Conf-931108--27

PNL-SA-23098

NUCLEAR WASTE ANALYTICAL ROUND
ROBINS 1-6 SUMMARY REPORT

G. L. Smith
S. C. Marschman

November - December 1993

Presented at the
Materials Society 1993 Fall Meeting
November 29 - December 3, 1993
Boston, Massachusetts

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

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ABSTRACT

The Materials Characterization Center (MCC) at Pacific Northwest Laboratory conducts Nuclear Waste Analytical Round Robins on simulated waste glasses with and without radionuclides. The analytical round robins are used to provide analytical laboratories with a forum for improving the accuracy and precision of analytical techniques that will be used for characterizing nuclear waste glasses. Chemical analysis data on glass waste forms produced by the nuclear waste community may need to withstand legal challenges for waste material storage qualification and for licensing repositories. Determining the quality of analytical data is important for meeting these challenges, making process operation decisions, and predicting long-term waste behavior.

The MCC has conducted six round robins for the waste management, research, and development community from 1987 to the present time. The laboratories that have participated regularly are Ames, Argonne, Catholic University, Lawrence Livermore, Pacific Northwest Laboratory, Savannah River, and West Valley Nuclear. The glass types analyzed in these round robins all have been simulated nuclear waste compositions expected from the vitrification of high-level nuclear waste. A wide range of analytical procedures have been used by the participating laboratories including Atomic Absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, direct current plasma-emission spectroscopy, and inductively coupled plasma-mass spectroscopy techniques. The consensus average relative error for Round Robins 1 through 6 is 5.4%, with values ranging from 9.4 to 1.1%. The trend on the average improved with each round robin. When the laboratories analyzed samples over longer periods of time, the intralaboratory variability increased. Lab-to-lab variation accounts for most of the total variability found in all the round robins. To date, participation in the radiochemistry portion has been minimal, and the analytical results poor when compared to the nonradiochemistry portion of the round robins. Additional radiochemical work is needed in future round robins.

INTRODUCTION

The Materials Characterization Center (MCC) at Pacific Northwest Laboratory (PNL) has been conducting interlaboratory test programs (Nuclear Waste Analytical Round Robins) that focus on analysis of glasses pertinent to nuclear waste repository programs. The program goal is to demonstrate and document achievable levels of performance in the analysis of nuclear waste glass. Chemical analysis data on glass waste forms produced by the nuclear waste community may need to withstand legal challenges for waste material storage qualification and for licensing repositories. Determining the quality of analytical data is important for meeting these challenges, making process operation decisions, and predicting long-term waste behavior. Methods to document the quality and reliability of the analytical data will include selection of appropriate facilities and instrumentation, use of reliable analytical methods/procedures, and application of laboratory quality control and quality assurance procedures.

Round robins give the individual analytical laboratories an opportunity to evaluate their current analytical capability. This evaluation is done in an absolute sense by comparison against a target composition and in a relative sense by comparison with other laboratories. These round robins are not initiated to foster competition among the participating laboratories, but instead to instill a spirit of cooperation and learning through interaction at the subsequent workshops. Although each round robin has a slightly different protocol, participating laboratories are always asked to analyze the glasses by using their normal laboratory procedures. This approach enables the participating laboratories to judge how well their laboratory procedures work. Through

the interaction at the workshops, many of the participating laboratories have been able to improve their analytical capability.

The results of each analytical round robin (1 through 6) were compiled in summary letter reports and sent by the MCC to a limited distribution of meeting participants, their managers, and managers of DOE supporting offices. Toward the goal to determine what constitutes "normal" precision and accuracy when nuclear waste glass components and products are chemically analyzed, participants feel that the round robin results should be published in open literature. Such reports would inform clients about "normal" analytical limitations and encourage the development and testing of improved analytical equipment and methods. All analytical laboratories face similar limitations and problems; this paper will point out the level of interlaboratory agreement to be expected in data comparisons so that comparison of values determined at different laboratories are not overrated as significant.

Researchers who use the services of analytical laboratories need to distinguish between the results that are "routinely achievable and cost-effective" and "best achievable regardless of cost," and when to request and expect these results. Often, because of sample inhomogeneity, field sampling is the limiting step in determining accuracy and intrasample analytical precision. Clients of analytical laboratories need to be aware of this factor and work with the analytical staff to achieve results appropriate for the intended use. It is hoped that this paper will be useful to drafters of waste acceptance criteria, will foster further laboratory interaction to solve existing and future problems,

and will publicize analytical methods suitable for the nuclear waste community and encourage their use at additional laboratories.

BACKGROUND

Analytical workshops following the round robins are conducted by the MCC in an informal environment to encourage participation in open discussions of analytical data, laboratory successes, and laboratory problems. In addition, participants can exchange critical appraisal of analytical methods and evaluate new instrumentation and techniques. Laboratories that would benefit most from the round robins include those currently involved in production and waste form qualification of glass waste forms. For this reason, the laboratories that have regularly participated in the round robins by analyzing unknowns are Ames Laboratory, Argonne National Laboratory, Catholic University of America, Lawrence Livermore National Laboratory, Pacific Northwest Laboratory, Savannah River Laboratory, and West Valley Nuclear Services. Hahn-Meitner Institute and Mobay Company have both participated in a single round robin in which they analyzed unknowns, and the National Institute of Standards & Technology (NIST), formerly the National Bureau of Standards, participated in one workshop.

The glass types analyzed in these round robins all have been simulated nuclear waste compositions expected from the vitrification of high-level nuclear waste. All the glasses have been composed largely of the oxides of Al, B, Fe, Li, Na, Si, Ti, and Zr. Other elements in the glasses at concentrations greater than 0.5 wt% have been Ba, Ca, Ce, Cs, K, Mg, Mn, Mo, Nd, P, and Zn. Additional elements that have been

incorporated in the glasses as oxides at concentrations below 0.5 wt% include Cr, Rh, Ru, S, Sr, and Y. The oxides of La, Ni, and U also have been minor constituents in the glass compositions with each oxide greater than 0.5 wt% in a single glass composition. Table 1 lists, by round robin, the elements present in each glass as oxides at greater than 0.5 wt%. The compositions for each round robin glass will be given in the results section. Table 1 also lists dates each round robin was initiated.

The most common technique used to analyze the glass composition has been inductively coupled plasma-atomic emission spectroscopy, (ICP-AES) from Round Robin 1 through Round Robin 6. Atomic Absorption spectroscopy (AA) was used more often in the earlier Round Robins, 1-4, and used sparingly or not at all in Round Robins 5 and 6. Direct current plasma-emission spectroscopy (DCP) was used consistently during all six round robins by one or two laboratories. Inductively coupled plasma-mass spectroscopy (ICP-MS) was first used in Round Robin 2, and was in a developmental stage for most applications. This technique has become more widely used as the round robins progress largely because ICP-MS has the ability to use very small samples of the solid glass, which reduces the personnel radiation hazard associated with handling of radioactive waste forms.

Alkaline fusions have been the preferred choice for preparing glass samples, with microwave-assisted acid dissolution being a distant second choice. For example, the preparation methods used in Round Robin 6 include Na peroxide fusion, microwave dissolution - B, micro acid dissolution (HF, HNO₃), Rb hydroxide fusion, HF dissolution, and a crucible fusion (HF, HNO₃, KOH, Ni). It has been noted that data submitted by

laboratories using heat-assisted HF plus other acid dissolutions to prepare glass samples for analysis (Round Robin 4 time frame) were biased low for rare- and alkaline-earth elements. This was thought to be due to the fluoride ion causing precipitation problems by formation of filterable rare- and alkaline-earth fluoride salts. Various sample preparation techniques may be found or soon will be found in the DOE analytical methods compendium [1]. For this reason, sample preparation procedures will not be found in this document.

The radiochemical aspect of the round robins was initiated in Round Robin 5, and continued in Round Robin 6. A spectrum of radioactive elements expected to be found in nuclear waste glass was supplied to each participant upon request. The radionuclides were contained in a nitric acid solution. In Round Robin 5, the participants added the radionuclide-containing solution to the digested glass solution, simulating the actual digestion of a radioactive glass. In Round Robin 6, participants were asked to analyze the two solutions independently.

RESULTS

Round Robin 1

Each participating laboratory was provided with approximately a 1-cm cube of a solid reference glass, ATM-WV/205 [2], typical of a nuclear waste form. They were asked to use their normal analytical instrumentation and preparation methods to determine the composition of the glass. The pre-round robin analysis or "nominal composition" and the associated standard deviation shown in Table 2 are based on

analyses of 19 replicate specimens by X-ray fluorescence (XRF) and ICP methods in two independent PNL laboratories. The reported oxide wt% values are consistent with known values based upon the amount weighed during conventional glass fabrication procedures. Table 2 also lists the round robin participants' consensus mean, the associated standard deviation (SD), and the number of labs that analyzed for each particular element converted to the oxide. The consensus mean, as used in this paper, is the mean of all available results reported for each oxide.

Round Robin 2

Analytical Round Robin 2 was conducted using crushed glass samples provided by the MCC. The crushed glass samples were made by grinding two separate glasses, ARM-1 [3] and ATM-WV/205 [2], and sieving to a -100 mesh powder. The two powdered glass samples were blended in the proportion of 60 wt% ATM-WV/205 and 40 wt% ARM-1. This final blended powder was split into two approximately equal portions and then packaged into approximately 5-g batches. A 5-g sample of each split was sent to all participating laboratories. The pre-round robin analysis or "nominal composition" shown in Table 3 is based on analyses of ARM-1 by both the NIST, which analyzed 10 samples of ARM-1 in duplicate, and the MCC, which analyzed three samples in duplicate. Analysis of ATM-WV/205 was described previously in the Round Robin 1 section. Table 3 lists the nominal and consensus compositions in wt%, the difference, and the 95% confidence interval for Round Robin 2.

Round Robin 3

Analytical Round Robin 3 was conducted using crushed samples of MCC reference glasses, made by grinding two separate glasses, ARM-1 and ATM-1b [3], and sieving to a -100 mesh powder. The two powdered glass samples were blended in the proportion of 50 wt% ARM-1 and 50 wt% ATM-1b. This final blended powder was split into three approximately equal portions. A sample from each of the three splits was sent to each participating laboratory. The pre-round robin analysis or "nominal composition" shown in Table 4 is based on analyses of 12 samples of ATM-1b glass. The basis for the ARM-1 analysis was discussed in the Round Robin 2 section. Table 4 lists the nominal and consensus compositions in wt%, the difference, and the 95% confidence interval for Round Robin 3.

Round Robin 4

Analytical Round Robin 4 was conducted using crushed samples of an MCC reference glass, ATM-WV/205. An amount of ATM-WV/205 glass made up of three different bars (7, 8, and 9) was crushed, ground, and sieved to a -100 mesh powder. Each participating laboratory was given three separate samples of the powdered glass. The nominal composition reported in Table 5 was derived from the analytical statistics given in a PNL document [2]. The following instructions were given to each participating laboratory:

1. Prepare each of three samples once, and conduct, over a period of three weeks, replicate analyses for elements normally determined in the laboratory.

2. Apply normal sample preparation procedure (according to the accompanying schedule) to each of the three samples of powdered glass provided herewith. Each sample has been crushed and screened to -100 mesh.
3. Analyze each of the three samples as specified on the schedule. Note that Sample A will be prepared once, and analyzed a total of 18 times during the three-week period. Assuming the use of ICP methods, the 8 g of sample should be adequate, Samples B and C are to be prepared and analyzed six times each during the second and third week, respectively; 5 g each of Samples B and C are provided.

By use of this sample preparation schedule and subsequent analyses: 1) Round Robin 4 was to quantify the bias (accuracy) and the normal data variability in analysis of nuclear waste glass within and between laboratories; and 2) The bias (accuracy) and the normal data variability would also be tested relative to short, moderate, and longer time periods. Table 5 lists the nominal and consensus compositions in wt% and the lab-to-lab (interlab) percent relative standard deviation (%RSD) for Round Robin 4.

Round Robin 5

Analytical Round Robin 5 was the first round robin to initiate the radiochemical aspect of analysis. Participants were supplied with powdered samples of ARM-1, and asked to first digest the powdered glass sample and then to add a specific portion of a nitric acid solution, which contained various radionuclides, to the previously digested solution. This was to simulate the actual digestion of a radionuclide-containing glass. Again, the nominal composition of ARM-1 is given in a PNL document [3].

Laboratories also were able to participate in the nonradiochemical portion of the round robin by not adding or receiving the radionuclide solution. Each laboratory then was instructed to analyze for radionuclide and/or nonradionuclide elements using their normal procedures and instrumentation. Table 6 lists the nominal and consensus compositions in wt% for the nonradionuclides and in $\mu\text{Ci/ml}$ for the radionuclides, and the lab-to-lab (interlab) %RSD for Round Robin 5.

Round Robin 6

Analytical Round Robin 6 was very similar to Round Robin 5. Because so few laboratories participated in the radiochemical portion of Round Robin 5 it was decided that Round Robin 6 would allow for a repeat of the analysis. By repeating the radiochemical analysis, it was hoped that the consistency of the results could be improved. The glass used for this round robin was ARG-1, which had been extensively analyzed by Corning Incorporated. Participating laboratories were issued two -100 mesh powdered samples, 5 g each; those laboratories participating in the radiochemistry portion received a 5-ml sample of the nitric acid solution containing radionuclides (from the same 100-ml solution used for Round Robin 5). Due to some short half lives of some radionuclides, the nominal values reported in Table 7 were decay-corrected for Co-60 ($t_{1/2} = 1925$ days) and Pm-147 ($t_{1/2} = 958$ days). A short description of the protocol used in Round Robin 6 follows.

In this round robin, participants were not asked to combine the radiochemical solution with the digested glass solution, but to analyze them separately. They were given two 5-g samples of ARG-1. One sample was representative of a 1-kg lot of ARG-1; the other was representative of a composite sample made up of more than 20 10-g samples taken from every fifth kilogram as the 110+ kg of ARG-1 was being repackaged into 1-kg lots. Participants were instructed to take three 0.5-g splits from each powdered glass sample, treating each split as a separate sample, and to analyze the liquid sample containing radionuclides in triplicate.

Each laboratory was instructed to analyze for the radionuclide and/or nonradionuclide elements using their normal procedures and instrumentation. Table 7 lists the nominal and consensus compositions in wt% for the nonradionuclides and in $\mu\text{Ci}/\text{ml}$ for the radionuclides, and the lab-to-lab %RSD for Round Robin 6.

DISCUSSION

Comparison of intralab and interlab SDs and %RSDs clearly show that interlab variation is large relative to intralab variation throughout all six round robins. The intralab variation is generally the largest contributor to the total variation for a single observation. Difficulty in dissolution (sample preparation) of the powdered glasses is a significant potential contributor to analytical variability, and would cause greater interlab variability. It was observed that field and process sampling operations that proceed

submission of samples to the analytical laboratory are often the source of large sample-to-sample variation, causing greater intralab variability.

High intralab %RSDs also were attributed to "long-term" analytic variation. Labs that performed their replicate analyses during a span of several days showed poorer results than labs which conducted their replicate analyses on the same day. Due to the protocol used in Round Robin 4, long-term variability was evidenced by a week-to-week drift on analyses performed during the three-week time period. This points out the need for frequent recalibrations on a daily basis, and use of control limits and working standards. Short-term scatter of individual data points appears to reflect the "tightness" of controls in the laboratory, most likely quality assurance and control procedures.

The question of which elements are the most problematic to analyze for is difficult. In Round Robin 1, four of the six participating laboratories reported concentrations that differed significantly from the nominal and consensus value for three or more oxides. In Round Robin 2, the interlaboratory agreement for major elements was considered to be much better. The most common major elements that laboratories had trouble with were K and P. For 16 of 21 elements tested in Round Robin 3, the nominal and consensus values were not statistically different. For the five remaining oxides (Cs_2O , Fe_2O_3 , Li_2O , Na_2O , and NiO) Cs_2O could not be compared due to insufficient data; Fe, Li, Na, and Ni oxides were significantly different at the 95% confidence level, but only Na_2O showed a very substantial bias. In Round Robin 3 the most commonly reported "false positive" was Ca. By the conclusion of Round Robin 4, there was no apparent overall analytical bias and the average analyzed values from each

laboratory agreed with the nominal concentrations within one to two lab-to-lab SDs. The nonradiochemistry portion of Round Robins 5 and 6 showed that the average values compared well with the nominal analysis values. Much of the variability present for specific elements (elements differed between round robins) often was due to a particular laboratory. Primary sources of variation from the two most recent round robins are listed in Tables 8 and 9. Tables 8 and 9 indicate which analytical procedures gave the most off-average data for the specific oxides. The method used to choose these data sets was purely subjective; the only strict rule followed in deciding which information would be included in the tables was that the data clearly be extreme.

The radiochemistry data from Round Robins 5 and 6 are sparse. In Round Robin 5, the reported values are all within a factor of two when compared to the nominal values, except for Pm-147, which was high by greater than two orders of magnitude. Due to a lack of participation in Round Robin 5, the same radionuclide doped solution was used in Round Robin 6. The Round Robin 6 data (Table 6 *versus* 7) shows an increase in participation over Round Robin 5, but fairly similar results. Similar biases to those obtained during Round Robin 5 were found for Tc-99, Np-237, Pu-239, Pu-240, Am-244, Cm-244, and U. Although only a single value for Pm-147 was reported in Round Robin 6 and it is a difficult element to analyze, the value was considerably closer to the nominal value. To date, participation in the radiochemistry portion has been sparse and the analytical results have not been as accurate when compared to the nonradiochemistry portion of the round robins. Additional radiochemical work is needed in future round robins.

The consensus "average relative error" was used to compare all six round robin data sets. First, the bias of the analytical results from each laboratory for each round robin was calculated. Only data from the major constituents (oxides present in the glass at greater than 0.5 wt%) were used in the calculation. The average relative error for each laboratory was calculated using

$$\text{Ave. Rel. Err. (\%)} = 100 \left[\sum \left| \frac{\Delta}{\text{nom}} \right| \right] \frac{1}{N}$$

where nom is the nominal concentration in the samples for each element, Δ is the difference between nominal and average analyzed values, and N is the number of elements included. The consensus average relative error for each round robin was then calculated from this data, and determined to be 6.4%, 6.4%, 9.4%, 3.1%, 5.6%, and 1.1% respectively for round robins 1 through 6. The mean consensus average relative error for all six round robins is 5.4%. The trend on the average has improved with each round robin. These numbers reflect the inclusion of long-term variability and would likely be smaller if only short-term variability was used.

CONCLUSIONS

1. Statistical analysis of different splits of glass shows that powdered and mixed -100 mesh samples are homogenous to well within analytical precision.
2. Dissolution of glasses during sample preparation is a significant real contributor to analytical variability.

3. Intralaboratory variance is smaller than interlaboratory variance for most elements. Specifically, the scatter of results for an element in a given laboratory are smaller than the difference between laboratory averages, indicating that instrument precision would contribute little to the overall variability of results.
4. Based upon results from Round Robin 4; long-term analytic variation is a large contributor to variability of data when replicate analysis is performed during a span of several days or weeks. Better quality control would eliminate this type of variability.
5. For nonradiochemistry data the overall agreement of the round robin mean consensus values with the nominal analysis is within one to two lab-to-lab SDs. No overall analytical bias is evident.
6. The consensus average relative error has been 6.4%, 6.4%, 9.42%, 3.14%, 5.62%, and 1.09% respectively for round robins 1 through 6. The trend, in general, has improved during the round robin program (note the over all improvement between Round Robin 1 and 4 using the same glass); the mean consensus average relative error for all six round robins is 5.4%.
7. Careful and complete definition of conditions under which data are generated during the round robins must be supplied with results to accurately characterize actual analytical laboratory performance. Additionally, laboratories must adhere to the specific round robin protocol if data are to be compared directly.
8. Participation in the radiochemistry portion of the round robins has been sparse and the analytical results have not been accurate when compared to the nonradiochemistry

portion of the round robins. Additional radiochemical work is needed in future round robins.

As a result of the six-year series of round robins, we have achieved a "warm fuzzy feeling" that the average results and conclusions from the data are reliable, as demonstrated repeatedly under a variety of experimental conditions in several laboratories. We can also conclude confidently that further improvements are not likely to be achieved until tighter control is exercised over all the participants regarding sample preparation procedures and analytical methods used, a consensus reference standard is used by all labs consistently, and QA/QC practices are implemented by all.

ACKNOWLEDGEMENTS

The authors thank J. Leland Daniel, Carrie Matsuzaki, Karl H. Pool, Gregory F. Piepel, Dennis L. Eggett, and Harry D. Smith for their extensive work in coordination, data analysis, and report-writing for Round Robins 1 through 6. Without their previous work, this paper would not be possible. Finally, the authors express their gratitude to the U. S. Department of Energy and both West Valley Nuclear Services and Savannah River Laboratory for the financial support of this work.

REFERENCES

1. Goheen, S. C., M. McCulloch, B. L. Thomas, R. G. Riley, D. S. Sklarew, G. M. Mong, and S. K. Fadeff. 1993. *DOE Methods for Evaluating Environmental and Waste Management Samples*. DOE/EM-0089T, Rev 1, Pacific Northwest Laboratory, Richland, Washington.

2. Maupin, G. D., W. M. Bowen, and J. L. Daniel. 1988. *Fabrication and Characterization of MCC Approved Testing Material-ATM-WV/205 Glass*. PNL-5577-WV/205, Pacific Northwest Laboratory, Richland, Washington.
3. Mellinger, G. B., and J. L. Daniel. 1984. *Approved Reference and Testing Materials for Use in Nuclear Waste Management Research and Development Programs*. PNL-4955-2, Pacific Northwest Laboratory, Richland, Washington.

Table 1. Elements Present in Round Robin Glass Samples as Oxides at ≥ 0.5 wt%

Round Robin 1 Spring 1987	Round Robin 2 Fall 1987	Round Robin 3 Fall 1988	Round Robin 4 Fall 1989	Round Robin 5 Spring 1990	Round Robin 6 Winter 1991
Al B Fe Li Na Si Ti Zr	Al B Fe Li Na Si Ti Zr	Al B Fe Li Na Si Ti Zr	Al B Fe Li Na Si Ti Zr	Al B Li Na Si Ti Zr	Al B Fe Li Na Si Ti
Ca	Ca Ce	Ba Ca Ce Cs	Ca	Ba Ca Ce Cs	Ca
K	K	La	K		K
Mg Mn	Mg Mn Mo Nd	Mo Nd	Mg Mn	Mo Nd	Mg Mn
P	P Zn	P U Zn	P	P Zn	Ni
Total: 13	Total: 17	Total: 18	Total: 13	Total: 15	Total: 12

Table 2. Statistical Comparison of Nominal Concentrations and Consensus Analytical Results of Solid Samples in Round Robin 1 (results are shown as wt% values)

Oxide	Nominal		#Labs	Mean	SD(a)	Consensus	
	Mean	SD				Mean	SD
Al ₂ O ₃	6.54	0.047	6	6.45	0.047	6.45	0.387
B ₂ O ₃	9.34	0.069	5	9.12	0.069	9.12	0.690
BaO	0.05	0.002	4	0.05	0.002	0.05	0.009
CaO	0.61	0.010	6	0.68	0.010	0.68	0.200
CeO ₂	0.31	0.006	5	0.30	0.006	0.30	0.080
Cr ₂ O ₃	0.26	0.009	5	0.25	0.009	0.25	0.030
Cs ₂ O	0.07	0.002	4	0.05	0.002	0.05	0.022
Fe ₂ O ₃	11.68	0.305	6	11.59	0.305	11.59	0.493
K ₂ O	3.59	0.216	5	3.20	0.216	3.20	0.287
La ₂ O ₃	0.02	0.001	4	0.03	0.001	0.03	0.007
Li ₂ O	2.90	0.014	4	2.98	0.014	2.98	0.210
MgO	1.19	0.015	5	1.12	0.015	1.12	0.115
MnO ₂	1.25	0.034	6	1.21	0.034	1.21	0.082
MoO ₃	0.002	0.0002	3	0.005	0.0002	0.005	0.003
Na ₂ O	10.26	0.099	5	9.99	0.099	9.99	0.884
Nd ₂ O ₃	0.18	0.004	2	0.15	0.004	0.15	0.054
NiO	0.31	0.012	6	0.38	0.012	0.38	0.216
P ₂ O ₅	2.39	0.038	6	2.43	0.038	2.43	0.637
RhO ₂	0.01	0.001	1	0.01	0.001	0.01	-----
RuO ₂	0.07	0.004	4	0.08	0.004	0.08	0.030
SO ₃	0.23	0.009	2	0.15	0.009	0.15	0.078
SiO ₂	48.0	1.662	6	45.8	1.662	45.8	1.679
StO	0.03	0.001	5	0.02	0.001	0.02	0.007
TiO ₂	0.86	0.030	6	0.91	0.030	0.91	0.062
Y ₂ O ₃	0.02	0.000	1	0.02	0.000	0.02	-----
ZrO ₂	1.41	0.025	5	1.44	0.025	1.44	0.072

(a) Standard Deviation

Table 3. Statistical Comparison of and Nominal Concentrations and Consensus Analytical Results of Solid Samples in Round Robin 2 (results are shown as wt% values)

Oxide	Nominal		Consensus		Difference		95% Conf. Int.	
	Mean	SD ^(a)	Mean	SD	Mean	SD	LCL ^(b)	UCL ^(c)
Al ₂ O ₃	6.285	0.015	6.096	0.065	-0.190	0.067	-0.345	-0.034
B ₂ O ₃	10.326	0.022	10.363	0.102	0.038	0.104	-0.224	0.300
BaO	0.295	0.000	0.285	0.006	-0.010	0.006	-0.026	0.006
CaO	1.275	0.006	1.195	0.066	-0.081	0.067	-0.237	0.076
CeO ₂	0.732	0.003	0.607	0.038	-0.125	0.038	-0.222	-0.028
Cr ₂ O ₃	0.157	0.001	0.164	0.003	0.007	0.003	-0.002	0.015
Cs ₂ O	0.482	-----	0.400	0.036	-0.082	-----	-----	-----
Fe ₂ O ₃	7.009	0.042	6.976	0.058	-0.033	0.071	-0.185	0.119
K ₂ O	2.156	0.030	1.991	0.098	-0.165	0.102	-0.399	0.069
La ₂ O ₃	0.011	0.000	0.016	0.004	0.005	0.004	-0.007	0.016
Li ₂ O	3.771	0.014	3.650	0.047	-0.122	0.049	-0.241	-0.002
MgO	0.713	0.004	0.717	0.015	0.004	0.015	-0.031	0.040
MnO ₂	0.747	0.005	0.719	0.026	-0.028	0.026	-0.091	0.035
MoO ₃	0.753	0.005	0.745	0.010	-0.008	0.011	-0.034	0.018
Na ₂ O	10.081	0.031	10.064	0.245	-0.018	0.247	-0.618	0.583
Nd ₂ O ₃	2.440	0.009	2.133	0.170	-0.307	0.171	-0.779	0.166
NiO	0.190	0.002	0.249	0.052	0.059	0.052	-0.063	0.182
P ₂ O ₅	1.662	0.010	1.691	0.139	0.029	0.139	-0.326	0.385
RhO ₂	0.006	0.000	0.005	-----	-0.001	-----	-----	-----
RuO ₂	0.044	0.001	0.051	0.014	0.007	0.014	-0.038	0.053
SO ₃	0.138	0.002	0.177	0.008	0.039	0.008	-0.033	0.111
SiO ₂	47.213	0.235	47.139	0.127	-0.074	0.267	-0.623	0.475
SrO	0.204	0.000	0.196	0.003	-0.008	0.003	-0.016	-0.001
TiO ₂	1.888	0.006	1.875	0.042	-0.013	0.043	-0.113	0.086
Y ₂ O ₃	0.011	0.000	0.012	0.001	0.001	0.001	-0.004	0.006
ZnO	0.608	0.002	0.589	0.016	-0.019	0.016	-0.061	0.022
ZrO ₂	1.626	0.006	1.301	0.185	-0.325	0.185	-0.762	0.112

(a) Standard Deviation

(b) Lower Confidence Level

(c) Upper Confidence Level

Table 4. Statistical Comparison of Nominal Concentrations and Consensus Analytical Results of Solid Samples in Round Robin 3 (results are shown as wt% values)

Oxide	Nominal		Consensus			Difference		95% Conf. Int.	
	Mean	SE ^(a)	#Labs	Mean	SE	Diff.	SD ^(b)	LCL ^(c)	UCL ^(d)
Al ₂ O ₃	3.375	0.012	7	3.512	0.094	0.137	0.094	-0.091	0.365
B ₂ O ₃	10.175	0.021	5	10.473	0.293	0.298	0.293	-0.509	1.105
BaO	0.640	0.000	6	0.600	0.025	-0.040	0.025	-0.103	0.023
CaO	2.195	0.005	7	2.278	0.051	0.083	0.052	-0.042	0.208
CeO ₂	1.170	0.013	6	1.096	0.083	-0.074	0.084	-0.286	0.139
Cr ₂ O ₃	0.225	0.006	6	0.209	0.016	-0.016	0.017	-0.057	0.025
Cs ₂ O	0.935	-----	5	1.146	0.022	0.212	-----	-----	-----
Fe ₂ O ₃	4.080	0.006	7	4.248	0.049	0.168	0.049	0.052	0.284
La ₂ O ₃	2.535	0.003	4	2.383	0.072	-0.152	0.072	-0.375	0.071
Li ₂ O	2.540	0.017	5	2.411	0.027	-0.129	0.032	-0.206	-0.052
MoO ₃	1.935	0.007	6	1.999	0.049	0.064	0.050	-0.062	0.190
Na ₂ O	9.740	0.026	6	10.973	0.167	1.233	0.169	-0.808	1.658
Nd ₂ O ₃	3.720	0.012	6	3.813	0.105	0.093	0.106	-0.173	0.359
NiO	0.110	0.004	7	0.134	0.004	0.024	0.006	0.012	0.036
P ₂ O ₅	0.585	0.009	5	0.620	0.026	0.036	0.027	-0.033	0.105
SiO ₂	43.300	0.078	6	42.845	0.403	-0.455	0.410	-1.472	0.562
SrO	0.465	0.001	6	0.430	0.019	-0.035	0.019	-0.083	0.013
TiO ₂	3.015	0.006	7	3.169	0.093	0.154	0.093	-0.073	0.381
UO ₂	2.080	0.012	5	1.964	0.070	-0.116	0.071	-0.298	0.067
ZnO	2.930	0.005	5	2.941	0.015	0.011	0.016	-0.022	0.044
ZrO ₂	1.915	0.010	7	2.059	0.069	0.144	0.069	-0.023	0.311

(a) Standard Error

(b) Standard Deviation

(c) Lower Confidence Level

(d) Upper Confidence Level

Table 5. Statistical Comparison of Nominal Concentrations and Consensus Analytical Results of Solid Samples in Round Robin 4 (results are shown as wt% values)

Oxide	Nominal		Consensus			Lab to Lab
	Mean	SD ^(a)	#Labs	Mean	SD	% RSD ^(b)
Al ₂ O ₃	6.54	0.047	9	6.54	0.437	6.68
B ₂ O ₃	9.34	0.069	6	9.952	0.339	3.40
BaO	0.052	0.002	7	0.052	0.004	7.34
CaO	0.61	0.040	8	0.604	0.110	18.30
CeO ₂	0.307	0.007	5	0.301	0.039	12.83
Cr ₂ O ₃	0.262	0.009	7	0.234	0.039	16.66
Cs ₂ O	0.070	0.002	5	0.073	0.009	12.80
Fe ₂ O ₃	11.68	0.305	9	11.827	0.480	4.06
La ₂ O ₃	0.019	0.002	4	0.025	0.007	26.34
Li ₂ O	2.90	0.015	6	2.858	0.159	5.57
K ₂ O	3.59	0.216	6	3.419	0.103	3.01
MgO	1.19	0.015	9	1.195	0.072	6.03
MnO ₂	1.25	0.036	9	1.295	0.072	5.56
MoO ₃	0.002	0.000	3	0.006	0.006	100.0
Na ₂ O	10.26	0.099	8	10.056	1.204	11.97
Nd ₂ O ₃	0.18	0.004	5	0.148	0.042	28.75
NiO	0.31	0.012	9	0.322	0.023	7.09
P ₂ O ₅	2.39	0.038	6	2.394	0.122	5.11
SiO ₂	48.0	1.66	9	46.279	1.360	2.94
SrO	0.027	0.001	8	0.029	0.004	14.27
TiO ₂	0.86	0.030	9	0.982	0.049	4.96
Y ₂ O ₃	0.019	0.000	3	0.019	0.001	5.26
ZrO ₂	1.41	0.025	8	1.462	0.109	7.43

(a) Standard Deviation

(b) Percent Relative Standard Deviation

Table 6. Statistical Comparison of Nominal Concentrations and Consensus Analytical Results of the Solid Glass Sample and the Radionuclide Doped Solution in Round Robin 5

Oxides	Nominal Composition		Consensus Composition			
	Mean wt%	SD ^(a)	No. Data Sets	Mean wt%	Total SD	Lab-to-Lab % RSD ^(b)
Al ₂ O ₃	5.90	0.04	11	5.69	0.59	8.354
B ₂ O ₃	11.80	0.06	10	11.93	0.73	4.578
BaO	0.66	0.00	10	0.67	0.078	7.810
CaO	2.28	0.01	11	2.32	0.254	9.530
CeO ₂	1.37	0.01	5	1.23	0.312	0.000
Cs ₂ O	1.10	---	6	1.20	0.483	39.517
Li ₂ O	5.08	0.06	9	4.95	0.276	4.139
MoO ₃	1.88	0.02	11	1.98	0.128	4.494
Na ₂ O	9.82	0.08	9	9.96	1.486	0.000
Nd ₂ O ₃	5.83	0.04	7	5.58	1.267	0.000
P ₂ O ₅	0.57	0.01	10	0.70	0.172	0.000
SiO ₂	46.10	0.23	11	49.65	6.878	10.638
SrO	0.47	0.00	11	0.48	0.074	12.197
TiO ₂	3.43	0.02	12	3.55	0.264	6.639
ZnO	1.52	0.01	11	1.43	0.261	17.812
ZrO ₂	1.95	0.02	12	2.02	0.207	8.293
Radionuclides - µg/g						
Co-60	0.001804	---	2	0.0018	0.000	0.000
Sr-90	0.01518	---	1	0.0127	0.001	0.000
Tc-99	1267.0	---	3	1337.6	39.737	1.555
Cs-137	0.04583	---	2	0.0457	0.002	0.000
Pm-147	0.01452	---	2	4.1061	4.001	90.497
Np-237	306.5	---	4	362.1667	61.408	14.557
Pu-238	0.07009	---	0	---	---	---
Pu-239	13.38	---	2	15.1125	3.011	19.518
Pu-240	4.183	---	2	4.8867	0.869	15.375
Am-243	15.35	---	4	14.0148	2.869	17.318
Cm-244	0.05192	---	1	0.1150	0.000	0.000
U	2180.0	---	2	2402.9	474.2	19.491

(a) Standard Deviation

(b) Percent Relative Standard Deviation

Table 7. Statistical Comparison of Nominal Concentrations and Consensus Analytical Results of the Solid Glass Sample and the Radionuclide Doped Solution in Round Robin 6

Oxides	Nominal Composition		Consensus Composition			
	Mean wt%	SD ^(a)	No. Data Sets	Mean wt%	Total SD	Lab-to-Lab % RSD ^(b)
Al ₂ O ₃	4.73	0.022	7	4.66	0.152	2.48
B ₂ O ₃	8.67	0.040	7	8.54	0.344	3.243
BaO	0.09	0.001	6	0.09	0.01	8.408
CaO	1.43	0.009	7	1.42	0.055	2.973
Cr ₂ O ₃	0.09	0.001	7	0.10	0.010	9.342
CuO	0.00	0.000	5	0.01	0.009	116.050
Fe ₂ O ₃	14.00	0.073	7	14.02	0.439	2.561
K ₂ O	2.71	0.016	7	2.68	0.182	3.794
Li ₂ O	3.21	0.015	7	3.18	0.237	7.112
MgO	0.86	0.005	7	0.87	0.034	2.886
MnO ₂	2.31	0.012	7	2.32	0.057	1.576
Na ₂ O	11.50	0.023	7	11.20	0.791	6.818
NiO	1.05	0.006	7	1.04	0.104	9.698
P ₂ O ₅	0.22	0.011	6	0.27	0.070	23.682
SiO ₂	47.90	0.157	7	47.75	1.531	2.210
SrO	0.00	0.000	6	0.00	0.001	0.000
TiO ₂	1.15	0.007	7	1.17	0.063	5.055
ZnO	0.02	0.000	6	0.02	0.010	35.376
ZrO ₂	0.13	0.005	7	0.14	0.019	12.860
Radionuclide Solution - $\mu\text{Ci/ml}$						
Co-60	0.0880	---	4	0.0840	---	---
Sr-90	0.0993	---	1	0.0498	0.001	0.000
Tc-99	1.0390	---	4	1.3478	0.064	4.350
Cs-137	0.1916	---	4	0.1679	0.019	10.975
Pm-147	0.5309	---	1	0.2520	---	---
Np-237	0.0100	---	4	0.0114	0.002	14.420
Pu-238	0.0580	---	2	0.0654	0.001	0.000
Pu-239	0.0400	---	2	0.0469	0.006	13.003
Pu-240	0.0450	---	2	0.0601	0.010	15.831
Am-243	0.1489	---	4	0.1395	0.017	10.683
Cm-244	0.2034	---	3	0.3295	0.050	9.461
U	0.1050	---	3	0.1188	0.048	39.991

(a)Standard Deviation

(b)Percent Relative Standard Deviation

Table 8. Primary Sources of Variation Found in Round Robin 5

Oxide	Lab Code Number	Observation Period	Direction of Bias	Sample Prep. Method	Analytical Method
Al ₂ O ₃	7	Wk #1	low	KOH Fusion	ICP-MS
BaO	9M	Wk #2	low	Micro. Diss.	ICP-AES
	10A	Wk #2	high	Micro. Diss.	ICP-AES
CaO	7	Wk #2	low	KOH Fusion	ICP-MS
	8	Both	high	Fused Glass	Wave. XRF
	9M	Wk #2	low	Micro. Diss.	ICP-AES
	10A	Wk #2	high	Micro. Diss.	ICP-AES
CeO ₂	10A, 10C	Both	(scatter)	Micro. Diss.	ICP-AES
Ce ₂ O	3	Both	low	KOH Fusion	GFAA
	9R	Both	high	RbCarbonate Fusion	ICP-AES
Na ₂ O	10A	Both	(scatter)	Micro. Diss.	ICP-AES
Nd ₂ O ₃	10A, 10C	Both	(scatter)	Micro. Diss.	ICP-AES
P ₂ O ₅	3	Both	(scatter)	KOH Fusion	ICP-AES
	9M	Both	(scatter)	Micro. Diss.	ICP-AES
SiO ₂	10A	Both	high(scatter)	Micro. Diss.	ICP-AES
SrO	8	Both	high	Fused Glass	Wave. XRF
	9M	Wk #2	low scatter	Micro. Diss.	ICP-AES
TiO ₂	7	Both	high	KOH Fusion	ICP-MS
	8	Both	v. high	Fused Glass	Wave. XRF
	10A	Wk #2	(scatter)	Micro. Diss.	ICP-AES
ZnO	8	Both	low	Fused Glass	Wave. XRF
ZrO ₂	7	Wk #2	high	KOH Fusion	ICP-MS
Radionuclides					
Co-60	4C	—	high	Micro. Diss.	Gamma Count
Sr-90	11	—	low	Micro. Diss.	Gamma Spec./Liq. Scin.
Tc-99	4C,7,11	—	high	Micro. Diss.	#7-ICP-MS
Cs-137	7,11	—	low/high	Micro. Diss.	ICP-MS/Gamma Spec./Liq. Scin.
Pm-147	7	—	very high	Micro. Diss.	ICP-MS
Np-237	4C,4I	—	high	Micro. Diss.	#4I- ICP-MS
Pu-238	—	—	—	—	—
Pu-239	4I	—	high	Micro. Diss.	ICP-MS
Pu-240	4I	—	high	Micro. Diss.	ICP-MS
Am-243	4C,7	—	low	Micro. Diss.	Gamma Count/ICP-MS
Cm-244	4I	—	very high	Micro. Diss.	ICP-MS
U	4I	—	high	Micro. Diss.	ICP-MS

Table 9. Primary Sources of Variation Found in Round Robin 6

Oxide	Lab Code Number	Direction of Bias	Sample Prep. Method	Analytical Method
Al ₂ O ₃	2,3M,5	low scatter	Micro. Diss.	ICP-AES or not reported
	3R	low scatter	RbOH Fusion	DC Plasma
	8	low scatter	HF Diss.	No Info.
B ₂ O ₃	All	scattered	No Info.	No Info.
BaO	3R	scattered	RbOH Fusion	ICP
	8	high	HF Diss.	DC Plasma
CaO	3R	low	RbOH Fusion	ICP
	5	low	No Info.	No Info.
Cr ₂ O ₃	5	low scatter	No Info.	No Info.
	7	low	No Info.	ICP-AES
CuO	3M	high	Micro. Diss.	ICP
	3R	high	RbOH Diss.	ICP
Fe ₂ O ₃	3M	high scatter	Micro. Diss.	ICP
	3R	low scatter	RbOH Fusion	ICP
	5	low	No Info.	No Info.
	8	low	HF Diss.	DC Plasma
K ₂ O	3R	scattered	RbOH Fusion	ICP
	10	low	KOH Fusion	ICP
Li ₂ O	3M	high	Micro. Diss.	ICP
	3R	low	RbOH Fusion	ICP
MgO	8	high	HF Diss.	DC Plasma
MnO ₂	5	low scatter	No Info.	No Info.
Na ₂ O	3R	low	RbOH Fusion	ICP
NiO	3R	low	RbOH Fusion	ICP
P ₂ O ₅	3R	high	RbOH Fusion	ICP
SiO ₂	3R	high	RbOH Fusion	ICP
	10	low scatter	KOH Fusion	ICP
SrO	3R	scattered	RbOH Fusion	ICP
	5	low	No Info.	No Info.
TiO ₂	8	high	HF Diss.	DC Plasma
ZnO	3M	high	Micro. Diss.	ICP
	3R	scattered	RbOH Fusion	ICP
	10	low	KOH Fusion	ICP
ZrO ₂	8	high	HF Diss.	DC Plasma
Radionuclides				
Co-60	1	low	Note: All radionuclides were provided in solution.	Gamma Spectr.
Sr-90	6	low		Beta Counting
Tc-99	All	high		All methods
Cs-137	1,19	low		Gamma Spectr.
Pm-147	19	high		not reported
Np-237	1	high		ICP-MS
Pu-238	6,17	high		Alpha Spec.
Pu-239	1	high		ICP-MS
Pu-240	1	high		ICP-MS
Am-243	1,6	high/low		ICP-MS, Alpha Spec.
Cm-244	All	high		All methods
U	1	high		ICP-MS

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