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MEMORANDUM

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VERIFICATION AND STANDARDIZATION OF REDOX MEASUREMENT FOR DWPF

SUMMARY

The colorimetric procedure for DWPF glass redox measurement developed by Baumann,[1,2] was verified by analyzing a series of reduced glasses using multiple techniques. The glasses were analyzed by (1) SRL-ADD using the colorimetric procedure, (2) SRL using Mossbauer spectroscopy, (3) Corning Glass Works (CGW) using the colorimetric procedure, and (4) CGW using a titration procedure. The results of the interlaboratory redox measurements indicated the following:

- the results of the colorimetric procedure were reproducible at SRL and CGW
- the Fe^{2+}/Fe^{3+} redox ratios correlated poorly
- the $Fe^{2+}/\Sigma Fe$ redox ratios correlated well
- the $Fe^{2+}/\Sigma Fe$ ratio can potentially be used to standardize the DWPF redox measurement

It is recommended that the DWPF redox measurement be based on the $Fe^{2+}/\Sigma Fe$ ratio rather than on the Fe^{2+}/Fe^{3+} ratio. The acceptable DWPF redox range based on the $Fe^{2+}/\Sigma Fe$ is 0.09-0.33 rather than the range of 0.1-0.5 based on the Fe^{2+}/Fe^{3+} ratio.

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BACKGROUND

The oxidation/reduction (redox) equilibrium in the Defense Waste Processing Facility (DWPF) melter is critical to the processing of high-level nuclear waste glass. The glass needs to be somewhat reducing to minimize glass foaming[3,4] and devitrification.[5] However, overly reducing conditions may cause metallic species to form in the melt. The metallic species can agglomerate, settle to the floor of the melter, and potentially short the joule-heated electrodes.[6-9] Reducing conditions in the DWPF melter can be caused by formic acid additions during waste sludge processing, aromatics from the tetraphenylborate (TPB) precipitate hydrolysis, and the presence of activated charcoal in some of the DWPF wastes. Oxidizing conditions can be caused by nitrate formed from the sodium nitrite corrosion inhibitors in the sludge, and from air inleakage into the melter.

The melter redox state can be measured from the Fe^{2+}/Fe^{3+} ratio of the final solidified glass. An Fe^{2+}/Fe^{3+} ratio between 0.1-0.5 has been recommended as an acceptable range for glasses produced in the DWPF.[10] This range appears optimal in terms of avoiding both (1) foaming, and (2) precipitation of metallic species during glass melting. This redox range agrees with the range determined at Pacific Northwest Laboratory in support of the West Valley project,[9,11] and redox determinations from Case Western University.[4] Fe^{2+}/Fe^{3+} ratios of 0.1-0.5 correspond to melter fugacities between 10^{-4} and 10^{-8} atmospheres based on calibration curves developed by Schreiber[12] for DWPF glasses.

Redox Ratios Determined from Wet Chemical Methods

1. Colorimetric Procedure

A rapid and reliable method for predicting the melter redox conditions using the Fe^{2+}/Fe^{3+} ratio determined from a vitrified feed sample has been developed by Baumann.[1,2,13] In this procedure the feed sample is vitrified in a closed crucible at 1150°C and then cooled to room temperature. A sample of the cooled glass is dissolved in HF/H_2SO_4 in the presence of NH_4VO_3. The ammonium vanadate protects the Fe^{2+} so the procedure can routinely be performed in air.[1,2,13] The dissolution portion of the technique is similar to that developed by Wilson.[14] Boric acid is added to complex the fluoride. The Fe^{2+}-specific chromogen Ferrozine (Trademark Hach Chemical Company) is added and the absorbance attributable to the Fe^{2+} is measured colorimetrically. The analytic methodology is similar to the photometric technique described by Jeffery.[15] Ascorbic acid is added to the same solution to reduce the Fe^{3+} to Fe^{2+} so that the absorbance attributed to the total iron can be measured colorimetrically. Fe^{3+} is calculated as the difference between the Fe^{2+} absorbance measured and the total Fe absorbance measured. The Fe^{2+}/Fe^{3+} ratio is determined directly from the absorbance values and the absolute value of each species is not determined. The relative uncertainty is estimated at ±5%.

2. ASTM C-169 and CGW Procedures

The ASTM C-169 procedure for measuring Fe^{2+} in soda-lime and borosilicate glasses is in draft form and will not be formally issued until 1990. A copy of this draft procedure became available to SRL in June, 1988.[16] Since the procedure is primarily used to determine small amounts of FeO in Fe_2O_3-containing bottle glass, it is similar to the procedure currently used by CGW to determine Fe^{2+}/Fe^{3+}.

The details of Corning's procedure are given in Appendix I. It is primarily a combination of the Pratt dissolution methodology[17] in an inert atmosphere and the Close and Tillman measurement methodology[18] by ceric sulfate titration. The ASTM procedure is a combination of the Pratt dissolution methodology[17] and the photometric measurement methodology of Jeffrey.[15] The measurement methodology is, therefore, similar to that used in SRL's colorimetric[1,2,13] procedure except that Baumann chose Ferrozine instead of 1,10 Phenanthroline (phen) because the Ferrozine develops a stable color more rapidly.

In both the CGW and the ASTM procedures, a glass sample is dissolved in an HCl/HF mixture under an atmosphere of CO_2, N_2 or Ar. This is a deviation from the Pratt methodology which specifies dissolution in a less oxidizing mixture of acids, e.g. HF/H_2SO_4. In the CGW technique, ferrous iron is determined by titration with standardized ceric sulfate. In the ASTM procedure the Fe^{2+} is determined colorimetrically using phen. In the CGW technique, the remaining Fe^{3+} is reduced with stannous chloride and the total iron determined by titration with ceric sulfate. The Fe^{3+} is calculated as the difference between the total iron and the Fe^{2+} so that the Fe^{2+}/Fe^{3+} ratio can be determined. In the ASTM procedure only the Fe^{2+} is measured and the total iron as Fe^{3+} is determined by a separate dissolution in $HF/HClO_4$ followed by colorimetric determination using phen.

Comparison of Redox Measurements Determined by Wet Chemical Methods and Mossbauer Spectroscopy

Mossbauer spectroscopy is capable of measuring glass redox non-destructively. Since no dissolution is necessary, the Fe^{2+}/Fe^{3+} ratio is determined directly from the relative areas of the Fe^{2+} and Fe^{3+} spectra. The Mossbauer spectroscopy results are, however, dependent on the curve fitting technique used to deconvolute the spectra.

Mossbauer spectroscopy has been extensively examined[19-21] for measurement of the Fe^{2+}/Fe^{3+} ratio of vitrified melter feed samples. A comparison of the ferrous iron to total iron ratio, expressed as $Fe^{2+}/\Sigma Fe$ by wet chemical techniques and Mossbauer spectroscopy has been conducted at Pacific Northwest Laboratory.[11,22] These results indicated that the ratios from the Mossbauer spectra overestimated the proportion of $Fe^{2+}/\Sigma Fe$ by a factor of 1.2 and the Fe^{2+}/Fe^{3+} ratio by 1.5. The slope was shown to invert when the dependent variable was switched during regression analysis[22] and hence the $(Fe^{2+}/Fe^{3+})_{chemical} = 0.66(Fe^{2+}/Fe^{3+})_{Mossbauer}$. The authors attributed the bias to the Mossbauer curve fitting technique and not to errors in the wet chemical methodology. However, the wet chemical technique used in the PNL study was performed in air and did not use the NH_4VO_3 to protect the Fe^{2+}. This could, indeed, cause the lower Fe^{2+} ratios for the wet chemical methodology[1,2] and the observed bias.

Comparisons of the redox ratios determined by Mossbauer and wet chemical techniques was also investigated at The Carnegie Institute of Washington Geophysical Laboratory,[23] at Clemson University,[19,21] and at SRL.[20] No systematic bias was found in any of these studies. The Clemson study found that $(Fe^{2+}/Fe^{3+})_{chemical} = 0.91 (Fe^{2+}/Fe^{3+})_{Mossbauer}$. The SRL study[20] found that the $(Fe^{2+}/Fe^{3+})_{chemical} = 1.03 (Fe^{2+}/Fe^{3+})_{Mossbauer}$ and the Geophysical Laboratory determined a correlation of $(Fe^{2+}/Fe^{3+})_{chemical} = 1.01 (Fe^{2+}/Fe^{3+})_{Mossbauer}$. All these studies used a wet chemical technique which was performed in air but used NH_4VO_3 to protect the Fe^{2+} species.

The Clemson study[19,21] also compared Baumann's colorimetric procedure to other wet chemical procedures. That study concluded that the colorimetric procedure was more reliable and reproducible than the other wet chemical methods. However, it was noted that neither Baumann's procedure nor the other analytic techniques gave reliable results for highly oxidized or highly reduced glasses.

This study was initiated to compare the Fe^{2+}/Fe^{3+} ratios determined by Baumann's colorimetric procedure with ratios determined by the CGW procedure and by Mossbauer spectroscopy. The ASTM C-169 procedure for ferrous iron determination has not been examined because it is in draft form and it only measures Fe^{2+} and not a redox ratio such as Fe^{2+}/Fe^{3+} or $Fe^{2+}/\Sigma Fe$. The reproduciblility of redox ratios determined at SRL and at CGW using Baumann's technique were also investigated.

EXPERIMENTAL

Three samples of glass were fabricated under varying redox conditions. The sludge-only glass compositions were made from TDS-3A average calcined waste (without coal) and 165 frit.[24] Varying amounts of a resorcinol-formaldehyde ion exchange resin,[25] $(Na,K)_{0.53}C_7H_{6.47}O_2 \cdot 2.36\ H_2O$,[26] were added to each glass before melting. Melting in closed crucibles for 4 hours at 1150°C imparted varying redox conditions to the three glasses. Addition of 1.0, 3.5, and 7 grams of resin produced three glasses doped with 0.039, 0.135, and 0.271 moles of carbon since 1 gram of resin equals 0.039 moles of carbon. The glasses were designated Resin-1, -2, and -3, respectively.

The Fe^{2+}/Fe^{3+} ratios were determined by the colorimetric procedure at both SRL and at Corning Glass Works. The Fe^{2+}/Fe^{3+} ratio was determined by Corning Glass Works using their own dissolution procedure which is similar to the draft ASTM C-169 dissolution procedure.[19] The redox ratio was also determined by Mossbauer Spectroscopy at SRL. X-ray diffraction analyes were conducted to determine if reduced metallic species were present in the glass.

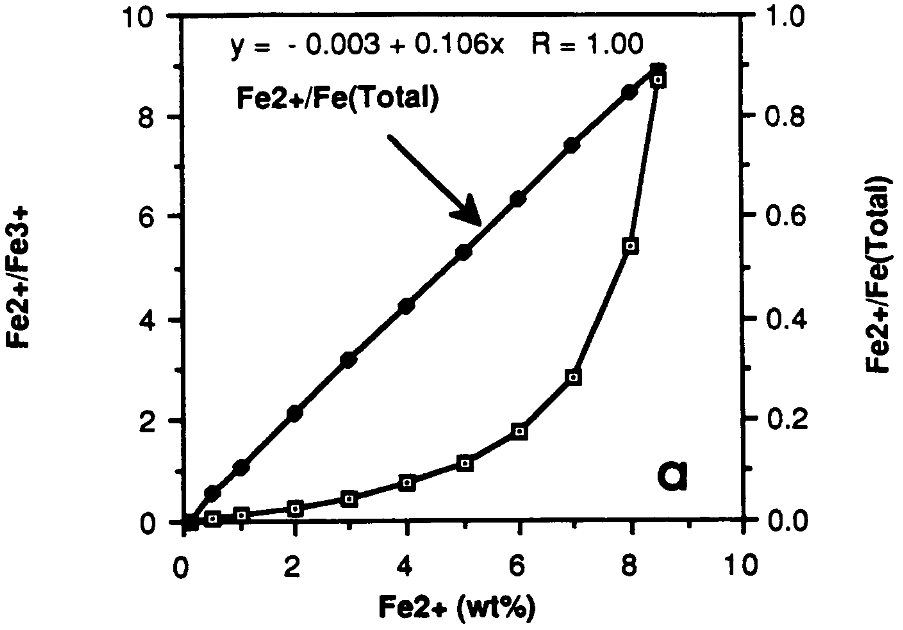
RESULTS AND DISCUSSION

Validation of Measurement Techniques

No glass redox standards are available for evaluating various redox measurement techniques. Since these three glasses were made from batch chemicals, the total iron content was known ($\Sigma Fe=9.48$ wt%).[24] An idealized plot of Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ can be derived by assuming Fe^{2+} (wt%) = 1,2,3, etc (Figure 1a). Graphically, Figure 1a demonstrates why large errors are to be expected with any Fe^{2+}/Fe^{3+} measurment technique in highly oxidized (high Fe^{3+}) or highly reduced (high Fe^{2+}) glasses, e.g. small errors in measurement at high Fe^{2+} or high Fe^{3+} lead to large errors in the Fe^{2+}/Fe^{3+} ratio.

The relationship between Fe^{2+} (wt%) and $Fe^{2+}/\Sigma Fe$ is linear with an intercept of 0.0 and a slope of 0.106 (Figure 1a) which is equal to $1/\Sigma Fe$. The values of $Fe^{2+}/\Sigma Fe$ range from 0.0 to 1.0. For the range of Fe^{2+}/Fe^{3+} ratios anticipated in DWPF, 0.1-0.5, the deviation between Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ is not significant (Figure 1b). In the event that more reducing or more oxidizing conditions are encountered, reporting the $Fe^{2+}/\Sigma Fe$ rather than the Fe^{2+}/Fe^{3+} ratio would be more accurate.

For the purpose of this study, plots of Fe^{2+}(wt%) versus Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ were compared. Since the colorimetric procedure and the Mossbauer technique measure the Fe^{2+}/Fe^{3+} ratio and the ΣFe was known, a Fe^{2+} content could be calculated. The CGW report (Appendix I - Exhibit A) gives both Fe^{2+} and ΣFe in wt% for the titration procedure. For the colorimetric procedure the $Fe^{2+}/\Sigma Fe$ can be calculated directly from the absorbance data in Appendix I - Exhibit D. The values calculated agree with those calculated from the Fe^{2+}/Fe^{3+} and $\Sigma Fe=9.48$ wt%.



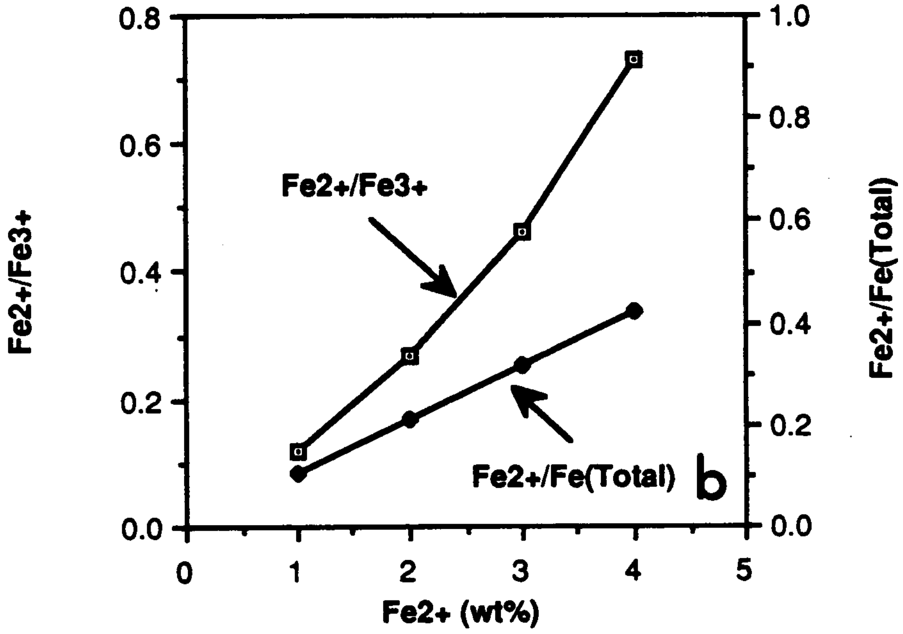


Figure 1. Graphical relationship of the ideal Fe^{2+}/Fe^{3+} ratio and the $Fe^{2+}/\Sigma Fe$ ratio with Fe^{2+} (wt%) at ΣFe=9.48 wt%.

(a) over entire range of $Fe^{2+}/\Sigma Fe$

(b) over anticipated range of DWPF glass redox conditions, e.g. Fe^{2+}/Fe^{3+} = 0.1-0.5

The Fe^{2+} content of reduced waste glasses should be proportional to the number of moles of carbon reacted during glass melting under closed system conditions. The overall oxidation-reduction equation by which Fe_2O_3 in the calcined waste reacts with carbon in the organic resin can be written on either a CO or CO_2 basis.[25] X-ray diffraction analyses revealed that the glass containing the most resin had precipitated metallic nickel. The precipitation of nickel is known[27] to be dominated by redox reactions involving CO. Therefore, the overall redox reaction can be written as:

$$Fe_2O_3 + C \longrightarrow 2FeO + CO \qquad (1)$$

so that 1 mole of carbon should create 2 moles of Fe^{2+}. Therefore, the number of moles of Fe^{2+} should be a linearly related to the number of moles of carbon with an ideal slope of 0.5. Likewise, the Fe^{2+} in wt% should be a linear function of the carbon reacted and, at constant total iron, the number of moles of carbon should also be linearly related to the $Fe^{2+}/\Sigma Fe$ ratio.

In this study, plots of Fe^{2+} (wt%) and carbon (moles) versus Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ were compared. In addition plots of Fe^{2+}(both in wt% and moles) and moles of carbon reacted were compared. Validation of the measuement methodologies was based on the following criteria:

- Linearity of Fe^{2+} (wt%) versus $Fe^{2+}/\Sigma Fe$ with a theoretical slope of $1/\Sigma Fe$.
- Linearity of carbon (moles) consumed during reaction versus $Fe^{2+}/\Sigma Fe$.
- Linearity of Fe^{2+} (wt%) and Fe^{2+} (moles) versus carbon (moles) consumed during reaction.
- Linearity of Fe^{2+} (moles) versus carbon (moles) with a theoretical slope of 1/2.

1. SRL/ADD Colorimetric Procedure

The values of the Fe^{2+}/Fe^{3+} ratio determined by the Analytical Development Division (ADD) at the Savannah River Laboratory (SRL) are given in Table I. Standard deviations are not shown since replicate analyses were not performed. Since the Baumann procedure measures the Fe^{2+}/Fe^{3+} ratio from the relative colorimetric absorbances, the values for the $Fe^{2+}/\Sigma Fe$ ratio (Table II) and Fe^{2+} in wt% (Table III) were calculated from the Fe^{2+}/Fe^{3+} ratio and the known as-made total Fe content (ΣFe= 9.48 wt%).

Table I. Comparative Analyses of Fe^{2+}/Fe^{3+} Ratio for Resin-Doped Sludge-Only 165 Glass.

Sample	SRL[t] Colorimetric Procedure	CGW* Colorimetric Procedure	CGW* Titration Procedure	SRL Mossbauer Technique
Resin-1	0.18	0.28 ± 0.03	0.16 ± 0.05	0.11 ± 0.04
Resin-2	0.66	0.69 ± 0.02	0.59 ± 0.05	0.26 ± 0.07
Resin-3	5.60	17.87 ± 11.6	3.13 ± 0.54	5.78 ± 4.15

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[t] only one sample of each glass was analyzed at SRL using the colorimetric procedure and standard deviations were not calculated

* Data for calculation of average values and standard deviations given in Appendix I (Exhibits A and D).

Table II. Comparative Analyses of $Fe^{2+}/\Sigma Fe$ for Resin-Doped Sludge-Only 165 Glass.

Sample	SRL[t] Colorimetric Procedure	CGW* Colorimetric Procedure	CGW** Titration Procedure	SRL[t] Mossbauer Technique
Resin-1	0.15	0.22 ± 0.02	0.14 ± 0.03	0.10
Resin-2	0.40	0.41 ± 0.01	0.37 ± 0.02	0.21
Resin-3	0.85	0.95 ± 0.03	0.75 ± 0.04	0.85

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t calculated from data in Table I and known $\Sigma Fe=9.48$ wt%

* average value calculated from data in Table I and known $\Sigma Fe=9.48$ wt%. Standard deviation calculated from absorbance data given in Appendix I (Exhibit D). If the $Fe^{2+}/\Sigma Fe$ ratios are calculated from the relative absorbance values given in Exhibit D values of 0.22, 0.41, and 0.93 are obtained for the Resin-1, -2, and -3 glasses, respectively.

** average value and standard deviation calculated from measured values given in Appendix I (Exhibit A) in wt%.

Table III. Comparative Analyses of Fe^{2+}(wt%) for Resin-Doped Sludge-Only 165 Glass.

Sample	SRL[t] Colorimetric Procedure	CGW* Colorimetric Procedure	CGW** Titration Procedure	SRL[t] Mossbauer Technique
Resin-1	1.45	2.07 ± 0.04	1.31 ± 0.33	0.94
Resin-2	3.77	3.87 ± 0.05	3.48 ± 0.20	1.96
Resin-3	8.04	8.98 ± 0.10	6.63 ± 0.30	8.08

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t calculated from ratio given in Table I at known ΣFe=9.48 wt%

* average value calculated from ratio given in Table I and known ΣFe=9.48 wt%. Standard deviation calculated from absorbance data given in Appendix I (Exhibit D).

** average value and standard deviation calculated from measured values given in Appendix I (Exhibit A) in wt%.

When the Fe^{2+}/Fe^{3+} ratios for the SRL colorimetric data (Table I) are plotted against either the calculated Fe^{2+} (wt%) data or against the moles of carbon reacted a hyperbolic curve is observed similar to the ideal behavior (Figures 2a and 2b). When the $Fe^{2+}/\Sigma Fe$ data from SRL (Table II) is plotted against the calculated Fe^{2+} (wt%) data a straight line with a 0.0 intercept and the ideal slope of $1/\Sigma Fe$ is observed (Figure 2a). When either the $Fe^{2+}/\Sigma Fe$ ratio (Table II) or the Fe^{2+} in wt% (Table III) is plotted against the moles of carbon reacted a linear relationship is also observed as expected (Figures 2b and 2c). A straight line with the ideal slope is also observed for the relationship between the moles of carbon reacted and the moles of Fe^{2+} formed (Figure 2c). The linear relationships between (a) $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%), (b) the $Fe^{2+}/\Sigma Fe$ versus moles of carbon, (c) Fe^{2+} (wt%) versus moles of carbon, and (d) Fe2+ (moles) versus moles of carbon, all have correlation coefficients of 1.00.

2. CGW Colorimetric Procedure

The values of the Fe^{2+}/Fe^{3+} ratio determined by Corning Glass Works (CGW) are given in Table I and in Appendix I (Exhibit D). The absorbance values for Fe^{2+}, ΣFe, and the calculated Fe^{3+} values are also given in Appendix I (Exhibit D). Since the Fe^{2+}/Fe^{3+} ratio, the Fe^{2+}, and the ΣFe are reported as relative colorimetric absorbances, the values for the $Fe^{2+}/\Sigma Fe$ ratio (Table II) and Fe^{2+} in wt% (Table III) were calculated from the Fe^{2+}/Fe^{3+} ratio and the known as-made total Fe content ($\Sigma Fe = 9.48$ wt%). Four replicate measurements of Fe^{2+} and ΣFe absorbances were made and the within sample standard deviations given in Tables I-III were calculated from the absorbance values.

Comparison of the data for the Fe^{2+}/Fe^{3+} ratios in Table I with the $Fe^{2+}/\Sigma Fe$ ratios in Table II and the Fe^{2+} values in Table III demonstrates that the Fe^{2+}/Fe^{3+} ratio values have higher standard deviations than either $Fe^{2+}/\Sigma Fe$ ratio or the Fe^{2+} measurement. If the within sample standard deviations for the ΣFe values given in Appendix I (Exhibit D) are calculated they are 0.13, 0.13, and 0.11 compared to the standard deviations for the Fe^{2+} measurement (Table III) which are 0.04, 0.05, and 0.10. Since each sample was known to have the same total iron content, a between sample standard deviation was also calculated from the absorbance data in Appendix I and the between sample standard deviation was 0.19. This indicates that the greatest error in Corning's data was the measurement of ΣFe.

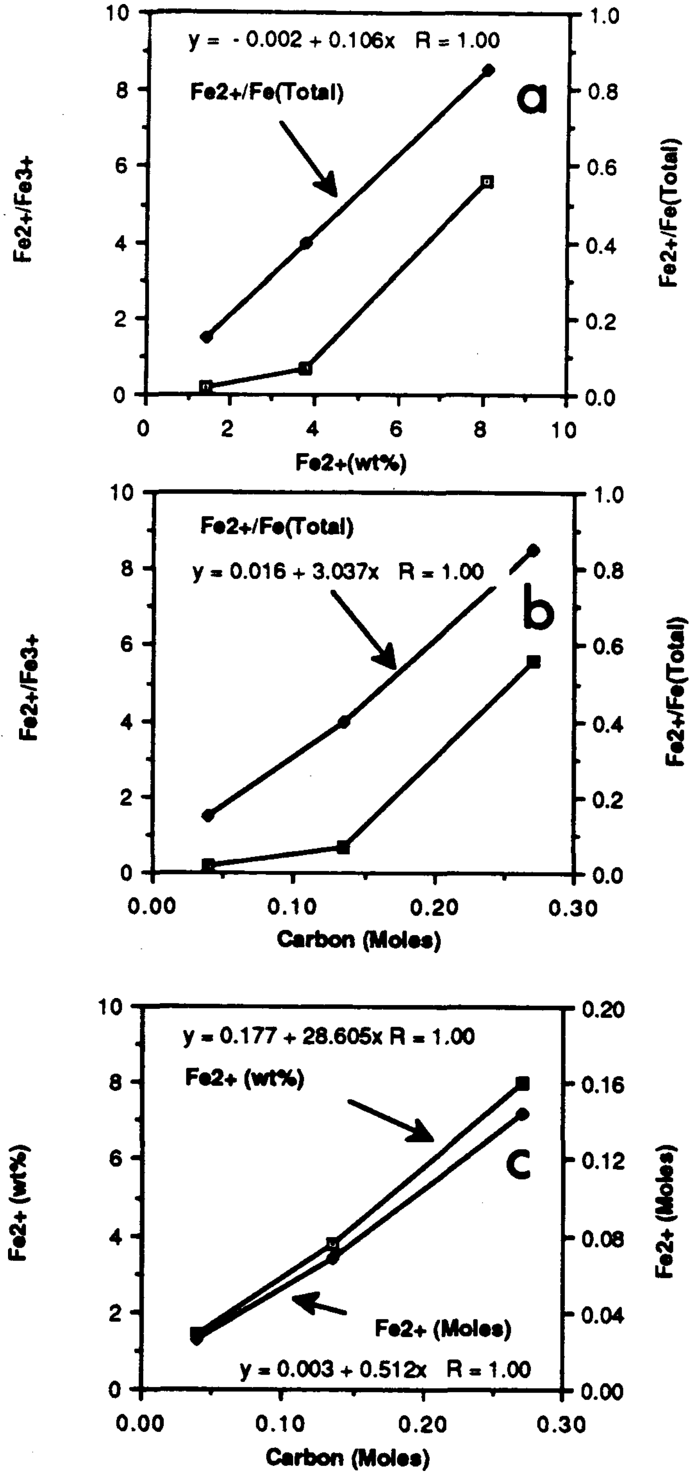

Figure 2. The graphical relationship of the SRL/ADD colorimetric data

(a) Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%),

(b) between Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus carbon (moles)

(c) between Fe^{2+} (wt%) and Fe^{2+} (moles) versus carbon (moles)

When the Fe^{2+}/Fe^{3+} ratios for the CGW data (Table I) are plotted against either the calculated Fe^{2+} (wt%) data or against the moles of carbon reacted a hyperbolic curve is observed similar to the ideal behavior (Figures 3a and 3b). When the $Fe^{2+}/\Sigma Fe$ data from CGW (Table II) is plotted against the calculated Fe^{2+} (wt%) data a straight line with a 0.0 intercept and the ideal slope of $1/\Sigma Fe$ = 0.106 is observed (Figure 3a). When the $Fe^{2+}/\Sigma Fe$ ratios calculated from the relative absorbances (Table II footnote) are plotted the slope is only slightly lower, 0.103.

When the $Fe^{2+}/\Sigma Fe$ ratio calculated from ΣFe = 9.48 wt% (Table II) or the Fe^{2+} in either wt% or moles (Table III) is plotted against the moles of carbon reacted some non-linearity is observed (Figures 3b and 3c). This may be caused by the inaccuracies in the calculation of the $Fe^{2+}/\Sigma Fe$ ratio and Fe^{2+} from the Fe^{2+}/Fe^{3+} ratio and the known ΣFe. The plot of Fe^{2+} (moles) against the moles of carbon reacted has the ideal slope of ~0.5. The relationships between (a) $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%), (b) the $Fe^{2+}/\Sigma Fe$ versus moles of carbon, (c) Fe^{2+} (wt%) versus moles of carbon, and (d) Fe^{2+} (moles) versus moles of carbon all have correlation coefficients of 0.99-1.00.

3. CGW Titration Procedure

The values of the Fe^{2+}/Fe^{3+} ratio determined by Corning Glass Works (CGW) are given in Table I and in Appendix I (Exhibit A). The values for Fe^{2+}, ΣFe, and the calculated Fe^{3+} values in wt% are also given in Appendix I (Exhibit A). Four replicate measurements of Fe^{2+} and ΣFe were made and the within sample standard deviations are given in Tables I-III.

Comparison of the data for the Fe^{2+}/Fe^{3+} ratios in Table I with the $Fe^{2+}/\Sigma Fe$ ratios in Table II and the Fe^{2+} values in Table III demonstrates that the Fe^{2+}/Fe^{3+} ratio values have higher standard deviations than either $Fe^{2+}/\Sigma Fe$ ratio or the Fe^{2+} measurement. If the within sample standard deviations for the ΣFe values given in Appendix I (Exhibit A) are calculated they are 0.02, 0.01, and 0.02 compared to the standard deviations for the Fe^{2+} measurement (Table III) which are 0.33, 0.20, and 0.30. This indicates that the greatest within sample error in Corning's data was the measurement of Fe^{2+} (Table III). The absolute values for Fe^{2+} measured are low by comparison with the other values in Table III indicating, perhaps, oxidation of Fe^{2+} during the initial dissolution step.

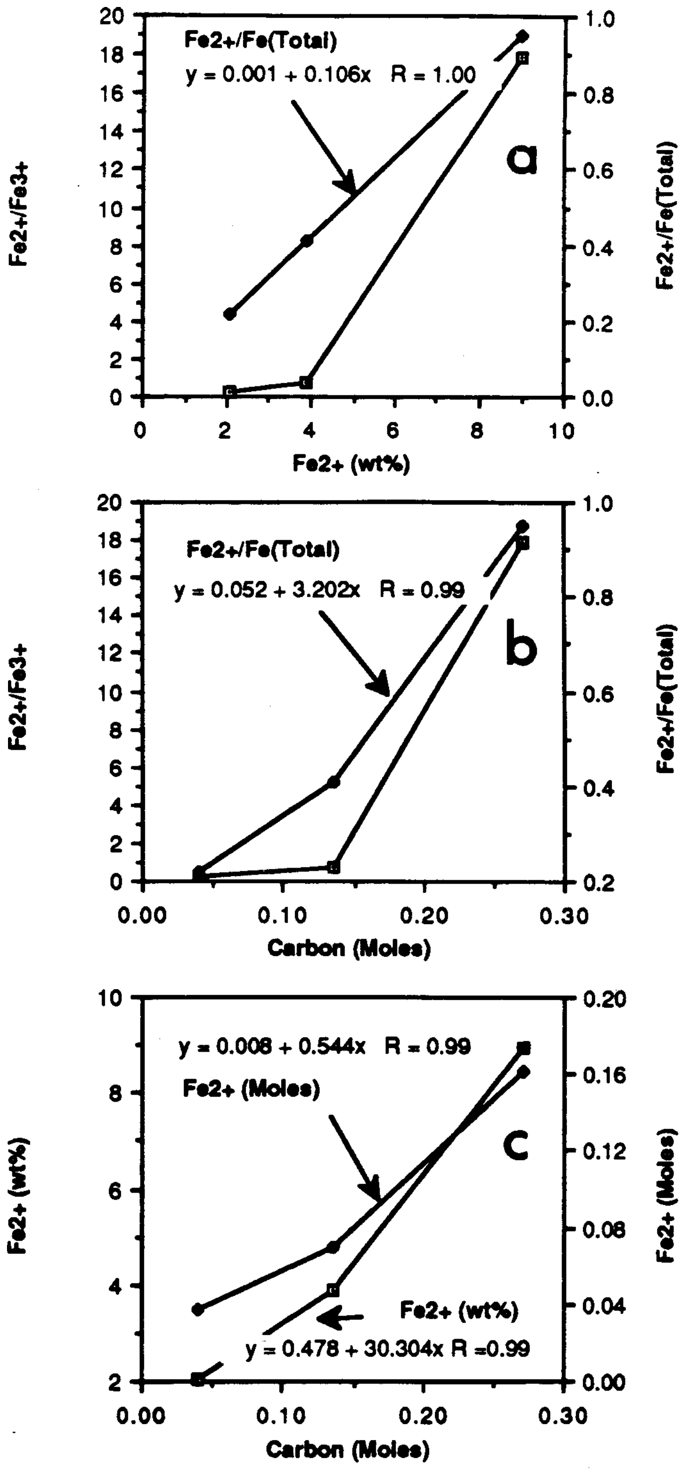

Figure 3. The graphical relationship of the CGW colorimetric data
(a) Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%),
(b) between Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus carbon (moles)
(c) between Fe^{2+} (wt%) and Fe^{2+} (moles) versus carbon (moles)

Since each sample was known to have the same total iron content, a between sample standard deviation was also calculated from the data in Appendix I. The average ΣFe measured was 9.20 ± 0.31 wt%. This between sample standard deviation indicates that the error from the titration procedure is greater than the error, 0.19 wt%, for the colorimetric procedure.

The value of ΣFe for Resin Glass-3 is extremely low (Appendix I - Exhibit A) which lowers the average ΣFe values and accounts for the large between sample standard deviation. This glass had metallic Ni present which could have caused some interferences in the titration measurement. The ΣFe values for the remaining glasses was 9.40 ± 0.07 which is in good agreement with the as-made ΣFe=9.48 wt%.

When the Fe^{2+}/Fe^{3+} ratios for the CGW titration data (Table I) are plotted against either the calculated Fe^{2+} (wt%) data or against the moles of carbon reacted a more shallow curve is observed (Figures 4a and 4b). This is caused by the low Fe^{2+} values divided by the low Fe^{3+} values which gives an abnormally low Fe^{2+}/Fe^{3+} ratio. When the $Fe^{2+}/\Sigma Fe$ data from CGW's titration procedure (Table II) is plotted against the calculated Fe^{2+} (wt%) data a straight line curve with a ~0.0 intercept is obtained but the slope is not the ideal value of $1/\Sigma Fe$ (Figure 4a). However, when either the $Fe^{2+}/\Sigma Fe$ ratio (Table II) or the Fe^{2+} in wt% (Table III) is plotted against the moles of carbon reacted a linear relationship is observed (Figures 4b and 4c). The relation between the Fe^{2+} in moles and the moles of carbon reacted is linear but the slope is lower than the ideal 0.5 for 1 mole of carbon reducing 2 moles of iron. The relationships between (a) $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%), (b) the $Fe^{2+}/\Sigma Fe$ versus moles of carbon, (c) Fe^{2+} (wt%) versus moles of carbon, and (d) Fe^{2+} (moles) versus moles of carbon, all have correlation coefficients of 1.00. The analytic results are self consistent but the Fe^{2+} values are biased toward lower (oxidizing) values.

4. Mossbauer Technique

The values of the Fe^{2+}/Fe^{3+} ratio determined by the Mossbauer technique at Savannah River Laboratory are given in Table I. The Mossbauer technique only measures the Fe^{2+}/Fe^{3+} ratio and, hence, the values for the $Fe^{2+}/\Sigma Fe$ ratio (Table II) and Fe^{2+} in wt% (Table III) had to be calculated from the Fe^{2+}/Fe^{3+} ratio and the known as-made total Fe content (ΣFe= 9.48 wt%). The standard deviations given in Tables I were those reported by the analyst.

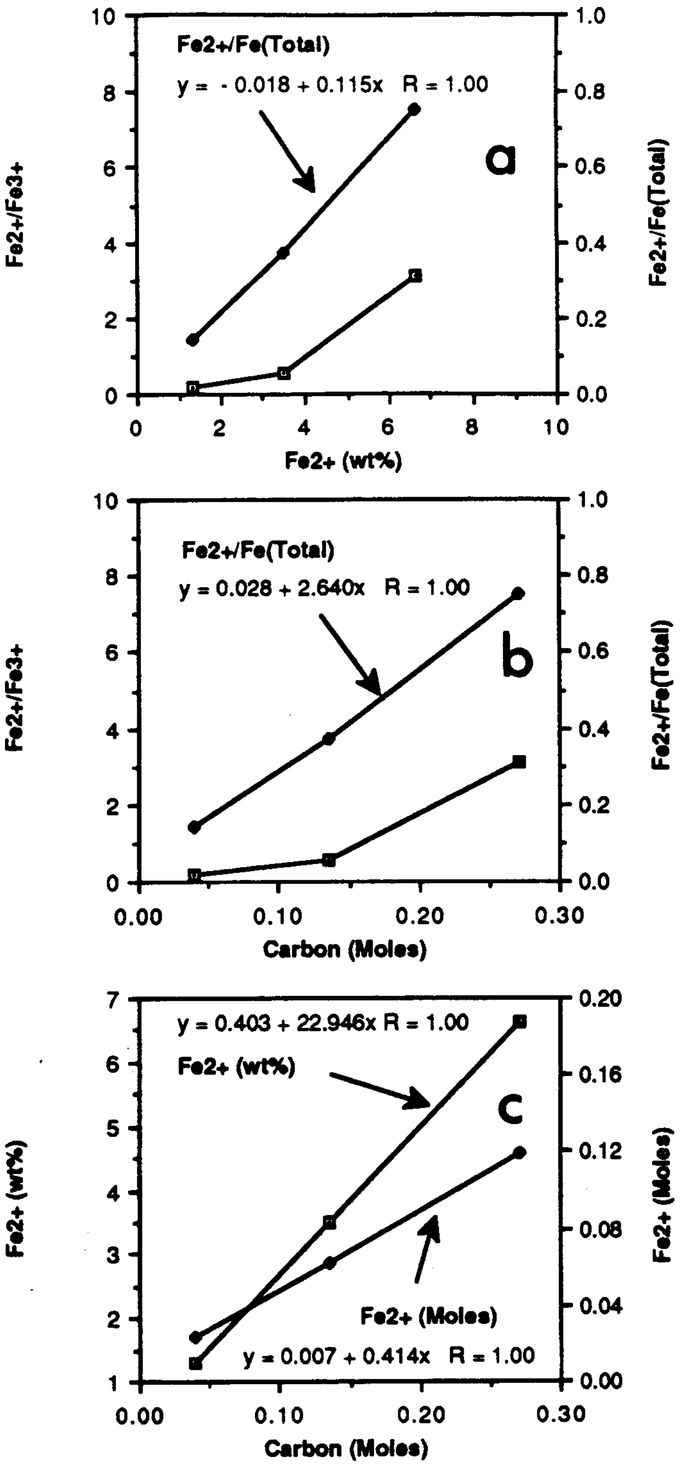

Figure 4. The graphical relationship of the CGW titration data
(a) Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%),
(b) between Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus carbon (moles)
(c) between Fe^{2+} (wt%) and Fe^{2+} (moles) versus carbon (moles)

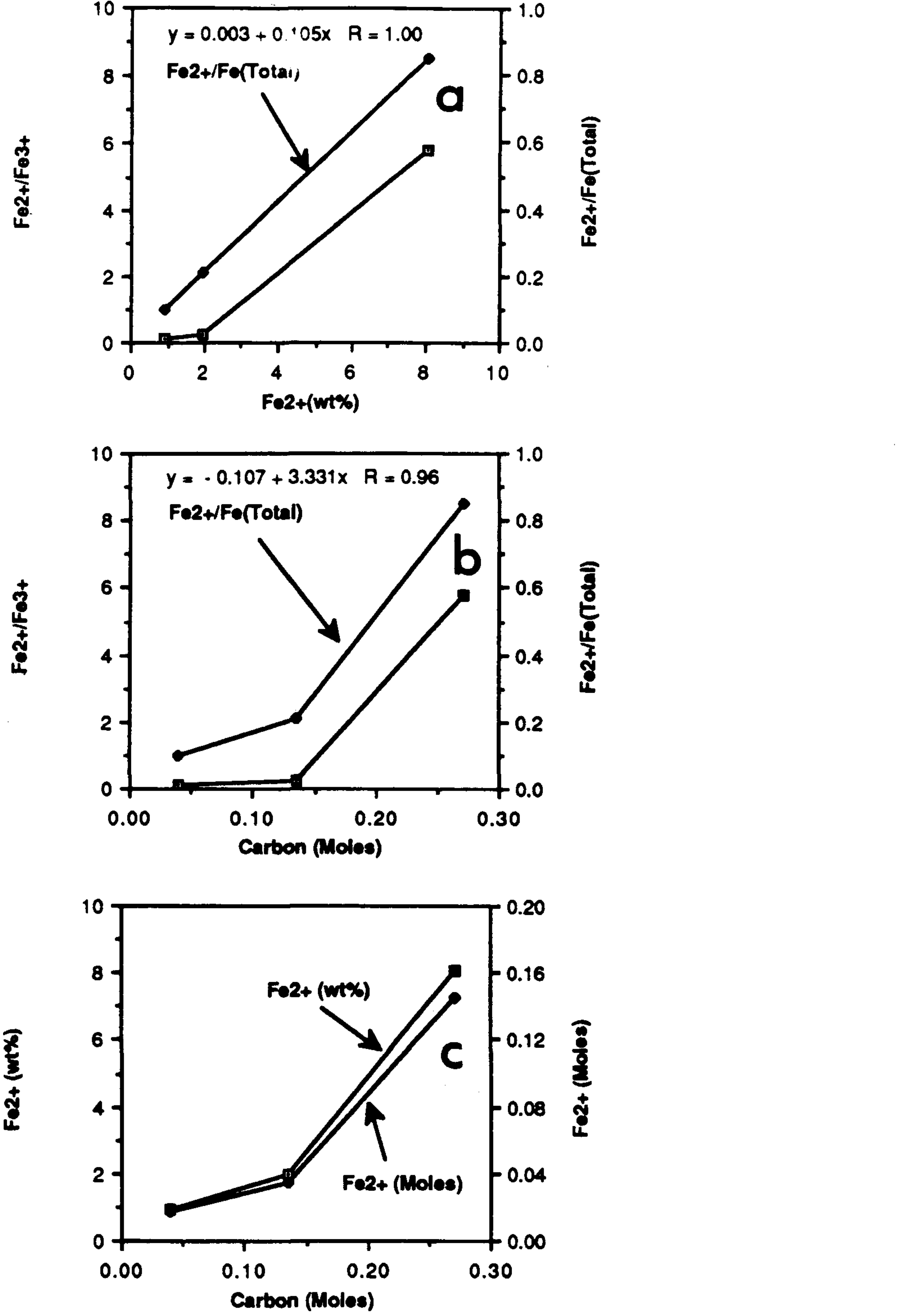

Figure 5. The graphical relationship of the Mossbauer spectroscopy data

(a) Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%),

(b) between Fe^{2+}/Fe^{3+} and $Fe^{2+}/\Sigma Fe$ versus carbon (moles)

(c) between Fe^{2+} (wt%) and Fe^{2+} (moles) versus carbon (moles)

When the Fe^{2+}/Fe^{3+} ratios for the Mossbauer data from Table I are plotted against either the calculated Fe^{2+} (wt%) data or against the moles of carbon reacted a curve similar to those obtained from the wet chemical methods is observed (Figures 5a and 5b). When the $Fe^{2+}/\Sigma Fe$ data (Table II) is plotted against the calculated Fe^{2+} (wt%) data a linear curve with a 0.0 intercept and the theoretical slope $1/\Sigma Fe$ is observed as predicted (Figure 5a). However, when either the $Fe^{2+}/\Sigma Fe$ ratio (Table II) or the Fe^{2+} in wt% (Table III) is plotted against the moles of carbon reacted, some non-linearity is observed (Figures 5b and 5c). This may be caused by the inaccuracies in the calculation of the $Fe^{2+}/\Sigma Fe$ ratio and Fe^{2+} from the Fe^{2+}/Fe^{3+} ratio. The relationships between $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%) has a correlation coreefficient of 1.00 but the inter-relationships between $Fe^{2+}/\Sigma Fe$ versus moles of carbon, and Fe^{2+} (wt%) versus moles of carbon have the poorest correlations of any of the measurement methodologies. This is because the Mossbauer technique does not measure ΣFe nor the Fe^{2+} directly, but only the ratio of the Fe^{2+}/Fe^{3+} spectral areas.

Intercomparison of Redox Measurements Determined by Wet Chemical Methods and Mossbauer Spectroscopy

1. By linearity of Fe^{2+} (Wt%) vs. $Fe^{2+}/\Sigma Fe$

Since large standard deviations are observed for the Fe^{2+}/Fe^{3+} ratios given in Table I, the intercomparison of the measurement techniques was based primarily on the $Fe^{2+}/\Sigma Fe$ values. The graphical plots of Fe^{2+} versus $Fe^{2+}/\Sigma Fe$ for the colorimetric procedure results (both SRL and CGW) and the Mossbauer data were linear with slopes of $1/\Sigma Fe$ (Figures 2a,3a, and 5a). Since both the SRL and CGW data using the colorimetric procedure (from Table II) were calculated from the known $\Sigma Fe = 9.48$ wt%, the data fall on the same line (Figure 6). However, the bias in the CGW data toward overestimation of the Fe^{2+} values is readily apparent. Errors in the Wilson type dissolution step are most likely caused by (1) the slow oxidation of the V(IV) on standing in solution; (2) the oxidation of V(IV) or Fe(II) by atmospheric oxygen; (3) the coprecipitation or adsorption of Fe(II) by residues which form during dissolution; or (4) incomplete sample dissolution.[28-29] All of these would cause the Fe^{3+} to be high rather than the Fe^{2+}. Hence, the CGW colorimetric procedure bias cannot be readily explained.

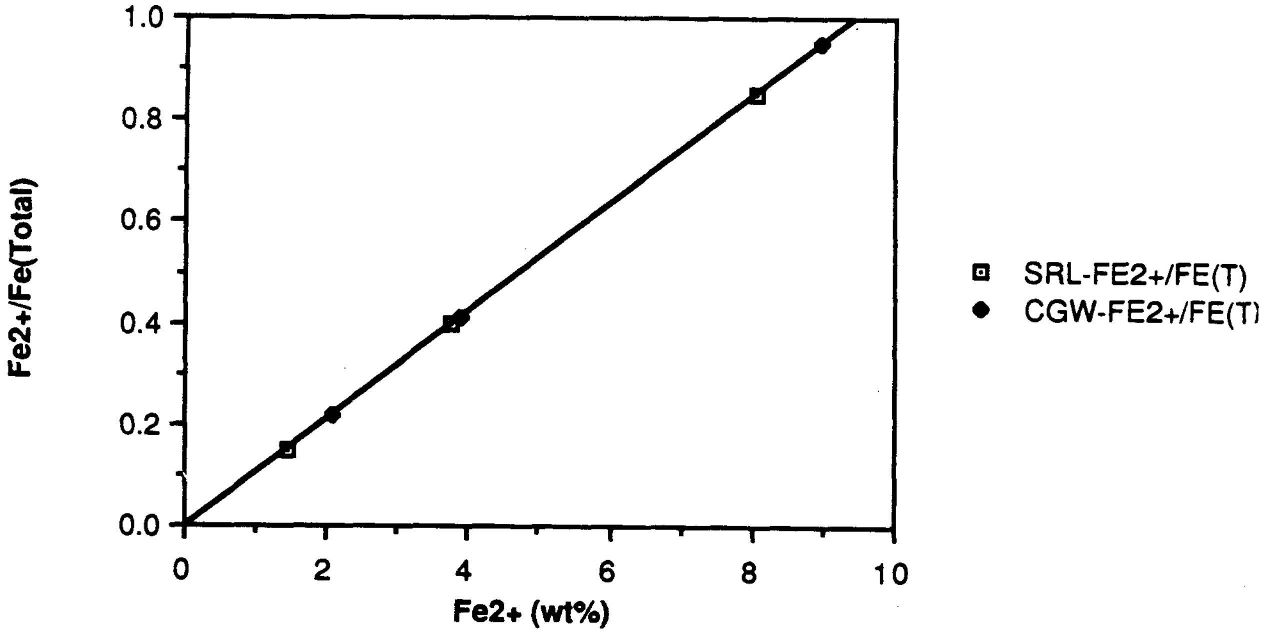

Figure 6. Comparison of the $Fe^{2+}/\Sigma Fe$ versus Fe^{2+} (wt%) for SRL and CGW data using the colorimetric procedure.

When the data for all four redox measurement techniques are plotted as Fe^{2+} (wt%) versus $Fe^{2+}/\Sigma Fe$, the data from the Mossbauer technique is observed to fall on the same line since $\Sigma Fe = 9.48$ wt% was also used to calculate these values (Figure 7). When the CGW-titration data is compared with the colorimetric and Mossbauer results, the data deviates significantly at higher Fe^{2+} values because the Fe^{2+} values measured are proportionately lower due to air oxidation during the dissolution step. The slope is 0.115 (Figure 4a) which would indicate a $\Sigma Fe = 8.70$ wt%. This total iron value is also biased low (more oxidizing).

The largest statistical error in the colorimetric procedure data from CGW is the ΣFe measurement. However, the error in the ΣFe measured for the colorimetric procedure was lower than the ΣFe error measured in the CGW titration technique. Moreover, the measurement of Fe^{2+} by the CGW titration technique was statistically much poorer than the Fe^{2+} data from the colorimetric procedure. Overall, the colorimetric procedure errors measured by Corning are lower than those of the titration technique.

2. By Linearity of Carbon (moles) vs. $Fe^{2+}/\Sigma Fe$

The comparison of the $Fe^{2+}/\Sigma Fe$ vs. the moles of carbon consumed during the glass melting reaction also demonstrated that the CGW data using the colorimetric methodology is biased toward more reduced ratios while the CGW/ASTM methodology is biased toward more oxidizing ratios. The SRL colorimetric procedure and Mossbauer data are in quantitative agreement with each other and give values intermediate between the two CGW sets of data (Figure 8). The SRL Baumann procedure data and the CGW/ASTM data are linear functions of the carbon consumed in moles (Figures 2b and 4b) while the other data deviate from linearity in the $Fe^{2+}/\Sigma Fe$ vs. carbon (moles) plots (Figures 3b and 5b) as discussed above.

3. By Linearity of Carbon (moles) vs. Fe^{2+} (wt%) and Fe^{2+} (moles)

The comparison of the Fe^{2+} (wt%) vs the moles of carbon consumed during the glass melting reaction provides one of the best validations of the wet chemical methodologies because the Fe^{2+} measured should be a direct result of the titration reaction involved in the measurement. Likewise, the comparison of the number of moles of Fe^{2+} formed per moles of carbon reacted should have ideal slope of 1/2 according to the mass balance (Equation 1). Figures 2c, 3c, and 4c demonstrate that the Fe^{2+} in either moles or

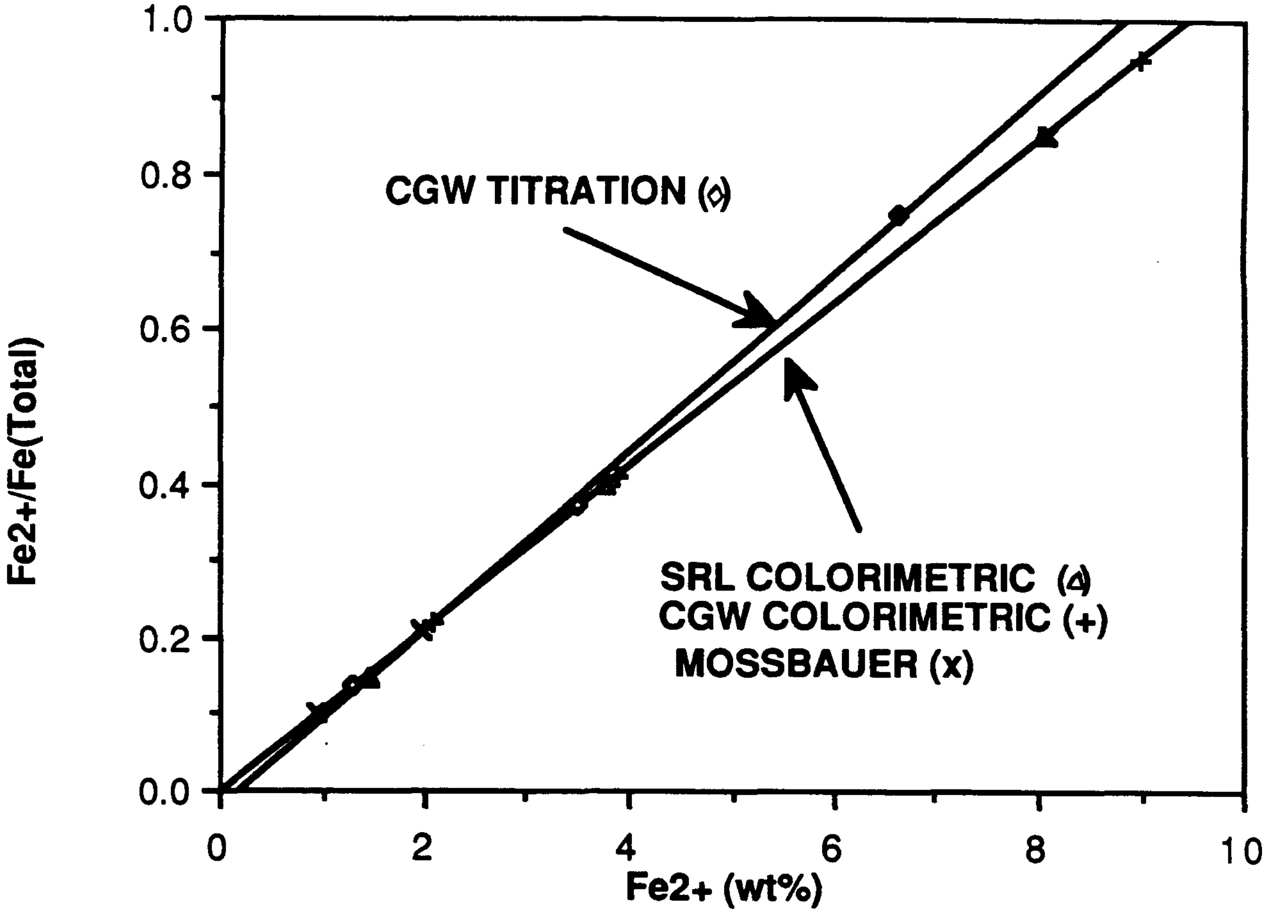

Figure 7. Comparison of the $Fe^{2+}/\Sigma Fe$ ratio vs Fe^{2+} (wt%) for all the redox measurement methologies. The data for the CGW/ASTM dissolution procedure gives Fe^{2+} values which are too low and inconsistent with the data from the colorimetric and Mossbauer methodologies.

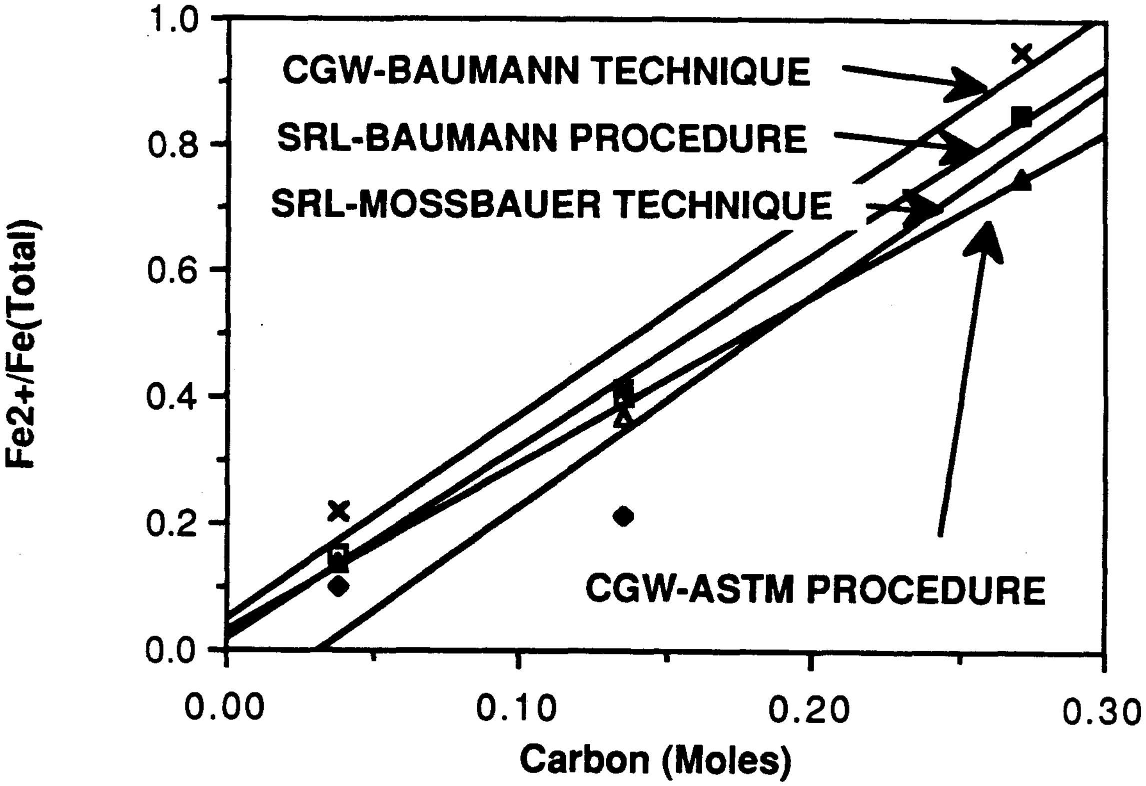

Figure 8. Comparison of the $Fe^{2+}/\Sigma Fe$ measured by four methods against the moles of carbon reacted during the glass melting reaction with an organic resin.

wt% is a linear function of the moles of carbon for the three wet chemical methologies. The Mossbauer data deviates considerably from a linear relationship (Figure 5c), and is not recommended for DWPF use.

Comparing the values of Fe^{2+} (wt%)for the three wet chemical methods demonstrates that the CGW data using the colorimetric procedure is biased toward higher Fe^{2+} values while the CGW data using the titration procedure is biased toward lower Fe^{2+} values as discussed above (Figure 9). When the slopes of the moles of carbon reacted versus the moles of Fe^{2+} formed are compared, the SRL and CGW data sets have approximately the ideal slope of 0.5. The CGW titration data is linear but has a lower slope of ~0.4 indicating that less Fe^{2+} was measured by this technique. All three chemical methologies gave correlation coefficients of 0.99-1.00 when the Fe^{2+} contents and the moles of carbon reacted were compared.

Standardization of $Fe^{2+}/\Sigma Fe$ Measurement

During DWPF operation, the redox ratio will be measured on vitrified feed from the Slurry Mix Evaporator (SME). Achievement of the correct redox is a process control hold point before the feed can be sent to the melter. Since glass redox standards are not available a way to standardize the measurement is desireable. Since the redox ratio, $Fe^{2+}/\Sigma Fe$, is a linear function of the Fe^{2+} content in wt%, a standard $Fe^{2+}/\Sigma Fe$ vs. Fe^{2+} curve like the one given in Figure 1b could be drawn if the ΣFe were known.

The total iron content of a two year batch of DWPF sludge will be known from inductively coupled plasma (ICP) analysis before the waste enters the DWPF. The DWPF sludge composition will be fairly constant over a 2 year period and the waste-frit-precipitate hydrolysis product blending schemes will dampen any large swings in ΣFe.[30] This information could be used to calculate a "standard" $Fe^{2+}/\Sigma Fe$ vs. Fe^{2+} curve, with the ideal slope of 0.106, in terms of measured absorbances. The standard plot could then potentially be used to validate the $Fe^{2+}/\Sigma Fe$ measured for each batch of slurry.

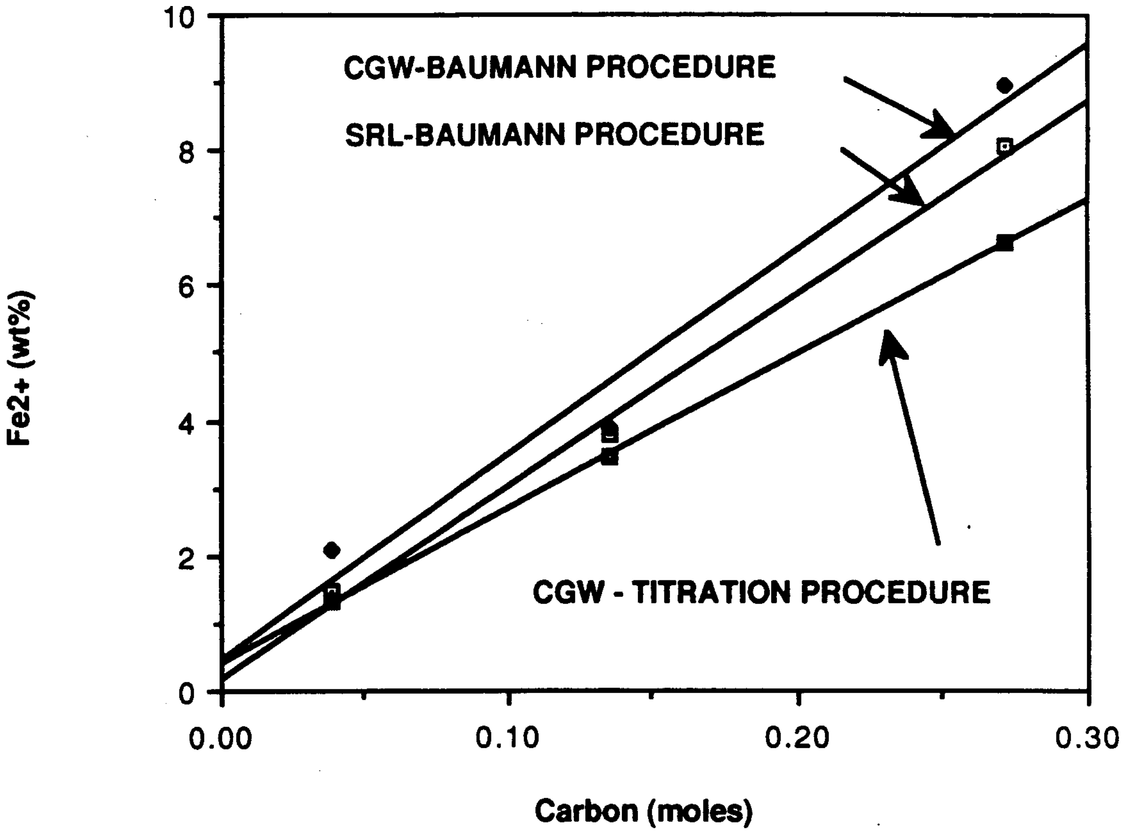

Figure 9. Comparison of the Fe^{2+} measured by three wet chemical methologies against the moles of carbon reacted during the glass melting reaction with an organic resin.

CONCLUSIONS

Verification of the colorimetric procedure selected for the measurement of the Fe^{2+}/Fe^{3+} redox ratio in DWPF glass was achieved. Three glasses of varying iron redox ratio were analyzed by the colorimetric Baumann procedure (at SRL and CGW), by a titration prodedure (at CGW), and by Mossbauer spectroscopy (SRL).

The analytic data agreed when the linear $Fe^{2+}/\Sigma Fe$ ratio was plotted against either the Fe^{2+}(wt%) or the number of moles of reductant reacted with the glass. Comparison of the three sets of wet chemical data in Fe^{2+} vs. moles of reductant reacted indicate that the CGW results using the colorimetric prodecure are biased toward reducing ratios while the CGW/ASTM dissolution procedure gives results which have lower Fe^{2+} values. The simpler colorimetric procedure is, therefore, more conservative than the more difficult CGW/ASTM dissolution procedure in inert atmospheres. This bias is favorable for DWPF operation in which overly reducing melt conditions might endanger melter operation.

For the range of Fe^{2+}/Fe^{3+} ratios anticipated in DWPF, e.g. 0.1-0.5, the difference between reporting Fe^{2+}/Fe^{3+} or $Fe^{2+}/\Sigma Fe$ would not be significant except that the $Fe^{2+}/\Sigma Fe$ is a more accurate representation of the glass redox state. In the event that more reducing or more oxidizing conditions are encountered, reporting the $Fe^{2+}/\Sigma Fe$ rather than the Fe^{2+}/Fe^{3+} ratio is necessary. The acceptable DWPF range of Fe^{2+}/Fe^{3+} between 0.1-0.5 is equivalent to 0.09-0.33 $Fe^{2+}/\Sigma Fe$.

Reviewed: EWBaumann Date: 1/17/89

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APPENDIX I. DATA FROM CORNING ENGINEERING LABORATORY SERVICES REPORT CELS-11988-019

(March 23, 1988)

CORNING

Corning Engineering
Laboratory Services
Corning Glass Works
Houghton Park, ME-02-041
Corning, New York 14831
Tel: 607-974-6360
800-235-2357

March 23, 1988

Laboratory Analysis Report for:

Ms. Carol M. Jantzen
E. I. duPont de Nemours Co.
Savannah River Laboratory
Aiken, SC 29808-0001

CELS Client No.: 11988-019
Date Received : 02-05-88
Date Reported : 03-23-88
Approved by LPA.

Copy to: CELS File

SAMPLE IDENTIFICATION:

LAB SAMPLE NO.	Sample Description
1343	Three (3) Simulated Waste Glass Samples: Resin-1 Resin-2 Resin-3

ANALYSES REPORTED:

Exhibit	Test Description
(Method 1)	
A	Quantitative Chemical Analysis (Titration)
B	Statistical Data
C	Analytical Procedures
(Method 2)	
D	Quantitative Chemical Analysis (Colorimetric)
E	Statistical Data
F	Discussion

COMMENTS:

Client Purchase Order No. AX814100

Direct questions regarding this report to Linda Adams, CELS office.

CONFIDENTIAL:
This CELS report information is to be used only for account 11988.

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Method 1
Exhibit A: Quantitative Chemical Analysis (Titration)

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

	Results (Wt. %)				
Sample	% Fe+2		% Fe Total	% Fe3*	Ratio (Fe+2/Fe+3)
Resin-1	1.08		9.33	8.25	0.13
	0.96	1.3	9.32	8.36	0.11
	1.60		9.37	7.77	0.21
	1.56		9.34	7.78	0.20
Resin-2	3.58		9.47	5.89	0.61
	3.50	3.49	9.46	5.96	0.59
	3.20		9.48	6.28	0.51
	3.67		9.45	5.78	0.63
Resin-3	6.79		8.78	1.99	3.41
	6.65	6.63	8.79	2.14	3.11
	6.20		8.81	2.61	2.38
	6.86		8.76	1.90	3.61

* % Fe+3 = % Fe Total - % Fe+2

Total iron [illegible] 9.48 in
28% TDS-3A sludge % coal

CONFIDENTIAL:
This CELS report information is to be used only for account 11988.

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Method 1
Exhibit B: Statistical Data

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

Sample/Analyte	No. of Determinations	Standard Deviation
Resin-1/Fe+2	4	0.33
Resin-1/Fe Total	4	0.02
Resin-1/Ratio	4	0.05
Resin-2/Fe+2	4	0.20
Resin-2/Fe Total	4	0.01
Resin-2/Ratio	4	0.05
Resin-3/Fe+2	4	0.30
Resin-3/Fe Total	4	0.02
Resin-3/Ratio	4	0.54

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Method 1
Exhibit C: Analytical Procedures

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

1. Abstract

The sample is dissolved in a HCl-HF mixture under an atmosphere of CO2. Ferrous iron is then determined by titration with standardized ceric sulfate.

Total iron is determined after reduction with stannous chloride and titration as for ferrous iron.

2. Procedure

A. Weigh 0.5g of glass sample to the nearest 0.1mg into a Teflon disk.
B. Dissolve the sample in 15ml of HCl-HF solution (100ml 1:1HCl + 200ml HF) under a steady stream of CO2.
C. After sample is dissolved (~10min.), add 200ml of warm saturated boric acid solution.
D. Cool sample to room temperature with CO2 purge.
E. Titrate cooled solution vs. standardized ceric sulfate using diphenylamine sulphonate indicator to permanent (120sec.) color.
F. Calculate

$$\%\text{Fe+2} = \frac{(\text{ml titrated})(\text{N of Ceric Sulfate})(0.05585\text{x}100\%)}{\text{Sample Weight}}$$

3. Total Fe

A. Dissolve 0.5grams of sample with HF + HClO4 in a Teflon dish. Take to dryness.
B. Dissolve residue with 10ml H20+3ml of warm HCl on a hotplate.
C. Transfer sample to a plastic beaker and make to ~100ml volume with D.I. water.
D. Warm on a steambath.
E. Add stannous chloride until iron is reduced (i.e.; color change from yellow to clear).
F. Remove any excess stannous chloride with mercuric chloride.
G. Add 5ml HCl-HF mix and 100ml saturated boric acid.
H. Titrate as in Fe+2 procedure.

$$\%\ \text{Fe3+ Total} = \frac{\text{ml Titrated (N.F.)}(0.05585)(100\%)}{\text{Sample Weight}}$$

% Fe3= Total = Fe2+ + Fe3+ as Fe3+

Method 1
Exhibit C: Analytical Procedures (Continued)

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

4. Reagents

Boric Acid Solution: Dissolve 50grams of H_3BO_3 in 500ml of recently boiled H_2O. Cover beaker with watch glass and keep solution hot on hot plage during run.

A. Add teflon stirrer bar and set on magnetic stirrer.
B. Cool to room temperature in cold water bath.
C. Add 1 drop of 0.025M 1,10-Phenanthroline Ferrous Sulfate solution (Ferroin).
D. Turn stirrer ON. Titrate dropwise with standard 0.0003N $Ce(SO_4)_2$ solution until orange disappears. Run blank and correct.
Calculate:

$$\% \, Fe^{+2} = \frac{\text{ml } Ce(SO_4)_2 \times \text{N.F.} \times 0.05585 \times 100}{\text{Sample Weight}}$$

Preparation and Standardization:

Standard 0.05N Ceric Sulfate Solution

A. Transfer 35grams of Ceric Sulfate reagent $H_4Ce(SO_4)_4$' G. Frederick Smith Chemical Co., Cat. No. 24, to a 1000ml PYREX (R) brand beaker.
B. Add 57ml of 1-1 H_2SO_4 plus about 800ml of H_2O. Stir and heat until reagent is completely dissolved.
C. Transfer to a 1 liter volumetric flask. Cool to room temperature and dilute to volume with H_2O. Mix.

Standardization of 0.05N $Ce(SO_4)_2$

A. Transfer 0.1000gram sodium oxalate (National Bureau of Standards) to a 400ml beaker.
B. Dissolve reagent in 200ml H_2O.
C. Add 40ml of concentrated HCl and 10ml of 0.05M Iodine Monochloride solution.
D. Heat to 50C. Use thermometer as stirring rod to control temperture.
E. Add 1 drop of Ferroin indicator.

Method 1
Exhibit C: Analytical Procedures (Continued)

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

Preparation and Standardization: (Continued)

Standardization of 0.05N $Ce(SO_4)_2$

F. Titrate with 0.05N Ceric Sulfate solution to a pale blue end point with no return of pink color for an interval of 1 to 2 minutes. (If during the titration, the temperature falls below 45C, reheat solution to 50C. DO NOT HEAT ABOVE 50C. Keep solution between 40 and 50C during titration.
Subtract blank titration

$$\text{Normality Factor} = \frac{\text{wt. of } Na_2C_2O_4}{\text{ml } Ce(SO_4)_2 \times 0.067}$$

Diluted Standard ~ 0.003N $Ce(SO_4)_2$

A. Pipet 30ml of the standard $Ce(SO_4)_2$ solution and transfer to a 500ml volumetric flask.
B. Add 27ml of 1-1 H_2SO_4 and dilute to volume with H_2O. Mix.
C. Calculate:

$$HF = \frac{30}{500} \times \text{N.F. of the 0.05N } Ce(SO_4)_2$$

5. Standard Solution Normality used in Analysis

A. Normality of Ceric Sulfate versus Oxalate:
Titration 1 - 0.0340
2 - 0.0342
3 - 0.0342

B. Normality of Ceric Sulfate versus 99.999% Standard Iron:
Titration 1 - 0.0343
2 - 0.0343
3 - 0.0344
4 - 0.0343

6. Control Sample

There are not commercial glass standards available with a known Fe+2/Fe+3 ratio. Therefore, with the exception of the primary standards used to standardize the titrant, no standards or control samples were used in this analysis.

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Method 2
Exhibit D: Quantitative Chemical Analysis (Colorimetric)

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

	Results (Absorbance)			
Sample	% Fe+2	% Fe Total	% Fe3*	Ratio (Fe+2/Fe+3)
Resin-1	0.134	0.642	0.508	0.26
	0.104	0.513	0.409	0.25
	0.124	0.532	0.418	0.30
	0.187	0.806	0.619	0.30
Resin-2	0.182	0.438	0.256	0.71
	0.173	0.423	0.250	0.69
	0.187	0.458	0.271	0.69
	0.282	0.702	0.420	0.67
Resin-3	0.383	0.408	0.025	15.32
	0.384	0.395	0.011	34.91
	0.373	0.408	0.035	10.66
	0.572	0.626	0.054	10.59

* [% Fe+3 Content] = [% Fe Total Content] - [% Fe+2 Content]

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Method 2
Exhibit E: Statistical Data of Colorimetric Ratio (Fe^{+2}/Fe^{+3})

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

Sample	No. of Determinations	Standard Deviation
Resin-1	4	0.03
Resin-2	4	0.02
Resin-3	4	11.57

LABORATORY ANALYSIS REPORT

CELS Client No.: 11988-019

Exhibit F: Discussion

Sample Description: Three (3) Simulated Waste Glass Samples

Lab I.D. No.: 1343

The Titration Analytical Procedure was supplied by the Corning Laboratory. The results are expressed as weight percent; 4 determinations of the Fe+2 and the Fe Total were recorded for each sample.

The Colorimetric Analytical Procedure was supplied by the Savannah River Laboratory. The results are expressed as absorbance readings; 4 determinations of the Fe+2 and Fe Total were recorded for each sample. Statistical Data was determined for the Fe+2/Fe+3 ratio only.

1) There are many possible reasons for the varying results:
    A) Mn Interference
    B) Shelf Life
    C) Grinding Procedure
    D) Inhomogeneous Sample

2) The total Fe measured in the titration process were consistent. It was the Fe+2 that varied.

3) The colorimetric technique appears consistent for the lower levels of Fe+2 but varies a great amount for the higher levels. A cut-off level could not be deduced from the limited amount of samples analyzed.

4) Ratio agreement between the two (2) methods was not good, especially for sample 3.

5) EPR (Electron Paramagnetic Resonance) is another valance state technique that can be used in conjunction with the wet chemical analysis. This may overcome interfernce from other redox pairs present as it is non-destructive. A standard is needed for the initial work.
