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S-Glass Analysis by X-Ray Spectroscopy



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S-GLASS ANALYSIS BY X-RAY SPECTROSCOPY

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ABSTRACT

A rapid and accurate x-ray fluorescence (XRF) method for estimating concentrations of K_2O , SiO_2 , Al_2O_3 , P_2O_5 , and $(Li_2O + B_2O_3)$ in S-glass was developed based on the use of a fundamental parameters program, a set of secondary S-glass standards, and an iterative adjustment of Li_2O and/or B_2O_3 to a total unnormalized sample composition of 100 ± 0.01 percent. The errors introduced by the use of arbitrary and nonunique values of the light element unknown concentrations at the iterative endpoint were found to be small. The results obtained for S-glass ceramic lot 84-132 samples using this procedure compared well with the results of a round-robin study on the same glass. A statistical study on samples from lots 84-132 and 84-133 showed good analytical precision with relative measurement errors on the order of 0.5 percent for all components. This precision allowed detection of relatively small, but significant, sample-to-sample variations in chemical composition. In addition, it was demonstrated that the quality of the standards influences the accuracy of the results.

CONTENTS

	<u>Page</u>
Introduction.	1
Experimental.	2
Procedure.	2
Software	2
Standards.	3
Iterative Adjustment of Li_2O and B_2O_3	3
Analysis of Measurement and Sample-to-Sample Errors	5
Accuracy of Results	6
Conclusions	8
Acknowledgment.	8
References.	8
Distribution.	14

TABLES

I. S-Glass Measuring Parameters.	9
II. Composition of S-Glass Samples 83-455-3 and 83-458-4 in Weight Percent	9
III. Concentration Changes During a Typical Light Element Iteration.	10
IV. Estimated Composition of Lot 84-133 S-Glass Samples Found by XRF-11 Using the Secondary Standard Set with Iterative Adjustment of the Light Element Concentrations. Effect of the Final $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$ Ratio on the Results.	10
V. Analysis of Individual Standards Using XRF-11 with the Several Standard Sets. Iterative Adjustment of the Light Element Components. Comparison with Chemical Data.	11
VI. Average Composition of S-Glass Samples Found by XRF-11 Using Secondary Standards with Iterative Adjustment of the Light Element Unknowns.	11
VII. Analysis of Measurement and Sample-to-Sample Errors	12
VIII. Comparison of Results for Lot 84-132 S-Glass.	12
IX. Fundamental Parameter Results for 84-132 and 84-133 Samples Using Standard Set A with Iterative Adjustment of Light Element Components.	13

S-GLASS ANALYSIS BY X-RAY SPECTROSCOPY

INTRODUCTION

S-glass is a high-strength insulator material with properties that make it ideal for use in glass sealing technology with some alloys. In particular, this glass has a coefficient of expansion that matches that of Inconel 718 and a molten viscosity low enough for it to flow into tight configurations without void or bubble formation. Because these desirable physical characteristics are sensitive to compositional variations, quality control analyses are needed during production.

Chemical analyses are difficult, time-consuming, and expensive. Therefore, we used x-ray fluorescence (XRF) spectroscopy during early S-glass development studies to analyze for K_2O , SiO_2 , Al_2O_3 , P_2O_5 and $(Li_2O + B_2O_3)$. Because these analyses were precise and rapid, they were used to monitor and model volatilization losses from the melt. Based on these studies, it was possible to predict final composition and properties from initial batching composition and processing conditions and to upscale the process to larger "production-size" melts.

The wavelength-dispersive XRF technique for S-glass analysis involves the use of a fundamental parameters program[1] for data reduction with a special iterative adjustment for the unknown concentrations of Li_2O and B_2O_3 in the glass. This procedure is not typical of fundamental parameter analyses because such unmeasured components are usually known or can be found by difference. In this report, we describe the XRF method for S-glass analysis, its

application to samples from two S-glass lots, a statistical study that defined the analytical precision of the method, and a study of the quality of the standards used and their effect on the accuracy of the results.

EXPERIMENTAL

1. Procedure

The preparation of lots 84-132 and 84-133 S-glass samples for analysis was described by Merrill, et al.[2]. After calcining, the batched chemicals were melted at 1600°C with stirring in a dry room for about 16 hours. Six pours were then made into hot molds and extruded into rods for chemical analyses. Three discs about 3 cm in diam and 0.5 cm thick were also made in a carbon mold for XRF analysis during some of these pours. All glass samples were ground flat and polished to a 6 μm diamond finish on each side. They were then centered over a 23 mm diam Au-plated mask in a Siemens SRS 200 XRF spectrometer with a Cr target x-ray tube. The net $K\alpha$ spectral line intensity was determined for K, Si, Al, and P (using the basic measuring parameters presented in Table I) by duplicate intensity measurements at appropriate peak and two background positions. Li and B are not seen by the spectrometer. The results were then analyzed by the J. Criss fundamental parameters program XRF-11[1] from Criss Software, Inc.

2. Software

The measured spectral line intensities for the unknowns were converted to sample composition by use of XRF-11 and other supporting routines. XRF-11 uses mass absorption coefficients, fluorescence yields, and other "fundamental" parameters in theoretical expressions that model the primary and

secondary fluorescent intensities from any sample composition for the given incident spectrum. These predicted intensities for the unknowns, rescaled to conform to the experimental system by the use of standards, are compared to the measured intensities. Successive adjustments of the sample composition are then made to minimize the differences between theoretical and measured intensities.

Another software routine was used to prepare driver files for the fundamental parameters program. These driver files caused XRF-11 to automatically read data for the selected standards and unknowns and to calculate the composition of the unknown and the normalized chi (a statistic describing the goodness of fit between the theoretical and experimental intensities) for the calculated composition. A large value of chi indicates a poor fit while a small value indicates a good fit.

3. Standards

Two S-glass samples, 83-455-3 and 83-458-4, were analyzed by the Analytical Chemistry Division at Sandia National Laboratories for use as secondary standards for the fundamental parameters program. Table II presents the estimated chemical composition of these two samples. The uncertainties in the estimated percentages are about 8 percent relative for all components.

4. Iterative Adjustment of Li_2O and B_2O_3

The Li_2O and B_2O_3 content of the S-glass samples are unknown because of vaporization losses during fabrication. The fundamental parameters program calculates the amount of each measured component in the unknown based on measured intensities, known amount of other components, composition of the standards, and experimental conditions. Our past experience has shown that if the

initial batched values for the two unknown component (Li_2O and B_2O_3) concentrations were used arbitrarily, then the final calculated sum of all component concentrations found by XRF-11 would differ from 100 percent. Moreover, the normalized chi would be variable and often large, indicating a poor fit. To correct this problem, we adjusted the concentrations of Li_2O and/or B_2O_3 , since the nominal batched values were known to be incorrect in the final sample, and repeated the fundamental parameters calculation. This adjustment and recalculation was continued until the sum of all concentrations was 100 ± 0.01 percent. The normalized chi was then always found to be small, indicating a good fit between theoretical and measured intensities. With experience, we seldom exceeded four adjustments of the light elements so that the iteration converged rapidly. A summary of the concentration changes in a typical light element iteration is displayed in Table III. The total measurement and computation time per sample was of the order of 15 minutes.

To evaluate the errors introduced by the assumed values of Li_2O and B_2O_3 at the iterative endpoint, lot 84-133 S-glass samples were analyzed using XRF-11 with the secondary standards. In this particular study, the B_2O_3 concentration was fixed arbitrarily at a low or a high value, and the Li_2O concentration was adjusted to the iterative end point. A wide range of values of the ($\text{Li}_2\text{O}/\text{B}_2\text{O}_3$) ratio at the end point was achieved by this procedure. The average results of this study are summarized in Table IV, and they clearly demonstrate that changes in the calculated values of the measured components are small for a large change in the ($\text{Li}_2\text{O}/\text{B}_2\text{O}_3$) ratio at the iterative endpoint. It is observed, in addition, that changes in the sum ($\text{Li}_2\text{O} + \text{B}_2\text{O}_3$) are also relatively small. It is therefore concluded that errors caused by the use of non-unique values of the two unmeasured unknowns at the iterative end point are small.

Each of the S-glass secondary standards was also analyzed against the secondary standard set using the iterative adjustment procedure for the light element components. The results are presented in Table V together with those obtained by using standard sets A and B (which are described later). The good agreement between the chemical data and the XRF results with the secondary standard set only provides additional support for the iterative procedure but does not confirm the chemical analysis since the analyzed samples form the secondary standard set. The errors observed in the analysis of 83-455-3 by standard sets A and B are described later.

ANALYSIS OF MEASUREMENT AND SAMPLE-TO-SAMPLE ERRORS

Six S-glass samples (three from lot 84-132 and three from 84-133) were analyzed 5 times on each face for K_2O , SiO_2 , Al_2O_3 , P_2O_5 , and $(Li_2O + B_2O_3)$ by XRF-11 using the secondary standard set with an iterative adjustment, as described above, for the light element unknowns. The experimental estimate of the composition of each sample and the overall estimated composition for each lot based on the use of the secondary standards are presented in Table VI.

Useful measures of sample-to-sample variability and measurement variability are the sample-to-sample variance (σ_s^2) and the measurement variance (σ_m^2). The square roots of the estimates of each of these two variance components ($\hat{\sigma}_s$, $\hat{\sigma}_m$) were obtained for the four chemical components of each melt and are displayed in Table VII. In addition, F-tests were performed in order to assess the significance of the sample-to-sample variability of each chemical constituent for each melt, given the associated measurement variability. Note that the relative measurement-to-measurement errors are about 0.5 percent for each component in both lots. Due to this good measurement precision some

small, but significant, sample-to-sample variability was detected. Because, however, of the relatively few samples (3/lot), the sample-to-sample error effect could not be precisely estimated. It was also observed that measurement errors associated with SiO_2 , Al_2O_3 , and P_2O_5 appear to be highly correlated. We tentatively attribute this effect to a combination of secondary enhancement by K and instrumental sensitivity to K.

While the precision of the XRF procedure is good, the accuracy depends on the quality of the standards used as shown in the next section.

ACCURACY OF RESULTS

To gain some insight on the quality of the secondary standards and the accuracy of the results, two additional standards sets were developed. Each of the secondary standards was then analyzed using the new standard sets with an iterative adjustment of the light elements using XRF-11. Then each of the 84-132 and 84-133 samples was analyzed once using one of the new standard sets.

Standard set A was formed from NBS SRM 93a borosilicate glass and a pressed disc of K_2HPO_4 . During XRF studies, dead-time corrections were made for K and P intensity measurements.

Standard set B was formed from NBS SRM 93a borosilicate glass and two fusion standards prepared in a Claisse fluxer. One fusion standard, prepared from K_2CO_3 and $\text{Li}_2\text{B}_4\text{O}_7$, contained 2.056 weight percent K_2O . The other fusion standard, prepared from Li_3PO_4 and $\text{Li}_2\text{B}_4\text{O}_7$, contained 0.984 weight percent P_2O_5 .

Results for the analysis of the secondary standards using the two new standard sets are presented in Table V. Except for SiO_2 , the results obtained

with the two new standard sets are reasonably self-consistent and agree well with the chemical values for 83-458-4. They differ from the chemical analysis of 83-455-3 (Al_2O_3 and P_2O_5) and highlight the 8 percent relative uncertainty in the chemical analysis.

The overall average estimated composition of lot 84-132 is presented with the results from a round robin study[2] on the same lot in Table VIII. The results obtained using standard set A are also presented in Table VIII. With the exception of SiO_2 , the average XRF determinations are within the error bars of the round robin results. Note that the round robin estimates of component percentages sum to less than 100 percent (99.16 percent). This deficiency is approximately equal to the difference between the XRF and round robin SiO_2 analyses.

The XRF analysis of 84-132 and 84-133 samples using standard set A with an iterative adjustment of the light element components is presented in Table IX. The average value for 84-132 samples is also presented in Table VIII for comparison with the round-robin results and those obtained from the secondary standards. If we assume that the results for 84-132 S-glass, displayed in Table VIII, obtained by both sets of XRF standards are inherently accurate, then there is a significant discrepancy between the two results based on the estimated relative measurement error of ~ 0.5%. Furthermore, by examining Table V, it is apparent that the analysis of 83-455-3 was probably inaccurate. Therefore 83-455-3, a member of the secondary standard set, is most likely the cause of this discrepancy. We assume that the results due to standard set A are more accurate because the composition of this standard set is known more accurately. Thus, the differences in Table VIII clearly demonstrate that the accuracy of the XRF results depends on the quality of the standards used.

CONCLUSIONS

We have shown that accurate and rapid analyses of S-glass can be made using XRF techniques, fundamental parameters, a suitable set of standards, and an iterative procedure for two unmeasured light element unknowns. The precision of measurement was found to be good. The accuracy, however, depends on the quality of the standards used.

ACKNOWLEDGMENT

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2. Raymond M. Merrill, James P. McCarthy, and Richard J. Antepencko, "The Analysis of S-Glass Ceramic Lot #84-132 For Use as a Standard Reference Material," SAND86-0065, April 1986.

Table I. S-Glass Measuring Parameters.

<u>Element</u>	<u>Crystal</u>	<u>Collimator</u>	<u>Counting Time (Sec)</u>	<u>kV/mA</u>
K	LiF(200)	0.15°	20	20/30
Si	PET	0.15°	20	20/50
Al	PET	0.40°	20	50/55
P	Ge(111)	0.40°	40	50/55

Table II. Composition of S-Glass Samples 83-455-3 and 83-458-4 in Weight Percent.

	<u>83-455-3</u>	<u>83-458-4</u>
K_2O^{**}	4.04	4.82
SiO_2^{***}	(73.48)	(72.37)
$Al_2O_3^*$	5.37	5.31
$P_2O_5^*$	2.72	2.78
$B_2O_3^{**}$	2.09	2.22
Li_2O^*	12.3	12.5
$Li_2O+B_2O_3$	14.39	14.72

* ICP
 ** Flame AES
 *** By difference

Table III. Concentration Changes During a Typical Light Element Iteration.

Iteration #	K ₂ O	Weight Percent						Total	Norm. CHI	Li ₂ O/ B ₂ O ₃
		SiO ₂	Al ₂ O ₃	P ₂ O ₅	Assumed		Li ₂ O+ B ₂ O ₃			
					B ₂ O ₃	Li ₂ O				
1	4.542	72.350	5.177	2.379	1.500	12.600	14.100	98.548	3.40	8.40
2	4.460	71.799	5.152	2.340	1.500	14.600	16.100	99.851	0.35	9.73
3	4.452	71.741	5.150	2.336	1.500	14.810	16.310	99.989	0.03	9.87
4	4.451	71.736	5.149	2.336	1.500	14.825	16.325	99.998	0.00	9.88

Table IV. Estimated Composition of Lot 84-133 S-Glass Samples Found by XRF-11 Using the Secondary Standard Set with Iterative Adjustment of the Light Element Concentrations. Effect of the Final Li₂O/B₂O₃ Ratio on the Results.

Sample	Weight Percent					
	K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Li ₂ O+B ₂ O ₃	Li ₂ O/B ₂ O ₃
84-133-2	4.62	71.01	4.35	3.06	16.96	2.73
	4.58	70.37	4.31	3.03	17.70	7.08
84-133-4	4.60	71.44	4.36	3.06	16.54	3.00
	4.57	70.87	4.32	3.04	17.20	7.53
84-133-5	4.50	71.68	4.43	3.09	16.31	3.17
	4.46	71.16	4.40	3.07	16.90	7.45

Table V. Analysis of Individual Standards Using XRF-11 with the Several Standard Sets. Iterative Adjustment of the Light Element Components. Comparison with Chemical Data.

Sample	Standards Used	Weight Percent						
		K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Li ₂ O	B ₂ O ₃	Li ₂ O+B ₂ O ₃
83-455-3	Chem. Data*	4.04	73.48	5.37	2.72	2.09	12.3	14.39
	Sec.Std.Set	4.04	73.37	5.39	2.71			14.50
	Std. Set A	4.20	74.17	5.59	2.52			13.52
	Std. Set B	4.15	74.97	5.62	2.49			12.77
84-458-4	Chem. Data*	4.82	72.37	5.31	2.78	2.22	12.5	14.72
	Sec.Std.Set	4.82	72.49	5.30	2.79			14.60
	Std. Set A	4.95	72.55	5.29	2.80			14.43
	Std. Set B	4.95	73.82	5.34	2.76			13.12

*Results from chemical analysis of sample (from Table II).

Table VI. Average Composition of S-Glass Samples Found by XRF-11 Using Secondary Standards with Iterative Adjustment of the Light Element Unknowns.

Sample	Weight Percent				
	K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Li ₂ O+B ₂ O ₃
84-132-4	4.37	74.54	5.04	2.48	13.59
84-132-5	4.39	74.97	5.06	2.50	13.12
<u>84-132-7</u>	<u>4.34</u>	<u>74.97</u>	<u>5.06</u>	<u>2.51</u>	<u>13.12</u>
Average	4.37	74.83	5.05	2.50	13.28
84-133-2	4.62	71.01	4.35	3.07	16.94
84-133-4	4.57	70.78	4.35	3.06	17.24
<u>84-133-5</u>	<u>4.46</u>	<u>70.96</u>	<u>4.39</u>	<u>3.08</u>	<u>17.10</u>
Average	4.55	70.92	4.36	3.07	17.09

Table VII. Analysis of Measurement and Sample-to-Sample Errors.

S-Glass Lot	Component	Weight Percent	Estimated Measurement	Relative Measurement	Estimated Sample-to-Sample
			Error ($\hat{\sigma}_m$)	Error	Error ($\hat{\sigma}_s$)
84-132	K ₂ O	4.37	0.022	0.005	0.020
	SiO ₂	74.8	0.25	0.003	0.24
	Al ₂ O ₃	5.05	0.018	0.004	0.013
	P ₂ O ₅	2.50	0.012	0.005	0.014
84-133	K ₂ O	4.55	0.018	0.004	0.083
	SiO ₂	70.9	0.28	0.004	0.086
	Al ₂ O ₃	4.36	0.018	0.004	0.022
	P ₂ O ₅	3.07	0.013	0.004	0.0085

Table VIII. Comparison of Results for Lot 84-132 S-Glass.

Component	Weight Percent		
	Round Robin Values[2]	Secondary Standards	XRF-11 Standard Set A
K ₂ O	4.26±0.34	4.37	4.48
SiO ₂	74.05±0.20	74.83	74.81
Al ₂ O ₃	5.05±0.25	5.05	5.16
P ₂ O ₅	2.47±0.13	2.50	2.35
B ₂ O ₃	0.96±0.10		
Li ₂ O	12.37±0.36		
Li ₂ O+B ₂ O ₃	13.33±0.37	13.28	13.20
Total	99.16±0.61	100.03	100.00

Table IX. Fundamental Parameter Results for 84-132 and 84-133 Samples Using Standard Set A with Iterative Adjustment of Light Element Components.

Sample	Weight Percent				
	K_2O	SiO_2	Al_2O_3	P_2O_5	$Li_2O+B_2O_3$
84-132-4	4.51	74.83	5.16	2.35	13.14
84-132-5	4.48	75.05	5.17	2.36	12.94
<u>84-132-7</u>	<u>4.46</u>	<u>74.54</u>	<u>5.14</u>	<u>2.34</u>	<u>13.53</u>
Average	4.48	74.81	5.16	2.35	13.20
84-133-2	4.57	70.66	4.39	2.95	17.43
84-133-4	4.75	70.59	4.35	3.00	17.30
<u>84-133-5</u>	<u>4.67</u>	<u>70.54</u>	<u>4.36</u>	<u>2.99</u>	<u>17.43</u>
Average	4.66	70.60	4.37	2.98	17.39

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