Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

SRNL-STI-2011-00555
Revision 1

Keywords: *DWPF*
Glass
Sludge Batch 6

Retention: *Lifetime*

Analysis of DWPF Sludge Batch 6 (Macrobatch 7) Pour Stream Glass Samples

F.C. Johnson

October 2022

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2011-00555
Revision 1

Keywords: *DWPF*
Glass
Sludge Batch 6

Retention: *Lifetime*

Analysis of DWPF Sludge Batch 6 (Macrobatch 7) Pour Stream Glass Samples

F.C. Johnson

October 2022

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

ACKNOWLEDGEMENTS

The author would like to acknowledge the support provided by Amanda Billings and John Pareizs for testing and sampling in the Shielded Cells, the Shielded Cells Organization (Phyllis Burkhalter, Dee Wheeler, Rita Sullivan, Jane Howard and Monica Jenkins) as well as SRNL Analytical Development personnel (Damon Click, Boyd Wiedenman, Mark Jones, David Missimer, Ronnie Rutherford, Beverly Burch, and Loretta Farrow) for the chemical analysis and X-ray diffraction data.

EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) began processing Sludge Batch 6 (SB6), also referred to as Macrobatch 7 (MB7), in June 2010. SB6 is a blend of the heel of Tank 40 from Sludge Batch 5 (SB5), H-Canyon Np transfers and SB6 that was transferred to Tank 40 from Tank 51. SB6 was processed using Frit 418.

During processing of each sludge batch, the DWPF is required to take at least one glass sample to meet the objectives of the Glass Product Control Program and to complete the necessary Production Records so that the final glass product may be disposed of at a Federal Repository. Four pour stream glass samples and two Melter Feed Tank (MFT) slurry samples were collected while processing SB6. The samples were transferred to the Savannah River National Laboratory (SRNL) where they were analyzed. The following conclusions were drawn from the analytical results provided in this report:

- The sum of oxides for the official SB6 pour stream glass is within the Product Composition Control System (PCCS) limits (95-105 wt%).

- The average calculated Waste Dilution Factor (WDF) for SB6 is 2.3. In general, the measured radionuclide content of the official SB6 pour stream glass is in good agreement with the calculated values from the Tank 40 dried sludge results from the SB6 Waste Acceptance Product Specification (WAPS) sample; however, the measured value of Cs-137 is an order of magnitude higher than calculated, which is expected since the Tank 40 sample does not account for salt addition.

- As in previous pour stream samples, ruthenium and palladium inclusions were detected by Scanning Electron Microscopy (SEM)-Electron Dispersive Spectroscopy (EDS) in the official SB6 pour stream sample.

- The Product Consistency Test (PCT) results indicate that the official SB6 pour stream glass meets the waste acceptance criteria for durability with a normalized boron release of 0.69 g/L, which is an order of magnitude less than the Environmental Assessment (EA) glass.

- The measured density of the SB6 pour stream glass was in the range of 2.5 – 2.6 g/cm^3.

- The $Fe^{2+}/\sum Fe$ ratio of the SB6 pour stream samples were in the range of 0.25 – 0.41, while the MFT-558 sample was in the range of 0.44 – 0.50 and the MFT-568A sample was in the range of 0.02 – 0.16.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytical Development
AR	Aqua Regia
ARG-1	Analytical Reference Glass 1
ARM	Approved Reference Material
ASP	Analytical Study Plan
CPC	Chemical Processing Cell
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	Electron Dispersive Spectroscopy
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
MB7	Macrobatch 7
MFT	Melter Feed Tank
PCCS	Product Composition Control System
PCT	Product Consistency Test
PF	Peroxide Fusion
PS	Pour Stream
REDOX	REDuction/OXidation
RSD	Relative Standard Deviation
SB	Sludge Batch
SEM	Scanning Electron Microscopy
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt Adjustment Tank
SRNL	Savannah River National Laboratory
St. Dev.	Standard Deviation
THERMO	Thermodynamic Hydration Energy Reaction MOdel
TTQAP	Task Technical and Quality Assurance Plan
WAPS	Waste Acceptance Product Specification
WDF	Waste Dilution Factor
XRD	X-ray Diffraction

1.0 Introduction

The Defense Waste Processing Facility (DWPF) began processing Sludge Batch 6 (SB6), also referred to as Macrobatch 7 (MB7), in June 2010. SB6 is a blend of the heel of Tank 40 from Sludge Batch 5 (SB5), H-Canyon Np transfers and SB6 that was transferred to Tank 40 from Tank 51.[1] SB6 was processed using Frit 418.[2,3]

Sludge is received into the DWPF Chemical Processing Cell (CPC) and is processed through the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator Tank (SME). The treated sludge slurry is then transferred to the Melter Feed Tank (MFT) and fed to the melter. During processing of each sludge batch, the DWPF is required to take at least one glass sample to meet the objectives of the Glass Product Control Program[4] (GPCP) and to complete the necessary Production Records so that the final glass product may be disposed of at a Federal Repository.

The DWPF requested various analyses of radioactive glass samples obtained from the melter pour stream during processing of SB6 as well as reduction/oxidation (REDOX) analysis of MFT samples to determine the impact of Argon bubbling.[5] Sample analysis followed the Task Technical and Quality Assurance Plan (TTQAP)[6] and an Analytical Study Plan (ASP).[7] Four Pour Stream (PS) glass samples and two MFT slurry samples[a] were delivered to the Savannah River National Laboratory (SRNL) from the DWPF. Table 1-1 lists the sample information for each pour stream glass sample. SB6 PS#3 (S03472) was selected as the official pour stream sample for SB6 and full analysis was requested. This report details the visual observations of the as-received SB6 PS#3 glass sample as well as results for the chemical composition, Product Consistency Test (PCT), radionuclide content, noble metals, and glass density. REDOX results will be provided for all four pour stream samples and vitrified samples of MFT-558 and MFT-568A. Where appropriate, data from other pour stream samples will be provided.

The SB6 PS#2 sample (collected while filling glass canister S03469) was received in Primary Container 104 (PC0104) and was originally designated as the archive sample. Limited analyses were performed on this sample. When the decision was made to utilize the remaining glass from canister S03469 as the archive sample, the original Primary Container (PC0104) had already been discarded. The remaining glass from PC0104 was placed in Primary Container 106 (PC0106), which originally contained the glass sample from canister S03506. In summary, PC0106 contains the archive glass sample collected from canister S03469 for Macrobatch 7.

Table 1-1. DWPF Pour Stream Glass Sample Information

Glass Canister	Sample Date	MFT Batch	Sample ID
S03465	Dec-10	549	SB6 PS#1
S03469	Dec-10	550	SB6 PS#2
S03472	Dec-10	551	SB6 PS#3
S03506	Feb-11	558	SB6 PS#4

2.0 Experimental Procedure

2.1 Visual Examination, Extraction and Washing

Upon arrival at SRNL, each of the pour stream glasses were inspected, and then samples were removed from the Pt/Au collection boats and washed according to procedure prior to analysis.[8]

[a] MFT Batch 558 and MFT Batch 568A, which will be denoted as MFT-558 and MFT-568A in the text.

2.2 Chemical Composition

A sample of SB6 PS#3 was ground and then sieved to -200 mesh. Quadruplicate samples of the pour stream glass were digested by two separate methods: aqua regia (AR)[9] and sodium peroxide fusion (PF).[10] Three Analytical Reference Glass (ARG-1) standards were also digested by each method and submitted along with the samples. All of the prepared samples were submitted to Analytical Development (AD) and analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). A multi-element standard and blank were also included in the analyses in order to assess the performance of the instrument over the course of the analyses.

2.3 Radionuclide Composition

The SB6 PS#3 glass sample was prepared in quadruplicate using peroxide fusion and was analyzed by AD using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) to determine actinide and fission product content. The glass was also dissolved by a mixed acid dissolution[11] and was analyzed by counting methods to calculate the radionuclide concentration. The reportable radionuclides for the Glass Product Control Program not measured in this study were calculated from the slurry results using a calculated Waste Dilution Factor (WDF).

2.4 Noble Metals

Noble metal concentrations were analyzed in SB6 PS#3 using ICP-MS from the peroxide fusion dissolution. The total silver concentration is calculated using the measured concentration of ^{109}Ag and the calculated concentration of ^{107}Ag.[12] Due to interference from Cd, the palladium concentration is calculated using the sum of the measured concentration of ^{105}Pd and the calculated concentrations of ^{106}Pd, ^{107}Pd, ^{108}Pd, and ^{110}Pd using their fission yields.[12] The total concentration of ruthenium is calculated from the sum of the measured concentrations of three isotopes: ^{101}Ru, ^{102}Ru, and ^{104}Ru. The reported concentration of rhodium is from the measured concentration of a single isotope, ^{103}Rh.

In addition, a sample of SB6 PS#3 was analyzed using Scanning Electron Microscopy (SEM) along with Energy Dispersive Spectroscopy (EDS) to image and analyze any inhomogeneities, including noble metal inclusions, in the glass. Samples of SB6 PS#1, #2 and #3 were also submitted for X-ray Diffraction (XRD) analysis.

2.5 Product Consistency Test (PCT)

The PCT was performed on quadruplicate samples of SB6 PS#3 to assess chemical durability using Method A of the procedure.[13] Also included was the Environmental Assessment (EA) glass, the Approved Reference Material (ARM) glass, and blanks from the sample cleaning batch. Samples were ground, washed, and prepared according to the standard procedure. ARM and EA were prepared in triplicate whereas the SB6 PS#3 sample was prepared in quadruplicate. The resulting solutions were sampled (filtered and acidified) and analyzed by AD. Samples of a multi-element, standard solution were also included with the glass samples as a check on the accuracy of the ICP-AES. Normalized release rates were calculated based on the measured composition using the average[b] of the leachate concentrations.

2.6 Density

The densities of SB6 PS#2 and SB6 PS#4 were measured with a Gay-Lussac pycnometer.[c] By

[b] It should be noted that one of the sets of triplicate values for EA was not used in the calculation due to erroneous results. It appears that a sample of ARM was used instead of EA.
[c] No glass was available to measure the density of SB6 PS#3; however measurement of SB6 PS#2 and #4 should be bounding.

using the mass of the empty pycnometer (m_0), pycnometer and sample (m_1), pycnometer and sample and water (m_2) and pycnometer and water (m_3), the density of the sample (ρ_s) is calculated by

$$\rho_s = \frac{\rho_{H2O}(m_1 - m_0)}{(m_3 - m_0) - (m_2 - m_1)}$$

where ρ_{H2O}[d] is the density of water at the measurement temperature. A reference glass[e] was included in the set of measurements as an internal check of the measurement technique in the shielded cells.

2.7 REDOX

2.7.1 *Pour Stream Samples*

A sample of each pour stream glass was ground and then sieved to -200 mesh. All samples were prepared for REDOX measurement and analyzed via UV-Vis spectroscopy according to procedure.[14] In addition to the pour stream samples, the EA glass was included in each set of measurements as an internal check of the measured REDOX value.

2.7.2 *MFT Samples*

Both of the MFT slurry samples were prepared in triplicate and vitrified via the sealed crucible method according to procedure.[15] All of the samples were removed from the alumina crucibles, ground and sieved to -200 mesh. The samples were then prepared and analyzed in a similar manner as the pour stream samples (Section 2.7.1).

2.8 Summary

A summary of the analyses for each pour stream sample is shown in Table 2-1.

Table 2-1. Summary of SB6 Pour Stream Glass Analyses

Sample ID	Analyses
SB6 PS#1	REDOX and XRD
SB6 PS#2	REDOX, XRD, density
SB6 PS#3	Chemical composition, radionuclides, noble metals, PCT, SEM-EDS, REDOX and XRD
SB6 PS#4	REDOX and density

3.0 Results and Discussion

3.1 Visual Examination and Analysis

Upon the receipt inspection, none of the pour stream glasses appeared to have a significant surface film (if any); however, the surface rinse water[f] from SB6 PS#2 and SB6 PS#3 did contain

[d] The density of H_2O was assumed to be 1 g/cm^3 for all measurements.
[e] The density of a sample of NIST 1830 glass was determined to be 2.49 g/cm^3 using the Archimedes method (ITS-0057) prior to its placement in the shielded cells.
[f] Samples were rinsed with de-ionized water prior to removal from the Pt-Au collection boat and submitted to AD for Ion Chromatography (IC) anion analysis.

a detectable amount of sulfate as shown in Table 3-1. Presence of a sulfate layer, specifically Na_2SO_4, was also detected on the surface of the SB5 pour stream glass.[16]

Table 3-1. Analysis of Glass Surface Rinse Water

Anion	Concentration (µg/mL)
Fluoride	<10
Formate	<10
Chloride	<10
Nitrite	<10
Nitrate	17
Phosphate	<10
Sulfate	161
Oxalate	<10
Bromide	<10

(a) SB6 PS#2

Anion	Concentration (µg/mL)
Fluoride	2
Formate	<1
Chloride	4
Nitrite	<1
Nitrate	10
Phosphate	<1
Sulfate	292
Oxalate	<1
Bromide	<1

(b) SB6 PS#3

3.2 Chemical Composition

Table 5-1 and Table 5-2 in Appendix A provide the measured elemental data from glasses prepared using aqua regia and peroxide fusion, respectively.

3.2.1 *ARG-1*

Table 3-2 shows a comparison of the published[17] and measured composition of the ARG-1 glass. The measured value is the average of the six replicates (three from each dissolution method) unless otherwise noted. In general, the measured values are consistent with the published values; however, there was some variation in the measurement of SiO_2 as shown by the Relative Standard Deviation (%RSD). The sum of oxides is within the Product Composition Control System (PCCS) acceptance limits (the interval of 95 to 105 wt%).

3.2.2 *SB6 PS#3*

Table 3-3 lists the oxide composition of the SB6 PS#3 glass. The measured value is the average of the eight replicates (four from each dissolution methods) unless otherwise noted. Some of the analytes were below the detection limit of the instrument and are noted by a result preceded with a "<." The %RSD for the major glass components (> 0.5 wt%) is less than 10%, indicating good precision in the results.

3.2.3 *WDF*

The WDF for a specific sludge batch is given by

$$WDF(i) = \frac{CS(i)}{CG(i)}$$

where *CS(i)* is the concentration of component *i* in the dried Tank 40 sludge[18] and *CG(i)* is the concentration of component *i* in the corresponding pour stream glass sample. Table 3-4 contains the calculated WDF values for Al, Ca, Fe and Mn for SB6. The average WDF value will be used in Section 3.3 to calculate the concentration of radionuclides that were not directly measured in the glass.

Table 3-2. Published[17] and Measured Values of ARG-1

Oxide	Published (wt%)	Measured (wt%)	% RSD	Digestion Method
Al_2O_3	4.73	4.48	6.5	PF, AR
B_2O_3	8.67	7.92	5.4	PF, AR
BaO	0.088	0.09	5.0	PF, AR
CaO	1.43	1.49	3.8	AR
Cr_2O_3	0.093	0.10	6.0	PF, AR
Fe_2O_3	14.0	13.96	5.5	PF, AR
K_2O	2.71	2.64	3.6	AR
Li_2O	3.21	3.15	4.9	PF, AR
MgO	0.86	0.85	5.0	PF, AR
MnO	1.88	1.81	4.7	PF, AR
Na_2O	11.5	11.18	3.8	AR
NiO	1.05	1.02	4.9	PF, AR
P_2O_5	0.22	0.25	9.9	PF, AR
SiO_2	47.9	48.21	10.7	PF
TiO_2	1.15	1.02	10.3	PF, AR
ZnO	0.02	0.02	16.1	PF, AR
ZrO_2	0.13	0.07	11.6	AR
Total	99.64	98.26	---	---

Table 3-3. Average Measured Composition of SB6 PS#3

Oxide	Measured (wt%)	%RSD	Digestion Method	Oxide	Measured (wt%)	%RSD	Digestion Method
Al_2O_3	8.63	5.7	PF, AR	MoO_3	<0.02	NA	PF, AR
B_2O_3	4.55	7.3	PF, AR	Na_2O	14.86	5.0	AR
BaO	0.06	7.0	PF, AR	NiO	1.02	6.6	PF, AR
BeO	<0.001	NA	PF, AR	P_2O_5	<0.17	NA	PF, AR
CaO	0.61	4.5	AR	PbO	<0.04	NA	PF, AR
CdO	0.01	7.8	PF, AR	SO_4	<0.18	NA	AR
Ce_2O_3	<0.08	NA	PF, AR	Sb_2O_3	<0.08	NA	PF, AR
Cr_2O_3	0.16	4.3	PF, AR	SiO_2	49.10	5.1	PF
CuO	0.21	5.8	PF, AR	SnO_2	<0.03	NA	PF, AR
Fe_2O_3	8.74	4.6	PF, AR	SrO	0.02	5.2	PF, AR
Gd_2O_3	0.04	23.4	PF, AR	ThO_2	1.00	9.9	PF, AR
K_2O	0.09	1.9	AR	TiO_2	0.35	4.7	PF, AR
La_2O_3	0.04	8.1	PF, AR	U_3O_8	1.83	5.3	PF, AR
Li_2O	4.92	5.2	PF, AR	ZnO	0.06	4.2	PF, AR
MgO	0.33	5.4	PF, AR	ZrO_2	0.12	9.6	AR
MnO	2.19	5.2	PF, AR	Total	99.57	---	---

Table 3-4. Waste Dilution Factor for SB6 PS#3

Element	Concentration (wt%)		WDF
	Dried Sludge Slurry[18]	Glass	
Al	10.6	4.57	2.3
Ca	0.868	0.44	2.0
Fe	14.0	6.11	2.3
Mn	4.30	1.70	2.5
Average	---	---	2.3
Std. Dev.	---	---	0.2

3.3 Radionuclide Composition

Based on measurements and analytical detection limits, thirty radionuclides have been identified as reportable for DWPF SB6 (MB7) as specified by the Waste Acceptance Product Specification (WAPS) 1.2.[1,g] Selected radionuclides were directly measured in quadruplicate either by gamma counting, beta counting, alpha spectroscopy or ICP-MS. Table 5-3 lists the average concentration of these radionuclides in the SB6 pour stream glass.[h] Table 5-3 and Table 5-4 in Appendix A provide the actual measured radiological chemical and ICP-MS data, respectively. Some of the analytes were below the detection limit of the instrument and are noted by a result preceded with a "<." The content of each radionuclide was also calculated from measured values of the Tank 40 dried SB6 sludge and the average WDF value shown in Table 3-4.[1]

3.4 Noble Metals

The average measured concentrations of the noble metals based on quadruplicate measurements of SB6 PS#3 are listed in Table 3-6. Table 5-4 in Appendix A provides the actual measured ICP-MS data. The calculated noble metal concentration in the glass is determined from the concentration in the Tank 40 sludge[18] and the average WDF value (Table 3-4).

In addition to ICP-MS, the SB6 PS#3 glass was also analyzed with SEM-EDS for noble metal inclusions. Examination of the glass with EDS indicated the presence of both Ru and Pd, which corresponds to the results of the ICP-MS noble metals analysis in Table 3-6.[i] Noble metal inclusions have been observed in previous pour stream samples, including SB4 and SB5.[16]

Ru was also detected via XRD in SB6 PS#1 as shown in Figure 3-1. No crystalline phases were detected in SB6 PS#2 and #3.

[g] Th-229 was identified as reportable for SB6; however, there is no direct method for measuring its concentration, so its value will not be presented in this report. Based on the calculated values presented in SRNL-STI-2011-00189, Th-229 becomes reportable in the year 2715, which is of no practical significance to this study.
[h] Th-232 was also added to the list as it was measured at greater than 0.2 wt% by ICP-MS.
[i] More details can be found in notebook SRNL-NB-2011-00029 (pages 74-77).

Table 3-5. Reportable Radionuclide Content of the SB6 PS#3 Glass

Radionuclide	Tank 40 SB6 Dried Sludge[1]	Calculated SB6 Glass	Measured SB6 Glass
	(Ci/kg)		
Ni-59	1.1E-03	4.6E-04	---
Ni-63	1.1E-01	4.7E-02	---
Se-79	9.1E-06	4.0E-06	---
Sr-90	1.9E+01	8.1E+00	5.9E+00
Zr-93	4.6E-04	2.0E-04	5.3E-04
Nb-93m	3.8E-04	1.6E-04	---
Tc-99	<1.1E-04	<2.5E-04	<1.3E-04
Sn-121m	<4.7E-03	<2.0E-03	---
Sn-126	<1.5E-04	<6.5E-05	---
Cs-137	3.9E-01	1.7E-01	1.3E+00
Sm-151	2.6E-01	1.1E-01	---
Th-232	2.4E-06	1.1E-06	9.3E-07
U-233	9.0E-05	3.9E-05	7.0E-05
U-234	8.4E-05	3.6E-05	4.2E-05
U-235	6.0E-07	2.6E-07	2.3E-07
U-236	1.3E-06	5.8E-07	6.3E-07
U-238	1.2E-05	5.3E-06	5.1E-06
Np-237	3.6E-05	1.6E-05	1.7E-05
Pu-238	3.8E-01	1.7E-01	1.4E-01
Pu-239	1.8E-02	7.9E-03	7.7E-03
Pu-240	6.5E-03	2.8E-03	2.9E-03
Pu-241	<8.3E-02	<3.6E-02	3.7E-02
Pu-242	<1.5E-05	<6.5E-06	<1.4E-05
Am-241	3.3E-02	1.4E-02	1.4E-02
Am-242m	2.3E-04	9.8E-05	---
Am-243	4.3E-03	1.9E-03	---
Cm-244	1.5E-01	6.5E-02	---
Cm-245	2.0E-05	8.9E-06	---
Cm-246	6.5E-05	2.8E-05	---
Cm-248	<7.1E-06	<3.1E-06	---
Cf-249	<2.3E-05	<1.0E-05	---
Cf-251	<5.5E-05	<2.4E-05	---

Alpha Spectroscopy:	Pu-238
Beta Counting:	Sr-90 and Pu-241
Gamma Counting:	Cs-137 and Am-241
ICP-MS:	Zr-93, Tc-99, Th-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-239, Pu-240 and Pu-242

Table 3-6. Noble Metal Concentration in the SB6 PS#3 Glass

Noble Metal	Tank 40 SB6 Dried Sludge[18]	Calculated SB6 Glass	Measured SB6 Glass
	(wt%)		
Ag	0.01	0.006	0.008
Pd	0.003	0.001	0.002
Rh	0.02	0.009	0.01
Ru	0.09	0.04	0.05

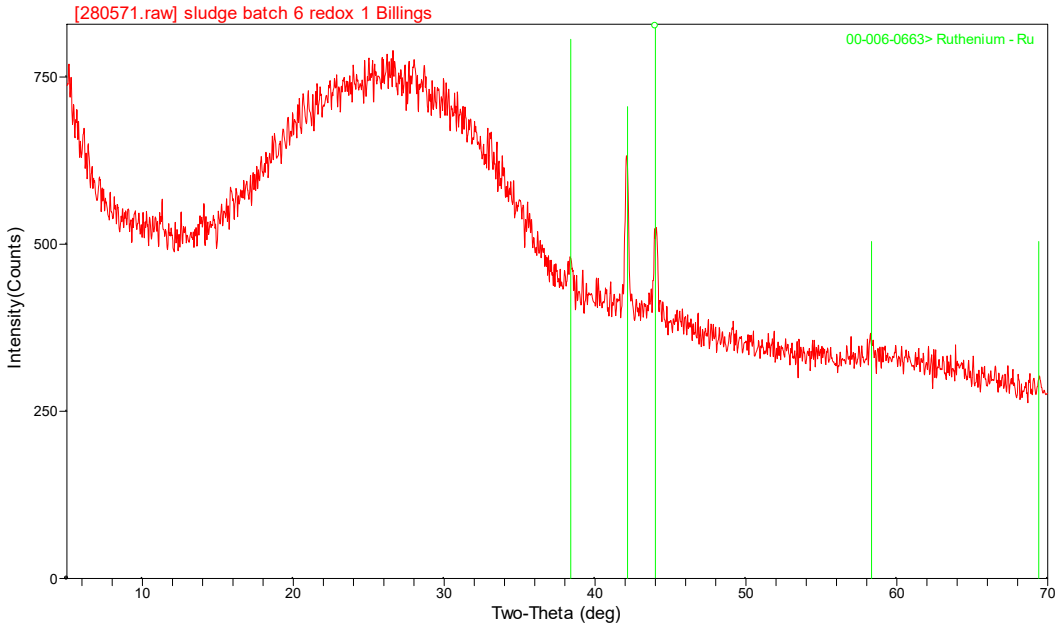

Figure 3-1. XRD spectrum of SB6 PS#1.

3.5 PCT

The average normalized release values for ARM [j], EA and SB6 PS#3 are shown in Table 3-7.[19,20] No water loss issues were observed over the course of the test. Table 5-5 in Appendix A provides the elemental leachate concentrations for the solution samples generated by the PCTs. The normalized release values of the pour stream glass for B, Li, Na and Si are below 1 g/L, which is very acceptable with respect to the EA glass benchmark value of 16.7 g/L.

3.6 Density

The densities of SB6 PS#2 and #4 were determined to be 2.6 g/cm^3 and 2.5 g/cm^3, respectively. Data from the density measurements are shown in Table 5-6 in Appendix A.

3.7 REDOX

Summaries of the REDOX results of the pour stream samples and vitrified MFT samples were communicated to DWPF in a series of brief memoranda.[21-23] Table 3-8 and Table 3-9 list the

[j] The concentrations of each element of interest for ARM are within the control limits stated in THERMO™.

average calculated values for $Fe^{2+}/\sum Fe$ and Fe^{2+}/Fe^{3+} for the pour stream samples and MFT samples, respectively. Complete sets of data for each of the replicates and EA samples included with individual sets are shown in Table 5-7 and Table 5-8 in Appendix A.

Table 3-7. Normalized PCT Results for SB6 PS#3 (g/L)

Glass ID	NL B	NL Li	NL Na	NL Si
ARM	0.46	0.54	0.48	0.27
St. Dev.	0.004	0.004	0.003	0.002
% RSD	0.8	0.7	0.6	0.6
EA	16.60	9.56	13.36	3.96
St. Dev.	0.02	0.04	0	0
% RSD	0.1	0.4	0	0
SB6 PS#3	0.69	0.81	0.85	0.49
St. Dev.	0.02	0.01	0.02	0.01
% RSD	2.5	1.6	2.8	2.8

Table 3-8. SB6 Pour Stream Glass REDOX Data

Sample ID	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
SB6 PS#1	0.25	0.34
SB6 PS#2	0.32	0.47
SB6 PS#3	0.38	0.60
SB6 PS#4	0.41	0.69

Table 3-9. SB6 MFT Glass REDOX Data[k]

Sample ID	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
MFT-558-1	0.50	1.00
MFT-558-2	0.44	0.81
SB6 MFT 568A-A	0.16	0.20
SB6 MFT 568A-B	0.06	0.06
SB6 MFT 568A-C	0.02	0.03

[k] Due to time restraints only two of the three samples were prepared for REDOX measurements.

4.0 Conclusions

- The sum of oxides for the official SB6 pour stream glass is within the PCCS limits (95-105 wt%).

- The average calculated WDF for SB6 is 2.3. In general, the measured radionuclide content of the official SB6 pour stream glass is in good agreement with the calculated values from the Tank 40 dried sludge results from the SB6 WAPS sample; however, the measured value of Cs-137 is an order of magnitude higher than calculated, which is expected since the Tank 40 sample does not account for salt addition.

- As in previous pour stream samples, ruthenium and palladium inclusions were detected by SEM-EDS in the official SB6 pour stream sample.

- The PCT results indicate that the official SB6 pour stream glass meets the waste acceptance criteria for durability with a normalized boron release of 0.69 g/L, which is an order of magnitude less than the EA glass.

- The measured density of the SB6 pour stream glass was in the range of 2.5 – 2.6 g/cm^3.

- The $Fe^{2+}/\sum Fe$ ratio of the SB6 pour stream samples were in the range of 0.25 – 0.41, while the MFT-558 sample was in the range of 0.44 – 0.50 and the MFT-568A sample was in the range of 0.02 – 0.16.

5.0 References

1. C.J. Bannochie and D.P. DiPrete, "Determination of Reportable Radionuclides for DWPF Sludge Batch 6 (Macrobatch 7)," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2011-00189, 2011.

2. K.M. Fox and T.B. Edwards, "Glass Frit Composition for Sludge Batch 6 Vitrification at the Defense Waste Processing Facility," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2010-00043, 2010.

3. K.M. Fox, T.B. Edwards, and J.R. Zamecnik, "Frit Development for Sludge Batch 6," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2010-00137, 2010.

4. J.W. Ray, B.H. Culbertson, S.L. Marra, and M.J. Plodinec, "DWPF Glass Product Control Program," Washington Savannah River Company, Aiken, SC, WSRC-IM-91-116-6, Rev. 7, 2007.

5. T.L. Fellinger, "Analysis of Sludge Batch 6 and 7 Pour Stream Samples," Savannah River Remediation, Aiken, SC, HLW-DWPF-TTR-2010-0047, 2010.

6. J.W. Amoroso and A.L. Billings, "Task Technical and Quality Assurance Plan for Analysis of Sludge Batch 6 and 7 Pour Stream Samples and Melter Feed Tank (MFT) Slurry Samples," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2011-00104, 2011.

7. J.W. Amoroso and A.L. Billings, "Analytical Study Plan for Analysis of Sludge Batch 6 and 7 Pour Stream Samples and Melter Feed Tank (MFT) Slurry Samples," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2011-00105, 2011.

8. C.J. Bannochie and N.E. Bibler, "Current and New Controls in the Shielded Cells for Handling DWPF Pour Stream Glasses and Comments Concerning S02244 and S02247 Glasses," Savannah River National Laboratory, Aiken, SC, SRNL-ITS-2005-00127, 2005.

9. "Aqua Regia Dissolution of Sludge for Elemental Analysis," Savannah River National Laboratory, Aiken, SC ADS-2226, Latest Revision.

10. "Alkali Fusion Dissolutions of Sludge and Glass for Elemental and Anion Analysis," Savannah River National Laboratory, Aiken, SC, ADS-2502, Latest Revision.

11. "Acid Dissolution of Glass and Sludge for Elemental Analysis," Savannah River National Laboratory, Aiken, SC, ADS-2227, Latest Revision.

12. N.E. Bibler, "Measuring and Predicting Fission Product Noble Metals in Savannah River Site High Level Waste Sludges," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-2005-0098, 2005.

13. "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)," ASTM International, West Conshohocken, PA, ASTM C 1285-02, 2002.

14. "Determining Fe^{2+}/Fe^{3+} and Fe^{2+}/Fe(Total) Using UV VIS Spectrometer," Savannah River National Laboratory, Aiken, SC, ITS-0042, Latest Revision.

15. "Heat Treatment of Waste Slurries for REDOX (Fe^{2+}/Fe Total) and Chemical Composition Measurement," Savannah River National Laboratory, Aiken, SC, ITS-0052, Latest Revision.

16. M.M. Reigel and N.E. Bibler, "Analysis of Sludge Batch 4 (Macrobatch 5) for Canister S02902 and Sludge Batch 5 (Macrobatch 6) for Canister S03317 DWPF Pour Stream Glass Samples," Savannah River National Laboratory, Aiken, SC SRNL-STI-2010-00435, 2010.

17. G.L. Smith, "Characterization of Analytical Reference Glass-1 (ARG-1)," Pacific Northwest National Laboratory, Richland, WA, PNL-8992, 1993.

18. C.J. Bannochie, "Tank 40 Final SB6 Chemical Characterization Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2010-00441, 2010.

19. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, and M.A. Pickett, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-92-346, Rev. 1, 1993.

20. C.M. Jantzen, J.B. Pickett, K.G. Brown, T.B. Edwards, and D.C. Beam, "Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction

Model (THERMO)," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-93-672, Rev. 1, 1995.

21. A.L. Billings, M.M. Reigel, and D.R. Click, "REDOX Analysis of SB4, SB5, and SB6 Pour Stream Glass Samples," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00007, 2011.

22. F.C. Johnson, "REDOX Analysis of a Melter Feed Tank Batch 568a Sample," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00140, 2011.

23. F.C. Johnson and D.R. Click, "REDOX Analysis of a SB6 Pour Stream Sample and Melter Feed Tank Batch 558 Sample," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00092, 2011.

Appendix A. Supplemental Data Tables

Table 5-1. Measured Elemental Concentrations (µg/g) for Glasses Prepared Using an Aqua Regia Dissolution

Replicate	Glass ID	Lab ID	Al	B	Ba	Be	Ca	Cd	Ce	Cr	Cu	Fe	Gd	K	La	Li	Mg
1	ARG	300294848	22500	24700	796	23.1	10400	< 24.7	< 48	632	< 50.2	93800	< 17.1	22200	< 43	14900	5130
2		300294850	22500	24700	806	23.9	10400	< 23.9	< 46.6	643	< 48.6	93400	< 16.6	22500	< 41.7	15100	5220
3		300294852	24200	26200	756	24.6	11100	< 24.6	< 47.9	611	< 50	99300	< 17.1	21000	< 42.9	14200	4880
1	SB6 PS#3	300294847	47300	14800	560	< 4.6	4370	117	674	1150	1820	61700	415	786	374	24200	2110
2		300294849	50100	15900	502	< 4.86	4610	110	633	1070	1650	65700	381	809	349	22700	1990
3		300294851	44700	14300	494	< 4.78	4140	107	612	1050	1610	58700	380	784	340	22300	1940
4		300294853	45800	14600	538	< 4.86	4280	115	682	1140	1750	60300	409	773	371	24300	2120
1	Blank	300294846	< 40	< 30	< 0.48	< 0.48	< 32	< 24.8	< 48.2	< 8.16	< 5.04	< 40	< 17.2	< 241	< 4.32	< 11.7	< 6

Replicate	Glass ID	Lab ID	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sn	Sr	Th	Ti	U	Zn	Zr
1	ARG	300294848	13700	< 21.4	81000	7940	1080	< 57.1	< 598	< 425	< 89.4	29.8	< 214	5400	< 6380	170	556
2		300294850	13700	< 20.7	81300	7970	1010	< 55.3	< 579	< 412	< 86.6	30.3	< 207	5680	< 6180	173	454
3		300294852	14500	< 21.3	86600	8460	1010	< 56.8	< 595	< 423	< 89	28.4	< 213	5650	< 6360	160	562
1	SB6 PS#3	300294847	17400	44.2	110000	8320	652	161	< 575	< 409	< 86	222	9830	2220	15500	524	766
2		300294849	18500	41.5	118000	8910	749	143	< 607	< 432	< 90.8	208	9220	2090	16700	489	930
3		300294851	16600	33.9	105000	7960	708	132	< 598	< 425	< 89.4	204	9040	2050	15100	475	851
4		300294853	17000	49.2	108000	8230	788	145	< 607	< 432	< 90.8	222	9800	2230	15100	513	949
1	Blank	300294846	< 4.24	< 21.4	< 265	< 36.4	< 69.3	< 57.3	< 600	< 427	< 44.9	< 0.4	< 21.4	< 3.04	< 641	< 7.2	< 4.4

Table 5-2. Measured Elemental Concentrations (µg/g) for Glasses Prepared Using a Peroxide Fusion Dissolution

Replicate	Glass ID	Lab ID	Al	B	Ba	Be	Ca	Cd	Ce	Cr	Cu	Fe	Gd	K	La	Li
1	ARG	300294829	25200	24600	802	25.1	12100	< 24.3	< 666	675	80.8	101000	< 169	23500	< 42.4	15100
2		300294831	22100	22200	727	23.7	11100	< 25.3	< 693	624	< 51.4	92500	< 176	20800	< 44.1	13400
3		300294833	25700	25200	838	25.4	12900	< 29.1	< 797	717	< 59.2	106000	< 202	24600	< 50.7	15200
1	SB6 PS#3	300294828	42500	12800	461	< 4.58	5550	99.2	< 648	1050	1580	57900	273	< 2300	320	21700
2		300294830	47600	14300	521	< 4.58	5990	101	< 648	1170	1750	64700	291	< 2300	364	24000
3		300294832	44700	13500	491	< 4.49	5180	95.9	< 636	1090	1590	61200	250	< 2250	300	22300
4		300294834	42500	12900	460	< 4.51	5030	97	< 638	1070	1560	58800	223	< 2260	315	21200
1	Blank	300294827	330	< 162	< 41.6	< 4.8	2070	< 24.8	< 679	< 81.6	< 50.4	210	< 172	< 2410	< 43.2	< 117

Replicate	Glass ID	Lab ID	Mg	Mn	Mo	Ni	P	Pb	S	Sb	Si	Sn	Sr	Th	Ti	U	Zn
1	ARG	300294829	5290	14300	< 176	8090	1230	< 562	< 5880	< 1000	235000	< 440	46.3	< 210	6750	< 6340	176
2		300294831	4800	13000	< 184	7360	1040	< 584	< 6120	< 1040	198000	< 458	43.3	< 219	6110	< 6600	166
3		300294833	5490	14800	< 211	8390	1250	< 672	< 7040	< 1200	243000	< 527	51.6	< 252	6920	< 7590	239
1	SB6 PS#3	300294828	1870	15900	< 172	7250	< 661	< 547	< 5730	< 975	219000	< 428	204	8060	2000	15500	471
2		300294830	2090	17700	< 172	8140	904	< 547	< 5730	< 975	245000	< 428	225	8900	2220	16800	527
3		300294832	1930	16700	< 169	7900	< 649	< 536	< 5620	< 957	232000	< 420	205	7800	2080	14900	506
4		300294834	1850	16000	< 169	7400	720	< 538	< 5640	< 960	222000	< 422	195	7610	1990	14500	493
1	Blank	300294827	< 24	< 42.4	< 180	< 364	< 693	< 573	< 6000	< 1020	< 782	< 449	< 32	< 214	< 30.4	< 6470	< 73.6

Table 5-3. Measured Radionuclide Concentrations (dpm/g) via Gamma and Beta Counting and Alpha Spectroscopy

Replicate	Glasss ID	Lab ID	Am-241	Cs-137	Pu-238	Pu-241	Sr-90
1	SB6 PS#3	300289390	3.14E+07	2.85E+09	3.04E+08	7.17E+07	1.27E+10
2		300289391	3.07E+07	2.95E+09	3.16E+08	8.09E+07	1.35E+10
3		300289392	2.89E+07	3.01E+09	3.27E+08	8.71E+07	1.51E+10
4		300289393	3.13E+07	2.92E+09	3.27E+08	8.46E+07	1.11E+10
1	Blank	300289389	<1.82E+04	<2.86E+06	<3.20E+05	<6.46E+04	3.47E+07

Table 5-4. Measured Concentrations of m/z (µg/g) via ICP-MS

Replicate	Glass ID	Lab ID	m/z						
			93	99	101	102	103	104	105
1	SB6 PS#3	300294837	2.12E+02	< 7.63E+00	1.96E+02	1.83E+02	9.78E+01	9.48E+01	1.40E+01
2		300294838	2.20E+02	< 7.63E+00	2.09E+02	1.98E+02	1.02E+02	1.06E+02	1.71E+01
3		300294839	2.05E+02	< 7.49E+00	1.83E+02	1.69E+02	8.81E+01	8.36E+01	1.16E+01
4		300294840	2.06E+02	< 7.52E+00	1.99E+02	1.77E+02	9.75E+01	1.02E+02	1.43E+01
1	Blank	300294836	1.43E+01	< 8.00E+00	< 4.00E+00	< 4.00E+00	< 4.00E+00	< 4.00E+00	< 1.00E+01

Replicate	Glass ID	Lab ID	m/z						
			106	107	108	109	110	232	233
1	SB6 PS#3	300294837	9.35E+01	5.36E+01	2.98E+01	3.08E+01	4.01E+01	8.96E+03	8.19E+00
2		300294838	8.39E+01	4.98E+01	2.62E+01	2.95E+01	3.60E+01	8.93E+03	6.69E+00
3		300294839	7.49E+01	4.78E+01	2.34E+01	2.81E+01	3.43E+01	7.80E+03	6.22E+00
4		300294840	1.04E+02	5.63E+01	3.41E+01	2.58E+01	4.39E+01	8.36E+03	7.92E+00
1	Blank	300294836	2.05E+02	6.58E+01	7.01E+01	< 6.00E+00	8.36E+01	5.54E+00	< 4.00E+00

Replicate	Glass ID	Lab ID	m/z							
			234	235	236	237	238	239	240	242
1	SB6 PS#3	300294837	7.44E+00	1.13E+02	7.62E+00	2.29E+01	1.65E+04	1.33E+02	1.18E+01	< 3.82E+00
2		300294838	6.63E+00	1.06E+02	1.03E+01	2.11E+01	1.55E+04	1.27E+02	1.45E+01	< 3.82E+00
3		300294839	6.71E+00	1.03E+02	1.08E+01	2.26E+01	1.44E+04	1.13E+02	1.19E+01	< 3.75E+00
4		300294840	5.84E+00	9.62E+01	1.02E+01	2.83E+01	1.46E+04	1.20E+02	1.30E+01	< 3.76E+00
1	Blank	300294836	< 4.00E+00	< 4.00E+00	< 4.00E+00	< 4.00E+00	1.11E+01	< 4.00E+00	< 4.00E+00	< 4.00E+00

Table 5-5. As-Received and Adjusted Measurements of the PCT Solutions

Replicate	Glass ID	Lab ID	As Received (mg/L)				Adjusted (ppm)			
			B	Li	Na	Si	B	Li	Na	Si
1	ARM	300289740	9.88	7.68	20.8	36.1	16.47	12.80	34.67	60.17
2		300289741	9.75	7.54	20.6	35.5	16.25	12.57	34.33	59.17
3		300289742	9.61	7.52	20.4	35.4	16.02	12.53	34.00	59.00
1	EA	300289737	34.9	11.3	99.9	54.1	581.67	188.33	1665.00	901.67
2		300289738	35	11.4	99.9	54.1	583.33	190.00	1665.00	901.67
3		300289739	1.02	0.767	<2.95	3.63	17.00	12.78	49.17	60.50
1	SB6 PS#3	300289747	5.84	10.9	55.7	67.2	9.73	18.17	92.83	112.00
2		300289748	5.68	10.8	54.7	65.9	9.47	18.00	91.17	109.83
3		300289749	5.92	11.3	57.5	69.2	9.87	18.83	95.83	115.33
4		300289799	5.96	11.4	57.4	69.2	9.93	19.00	95.67	115.33
1	Soln Std	300289800	19.7	9.98	83.5	51.6	19.7	9.98	83.5	51.6
1	Blank	300289735	0.108	<0.058	<2.95	<0.176	---	---	---	---
2		300289736	<0.081	<0.058	<2.95	<0.176	---	---	---	---

Table 5-6. Density Measurements

Parameter	Reference Glass	SB6 PS#2	SB6 PS#4
m0 (g)	32.105	31.746	32.085
m1 (g)	33.564	33.668	33.142
m2 (g)	82.828	82.808	82.573
m3 (g)	81.953	81.638	81.953
Vessel ID	53	69	53
Density (g/cm^3)	2.50	2.56	2.53

Note: m3 was only measured once for vessel 53

Table 5-7. SB6 Pour Stream REDOX Data

Sample	Replicate	Fe^{2+}	$\sum Fe$	Fe^{3+}	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
EA	---	0.1429	0.761	0.6181	0.188	0.231
SB6 PS#1	1	0.2571	1.0508	0.7937	0.245	0.324
	2	0.2627	1.0069	0.7442	0.261	0.353
EA	---	0.1941	1.0646	0.8705	0.182	0.223
SB6 PS#2	1	0.2398	0.8347	0.5949	0.287	0.403
	2	0.3323	0.8946	0.5623	0.371	0.591
SB6 PS#3	1	0.2532	0.683	0.4298	0.371	0.589
	2	0.2977	0.7978	0.5001	0.373	0.595
EA	---	0.1665	0.8694	0.7029	0.192	0.237
SB6 PS#2	3	0.1967	0.649	0.4523	0.303	0.435
	4	0.2374	0.79	0.5526	0.301	0.430
SB6 PS#3	3	0.3354	0.8816	0.5462	0.380	0.614
	4	0.3223	0.8608	0.5385	0.374	0.599
EA	---	0.1645	0.9301	0.7656	0.177	0.215
SB6 PS#4	1	0.3856	0.9236	0.5380	0.417	0.717
	2	0.3272	0.7971	0.4699	0.410	0.696
	3	0.3489	0.8875	0.5386	0.393	0.648

Table 5-8. SB6 MFT REDOX Data

Sample	Replicate	Fe^{2+}	$\sum Fe$	Fe^{3+}	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
EA	---	0.1645	0.9301	0.7656	0.177	0.215
SB6 MFT 588-1	1	0.238	0.499	0.2610	0.477	0.912
	2	0.203	0.429	0.2260	0.473	0.898
	3	0.262	0.483	0.2210	0.542	1.186
SB6 MFT 588-2	1	0.206	0.402	0.1960	0.512	1.051
	2	0.225	0.547	0.3220	0.411	0.699
	3	0.199	0.487	0.2880	0.409	0.691
EA	---	0.088	0.52	0.4320	0.169	0.204
SB6 MFT 568A-A	1	0.06	0.293	0.2330	0.205	0.258
	2	0.059	0.402	0.3430	0.147	0.172
	3	0.061	0.453	0.3920	0.135	0.156
SB6 MFT 568A-B	1	0.022	0.5	0.4780	0.044	0.046
	2	0.046	0.645	0.5990	0.071	0.077
	3	0.02	0.39	0.3700	0.051	0.054
SB6 MFT 568A-C	1	0.013	0.518	0.5050	0.025	0.026
	2	0.011	0.473	0.4620	0.023	0.024
	3	0.012	0.458	0.4460	0.026	0.027