A Spectroscopic Analysis of a Multiglaze Blend; Understanding Components Used in Ceramic Glazes

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May 15th, 2023

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Abstract

This research paper investigates the production of ceramic glazes through the understanding of multiple glaze components. Three separate tests were conducted to explore the roles of colorants, acids, and amphoteric agents in the overall recipe of a glaze. This study focuses on controlling these agents to achieve specific physical characteristics such as color and texture. A spectroscopic analysis was conducted to gain quantitative data on pigmentation for five different multi-glaze blends. The results are analyzed to show the relationship between the light absorbance of the unfired glaze and fired ceramic piece and to show differences in values between the five glazes prepared. This research experiments with the composition of ceramic glazes for glaze development with specific goals in aesthetic visuals in pottery.

I. Introduction

Understanding the components used in glazes and their interactions is important in order to accomplish a desired or predicted outcome. In this research paper, the effects on the final product of the ceramic components such as colorants, fluxes, amphoteric agents and acids are explored. The focus is specifically on multi-glaze blends as there are more factors that are involved, resulting in a wider range of samples. With this test, a spectroscopic analysis of the glazes is conducted to better understand glaze composition.

The results of this study can be applied to the development of new and innovative ceramic glazes with unique qualities. By gaining a deeper understanding of the composition and behavior of ceramic glazes, a wide variety of glazes can be produced for decoration and functionality as protection for electronic or automotive industries.

II. Background

A. Ceramic Components

The three main materials in a glaze are fluxes, amphoterics, and acids. Fluxes are mostly alkaline and is used to lower the high melting point of the acids in the glaze. In this way, the kiln does not have to be fired at a high temperature for the glazes to melt into the piece. Amphoterics are also known as neutrals and are mainly made of clay or alumina. The amphoteric agents binds the glaze to the clay body piece and prevents the glaze from running off the piece. The acids, mainly silica, are the glass-forming agents. Silica is the main component in the glaze that determines the strength and contributes to the shine of the fired glaze. To elaborate, silica has a melting point of 3110°F and the campus kiln reaches 2350°F (NCBI, 2023). In order for the glaze to be fully fired, the addition of flux is used to lower the melting point, as mentioned previously. Additionally, colorants are added for pigmentation.

Aside from the components listed above, firing techniques can also affect a piece's color and texture. The temperature and atmospheric type of the kiln are taken into consideration. The

atmosphere could be oxidation or reduction. Oxidation atmosphere is when there is plenty of oxygen present in the kiln; reduction atmosphere is when there is only a small amount of oxygen present (Hopper, 2001). According to Hopper, as the glaze materials are in oxide form, the atmospheric state of reduction robs the glaze of its oxygen content, causing the return to their metal state. As further description, "copper when oxidized is greenish, but when reduced it is reddish (Hopper, 2001)." In this research, the kiln will be in a $\Delta 10$ (2284 - 2381°F) temperature and reduction atmosphere.

B. Preparation of Ceramic Pieces

The test tile clay bodies are prepared by a clay extruder die to create uniform products. These are then bisque fired as a batch to be glazed after. The measurements of the tiles after firing are as follows 1.5 inches in length, 1.25 inches in width, and 2.5 inches in height. There are multiple ways to glaze a clay body: dipping, brushing, spraying, splattering and more. As the test tiles are small, the pieces are glazed by dipping. With the pieces that are double dipped, the first layer is left to dry before adding another layer. It is important that each layer is not heavily applied. This prevents glaze defects such as crawling and blistering.

C. Determining How to Analyze the Glazes Chemically

To gain further understanding in glaze composition, the materials and methods of multiple research papers were taken into consideration. Although there is limited research capacities on campus, the following papers will shed light on possible methods that this research could develop further.

In *The Microscopy and Microanalysis of Crystalline Glazes*, the glazes were tested using X-ray diffraction, optical microscopy, and scanning electron microscopy. X-ray diffraction was used to analyze the light micrographs of speherulites (crystalline regions) present in fired glazes. The diffraction peaks were compared to examine particle size and defects. Optical microscopy was used

to analyze crystal growth. Lastly, the scanning electron microscopy is used as a visual examination of the crystal morphologies. To summarize, this paper written by Knowles and Freeman focuses on the comparison of crystal growth by the glass-former agents in different glazes (2004).

In *The Synthesis and Colour Properties of Blue–violet Cassiterite Pigments Doped by Terbium Ions,* an X-ray diffraction and spectrophotometer was used to analyze the glazes. X-ray diffraction was used to identify peak intensities of the samples are increased with the calcination temperature of 1450°C. It was observed that an increased temperature resulted in darker hues. The spectrophotometer was used to measure the colour properties of applied cassiterite pigments when terbium ions and increasing calcination temperature was applied (2018).

In *The Thermal Analysis of Doped Bi*₂ O_3 by Sulcová, Vecera, and Bystrzycki, a Ultraviolet-visible spectrophotometer to evaluate color changes by measuring spectral reflectance in the visible region of light (wavelength 400-700 nm). The paper concludes that the increase of dysprosium and zirconium content and calcination temperature had no great influence in the color of the powder materials (2012). Utilizing the authors' UV-Vis spectrophotometer values, this research paper will use a similar wavelength value of 350-750 nm to analyze the multi-glaze blends.

III. Research

A. Colorant Line Blend

This test is conducted to analyze how strong Cobalt (II) Carbonate is as a colorant. Based on Mentor Ed Stein's experience with Cobalt (II) Carbonate, he advised that this should be increased by smaller increments. Therefore, it was decided that the colorant will be increased by 0.5 grams increments. A Shiny White Glaze is used as a base so that the pigmentation of Cobalt (II) Carbonate is evident upon observation. The table shown is the recipe for the Shiny White base glaze and the tile classification for the samples.

| Shiny White | | | Shiny White 200 g | |
|--------------|-------|---|----------------------|-----------------------------|
| Base Glaze | % | * | Test Tile label | Amount of CoCO ₃ |
| Bentonite | 3.36 | * | 11 | 0 g |
| EPK | 4.6 | * | 12 | 0.5 g |
| Zircopax | 7.1 | * | 13 | 1.0 g |
| Whiting | 14.2 | | 14 | 1.5 g |
| Flint/Silica | 20.84 | | 15 | 2.0 g |
| Minspar | 49.7 | | 16 | 2.5 g |
| Water | 100 | | 17 | 3.0 g |

The base glaze is already prepared and is available in the studio. 200 ml of Shiny White Glaze is collected after thorough mixing. It is then placed in a blender so that the colorant is evenly blended in the mixture. After each addition of grams of the colorant, a numbered tile is then dipped into the mixture. There is a total of seven samples; labeled #11-17.



As a result of the colorant line blend, the pigmentation gradually became stronger, reaching a bolder blue hue. As expected, the texture remained consistent throughout. It is observed to be smooth and shiny, with no crackles or runs in all the samples. Overall, this demonstrates that the amount variation of colorants does not compromise the overall texture of the ceramic pieces.

B. Alumina/Silica Variations

The purpose of this test is to analyze how increasing one component will affect the overall texture of the glaze This means controlling the quantities of alumina and silica to reach textures such as glossy, semi-matte, and matte. Silica or Flint is a glass-forming agent that allows the materials to fuse together. Alumina stiffens the glaze so that it does not slide off the clay body. Examples are EPK, kaolin clay, ball clay, fire clay, or alumina hydrate. A Stull chart is used to determine the ratio between alumina and silica for a specific vision of texture.



The Stull chart above, left was used to obtain four samples: glossy (a), semi-matte (b), matte (c), and a more concentrated matte (d). The glaze chosen for this test is named "Whale Watching." It is a light purple glaze with speckles of darker purple. The chosen ratio of silica and alumina are as follows: 20g Si/ 2.5g Al, 20g Si/ 50g Al, 5g Si/ 50g Al, and 0g Si/ 60g Al. Although the changes between the silica and alumina are in greater increments, the goal is to control the components to become a certain texture. The Stull chart was applied to the recipe listed below to determine the ratios to reach the different goals of texture.

| Base Glaze | % | Colorant | % |
|-----------------|------|------------------|-----|
| Custer Feldspar | 46 | Bentonite | 2 |
| Silica | 20 | Copper Carbonate | 1 |
| Gerstley Borate | 13.5 | Tin | 1 |
| Whiting | 8 | Cobalt Carbonate | 0.5 |
| Dolomite | 6 | Rutile | 0.5 |
| Zinc | 4 | | |
| EPK (Alumina) | 2.5 | Water | 100 |

To prepare the following glazes, all the ingredients aside from silica and alumina were combined and dry-sieved multiple times. The composition was then separated to four equal parts, in which the ratios of silica and alumina mentioned above were added. Equal parts water is then added to each of the four containers. The labeled test tiles are dipped once and dried to be prepared for firing.



Although the planned textures came out as predicted, the concentration of the alumina overpowered the silica. This resulted in a thicker tecture and crawling on the test pieces. The left-most sample is the original recipe with no variations; the rest is with varied ratio of silica and alumina. To avoid the outcome of runny glaze, the concentration of alumina has to be lowered. In doing so, the amount of silica was also determined by trial and error with the use of the Stull chart to address the issue of crawling.

C. Multi-Glaze Blend

In this test, two types of glazes are mixed together to obtain an entirely new glaze. As both glazes are different in ratios of silica and alumina, and use different types of colorants, the resulting mixed glaze can be unpredictable. This test is to analyze how texture and color changes once two different glazes are blended together.

There are two total combinations in this section: Mark's Tommoku/Breakfast Special and Seafoam Green/Cherry Blossom. The preparation for both combinations are consistent. Five total samples are collected from each combination. 200 ml total is prepared for each glaze. The first glaze consists of 100% Glaze A and 0% Glaze B. For the five samples, Glaze A decreases by 25% increments and Glaze B increases by 25% increments. These are the following ratios:

200 ml Glaze A / 0 ml Glaze B 150 ml Glaze A / 50 ml Glaze B 100 ml Glaze A / 100 ml Glaze B 50 ml Glaze A / 150 ml Glaze B 0 ml Glaze A / 200 ml Glaze B

1. Mark's Tommoku and Breakfast Special

| Mark's Tommoku | | Breakfast Special | | |
|-----------------|-----|---------------------|-------|--|
| Base Glaze | % | Base Glaze | % | |
| Custer Feldspar | 45 | Dolomite | 11.9 | |
| Flint | 27 | Strontium Carbonate | 6.34 | |
| Whiting | 17 | Whiting | 8.1 | |
| ЕРК | 11 | Nepheline Syenite | 36.85 | |
| | | EPK | 2.06 | |
| | | Flint | 34.75 | |
| | | | | |
| Colorant | % | Colorant | % | |
| Red Iron Oxide | 10 | Cobalt Carbonate | 0.3 | |
| | | Red Iron Oxide | 2.58 | |
| | | Rutile | 4.83 | |
| | | | | |
| Water | 100 | Water | 100 | |

Listed below is the recipe for each glaze:



As the colorants for both glazes are too strong, the resulting mixed glaze did not show evident changes in color. As a result, a different combination is tested for a better observation.

2. Seafoam Green and Cherry Blossom

Listed is the following recipe for each glaze:

| Seafoam Green | | Cherry Blossom | | |
|------------------|-----|-------------------|-----|--|
| Base Glaze | % | Base Glaze | % | |
| Custer Feldspar | 36 | Nepheline Syenite | 60 | |
| Silica | 28 | Spodumene | 20 | |
| Gerstley Borate | 20 | Ball Clay | 12 | |
| Whiting | 11 | Soda Ash | 8 | |
| Dolomite | 3 | | | |
| ЕРК | 2 | | | |
| Colorant | % | Colorant | 9⁄0 | |
| Copper Carbonate | 3 | Tin Oxide | 4 | |
| | | | | |
| Water | 100 | Water | 100 | |



Seafoam Blue is light blue in color, and Cherry Blossom is white in color with orange hues, if in a thinner coat. When dipped in Seafoam first, then Cherry Blossom, the result would be a purple hue with streaks of blue. In this test, the tiles were expected to be in varying intensities of purple. However, from Tile #01 to Tile #03, it turned from light blue to darker green. Then, in Tile #04, it turned to a purple color, as was expected. #05 is 100% Cherry Blossom, so only one shade of purple is observed.



Another test was conducted to observe at what ratio of Seafoam Blue and Cherry Blossom will reach a purple hue from green. Smaller percent increments was used and is specified above. Starting from the 50/50 ratio, Glaze A decreases by 5% and Glaze B decreases by 5%. In the 45/55 and 15/85 ratio, the purple hue began to show.

As the glazes were too thick to be measured by the spectrophotometer, the glazes had to be diluted with water. The following concentrations were tested for one glaze to determine if it is readable by the machine (glaze:water in ml), 4:4, 1:99, 1:144, 1:249, and 1:149. The glaze to water concentration used is 1:149 as it was readable by the machine from wavelengths 350-750 nm.

Due to time constraints, only the first set of the Seafoam Green and Cherry Blossom was sampled with the spectrophotometer. The light absorbance from wavelength 350 to 750 nm was collected and is shown below.

| Wavelength | Absorbance | | | | |
|------------|------------|-------|-------|-------|-------|
| (nm) | 1 | 2 | 3 | 4 | 5 |
| 350 | 1.254 | 1.381 | 1.318 | 1.419 | 1.592 |
| 400 | 1.218 | 1.338 | 1.256 | 1.353 | 1.52 |
| 450 | 1.208 | 1.303 | 1.218 | 1.303 | 1.468 |
| 500 | 1.146 | 1.221 | 1.131 | 1.211 | 1.348 |
| 550 | 1.129 | 1.194 | 1.074 | 1.117 | 1.241 |
| 600 | 1.093 | 1.157 | 1.017 | 1.105 | 1.227 |
| 650 | 1.061 | 1.118 | 1.02 | 1.067 | 1.161 |
| 700 | 1.054 | 1.104 | 0.978 | 1.031 | 1.125 |
| 750 | 1.046 | 1.058 | 0.948 | 0.989 | 1.079 |

As the wavelength increases, the light absorbance for each glaze decreases. Furthermore, as Glaze A decreases and Glaze B increases, the ligh absorbance for each wavelength increases. As Cherrry Blossom (Glaze B) is thicker in texture, more light is absorbed for each wavelength. The highest light absorbance value for each glaze occurs at 350 nm, falling in the violet region of the light spectrum. The graph below visualizes the pattern between the wavelength and light absorbance for each glaze.



IV. Future Work

Due to time constraints and studio firing schedules, conducting multiple or larger tests are limited. Another objective is to expand the spectroscopic data collection for all glazes is an objective. More data will lead to a further understanding of how the physical characteristics relate to light absorbance. It is also a goal to find a better way to test the samples in which more variety in results are collected. Furthermore, for the alumina/silica variation test, adjusting the values to smaller increments to showcase a gradual change would show a more valuable comparison between the ratios. In terms of glaze production, it is a personal goal to perfect the 75% Seafoam Green and 25% Cherry Blossom glaze with consistent pigmentation and less crazing and runs. In improving the crazing, the glaze will become food-safe without having to use another glaze to precoat the ceramic piece.

V. Conclusion

The application process of the glaze drastically changes the composition of the final piece. In ceramics, a piece can be dipped into more than one type of glaze, resulting in unique patterns and colors. However, the same result cannot be expected if the two glazes are mixed into the same container as the overall recipe changes. In the multi-glaze blend of Seafoam Blue and Cherry Blossom, shades of green, blue, and purple are shown depending on the applied ratio.

As different colors were observed, the spectroscopic results shows consistent patterns between the five glazes. However, it was expected that he max absorption values would differ throughout as each glaze present different pigments. However, as the glazes had similar components, the spectrophotometer showed the same max wavelength as all the glazes were in similar conditions before firing. The pigments that show after firing in a reduction atmosphere was not present for the spectrophotometer to measure as the glaze components were all similar in its unfired condition. Therefore, it would be more valuable to compare spectroscopic results between glazes that are vastly different in formula.

Acknowledgments

This work was supported by the New Jersey Space Grant Consortium and Brookdale Community College. I would like to thank Professor Ed Stein for guidance in the preparation of ceramic glazes, Professor Thomas Riley for directing me throughout the research, Professor Ana Teodorescu, and Professor Karina Ochs for supporting me throughout the project.

Special thanks to Viviana Ma and Ellen Kiyler for assistance in glaze production, and Professor Jennifer Riley for assistance in spectrophotometer samplings.

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