed in all microscopy samples. The autoradiography demonstrated uniform activity throughout the samples. This observation suggests homogeneous distribution of the radionuclides. However, because of the differences in specific activity and concentration of the radionuclides, the radiographs primarily represent the distribution of ^{241}Am .

Fractured surfaces of three bars were observed by scanning electron microscopy (SEM). Observed pore diameters ranged from 30 to 250 μm . Cubic second phase features, similar to those observed by optical microscopy, were

TABLE 2.1. Summary of ATM-10 Characterization Results

Composition:

Oxide	Target wt%	Sample Mean wt%	Sample Std. Dev.	Acceptable
Al ₂ O ₃	6.50	6.65	0.0209	Yes
AmO ₂	0.0068	0.0064	0.000073	Yes
B ₂ O ₃	9.26	9.17	0.082	Yes
BaO	0.05	0.045	0.00131	Yes
CaO	0.56	0.60	0.0354	Yes
CeO ₂	0.07	0.072	0.00127	Yes
Cr ₂ O ₃	0.29	0.253	0.0107	Yes
CsO ₂	0.07	0.062	0.0015	Yes
Fe ₂ O ₃	11.31	11.5	0.2065	Yes
K ₂ O	3.33	3.34	0.125	Yes
La ₂ O ₃	0.03	0.025	0.0020	Yes
Li ₂ O	2.82	2.88	0.0281	Yes
MgO	1.21	1.15	0.0296	Yes
MnO ₂	1.22	1.29	0.0219	Yes
Na ₂ O	10.17	10.5	0.150	Yes
Nd ₂ O ₃	0.17	0.168	0.0023	Yes
NiO	0.32	0.296	0.0135	Yes
NpO ₂	0.0208	0.021	0.00041	Yes
P ₂ O ₅	2.33	2.34	0.258	Yes
PuO ₂	0.0085	0.0081	0.000527	Yes
RhO ₂	0.01	0.012	0.0018	Yes
RuO ₂	0.07	0.061	0.0108	Yes
SO ₃	0.27	0.31	0.090	Yes
SiO ₂	44.9	45.8	2.391	Yes
SrO	0.03	0.025	0.00096	Yes
Tc ₂ O ₇	0.003	0.0031	0.000083	Yes
ThO ₂	3.34	3.29	0.0336	Yes
TiO ₂	0.91	0.858	0.0245	Yes
UO ₂	0.52	0.527	0.0171	Yes
Y ₂ O ₃	0.02	0.017	0.00082	Yes
ZrO ₂	0.27	0.247	0.00513	Yes
Total	100.09	101.5		

Oxidation State:

Target Fe²⁺/Fe³⁺ of 0.10
Ave Fe²⁺/Fe³⁺ of 0.12 (±20%)
Acceptable: Yes

Microstructure:

3 μm Fe,Cr,Mn,Ni crystals (spinel)
0.5 μm Ru inclusions
Closed porosity, 5-250 μm diameter
Acceptable: Yes

Devitrification:

No crystalline material detectable by XRD
(less than 2 wt% spinel)
Acceptable: Yes

Bulk Density:

2.707 g/cm³ (±0.07%)
Acceptable: Yes

CONCLUSION:

ATM-10 is an acceptable reference material

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 (Chick 1980). Associated with some of the cubic-clustered regions were ~0.5- μ m-diameter inclusions of high ruthenium concentration. The individual samples appeared to be of uniform composition and structure.

X-ray diffraction analysis (XRD) was conducted on powder samples taken from the same three bars as used for microscopy. No XRD peaks indicative of crystalline materials were observed in the XRD pattern. This observation indicates ATM-10 glass contains very little (less than 2 wt% in the case of spinel) crystalline material.

Water immersion bulk-density determinations were performed on sections taken from six bars. Small differences ($\pm 0.07\%$ from mean) were observed in the densities of these samples. The mean density of the six samples was 2.707 g/cm³.

The ATM-10 glass meets all specifications. It is considered suitable for use as a reference material. ATM-10 glass has been provided to PNL, Lawrence Livermore National Laboratory (LLNL), and Savannah River Laboratory (SRL) for use in their test programs. As of March 1987, approximately 650 g of ATM-10 are available for distribution.

3.0 FABRICATION

The fabrication of ATM-10 began on May 19, 1986, and was completed September 12, 1986. The procedures and methods used in fabrication were described in two run plans. Supporting analytical data is retained in the PNL Records Center. The ATM-10 glass was produced in accordance with MCC Program Technical Procedures.

3.1 STARTING MATERIALS

The batch glass, or frit, was produced from the reagent grade chemicals listed in Table 3.1 (see Appendix A for manufacturer and lot numbers). The radioactive dopants (^{241}Am , ^{237}Np , ^{239}Pu , ^{99}Tc , ^{232}Th , and ^{238}U) were produced from existing stock materials (see Appendix B, Jack Ryan Memorandum, for original sources).

3.2 INITIAL TEST BATCH

An initial 500-g test batch of the undoped frit glass 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 "DT-31-RS" furnace. 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 μm using an Angstrom mill and tungsten-carbide grinding chamber. Three powder samples were randomly selected and submitted for ICP (by two separate laboratories) and EDXRF analysis. Table 3.2 lists the analytical results from

TABLE 3.1. Worksheet for Undoped Preliminary
Test Batch (500 g)

Oxide	Target wt%	Compound Used	Theoretical Compound:Oxide Factor	Quantity of ^(a) Compound Used, g
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	0.15
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	0.30	ZrO ₂	1.000	1.50
	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.

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 BATCH, FRIT FABRICATION

The compounds in Table 3.3 were combined in the quantities listed 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 foamed out of the crucible.^(a) 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. 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. EDXRF was required for the low-concentration, higher atomic number elements. ICP analysis was required for the lower atomic number elements (Al, B, Li, Mg, Na) and for Nd. For those elements with analyses common to both techniques, the data generally agree. In the case 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 the frit composition was acceptable. The "actual batch" fabrication resulted in 5.5 kg of powdered glass, or frit. Only 2.9 kg

(a) We do not know why these four melts foamed more than the other melts.

TABLE 3.2. Chemical Analysis of ATM-10 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, wt%				Dev. from Target, %	Allow. Dev., %	Adjust Factor
		P1	P2	P3	P1	P2	P3	P1	P2	P3	Mean			
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-10 Frit Fabrication (6 kg)

Oxide	Target wt%	Compound Used	Compound:Oxide Factor	Quantity of ^(a) Compound Used, g
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-10 Frit by Inductively Coupled Plasma Spectroscopy (ICP) and Energy Dispersive X-Ray Fluorescence (EDXRF)

ATM-10 Oxide	ICP Data, wt%								Oxide	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	Al ₂ O ₃	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	B ₂ O ₃								
BaO	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	BaO	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	CaO	0.638	0.677	0.694	0.662	0.659	0.659	0.700	0.642
CeO ₂									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	Cr ₂ O ₃	0.292	0.299	0.296	0.302	0.305	0.294	0.296	0.292
Cs ₂ O									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	Fe ₂ O ₃	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	K ₂ O	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	La ₂ O ₃	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	Li ₂ O								
MgO	1.25	1.26	1.25	1.26	1.26	1.27	1.28	1.27	MgO								
MnO ₂	1.34	1.35	1.35	1.35	1.35	1.35	1.37	1.35	MnO ₂								
Na ₂ O	11.30	11.20	11.10	11.10	11.10	11.10	11.10	11.10	Na ₂ O								
Nd ₂ O ₃ (a)	0.18	0.18	0.18	0.18	0.19	0.19	0.18	0.19	Nd ₂ O ₃								
NiO	0.32	0.33	0.33	0.33	0.34	0.34	0.36	0.34	NiO	0.356	0.354	0.359	0.360	0.357	0.357	0.360	0.362
P ₂ O ₅									P ₂ O ₅	2.37	2.40	2.47	2.42	2.28	2.26	2.36	2.22
RhO ₂									RhO ₂	0.013	0.013	0.013	0.012	0.013	0.012	0.012	0.012
RuO ₂									RuO ₂	0.095	0.095	0.093	0.093	0.095	0.092	0.096	0.094
SO ₃									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	SiO ₂	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	SrO	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	TiO ₂	0.939	0.934	0.922	0.952	0.936	0.921	0.954	0.917
Y ₂ O ₃									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					ZrO ₂	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	Total	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 3.5. Combined ICP and TOXRI Data and Statistical Test for Predoped AIM-104111

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						

of this frit were used in the production of ATM-10 glass. The remaining frit was reserved for production of another approved test material (ATM-WV/205).

3.4 DOPANT SOLUTIONS

The radioactive elements (^{241}Am , ^{237}Np , ^{239}Pu , ^{99}Tc , ^{232}Th , and ^{238}U) were prepared as separate nitrate solutions. Only a brief description of dopant preparation is given here. A detailed description is provided in Appendix B. The ^{241}Am and ^{237}Np dopants were both prepared by dissolving the oxides in nitric acid and small amounts of hydrofluoric acid. These solutions were diluted to 25 mL. The ^{239}Pu dopant was prepared from an existing analyzed Pu-nitrate solution that was diluted to 25 mL. The ^{99}Tc dopant was made by dissolving ammonium pertechnetate in dilute nitric acid/hydrogen peroxide which was then diluted to 25 mL. The ^{232}Th dopant was prepared from thorium nitrate which was dissolved in nitric acid and diluted to 250 mL. The ^{238}U dopant was prepared from UO_2 dissolved in nitric acid and hydrogen peroxide diluted to a final volume of 100 mL. Samples were prepared from each of the dopant solutions and submitted for analysis.

3.5 DOPANT ADDITION TO FRIT

The results of the radiochemical analysis for the dopant solutions described above are shown in Table 3.6. Originally, all of the remaining dopant solutions (after sampling) were intended to be added to the frit. The ^{239}Pu and ^{232}Th dopants, however, were found to be more concentrated than intended. Portions of these two dopants were withheld in order to obtain the specified target composition. As shown in Table 3.6, the anticipated errors for the dopant elements were well within the sponsor's allowable limits.

Working in a glove box, the indicated volumes of dopant solutions were combined in a 3.5-L polyethylene beaker and diluted to 750 mL using deionized water. A total of 2874.3 g of the frit (described in Section 3.3) was then added to the beaker. The resulting slurry was mixed and dried in two batches.

TABLE 3.6. Dopants Added to ATM-10 Frit

Isotope	Target Conc., mg/mL	Analyzed Conc., mg/mL	Adjusted Vol.	Added to 2874.3 g Frit			
				Volume, mL	Mass (Element)	Oxide	Mass (Oxide), g
^{241}Am	7.79	7.47	No	24.85	185.6 mg	AmO_2	0.210
^{237}Np	23.64	22.64	No	24.85	562.7 mg	NpO_2	0.639
$^{239/240}\text{Pu}$	8.04	8.66	Yes	23.3	201.8 mg	PuO_2	0.229
^{99}Tc	1.68	1.65	No	24.85	41.0 mg	Tc_2O_7	0.064
U depleted	148.1	150.2	No	98.0	14.72 g	UO_2	16.70
Th natural	378.7	398.0	Yes	244.7	97.37 g	ThO_2	<u>110.80</u>
							128.64

Oxide	Calculated wt% in Glass	Target wt % in Glass	Calculated Error, %	Allowable Error, %
AmO_2	0.0070	0.0073	-4.1	15
NpO_2	0.0213	0.0224	-5.1	15
PuO_2	0.0076	0.0076	0.3	10
Tc_2O_7	0.0021	0.0021	1.7	25
UO_2	0.556	0.56	-0.7	15
ThO_2	<u>3.690</u>	<u>3.59</u>	2.8	15
	4.28	4.19		

3.6 DRYING AND DENITRATING OF THE DOPED FRIT

Approximately half of the slurry (~500 mL) was transferred to a 1.2-L stainless steel beaker. The beaker was then heated to 200°C using a Hoskins pot furnace. The slurry was stirred during the first 5 h of drying. At this point, the doped frit appeared relatively dry, and the material was left overnight at 200°C. After a total drying time of 20 h, the powder was removed. Much of the powder had caked overnight. It was necessary to scrape this material from the walls of the stainless steel beaker. The other half of the frit/dopant slurry was dried in the same manner.

Severe foaming was encountered during the first attempts at melting the doped frit that had been dried at 200°C (Section 3.7). The residual nitrates were believed to be the cause of the severe foaming. Because the decomposition temperature of thorium nitrate is about 500°C (Weast 1985), the nitrates were not effectively removed at 200°C. The doped frit was subjected to another heat treatment prior to melting.

A sodium hydroxide scrubber system was employed in order to capture NO_x fumes and avoid damage to the glove box. Approximately one-third of the doped frit was placed in the pot furnace. The temperature was increased to 550°C; prolonged higher temperatures were not practical, as the frit would have fused. The frit was stirred occasionally, and brown NO_x fumes were observed at temperatures above 500°C. After about 3 h at 550°C, the NO_x fumes were no longer visible. The furnace temperature was increased momentarily to 600°C; only slight NO_x off-gassing was observed. The furnace was then turned off and the denitrated doped-frit removed. The remaining doped frit was denitrated in a similar manner.

3.7 MELTING OF THE DOPED FRIT

A Deltech "DT-31-RS" furnace, located in a nitrogen atmosphere glove box, was used to melt the doped frit. Temperature was monitored using a calibrated type "S" thermocouple and a Omega (model 650) digital thermometer.

The first attempt at melting involved the doped frit that had been dried at 200°C (Section 2.6). Approximately 130 g, or 100 mL, of this doped frit were placed in a 250 mL Denver Fire Clay (DFC) crucible. The cold crucible was then placed in the furnace at 1150°C. After 20 min, most of the glass (~80 g) had foamed out of the crucible. The furnace was shut down; too much glass was being lost.

The second attempt using a DFC crucible involved doped frit that had been denitrated at 550°C. Process loss was still unacceptably high because of foaming. Other attempts involved preheating the DFC crucible and preheating both the DFC crucible and the doped frit before they were placed in the Deltech furnace at 1150°C. The foaming behavior continued.

Eventually, a larger (500 mL) platinum crucible was used with five ~110-g frit additions. Each addition required about 20 min to subside. After the fifth addition, the glass was held at 1150°C for 30 min. The molten glass was then poured onto a stainless steel plate and allowed to cool. A total of five of these "melt cycles" were required to process the remainder of the 3 kg of denitrated doped frit. Despite these efforts, 530 g of glass were lost due to foaming. The 2470 g of doped glass were crushed and sieved to less than 150 μ m using a Fritsch Alumina Auto-Mortar and Pestle.

The cause of the foaming is not understood. At first, the problem was believed to be residual nitrates from dopants. However, denitrating at 550°C did not seem to help. And, recently, we found that glass of a very similar composition and fabrication history, ATM-WV/205,^(a) did not exhibit severe foaming when melted in air. The ATM-10 foaming problem may relate to the nitrogen atmosphere in the glove box or perhaps to the presence of Th or U.

While foaming made processing difficult and resulted in loss of material, it had no apparent detrimental effect on the glass product. The doped glass appeared very glossy and homogeneous after this first melt. There were no signs of macroscopic phase separation.

(a) ATM-WV/205 is a nonradioactive Approved Test Material, similar to ATM-10, which is also being produced at the request of West Valley Nuclear Service.

3.8 OXIDATION TEST MELTS

The purpose of the oxidation test melts was to determine how much graphite should be added to the final glass melt. The graphite acts as a reductant and was used to achieve the desired $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.10 ± 0.08 . For this test, 25 g of undoped frit was combined with 0.0 to 0.5 wt% graphite.^(a) The five samples were melted in the nitrogen atmosphere glove box using 100-mL DFC crucibles. After 1 h at 1150°C, the samples were poured onto a stainless steel plate. The samples were submitted for $\text{Fe}^{2+}/\text{Fe}^{3+}$ analysis. The resulting $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is presented as a function of added graphite in Figure 3.1. Notice that the data indicate an addition of 0.18 wt% graphite should result in the desired $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.10.

3.9 FIRST TEST MELT

The purpose of the test melt was to demonstrate whether the final ATM-10 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 the nitrogen glove box using the Deltech furnace described in Section 3.7. A Hoskins pot furnace, monitored with a calibrated type "K" thermocouple, Omega (model 650) thermometer, and a Kipp Zonnen strip chart recorder, was used for the annealing of the glass bars.

Three hundred fifty grams of the doped glass described in Section 3.8 were combined with 0.63 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 melts described in Section 3.8. Approximately 100 g of the graphite spiked glass was placed in a 250-mL DFC crucible. The crucible was then placed in the Deltech furnace at 1150°C. Twenty minutes later, another 120 g of glass was added to

(a) Originally, the glass produced from the initial test batch (Section 3.2) was to be used for this oxidation test. However, the initial test batch glass was reduced before graphite was ever added. The initial test batch was not representative of the doped glass. See Appendix C for further discussion.

FIGURE 3.1. Oxidation Test Using ATM-10 Predoped Frit in Glove Box with Nitrogen Atmosphere. Test indicates a 0.18 wt% addition of graphite is needed for the target $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.10.

the crucible. Two more additions of about 65 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 an additional 30 min at 1150°C (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, a "dimple" was indented 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) Hoskins pot furnace for annealing.

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Two more glass bars were poured and placed in the Hoskins furnace. The three bars were annealed for 2 h at 500°C. The Hoskins furnace was then turned off, and the bars were allowed to cool undisturbed. The cooling behavior of the Hoskins furnace is presented in Figure 3.2. As expected, the cooling rate is not linear with time. However, the average cooling rate of the Hoskins furnace between 500 and 100°C was ~75°C/h.

After the three bars had cooled to less than 50°C, they were removed from the Hoskins 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 last bar poured, Bar 3, was sectioned using a Buehler Isomet, low-speed diamond saw with deionized water coolant. Three cross sections ~5 mm thick were taken, one from each end and one from the center of the bar. The sections were individually crushed and sieved to less than 75 μm using a hand alumina mortar and pestle. Portions of

FIGURE 3.2. Observed Cooling Rate of Hoskins Pot Furnace Used for Annealing ATM-10 Glass Bars. Average cooling rate between 500 and 100°C was 75°C/h.

these powders were submitted for ICP, radiochemistry, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ analyses. The smearable radioactive material on the surface of Bar 2 was removed by wiping with lint-free towels saturated with deionized water and ethanol. Each end and the center of this decontaminated bar were subjected to nondestructive EDXRF analysis.

The analytical results from the first test melt are shown in Tables 3.7 and 3.8. A statistical test was performed to determine if the observed mean composition met the sponsor's specifications. As shown in Table 3.8, the confidence intervals for the elements Ca, K, Nd, Pu, S, Tc, and Ti did not meet the specifications. Also, the oxidation state of the first test melt glass indicated that it was over-reduced.

For the elements Ca, K, and Ti, the observed mean compositions met the specifications. However, considering the scatter in the data and the limited number of samplings, the statistical results for the concentrations of these elements were inconclusive. The Ca, K, and Ti concentrations would likely be demonstrated to be acceptable if more samples were analyzed. This was not the case for Nd, Pu, S, or Tc, or the $\text{Fe}^{2+}/\text{Fe}^{3+}$, however.

The source of the extra Pu is unknown. Pu contamination to the doped glass (or the analytical samples) may have resulted from the equipment used in the glove box. ICP analysis for Nd in these samples indicated concentrations near the detection limit; a fusion technique for increasing the sensitivity to Nd was being developed but was not available for radioactive samples at this time.^(a) Concentrations of S in these samples were also near the EDXRF detection limit. No better method for determining S concentration in actinide glass was available, however. Apparently, over half of the added Tc evaporated during processing. Such evaporation is not unreasonable; the reported boiling point of Tc_2O_7 is 311°C (Rard 1985). The amount of added graphite had been determined by the oxidation test melts (Section 3.8). The oxidation test melts used 25-g melts of frit to represent 350-g doped-glass melts. Owing to the

(a) Based on ASTM Method C-146 for sample preparation.

TABLE 3.7. Analysis of ATM-10 First Test Melt by Inductively Coupled Plasma Spectroscopy (ICP),^(a) Energy Dispersive X-Ray Fluorescence (EDXRF),^(b) Radiochemistry (RC)^(a) and Spectrophotometric Determination of Reduced and Total Iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$)^(a)

Oxide	ICP Data, wt%			XRF Data, wt%			RC Data, wt%		
	TM-1	TM-2	TM-3	TMP1	TMP2	TMP3	TM-1	TM-2	TM-3
Al_2O_3	2.90	2.93	2.90						
AmO_2							0.00694	0.00706	0.00704
B_2O_3	10.1	10.1	10.0						
BaO	0.06	0.06	0.06	0.052	0.051	0.052			
CaO	0.68	0.66	0.65	0.672	0.631	0.576			
CeO_2				0.078	0.081	0.076			
Cr_2O_3	0.25	0.27	0.26	0.272	0.272	0.279			
Cs_2O				0.068	0.070	0.071			
Fe_2O_3	11.7	11.7	11.6	12.15	12.18	11.88			
K_2O	3.27	3.53	3.17	3.578	3.361	3.554			
La_2O_3	0.02	0.02	0.02	0.030	0.028	0.028			
Li_2O	3.12	3.09	3.11						
MgO	1.21	1.20	1.20						
MnO_2	1.29	1.30	1.28	1.375	1.377	1.312			
Na_2O	10.9	10.9	10.7						
Nd_2O_3	0.09	0.09	0.10						
NiO	0.31	0.49	0.32	0.312	0.324	0.296			
NpO_2							0.021	0.021	0.022
P_2O_5	3.1	3.3	3.4	2.246	2.429	2.269			
PuO_2							0.0106	0.0099	0.0100
RhO_2				0.014	0.013	0.010			
RuO_2				0.068	0.072	0.094			
SO_3				0.250	0.312	0.332			
SiO_2	45.2	45.2	44.8	44.28	45.57	45.35			
SrO	0.03	0.03	0.03	0.028	0.027	0.027			
Tc_2O_7							0.00075	0.00109	0.00091
ThO_2	3.7	3.3	3.8	3.710	3.493	3.493			
TiO_2	0.95	0.95	0.95	0.862	0.887	0.856			
UO_2				0.571	0.534	0.534			
Y_2O_3				0.019	0.019	0.019			
ZrO_2	0.29	0.29	0.27	0.285	0.267	0.255			
Total	99.17	99.41	98.62	70.92	72.00	71.37	0.04	0.04	0.04

Oxidation State	$\text{Fe}^{2+}/\text{Fe}^{3+}$		
	TM-1	TM-2	TM-3
	0.289	0.239	0.279

(a) Conducted on powder samples taken from three locations on bar 3.

(b) EDXRF performed on solid glass bar 2 in three locations.

TABLE 3.8. Combined Analytical Data and Statistical Test for
ATM-10 First 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	2.83	2.91	ICP	2.689	2.867	2.953	2.972	Yes
AmO ₂	0.0073	0.00701	RC	0.0062	0.0068	0.0072	0.0084	Yes
B ₂ O ₃	9.96	10.07	ICP	9.462	9.923	10.210	10.458	Yes
BaO	0.05	0.052	XRF	0.030	0.050	0.053	0.070	Yes
CaO	0.6	0.626	XRF	0.480	0.508	0.745	0.720	No
CeO ₂	0.07	0.078	XRF	0.035	0.072	0.085	0.105	Yes
Cr ₂ O ₃	0.31	0.274	XRF	0.248	0.264	0.285	0.372	Yes
Cs ₂ O	0.08	0.070	XRF	0.056	0.066	0.074	0.104	Yes
Fe ₂ O ₃	12.16	12.07	XRF	11.309	11.660	12.483	13.011	Yes
K ₂ O	3.58	3.50	XRF	3.222	3.202	3.793	3.938	No
La ₂ O ₃	0.03	0.029	XRF	0.015	0.027	0.031	0.045	Yes
Li ₂ O	3.03	3.11	ICP	2.879	3.069	3.145	3.181	Yes
MgO	1.3	1.20	ICP	1.105	1.203	1.203	1.495	Yes
MnO ₂	1.31	1.355	XRF	1.114	1.263	1.447	1.507	Yes
Na ₂ O	10.94	10.83	ICP	9.846	10.546	11.120	12.034	Yes
Nd ₂ O ₃	0.18	0.09	ICP	0.133	0.079	0.108	0.227	No
NiO	0.34	0.311	XRF	0.289	0.276	0.346	0.391	Yes
NpO ₂	0.0224	0.0215	RC	0.0190	0.0205	0.0225	0.0258	Yes
P ₂ O ₅	2.51	2.314	XRF	2.008	2.066	2.563	3.012	Yes
PuO ₂	0.0076	0.0102	RC	0.0068	0.0093	0.0111	0.0084	No
RuO ₂	0.01	0.012	XRF	0.003	0.006	0.018	0.018	Yes
RuO ₂	0.08	0.078	XRF	0.040	0.044	0.112	0.120	Yes
SO ₃	0.22	0.298	XRF	0.110	0.191	0.405	0.330	No
SiO ₂	44.9	45.07	XRF	42.655	43.360	46.777	47.145	Yes
SrO	0.03	0.027	XRF	0.010	0.025	0.030	0.050	Yes
Ta ₂ O ₅	0.0021	0.00092	RC	0.00158	0.00049	0.00134	0.00262	No
ThO ₂	3.59	3.565	XRF	3.052	3.255	3.876	4.129	Yes
TiO ₂	0.98	0.868	XRF	0.833	0.827	0.910	1.127	No
UO ₂	0.56	0.546	XRF	0.476	0.494	0.598	0.644	Yes
Y ₂ O ₃	0.02	0.019	XRF	0.005	0.018	0.020	0.035	Yes
ZrO ₂	0.29	0.269	XRF	0.203	0.232	0.306	0.377	Yes
Total	100.00	99.68						
Fe ²⁺ /Fe ³⁺	0.10	0.269		0.02	N/A	N/A	0.18	No

differences in surface area-to-volume ratios of the melts, or composition of the melts, the oxidation test melts did not adequately represent the effect of graphite in the larger test melt.

West Valley management was notified of the results of the first test melt and of our intentions of performing a second test melt with added Tc and less graphite. At this time, West Valley requested that the target composition be changed to include more Al_2O_3 and SiO_2 . This new target composition is shown as Revision 1 on Table 3.9. Notice that the allowable deviations for Al_2O_3 and SiO_2 were also changed.

3.10 SECOND TEST MELT

A portion of the powdered doped glass (329.5 g), 13.71 g of Al_2O_3 , and 11.17 g of SiO_2 were combined in a plastic bag. This powder mixture was added to a stainless steel beaker containing 84 mL of dilute nitric acid/ammonium pertechnetate solution. The 84 mL of solution contained the equivalent of 0.015 g Tc_2O_7 . The resulting slurry was mixed and denitrated at 550°C for 1 h. The denitrated powder was then melted at 1150°C for 1 h in a 500-mL platinum beaker and poured onto a stainless steel plate. The resulting glass was crushed and sieved to less than 150 μm and spiked with 0.08 wt% graphite.

Similar to the first test melt, approximately 100 g of the graphite-spiked glass was placed in a 250 mL OFC crucible. The crucible was then placed in the Deltech furnace at 1150°C. Unlike the first melt, however, the modified glass foamed over. The remainder of the modified glass was added in three increments at 20-min intervals. Further foaming was observed (an estimated 75 g lost). The melt was stirred twice in the hour following the last glass addition. After 1 h at 1150°C, two ~90-g bars and a 32-g bar were poured and transferred to the Hoskins furnace. This glass appeared more viscous than the glass poured in the first test melt. The greater foaming tendency of this glass might also be related to an increased viscosity; CO and CO_2 gasses generated from the added graphite may dissipate more slowly in the higher-viscosity glass.

After 2 h at 500°C and following furnace cooling, the three bars were removed. The bars looked uniformly glassy with no surface porosity or apparent

TABLE 3.9. ATM-10 Target Composition Revisions

Oxide	Initial (Run Plan 4/1/86)		Revision 1 (WV TA 13, 7/25/86)		Revision 2 (WV TA 336, 9/11/86)	
	Conc., wt%	Allowable Deviation, wt%	Conc., wt%	Allowable Deviation, wt%	Conc., wt%	Allowable Deviation, wt%
Al ₂ O ₃	2.83	5	6.50	10	6.50	10
B ₂ O ₃	9.96	5	9.26	5	9.26	5
BaO	0.05	40	0.05	40	0.05	40
CaO	0.60	20	0.56	20	0.56	20
CeO ₂	0.07	50	0.07	50	0.07	50
Cr ₂ O ₃	0.31	20	0.29	20	0.29	20
Cs ₂ O	0.08	30	0.07	30	0.07	30
Fe ₂ O ₃	12.16	7	11.31	7	11.31	7
K ₂ O	3.58	10	3.33	10	3.33	10
La ₂ O ₃	0.03	50	0.03	50	0.03	50
Li ₂ O	3.03	5	2.82	5	2.82	5
MgO	1.30	15	1.21	15	1.21	15
MnO ₂	1.31	15	1.22	15	1.22	15
Na ₂ O	10.94	10	10.17	10	10.17	10
Nd ₂ O ₃	0.18	26	0.17	26	0.17	26
NiO	0.34	15	0.32	15	0.32	15
P ₂ O ₅	2.51	20	2.33	20	2.33	20
RhO ₂	0.01	75	0.01	75	0.01	75
RuO ₂	0.08	50	0.07	50	0.07	50
SO ₃	0.22	50	0.20	50	0.27	65
SiO ₂	44.90	5	44.90	10	44.90	10
SrO	0.03	67	0.03	67	0.03	67
ThO ₂	3.59	15	3.34	15	3.34	15
TiO ₂	0.98	15	0.91	15	0.91	15
UO ₂	0.56	15	0.52	15	0.52	15
Y ₂ O ₃	0.02	75	0.02	75	0.02	75
ZrO ₂	0.29	30	0.27	30	0.27	30
AmO ₂	0.0073	15	0.0068	15	0.0068	15
NpO ₂	0.0224	15	0.0208	15	0.0208	15
PuO ₂	0.0076	10	0.0071	10	0.0085	15
Tc ₂ O ₇	0.0021	25	0.0020	25	0.0030	25
TOTAL	100.00		100.02		100.09	
Fe ²⁺ /Fe ₃₊	0.10	0.08	0.10	0.08	0.10	0.08

phase separation. Bar 1 was sectioned and powder samples were prepared just as for Bar 3 of the first test melt. Bar 2 of this second test melt was also decontaminated and subjected to EDXRF as before.

Tables 3.10 and 3.11 show the analytical results from this second test melt. Although the elements Pu, S, and Tc were found to be outside the Revision 1 target composition listed in Table 3.9, the sponsor reviewed the data and accepted the second test melt composition shown as Revision 2 on Table 3.9. Table 3.11 demonstrates that the analyzed composition of the second test melt meets the Revision 2 specifications.

3.11 FABRICATION OF ATM-10 PRODUCTION BARS

Production of the ATM-10 glass bars essentially duplicated the procedure used for the second test melt (Section 3.10). The remaining 1774 g of doped glass (Section 2.7) were mixed with 73.82 g Al_2O_3 and 60.15 g SiO_2 . The powder mixture was added to 450 mL dilute nitrate and ammonium pertechnetate solution (solution contained equivalent of 0.083 g Tc_2O_7). The resulting slurry was denitrated in two batches, each at 550°C for 1 h. The denitrated powder was melted at 1150°C for 1 h using a 500-mL platinum crucible. Foaming was not observed. The molten glass was poured onto a stainless steel plate. This glass was crushed and sieved to less than 150 μm . A total of 1866 g of powdered glass resulted. Graphite, amounting to 0.08 wt% (1.494 g), was mixed with the powdered glass in a plastic bag.

The glass/graphite mixture was melted in DFC crucibles as described in Sections 3.9 and 3.10. A total of five melt cycles, over two days, were required to process all of the glass. Three glass bars, measuring nominally 1.9 x 1.9 x 10 cm and 93 g, were produced from each melt cycle. Each bar was "dimpled" as described in Section 3.9. Two identical Hoskins furnaces were used to anneal the glass bars at 500°C for 2 to 6.3 h. An estimated 200 g of glass were lost to foaming; an additional 150 g of glass was trapped in the three DFC crucibles that were used. A single partial bar of ~40 g was also produced, but is not included as an "ATM-10 production bar."

The fifteen ATM-10 production bars were removed from the annealing ovens. The first glass bar poured was labeled ATM-10-1; the second bar poured,

TABLE 3.10. Analysis of ATM-10 Second Test Melt by Inductively Coupled Plasma Spectroscopy (ICP),^(a) Energy Dispersive X-Ray Fluorescence (EDXRF),^(b) Radiochemistry (RC),^(a) and Spectrophotometric Determination of Reduced and Total Iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$)^(a)

Oxide	ICP Data, wt%						XRF Data, wt%			RC Data, wt%		
	[<-----1st Run----->]			[<-----2nd Run----->]			ZTMP1	ZTMP2	ZTMP3	ZTM-2	ZTM-2	ZTM-3
	ZTM-1	ZTM-2	ZTM-3	ZTM-1	ZTM-2	ZTM-3						
Al_2O_3	6.55	6.57	6.62	6.46	6.45	6.42						
AmO_2										0.00641	0.00648	0.00645
B_2O_3	9.27	9.33	9.34	9.07	9.06	9.11						
BaO	0.06	0.06	0.06	0.064	0.069	0.063	0.047	0.045	0.047			
CaO	0.71	0.71	0.71	0.648	0.669	0.682	0.585	0.617	0.561			
CeO_2							0.075	0.072	0.074			
Cr_2O_3	0.21	0.20	0.21	0.223	0.225	0.206	0.272	0.267	0.260			
Cs_2O							0.064	0.061	0.063			
Fe_2O_3	11.1	11.0	11.0	10.9	10.8	10.7	11.71	11.75	11.68			
K_2O	3.15	2.97	3.00	2.97	2.84	2.68	3.517	3.385	3.421			
La_2O_3				0.022	0.021	0.021	0.025	0.024	0.025			
Li_2O	2.88	2.88	2.88	2.86	2.84	2.84						
MgO	1.17	1.16	1.16	1.18	1.13	1.13						
MnO_2	1.20	1.19	1.20	1.18	1.17	1.17	1.268	1.275	1.260			
Na_2O	10.7	10.8	11.0	10.3	10.4	10.3						
Nd_2O_3				0.128	0.122	0.123						
NiO	0.26	0.27	0.26	0.261	0.256	0.249	0.298	0.305	0.298			
NbO_2										0.023	0.023	0.023
P_2O_5							2.314	2.360	2.314			
PuO_2										0.0080	0.0087	0.0087
RhO_2							0.011	0.013	0.013			
RuO_2				0.137	0.133	0.149	0.065	0.063	0.064			
SO_3							0.345	0.207	0.260			
SiO_2	45.5	45.8	45.8	44.7	45.3	44.8	46.64	44.71	45.78			
SrO	0.03	0.03	0.03	0.026	0.026	0.025	0.025	0.025	0.025			
Ta_2O_5										0.00310	0.00305	0.00313
TbO_2							3.357	3.345	3.300			
TiO_2	0.82	0.83	0.83	0.84	0.83	0.813	0.789	0.879	0.864			
UO_2							0.513	0.509	0.506			
Y_2O_3							0.017	0.017	0.016			
ZrO_2	0.44	0.41	0.41	0.23	0.629	0.233	0.243	0.250	0.247			
Total	94.05	94.21	94.51	92.20	92.97	91.71	72.18	70.18	71.08	0.04	0.04	0.04
Fe ²⁺ /Fe ³⁺												
Oxidation State	ZTM-1	ZTM-2	ZTM-3									
	0.154	0.151	0.113									

(a) Conducted on powder samples taken from three locations on Bar 1.

(b) EDXRF performed on solid glass Bar 2 in three locations.

TABLE 3.11. Combined Analytical Data and Statistical Test for ATM-10 Second Test Melt

Oxide	Target (a) 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	6.5	6.5112	ICP	5.850	6.428	6.595	7.150	Yes
AmO ₂	0.0068	0.00645	RC	0.0058	0.0064	0.0065	0.0078	Yes
B ₂ O ₃	9.26	9.20	ICP	8.797	9.059	9.334	9.723	Yes
BaO	0.05	0.046	XRF	0.030	0.043	0.050	0.070	Yes
CaO	0.56	0.588	XRF	0.448	0.518	0.657	0.672	Yes
CeO ₂	0.07	0.074	XRF	0.035	0.070	0.077	0.105	Yes
Cr ₂ O ₃	0.29	0.266	XRF	0.232	0.252	0.281	0.348	Yes
Cs ₂ O	0.07	0.063	XRF	0.049	0.060	0.066	0.091	Yes
Fe ₂ O ₃	11.31	11.71	XRF	10.518	11.625	11.803	12.102	Yes
K ₂ O	3.33	3.44	XRF	2.997	3.271	3.611	3.663	Yes
La ₂ O ₃	0.03	0.024	XRF	0.015	0.023	0.026	0.045	Yes
Li ₂ O	2.82	2.86	ICP	2.679	2.843	2.884	2.961	Yes
MgO	1.21	1.16	ICP	1.029	1.155	1.155	1.392	Yes
MnO ₂	1.22	1.268	XRF	1.037	1.248	1.287	1.403	Yes
Na ₂ O	10.17	10.58	ICP	9.153	10.276	10.891	11.187	Yes
Nd ₂ O ₃ (b)	0.17	0.16	ICP	0.126	0.138	0.183	0.214	Yes
NiO	0.32	0.300	XRF	0.272	0.289	0.311	0.368	Yes
NpO ₂	0.0208	0.0226	RC	0.0177	0.0226	0.0226	0.0239	Yes
P ₂ O ₅	2.33	2.330	XRF	1.864	2.264	2.395	2.796	Yes
PuO ₂	0.0085	0.0085	RC	0.0072	0.0074	0.0096	0.0098	Yes
RhO ₂	0.01	0.012	XRF	0.003	0.009	0.015	0.018	Yes
RuO ₂	0.07	0.064	XRF	0.035	0.061	0.067	0.105	Yes
SO ₃	0.27	0.271	XRF	0.095	0.098	0.443	0.446	Yes
SiO ₂	44.90	45.71	XRF	40.410	43.313	48.106	49.390	Yes
SrO	0.03	0.026	XRF	0.010	0.025	0.026	0.050	Yes
Tc ₂ O ₇	0.003	0.00309	RC	0.00225	0.00300	0.00319	0.00375	Yes
ThO ₂	3.34	3.334	XRF	2.839	3.259	3.409	3.841	Yes
TiO ₂ (c)	0.91	0.844	XRF	0.774	0.786	0.902	1.047	Yes
UO ₂	0.52	0.509	XRF	0.442	0.501	0.518	0.598	Yes
Y ₂ O ₃	0.02	0.017	XRF	0.005	0.016	0.018	0.035	Yes
ZrO ₂	0.27	0.247	XRF	0.189	0.238	0.255	0.351	Yes
Total	100.09	101.66						
Fe ²⁺ /Fe ⁺	0.10	0.139		0.02	N/A	N/A	0.18	Yes

(a) ATM-10 target composition Revision 2. See Table 3.9.

(b) Nd concentration is near detection limit of ICP analysis in this matrix. Nd₂O₃ data reported are based on direct ICP analysis of three samples, with a calibration factor applied for a bias correction based on independent analysis of six similar nonradioactive samples using ASTM Method C-146 for sample preparation. Confidence intervals shown include uncertainties for both the sample analyses and the calibration factor.

(c) TiO₂ standard deviation and confidence interval are calibrated from six XRF analyses: three from the previous ATM-10 first test melt. This method is justified because in both cases a) the actual physical content of TiO₂ in the starting material is identical; b) the analytical method is the same. The standard statistical method for calculating pooled standard deviation and the resulting confidence intervals was used.

ATM-10-2, and so on. All the bars appeared very uniform and glassy. A slight metallic sheen was observed on most bars. There were no indications of phase separation or surface porosity. The fifteen glass bars weighed a total of 1394 g.

4.0 CHARACTERIZATION

The characterization of ATM-10 began on September 19, 1986, and was completed January 2, 1987. The procedures and methods used for characterization of the ATM-10 production bars were described in a characterization plan. Documentation of the characterization is contained in PNL Laboratory Record Books. Supporting analytical data are retained in the PNL Records Center. The ATM-10 glass was characterized under the guidance of the MCC's Quality Assurance Plan.

The purpose of characterizing the ATM-10 material was to 1) determine if the ATM-10 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 3.9 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-10 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-10 glass meet the specifications. Within the limits of analytical precision and sampling, the ATM-10 glass is acceptably uniform. Except for small ($\sim 3 \mu\text{m}$), uniformly dispersed Fe, Cr, Mn, Ni crystals (probable spinel) and Ru inclusions ($\sim 0.5 \mu\text{m}$), which are typical of waste glasses, there were no indications of phase separation on the micron scale. Closed porosity ranging in diameter from 5 to $250 \mu\text{m}$ was found randomly distributed throughout the interior of all observed samples.

The ATM-10 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-10

Table 4.1 shows the sampling and analytical scheme that was used. A summary of the statistical design basis is given in Appendix D. 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 all fifteen bars. ICP analysis was performed in duplicate on powder samples taken from six bars. Radiochemistry and $\text{Fe}^{2+}/\text{Fe}^{3+}$ determinations were also performed on the powders taken from the six bars. SEM/optical microscopy, autoradiography, and x-ray diffraction were performed on samples taken from three different bars.

4.2 CHEMICAL ANALYSIS

Three separate techniques were required to determine the elemental composition of ATM-10 glass. All fifteen 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. Density determinations were performed on samples from six different bars. A U.S. Geological Survey (USGS) AGV-1 sample was used as a reference standard. Background radiation from the radionuclides contained in ATM-10 glass was measured and subtracted from the observed fluorescence spectra. Corrections for matrix absorptions, enhancement, and interference were applied. The results are shown in Table 4.2.

Aqueous solutions prepared from powder samples taken from six ATM-10 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.

TABLE 4.1. Sampling of the ATM-10 Production Bars for Characterization

ATM-10 Bar #	Bar Weight, g	Sampling Location ^(a)	Chemical Analysis				Microscopy		Other	
			EDXRF ^(b)	ICP ^(c)	RC	Fe ²⁺ /Fe ³⁺	SEM	Optical/ Autoradiography	XRD	Density
1	90.4	: end 1	run 3							
2	87.0	: middle	run 11	F12,F13	F13	F	ATM-10-2	ATM-10-2	ATM-10-2	ATM-10-2
3	85.5	: end 2	run 13							ATM-10-3
4	93.6	: middle	run 5	F2,F10	F2	A				
5	94.4	: middle	run 8							ATM-10-5
6	95.3	: end 1	run 12	F7,F1	F7	C				ATM-10-6
7	92.0	: end 2	run 7	F14,F3	F14	G	ATM-10-7	ATM-10-7	ATM-10-7	ATM-10-7
8	89.5	: middle	run 1							
9	94.9	: end 2	run 4							
10	94.1	: middle	run 10							
11	94.3	: middle	run 2	F8,F4	F8	D				
12	98.6	: end 2	run 9							
13	85.1	: end 2	run 15							
14	99.8	: middle	run 6							
15	99.9	: end 1	run 14	F5,F9	F5	B	ATM-10-15	ATM-10-15	ATM-10-15	ATM-10-15
Total	1394.4									

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

(b) Run number indicates random order in which the runs were analyzed by EDXRF.

(c) F6 and F11 were included as standards.

TABLE 4.2. Energy Dispersive X-Ray Fluorescence Analysis (EDXRF) of ATM-10 Production Bars 1 through 15

Oxide	Production Bar No.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Al ₂ O ₃															
AmO ₂															
B ₂ O ₃															
BaO	0.045	0.046	0.045	0.045	0.042	0.046	0.043	0.045	0.046	0.045	0.044	0.045	0.047	0.046	0.044
CaO	0.624	0.630	0.578	0.590	0.670	0.578	0.630	0.585	0.609	0.620	0.620	0.620	0.514	0.581	0.607
CeO ₂	0.073	0.074	0.070	0.072	0.074	0.073	0.071	0.071	0.071	0.072	0.072	0.073	0.071	0.071	0.069
Cr ₂ O ₃	0.256	0.251	0.259	0.267	0.253	0.240	0.266	0.257	0.244	0.251	0.251	0.240	0.266	0.232	0.265
Cs ₂ O	0.063	0.062	0.063	0.061	0.060	0.063	0.059	0.063	0.061	0.062	0.061	0.063	0.064	0.063	0.059
Fe ₂ O ₃	11.42	11.60	11.92	11.64	11.75	11.24	11.54	11.50	11.72	11.61	11.40	11.18	11.40	11.31	11.70
K ₂ O	3.156	3.361	3.397	3.385	3.264	3.264	3.373	3.337	3.289	3.445	3.337	3.060	3.469	3.517	3.505
La ₂ O ₃	0.026	0.024	0.026	0.027	0.021	0.025	0.024	0.026	0.025	0.025	0.025	0.025	0.024	0.026	0.024
Li ₂ O															
MgO															
MnO ₂	1.28	1.31	1.34	1.29	1.33	1.25	1.28	1.30	1.30	1.30	1.29	1.27	1.28	1.29	1.29
Na ₂ O															
Nd ₂ O ₃															
NiO	0.298	0.298	0.318	0.304	0.304	0.283	0.300	0.298	0.307	0.302	0.289	0.288	0.294	0.258	0.303
NpO ₂															
P ₂ O ₅	2.39	2.75	2.45	2.61	2.41	2.02	2.34	2.10	2.38	2.20	1.83	2.20	2.36	2.80	2.27
PuO ₂															
RhO ₂	0.010	0.011	0.011	0.011	0.014	0.009	0.015	0.011	0.012	0.011	0.014	0.012	0.010	0.011	0.014
RuO ₂	0.070	0.062	0.068	0.057	0.045	0.076	0.041	0.070	0.063	0.067	0.052	0.057	0.067	0.068	0.044
SO ₃	0.247	0.277	0.474	0.277	0.395	0.407	0.280	0.312	0.295	0.340	0.325	0.375	0.110	0.317	0.182
SiO ₂	45.4	44.9	41.5	45.4	45.1	48.6	44.7	44.5	46.6	45.6	45.4	43.9	50.1	50.9	45.1
SrO	0.026	0.025	0.027	0.025	0.025	0.024	0.026	0.026	0.023	0.024	0.025	0.026	0.025	0.026	0.025
Tc ₂ O ₇															
ThO ₂	3.24	3.25	3.37	3.28	3.30	3.29	3.28	3.30	3.32	3.27	3.30	3.24	3.28	3.32	3.31
TiO ₂	0.853	0.841	0.871	0.831	0.893	0.863	0.881	0.812	0.886	0.834	0.837	0.846	0.879	0.858	0.889
UO ₂	0.479	0.518	0.535	0.525	0.523	0.529	0.529	0.558	0.528	0.524	0.548	0.517	0.528	0.530	0.537
Y ₂ O ₃	0.018	0.018	0.017	0.017	0.017	0.016	0.017	0.017	0.015	0.017	0.017	0.016	0.015	0.016	0.018
ZrO ₂	0.246	0.243	0.246	0.243	0.244	0.254	0.244	0.249	0.238	0.249	0.254	0.242	0.253	0.253	0.254
Total	70.2	70.6	67.6	70.9	70.8	73.1	69.9	69.4	72.1	70.8	69.9	68.2	75.0	76.5	70.5

The resulting salt fusions were dissolved in water, acidified, and then analyzed using a Bausch and Lomb ARL-3580 ICP unit in which the plasma torch is located inside a glove box. The ICP results are listed in Table 4.3.

Portions of the K/Ni fusions mentioned above (one sample from each of the six bars) were also used for radiochemical (RC) analysis. After further solution treatment to concentrate and isolate the radioisotopes, Am, Np, and Pu concentrations were determined by alpha energy analysis (counting) techniques. Tc concentrations were determined by beta counting. Ludlum/Tracor Northern detectors and counting systems were used. The RC results are presented in Table 4.4.

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 3.9. The tolerance intervals provide a predicted range of possible compositions for individual samples (or specimens) from this lot of ATM-10 glass.

For each element in the ATM-10 glass, the analytical results were used to construct a 95% confidence interval for the overall true mean wt% oxide in the ATM-10 production bars. The determination and justification of the statistical estimation methods that were used to construct the confidence intervals are discussed in Appendix E.

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-10 glass is between 6.625 and 6.668 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-10 production

(a) This corresponds to "Target Composition, Revision 2" in Table 3.9.

TABLE 4.3. Inductively Coupled Plasma Spectroscopy (ICP) of ATM-10 Production Bar Samples F1 through F14

T4.3

Oxide	Production Bar Sample (ATM-M-10 Bar Sample)																							
	F1 (6b)		F2 (4a)		F3 (7b)		F4 (11b)		F5 (15a)		F7 (6a)		F8 (11a)		F9 (15b)		F10 (4b)		F12 (2b)		F13 (2a)		F14 (7a)	
	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI	Ma/Zr	K/NI
Al ₂ O ₃	6.62	6.62	6.68	6.63	6.79	6.57	6.64	6.63	6.67	6.58	6.75	6.59	6.90	6.56	6.62	6.60	6.70	6.55	6.66	6.55	6.82	6.52	6.80	6.48
As ₂ O ₃																								
B ₂ O ₃	9.21	9.18	9.11	9.09	9.38	9.21	9.18	9.18	9.19	9.08	9.42	9.05	9.45	9.08	8.86	9.17	9.11	9.09	8.94	9.22	9.11	9.15	9.38	9.13
BaO	0.05	0.06	0.04	0.06	0.05	0.06	0.04	0.06	0.05	0.06	0.05	0.06	0.05	0.06	0.04	0.06	0.04	0.06	0.05	0.06	0.04	0.06	0.05	0.06
CaO		0.77		0.76		0.81		0.83		0.76		0.78		0.81		0.78		0.76		0.78		0.83		0.80
CeO ₂																								
Cr ₂ O ₃		0.30	0.17	0.25	0.17	0.30	0.16	0.25	0.15	0.25	0.14	0.25	0.15	0.25	0.14	0.25	0.19	0.24	0.13	0.25	0.14	0.23	0.17	0.24
Cs ₂ O																								
Fe ₂ O ₃	10.5	10.9	10.6	10.6	10.8	10.9	10.6	10.8	10.6	10.6	10.8	10.6	10.8	10.5	10.5	10.5	10.6	10.4	10.6	10.5	10.8	10.5	10.9	10.4
K ₂ O	3.19		2.90		3.46		3.02		2.98		3.43		3.45		3.00		3.19		2.98		3.15		3.45	
La ₂ O ₃																								
Li ₂ O	2.89	2.87	2.91	2.88	2.93	2.90	2.91	2.90	2.91	2.87	2.93	2.84	2.96	2.90	2.77	2.88	2.88	2.85	2.79	2.87	2.81	2.90	2.92	2.86
MgO	1.12	1.14	1.13	1.14	1.16	1.16	1.13	1.17	1.13	1.14	1.43	1.15	1.16	1.13	1.11	1.13	1.15	1.12	1.63	1.14	1.16	1.15	1.16	1.13
MnO ₂	1.15	1.19	1.16	1.18	1.19	1.19	1.16	1.19	1.17	1.17	1.18	1.18	1.19	1.16	1.13	1.16	1.16	1.14	1.15	1.17	1.16	1.16	1.19	1.16
Na ₂ O		10.4		10.5		10.6		10.9		10.6		10.4		10.7		10.5		10.4		10.4		10.5		10.5
Nd ₂ O ₃ (a)				0.169						0.166		0.170		0.166					0.169					0.171
NiO	0.26		0.27		0.29		0.27		0.27		0.27		0.29		0.26		0.28		0.26		0.29		0.30	
NpO ₂																								
P ₂ O ₅																								
PuO ₂																								
RhO ₂																								
RuO ₂	0.14		0.12		0.17		0.12		0.12		0.15		0.17		0.14		0.14		0.13		0.18		0.17	
SO ₃																								
SiO ₂	45.2	45.2	45.3	45.2	46.0	44.9	45.8	45.2	44.9	45.0	46.1	44.2	46.5	44.1	44.8	44.4	45.2	43.7	44.6	44.1	44.6	44.2	45.9	43.9
SrO	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.03
Tc ₂ O ₇																								
ThO ₂																								
TiO ₂	0.77	0.89	0.93	0.89	0.77	0.89	0.79	0.91	0.80	0.96	0.80	0.87	0.81	1.23	0.79	0.91	0.82	0.87	0.77	0.88	0.80	0.96	0.78	0.86
UO ₂																								
Y ₂ O ₃																								
ZrO ₂		0.52		0.51		0.52		0.52		0.53		0.52		0.63		0.51		0.50		0.52		0.54		0.50

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

TABLE 4.4. Radiochemical Analysis of ATM-10 Production Bars

Oxide	Sample (Bar)					
	F2 (ATM-10-4) wt%	F5 (ATM-10-15) wt%	F7 (ATM-10-6) wt%	F8 (ATM-10-11) wt%	F13 (ATM-10-2) wt%	F14 (ATM-10-7) wt%
AmO ₂	0.00656	0.00646	0.00640	0.00634	0.00642	0.00640
PuO ₂	0.00889	0.00738	0.00823	0.00778	0.00839	0.00789
NpO ₂	0.02054	0.02111	0.02009	0.02077	0.02077	0.02122
Tc ₂ O ₇	<u>0.00310</u>	<u>0.00316</u>	<u>0.00307</u>	<u>0.00313</u>	<u>0.00307</u>	<u>0.00329</u>
Total	0.0391	0.0381	0.0378	0.0380	0.0387	0.0388

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 eight 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 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-10 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-10 characterization data. If the sample averages and confidence intervals

TABLE 4.5. Comparison of 95% Confidence Intervals with the Acceptable Error Ranges of Elements in ATM-10 Glass^(a)

Oxide	Method	Sample Mean wt%	Sample Std. Dev.	95% Confidence Interval	Target, wt%	Allowable Error Range	Question ^(b)		
							1	2	3
Al ₂ O ₃	ICP	6.64646	0.020889	(6.62454, 6.66838)	6.50	(5.85 , 7.15)	No	Yes	Yes
AmO ₂	RC	0.00643	7.295EE-5	(0.00635, 0.00651)	0.0068	(0.00578, 0.00782)	No	Yes	Yes
B ₂ O ₃	ICP	9.16570	0.08174	(9.07990, 9.25150)	9.26	(8.897 , 9.723)	No	Yes	Yes
BaO	XRF	0.04497	0.0013119	(0.04424, 0.04569)	0.05	(0.03 , 0.07)	No	Yes	Yes
CaO	XRF	0.60362	0.353886	(0.58402, 0.62322)	0.56	(0.448 , 0.672)	No	Yes	Yes
CeO ₂	XRF	0.07162	0.001274	(0.07091, 0.07232)	0.07	(0.035 , 0.105)	No	Yes	Yes
Cr ₂ O ₃	XRF	0.25324	0.107042	(0.24731, 0.25917)	0.29	(0.232 , 0.348)	No	Yes	Yes
CsO ₂	XRF	0.06179	0.00154	(0.06094, 0.06265)	0.07	(0.049 , 0.091)	No	Yes	Yes
Fe ₂ O ₃	XRF	11.52720	0.20651	(11.4128, 11.6416)	11.31	(10.5183, 12.1017)	No	Yes	Yes
K ₂ O	XRF	3.34397	0.125252	(3.27460, 3.41334)	3.33	(2.997 , 3.663)	Yes	Yes	Yes
La ₂ O ₃	XRF	0.02500	0.001984	(0.02426, 0.02575)	0.03	(0.015 , 0.045)	No	Yes	Yes
Li ₂ O	ICP	2.88062	0.02812	(2.85111, 2.91014)	2.82	(2.679 , 2.961)	No	Yes	Yes
MgO	ICP	1.15345	0.02963	(1.12235, 1.18455)	1.21	(1.0285 , 1.391)	No	Yes	Yes
MnO ₂	XRF	1.29297	0.0218983	(1.28084, 1.30510)	1.22	(1.037 , 1.403)	No	Yes	Yes
Na ₂ O	ICP	10.52518	0.14978	(10.3680, 10.6824)	10.17	(9.153 , 11.1870)	No	Yes	Yes
Nd ₂ O ₃	ICP	0.16802	0.002278	(0.16563, 0.17041)	0.17	(0.1258 , 0.2142)	Yes	Yes	Yes
NiO	XRF	0.29618	0.013549	(0.28867, 0.30368)	0.32	(0.272 , 0.368)	No	Yes	Yes
NpO ₂	RC	0.02075	4.087EE-4	(0.02032, 0.02118)	0.0208	(0.01768, 0.02392)	Yes	Yes	Yes
P ₂ O ₅	XRF	2.33995	0.25842	(2.19683, 2.48307)	2.33	(1.864 , 2.796)	Yes	Yes	Yes
PuO ₂	RC	0.00809	5.269EE-4	(0.00754, 0.00865)	0.0085	(0.00723, 0.00978)	Yes	Yes	Yes
RhO ₂	XRF	0.01176	0.001079	(0.01077, 0.01275)	0.01	(0.0025 , 0.0175)	No	Yes	Yes
RuO ₂	XRF	0.06050	0.0108053	(0.05452, 0.06649)	0.07	(0.035 , 0.105)	No	Yes	Yes
SO ₃	XRF	0.30748	0.0896172	(0.25784, 0.35711)	0.27	(0.0945 , 0.4455)	Yes	Yes	Yes
SiO ₂	XRF	45.83900	2.39112	(44.5147, 47.1633)	44.90	(40.41 , 49.39)	Yes	Yes	Yes
SrO	XRF	0.02513	9.564EE-4	(0.02460, 0.02566)	0.03	(0.0099 , 0.0501)	No	Yes	Yes
Tc ₂ O ₇	RC	0.00314	8.265EE-5	(0.00305, 0.00322)	0.003	(0.00225, 0.00375)	No	Yes	Yes
ThO ₂	XRF	3.29004	0.033554	(3.27146, 3.30863)	3.34	(2.839 , 3.841)	No	Yes	Yes
TiO ₂	XRF	0.85818	0.02446	(0.84463, 0.87173)	0.91	(0.7735 , 1.0465)	No	Yes	Yes
UO ₂	XRF	0.52713	0.017133	(0.51764, 0.53662)	0.52	(0.442 , 0.598)	Yes	Yes	Yes
Y ₂ O ₃	XRF	0.01681	8.222EE-4	(0.01635, 0.01726)	0.02	(0.005 , 0.035)	No	Yes	Yes
ZrO ₂	XRF	0.24737	0.0051276	(0.24453, 0.25021)	0.27	(0.189 , 0.351)	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 smaller than the allowable error?

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

are to be interpreted as representing the probable mean composition of the ATM-10 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 conclusion about the composition of the ATM-10 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 E.

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 6.557 and 6.736 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 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-10 production bars meets the client's stated requirements. Within the limits of analytical precision and sampling, the probable variation between ATM-10 bars is also acceptable.

TABLE 4.6. Tolerance Intervals for ATM-10 Components

Oxide	75/75 Tol. Int.		90/90 Tol. Int.		95/90 Tol. Int.		95/95 Tol. Int.	
Al ₂ O ₃	6.60835	6.68457	6.57349	6.71943	6.55718	6.73574	6.54039	6.75253
AmO ₂	0.00629	0.00657	0.00616	0.00670	0.00610	0.00676	0.00604	0.00682
B ₂ O ₃	9.01651	9.31489	8.88008	9.45132	8.81624	9.51516	8.75052	9.58088
BaO	0.04313	0.04681	0.04197	0.04797	0.04170	0.04824	0.04108	0.04886
CaO	0.55425	0.65299	0.52300	0.68424	0.51585	0.69139	0.49908	0.70816
CeO ₂	0.06983	0.07341	0.06870	0.07454	0.06844	0.07480	0.06783	0.07541
Cr ₂ O ₃	0.23830	0.26818	0.22885	0.27763	0.22669	0.27979	0.22161	0.28487
Cs ₂ O	0.05965	0.06393	0.05829	0.06529	0.05798	0.06560	0.05726	0.06632
Fe ₂ O ₃	11.23905	11.81535	11.05666	11.99774	11.01493	12.03947	10.91702	12.13737
K ₂ O	3.16924	3.51870	3.05864	3.62930	3.03334	3.65460	2.97397	3.71397
La ₂ O ₃	0.02314	0.02686	0.02196	0.02804	0.02169	0.02831	0.02105	0.02895
Li ₂ O	2.82931	2.93193	2.78239	2.97885	2.76043	3.00081	2.73782	3.02342
MgO	1.09937	1.20753	1.04992	1.25698	1.02678	1.28012	1.00296	1.30394
MnO ₂	1.26242	1.32352	1.24308	1.34286	1.23865	1.34729	1.22827	1.35767
Na ₂ O	10.25188	10.79848	10.00195	11.04841	9.88499	11.16537	9.76459	11.28577
Nd ₂ O ₃	0.16386	0.17218	0.16006	0.17598	0.15829	0.17775	0.15645	0.17959
NiO	0.27726	0.31510	0.26529	0.32707	0.26255	0.32981	0.25612	0.33624
NpO ₂	0.02000	0.02150	0.01932	0.02218	0.01900	0.02250	0.01867	0.02283
P ₂ O ₅	1.97946	2.70044	1.75128	2.92862	1.69908	2.98082	1.57659	3.10331
PuO ₂	0.00713	0.00905	0.00626	0.00992	0.00585	0.01033	0.00543	0.01075
RhO ₂	0.00927	0.01425	0.00769	0.01583	0.00733	0.01619	0.00648	0.01704
RuO ₂	0.04544	0.07556	0.03590	0.08510	0.03372	0.08728	0.02860	0.09240
SO ₃	0.18245	0.43251	0.10330	0.51166	0.08520	0.52976	0.04271	0.57225
SiO ₂	42.50336	49.17464	40.39199	51.28601	39.90898	51.76902	38.77559	52.90242
SrO	0.02380	0.02646	0.02295	0.02731	0.02276	0.02750	0.02230	0.02796
Tc ₂ O ₇	0.00298	0.00330	0.00284	0.00344	0.00277	0.00351	0.00270	0.00358
ThO ₂	3.24324	3.33684	3.21362	3.36646	3.20684	3.37324	3.19094	3.38914
TiO ₂	0.82405	0.89231	0.80245	0.91391	0.79751	0.91885	0.78591	0.93045
UO ₂	0.50323	0.55103	0.48810	0.56616	0.48464	0.56962	0.47651	0.57775
Y ₂ O ₃	0.01565	0.01797	0.01492	0.01870	0.01475	0.01887	0.01436	0.01926
ZrO ₂	0.24022	0.25452	0.23569	0.25905	0.23465	0.26009	0.23222	0.26252

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-10 production bars were determined. A solution chemistry, spectrophotometric technique using 1,10-phenanthroline to determine reduced and total iron in glass (Jones, Jansheski, and Goldman 1981) was used. The results are shown in Table 4.7. Notice that all six analyses are well within the client's specification of 0.10 ± 0.08 . The mean value was 0.12.

4.5 MICROSCOPY AND AUTORADIOGRAPHY

Optical and scanning electron microscopy were used to investigate the microstructure of the ATM-10 glass.

Reflected-light 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. An autoradiograph of the same sample area and magnification is shown in Figure 4.2. Notice the voids that range in size from ~5 to 250 μm . It is apparent that these voids are generally

TABLE 4.7. Oxidation State of ATM-10 Glass as Determined by Spectrophotometry for Total and Reduced Iron

<u>ATM-10 Bar</u>	<u>$\text{Fe}^{2+}/\text{Fe}^{3+}$</u>
ATM-10-2	0.114
ATM-10-4	0.139
ATM-10-6	0.111
ATM-10-7	0.118
ATM-10-11	0.105
ATM-10-15	<u>0.110</u>
Mean =	0.116
Sample Std. Dev. =	0.012
Target =	0.10
	(± 0.08)

FIGURE 4.1. Photograph of Cross Section of ATM-10 Bar 7. The closed porosity, ranging in diameter from 5 to 250 μm , is estimated to be 0.5 vol% of the glass matrix.

FIGURE 4.2. Autoradiograph of Cross Section of ATM-10 Bar 7 (same region shown in Figure 4.1). Dark regions represent regions containing radioactive material. Even shading indicates even distribution of radioactive material (primarily sensitive to ^{241}Am).

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 0.5% of the sample matrix.^(a) These voids are shown in greater detail in Figure 4.2. The bright regions seen in Figures 4.3 and 4.4 are cubic features found individually and in clusters throughout all the viewed samples.

Autoradiography was also performed on these polished sections. An autoradiograph taken from the same sample area and magnification as seen in Figure 4.1 is presented in Figure 4.2. Dark regions represent areas of radioactivity. The uniform shading in Figure 4.2 suggests the radioisotopes are uniformly distributed. It should be noted, however, that the radiographs are most efficient at representing ^{241}Am distribution (~40 times for ^{239}Pu and ~60,000 times ^{238}U , for example).

Fractured samples taken from three bars were observed by SEM. As shown in Figure 4.5, voids were apparent in these samples as well. Higher magnification revealed the cubic features observed by optical microscopy (compare Figures 4.4 and 4.6). Energy dispersive x-ray spectra (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 0.5 μm regions associated with clusters of the larger spinel crystals were identified by EDXS as Ru inclusions of unknown oxidation state. As shown in Figure 4.7, comparison of EDXS taken from 100,000- μm^2 matrix regions and 4- μm^2 regions appeared identical. This similarity suggests that the glass matrix is homogeneous on a micron scale. In Figure 4.8, EDXS spectra of cubic crystals and a Ru inclusion are shown.

Observation by SEM and optical microscopy indicated the ATM-10 glass is generally uniform in microstructure.

4.6 X-RAY DIFFRACTION

X-ray diffraction (XRD) analysis was performed on powder samples taken from three glass bars. A General Electric XRD-5 goniometer and copper target

(a) See Appendix F for calculations.

FIGURE 4.3. Photomicrograph of Cross Section of ATM-10 Bar 7. Dark regions are pores or voids ranging from 5 to 30 μm in diameter. Bright dots are Fe, Cr, Mn, Ni cubic crystals (probably spinel crystals), which are about 3 μm across.

FIGURE 4.4. Photomicrograph of Cross Section of ATM-10 Bar 7. Individual and clustered cubic crystals (probably spinel crystals) shown in detail.

FIGURE 4.5. Fractured Sample of ATM-10 Bar 7 as Seen by Scanning Electron Microscopy (SEM). Notice the pores ranging from 30 to 250 μm in diameter. The square indicates the $\sim 100,000 \mu\text{m}^2$ area, region 1, which was analyzed by EDXS (see Figure 4.7).

x-ray tube located in a glove box were used. No XRD peaks characteristic of crystalline material could be detected. Subsequent tests were made using the same ATM-10 powder samples spiked with magnetite (Fe_3O_4 having a spinel structure). The spiked samples were run under operating conditions identical to those used for the original ATM-10 glasses. As little as 2 wt% added spinel resulted in a detectable diffraction peak. This observation implies that there is less than 2 wt% spinel (and very little of any other type of crystalline material) contained in the ATM-10 production glass.

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-10 density results. The mean bulk density for the six samples was 2.707 g/cm^3 . Small ($\pm 0.07\%$ from mean) differences in bulk density were

FIGURE 4.6. Fractured Sample of ATM-10 Bar 7 by Scanning Electron Microscopy (SEM). The white region is a cluster of 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. Located near the center of the cluster is a $\sim 0.5 \mu\text{m}$ diameter Ru inclusion. The $\sim 4 \mu\text{m}^2$ matrix region #2, which was used for EDXS analysis (see Figure 4.7), is also indicated.

observed among the samples. Bulk density is a function of the total volume of a solid sample (including voids) and the sample mass. Because the differences in observed densities were small, it is probable that the differences among the void volumes of the samples are also small.

FIGURE 4.7. Energy Dispersive X-Ray Spectra (EDXS) Collected from Fractured Sample of ATM-10 Bar 7 (see Figures 4.5 and 4.6 for regions). The similarity between EDXS from regions 1 and 2 indicates homogeneity of the glass matrix on the micron scale.

FIGURE 4.8. Energy Dispersive X-Ray Spectra (EDXS) of Cubic Crystals and Ruthenium Inclusion Observed on a Fractured Surface of ATM-10 Bar 7 (see Figure 4.6)

TABLE 4.8. Bulk Density Determination of ATM-10 Glass by
Water Immersion Technique

Sample	Measurement #				Mean	St. Dev.	% Dev. from Mean
	1	2	3	4			
ATM-10-2	2.7086	2.7086	2.7091	2.7083	2.7086	0.0003	0.074
ATM-10-3	2.7066				2.7066	N/A	-0.000
ATM-10-5	2.7064				2.7064	N/A	-0.010
ATM-10-6	2.7065				2.7065	N/A	-0.004
ATM-10-7	2.7050	2.7052	2.7054	2.7050	2.7051	0.0002	-0.056
ATM-10-15	2.7062	2.7071	2.7067	2.7062	<u>2.7065</u>	0.0004	-0.004

Overall Mean = 2.707

5.0 REFERENCES

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APPENDIX A

BASE CHEMICALS USED TO PRODUCE ATM-10 FRIT

APPENDIX A

BASE CHEMICALS USED TO PRODUCE ATM-10 FRIT

The following represents an inventory of the base chemicals that were ordered for ATM-10 glass fabrication on PNL 90 M5364 and received at PNL on 12/16/85.

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

APPENDIX B

RADIOISOTOPE DOPING OF ATM-10 FRIT

Date June 20, 1986
To Gary Maupin
From Jack Ryan *Jack Ryan*
Subject RADIOISOTOPE DOPING OF MCC GLASS FRIT ATM-10

The subject glass frit was to be doped with the following radioisotopes: ^{99}Tc , ^{232}Th , ^{238}U , ^{237}Np , ^{239}Pu , and ^{241}Am . The ^{99}Tc was obtained as NH_4TcO_4 from ORNL, Isotope Sales as Isotope Order No. 37-1174 shipped August 23, 1984. It was specified to be 52.3% ^{99}Tc and to contain $\text{Na}=40.2 \mu\text{g/g}$, $\text{Re}=120 \mu\text{g/g}$, and $\text{Au}=0.15 \mu\text{g/g}$. It was used as received. ^{232}Th was obtained from Tennessee Nuclear Specialties as crystalline $\text{Th}(\text{NO}_3)_4 \cdot X \text{H}_2\text{O}$ ($X \sim 5$). It was identified as Sample # PO No. 22 151AR. It has been on site for about eight years. It was used directly as received. The ^{238}U was depleted uranium as UO_2 supplied for this use by John Wald. The ^{237}Np was as NpO_2 obtained in the past for use in glass preparation and has been used in prior glasses. John has as much or more information on this as I do.^(a) The ^{239}Pu is old weapons grade material (isotopic analysis provided to you) of my stock. It has been purified by anion exchange in nitric acid and as such should be very pure except for ^{241}Am which has grown in over the few years since last purification. The ^{241}Am was as AmO_2 purchased from ORNL Isotope Sales (Isotope Order No. 39-0258 shipped Jan. 24, 1986). It was used as received.

The ^{99}Tc solution was prepared from the above source material by dissolving 76.8 mg of the ammonium pertechnetate in 0.05 M HNO_3 containing 0.10 mL of 30% H_2O_2 per 25 mL. The solution was made up to 25.00 ± 0.05 mL. An 0.150 mL sample of this solution was taken and diluted into 5.00 mL to give a dilution factor of $\frac{5.15}{0.150} = 34.33$ and this solution, designated A10-TC, was submitted to Clyde Leaf for analysis. The remaining 24.85 mL of the Tc solution was used for frit doping.

(a) The source of the depleted uranium was from on-hand stock of UO_2 powder (0.15% ^{235}U). The Neptunium used in the previous ATM-9 and ATM-11 glasses was from ORNL Isotope Sales batch number 112HB-11.

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The ^{232}Th solution was made on 5-2-86 by dissolving 246.0 g of the $\text{Th}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ (X~5) described above and making up to 250.00 ± 0.08 mL with 0.5 M HNO_3 . Using a tared micropipette, a 1.000 mL sample was taken. The 1.00 mL sample weight was 1.672 g resulting in a density of 1.672 g/mL. This was drained into a tared sample vial and 1.648 g of sample was delivered to Frank Hara as sample number A10-TH, along with sample and tare weights and density. The remaining 249.00 mL was saved for doping. A 4.35 mL aliquot of this was removed, and the remaining 244.65 mL was used for frit doping.

The depleted uranium solution was made up on 5-1-86 by dissolving 16.80 g of the above UO_2 . The UO_2 was dissolved in 1 M HNO_3 by addition of increments of 30% H_2O_2 which rapidly converts dark brown UO_2 to light yellow $\text{UO}_3 \cdot \text{XH}_2\text{O}$ or uranyl peroxide. The material was heated to decompose peroxide and a few small increments of conc. HNO_3 were added to dissolve remaining $\text{UO}_3 \cdot \text{XH}_2\text{O}$ since acid is consumed by the reaction:

The final acidity was ~1 M HNO_3 . The solution was made up to 100.00 ± 0.08 mL. A 2.00 mL sample of this material labeled A10-U was supplied to Merrill Burt for U analysis. The density of this solution was determined by weighing in a tared 50.00 ± 0.05 mL flask to be 1.2367 g/mL, and you have the lab notes on this. The 98.00 mL of solution was used for frit doping.

The Np solution was made up by weighing 0.6708 g of the above NpO_2 and heating this gently with 1.6 mL of 15.8 M HNO_3 plus 0.3 ± 0.2 mL of 2.7 M HF on 5-6-86. The resulting crystalline mass was dissolved and made up to 25.00 ± 0.03 mL on 5-7-86. An aliquot of 0.150 mL was diluted to

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10.00 mL to give a dilution factor of $\frac{10.150}{0.150} = 67.67$, and this solution, designated A10-Np, was submitted to Clyde Leaf for analysis. The remaining 24.85 mL of the Np solution was used for frit doping.

The ^{239}Pu solution was made up from a stock solution which had been purified several years before by anion exchange in nitric acid and which had analyzed as 29.1 g/L. An aliquot of 6.90 mL was diluted to 25.00 ± 0.03 mL with 0.3 M HNO_3 on 5-7-86. An 0.100 mL aliquot of this was diluted into 100.0 mL giving a dilution factor of $100.1/0.1 = 1.001 \times 10^3$, and this sample, designated A10-PU, was submitted to Clyde Leaf for analysis. An additional 1.60 mL was removed from the Pu solution, and the remaining 23.30 mL was used for frit doping.

The ^{241}Am was prepared on 5-8-86 by weighing 0.2205 g of the above described AmO_2 and dissolving by heating in conc. HNO_3 containing a trace of fluoride. It was taken to incipient dryness and then taken up in 0.2 M HNO_3 . An aliquot of 0.150 mL was diluted into 100 mL and 0.10 mL of this dilution was diluted into 10.00 mL to give a dilution factor of $\frac{100.15}{0.150} \times \frac{10.1}{0.1} = 6.743 \times 10^4$ for sample A10-AM which was submitted to Clyde Leaf. The remaining 24.85 mL of the Am solution was used for frit doping.

The glass frit was doped by combining all of the actinide (and Tc) solutions above along with 0.2 M HNO_3 rinses of all the flasks in an approximately 3.5 L polyethylene beaker (made from 1 gal. poly. bottle) and bringing up to 750 mL with water. The glass frit was then added (the entire weighed amount delivered to me). The mixture was stirred thoroughly and was dried in two batches in a stainless steel beaker in a pot furnace controlled at 200°C. Each batch was dried overnight to give total drying times of about 18-22 hours each. The mix was stirred frequently through the slurry step and virtually continuously through the "heavy mud" through "crumb" stage. Despite this, some hard caking

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occurred in the bottom of each batch, and this was broken loose and crushed with the 1/2-inch stainless steel pipe stirring bar. You have the lab notes for this portion of the work. The two batches were combined and mixed in the one gallon can in which the frit was delivered to you.

My calculations based on the desired percentages for 3.00 kg of glass and the analytical results and dilution factors give the following:

<u>Component Form</u>	<u>Planned Amount</u>	<u>Analyzed Amount Added to Frit</u>
Tc	40.2 mg	40.2 mg
UO ₂	16.8 g	16.70 g
Th	94.65 g	97.37 g
NpO ₂	672 mg	638.6 mg
Pu	201.1 g	201.6 mg
AmO ₂	219 mg	210.6 mg

JLR:lm

Pacific Northwest Laboratories

Project Number _____

Internal Distribution

Date September 19, 1986

To Gary Maupin

From Jack Ryan

Subject AMMONIUM PERTECHNETATE SOLUTION(a)

The $\text{NH}_4 \text{TcO}_4$ solution was prepared by weighing 1.00 ± 0.01 g and dissolving this directly into 500 mL of 0.05 M HNO_3 which had been made 0.1% H_2O_2 by dilution of reagent grade 30% H_2O_2 .

(a) Tc solution used in Sections 3.10 and 3.11 of this report.

APPENDIX C

OXIDATION STATE OF ATM-10 INITIAL TEST BATCH

APPENDIX C

OXIDATION STATE OF ATM-10 INITIAL TEST BATCH

The initial test batch of ATM-10 was found to have an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.1 before graphite was added. The ATM-10 frit, however, was found to be highly oxidized ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.0). Because these two materials were made from the same starting chemicals by essentially the same procedure, it was not immediately clear why they differed in oxidation state. A review of the laboratory record books indicated that the intense smell of ammonium had been detected during the V-blending of the large frit batch. No ammonium was detected during blending of the smaller initial test batch. Also, a 135.3-g loss was observed during blending of the frit batch, but only a 6.6-g loss was observed in the test batch. The difference in weight loss can be attributed to NH_3 and water loss from the ammonium phosphate. The size of the batches appears to be important. The larger frit batch generated and contained sufficient heat during blending to result in the dissociation of the ammonium phosphate. The smaller test batch did not.

The ammonium phosphate that was used in the frit batch dissociated prior to melting (i.e., in the V-blender). In the test batch, however, the ammonium was not liberated prior to melting of the glass. The NH_3 that was liberated during melting of the test batch may have acted as a reductant to the glass. This action would explain the difference in oxidation state between the two melts.

Because the test batch material was not representative of the oxidation state of the frit, the oxidation test melts were performed on actual frit material.

APPENDIX D

STATISTICAL DESIGN FOR SAMPLING OF
ATM-10 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 E

STATISTICAL ANALYSIS FOR THE ATM-10 CHARACTERIZATION

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Compositional analysis of the ATM-10 glass product was performed as outlined in the formal characterization plan. The analytical methods included x-ray fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP), and radiochemistry (RC). The details of the sampling, specimen preparation, and compositional analysis are described in the formal ATM-10 characterization report. Therefore, the only details repeated here are those 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-10 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-10 glass product, 2) construct a 95% confidence interval (CI) for the true batch mean of each component, and 3) use these CIs 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 that indicate the expected range of composition of individual samples (or specimens) taken from this batch of ATM-10 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 proper 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 and RC 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 discussed below.

The analysis of variance results indicated that none of the components has a significant position effect. However, some caution must be exercised in interpreting this conclusion. Because multiple locations were not analyzed on any of the bars, the position effect referred to above would be a compositional "trend" over each bar that would be the same for every bar. The analysis of variance results indicate only that this common "trend" is not significant and can be ignored. It could be, however, that a different compositional "trend" is present for each bar, in which case its contribution to the overall variability can not be separately estimated from these data.

Therefore, for the purpose of computing the sample average and its variance, the position was ignored. The XRF and RC 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 in exactly the same manner as for the RC analysis. 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 1) test for the position effect discussed above and 2) test for 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 which 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 available 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. As previously noted, none of the components had a significant position effect. In addition, B, Li, and Mg had no significant fusion effect. However, Al did have a significant fusion effect. Specifically, the average of the Na fusion results for Al is significantly larger than the average of the K fusion results. This fusion effect for Al was dealt with as described in the subsequent discussion. Since, of course, only K fusion results were reported for Na, there was no test for a fusion effect.

For the purpose of constructing confidence intervals from the ICP data, the analysis of variance results indicate that the difference in the fusion results can be ignored for all elements except Al. Therefore, the data for B, Li, and Mg were reduced by averaging the two fusion results for each material sample. The Al data were separated into two data sets, one containing the Na fusion results and one containing the K fusion results.

Then, because position can be ignored, the variability in the data for B, Li, Mg, Na, and both sets of Al data 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.

The two sets of Al data, from the Na and K fusions, were used to construct two 95% confidence intervals for the overall true mean wt% oxide. Because both confidence intervals were well within the specified allowable error range, it was decided that the Na and K fusion results for Al should be averaged. Since 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 for B, Li, Mg, and Na. That is, the correct approach for combining the Al 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 $n=15$. The RC results for each component were treated as a simple random sample of size $n=6$. 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

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

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, $t(14, 0.975) = 2.145$. For the RC and 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. 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-10 characterization data. Therefore, if the sample averages and confidence intervals are to be interpreted as representing the probable mean composition of the ATM-10 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-10 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

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

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 (1987) 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-10 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
15	1.395	2.278	2.480	2.954

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 Al_2O_3 . We can be 95% confident that 90% of the individual samples (or specimens) obtained from this batch of glass will have wt% Al_2O_3 between 6.557 and 6.736.

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 and RC 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 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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APPENDIX F

CALCULATION OF CLOSED POROSITY VOLUME FRACTION IN ATM-10 BAR 15 GLASS MATRIX

APPENDIX F

CALCULATION OF CLOSED POROSITY VOLUME FRACTION IN ATM-10 BAR 15 GLASS MATRIX

ATM-10-15 Micrographs 86890 F&G ~10X Magnification			ATM-10-15 Micrograph 86890 B ~100X Magnification		
Void #	Diameter, μm	Area, μm^2	Void #	Diameter, μm	Area, μm^2
1	125	12272	1-28	~5	550
2	75	4418	29	30	707
3	75	4418	30	10	79
4	125	12272	31	10	79
5	75	4418	32	12	113
6	100	7854	33	12	113
7	100	7854	34	12	113
8	75	4418	35	8	50
9	75	4418	36	15	177
10	100	7854	37	8	50
11	75	4418	38	10	79
12	100	7854	39	8	50
13	50	1963	40	8	50
14	75	4418	41	8	50
15	100	7854	42	8	50
16	100	7854	43	12	113
17	175	24053	44	8	50
18	35	962	45	12	113
19	50	1963	46	8	50
20	100	7854	47	8	50
21	50	1963	48	12	113
22	125	12272			
23	75	4418			
24	50	1963			
Void Total = $1.6\text{E}+0.5 \mu\text{m}^2$			Void Total = $2.8\text{E}03 \mu\text{m}^2$		
Area considered = $1.5\text{E}+08 \mu\text{m}^2$			Area Considered = $9.2\text{E}+05 \mu\text{m}^2$		
Ratio of Void/Sample areas = 0.0011			Ratio of Void/Sample areas = 0.0030		
30 to 250 μm dia. voids represent ^(a) : 0.11 vol%			5 to 30 μm dia. voids represent: 0.30 vol%		
Conclusion: ATM-10 bar 15 contains a total of about 0.5 vol% closed porosity.					

- (a) For random particles or voids, the average areal fraction of the voids, which is determined on sections through the microstructure, represents an estimate of the volume fraction of the voids in the matrix--Underwood et al. 1966. "Quantitative Relationships for Random Microstructures." In Ceramic Microstructures. R. M. Fulrath and J. A. Pask, ed., Robert E. Krieger Publishing Co., New York, p. 31.

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