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A Comparative Spectrophotometric Study Using Ferrozine and 1,10-*Ortho*-phenanthroline to Evaluate the Iron Redox Ratio ($\text{Fe}^{2+}/\Sigma\text{Fe}$) in Glass Prepared by Microwave Heating

Biswajit MANDAL,* Prasanta Kumar SINHA,** Ranjan SEN,* and Ashis Kumar MANDAL*†

*Glass Division, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S. C. Mullick Road, Kolkata-700032, India

**Materials Characterization and Instrumentation Division, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S. C. Mullick Road, Kolkata-700032, India

In the present study, Fe-doped barium borosilicate glass has been melted at 1250°C under microwave heating. The iron redox ratio ($\text{Fe}^{2+}/\text{total Fe}$) in the glass is investigated by two spectrophotometric methods. A novel decomposition technique has been optimized to measure the ferrous oxidation state in glass. Ferrozine was chosen as a specific complexing reagent; it forms a deep violet color complex with Fe^{2+} and has a broad absorbance peak centered at ~562 nm. 1,10-*ortho*-phenanthroline develops an orange color complex with Fe^{2+} (having an absorbance peak centered at ~510 nm) and has been used to determine ferrous ion in glass. Both the methods are compared and the estimated redox ratio was found to be higher in the ferrozine method. The error limit of measurement has been determined as 0.012 and 0.023 for the ferrozine and 1,10-*ortho*-phenanthroline methods, respectively.

Keywords Iron redox ratio in glass, microwave heating, barium borosilicate glass, spectrophotometric method, ferrozine, 1,10-*ortho*-phenanthroline

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Introduction

The iron redox ratio ($\text{Fe}^{2+}/\Sigma\text{Fe}$) plays an important role in glass to determine its optical properties, particularly in view of developing IR absorbing properties. Higher $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio in glass improves its optical absorbance at 1050–1200 nm wavelength owing to the absorbance of the ferrous oxidation state.^{1–3} However, higher ferrous oxidation state in glass is usually obtained by melting it in reducing atmosphere along with the addition of a reducing agent in glass in the conventional furnace. A complicated arrangement is indeed required to maintain reducing atmosphere during melting in the conventional furnace. Microwave-assisted material synthesis is a potential alternative method of synthesis mainly due to several advantages, which include rapid processing and less consumption of energy as elaborated elsewhere.^{4,5} Many authors have demonstrated microwave material processing to develop materials with improved or new properties.^{6–10} Improved properties such as micro-hardness and low OH content in borosilicate glasses have been identified elsewhere.^{11,12} Improved chemical durability and low contamination from the crucible wall has also been observed in borosilicate and phosphate glass.^{13,14} Zinc borate glass could not be melted using an alumina crucible in a conventional resistance heating furnace due to high corrosion leading to cracking of the crucible. However, the glass could be melted

using an alumina crucible with low OH content in microwave heating.¹⁵ Microwave heating yields higher ferrous oxidation state in glass as revealed in earlier reports.^{16–18}

UV-Vis-NIR spectroscopy is used to estimate the relative presence of Fe^{2+} from its absorbance at ~1100–1200 nm wavelengths. Determination of the iron redox ratio is done by measuring optical density (OD) at ~1050 nm for Fe^{2+} and 380 nm for Fe^{3+} .^{19,20} However, the actual determination of the redox ratio is very difficult due to the low intensity of the absorbance peak of Fe^{3+} within 380 to 650 nm wavelength owing to its spin forbidden transition.^{1,21} The absorption band centered at about 380 nm typical for Fe^{3+} species and used for redox ratio determination is not resolved; this band is obscured by strong charge transfer absorption. This prevents determination of either the precise position of this absorption band or its intensity. Although Mössbauer spectroscopy is another tool to evaluate the iron redox ratio,²² low concentration of iron (1% of Fe in precursor) limits its use for the said purpose. X-ray absorption near edge structure (XANES) spectroscopy is another useful technique to study the oxidation state and coordination geometry of metal ions in glass and therefore to quantify the $\text{Fe}^{2+}/\Sigma\text{Fe}$ in glass.²³

The determination of Fe^{2+} using permanganate by redox titration method is reported by Ceglia *et al.*²³ and accuracy of measurement is reported to be ~10% for this titration method. In another work, the titration method is adopted using cerium by Close *et al.*²⁴ However, poor accuracy of this titration method makes it a less preferable technique to determine Fe^{2+} . Use of the spectrophotometric method to determine the different

† To whom correspondence should be addressed.
E-mail: ashis@cgcri.res.in; ashismand@gmail.com

oxidation states of iron developing ferrozine color complex has been discussed elsewhere.²⁵⁻²⁷ However, the digestion of glass to develop the color complex is carried out either in an inert atmosphere or in reducing atmosphere in the reported works. Phenanthroline is also reported to have been used to investigate the iron redox ratio in solution.^{28,29} However, the above reports do not include the precision and accuracy of the two wet chemical analysis methods using ferrozine and phenanthroline.

In the present work, the main objective is to report the comparative studies of two spectrophotometric methods developing ferrozine and 1,10-*ortho*-phenanthroline color complexes with Fe²⁺ to estimate the iron redox ratio (Fe²⁺/ΣFe). Estimation of precision and accuracy of these two analytical methods is also presented and elaborated. In order to carry out the study, iron doped barium borosilicate glass has been melted by direct microwave heating as an alternate heating route. Microwave heating route for glass melting is preferred to retain higher Fe²⁺/ΣFe in glass.

Materials and Method

Microwave melting

Glass of batch composition (wt. %) SiO₂-46, B₂O₃-26, Na₂O-16.5, BaO-10.5 with 1% Fe metal powder was taken for this study. The source of SiO₂ and B₂O₃, primary glass-forming oxide in the glass batch was SiO₂ (from Bremthaler Quarzitwerk GmbH [BQW], Germany, 99% pure) and H₃BO₃ (Loba Chemie, India, 99.5% pure). Na₂O and BaO were obtained from carbonate sources (Na₂CO₃ and BaCO₃ from Merck, Darmstadt, Germany, 99% pure). Fe metal powder (Loba Chemie, India, 99.5% pure) was added in the batch. Approximately 50 g of each glass batch with above composition was mixed thoroughly in an agate mortar and pressed to form a pellet at 10 ton pressure in a hydraulically operated pellet press. The pellet was placed in a quartz crucible insulated in air atmosphere inside a 2.45 GHz, 3.0 kW multimode microwave furnace (from M/S Enerzi Microwave Systems Pvt. Ltd., India) and heated at a rate of 15 - 25°C/min up to 1250°C and held for 1 h. Temperature measurement of the sample was performed by online infrared non-contact Pyrometer 260 - 1800°C with an accuracy ±0.3% of the measured value +1°C. The molten glass was poured into a preheated steel mold and annealed at 560°C for 2 h followed by controlled cooling in a muffle furnace to eliminate thermal stresses in the glass. The glass sample is named SBNBM to denote the glass composition ("S" for silica (SiO₂); "B" for boric oxide (B₂O₃); "N" for sodium oxide (Na₂O); "B" for barium oxide (BaO) and "M" stands for microwave) and is shown in Fig. 1.

Spectrophotometric characterization

Method using ferrozine. Glass samples were ground to a fine powder using an agate mortar and pestle. Glass powder of 50.0 mg was taken in a Teflon beaker. Then, 20 mg of meta-NH₄VO₃, 0.5 ml of concentrated H₂SO₄ and 1.5 ml of concentrated HF were added into it. The liquids were added drop by drop and mixed well with the powder glass sample. The beaker was then heated on a hot plate maintained at 60°C for 10 min for digestion of powdered glass. After dissolution, 20 ml of a saturated boric acid solution was added and the total volume of the sample was made to 50 ml by adding distilled water. Then, the solution was filtered using Whatman 42 filter paper. Next, 5 ml aliquot and 5 ml ferrozine-buffer solution were mixed and allowed to develop a stable color complex for 2 h. The optical absorbance of the solution containing



Fig. 1 Polished glass sample melted in microwave furnace (SBNBM).

Fe²⁺-ferrozine color complex was recorded by UV-Vis spectrophotometer (Model Perkin Elmer, Lambda 45, USA) within the wavelength range 450 to 550 nm.

For the analysis of total iron, 5 ml of the aliquot was taken in another volumetric flask and then 5 ml of 5% ascorbic acid (Merck, Darmstadt, Germany, 99% pure) solution was added to reduce all the iron to Fe²⁺ state, followed by the addition of 5 ml ferrozine-buffer solution to develop the color complex. The intensity of optical absorbance of Fe²⁺-ferrozine color complex (at 562 nm) is the measure of total iron in the solution. Ratio of Fe²⁺/total Fe was estimated from the absorbance intensity of Fe²⁺-ferrozine color complex in the solution without and with the addition of ascorbic acid in the solution.

Method using 1,10-*ortho*-phenanthroline. In order to estimate the ferrous ion concentration using 1,10-*ortho*-phenanthroline, 50 mg of the glass powder was taken into a 100-ml Teflon beaker. Then, 0.5 ml of concentrated H₂SO₄ and 1.5 ml of concentrated HF were added into it, followed by heating it at 60°C for 10 min for sample digestion. An indicating solution was prepared simultaneously using 25 ml of 4% boric acid (Merck, Darmstadt, Germany, 99.5% pure), 7 ml of 10% potassium hydrogen phthalate (Merck, Darmstadt, Germany, 99% pure), 6 ml of 0.25% 1,10-*ortho*-phenanthroline (Merck, Darmstadt, Germany, 99.5% pure) solution, and 2 ml of concentrated NH₄OH in another Teflon beaker. After dissolution of the glass sample, the solution was allowed to cool to room temperature and the as prepared indicating solution was added into it. The pH of the mixed solution was adjusted to 3 - 4 using diluted NH₄OH and/or diluted H₂SO₄. The volume was made up to 100 ml by adding double distilled water.

A reducing agent, hydroquinone (25 mg, Merck, Darmstadt, Germany, 99.5% pure), was added to the 25 ml sample solution to reduce all iron into Fe²⁺ and indicating solution was added to develop color for 2 h. The absorbance intensity of this solution was measured after complete color development of the orange-red complex. This absorbance intensity is a direct measure of total iron content in solution and thereby in glass. Thus, the redox ratio is evaluated from the concentration of solution without and with the addition of hydroquinone.

Preparation of calibration standards

To investigate the concentration of Fe²⁺ in the glass sample solution, two calibration curves have been drawn using the standard iron solution.

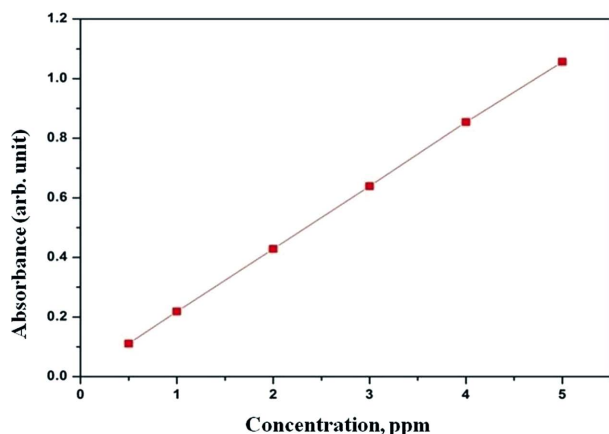


Fig. 2 Calibration curve drawn from the absorbance intensity of Fe^{2+} -phenanthroline color complex at 510 nm from six standard sets of iron solution.

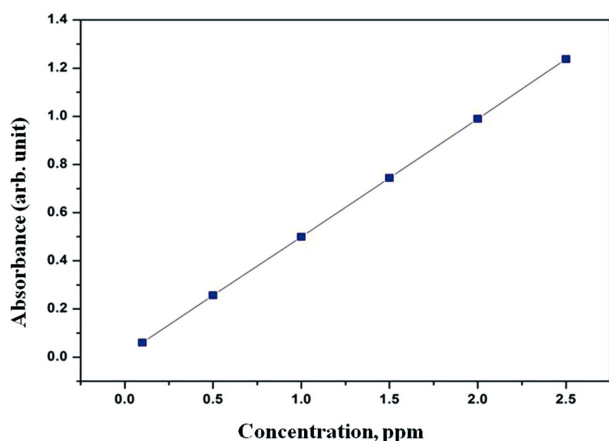


Fig. 3 Calibration curve drawn from the absorbance intensity of Fe^{2+} -ferrozine color complex at 562 nm from six standard sets of iron solution.

For 1,10-ortho-phenanthroline. The standard iron solution 0.25 – 2.5 ml of 50 $\mu\text{g}/\text{ml}$ was transferred into six sets of 25.0 ml volumetric flasks. Then, 50 mg of hydroquinone was added to 6 ml of aqueous solution of 1,10-ortho-phenanthroline (0.25% w/v) in each set. Finally, distilled water was added to make up the volume to 25 ml. The orange-red colored complex was formed and allowed to settle for 3 h. The optical absorbance of the solution was measured at 510 nm against the reagent blank. Figure 2 depicts the calibration curve obtained from the absorbance intensity at 510 nm of six sets of different standard iron solution using 1,10-ortho-phenanthroline.

For ferrozine. The standard iron solution 0.25 – 6.25 ml of 10 $\mu\text{g}/\text{ml}$ was transferred into six sets of 25.0 ml volumetric flasks. Then, 5 ml of ascorbic acid was added to 5 ml of the ferrozine buffer solution to each set. Finally, distilled water was added to make up the volume up to 25 ml. A deep violet color complex developed and was allowed to settle for 2 h. The optical absorbance of the color complex was measured at 562 nm. The measured absorbance intensities were plotted against the concentration of Fe^{2+} in the solution as shown in the calibration curve, Fig. 3.

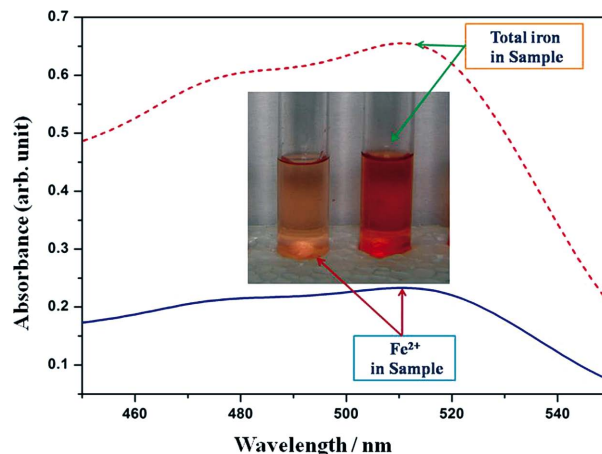


Fig. 4 Visible absorption spectra of samples SBNBMP (before addition of hydroquinone) and SBNBMPHQ (after addition of hydroquinone) in 1,10-ortho-phenanthroline method. Inset shows the orange, red color in the solution; left side, color of the solution without the addition of reducing agent; right side, color of the solution after addition of reducing agent (*i.e.* hydroquinone).

Results and Discussion

Visible absorption spectra of solutions containing samples SBNBM in the 1,10-ortho-phenanthroline method within the wavelength range of 450 – 550 nm are presented in Fig. 4. The maximum absorbance peak has been identified at the 510 nm wavelength from the absorbance spectra. Absorbance peak at 510 nm for the solution after addition of hydroquinone was found to be higher, indicating total iron concentration in the solution. Inset shows the photograph of the solution containing a sample solution of both with and without addition of hydroquinone. Fe^{2+} ions form an orange-red complex $[(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Fe}^{2+}]$, reacting with 1,10-ortho-phenanthroline in the solution over a pH range of 2 – 9.²⁸ The optical absorbance of this complex shows a broad peak centered at ~ 510 nm. Therefore, optical absorbance at 510 nm wavelength of the solution containing the complex could be converted to a concentration of Fe^{2+} in the solution from the calibration curve in Fig. 2. The ratio of $\text{Fe}^{2+}/\Sigma\text{Fe}$ is determined by the ratio of absorbance intensity of the solution without hydroquinone and after the addition of hydroquinone. The optical absorbance spectrum before adding hydroquinone is denoted as SBNBMP (“P” stands for phenanthroline method) and after adding hydroquinone in the solution has been noted as SBNBMPHQ (“HQ” stands for hydroquinone) in Fig. 4.

Figure 5 depicts the visible absorption spectra of solutions containing samples SBNBM in the ferrozine method within the wavelength range 500 – 600 nm. The maximum optical absorbance peak was recorded at the 562 nm wavelength. Optical absorbance peak at 562 nm for the solution after addition of 5% ascorbic acid was found to be higher, which represents the total iron concentration in the solution. Fe^{2+} ions form a magenta color complex with ferrozine in the solution over a pH range of 3 – 4. The optical absorbance intensity of the solution containing ferrozine color complex could be converted into concentration of Fe^{2+} in the solution from the calibration curves in Fig. 3. The ratio of $\text{Fe}^{2+}/\Sigma\text{Fe}$ is determined by the ratio of absorbance of the solution and that after the addition of ascorbic acid. The absorbance spectrum recorded for the solution before adding ascorbic acid is denoted as

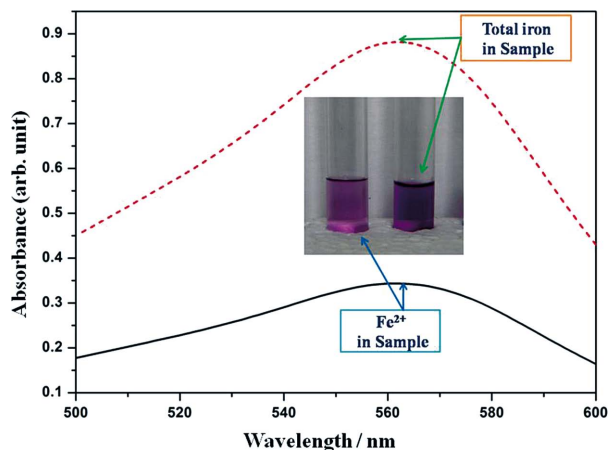


Fig. 5 Visible absorption spectra of SBNBMF (before addition of ascorbic acid) and SBNBMFA (after addition of ascorbic acid) in ferrozine method. Inset shows the violet color in the solution; left side, color of the solution without the addition of ascorbic acid; right side, dark color of the solution containing ascorbic acid.

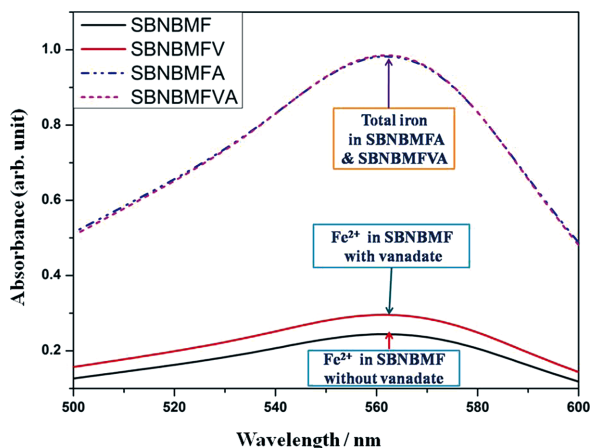
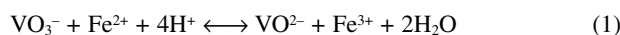


Fig. 6 Optical absorption spectra of solution prepared with and without the addition of meta-vanadate in ferrozine method.

SBNBMF ("F" stands for ferrozine) and after addition of ascorbic acid has been noted as SBNBMFA ("A" stands for ascorbic acid) in Fig. 5.

The effect of meta-vanadate on Fe^{2+} in the ferrozine method has been demonstrated in Fig. 6, which illustrates optical absorbance spectra of the solution prepared using ferrozine with and without the addition of meta-vanadate within the wavelength range 500 to 600 nm. The absorbance spectrum SBNBMF has been recorded from the solution prepared without the addition of meta-vanadate in ferrozine solution. SBNBMFV has been recorded from the sample solution prepared with the addition of meta-vanadate. The intensity of the absorbance peak for SBNBMFV at the 562 nm wavelength is noted to be higher than SBNBMF, indicating higher concentrations of Fe^{2+} in the solution containing ammonium meta-vanadate. Thus, ammonium meta-vanadate restricts aerial oxidation of Fe^{2+} to Fe^{3+} in the solution. SBNBMFVA and SBNBMFA, in Fig. 6, are the absorbance spectra recorded after addition of ascorbic acid in both the solution with and without ammonium meta-vanadate, respectively. All the iron is supposed to be reduced to the Fe^{2+} state after addition of ascorbic acid.

The intensity of the absorbance peak at 562 nm is found to be identical for both SBNBMFVA and SBNBMFA, signifying identical concentrations of Fe^{2+} in both the solutions. This confirms that total iron concentration remains the same in both solutions (containing meta-vanadate and without meta-vanadate). This justifies the use of ammonium meta-vanadate to prevent the aerial oxidation of Fe^{2+} with the acidic media, which preserves the Fe^{2+} by the following Eq. (1).²⁵



The equilibrium of Eq. (1) shifts towards the left hand side when the pH of the solution increases above 5 and also less than 1. To avoid this pH dependent oxidation/reduction of iron, the solution pH is carefully maintained within the pH range 3 – 4.

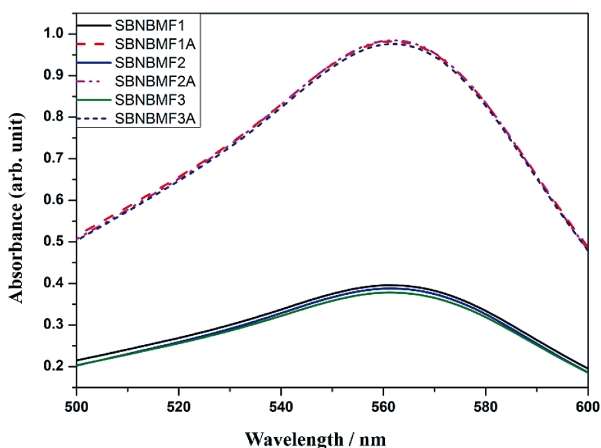
Precision and accuracy

Estimation of precision and accuracy of an analytical method is important for its validation. The use of standard reference materials and a synthetic standard enable the calculation of both accuracy and precision of the analytical method simultaneously. The two above mentioned methods, namely ferrozine and phenanthroline, are denoted as method A and method B, respectively. The precision and accuracy of the two proposed methods were evaluated by analyzing different standard reference materials having different concentrations of Fe (each sample analyzed for five times) in both methods. Here, NIST-SRM 1831 (soda-lime glass, $\text{FeO} = 0.025 \text{ wt\%}$ and $\text{Fe}_2\text{O}_3 = 0.087 \text{ wt\%}$), NIST-SRM 89 (lead alkaline silicate glass, $\text{Fe}_2\text{O}_3 = 0.049 \text{ wt\%}$) and SARM 49 (quartz, $\text{Fe}_2\text{O}_3 = 0.05 \text{ wt\%}$) are used as standard reference materials. Also, 0.1 g of powder sample of NIST-SRM 1831 was decomposed into 50 ml volume, 0.1 g of NIST-SRM 89 was taken into 25 ml and 0.1 g of SARM 49 was taken into 25 ml. The concentration of iron in the three sample solutions becomes 1.756, 1.368 and 1.398 ppm, respectively. The concentration of iron in all the sample solutions has been measured by both methods, and the results are shown in Table 1. Standard deviations were found in the range 0.009 – 0.024 and 0.037 – 0.057 for method A and method B, respectively. The results summarized that both the methods are highly precise and reproducible. However, the precision and accuracy of method A were found to be superior to method B due to aerial oxidation of Fe^{2+} in method B. Further, to study the effect of aerial oxidation in method A, NIST-SRM 1831 has been analyzed and FeO and Fe_2O_3 were found to be 0.0248 and 0.0868%, respectively. Thus, the measured value of FeO is much closer to the certified value, which reveals that aerial oxidation of FeO is almost inhibited in method A. The detection limit was evaluated as described elsewhere³⁰⁻³² and was found within 0.2 ppm.

Accuracy and precision of both methods for measurement of the iron redox ratio in glass have also been studied thrice in each method separately. The glass sample solution was prepared by following the sample solution procedure as elaborated in an earlier section. The optical absorbance spectra of three sets of Fe^{2+} -ferrozine color complex within spectral range 500 – 600 nm wavelength are displayed in Fig. 7 (SBNBMF1, SBNBMF2, SBNBMF3 indicates the Fe^{2+} concentration in the solution and SBNBMF1A, SBNBMF2A, SBNBMF3A denotes the total iron concentration in the solution). It is clearly seen from Fig. 6 that the optical absorbance spectrum of total iron for each measurement is closely overlapped as expected. A minor deviation is noticed in case of the Fe^{2+} spectrum. The intensity at 562 nm for Fe^{2+} and total Fe have been estimated to determine the ratio of iron redox ratio in the solution and has been

Table 1 Standard deviation RSD and % recovery data as estimated for ferrozine and orthophenotraline method using standard reference sample

| Sample ID | Ferozine method | | | | | 1,10- <i>Ortho</i> -phenanthroline method | | | | |
|---------------|-----------------|------------------|-------|------|-------------|---|-------|------|-------------|--|
| | Fe present, ppm | Fe measured, ppm | SD | RSD | Recovery, % | Fe measured, ppm | SD | RSD | Recovery, % | |
| NIST-SRM 89 | 1.37 | 1.36 | 0.009 | 0.69 | 99.27 | 1.35 | 0.037 | 2.68 | 98.54 | |
| SARM 49 | 1.40 | 1.41 | 0.017 | 1.24 | 100.71 | 1.38 | 0.040 | 2.88 | 98.57 | |
| NIST-SRM 1831 | 1.76 | 1.75 | 0.024 | 1.36 | 99.43 | 1.72 | 0.057 | 3.24 | 98.29 | |

Fig. 7 Optical absorption spectra of three sets of samples prepared using ferrozine method (SBNBMF1, SBNBMF2, SBNBMF3 indicates the Fe²⁺ concentration in the solution and SBNBMF1A, SBNBMF2A, SBNBMF3A denotes the total iron concentration in the solution).Table 2 Concentration of Fe²⁺, total iron, Fe²⁺/total Fe, average and tolerance limit for estimation of the iron redox ratio using the ferrozine method

| Set | C1 ^a | C2 ^b | Ratio of C1/C2 (Fe ²⁺ /ΣFe) | Average | Tolerance error limit |
|-------|-----------------|-----------------|--|---------|-----------------------|
| Set A | 0.7884 | 1.9680 | 0.400 | | |
| Set B | 0.7685 | 1.9844 | 0.387 | 0.388 | ± 0.012 |
| Set C | 0.7413 | 1.9703 | 0.376 | | |

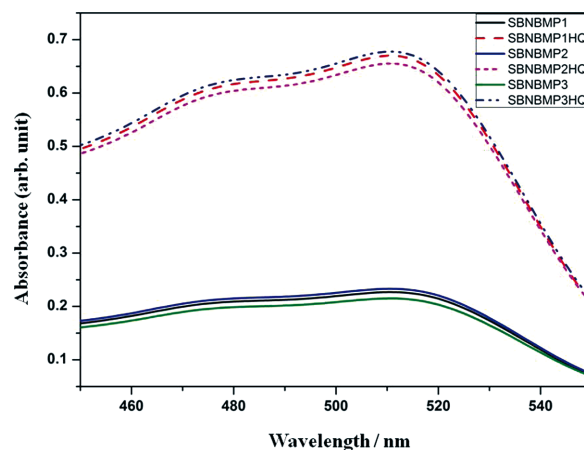
a. Conc. of Fe²⁺-ferrozine complex (ppm) before reduction.b. Conc. of Fe²⁺-ferrozine complex (ppm) after reduction.

presented in Table 2. The error range is evaluated as 0.012 in the case of method A.

The optical absorbance spectra of three sets of Fe²⁺-1,10-*ortho*-phenanthroline color solution within the 450 - 550 nm wavelength, as shown in the Fig. 8, illustrate the accuracy in determining Fe²⁺/ΣFe in solution. Figure 8 depicts that both spectra for Fe²⁺ as well as total iron are deviated slightly due to uncontrolled aerial oxidation. The absorbance intensity at 510 nm for Fe²⁺ and total Fe are identified from the Fig. 8 and presented in Table 3. The error limit is estimated at 0.023 in method B.

Conclusion

Barium borosilicate glass with Fe as dopant has been melted at

Fig. 8 Optical absorption spectra of the three sets of sample solutions prepared using 1,10-*ortho*-phenanthroline (SBNBMP1, SBNBMP2, SBNBMP3 indicates the Fe²⁺ concentration in the solution and SBNBMP1HQ, SBNBMP2HQ, SBNBMP3HQ denotes the total iron concentration in the solution).Table 3 Concentration of Fe²⁺, total iron, Fe²⁺/total Fe, average and tolerance limit for estimation of iron redox ratio using 1,10-*ortho*-phenanthroline

| Set | C1 ^a | C2 ^b | Ratio of C1/C2 (Fe ²⁺ /ΣFe) | Average | Tolerance error limit |
|-------|-----------------|-----------------|--|---------|-----------------------|
| Set A | 1.0123 | 3.1832 | 0.318 | | |
| Set B | 1.0853 | 3.1196 | 0.347 | 0.323 | ± 0.023 |
| Set C | 0.9713 | 3.2031 | 0.303 | | |

a. Conc. of Fe²⁺-phenanthroline complex (ppm) before reduction.b. Conc. of Fe²⁺-phenanthroline complex (ppm) after reduction.

1250°C in a microwave furnace to yield a higher redox ratio. Estimation of the Fe²⁺ oxidation state in glass with two spectrophotometric methods has been carried out, developing ferrozine and 1,10-*ortho*-phenanthroline color complexes. Further, the iron redox ratio (Fe²⁺/total Fe) in the studied glass has been evaluated as 0.388 and 0.323 from the ferrozine and phenanthroline methods, respectively. The lower value of the redox ratio in the phenanthroline method compared to the method using ferrozine is the result of aerial oxidation. The error limit is estimated at 0.012 in the case of ferrozine whereas it is evaluated at 0.023 in the 1,10-*ortho*-phenanthroline method. Thus, ferrozine is preferred to phenanthroline for the estimation of the iron redox ratio in glass.

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