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Analysis of Frit by Sodium Peroxide Fusion
and Flow Injection Analysis

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Abstract

Test runs for the immobilization of radioactive wastes in glass are now underway at the TNX Facility of the Savannah River Site. The wastes are immobilized by the Integrated Defense Waste Processing Facility Melter System (IDMS) process. The IDMS makes a borosilicate glass. To make the glass, certain quantities of boron and silicate must be maintained in the melter. The silicate is added to the melter in a substance called frit. To determine the amount of frit to add, it is necessary to calculate the percent silicate in the frit. The present method of determining the silicate content of frit has yielded inconsistent results. The focus of this project was to develop and implement a new process for determining the silicate content of frit. I chose to achieve this goal using a colorometric method.

Background Information

Frit is a substance that is made up primarily of silicate and boron, although there are a few metals present in small quantities. The frit is produced by a private contractor for the Savannah River Site. It has about the same properties as fine, white beach sand. The private contractor has been given strict guidelines for the composition of the frit. Before using a new shipment of frit, the Savannah River Site runs tests to see if the guidelines are being observed. The present method of testing has yielded inconsistent results and is not considered reliable.

During IDMS operation frit is placed in suspension in water and is added to the melter. The highly radioactive nuclear wastes are also added. The melter operates at 1050 degrees Celsius, and, as a result, water vapor and various gases are produced. These products are drawn off from the melter and pass through complex off-gas scrubbers and waste water treatment facilities before release into the environment. The liquid glass is poured into stainless steel cylinders 118 inches high by 24 inches in diameter which are temporarily stored at the Savannah River Site and then will be shipped to an underground storage facility in the western US for permanent storage.

The purpose of this project was to try to find a new method for measuring silicate content. I chose to use a colorometric method. This method consisted of two major steps: sample prep using sodium peroxide fusion and sample analysis using a flow injection analyzer (FIA) equipped with a spectrophotometer. The first step placed the silicate in a form that could be measured by a spectrophotometer. The second step required the addition of certain reagents to the solution from step one. These reagents caused a color change whose intensity could be measured on a spectrophotometer.

The FIA is a fairly complex instrument which consists of 3 components: the controller, the analyzer, and the autosampler. The sampler draws up a sample and pumps it to the analyzer via small Teflon tubing. The analyzer injects various chemicals into the sample causing a color change and then pumps the sample through its spectrophotometer which takes absorbance readings. Those readings are then relayed to the controller which prints

out the information numerically as well as graphically. From that information silicate content can be calculated.

Procedure

The total process each sample underwent was lengthy, although straightforward. Each of the two major steps, sample prep and sample analysis, is described below.

Sample Prep

The first step was sample prep by sodium peroxide fusion. This step transforms the silicate in frit form a solid to an aqueous solution.

Materials

Safety Equipment

- Hood
- Rubber gloves
- Safety glasses
- Face shield
- Lab coat

Lab Equipment

- Muffler furnace (capable of 750 degrees C)
- Hot plate
- Balance (accurate to .0001 g)
- pH meter (accurate to .01)
- Nickel crucible (130mL+)
- Beaker tongs
- 200 mL plastic volumetric flask
- 400 mL plastic beaker
- 2 100 mL graduated cylinders
- Funnel
- Wash bottle
- Stirring rod
- 400 mL plastic lab storage bottle
- Hot pad
- Mortar and pestle

Chemicals

- Conc. Hydrochloric acid
- Hydrofluoric acid
- Sodium peroxide
- De-ionized water (DI H₂O)

1. Place furnace and hot plate in the hood and preheat furnace to 725 degrees C and hot plate to just below the boiling point of water.
2. Label frit sample bottle.
3. Using mortar and pestle, grind entire sample into a fine powder.
4. Add .5000 g of sample to the nickel crucible. (Record exact weight on sample sheet.)
5. Add 5.00 g of sodium peroxide to crucible.
6. Place the crucible on the hot plate 10 minutes to evaporate any water present.

7. Place the crucible in the furnace at 725 degrees C for 10 minutes.
8. Remove. Allow contents to cool 5-10 minutes.
9. Add 60 mL DI H₂O to the crucible.
10. Heat crucible on hot plate and stir until no solids are present on the bottom of the crucible.
11. Pour solution into the 400 mL beaker. Rinse crucible into beaker with DI H₂O.
12. Add 10 mL of Conc. HCl to crucible to remove any residue. Heat on hot plate until just boils.
13. Pour Conc. HCl into beaker. Rinse crucible into beaker with DI H₂O.
14. Using the pH meter and HCl, lower pH from highly basic to approximately neutral. (5.50)
15. Pour contents of the beaker into the volumetric flask. Bring volume up to 200 mL by adding DI H₂O.
16. Pour contents of the volumetric flask into the lab storage bottle and label: "Frit", "HCl" and "Na₂O₂" per 200 mL, date, sample number, and your name.
17. Clean the crucible with soap and rinse with HF acid followed by DI H₂O. Clean beaker, volumetric flask, and funnel with soap and rinse with DI H₂O.

The following comments should be made. Approximately .5000 g of sample was used. The actual weights varied from .4996 g to .5032 g. The same was true for the Na₂O₂. Weights ranged from 4.98 g to 5.17 g. The reason for heating the sample before placing it in the furnace was to prevent splattering which would mean sample loss. (A reaction similar to water in hot grease would occur.) The Na₂O₂/SiO₂ reaction temperature was 725 degrees C. The sample melted to a liquid in the furnace and quickly returned to a solid as it cooled. All lab equipment that came in contact with the sample was either plastic or metal; no glass was used. This was a precaution taken to prevent silicate from possibly leaching out of the glass. The approximate time per sample was one hour. Up to four samples could be run in an assembly line fashion. For example, one sample could be on the hot plate while another was in the furnace, and one more sample could be cooling from the furnace while DI H₂O was being added to another sample.

Sample Analysis

The second step was to measure the silicate present in each sample. A flow injection analyzer (FIA) equipped with a spectrophotometer was used. Three chemical were mixed with the sample using a system of pumps, tubes, and valves.

First, the sample was injected into a carrier stream of oxalic acid. The oxalic acid complexed with any phosphates present. Second, ammonium molybdate was introduced into the carrier stream/sample. The ammonium molybdate reacted with the silicate to form a yellow molybdosilicate complex whose color intensity could be measured on the spectrophotometer. Last, ascorbic acid was added to reduce the molybdosilicate complex changing its color to blue. The spectrophotometer is more sen-

sitive to blue because it has a smaller wavelength group than yellow. The concentration was automatically calculated using a calibration curve, and the sample number, absorbance value, and concentration were printed out on hardcopy.

Materials

Safety Equipment

Safety glasses
Rubber gloves

Lab Equipment

Flow injection analyzer equipped with spectrophotometer
Balance (accurate .01 g)
Pipet or eyedropper
100 FIA sample cups
5 1.0 L plastic lab storage bottles
Stirring rod or magnetic stirrer
400 mL plastic lab storage bottle
1.0 L beaker

Chemicals

DI H₂O
Sodium metasilicate
Oxalic acid
Ascorbic acid
Ammonium molybdate
Sulfuric Acid

1. Make a 1000 ppm Si standard using sodium metasilicate.

$$1000 \text{ ppm Si} = \frac{284.064 \text{ (g/mole Na}_2\text{SiO}_3 * 9 \text{ H}_2\text{O)} * 1.00 \text{ (g Si/L)}}{28.086 \text{ (g/mole of Si)}}$$

2. Make the three reagents.
 - A. Add 35.2 g of ascorbic acid to 1.0 L of DI H₂O.
 - B. Add 25.0 g of oxalic acid to 960 mL of DI H₂O and approximately 40 mL of HCl (enough to lower pH to < .50).
 - C. Add 25.0 g of ammonium molybdate to 1.0 L of DI H₂O and 3 mL Conc. H₂SO₄.
 - D. Pour each reagent into one of the 1.0 L lab storage bottles and label. Place the three reagent bottles plus a bottle of DI H₂O and a waste bottle behind the analyzer.
3. Set up the FIA.
 - A. Run supply lines from the reagents, wash bottle, and sampler through pumps and to the silicate manifold.
 - B. Set up manifold mixing coils.
 - C. Run a line to the spectrophotometer from the silicate manifold.
 - D. Program the pump stop time (to allow reaction to progress sufficiently).
4. Run a 50 ppm Si standard. Do a wavelength scan to find optimal scan wavelength. (697 nm)
5. Program a calibration curve running 10, 20, 40, 60, 80, and 100 ppm Si standard concentrations.
6. Load sampler with samples.

7. Program number of samples and volume of sample to be injected into the carrier stream.
8. Press the "Run/Stop" key and wait for results to be printed out.

Comments: The FIA was very fast. It could accomplish in 20 minutes what would take days to do manually, and do it more accurately. Manually, the three reagents would have to be precisely added 1 at a time, allowed to react the exact same amount of time, the color change measured in a spectrophotometer, and then a calibration curve would have to be calculated the "old fashioned" paper and pen method. After all that, the concentration of each sample would have to be calculated by plugging the absorbance value into the quadratic calibration curve equation and be solved for the concentration. The calibration curve was quadratic, although there was only a slight curve among the concentrations (10, 20, 40, 60, 80, and 100 ppm). The sampler would then draw samples automatically as needed, but due to a communication failure the sampler functioned "semiautomatically"; the sample needle was moved by hand from sample to sample.

The above steps were the total process one sample underwent. Eight samples were tested. Each of the eight samples underwent sample prep in duplicate. Three standards were also run. The samples were labeled 5A through 12B. The standards were labeled 1A, 2A, and 3A. Those 19 samples were run in duplicate during sample analysis on the FIA for a total of 38 sample analyses. The samples were then labeled 5A.1 through 12B.2 and 1A.1 through 3B.2. Approximately twenty days has passed by this point in the experiment. Those days included lab training, safety training, ordering materials and getting lab equipment together, setting up the processes, and actually running the processes.

The next step was to calculate the actual percent silica present in the frit. The following data were gathered from sample analysis:

<u>Sample#</u>	<u>Conc.(ppm)</u>	<u>Sample#</u>	<u>Conc.(ppm)</u>	<u>Sample#</u>	<u>Conc.(ppm)</u>
5A.1	44.7	8A.2	50.2	11B.1	50.9
.2	45.0	B.1	52.1	.2	52.8
B.1	43.1	.2	51.2	12A.1	56.2
.2	43.6	9A.1	55.1	.2	54.9
6A.1	56.4	.2	54.4	B.1	49.9
.2	58.9	B.1	55.4	.2	50.5
B.1	54.9	.2	52.8	1A.1	56.8
.2	55.2	10A.1	50.9	.2	56.1
7A.1	54.3	.2	51.8	2A.1	56.9
.2	54.8	B.1	50.1	.2	56.9
B.1	45.4	.2	51.1	3A.1	55.3
.2	47.1	11A.1	48.7	.2	53.5
8A.1	49.4	.2	53.3		

Using the calculated silicate concentration, the sample weight (approximately .5000g), and the sample prep solution volume (.200 L), the percent silica and, therefore, silicate, for each sample was calculated as follows:

$$\% \text{ Si} = \frac{\text{Sample result (mG/L)}}{\text{Sample weight (G)} \cdot 1000 \text{ (mG/G)}} \times 100$$

.200 L

Using the above equation the following silica contents were calculated:

<u>Sample #</u>	<u>% Silicate Per Sample</u>	<u>Average % of .1-.2</u>	<u>Average % of A.1-B.2</u>	<u>Standard Dev. of A.1-B.2</u>
5A.1	1.78			
.2	1.79	1.79		
B.1	1.72			
.2	1.74	1.73	1.76	.0330
6A.1	2.25			
.2	2.35	2.30		
B.1	2.18			
.2	2.19	2.19	2.25	.0780
7A.1	2.18			
.2	2.19	2.19		
B.1	2.82			
.2	2.89	2.86	2.53	.388
8A.1	1.98			
.2	2.01	2.00		
B.1	2.09			
.2	2.05	2.07	2.04	.0479
9A.1	2.20			
.2	2.18	2.19		
B.1	2.21			
.2	2.10	2.16	2.18	.0499
10A.1	2.03			
.2	2.07	2.05		
B.1	2.01			
.2	2.05	2.03	2.04	.0258
11A.1	1.95			
.2	2.13	2.04		
B.1	2.04			
.2	2.11	2.08	2.06	.0814
12A.1	2.25			
.2	2.19	2.22		
B.1	1.99			
.2	2.01	2.00	2.11	.130
1A.1	2.27			
.2	2.25	2.26	----	.0141
2A.1	2.27			
.2	2.27	2.27	----	0
3A.1	2.21			
.2	2.14	2.18	----	.0495

Average percent Si of all 38 samples = 2.14

Standard Deviation = .230 (ppm)

Percent Variance of all 38 samples = 10.8

n = 38

Conclusion

The average percent silicate found in each of the 38 samples was 2.14. The original eight samples and three standards were known through previous testing and manufacturers specifications to be between 33 and 35 percent silicate. The results achieved by the experiment were extremely low. There are a couple of possible explanations for this discrepancy. Both are involved with the sample prep step.

One of the goals of sample prep was to lower the pH to a fairly neutral number, 5.5. Every sample had a pH of > 12.0 before hydrochloric acid was added in step 14 of sample prep. It was theorized that if the pH was highly basic, the later chemistry of sample analysis would not take place properly. At a pH of 12, many precipitants were present -- probably metal hydroxides. As hydrochloric acid was added, some precipitants dissolved into solution, but there were still many present. The solids could have contained silicate, and since only the liquid was used in sample analysis, the results could have been low. To test this theory, sample standard 1 was run through the whole process from the mortar and pestle to calculation of percent silicate, but this time hydrochloric acid was added until all solids dissolved into solution (pH < .15). The results were almost identical to sample standard 1A with solids. Two conclusions were made: solids did not seem to affect later chemistry of sample analysis and highly acidic pH did not affect the later chemistry of sample analysis.

The second reason and probably the more valid was that the oxidizer, sodium peroxide, was reacting "too far." The desired reaction between sodium peroxide and silicate was:

but the reaction that may have taken place was:

Ammonium molybdate will react with SiO_3 , but not SiO_4 . Therefore, there could not be a color change, and the spectrophotometer could not take an absorbance reading. There was not enough time to try another oxidizer that contained only one atom of oxygen. A good suggestion for further research would be to try an oxidizer in the sample prep step that only contains one oxygen.

Personal Experience

On a personal note, I would like to say that I learned more in this six week program than I have ever learned in any other six weeks. I learned everything from how to be brief and direct on the telephone concerning business to how to program a flow injection analyzer. I used or observed the use of many scientific instruments on the cutting edge of technology, and I also sharpened my skills using everyday lab equipment. It is going to be tough to go back to school in a few weeks after working

with such professionals in the workforce. This has been a great program, and I hope that other students also get a chance to participate in it in the coming years.

Acknowledgments

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