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G-Plus Report to Judel Products

Spectral Analysis and Imaging of Colored Glasses

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1. Introduction

Redox state is one of the most important factors that affect color of glasses. Recently, optical properties and redox state of the glass melts have been studied at TNO by A.J. Faber [1]. Spectral measurements up to 4 μm into the infrared region were taken. The focus of similar studies [2] was on the redox state of iron. In glassware production, the control of color is mainly dependent upon the experience of the operators. When the color varies due to changes in processing conditions, batching or furnace contamination, usually little can be done but to scrap the entire batch. This can result in significant down time and waste of energy to melt and refine the glass. For small glass companies, detecting out-of-specification color variation early in the melting process means savings on labor and energy costs. In larger color glass operations, early detection may provide means to correct or save the batch.

Monitoring the redox state of the glass melt can be used to effectively control the quality of glass products. An in-line redox sensor has been tested in industrial environment [3]. Thermal emission spectroscopy is a non-contact, real-time sensing technique. The collection of a spectrum takes only a few seconds or less. This may allow on-line analysis of the glass melt or hot glass products. For a specific glass product, a series of spectra with different processing parameters could be collected and analyzed. The sensing system would be able to detect a deviation from the normal conditions and signal the operator a change has occurred. The primary goal of this GPLUS effort is to find a practical solution for color monitoring.

In this project, we proposed to conduct initial experiments of spectral characterization of colored glasses from the designated glass industry members of the Society for Glass Science and Practices. The work plan contained three stages: 1) Obtain glass samples and use spectroscopy analysis at ORNL to measure basic spectral characteristics of various glass products; 2) collect emission spectra of the glasses using single-point spectrometers (UV to 2.5 microns) from glass melts; 3) Using a spectral imaging device (3-5 microns) at ORNL to obtain 2D hyper-spectra images to evaluate the emission of glass melts.

2. Experimental

2.1 Glass Specimens:

The specimens were provided by Judel Products Inc., Salem WV, in the form of wine glasses as shown in Figure 1. The colors of the glasses supplied were considered acceptable. Glasses of three basic colors of the products, blue, amber and green, were obtained. The specimens for color analysis were obtained from the top part (about 1 inch below the edge) of the glasses with thickness about 1 mm. For the melting study, glass chips were put into alumina crucibles and the glasses were melted at 1100ºC in a box furnace. Figure 2 shows the melted glasses in alumina crucibles.

Figure 1. Colored glass samples provided by Judel Products Inc.

Figure 2. Three colored glasses melted in alumina crucible

2.2 Spectral Analysis

Spectral analysis of the color glasses was conducted using a CVI Spectral Products, Model SM-240 spectrometer, which covers the spectral wavelength from 350-1100 nm. It is a portable system using a USB connection and can be controlled from a laptop computer. Fiber optic cables were connected to the spectrometer and light source via SMA connectors. The light source for the study was made by CVI Laser Corp with a model number ASB-W-020R. A piece of colored glass was placed between the spectrometer input fiber and light source fiber. A collimating lens was used at the end of each fiber. The absorption of the glass was compared with the light source emission.

2.3 High Temperature Emission Spectral Measurements

High temperature emission spectra were collected using a high temperature fiber optic probe as shown in Figure 4 and the SM-240 spectrometer. The steel casing of the probe allowed the maximum temperature for exposure to be at 700ºC. For short time exposure, i.e. 5-10 seconds, a maximum temperature of 900ºC was used. The probe was partially inserted into a vertical opening at the top of the box furnace and collected emission signals. The crucible with glass melt was placed right below the opening. When the glass was melted and became stable at 1100ºC, the emission spectrum was collected, as shown in Figure 5.

Figure 4. High temperature fiber optic probe

Figure 5. Glass melt in a crucible at 1100ºC

2.4 Near IR and mid-IR Hyperspectral Imaging

A hyperspectral imager, by Pacific Advanced Technology (PAT), HyPAT II, in the 3-5 micron range was made available to study the emission characteristics in that wavelength. The imager is an attachment on an Indigo Phoenix Mid-IR camera with a stand-alone computer system and image analysis. The system divides the 3-5 micron region into 200 bins. Hyperspectral imaging as a function of time and wavelength can be carried out. The imager was placed 8 feet away from the furnace. A 45º mirror was used to direct the images of the glass melt to the imager.

Figure 6. PAT hyperspectra imaging systems

3. Results and Discussion

For light transmission of a standard and the spectral absorption characteristics of three colored glasses are shown in Figure 7. It is clear that the three glasses have distinctive spectra which can be used as a signature for color monitoring. However, the influence of source makes the spectra more complicated. A source spectral was subtracted from the transmission spectra of each glass to obtain the absorption spectra. After normalizing the signal, the absorption spectra of the three glasses are shown in Figure 8. The results match literature reports on similar glasses. Because of the distinct spectral features of each glass, this method can be used to quickly and quantitatively determine the color of each glass. In a more analytical approach, the spectral method requires a sample taken from the melt and analyzed on site. The sample will need to be cooled down and shaped into a pre-determined thickness. The spectrum collection would take about 1 minute. The total time for color analysis will likely take a few minutes. Since the cost of the spectrometer and laptop is low, this could be a superior quality control tool for production of color glass.

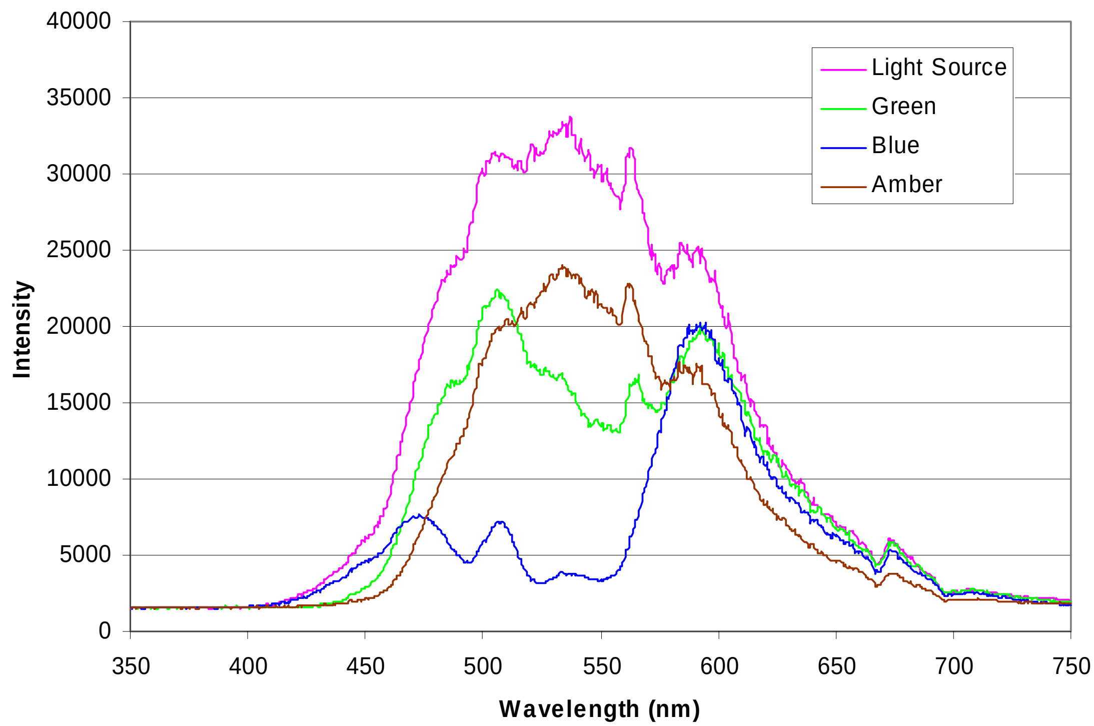

Figure 7. Transmission spectra of three color glasses including the light source

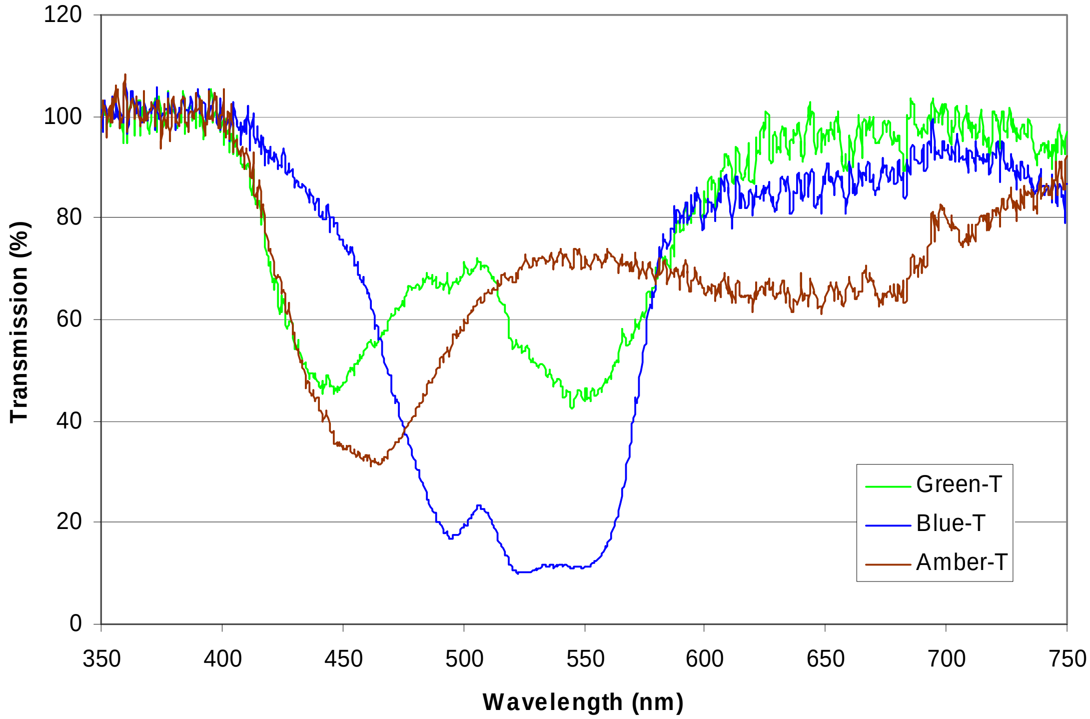

Figure. 8 Absorption spectra of 1 mm thick glasses.

The emission spectra was taken when the glasses were melted in a box furnace. Through the high temperature probe, the emission spectra of the blue glass at 900ºC, 1000ºC and 1100ºC were collected and shown in Figure 9. The intensities of the emission reduced greatly as a function decreasing temperature. However, the shape and features remained the same. The emission mainly came from blackbody radiation of the glass melt as indicated in the literature [1,3].

Figure 10 shows the emission spectra of three colored glasses. Besides differences in magnitudes, the three spectrums appear to be identical. These results indicate that the emission of the three colored glasses are the same in the visible range in terms of spectral features. No spectral differences on the redox states could be obtained even with drastically different colors. However, the results in Figure 10 indicated that there is a difference in radiative heat transfer power between different glasses, i.e. the color differences can be measured by the radiative thermal conductivity. In relative terms, the

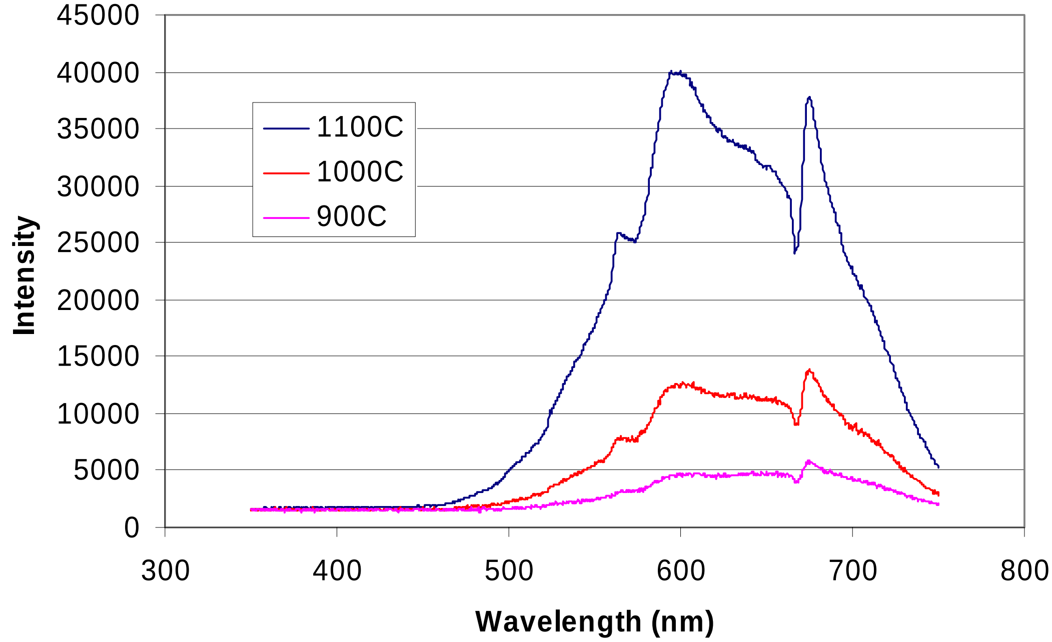

Figure 9. Blue glass melt at three different temperatures

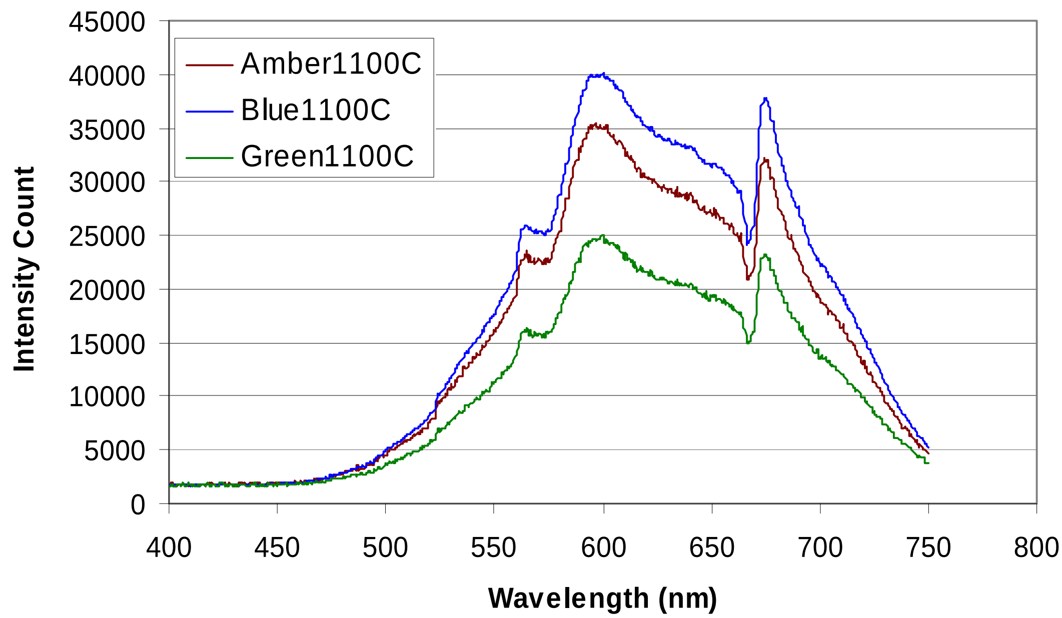

Figure 10. Emission at 1100 C for three different colors. A strong difference in emission power was observed.

blue glass seemed to have the strongest thermal radiation compared to the amber and green glasses.

To further investigate the effect on redox state, spectroscopy in the infrared region is needed. The disadvantage of going to an IR spectrum is that the cost of spectrometers goes up significantly, making it difficult for glass companies to adopt the technique in their production. The hyper spectral imager tests were not conducted due to lack of availability of the instrument and time constrains on the project.

Past tests by A.J. Faber [1] studied redox state of silicate glass melt using a Perkin Elmer FTIR system from 0.9-4.0 μm showed no obvious spectral features due to redox states. However, the effect of redox states (Fe^{2+}/Fe^{3+}) on radiative heat transfer was also observed in the near to mid-IR range. Therefore, it is reasonable to expect glasses with drastically different colors to show strong differences in radiation power.

In the current project, similar color glasses with different redox states were not available. It is expected that the relationship between radiation heat transfer and redox state can be established by measuring radiative thermal conductivity of the glass melt. This means at the same furnace temperature, the measure of emission under same instrument set up should show differences in total energy (or total intensity over the spectral range). A larger scale study is needed to further investigate this topic.

4. Summary:

Spectral transmissions of colored glasses were obtained from three major Judel products using a low-cost portable spectrometer. The instrument and set up is relatively low cost and capable of detecting differences between batches and has the potential to be used as a quality control tool. Spectral emission of the different color glasses were also studied using the same spectrometer. Thermal radiation differences were observed among the three glasses. This result is consistent with the variation in radiative thermal conductivity due to redox states reported in the literature.

References:

[1] A.J Faber, “Optical Properties and redox state of silicate glass melts”, C.R. Chimie, (5) pp1-8 (2002)
[2] Max Wilke, François Farges, Pierre-Emmanuel Petit, Gordon E. Brown Jr., And François Martin, “Oxidation state and coordination of Fe in minerals: An Fe *K*-XANES spectroscopic study”, *American Mineralogist, Volume 86, pages 714–730, 2001*
[3] A.J. Faber and M. J. van Kersbergen, “Development and industrial testing of a new in-line redox sensor”, Proc. XIX Int. Congr. Glass, Edinburg, July 1-6, 2001, Glass Technol, 43C, 242-4 (2002)