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An interlaboratory study of a standard glass for acceptance testing of low-activity waste glass

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Abstract

An interlaboratory study was conducted to determine the precision with which the composition and chemical durability of a borosilicate glass could be measured and to generate a data base of expected values for that glass. The study was conducted with a low-activity reference material (LRM) glass that was developed for use as a standard material for acceptance testing of immobilized low-activity waste (ILAW) products, including those to be made with Hanford tank wastes. The study provided nine independent measurements of the LRM glass composition and eight independent sets of triplicate product consistency tests (PCTs) at 40°C and 90°C. Statistical analysis of these data indicates that LRM glass is suitable for use as a composition and test standard. The results from this study can be used to evaluate the accuracy of composition analyses and PCTs conducted with LRM glass at other laboratories in conjunction with acceptance tests conducted with ILAW products. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Some of the low-activity radioactive wastes at US Department of Energy (DOE) facilities will be vitrified to produce glass waste forms for disposal. The largest volume of low-activity wastes (ILAW) will be generated during remediation of tank wastes at the Hanford, Washington site. Both high-level and low-activity glass waste forms will be produced from tank wastes by a private contractor and returned to DOE for eventual disposal. These waste forms must meet contractual product specifications regarding physical, chemical, and radiological properties to ensure their suitability for transfer, handling, and disposal for DOE acceptance [1].

Tests have been conducted at Argonne National Laboratory (ANL) to evaluate the adequacy of several of the tests and analyses specified in the Hanford contract for the immobilized ILAW products. A glass referred to as the low-activity reference material (LRM)

was formulated for use in those tests and for possible use as a composition and test standard for acceptance testing of DOE ILAW products [2]. Since the composition(s) of the waste forms for the Hanford tank wastes has not yet been finalized, the LRM glass was formulated based on the anticipated low-activity waste stream for pretreated Hanford wastes and contains chemical additives that might be used for vitrification of the waste. The responses of the LRM glass in the tests and analyses are expected to be representative of the responses of ILAW products.

About 1.5 kg of LRM glass was made at ANL for initial testing; this is referred to as LRM-1 glass to distinguish it from the LRM glass made for use as a standard material. Testing included analysis of the microstructure, density [3], and compressive strength [4] of this glass and measurement of its response in Toxicity Characteristic Leach Procedure (TCLP) tests [5], ANSI/ANS 16.1 leach tests [6], and American Society for Testing and Materials (ASTM) standard C1285-97, which is referred to hereafter as the Product Consistency Test (PCT) [7]. The results of tests and analyses with LRM-1 glass indicated that these test methods were appropriate for ILAW, and that LRM glass was a 'suitable' standard material [8], where suitability means

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that a property or response could be measured with sufficient precision by using the contractually prescribed method. In addition, the responses of LRM-1 glass in these tests were within the values required for ILAW products in the DOE contract. Subsequently, about 454 kg (1000 lb) of LRM glass was procured from Ferro Corp. (Cleveland, OH) for use as a standard test material. The target compositions of the LRM-1 and LRM glasses were identical except the LRM-1 glass contained small amounts of Cl and Sn whereas these components were excluded from the LRM glass.

Two key properties of ILAW products that must be determined are the chemical composition of the glass (elements present at > 0.5 mass% and elements required to meet regulator and contractual requirements must be quantified, see Section 2.2.2.6.1 in [1]) and its response in PCTs at 40°C and 90°C. The concentration of Na₂O in the waste form is used to determine the waste loading (see Section 2.2.2.2 in [1]), and the PCT results are used to determine the chemical durability and radionuclide release rates (based on the amounts of sodium, silicon, and boron released in the test, see Section 2.2.2.17.2 in [1]). The results for these and other analyses of ILAW products must be reported by the contractor. Note that the LRM glass does not contain and cannot be used as a standard for the concentrations of ⁹⁰Sr, ⁹⁹Tc, or ¹³⁷Cs in ILAW, for which limits are specified in the contract (see Section 2.2.2.8 in [1]). A separate composition standard is needed for these radionuclides.

The interlaboratory study (ILS) discussed in this paper was conducted to evaluate the use of LRM glass as: (1) a composition standard for non-radioactive components of the waste forms, including sodium, and (2) a standard material for a chemical durability test based on the PCT [7]. The results of the ILS were then used as data bases to establish expected values and precision for analysis of LRM glass conducted as a part of acceptance testing. The ILS was conducted as a two-part study following the procedure in ASTM standard E691-92 [9]. In the first part, participants analyzed the composition of the LRM glass by their method of choice. In the second part, participants conducted triplicate PCTs at 40°C and 90°C. Sample lots provided to participants were taken from a batch of glass that had been crushed, sieved, and washed to remove fines at ANL. This was done to maximize the homogeneity of the samples and to constrain the study of testing and analytical precision that can be 'attributed to unavoidable random errors inherent in every test procedure' [9]. This has the effect of eliminating possible variations due to sample preparation from the measured precision. The factors that may contribute to the variability in the test results include the operator, equipment used, calibration of equipment, and the laboratory environment.

The present authors have analyzed the data base generated in the ILS to determine the precision that can be expected for analysis of the glass composition and execution of the PCT. This information can be used to directly assess the analyses conducted by contractor laboratories with the LRM glass and indirectly assess the reliability of acceptance tests conducted with actual waste glasses. That is, the precision and accuracy with which a laboratory can analyze LRM glass provide an indication of the precision and accuracy with which that laboratory can analyze actual ILAW products. This paper summarizes the statistical analyses for the ILS with LRM glass and the expected intralaboratory and interlaboratory precision for composition and PCT analyses. A more detailed description of the ILS, test results, and statistical analysis is available elsewhere [10].

2. Experimental

About 250 g of glass received from Ferro Corp. was prepared at ANL for use in the ILS following the sample preparation steps given in the PCT procedure [7]. The glass was crushed and sieved to isolate the -100 +200 mesh size fraction (i.e., the size fraction between 74 and 140 μm) then repeatedly washed with absolute ethanol to remove fines. A small amount of washed glass was examined with a scanning electron microscope to verify that the particles were of the appropriate size and that fines had been removed. The glass was divided into aliquots of about 17 g, which were provided to each participant for use in both the composition analysis and PCT parts of the study.

No restrictions were placed on the method used to dissolve the glass for chemical analysis or the analytical techniques to be used, except that the methods used to dissolve and analyze the glass had to be reported with the analytical results. The composition of the prototype glass LRM-1 was provided to facilitate selection of the methods for composition analysis of the LRM glass.

The participants were instructed to follow the PCT procedure for tests at both 40°C and 90°C as closely as possible, except that the tests with a standard reference glass that are called for in the PCT were not required. Key aspects of the test procedure are summarized below:

- Three replicate tests were to be conducted at both 40°C and 90°C with between 1 and 1.5 g of crushed glass and a mass of demineralized water (ASTM Type I water) that was exactly 10 times the mass of glass used.
- Tests were to be conducted for seven days. The times of day a test vessel was placed in and removed from the oven were required to agree within 3.4 h.
- The use of unsensitized Type 304L stainless steel vessels was preferred, but tests could be conducted with Teflon vessels if steel vessels were not available. The

vessel type used in the tests were to be reported and cleaned according to the PCT procedure. (All participants used Type 304L stainless steel vessels.)

- Duplicate blank tests with demineralized water were to be conducted simultaneously with the tests with glass. The vessels used in the blank tests were to have been cleaned in the same batch as the vessels used in the tests with glass.
- The oven temperature was to remain within 2°C of the test temperature throughout the test.
- The total mass of the test vessel was not to have changed during the test by more than 5% of the mass of demineralized water that was initially added to the vessel.
- Solutions generated in the tests with glass and the blank tests were to be filtered through 0.45-µm pore size filters, acidified with concentrated nitric acid, and then analyzed for B, Na, and Si. Estimated detection limits were to be reported.

- While a particular analytical method was not required for solution analysis, the method(s) used was to be reported.

3. Results

In the following discussion, the ILS participants are designated by index letters. In some cases, the same participant or different scientists at the same participating laboratory conducted more than one composition analysis or set of PCTs. Some laboratories used more than one dissolution procedure or conducted replicate dissolutions following the same procedure. For the purpose of data analysis, all solution analyses conducted on the same instrument are treated as replicate tests, and the average values are used in the statistical analysis. The results of analyses performed at

Table 1
Compositions of LRM glass measured by participants, in oxide mass%

Oxide	A	B(2) ^a	C(2)	D(2)	E(5)	F(2)	G(3)	J	K
Al ₂ O ₃	9.33	9.90	10.05	9.69	9.01	9.25	9.39	9.91	9.33
B ₂ O ₃	8.19	7.49	8.23	7.86	7.68	7.41	8.25	7.97	8
BaO	0.0009	0.002	– ^b	<0.005	<0.004	<0.01	–	<0.003	<0.012
CaO	0.6	0.518	0.488	0.52	0.56	0.56	0.52	0.46	0.61
CdO	0.13	0.149	0.154	0.17	0.17	0.16	0.18	0.17	0.14
Cl	–	<0.1	–	0.15	–	–	–	<0.003	0.04
Cr ₂ O ₃	0.15	0.19	0.173	0.205	0.21	0.20	0.21	0.18	0.23
F	–	0.86	–	0.695	–	–	–	0.89	1
Fe ₂ O ₃	1.46	1.39	1.39	1.51	1.42	1.06	1.44	1.4	1.69
HgO	–	–	–	–	<0.004	–	–	–	<0.002
I	–	<0.02	–	–	–	–	–	<0.01	<0.004
K ₂ O	1.77	1.41	1.32	1.27	1.50	1.58	1.40	1.46	1.62
La ₂ O ₃	0.005	0.011	–	–	0.02	0.02	–	0.016	0.03
Li ₂ O	0.1	–	0.168	0.075	0.12	0.11	0.09	0.1	–
MgO	0.11	0.103	0.093	0.11	0.12	0.10	0.10	0.11	0.09
MnO	0.068	0.071	0.0785	0.075	0.11	0.07	0.08	0.093	0.09
MoO ₃	0.11	0.087	–	0.11	0.11	0.09	0.10	0.1	0.09
Na ₂ O	20.2	17.8	20.4	20.2	18.44	21.00	21.9	20.8	19.53
NiO	0.16	0.178	0.173	0.19	0.19	0.16	0.20	0.19	0.23
P ₂ O ₅	0.54	0.482	0.548	0.555	0.54	0.63	0.51	0.45	0.48
PbO	0.078	0.068	0.107	0.08	0.12	0.14	0.09	0.096	0.08
SO ₃	–	0.230	–	0.435	0.34	0.30	–	0.28	0.24
SiO ₂	55.7	51.99	54.2	55.27	51.94	53.65	55.2	55.1	55.28
SnO ₂	0.00007	–	–	–	0.02	0.10	–	–	0.01
TiO ₂	0.11	0.102	0.0885	0.095	0.11	0.10	0.10	0.1	0.14
ZrO ₂	0.82	0.973	0.866	1.01	0.99	0.92	0.97	0.95	0.84
Total	99.6538	93.995	98.522	99.9855	93.722	97.56	100.73	100.825	99.79

^a The value in parentheses is the number of replicate analyses performed. The average composition values are given in the column below.

^b ‘–’ indicates that no value was reported by participant.

Table 2
Results of PCT with LRM glass^a

Participant	pH	Al (mg/l)	B (mg/l)	Na (mg/l)	Si (mg/l)
<i>Tests at 40°C</i>					
A	10.24 ± 0.01	2.35 ± 0.08	2.05 ± 0.11	22.4 ± 0.4	15.5 ± 0.9
B	9.89 ± 0.08	2.30 ± 0.09	2.00 ± 0.08	19.1 ± 0.7	12.8 ± 0.6
C	9.95 ± 0.04	– ^b	2.59 ± 0.15	22.3 ± 0.9	13.5 ± 0.5
D	9.98 ± 0.03	–	2.47 ± 0.10	21.6 ± 0.6	12.5 ± 1.0
E	9.41 ± 0.01	1.93 ± 0.08	2.77 ± 0.27	17.9 ± 0.10	14.9 ± 0.2
F	9.90 ± 0.01	2.1 ± 0.1	2.3 ± 0.1	20 ± 0	12 ± 0
G	9.3 ± 0.1	1.6 ± 0.3	1.5 ± 0.02	15.3 ± 0.6	(8.1 ± 0.3) ^c
H	10.20 ± 0.01	2.56 ± 0.14	2.65 ± 0.27	18.5 ± 1.1	14.9 ± 0.9
Consensus ^d	9.86	2.15	2.30	19.6	13.7
<i>Tests at 90°C</i>					
A	10.98 ± 0.01	13.6 ± 0.2	25.0 ± 0.8	173 ± 3	83.2 ± 1.0
B	11.00 ± 0.04	14.5 ± 0.5	22.6 ± 0.3	158 ± 5	84.8 ± 1.0
C	11.03 ± 0.01	–	29.2 ± 0.8	169 ± 1	84.1 ± 1.5
D	11.05 ± 0.01	–	29.7 ± 0.5	170 ± 7	84.3 ± 1.5
E	10.81 ± 0.01	13.3 ± 0.1	27.9 ± 0.2	143 ± 2	85.7 ± 0.3
F	10.98 ± 0.02	12 ± 0.0	27 ± 1.2	150 ± 6	76 ± 1.5
G	10.6 ± 0.01	13 ± 0.6	26 ± 0.1	150 ± 0	75 ± 1.5
H	10.93 ± 0.07	19.0 ± 2.1	(36.3 ± 3.6)	(202 ± 1)	(112 ± 8)
Consensus	10.92	12.5	26.7	160	82.0

^a Mean ± standard deviation (s_p).

^b ‘–’ indicates that no value was reported by participant.

^c Numbers in parentheses were determined to be outliers and were excluded from the consensus value.

^d The consensus values are the averages of the mean values.

Table 3
Results of PCT blank tests^a

Participant	pH	Al (mg/l)	B (mg/l)	Na (mg/l)	Si (mg/l)
<i>Tests at 40°C</i>					
A	6.65 / 6.27	<0.1/<0.1	<0.1/<0.1	<0.07/<0.07	<0.08/<0.08
B	<7/<7	0.25/<0.2	0.13/0.10	<0.1/<0.1	<0.5/<0.5
C ^b	6.78 / 6.76	– ^c	0.30/<0.3	1.2/<0.9	<0.3/<0.3
D ^b	6.78/6.76	–	0.30/<0.3	1.2/<0.9	<0.3/<0.3
E	6.03/6.05	<0.11/<0.11	<0.54/<0.54	<0.1/<0.1	0.50/0.32
F	5.96/5.84	<0.04/<0.04	<0.01/<0.01	0.12/0.10	<0.01/<0.01
G ^d	5.5	<0.015	0.090	<0.022	<0.01
H	–	<0.02/<0.02	<0.01/<0.01	<0.02/0.04	<0.02/<0.02
<i>Tests at 90°C</i>					
A	6/42/6.53	<0.1/<0.1	<0.1/<0.1	<0.07/<0.07	<0.08/<0.08
B	<7/<7	0.26/0.29	0.12/0.14	<0.1/<0.1	<0.5/<0.5
C ^b	6.72/6.82	–	<0.3/<0.3	1.4/<0.9	<0.3/<0.3
D ^b	6.72/6.82	–	<0.3/<0.3	1.4/<0.9	<0.3/<0.3
E	6.12/6.14	<0.11/<0.11	<0.54/<0.54	<0.1/<0.1	1.3/1.3
F	5.80/5.75	<0.04/<0.04	<0.01/<0.01	0.068/0.098	<0.01/<0.01
G ^d	6.4	<0.015	0.044	<0.022	<0.010
H	–	<0.02/<0.02	<0.01/<0.01	0.053/0.38	<0.02/<0.02

^a Values for the two blank tests are separated by slash.

^b The same blank tests were utilized by participants C and D.

^c ‘–’ indicates that no value was reported by participant.

^d Average of duplicate tests was reported by participant.

the same laboratory but with different instruments are treated as being independent. Note that participant H did not provide composition results, participant I did not complete the ILS, and participant J did not provide PCT results.

3.1. Composition analysis

Results from nine independent participants were available for the composition analysis. (The results

provided by the glass supplier are included as an independent analysis.) The methods used by each participant to dissolve the glass and analyze the resulting solutions are summarized in Tables 8 and 9, respectively. The average results for each participant are given in Table 1 with the same number of significant figures reported by the participants. The values in Table 1 represent the averages of replicate dissolutions and analyses conducted at the same laboratory with the same analytical technique and the same instrument; the

Table 4
Summary of precision for glass composition data, in mass%^a

Component	\bar{x}	s_r	s_x	s_L	s_R	I(r)	I(R)
Al ₂ O ₃	9.51	0.119	0.346	0.336	0.356	0.335	1.008
B ₂ O ₃	7.85	0.146	0.327	0.311	0.343	0.413	0.971
BaO	0.00	nd ^b	0.001	nd	nd	nd	nd
CaO	0.54	0.003	0.086	0.086	0.086	0.008	0.244
CdO	0.16	0.003	0.015	0.015	0.015	0.008	0.042
Cr ₂ O ₃	0.19	0.005	0.021	0.021	0.022	0.013	0.061
F	0.86	0.035	0.109	0.106	0.112	0.100	0.317
Fe ₂ O ₃	1.38	0.042	0.184	0.181	0.186	0.120	0.526
I	nd	nd	nd	nd	nd	nd	nd
K ₂ O	1.48	0.008	0.489	0.489	0.489	0.022	1.383
La ₂ O ₃	0.02	nd	0.008	nd	nd	nd	nd
Li ₂ O	0.11	0.004	0.026	0.026	0.026	0.010	0.074
MgO	0.10	0.004	0.009	0.008	0.009	0.012	0.026
MnO	0.08	0.004	0.013	0.013	0.014	0.011	0.039
MoO ₃	0.10	nd	0.009	nd	nd	nd	nd
Na ₂ O	20.03	0.249	1.202	1.189	1.215	0.705	3.439
NiO	0.19	0.013	0.020	0.018	0.022	0.036	0.063
P ₂ O ₅	0.54	0.008	0.065	0.065	0.065	0.021	0.184
PbO	0.10	0.023	0.026	0.020	0.031	0.066	0.088
SO ₃	0.30	0.049	0.068	0.059	0.077	0.140	0.218
SiO ₂	54.20	0.752	1.318	1.206	1.421	2.128	4.022
TiO ₂	0.10	0.004	0.013	0.013	0.013	0.010	0.038
ZrO ₂	0.93	0.004	0.064	0.064	0.065	0.010	0.183

^a Symbols defined in text.

^b Value was not determined.

Table 5
Summary of precision for PCTs^a

	\bar{x}	s_r	s_x	s_L	s_R	I(r)	I(R)
<i>Tests at 40°C</i>							
pH	9.86	0.040	0.338	0.338	0.340	0.113	0.962
Al	2.15	0.131	0.341	0.333	0.358	0.372	1.012
B	2.30	0.156	0.423	0.413	0.441	0.441	1.249
Na	19.7	0.664	2.530	2.501	2.588	1.88	7.32
Si	13.7	0.640	2.372	1.321	1.468	1.81	4.15
<i>Tests at 90°C</i>							
pH	10.9	0.033	0.150	0.149	0.152	0.092	0.431
Al	14.3	0.922	2.415	2.415	2.585	2.61	7.32
B	26.7	0.647	2.479	2.451	2.535	1.83	7.17
Na	160	4.061	11.48	11.23	11.95	11.5	33.8
Si	82.0	1.247	4.360	4.302	4.479	3.53	12.67

^a Symbols defined in text. Concentrations of Al, B, Na, and Si in mg/l.

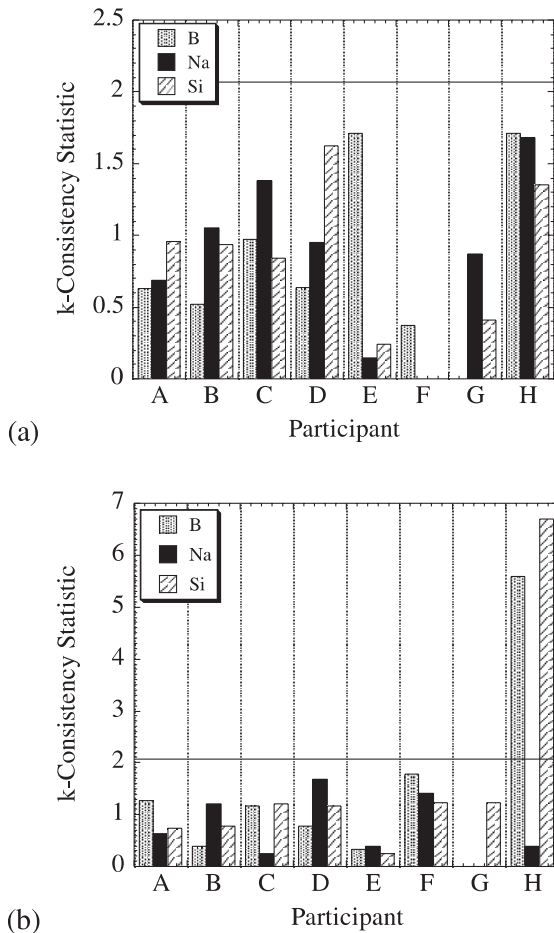


Fig. 1. Plot of intralaboratory consistency statistic (k) for concentrations of B, Na, and Si measured by participants in PCT at: (a) 40°C and (b) 90°C. The horizontal lines indicate the critical k -value of 2.06 for this data set.

numbers of replicate analyses that are included in the average are given in parentheses following the participant indices.

The objectives of this portion of the ILS were to determine the consensus concentration values of glass components, measure the interlaboratory precision for compositional analysis, and determine if the LRM glass was suitable for use as a composition standard (and for which elements). The objective was not to evaluate particular analytical methods used at different laboratories. Hence, the precision of the reported results includes uncertainties due to both the dissolution and analytical procedures.

3.2. Durability tests

Results from eight independent participants were available for PCTs conducted at 40°C and 90°C. The

mean and standard deviations (s_p , see below) of the reported solution concentrations of Al, B, Na, and Si measured in the PCTs are presented in Table 2. Results are for triplicate PCTs except for participant E (six replicate tests at both 40°C and 90°C) and participant H (four replicate tests at 40°C). Determination of the reproducibility of the PCTs includes variability in test performance and in solution analysis.

Whereas the PCT calls for subtracting the background concentration of an element from the concentration of that element in a test with glass, the results of the ILS were analyzed without background subtraction. This has the effect of combining the uncertainties of the test solutions and the blanks and provides a conservative measure of the precision of the PCTs.

The values of the duplicate blank tests for each participant are summarized in Table 3. The data reported show that analytical sensitivities (detection limits) for each component varied slightly among participants. Measurable concentrations of Al, B, Na, or Si were found in at least one blank test from at least one of the participants. At least one blank test had measurable concentrations of Al, B, Na, or Si for all participants except participant A. In most cases, measurable concentrations were found by a participant in tests at both temperatures. Three blank tests for participant B had measurable Al concentrations; four blank tests for participant B, one blank test for participants C/D, and blanks for participant G had measurable B concentrations; two blank tests for participants C/D and four blank tests for participant F had measurable Na concentrations; and four blank tests for participant E had measurable Si concentrations. In the 40°C tests, the concentrations measured in blank tests were significant with respect to the concentrations measured in tests with glass: the blank concentrations for various participants were as high as 11% of the Al concentrations measured in tests with glass, 12% for B, 6% for Na, and 3% for Si. The concentrations of Al, B, Na, and Si in the blank tests at 90°C were 2% or less of the concentrations measured in tests with glass. The blank tests give a measure of the accumulated contamination during vessel cleaning, testing, and solution analysis. These results suggest possible environmental contamination in some laboratories: participant B had measurable aluminum concentrations in three of four blank tests and measurable boron concentrations in all blank tests; participant F had measurable sodium concentrations in all blank tests; and participant E had measurable silicon concentrations in all blank tests.

Another potential source of variability in the PCTs is sample preparation, particularly the efficiency of removing fines. However, since all of the samples provided to the participants were taken from the same source prepared at ANL, variability due to sample preparation should not be a factor in the ILS. Because of the care

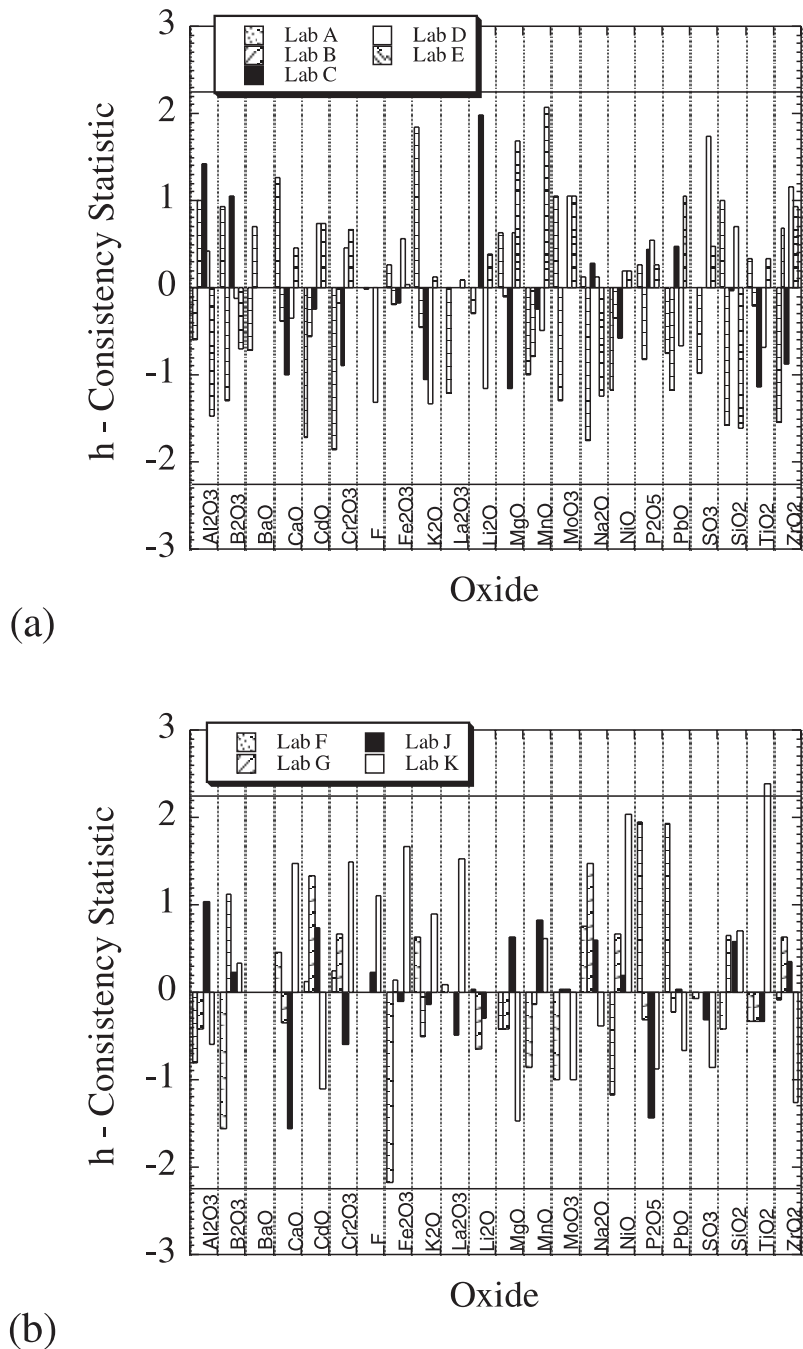


Fig. 2. Plot of interlaboratory consistency statistic (h) by glass component for: (a) Labs A, B, C, D, and E, and (b) Labs F, G, J, and K. The critical h -value for these analyses is ± 2.23 , which is shown by horizontal lines.

taken to remove fines from the material used in the ILS, the precision determined in this study is expected to provide a measure of the variation that should be expected in acceptance testing of actual ILAW products due to random uncontrollable errors.

4. Discussion

The results of the composition and PCT parts of the ILS were analyzed separately following the methods recommended in ASTM standard E691-92 [9] to assess

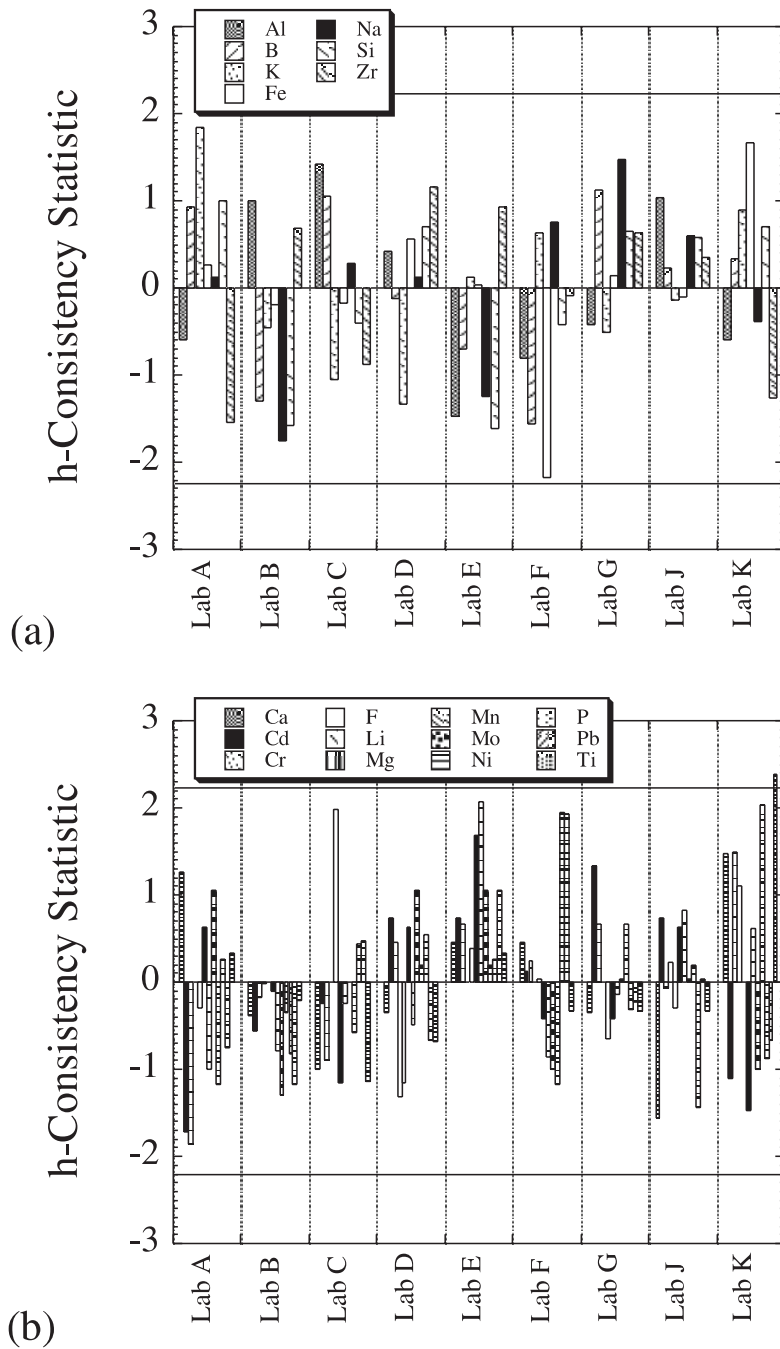


Fig. 3. Plot of interlaboratory consistency statistic (h) by Lab for components at (a) ≥ 0.5 element mass% and (b) < 0.5 element mass%. The critical h -value for these analyses is 2.23.

the repeatability and reproducibility. As defined in ASTM E691, Section 3.2.5, ‘repeatability concerns the variability between independent test results obtained within a single laboratory in the shortest practical period of time by a single operator with a specific set of test

apparatus using test specimens taken at random from a single quantity of homogeneous material obtained or prepared for the interlaboratory study. Reproducibility deals with the variability between single test results obtained in different laboratories, each of which has

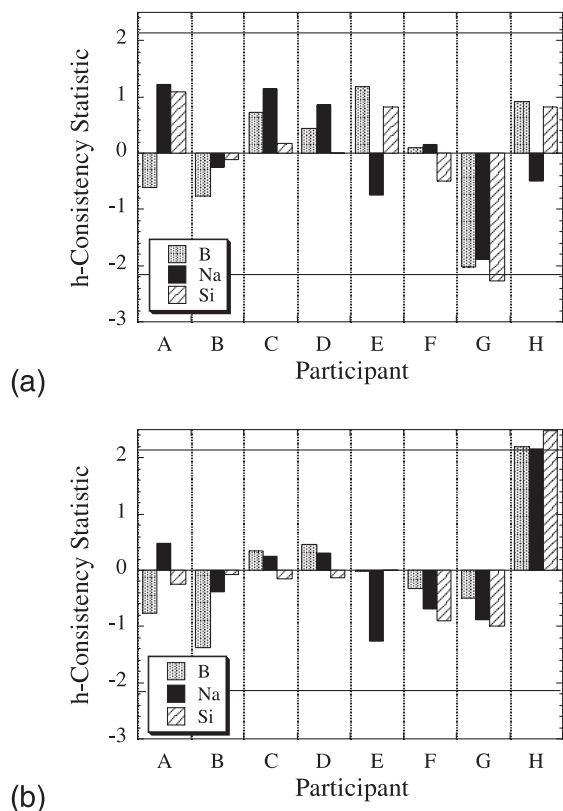


Fig. 4. Plot of interlaboratory consistency statistic (h) for concentrations of B, Na, and Si measured by participants in PCT at (a) 40°C and (b) 90°C. The horizontal lines indicate the critical h -value of ± 1.15 for this data set.

applied the test method to test specimens taken at random from a single quantity of homogeneous material obtained or prepared for the interlaboratory study' [9]. In the formulae that are summarized below, a 'cell' refers to the result of a measurement made by a partici-

Table 6
Repeatability^a and reproducibility^b for composition analysis of LRM glass

Component	Repeatability	Reproducibility
Al	5.03 ± 0.18	5.03 ± 0.53
B	2.44 ± 0.13	2.44 ± 0.30
Ca	0.386 ± 0.006	0.39 ± 0.17
Fe	0.965 ± 0.083	0.97 ± 0.37
K	1.23 ± 0.02	1.2 ± 1.2
Na	14.8 ± 0.5	14.8 ± 2.5
P	0.236 ± 0.009	0.236 ± 0.080
Si	25.3 ± 1.0	25.3 ± 1.9
Zr	0.689 ± 0.007	0.69 ± 0.14

^a Repeatability defined as $\bar{x} \pm I(r)$.

^b Reproducibility defined as $\bar{x} \pm I(R)$.

part, x refers to the value that is being measured, x_p is a measured value, n is the number of replicate measurements made by a participant, and p is the number of participants that provided a measurement of that value.

- The cell average of values measured by a participant in replicate tests (\bar{x}_p): $\bar{x}_p = \Sigma x_p / n$.
- The cell standard deviation for a participant (s_p): $s_p = [(\Sigma(x_p - \bar{x}_p)^2) / (n - 1)]^{1/2}$. This is a measure of the intralaboratory variability.
- The consensus average of the measured value (\bar{x}): $\bar{x} = \Sigma \bar{x}_p / p$. This is the average of the cell averages.
- The pooled intralaboratory standard deviation (s_r): $s_r = [\Sigma s_p^2 / p]^{1/2}$. This gives the estimated repeatability standard deviation for measurements made within a laboratory.
- The standard deviation of the cell averages for replicate tests by the same participant from the consensus average (s_x): $[\Sigma(\bar{x}_p - \bar{x})^2 / (p - 1)]^{1/2}$.
- The estimated interlaboratory variability, expressed as the square root of the component of variance (s_L): $s_L = [s_r^2 (s_x^2 / n)]^{1/2}$. This gives the standard deviation for the normal distribution of laboratory means.
- The interlaboratory estimate of precision (s_R): $s_R = (s_r^2 + s_L^2)^{1/2}$. This is the reproducibility standard deviation.

Two other expressions were used to express the repeatability and reproducibility:

- The estimated 95% repeatability level, $I(r)$: $I(r) = 2.83 \cdot s_r$. On the basis of test error alone, the absolute value of the difference of two test results obtained in the same laboratory will exceed $I(r)$ only approximately 5% of the time.
- The estimated 95% reproducibility level, $I(R)$: $I(R) = 2.83 \cdot s_R$. On the basis of test error alone (including intra- and inter-laboratory components), the absolute value of the difference between two test

Table 7
Repeatability^a and reproducibility^b for PCT with LRM glass

Component	Repeatability	Reproducibility
<i>Tests at 40°C</i>		
pH	9.86 ± 0.11	9.86 ± 0.96
Al	2.15 ± 0.37	2.15 ± 1.01
B	2.30 ± 0.44	2.30 ± 1.25
Na	19.7 ± 1.9	19.7 ± 7.3
Si	13.7 ± 1.8	13.7 ± 4.2
<i>Tests at 90°C</i>		
pH	10.9 ± 0.1	10.9 ± 0.4
Al	14.3 ± 2.6	14.3 ± 7.3
B	26.7 ± 1.8	26.7 ± 7.2
Na	160 ± 12	160 ± 34
Si	82.0 ± 3.5	82.0 ± 12.7

^a Repeatability defined as $\bar{x} \pm I(r)$.

^b Reproducibility defined as $\bar{x} \pm I(R)$.

Table 8
Sample preparation methods for composition analysis

Analysis no.	Sample preparation method
A	Digestion in mixture of HNO ₃ , HCl, and HF (analyzed for Al, B, Ba, Ca, Cd, Cr, Fe, Hf, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Sr, Ti, Zr)
B	Digestion in mixture of HNO ₃ , HCl, and HF (analyzed for Al, B, Ba, Ca, Cd, Cr, F, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, Ta, Th, Ti, V, Zn, Zr; for La analysis, HF was excluded and sample fumed into HClO ₄)
C1, C2	Na ₂ O ₂ /NaOH fusion in platinum crucible at 600°C followed by acidification with HCl and dilution with water (analyzed for Al, B, Li, Si)
C1, C2	LiBO ₂ fusion in platinum crucible at 900°C followed by acidification with HNO ₃ and dilution with water (analyzed for Ba, Ca, Cd, Cr, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sn, Te, Zr)
D1, D2	CsOH · H ₂ O fusion in zirconium crucible at 500°C followed by dilution with water and added H ₂ O ₂ and acidification with HNO ₃ (analyzed for Al, B, Ba, Cd, Fe, La, Mg, Mn, Mo, Ni, P, Pb, Si, Sn)
D1, D2	CsOH · H ₂ O fusion in nickel crucible at 500°C followed by dilution with water and added H ₂ O ₂ and acidification with HNO ₃ (analyzed for Zr)
D1, D2	Na ₂ O ₂ /NaOH fusion in zirconium or nickel crucible at 675°C followed by dilution with water and added H ₂ O ₂ and acidification with HNO ₃ (analyzed for Cl and F)
D1, D2	Microwave digestion in mixture of HF and HNO ₃ in Teflon vessel followed by acidification with H ₃ BO ₃ and HCl (analyzed for Ca, Cr, Hg, K, Li, Na, Ti)
E	Microwave digestion in mixture of HNO ₃ and HF (5:1 volume ratio) followed by dilution with water (analyzed for Al, B, Ba, Ca, Cd, Cr, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Ti, Zn)
F1	Na ₂ O ₂ /NaOH fusion in zirconium crucible followed by acidification with HNO ₃ (analyzed for Al, B, Ba, Ca, Cd, Cr, Fe, K, La, Li, Mg, Mn, Mo, Ni, P, Pb, S, Si, Sn, Ti)
F2	KOH/KNO ₃ fusion in nickel crucible followed by acidification with HNO ₃ (analyzed for Al, B, Ba, Ca, Cd, Cr, Fe, La, Li, Mg, Mn, Mo, Na, P, Pb, S, Si, Sn, Ti, Zn)
G	Microwave digestion in mixture of HNO ₃ , HCl, and HF in Teflon vessel (analyzed for Al, B, Cd, Cr, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Sn, Ti, Zn)
G	Microwave digestion in mixture of HNO ₃ , HCl, and HF in Teflon vessel followed by acidification with H ₃ BO ₃ and addition of EDTA (analyzed for Ca, Na, Si, Sn)
J	HF/HClO ₄ preparation (analyzed for Al, B, Ba, Ca, Cd, Cr, F, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Ti, Zn)
K	Glass was analyzed directly (analyzed for Al, B, Ba, Ca, Cd, Cr, F, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Ti, Zn)

results obtained in different laboratories will exceed I(R) only approximately 5% of the time.

The calculated values for these statistical parameters are summarized in Table 4 for the results of the composition analyses and Table 5 for the results of the PCTs. These parameters are used to evaluate the repeatability (the intralaboratory consistency) and the reproducibility (the interlaboratory consistency) that can be expected during ILAW product acceptance testing. Non-detects were excluded from the calculations.

The intralaboratory consistency is determined by the k -consistency statistic, which is defined as the standard deviation for a participant (s_p) divided by the repeatability standard deviation (s_r): $k = s_p/s_r$. It provides a measure of how the variability within a laboratory compares with that of all laboratories combined. The k -value is unitless. We deemed the data base for composition analysis to be too small to evaluate the k -consistency statistic, since participants were not requested to provide replicate composition analysis; however, this factor was evaluated for the PCTs conducted at 40°C and 90°C (Fig. 1). The critical k -value

for an ILS with eight participants conducting triplicate tests is 2.06 (see Table 12 in [9]). The critical value is provided in [9] to aid in the decision of whether or not the deviation in the results of a particular laboratory exceeds that expected due to random error and is sufficient to warrant investigation. We use the critical value to identify results to be excluded from the calculations of consensus values and the test precision. Examination of Fig. 1 shows that the k -values for all participants are less than the critical value for tests conducted at 40°C, but that the concentrations of B and Si measured by Lab H exceed the critical k -value in tests conducted at 90°C. This finding means that the variation in the 90°C PCT results for Lab H is inconsistent with (higher than) that for the other participants. It also indicates intralaboratory imprecision, which may be related to the test procedure or the solution analysis. Test results for which k -values exceeded the critical value were excluded from the calculations summarized in Table 5. Very small k -consistency parameter values indicate laboratories that have a less sensitive measurement scale than the other laboratories. For example, Fig. 1 indicates that the results of the 40°C PCT

Table 9
Analytical methods used at different laboratories^a

Element	A	B	C	D	E	F	G	J	K
Al	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
B	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	not determined
Ba	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	not determined	ICP/DCP	XRF
Ca	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Cd	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Cl	Not determined	IC	Not determined	ISE	Not determined	not determined	Not determined	Titration	XRF
Cr	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
F	Not determined	IC	Not determined	ISE	Not determined	ISE and XRF	Not determined	Pyrohydrolysis	Not determined
Fe	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Hg	Not determined	Not determined	Not determined	Cold vapor AA	DCP-AES	Not determined	Not determined	ICP/DCP	XRF
I	not determined	IC	Not determined	Not determined	Not determined	Not determined	Not determined	Titration	XRF
K	ICP-MS	ICP-AES	ICP-AES	Flame AA	DCP-AES	ICP-OES	ICP-AES	FES	XRF
La	not determined	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	not determined	ICP/DCP	XRF
Li	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	FES	not determined
Mg	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Mn	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Mo	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Na	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	FES	XRF
Ni	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
P	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Pb	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
S	Not determined	LECO	Not determined	IC	IC	ICP-OES	Not determined	LECO	XRF
Si	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Sn	ICP-MS	Not determined	Not determined	ICP-ES	DCP-AES	ICP-OES	ICP-AES	Not determined	XRF
Ti	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF
Zr	ICP-MS	ICP-AES	ICP-AES	ICP-ES	DCP-AES	ICP-OES	ICP-AES	ICP/DCP	XRF

^aAA – Atomic absorbance; ICP/DCP – Inductively coupled plasma-direct coupled plasma; IC – Ion chromatography; DCP-AES – Direct coupled plasma-atomic emission spectroscopy; ICP-ES – Inductively coupled plasma-emission spectroscopy; ISE – Ion selective electrode; FES – Flame emission spectroscopy; ICP-MS – Inductively coupled plasma-mass spectrometry; LECO – Combustion/infra-red spectroscopy; ICP-AES – Inductively coupled plasma-atomic emission spectroscopy; ICP-OES – Inductively coupled plasma-optical emission spectroscopy; XRF – X-ray fluorescence spectroscopy.

from Lab F and the results of the 90°C PCT from Lab E give k -values that are noticeably lower than the k -values for the other labs. This probably reflects the fact that the results from Lab F were reported to two significant figures (as were the results of Lab G), while other laboratories reported results to three significant figures. The lower k -value for Lab E may be because six replicates were conducted rather than three.

The interlaboratory consistency is determined by the h -consistency statistic, which is defined as the difference between the value measured by a participant (\bar{x}_p) and the consensus value (\bar{x}) divided by the standard deviation of the cell averages (s_x): $h = (\bar{x}_p - \bar{x})/s_x$. The h -value is unitless and can be used to evaluate the overall variability of the analyses among the participants and to compare the results of one participant against those of all the other participants. At the 0.5% significance level, the critical values of h for 8 and 9 participants are 2.15 and 2.23, respectively (see Table 12 in [9]).

The h -values calculated for the results of the nine independent measurements of the glass composition (represented on an oxide basis) are plotted in Fig. 2. Only the measurement of Ti (expressed as TiO₂) by Lab K (2.38) exceeds the critical h -value of 2.23. The TiO₂ content measured by Lab K was thus excluded from the calculations summarized in Table 4. The numbers of positive and negative h -values for each laboratory were evaluated to identify any bias. The h -values for the component concentrations are grouped by participant in Fig. 3. Components included in Fig. 3(a) are present at concentrations greater than 0.5 elemental mass%, and those included in Fig. 3(b) are present in LRM glass at concentrations less than 0.5 elemental mass%. The significance of this difference is that the DOE privatization contract requires that the concentrations of elements that are present in the ILAW waste forms at concentrations of 0.5 elemental mass% or higher be quantified. Inspection of Fig. 3(a) indicates no bias in the analysis of LRM glass for these elements by any of the participants. However, the h -values for Labs B and C are biased low and the h -values for Lab E are biased high for the components present in LRM glass at <0.5 elemental mass%.

Of particular interest is the reliability with which the Na₂O content can be quantified because it will be used as a measure of waste loading. The privatization contract specifies minimum concentrations of Na₂O for waste forms made with the three waste stream envelopes, namely, 16 mass% for Envelope A, 6 mass% for Envelope B, and 14 mass% for Envelope C. Based on the results of the ILS, the LRM glass contains 20.03 mass% Na₂O, and the estimated repeatability and reproducibility levels, $I(r)$ and $I(R)$, respectively, are 0.705 and 3.439 at the 95% confidence level. These values give the precision and accuracy for analysis of LRM glass in this ILS. They also provide expected values for the precision

and accuracy with which ILAW waste forms can be analyzed.

The h -values calculated for the concentrations of B, Na, and Si in PCTs conducted at 40°C and 90°C by eight participants are plotted in Fig. 4. Examination of these plots shows that the h -values for the results of Lab G for the 40°C PCT are all biased low, although only the value for the Si result (which is -2.28) exceeds the critical value of -2.15. In the 90°C results for Lab H, the h -values for the B, Na, and Si (2.19, 2.15, and 2.48, respectively) exceed or equal the critical value of 2.15; the h -value for Al (2.11) is slightly below the critical value. The results for Si in the PCT at 40°C from Lab G and for B, Na, and Si in the PCT at 90°C from Lab H were thus excluded from the calculations summarized in Table 5.

The expected values for product acceptance testing are given by consensus values and $I(r)$ for repeatability and $I(R)$ for reproducibility. Two values measured at the same laboratory that differ by more than $I(r)$ should be considered suspect, as should two values measured at different laboratories that differ by more than $I(R)$. The expected repeatability and reproducibilities for compositions of major glass components and for PCTs are summarized in Tables 6 and 7. Note that the compositions are expressed in units of elemental mass%. These tables give the expected values for compositional analysis and PCTs with LRM glass.

5. Conclusions

A study was conducted to determine the precision for compositional analysis and PCTs at 40°C and 90°C with LRM glass. The data base was used to determine the repeatability (intralaboratory precision) of the composition analysis and PCTs and the reproducibility (interlaboratory precision) of the PCTs following guidelines in ASTM Standard E691-92. This data base and the statistical calculations provided in this paper can be used to determine the precision of results from laboratories contracted to evaluate ILAW products of Hanford tank wastes. In addition to random errors, the precision for composition analysis accounts for the use of several sample preparation methods and analytical techniques. The PCTs were conducted with material prepared as ANL. This was done to (1) conduct the ILS with samples that were as homogeneous as possible and (2) eliminate variance due to sample preparation from the ILS so that the precision reflected the effects of uncontrollable random errors. The ability of a laboratory to demonstrate that it meets the repeatability and reproducibility limits determined in this ILS for analysis of LRM glass will add confidence to the results that laboratory obtains when conducting the same analyses with actual ILAW products.

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Appendix A

The methods used by participants to dissolve and analyze the glass are summarized in Tables 8 and 9.

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