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In-House Alternative for Chemical Analyses of Rhenium and Sulfur in Glass

October 2019

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Prepared for the U.S. Department of Energy
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Abstract

Accurate measurements of rhenium (Re) and sulfur (S) concentrations in solid samples are of critical importance for the key research activities at the Pacific Northwest National Laboratory (PNNL) Waste Form Development Laboratory (WFDL) related to Re behavior during waste glass melting process and solubility of S in glass. Southwest Research Institute (SwRI) has provided reliable services for chemical analysis needs at WFDL; however, its long turnaround time, occasionally up to 5 months, has caused some difficulties. An in-house method was developed for dissolving and fusing glass and feed samples in preparation for analyses by inductively coupled plasma-optical emission spectrometry and -mass spectrometry at a PNNL facility.

Using a previously developed sodium hydroxide fusion method as a basis, four groups of samples from Hanford waste glass research were digested and fused at WFDL. The samples included 1) Enhanced low-activity waste glass correlation phase 2/3 melter glasses from the Vitreous State Laboratory at the Catholic University of America, 2) AN-102 dried feeds and glasses, 3) SS-AN-102 dried feeds and glasses, and 4) Integrated Research Project S solubility study glasses. We evaluated three different sets of solution preparation and analysis combinations, which included 1) a WFDL-prepared solution analyzed at SwRI, 2) a PNNL-prepared solution analyzed at a laboratory in the Building-331at PNNL, and 3) an SwRI-prepared solution analyzed at SwRI.

We concluded that the PNNL in-house Re results can be used in parallel with the SwRI data based on the relative standard deviation values less than 6% from three different sets of solution preparation and analysis for all three groups of rhenium-containing samples tested. However, it was proposed that the in-house S data be used for the barium oxide-free glasses only because of the issue of barium sulfate precipitation in digestion/fusion solutions prepared from glasses containing barium oxide. In addition, higher analytical biases between the PNNL and SwRI S results are expected compared to the Re results, based on the relative standard deviation values of less than 10% from three different sets of solution preparation and analysis for two groups of S-containing samples.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the U.S. Department of Energy's Waste Treatment and Immobilization Plant Project of the Office of River Protection.

The authors also thank following staff at PNNL:

- Ian Leavy and Christopher Thompson for technical support for inductively coupled plasma-optical emission spectrometry and inductively coupled plasma mass spectrometry analyses of solution samples
- Dr. Tongan Jin for a providing a technical review of the report.

Acronyms and Abbreviations

DI	deionized
ICP-OES	inductively coupled plasma-optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
IRP	Integrated Research Project
LAW	low-activity waste
NaOH	sodium hydroxide
PNNL	Pacific Northwest National Laboratory
SwRI	Southwest Research Institute
VSL	Vitreous State Laboratory
WFDL	Waste Form Development Laboratory
WTP	Hanford Tank Waste Treatment and Immobilization Plant
wt%	weight percent
RSD	relative standard deviation

Contents

Figures

Tables

1.0 Introduction

As a result of past plutonium production, large volumes of radioactive and chemically hazardous wastes were generated and currently are stored in underground tanks at the Hanford Site. The U.S. Department of Energy has been focused on determining appropriate methods for cleaning up Hanford and properly disposing of the waste. The Waste Treatment and Immobilization Plant (WTP) currently under construction is designed to immobilize the waste [1, 2]. The WTP design included full pretreatment process to separate the tank wastes into high-volume, low-activity waste (LAW) and low-volume, high-level waste before vitrifying them into separate glass waste forms for permanent disposal. However, recent changes in the Hanford waste cleanup strategies involve directly feeding LAW to the LAW vitrification facility without full pretreatment [1], called direct-feed LAW, which is currently the first phase of the planned WTP startup and operation.

Hanford LAW generally consists of various anions such as NO_2^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, F^-, Cl^-, and CrO_4^{2-} and with predominantly Na^+ cations [3-5]. Because Hanford LAW contains radionuclides like technetium-99 (^{99}Tc), the waste poses a problem in the vitrification process. ^{99}Tc is a significant concern for various reasons—it has a long half-life of 2.1×10^5 years and it can become a water-soluble pertechnetate. In the pertechnetate form (TcO_4^-), the ion is highly mobile in oxidized aqueous environments and volatilizes at waste processing temperatures in the WTP melters [6, 7]. As a result, Tc retention in glass is rather low, 18%–66% [7-10].

In an attempt to study the behavior of ^{99}Tc incorporation and retention in glass, a non-radioactive surrogate, rhenium (Re), is studied because it is similar to Tc in chemistry, ionic size, speciation in glass, and volatility [11-13]. As much as the two elements have in common, their main difference lies in their behaviors under different reducing conditions. Studies by Kim et al. [13] and Luksic et al. [14] illustrated the two elements act in a similar manner for partitioning into salt phases and final retention in glass. Lukens et al. [15] provided further evidence that Re is a good substitute for Tc as long as an oxidizing condition was used.

Sulfur (S) has been identified as a critical component in glass formulation because it limits the fraction of waste in glasses [16-19]. A segregated sulfate salt layer may form around the top surface of the LAW glass melt during melter processing. This phenomenon occurs when the S content exceeds the melter tolerance and, as a result, needs to be controlled to avoid salt accumulation on the melt surface. The sulfate phases on top of the glass melt can cause potential problems such as corrosion of refractory materials and metallic components and increased volatility of components such as ^{99}Tc during melting.

To solve the Tc glass retention problem and to increase the loading of S in the glass, the behavior of Re during the glass melting process and the solubility of S in the glass have been the key research activities at Pacific Northwest National Laboratory's (PNNL's) Waste Form Development Laboratory (WFDL). For the success of these research activities, accurate measurements of Re and S concentrations in solid samples are of critical importance. Southwest Research Institute (SwRI) has provided reliable services for chemical analysis needs at WFDL [3,13]. One of the advantages of the SwRI services has been that the researchers can rely on the data without concerns about potential analytical biases that might be present when different analytical laboratories are used. However, the drawback of using SwRI has been the long turnaround times occasionally taking up to 5 months to receive the results. This is an issue for some research activities that need to plan the next set of tests based on the results of previous set of results. Therefore, a task was initiated to evaluate the feasibility of using the analytical services at PNNL specifically for Re and S analyses.

It has been learned that typical analytical biases and uncertainties (reproductivities) for chemical analyses of glass samples primarily originate from the solution preparation from solid samples rather than the solution analyses by inductively coupled plasma (ICP) optical emission spectrometry (OES) or mass spectrometry (MS). It was determined that in-house solution preparation methods could be developed based on recent success of the method designed to analyze ^{99}Tc in solid samples [14]. Existing samples of varying glass compositions with wide ranges of Re and S concentrations were collected and used in this study. The objective was to confirm that the in-house solution preparation and subsequent ICP-OES and ICP-MS analyses at PNNL generate comparable results with the existing SwRI data so that future PNNL results could be used in parallel with past SwRI data without concerns about potential biases. For all sample dissolutions done at PNNL, duplicates were prepared by two independent researchers.

2.0 Experimental

2.1 Sample Selection

Four sets of samples that were previously prepared for various studies were selected:

1. Enhanced LAW Glass Correlation Phase 2/3 melter glasses (labeled as “ORLEC”) from the Vitreous State Laboratory (VSL) at the Catholic University of America [20, 21]
2. AN-102 dried feeds and glasses[1]
3. SS-AN-102 dried feeds and glasses[2]
4. Integrated Research Project (IRP) S solubility study glasses [22]. A brief description of how each set of samples were prepared is provided below.

The SS-AN-102 feeds and glasses were used for Re analysis only while IRP S solubility study glasses were used for S analysis only. The other two sets were analyzed for both Re and S.

“VSL Phase 2/3 melter glasses” were the samples collected from DuraMelter® 100 (DM100) tests [20, 21]. Molten glass was discharged from the DM100 melter periodically into 5-gallon carbon steel pails using an air lift system. The discharge glass was sampled by removing glass from the top of each pail, and selected samples were sent to PNNL for testing.

“AN-102 dried feeds and glasses” were prepared as a part of the study to investigate the effect of reducing agent on Re retention in glass. The AN-102 slurry feeds were prepared by adding a mix of simulated waste components and additive chemicals and minerals into deionized (DI) water in a specific order, ensuring each chemical was completely dissolved before the next was added. After all the chemicals were mixed in, the slurry feed was dried at 105°C for 12 hours. The AN-102 glasses (1000°C in the glass ID) were obtained after thermal treatment in a platinum crucible by heating at 5°C/min to 1000°C. The treated samples were cooled in air.

“SS-AN-102 dried feeds and glasses” were prepared similarly to the set of AN-102 dried feeds and glasses, but with simplified glass compositions consisting of four to five components.

“IRP sulfur solubility study glasses” were prepared by saturating the glass with S following a method developed by Jin et al. [22]. Sodium sulfate at 7–10 wt% was added to a pre-crushed baseline glass and melted at 1150°C for 1 hour in a Pt/Rh crucible. Glasses were saturated with S by repeating the crushing, mixing, and melting of the glass and salt mixture for a total of three cycles.

2.2 Digestion/Fusion Procedure

Development of the standard operation procedure for preparation of solution samples via sodium hydroxide (NaOH) flux digestion/fusion was based on the method developed by Luksic et al. [14, 23] for measuring Tc. Samples were crushed into powder form and 50 mg of each

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[1] George J.L., D. Kim, and A.A. Kruger. "Effects of iron oxalate on rhenium incorporation into low-activity waste glass." submitted to *Journal of Non-crystalline Solids*.

[2] Unpublished work.

solid sample was weighed and placed into an empty nickel crucible for the digestion. A 20% NaOH solution was prepared beforehand and 2.5 mL of the solution was added to each nickel crucible. The contents were swirled to mix the solid powder with the NaOH solution before being placed on a hotplate (around 150–200°C) within a fume hood. A nickel crucible filled with only the NaOH solution was prepared alongside the other crucibles so that a “blank” was created. When essentially all the water had evaporated from the crucibles, all but one crucible was removed for the fusion process that was done for one crucible at a time. A glass beaker was placed over the top of the crucible and the hotplate was then turned to maximum heat. The inverted beaker and hotplates on maximum heat raised the temperature of the sample to approximately 400°C. When the NaOH was completely molten, the crucible was removed from the hotplate and cooled.

After cooling for about 5 minutes, DI water was added to the sides of the crucibles to help extract all the contents. The NaOH and solids mixture became suspended in water when all the contents were transferred to the centrifuge tube to separate the solids and liquid fractions. This mixture was centrifuged for 10 minutes. The resulting liquid fraction was transferred to the liquids tube and then decanted into a separate container. The solids were rinsed with approximately 5 mL of DI water, resuspended, and then centrifuged again. The 5 mL of centrifuged liquid was added to the liquid from the initial centrifuging. Concurrently, the nickel crucibles were cleaned with 1 mL of 16 M nitric acid. The nitric acid rinse was removed from the nickel crucibles and added to the solid fraction remaining after the second centrifuging. Additional DI water was used to clean any remaining bits in the crucible and was mixed along with the nitric acid rinse. The solids remaining after centrifuging generally dissolved in the nitric acid. The nitric acid and solids mix were combined with the decanted liquids, and the final contents were pH adjusted with the addition of nitric acid if needed to ensure that the solution was within pH 1-2 when checked by pH paper. The combined contents were placed inside a 25 mL volumetric flask and diluted up to the 25 mL mark with DI water. Ten milliliter aliquots were withdrawn and filtered through a 0.45 µm filter before being sent off for ICP-MS and ICP-OES analyses at SwRI or PNNL. Two PNNL staff members prepared one digestion each per sample so that duplicate solutions were made.

3.0 Results and Discussion

3.1 Rhenium Results

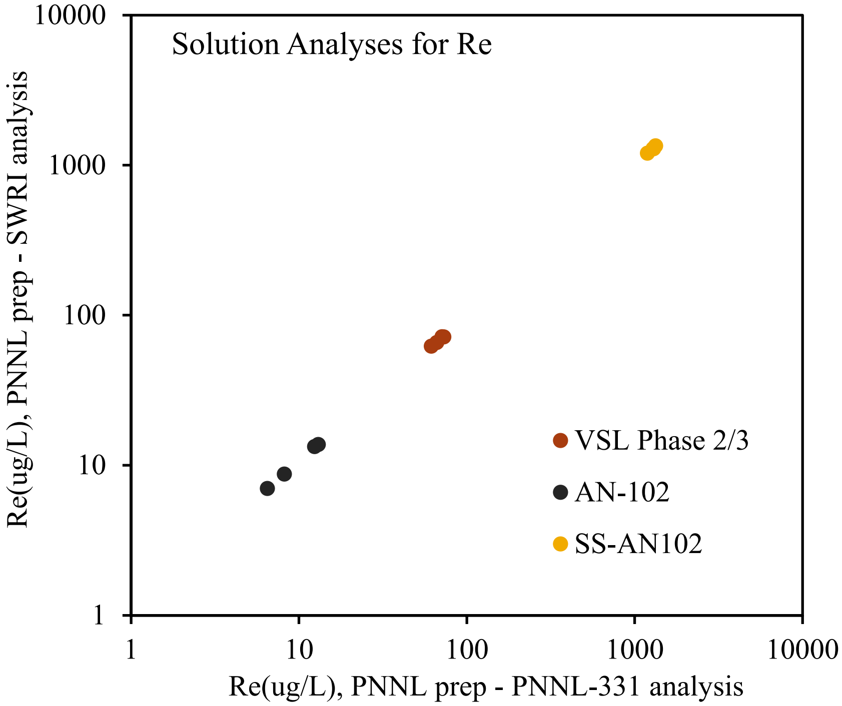
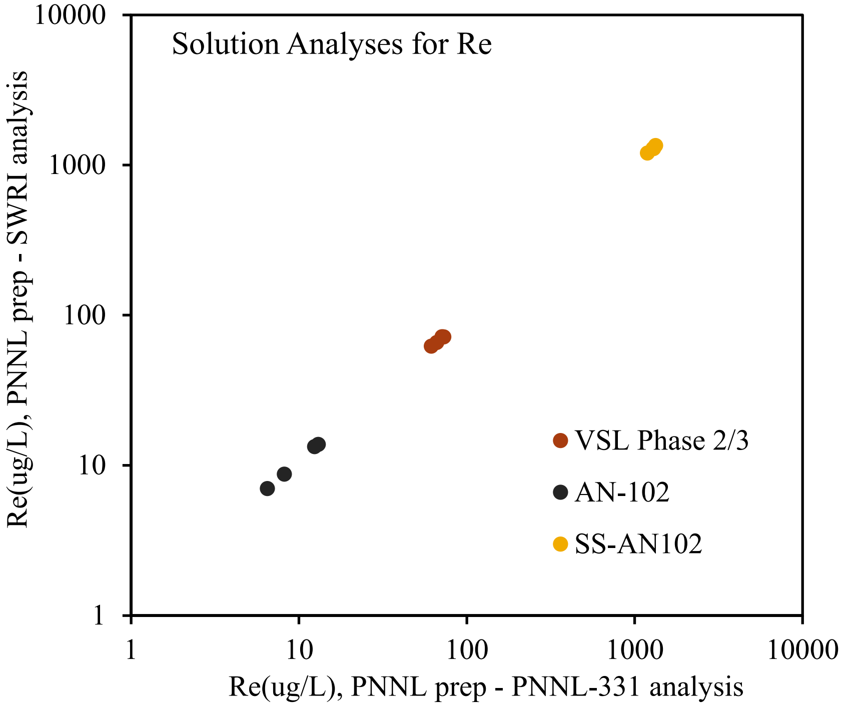


Figure 1 compares the as-measured concentrations of Re by ICP-MS at SwRI and PNNL-331 for all solutions prepared at PNNL. Because there were negligible differences between the duplicate solutions, average values were used for the plot. As shown in Figure 1, the solution analysis results from the two laboratories agree well across the wide range of Re concentrations with almost all data closely lying on the 45-degree reference line. More detailed comparisons for each group of samples including the results from SwRI preparation and analysis are given below.



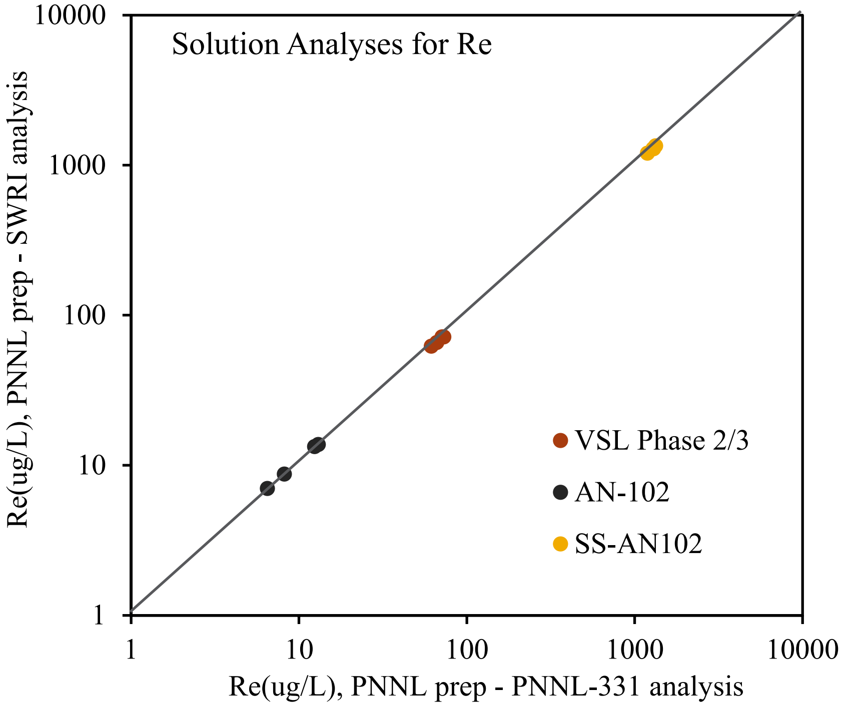


Figure 1. Rhenium Concentrations in PNNL-Prepared Solutions Analyzed by ICP-MS at PNNL-331 and SwRI

All the as-measured concentrations of Re in solution were converted to the concentration of Re in the solid. These calculations were done using the final volume of the solution and the mass of the sample that was digested/fused. The Re concentrations in VSL Phase 2/3 melter glasses from three sets of solution preparation and analysis, PNNL-prepared solution analyzed at SwRI, PNNL-prepared solution analyzed at PNNL-331, and SwRI-prepared solution analyzed at SwRI, are given in Table 1.

The average values from three sets of solution preparation and analysis and RSD are also given in Table 1.

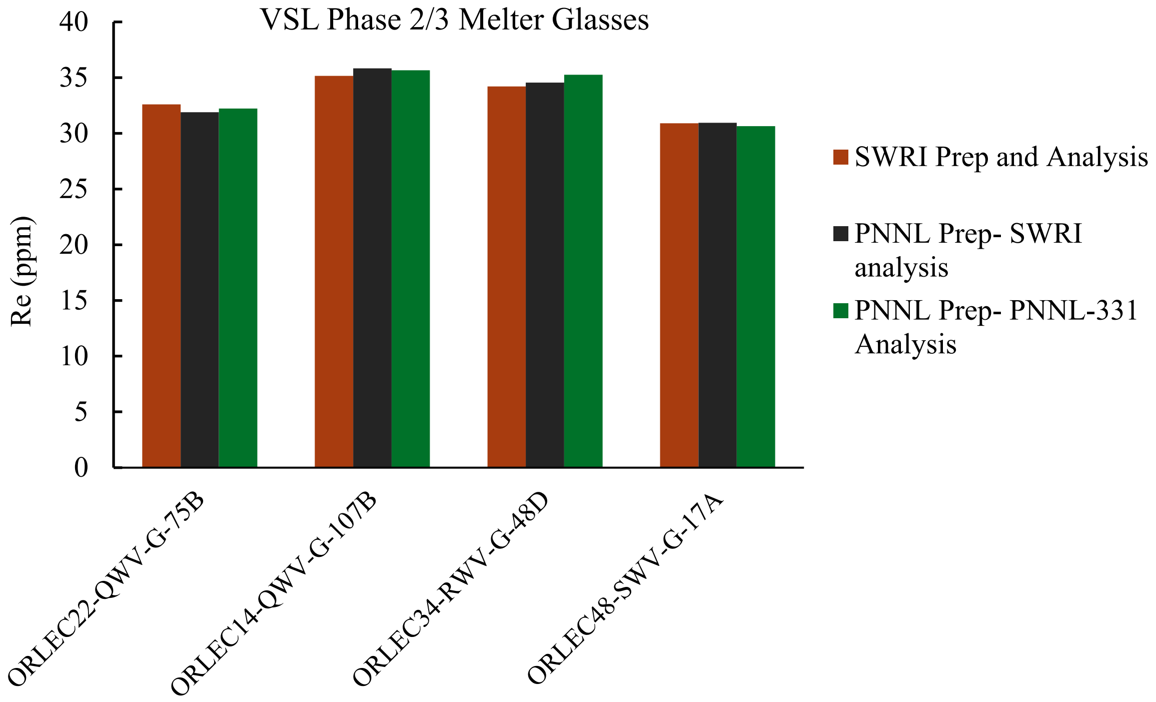


Figure 2 compares the Re concentrations in VSL Phase 2/3 melter glasses from three sets of solution preparation and analysis. From Table 1 and

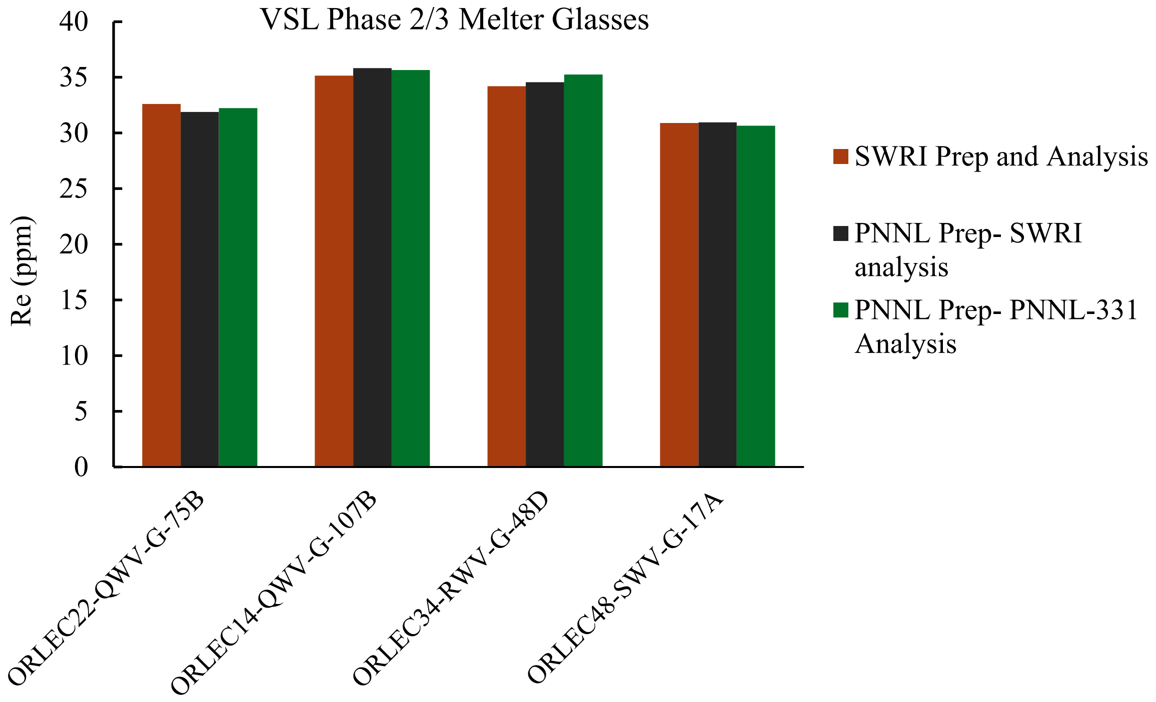


Figure 2, there was little difference between the results from different preparation and analyses for all these samples from melter tests.

Table 1. Rhenium Concentration (in Re ppm) in the VSL melter Phases 2/3 Glasses

Sample	PNNL Prep - SwRI Analysis	PNNL Prep - PNNL-331 Analysis	SwRI Prep - SwRI Analysis	Average	Relative Standard Deviation (RSD)
ORLEC22-QWV-G-75B	31.9	32.2	32.6	32.2	1.1%
ORLEC14-QWV-G-107B	35.8	35.7	35.2	35.5	1.0%
ORLEC34-RWV-G-48D	34.6	35.3	34.2	34.7	1.5%
ORLEC48-SWV-G-17A	31.0	30.6	30.9	30.8	0.5%

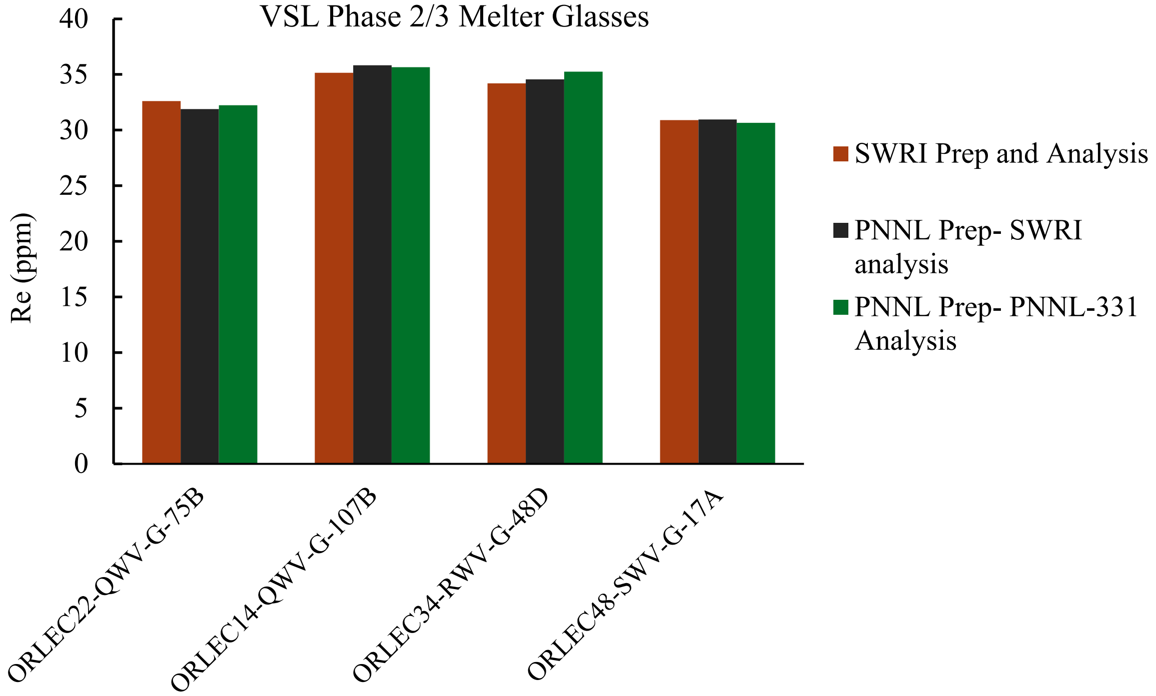


Figure 2. Rhenium Concentration in the VSL Phases 2/3 Melter Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI Analysis, and PNNL Preparation and PNNL-331 Analysis

Like Table 1, the Re concentrations in the AN-102 dried feeds and glasses and SS-AN-102 dried feeds and glasses are given in Table 2 and

Table 3, respectively. Average from three sets of solution preparation and analysis and RSD values also are given in Table 2 and

Table 3. Figure 3 and

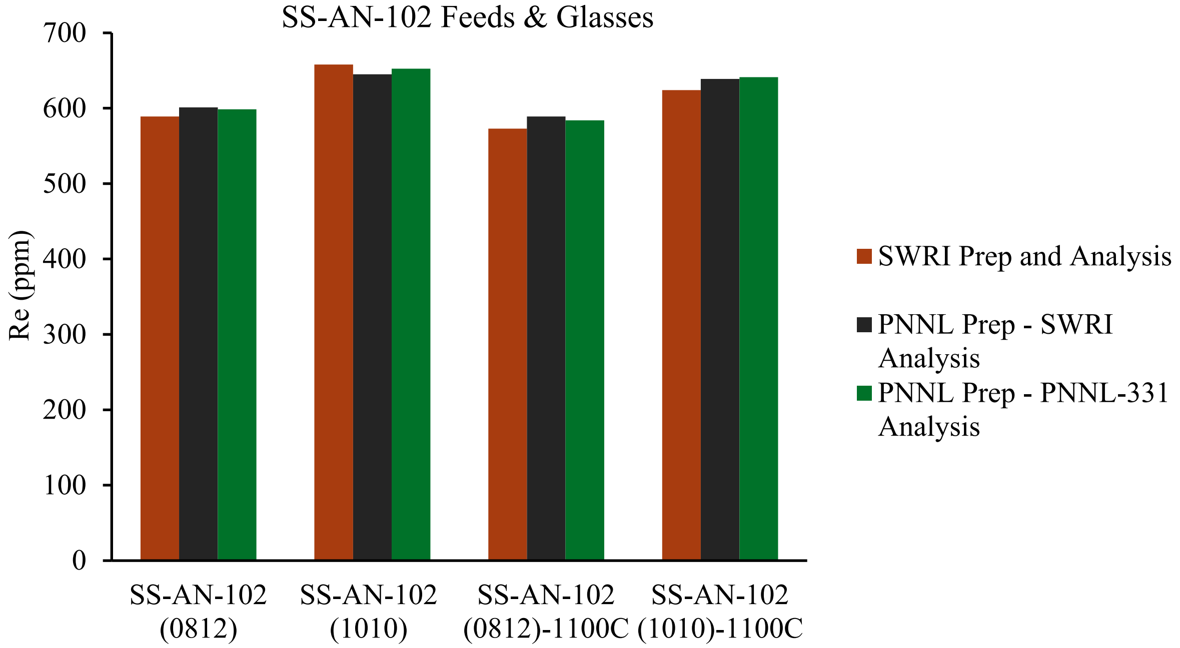


Figure 4 compare the Re concentrations in the AN-102 dried feeds and glasses and SS-AN-102 dried feeds and glasses, respectively. As shown in Table 2 and

Table 3 and Figure 3 and

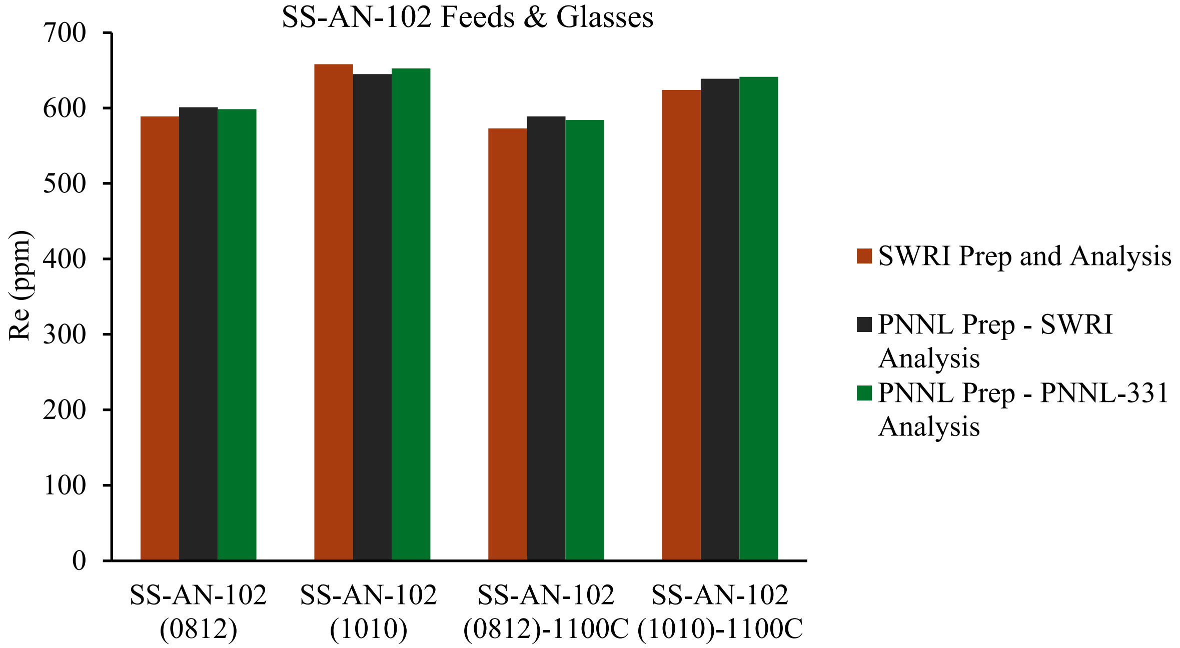


Figure 4, there was little difference between the results from different preparation and analyses for all these samples in each group of samples from crucible tests.

Table 2. Rhenium Concentration (in Re ppm) in AN-102 Feeds and Glasses

Sample	PNNL Prep - SwRI Analysis	PNNL Prep - PNNL-331 Analysis	SwRI Prep - SwRI Analysis	Average	RSD
AN-102 baseline feed	6.5	6.1	6.8	6.5	5.7%
AN-102 Sucrose feed	6.8	6.5	6.6	6.6	2.7%
AN-102 baseline 1000C	3.5	3.2	3.5	3.4	4.7%
AN-102 Sucrose 1000C	4.3	4.0	4.2	4.2	3.1%

Table 3. Rhenium Concentration (in Re ppm) in SS-AN-102 Feeds and Glasses

Sample	PNNL Prep - SwRI Analysis	PNNL Prep - PNNL-331 Analysis	SwRI Prep - SwRI Analysis	Average	RSD
SS-AN-102 (0812)	601.1	598.5	589.0	596.2	1.1%
SS-AN-102 (1010)	644.9	652.5	658.0	651.8	1.0%
SS-AN-102 (0812)-1100C	589.0	584.0	573.0	582.0	1.4%
SS-AN-102 (1010)-1100C	638.8	641.3	624.0	634.7	1.5%

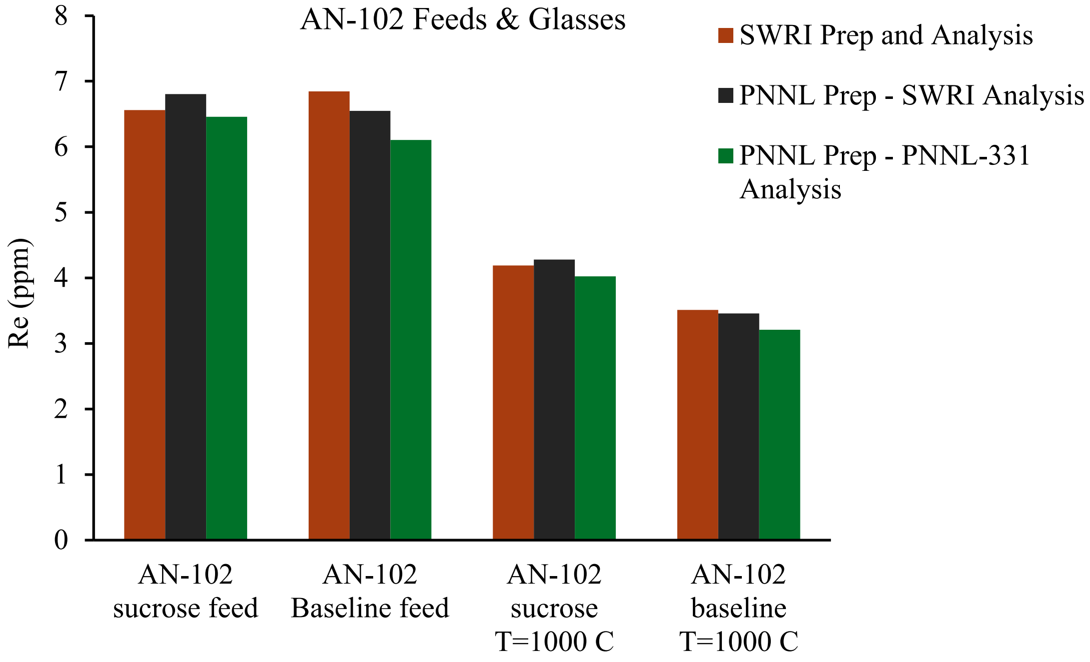


Figure 3. Rhenium Concentration in the AN-102 Feeds and Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI analysis, and PNNL Preparation and PNNL-331 Analysis

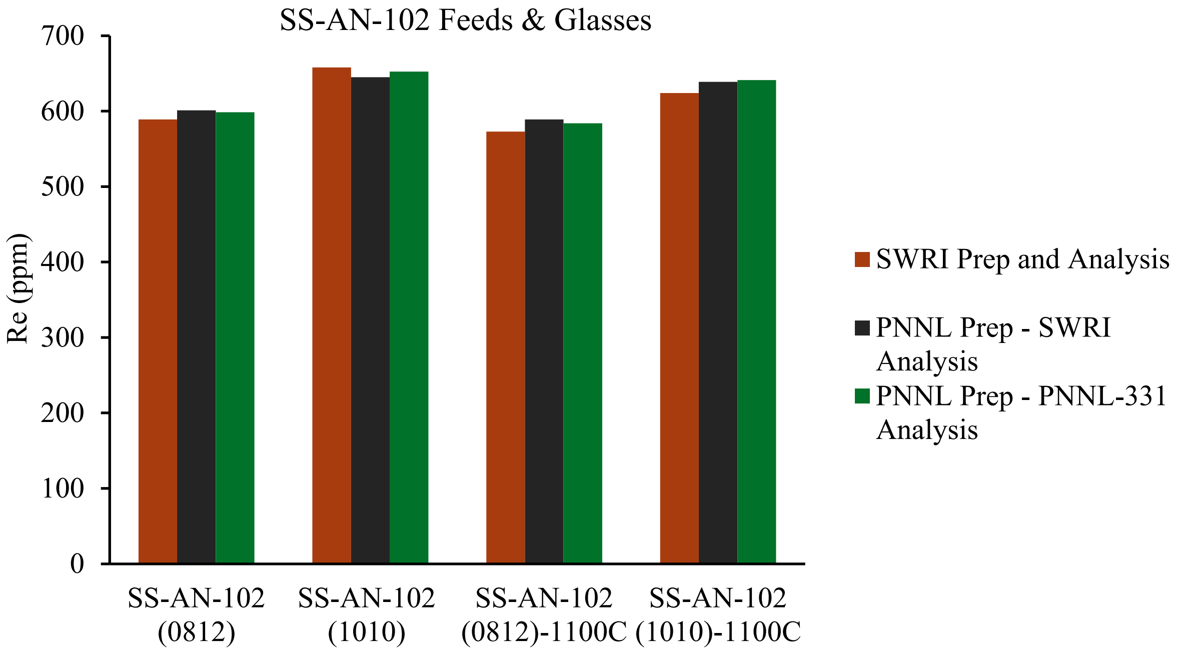


Figure 4. Rhenium Concentration in the SS-AN-102 Feeds and Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI analysis, and PNNL Preparation and PNNL-331 Analysis

3.2 Sulfur Results

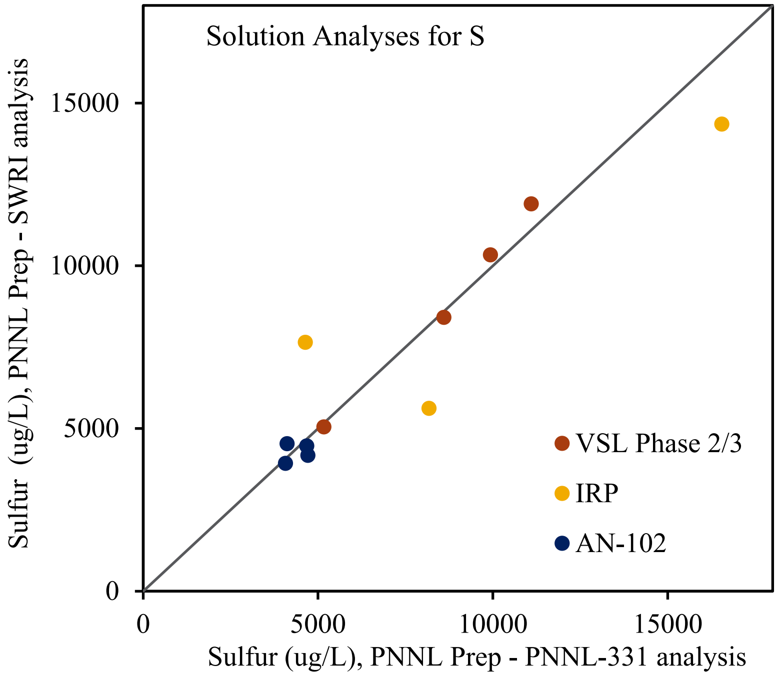
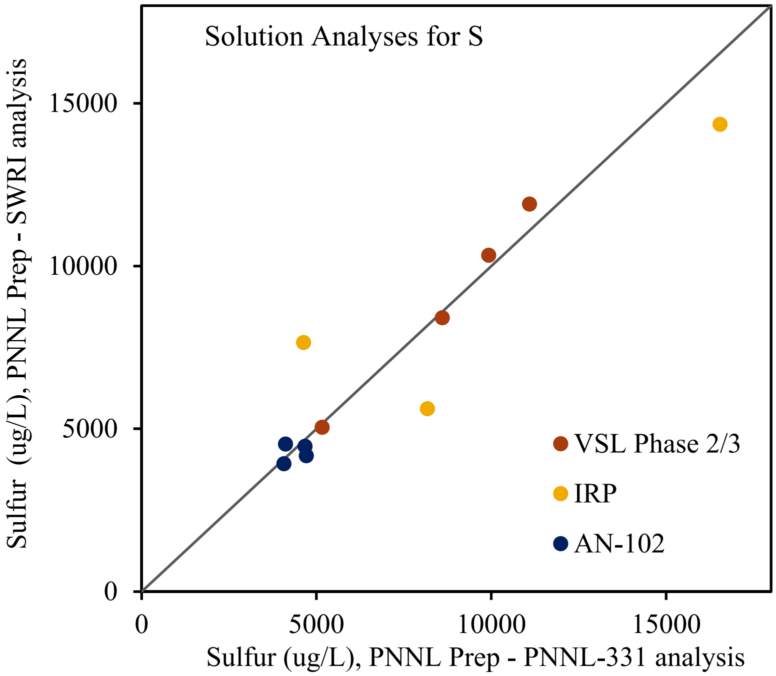


Figure 5 compares the as-measured concentrations of S measured at SwRI and PNNL-331 for all solutions prepared at PNNL. While ICP-MS was used for Re by both SwRI and

PNNL-331, ICP-OES was used for S analysis by both laboratories. Initial results that were received from PNNL-331 had to be rerun after learning that the wavelength used for S (180.667 nm) had interference from Ca. Switching the wavelength to 181.975 nm eliminated the Ca interference. There were negligible differences between the duplicate solutions, therefore, average values were used for the plot. As shown in Figure 5, the solution analysis results from the two labs showed reasonable agreement for two group of samples, VSL Phase 2/3 melter glasses and AN-102 dried feeds and glasses. However, poor agreement between the two labs was observed for the IRP S solubility study glasses. Detailed results for each group of samples including the results from SwRI preparation and analysis are discussed below.



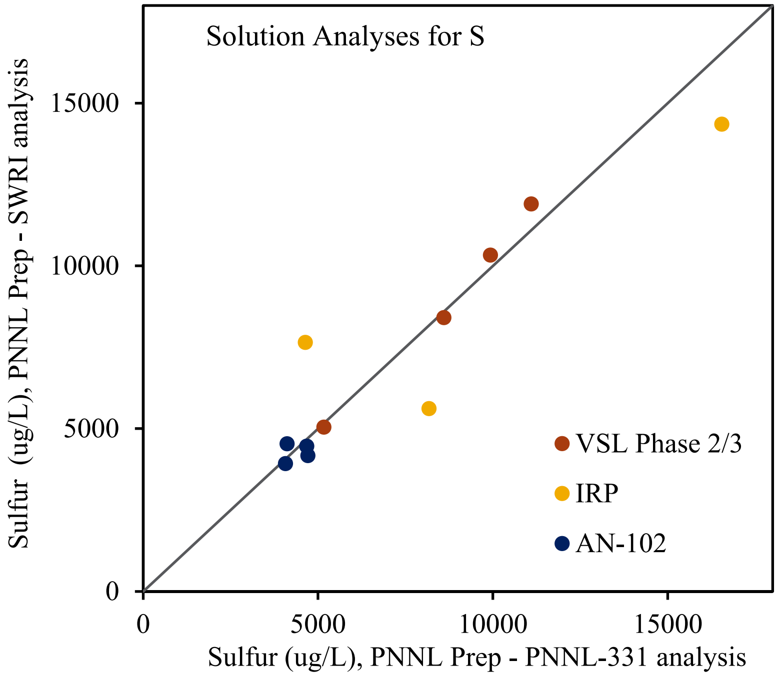
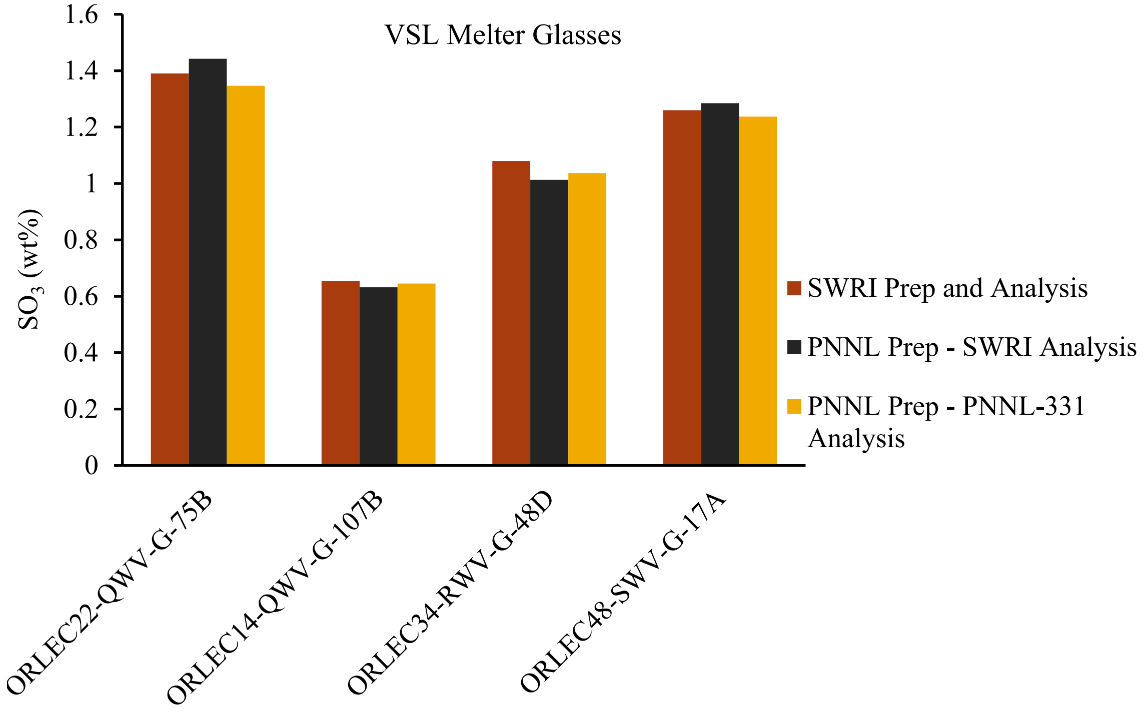


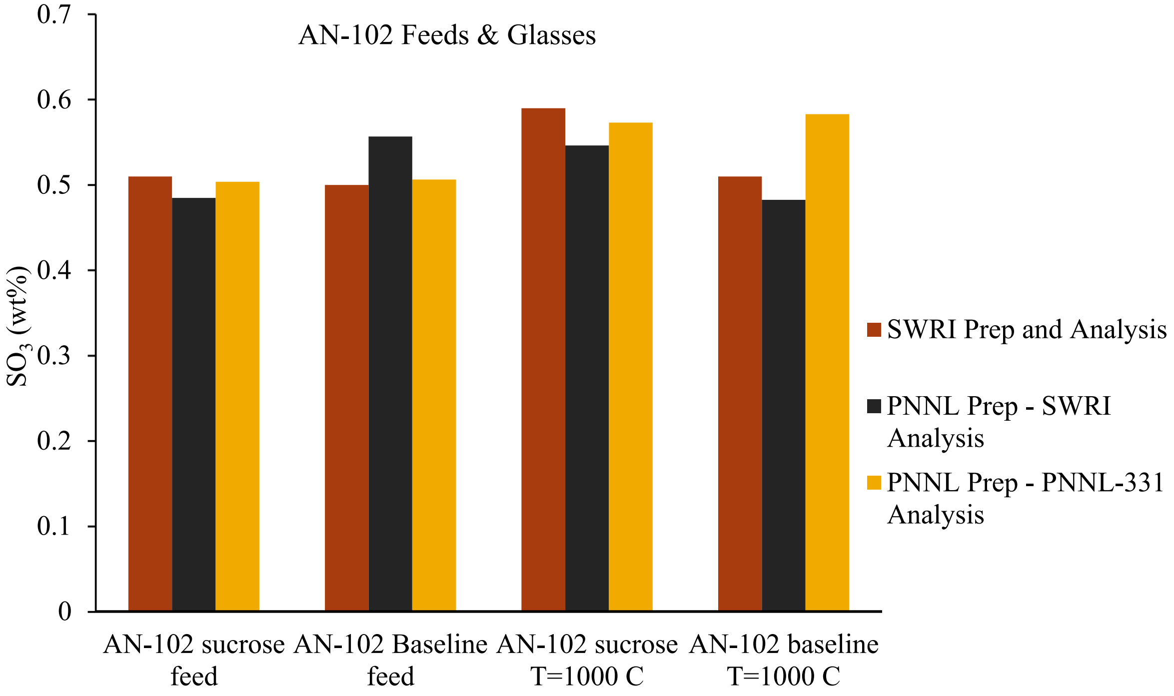
Figure 5. Sulfur Concentrations in PNNL-Prepared Solutions Analyzed by ICP-MS at PNNL-331 and SwRI

All the as-measured concentrations of S in solution were converted to the concentration of S (in terms of SO_3 wt%) in the solid. The calculations were done using the final volume of the solution and the mass of the sample that was digested/fused.

The SO_3 concentrations from three sets of solution preparation and analysis, PNNL-prepared solution analyzed at SwRI, PNNL-prepared solution analyzed at PNNL-331, and SwRI-prepared solution analyzed at SwRI are given in Table 4 (VSL Phase 2/3 melter glasses), **Error! Reference source not found.** (AN-102 feeds and gasses), and Table 6 (IRP glasses).

The SO_3 concentrations from three sets of solution preparations and analyses are compared in Figure 6 for VSL Phase 2/3 melter glasses, in





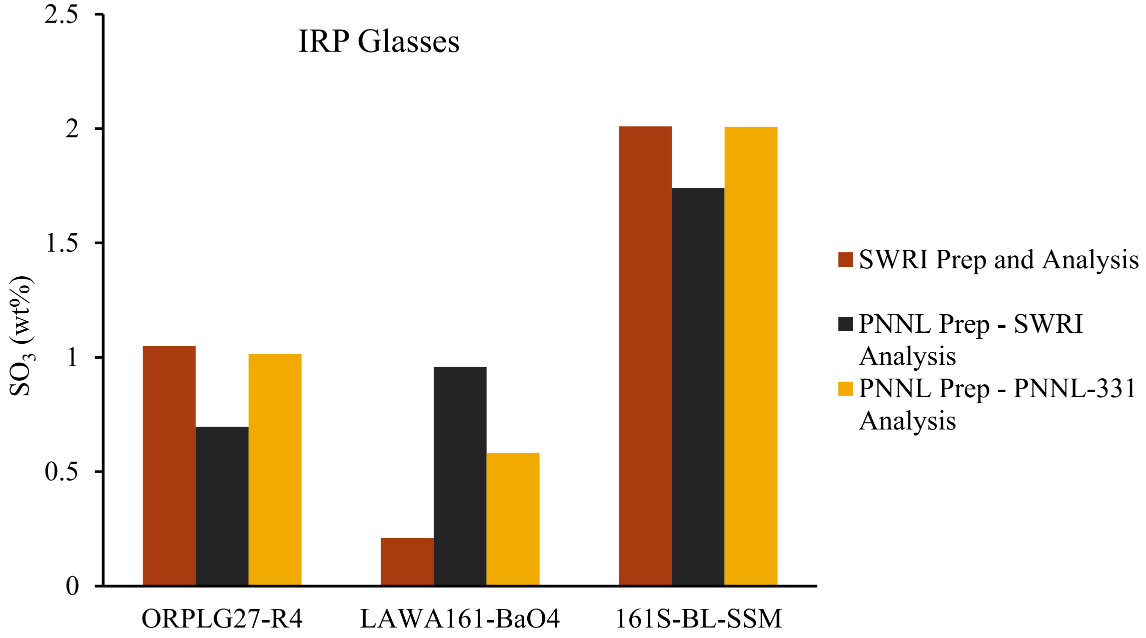
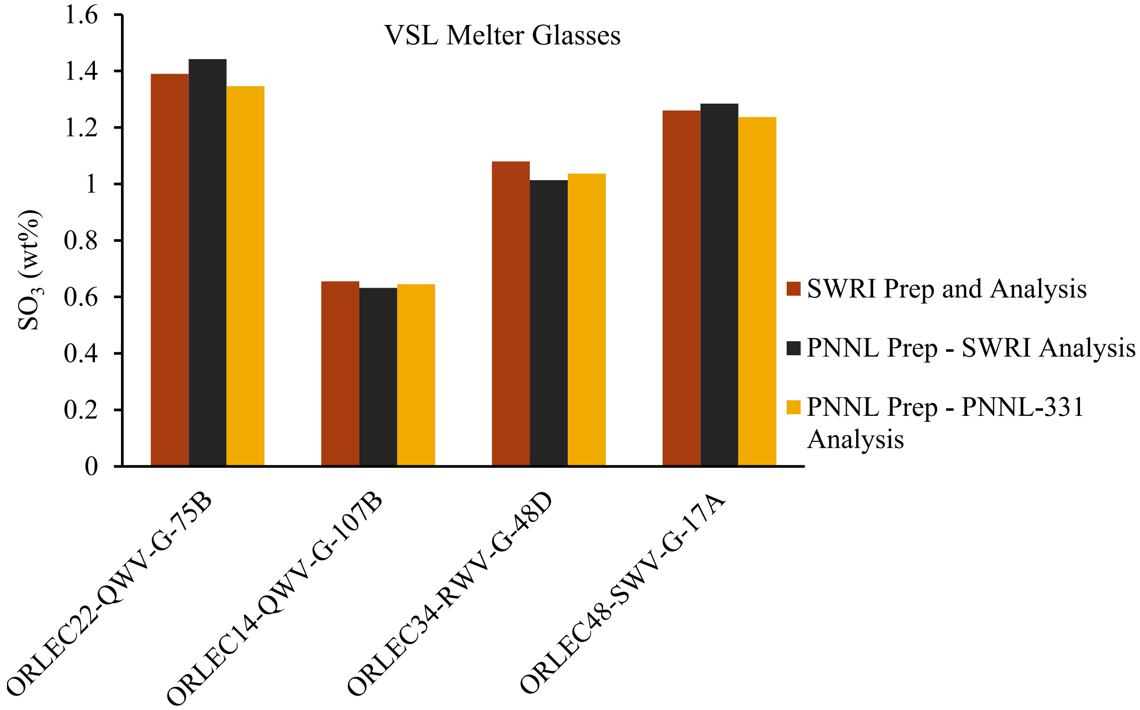
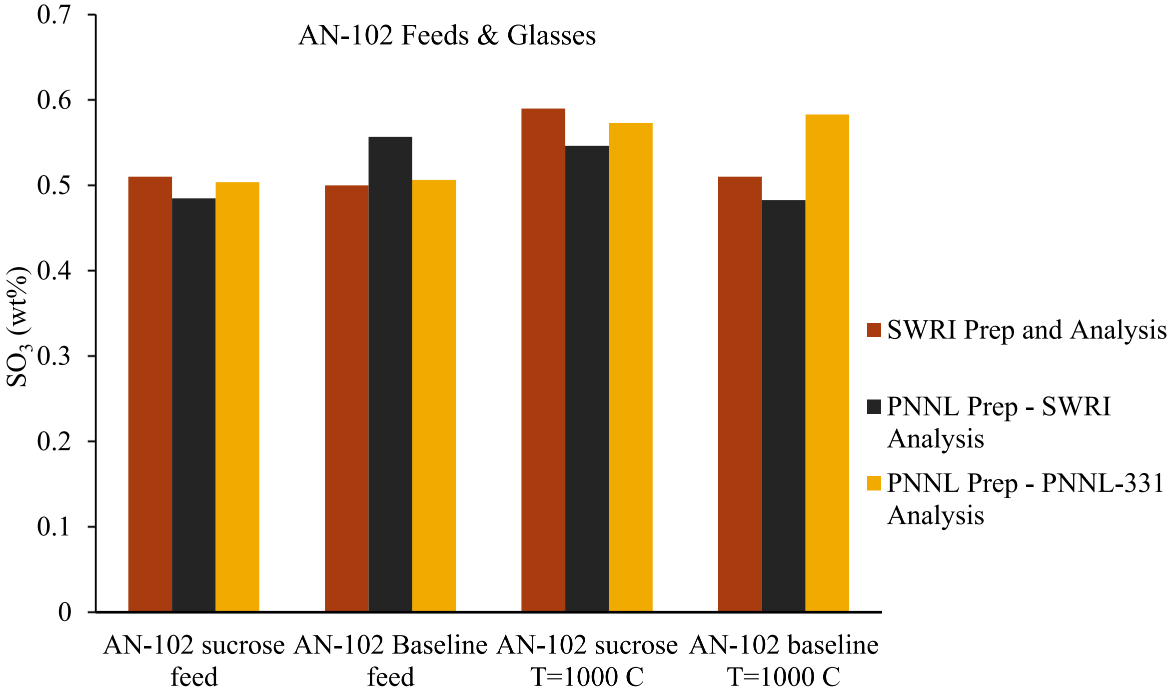


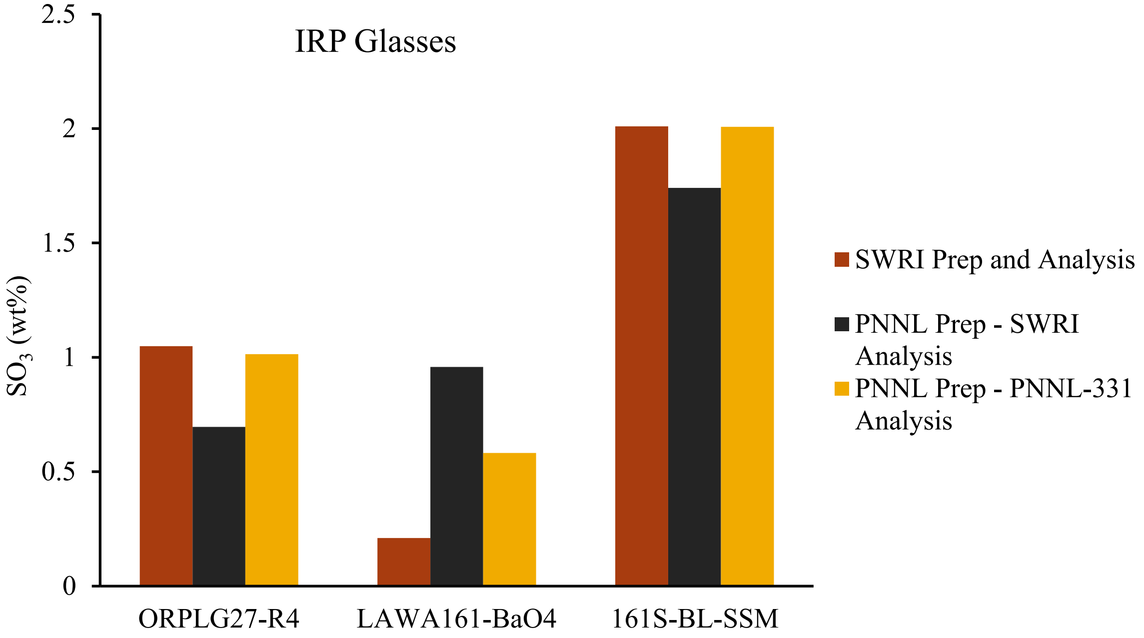
Figure 7 for AN-102 feeds and gasses, and in Figure 8 for IRP glasses. The average from the three sets of solution preparation and analysis along with RSD values are also given in Table 4 through Table 6.

There was a reasonable agreement between the results from different preparations and analyses for two groups of samples—VSL Phase 2/3 melter glasses (Table 4 and Figure 6) and AN-102 feeds and gasses (**Error! Reference source not found.** and Figure 7). The RSD values were 10% or less for these glasses, which were slightly higher than those for Re (<6%). However, the results from IRP glasses showed very poor agreement with the RSD values





between 8 and 64% (Table 6 and Figure 8).



In summary, unlike Re, the S concentrations showed reasonable agreement from three different sets of solution preparations and analyses only for two groups of samples, with RSD values less than 10%. Especially, an RSD value of 64% was observed in LAWA161-BaO4 sample from the IRP glasses. We performed a separate investigation and determined the cause of this large discrepancy was precipitation of $BaSO_4$ in digest/fusion solutions prepared from BaO-containing glasses. This issue of S analyses in BaO-containing glasses is being resolved within another project at WFDL.

Table 4. Sulfur Concentration (in SO_3 wt%) in the VSL melter Phases 2/3 Glasses

Sample	PNNL prep - SwRI analysis	PNNL prep - PNNL-331 analysis	SwRI prep - SwRI analysis	Average	RSD
ORLEC22-QWV-G-75B	1.4	1.3	1.4	1.4	3.4%
ORLEC14-QWV-G-107B	0.6	0.6	0.7	0.6	1.8%
ORLEC34-RWV-G-48D	1.0	1.0	1.1	1.0	3.2%
ORLEC48-SWV-G-17A	1.3	1.2	1.3	1.3	1.9%

Table 5. Sulfur Concentration in (SO_3 wt%) in the AN-102 Feeds and Glasses

Sample	PNNL prep - SwRI analysis	PNNL prep - PNNL-331 analysis	SwRI prep - SwRI analysis	Average	RSD
AN-102 Baseline feed	0.56	0.51	0.50	0.52	6.0%
AN-102 Sucrose feed	0.48	0.50	0.51	0.50	2.6%
AN-102 Baseline T=1000C	0.48	0.58	0.51	0.53	9.9%
AN-102 Sucrose T=1000C	0.55	0.57	0.59	0.57	3.9%

Table 6. Sulfur Concentration (SO_3 wt%) in the IRP Glasses.

	PNNL Prep - SwRI Analysis	PNNL Prep - PNNL-331 Analysis	SwRI Prep - SwRI Analysis	Average	RSD
ORPLG27-R4	0.70	1.01	1.05	0.92	21.2%
LAWA161-BaO4	0.96	0.58	0.21	0.58	64.1%
161S-BL-SSM	1.74	2.01	2.01	1.92	8.1%

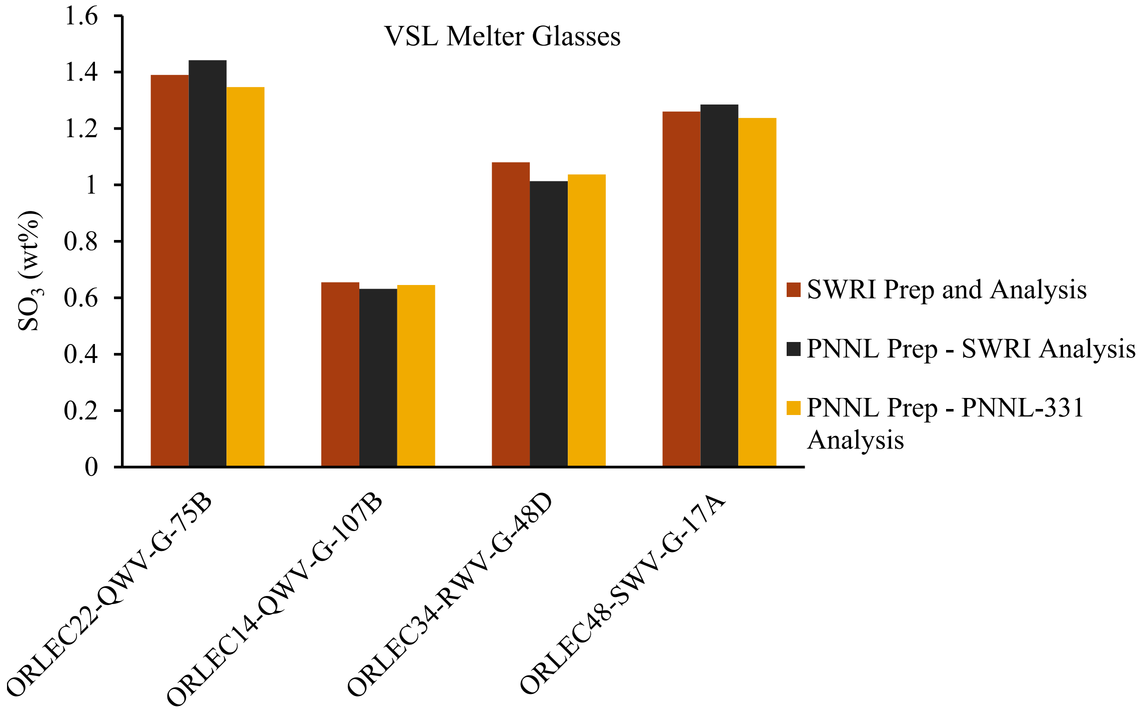


Figure 6. Sulfur Concentration in the VSL Phases 2/3 Melter Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI analysis, and PNNL Preparation and PNNL-331 Analysis

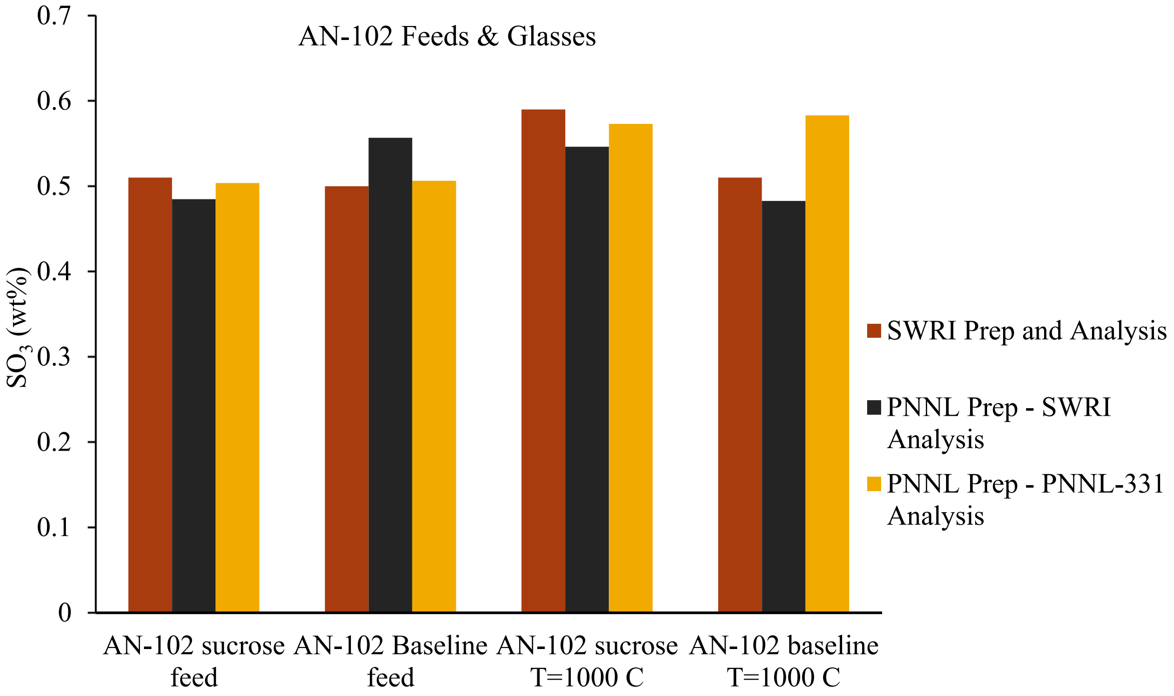


Figure 7. Sulfur Concentration in the AN-102 Feeds & Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI analysis, and PNNL Preparation and PNNL-331 Analysis

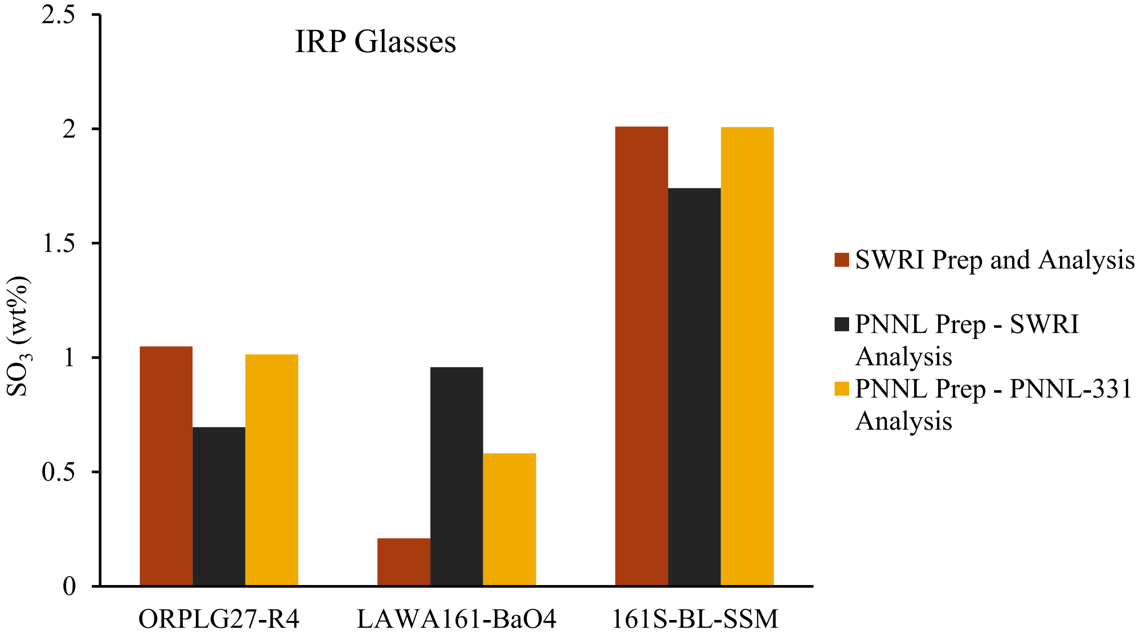


Figure 8. Sulfur Concentration in the IRP Glasses Comparing the Results from SwRI Preparation and Analysis, PNNL Preparation and SwRI analysis, and PNNL Preparation and PNNL-331 Analysis

4.0 Conclusions

Glass and feed samples with wide range of Re and S concentrations were tested to evaluate the feasibility of applying in-house solution preparation and subsequent ICP-OES and ICP-MS analyses at PNNL for Re retention and S solubility research activities at WFDL. The Re concentrations resulted in RSD values less than 6% from three different sets of solution preparations and analyses for all three groups of samples tested, suggesting that the PNNL in-house Re results can be used in parallel with the SwRI data. However, the S concentrations resulted in the RSD values of less than 10% from three different sets of solution preparations and analyses for only two groups of samples. A separate investigation identified the issue of $BaSO_4$ precipitation in digest/fusion solutions prepared from BaO-containing glasses. Until the $BaSO_4$ precipitation issue is resolved, it is proposed that the in-house S data be used for BaO free glasses, although with higher expected biases between the PNNL and SwRI results compared to Re in-house data.

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