The colour of glass

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Abstract

3D-printing, along with other additive manufacturing (AM) and rapid prototyping (RP) techniques, involves building up structures in a layer-by-layer fashion based upon a computer design file. Such techniques are well-suited to the production of one-off, complex structures that would often be difficult to produce using traditional manufacturing methods. There has been rapid growth and interest in this field during recent years, and a range of techniques are now available which make use of many common materials such as plastic, metal, wood and ceramic. However, relatively little has been done to develop AM using glass. Since glass was first made, thousands of years ago in Mesopotamia, it has been appreciated because of its vibrant colours. To allow a successful design and print of any glass object, these colours have to be captured and classified in such a way that they can be incorporated in the CAD design of the object and lead to the desired result in the print. The colours of architectural glass are often classified by RAL charts [1] or by BS4800:2100 colour codes [2]. Both colour classification systems have been developed for paints and coatings, but are a good first approximation. What they cannot capture is, for example, that some glasses display different colours in reflection and transmission and/or the colour change occurring in glass when it is reheated. In 3D printed glass, gas inclusions are another source of colour changes. Scattering at the air/glass interface leads to the addition of white to the underlying glass colour. Using CIE chromaticity coordinates [3], glass samples are characterized before and after processing. We used two different measurement methods to determine colour coordinates as a function of sample thickness and frit size, to check how robust the results were as a function of the measurement method.

Introduction

The colour of glass is generated by incorporating transition metal ions such as Cr^+, Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^+, Cu^{2+} into the SiO_2 matrix. The resulting colour depends on the atomic mass of the transition metal, the higher the atomic mass the more saturated the colour, but also on processing factors like [4]:

The preparation of the glass batch
Atmosphere in the kiln
Presence of crystalline opacifiers
Chemical environment
Heating schedule
Gas inclusions

The ingredients and the processing conditions are supplier trade secrets and, in general, glasses from different suppliers will lead to different results when processed, for example as a 3D print. 3D printing of glass is a two-step process: First, the so called greenware is printed using either extrusion or a powder bed as the print platform. Second the dry greenware is fused in a high temperature kiln. Indirect printing is a process where a mold is created by 3D printing and then filled with glass. The second step is the same as for direct printing: the glass is fused at high temperatures. During heating the glass melts completely, and, after the droplets have merged, is quenched in order to solidify in a glass state again. Exposure to high temperature and gas inclusions in the glass body will lead to colour changes in the final object.

Colour changes after secondary heating

In kiln glass processing, the heating process after the shape of the object has been determined either by direct print or by a mold, glass is heated up to temperatures between 720 to 820 °C. At these temperatures the glass is a viscous fluid and chemical reactions between the different components take place which influence the final colour.

In Figure 1 we present the colour shifts of three glass samples as a result of the following heating schedule in air: Ramp 280°C/h to 150°C, hold at 150°C for 5 min, ramp 444°C/h to 718°C, hold at 718°C for 10 min, ramp full to 510°C, hold at 510°C for 30 min, ramp 97°C/h to 427°C, hold at 427°C for 10 min, ramp full to room temperature. The kiln was a vented, top-heating, glass kiln.

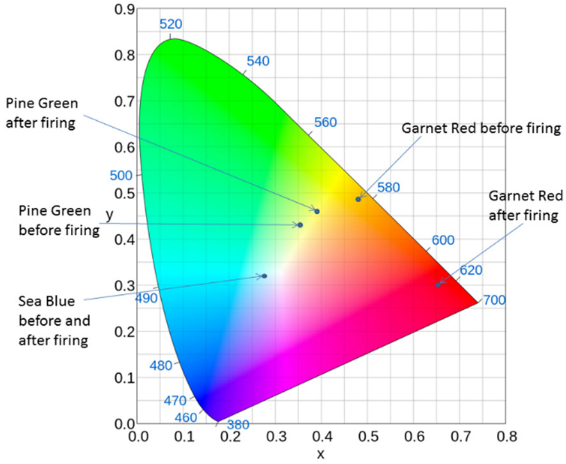

Figure 1: CIE chromaticity x,y coordinates of three glass samples before and after heating to 718°C.

All glass samples were Bullseye thin-rolled 2 mm sheet glass. Sea Blue is described as stable and does not show a colour shift after heating. Pine Green contains sulphur and is expected to wisp (to develop faint colour streaks) upon heating. We did not observe wisping but noticed a small colour shift. Garnet red contains selenium and sulphur and is a so called ‘striker’, a glass which shifts colour substantially upon heating as seen in Figure 1. The chromaticity coordinates were determined as follows: The transmittance of the samples was measured in 0/0 configuration [3] using a HP UV/VIS spectrometer. The spectrum was then used to calculate x, y chromaticity coordinates using D65 illumination and the colour-matching functions for the CIE standard colorimetric observer [3].

Using the HP UV/VIS spectrometer without an integrating sphere was problematic since none of the samples had truly flat surfaces. Therefore we used the measurement methods described below.

Experimental set up

To determine chromaticity coordinates of different samples and to explore how sensitive the results are to the measurement methods we used the following three set ups.

1. Setup 1: Lovibond Tintometer R400

The Lovibond Tintometer R400 is a handheld colorimeter based on diffuse reflectance spectroscopy, i.e. it consists of an integrating sphere illuminated by a tungsten lamp and a spectrometer. The integrating sphere has an opening under which the sample is positioned. The light reflected from the sample is then collected by the integrating sphere and part of it analyzed by the spectrometer. Both specular and diffuse reflectance contribute to the total reflectance. The CIE chromaticity coordinates are calculated from the collected spectra. The instrument is able to include specular reflection, SPIN, or exclude specular reflection, SPEX. The illumination, and the coordinate system can by chosen by the user. We used illuminant C, representing average daylight with a correlated colour temperature of 6800K and xyz colour coordinates. The tristimulus values X,Y,Z [3] are calculated using

$$X = k \sum_{\lambda} \phi(\lambda)\bar{x}(\lambda)\Delta\lambda$$

$$Y = k \sum_{\lambda} \phi(\lambda)\bar{y}(\lambda)\Delta\lambda$$

$$Z = k \sum_{\lambda} \phi(\lambda)\bar{z}(\lambda)\Delta\lambda$$

With $\phi(\lambda) = T(\lambda)C(\lambda)$ for transmittance or $\phi(\lambda) = R(\lambda)C(\lambda)$ for reflectance and $k = \frac{100}{\sum_{\lambda} D_{65}(\lambda) * \bar{y}(\lambda)\Delta\lambda}$.

T(λ) is the transmittance of a transparent glass sample illuminated and measured normal to the surface and $R(\lambda)$ is the reflectance.

The chromaticity coordinates are:

$$x = \frac{X}{X+Y+Z}$$

$$y = \frac{Y}{X+Y+Z}$$

And $z = 1 - x - y$.

To check how much the chromaticity coordinates are influenced by contributions from diffuse and specular reflections we measured the samples a) mounted on a mirror, b) mounted on a white diffuser and c) in transmittance using set up 1 for a) and b) and set up 2 for a) and c).

2. Setup 2: Integrating sphere and spectrometer

We used a Thorlabs 2″ integrating sphere, a Thorlabs cold white LED with a colour temperature of 6500K and the Ocean Optics USB4000 spectrometer coupled to the integrating sphere by an optical fiber perpendicular to the incident light. In a linear arrangement this set up allowed us to measure the spectra of the light transmitted through the glass samples without any contribution of reflectance. To mimic the experimental situation encountered when using the Tintometer we used the 20º setup, where the integrating sphere is next to the LED, the sample is mounted on a mirror and rotated at 20º to the incident light.

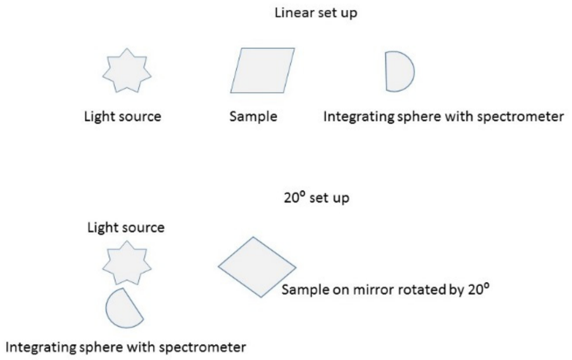

Figure 2: Schematics of the linear set up and the 20º set up described in the text.

Sample preparation

We used Bullseye Emerald Green glass in the following grades: 2 mm rolled, coarse frit, medium frit, fine frit and powder. The average thickness of the rolled glass was 2.25 mm. The average particle sizes of the frit were: 8 mm, 2 mm, 1 mm and 0.1 mm for the course, medium, fine and powdered frit, respectively. All frit grades had wide particle size distributions. In an attempt to achieve reproducible dimensions we used indirect printing and made 50 x 50 x 3 mm^3 molds. They were filled with 18.75 g of glass, expecting that after firing we would have 50 x 50 x 3 mm^3 samples. Surface tension of the molten glass led to shrinkage in the x,y direction and to an increase of height, see figure 3. In table 1 the average thickness of the samples are listed. The smallest frit size led to the largest increase in sample height.

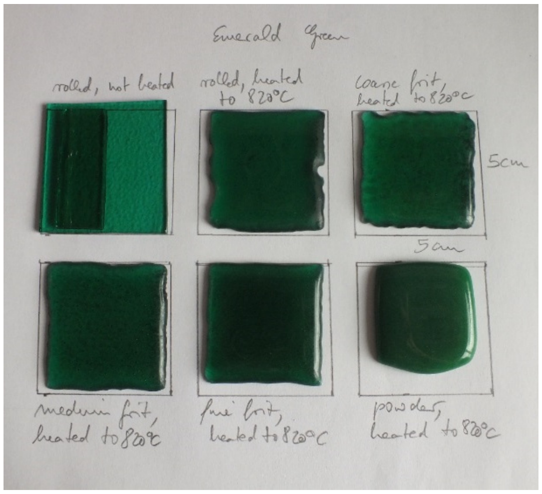

Figure 3: Emerald Green glass samples. On the left side of the rolled sample, a second sheet was put on top to show the colour difference between one and two layers.

Table 1: Thickness after firing

Sample material	Thickness after firing
Rolled glass sheets	4.83 mm
Coarse frit	4.86 mm
Medium frit	4.55 mm
Fine frit	5.01 mm
Powder	7.01 mm

The firing schedule can be found in table 2.

Table 2: Firing schedule

Ramp 100ºC/h	To 150ºC
Hold at 150ºC	For 30 min
Ramp 222ºC/h	To 677ºC
Hold at 677ºC	For 30 min
Ramp 333ºC/h	To 820ºC
Hold at 820ºC	For 60 min
Ramp full	To 482ºC
Hold at 482ºC	For 60 min
Ramp 55ºC/h	To 427ºC
Ramp 100ºC/h	To 371ºC
Ramp 330ºC/h	To 26ºC

After firing the glass/air interface was glossy but the glass/mold interface was matt. We did not polish the matt surface but used it to test the lack of specular reflection on the chromaticity results.

Results

Increasing the sample thickness by piling up rolled glass sheets showed that Emerald Green exhibits dichromatism which is a shift in colour, i.e. hue, as a function of thickness. The data points in Figure 4 represent 1 to 4 sheets of rolled glass. The colour shifts deeper into green with increasing thickness.

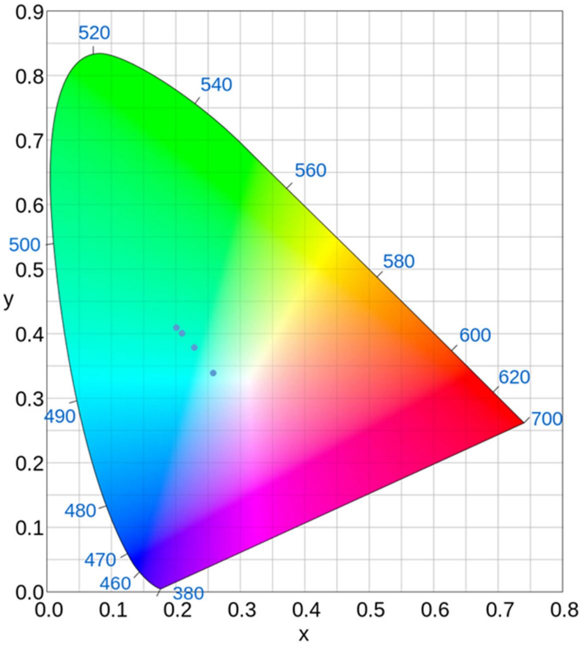

Figure 4: Dichromatism displayed by Emerald Green glass. The thickness of the glass sample from right to left are: 2.25mm, 4.5mm, 6.75mm and 9mm.

The measurements were performed using setup 2 in transmission. The colour coordinates of the fired glass samples were determined in the same way. Figure 5 shows that the chromaticity coordinates for the fired samples cluster near the value for two sheets of rolled glass, except for the powder sample. The powder sample is very different. It is opaque and transmits hardly any light. The cluster of the cut, coarse, medium and fine samples is shifted to the right of the trajectory between 1 sheet and 2 sheets of rolled glass which indicates a colour shift as a result of heating. The two data points for each heated sample are from orienting the sample in two different ways, a) with the air/glass interface (the glossy side of the sample) towards the light source and b) with the mold/glass interface (the matt side) towards the light source.

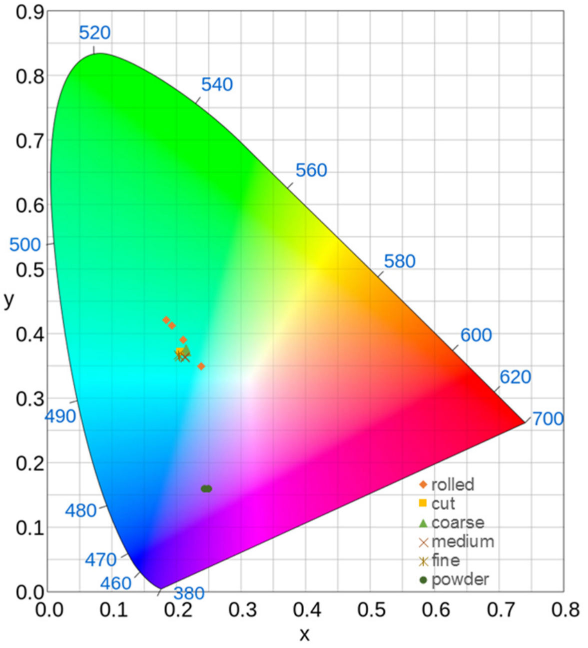

Figure 5: Chromaticity coordinates of cut, coarse, medium, fine and powder samples after heating to 820ºC in comparison to the chromaticity coordinates of unheated, rolled glass.

The chromaticity coordinates for Figure 4 and 5 were calculated from the recorded spectra using the CIE definitions. Setup 1, the Tintometer, does the calculations automatically. To determine how robust the results are with respect to measurement procedure, we measured the chromaticity coordinates of rolled sheets in the following arrangements:

- Setup 1, two sheets on matt white background
- Setup 1, two sheets on mirror
- Setup 2, 4 sheets in transmission
- Setup 2, 2 sheets at 20º with mirror behind them.

The 20º setup should mimic the Tintometer set up with a mirror behind the sample, since the optical path of light incident at 20º is only 3% longer than at 0º.

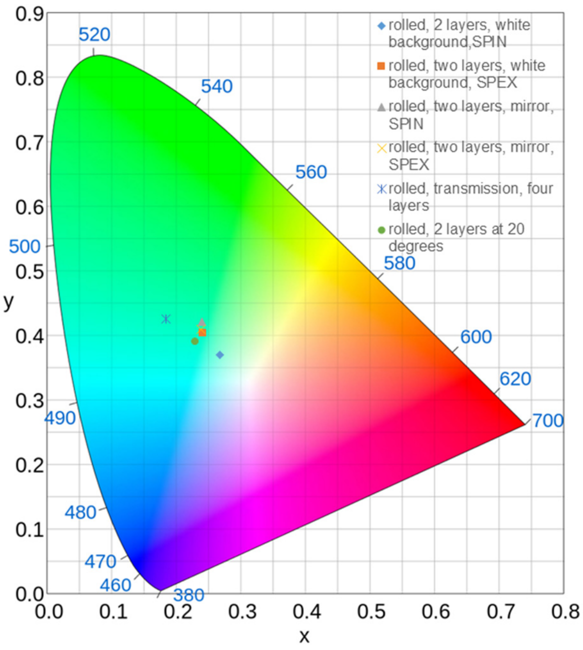

Figure 6: Chromaticity coordinates for rolled glass samples as a result of different measurement methods.

Figure 6 shows that:

- Four layers of rolled glass are not equivalent to two layers in reflection. This is a surprising result since Emerald Green is transparent.
- When specular reflection is not included, SPEX, the results for measurements with setup 1 are independent of the background the samples were mounted on, i.e. a mirror and a matt white background generate the same chromaticity coordinates.
- The difference between SPEX and SPIN are biggest when a matt white background is used.
- Two layers at 20º with a mirror as background are close to the results for Tintometer measurements with a mirror as background but not identical.

Considering only SPEX results, we compared colour coordinates for samples of different frit size on different backgrounds, with the air/glass interface towards the light source and with the plaster/glass interface towards the light source, measured with setup 1 and 2. Figure 7 shows two trends: There is a noticeable blue shift of the chromaticity coordinates when measured with setup 2 in the 20º configuration. The blue shift is clearly visible in the integrating sphere. It could be caused by mixing of the specular reflection from the surface of the samples with the reflection from the bulk of the sample. In all cases, measurements with the glossy side of the samples towards the light source and measurements with the matt side of the samples towards the light source lead to different sets of chromaticity coordinates, even though specular reflection was excluded in the case of measurements with the Tintometer. All samples show dichromatism as a function of frit size when measured in reflection. The smaller the particles size, the larger the x-coordinate and the smaller the y-coordinate. When measured in transmission, this effect is much reduced, see Figure 5.

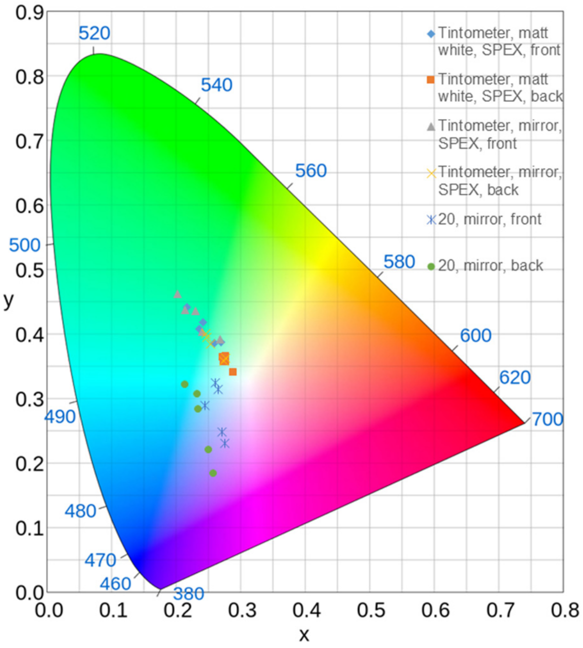

Figure 7: Comparison of different measurement methods and different frit sizes. 'matt white' refers to a matt white background the samples were mounted on, 'mirror' to a mirror as the background. '20' is the 20º configuration of setup2. The dependency of the chromaticity coordinates from the frit size is clarified in table 3.

Table 3: Chromaticity coordinates as a function of frit size, mirror background, glossy side towards light source, setup 1, SPEX

	x	y
Cut sheet, heated to 820ºC	0.2011	0.4621
Coarse frit, heated to 820ºC	0.2130	0.4379
Medium frit, heated to 820ºC	0.2397	0.4039
Fine frit, heated to 820ºC	0.2292	0.4367
Powder, heated to 820ºC	0.2676	0.3924

Conclusions

Most glass samples display a colour shift upon heating. This shift is unpredictable and differs from sample to sample and from batch to batch. The colour shift is not only dependent on how complete chemical reactions in the glass were before it was heated a second time, but also on the frit size of the glass used in the kiln glass process.

Whether a commercially available instrument, like the Lovibond Tintometer R 400, is suitable to determine the chromaticity coordinates of coloured glass, is debatable. It is known that many glass samples show different colours in transmission compared to reflection. The Tintometer uses diffuse reflectance spectroscopy to determine colour coordinates. The values of chromaticity coordinates measured in reflection shift noticeably with frit size and surface gloss. The dependency of the chromaticity coordinates on frit size is hugely reduced when measured in transmission, with the exception of the powder frit samples which are almost opaque. Even for a transparent glass sample, like Emerald Green in sheet form, the chromaticity coordinates of the same optical path length in transmission or reflection are not compatible.

More work is needed to separate the influence of the measurement method on the chromaticity coordinates from true colour shifts.

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Author Biography

Susanne Klein holds a Diploma in Physics and a PhD in Medical Physics from the University of Saarland. Since 1995 she has worked and lived in the UK, first as a Royal Society Research Assistant at the University of Bristol and then as a member of HP Labs. She has worked on colloidal liquid crystals, colloids in liquid crystals and new materials for 3D printing and is now working on optical cryptography.