

Polychrome Decoration on Staffordshire Figures:

The identification of a new enamel colorant and underglaze oxide recipes using technical analysis

by Lauren Fair and Jennifer Mass

In 2002, more than two hundred Staffordshire figures were given to Winterthur Museum by Thomas N. and A. Pat Bernard of New Orleans, with the wish that a large portion would be on display to museum visitors (*figure 1*). With this donation, Winterthur's collection of Staffordshire figures is now the largest of its kind in an American museum, with over 250 earthenware sculptures that represent the full range of manufacture and decoration techniques known to English potters at the time. Their dates range from 1740 to 1900, spanning the rise and fall of figure production in Staffordshire. Having such an extensive and representative group of objects in one location presents a unique opportunity for in-depth study and technical research.¹

The diligent work of scholars such as Robert Harrison, Patricia Halfpenny, and Myrna Schkolne, has given us a clear picture of the art historical context of these figures, their subject and design inspirations, and details of the lives of the potters who produced them.² Despite their appeal and importance within the ceramic arts, however, the production methods and decoration techniques of these figures are not well understood. Collections of European porcelain

have been systematically analyzed by museum scientists, but notwithstanding their significance, Staffordshire earthenware figures have not been paid this same attention. Were Staffordshire potters copying the same enamel and glaze recipes established at the leading European porcelain

factories? Or, were they paving the way with new methods and materials with which to decorate their figures?

In 2010 Winterthur started a year-long multidisciplinary project focused on condition assessment and technical analysis of the Staffordshire figure collection. The analysis focused on identifying the technology of manufacture of the polychrome decoration (colored glazes, slips, underglaze oxides, and



Figure 1: The Thomas N. and A. Pat Bernard Collection of Staffordshire Figures, Winterthur Museum Ceramic and Glass Galleries.

overglaze enamels) to provide a better understanding of their compositional evolution over time. Through focused art historical research, conservation assessment, and scientific analysis, the goal of this project was to establish a baseline of information to be used for future research and the improved interpretation and preservation of these important and under-studied figures.

This paper will present a thorough summary of the historic methods of Staffordshire figure production, a detailed technical survey of the museum's collection, and the results of technical analysis of the polychrome decoration, including important discoveries made about the compositions of high temperature underglaze oxides (also known as "Pratt colors") and the identification of an orange enamel colorant unique to Staffordshire earthenwares.

Historical Context of the Staffordshire Figure

The Staffordshire figure, as we know it today, has many different origins. Some of the early figures seem to have been inspired by those from medieval times made in clay or wood.³ Later on, as porcelain became widely imported from China and then manufactured in Europe, more elegant figure forms in porcelain became a major source of inspiration for the Staffordshire figure.

While continental porcelain figures were in high demand in the eighteenth century, this was a time of great economic change in England, and the country bore witness to a growing middle class, with wars in Europe and America lessening the demand for costly English porcelain.⁴ Pottery manufacturers in Staffordshire took advantage of this changing market, and introduced lead-glazed

earthenware known as creamware and pearlware, which served as less expensive alternatives to porcelain. Like the high demand for table wares made of this less expensive material, earthenware decorative figures could be purchased by merchants and working class individuals, now able to afford what were considered to be luxury items for the home.

Earthenware manufacture thus became the dominant source of revenue for the Staffordshire potteries, and by 1810 they led the world in its production.⁵ At the same time, the market for English porcelain among the upper classes decreased significantly. Craftspeople who had long been employed as decorators of porcelain had to find work elsewhere, and some of them moved into Staffordshire from the porcelain factories.⁶

Figure design inspiration

The early stages of eighteenth-century Staffordshire figure manufacture and design were in part based on Chinese porcelain

prototypes, in part inspired by traditional tastes, and in part based on the practices established at the notable European porcelain factories, namely Meissen and, later, Sèvres. In 1751, for example, Sir Charles Henry Williams's collection of Meissen figures was lent to the Chelsea factory to be used as a source of design ideas.⁷ English factories capitalized on the public esteem held for Meissen wares and the demand for buying imitations, producing strikingly similar replications (*figure 2*), both in subject matter and in form.⁸

Inspiration for figures made at Meissen from the early eighteenth century was from Chinese prototypes; while in France, subjects in paintings by Watteau or Boucher were often represented in clay models. While English designs largely copied their continental European counterparts, there were also local sources of inspiration, such as the many statues that were made for new English homes and gardens.⁹ From the mid-century onward, scenes in popular prints, magazines and design books such as



Figure 2: (left) Tailor on goat, enameled and gilt hard-paste porcelain, Meissen c. 1740, antiques-meissen.com; (right) Tailor on goat, Staffordshire enameled earthenware, 1820-30, 6½" (16.6 cm) h., Winterthur (02.30.73.2).



Figure 3: Shepherd and shepherdess *bocage* group with polychrome enamel decoration, AL5434, Staffordshire, 1800-20, 11 2/5" (28.9 cm) h., Winterthur (02.30.571).



Figure 4: John Brown and the Prince of Wales, with polychrome enamel and "second overglaze blue" decoration, Staffordshire, 1850-1860, 7 4/5" (19.9 cm) h., Winterthur (02.30.130).

The Ladies Amusement,¹⁰ were also translated into ceramic figures.

Throughout the eighteenth century in England, figures from classical mythology and allegorical figures were highly popular, as well as romantic interpretations of everyday rural life, such as representations of shepherds, gardeners, hunters, and even animals. In the nineteenth century, from about 1810-1820 a style of figures with *bocage* was introduced; this referred to a woodland setting, incorporating a spreading, leafy tree behind the figures standing upon a grassy mound (*figure 3*).

Around the time of Queen Victoria's accession to the throne in 1837, figure production was at its peak. The royal family, as well as soldiers, politicians, and heroes or villains of the day became the main subjects of Staffordshire figures (*figure 4*). In addition, characters from popular paintings, plays, novels, or poems also found their way into representations in clay. Toward the later part of the nineteenth century, the trend moves away from classical inspirations to representations that are uniquely English, illustrating contemporary politics, society, and culture.¹¹

Figure collecting

The great variety of subjects pertaining to all aspects of contemporary life, style, and tastes made the collecting of earthenware figures attractive to many people. The sculptures represented personal interests and scenes of whimsical humor, but were also emblematic of the collector's degree of affluence. Ceramic figures were considered luxury items, and the growing middle class in eighteenth-century England readily followed the trend of collecting them for prominent display in their homes.¹² One common way to show off one's

figure collection in upper middling and wealthy homes was to have figure sculptures – some of them inspired by earlier confectionary figures – as decoration for dining tables and dessert services. A 1751 engraving by L.P. Boitard in *The Scribleriad*¹³ shows a picnic scene in the English countryside with ceramic figures surrounding and adorning the feast (figure 5).

Figure collecting even crossed the ocean, and by the 1820s, Staffordshire figures were being exported to the United States in large quantities. Called “images” or “image toys” in the eighteenth century, a fairly broad range was imported to America at that time, as known from period inventories and advertisements. This trend extended even into the twentieth century, with an article from the *Dallas Morning News* in March of 1909 noting that “Mantel ornaments of Staffordshire ware are being collected by women ... [but] a single piece does not satisfy the average woman. She wants half a dozen or more.” It continues, “It is a

fad to have at least one mantel in one’s country house literally packed with Staffordshire figures.”¹⁴

The passion for collecting and displaying figures goes beyond the interest in a certain subject matter or theme represented, and relates to the innovative technology of colorful decoration on ceramics. Staffordshire figures, painted with the full range of enamel colors known at the time, were a means of showcasing this novelty. Potters and craftsmen were always searching for new colors and methods to improve upon known ones in order to keep up with consumer demands.¹⁵

By the early twentieth century, the demand for figures had subsided; and while they were still sold, they were no longer mass-produced. Today, Staffordshire figures represent a unique slice of English history from the eighteenth and nineteenth centuries. Through niche enthusiasts, the appeal of Staffordshire figures lives on, but only as a pale comparison to the fervor and popularity they once

generated in English and American households.

Figure manufactories

Although the market for ceramic figures was growing in the eighteenth and nineteenth centuries, the main source of revenue for pottery manufactories remained in functional wares, such as dinner and dessert services, rather than luxury goods. Therefore, at an early date it was only the larger factories that produced figures as a secondary venture. By 1800 there were five small pottery factories that were reported to specialize in making figures; this number grew to fifteen in 1830, and to 36 by 1841.¹⁶ Smaller factories were better suited to the manufacture of figures, since their production required more specialized skills and handling.

Initially, enamel painters worked mostly as freelance artists. In the eighteenth century, some advertised their craft as painters of miniatures or of panels for the toy industry.¹⁷ Enameling shops appeared first in London, and then in Staffordshire around the early 1750s, but by the mid-1760s it became commonplace for potteries to include decorating facilities within their factories.¹⁸ By the 1780s porcelain works were bringing some of the most talented enamel painters to their factories to train and inspire other artists.¹⁹ Many of these artists then moved to Staffordshire, particularly once painted porcelain gave way to cheaper earthenware versions.

The ability to produce enamel colors was considered highly specialized, and it required a refined knowledge of chemistry and diligent control of firing atmospheres. Warner Edwards (d. 1753) is the earliest documented “color maker” in Staffordshire, with a pottery works in Albion Street in



Figure 5: L.P. Boitard, *Picnic with Porcelain Sculptures*, for Richard Owen Cambridge’s *The Scribleriad: an Heroic Poem*, Book 2 (London 1751). Cambridge University Library.

Shelton, where he made various wares and also manufactured enamel colors for “other houses”.²⁰ In Simeon Shaw’s 1829 *History of the Staffordshire Potteries*, he writes of Mr. Edwards, whose “chemical ability exceeded that of all other persons in the district; for he could make the various kinds of Pottery then in demand, and prepare and apply the different colours, to ornament them.”²¹ Enamel recipes

tended to be highly guarded, leaving enameling shops to explore color-making chemistry on their own, and the majority of enamel painters to purchase enamels from independent vendors. In fact, it was only on his deathbed that Edwards had his recipes published. It was partly because of this culture of secrecy that enamel technology during the eighteenth and nineteenth centuries consisted of a

wide variety of materials and technologies, and much experimentation to achieve the brightest and best colors on the market.

There is one known technical treatise available in the eighteenth century that detailed enamel production. This was Robert Dossie’s *Handmaid to the Arts*, published in 1758 and again in 1764, and he dedicates over eighty

Box 1: Examples of flux and enamel recipes from Dossie’s *Handmaid to the Arts* (1758)

Composition of a flux, for common purposes, moderately soft. N° 1.

Take of the glass of lead one pound, of pearl ashes six ounces, of sea salt two ounces. Treat them according to the general directions for fluxes.

This is a very cheap flux; and will serve extremely well for all purposes where a tinge of yellow will not be injurious; or where the flux is not required to be extremely soft.

Composition of a soft flux for common purposes. N° 2.

Take of the glass of lead one pound, of pearl ashes six ounces, of borax four ounces, of arsenic one ounce. Proceed according to the general directions.

This is a very soft flux; and will vitrify a very large proportion of zaffer,²³ or the precipitated powders, or calxes of metals. It is, therefore, very proper for forming strong glazing colours, where harder fluxes are used with the rest: or for all purposes, where there is any necessity for, or convenience in, burning the enamel with a slighter heat.

Composition for the brightest blue. N° 6.

Take of the fluxes N° 1. or N° 2. or of the Venetian glass six parts, of the finest ultramarine one part. Mixt them well for painting. If a transparent blue be desired from ultramarine, a sixth or eighth part must be added to the flux N° 2. and the mixture kept in fusion till the ultramarine be perfectly vitrified, and the whole become transparent.

If the body of colour be not sufficient, more ultramarine may be added: but in order to spare the ultramarine, a small proportion of zaffer, fluxed with four or six times its weight of borax, may be added: which, if the zaffer be perfectly good, will make the ultramarine appear much darker without impairing its brightness.

Composition of a cheaper opaque full yellow. N° 14.

Take the fluxes N° 1. or 2. Venetian glass, six parts, of antimony one part, and of the iron precipitated from vitriol half a part. Mix and flux them well together, till the matter be thoroughly vitrified; and then levigate them with one part of tin calcined to whiteness.

Composition of bright transparent green. N° 21.

Take of the fluxes N° 1. or 2. six parts, and of copper precipitated by alkaline salts one part. Mix and flux them till the mass be transparent.

This will be a very fine deep green; but inclining to the blue; which may be easily corrected, when not agreeable to the purpose, by adding a proper quantity of the transparent yellows N° 12. or 13.

Cheaper composition of an opaque green. N° 23.

Take of the fluxes N° 1. or 2. six parts, of copper calcined to a purple colour, and of the opaque yellow N° 14. each one part. Mix and flux them well; and then levigate them for use with one part of calx of tin.

pages to the manufacturing techniques “Of the nature, preparation, and use, of the several substances employed in enamel painting.”²² A few examples of enamel recipes from Dossie’s treatise are listed in box 1.

Although the majority of enamel production was done privately, there is evidence that some Staffordshire pottery factories produced their own enamel colors. Engravings were published in a pamphlet in 1827 that supposedly illustrate steps in earthenware manufacture at Enoch Wood’s factory.²⁴ This pamphlet included an engraving of women workers grinding and preparing “the various

colours for the Enameller or Painter” (*figure 6*).

A recipe book of Mr. Thomas Lakin²⁵ was published by his widow in 1824 that contains recipes for enamels, as well as colored glazes and underglaze colors.²⁶ A few examples are reproduced in box 2 below.

These examples demonstrate that not all factories sought out independent suppliers of enamel colors. However, by the turn of the twentieth century, it was common knowledge that the most economical way to obtain enamel colors was to purchase them from a color maker, rather than use the

factory’s time and resources to do so.²⁷

Enamels, which are almost always low fired lead silicates applied over the glazed and fired ceramic body, enabled new and brighter colors not seen before on Staffordshire figures (and not achievable using underglaze colors or colored glazes). As mentioned earlier, this held great appeal for the collector. The technique of enameling gave the consumer a greater variety of options for how the figure would be decorated. For instance, a customer could select the desired figure shape and then choose whether it be left pure “white” with china blue glaze only,

Box 2 Examples of glaze, underglaze, and enamel recipes from Lakin’s recipe book (1824)

To make a Green Glaze. Process 45.

Take 3 Parts of Blue Vitrol, Calcined; 1 Part of Flint Glass; 1 Part of Flint. When ground, take four quarts of the above mixture to thirty quarts of the following mixture, ground, viz.: Take 35 Parts of Litharge; 20 Parts of Flint; 10 Parts of Cornish Stone; 10 Parts of Frit, Process 32.

This glaze is sufficiently fired in the coolest part of the glazing oven. Particular attention should be observed as to the proper wash used for the seggars, for much depends on that simple process. The brightness and lustre of the glaze will be secured by adopting the following wash: five parts of the solution of quick lime, one part of clay slip, free from the least particle of flint, and applied about the thickness of common glaze.

To make a Green under Glaze. Process 53.

Take 12 Parts of Oxide of Yellow; 4 Parts of White Enamel (Flint Glass, Red Lead, Nitre, Arsenic); 2 Parts of Frit, Process 32; 1 ¼ Parts of Blue Calx. The green ingredients only require grinding.

To make an Enamel Blue. Process 77.

Take 16 Parts of Flint Glass; 5 Parts of Red Lead; 2 Parts of White Enamel; 2 Parts of Blue Calx; 1 Part of Common Salt; 1 Part of Potash. ... the materials must be calcined in an air furnace or glazing oven, and caution should be observed that they are not too finely ground at the mill, in order to prevent it from crazing or chipping after being burnt on the pieces of ware, which this colour is very susceptible of doing.

To make an Enamel Grass Green. Process 87.

Take 3 2/3 Parts of Blue Green Frit (Red Lead, Flint, Borax, Blue Vitrol Calcined); 1 Part of Enamel Yellow.

To make an Enamel Orange. Process 90.

Take 1 Part of Orange under Glaze; 2 Parts of Flux, Process 69 (Red Lead, Flint Glass, Borax, Flint); 1 Part of Flux, Process 72.

To make an Enamel Pomona Green. Process 93.

Take 1 Part of Oxide of Green Chroma; 1 ½ Parts of Flux, Process 69; 1 ½ Parts of Flux, Process 72.

This fine beautiful green is simply prepared by only grinding the above ingredients, and produces that dark colour equal to the French green, provided the oxide is genuine; and by adding a proportion more of flux and white enamel, there still will be a rich tint, though weaker and lighter in colour.



Figure 6: 1827 engraving showing enamel preparation, inside an earthenware factory (G. W. Elliot, *Some descriptions of Pottery Making and Working Conditions, 1557-1844* (Stoke-on-Trent, Staffordshire: Albion Galleries, 1970), 50.

or be colored in any number of ways with enamels. Gilding details could also be added at an additional expense. Therefore, whether the enameling was done by workers in the ceramic manufactory or sent out to a private enameler, the factory could offer a greater variety of wares to the growing number of consumers interested in collecting figures.

The three figures of Benjamin Franklin (*figure 7*) were each made in a similar mold, or possibly the same mold, but with different options for color. On the left, the

Franklin sculpture is left plain, the earthenware body glazed with china blue only; while the other two are decorated in very different color schemes of overglaze polychrome enamels.

As published by Halfpenny, transcripts of sales ledgers and order lists from John Wood, Enoch and Ralph Wood, demonstrate this ability of the consumer to select the kind of decoration desired on a figure. An excerpt from John Wood's sales ledger from 9 December 1785 lists items sold to Mr. John Edwards. Towards the top

of the list, he recorded "4 Toby Jugs coloured 10/-" and "2 China glaze 4/-", denoting a difference in cost between the various options of Toby Jugs for sale.²⁸ Notations and separate prices are also listed if the figure was gilded ("& Gilt") or enameled ("Enamiled").

Survey of Winterthur's Collection of Staffordshire Figures

For each of the 270 Staffordshire figures in the Winterthur collection, the following data was recorded: accession number, brief description, attributed date, provenance, and maker's marks. In addition, the type of colored decoration present was indicated, and for each decoration technique, the colors and the appearance, condition, and location of each color were also recorded. Finally, remarks on the general condition of the object were listed, including examination under long-wave ultraviolet light²⁹ and a categorization of conservation treatment priority.

The figures were divided into three groups based on time period: Early (1780-1820), Middle (1820-1860), and Late (1860-1900). In addition, five types of decoration techniques were identified: slips, colored glazes, underglaze oxides, overglaze enamels, and an additional overglaze blue decoration.

Table 1 shows the number of figures surveyed and how many fall

Table 1 Breakdown of figures surveyed by date range and type of decoration present

Period	Date range	Total # recorded	Slips	Colored glazes	Underglaze oxides	Enamels	Blue 'glaze' decoration
Early	1780-1820	97	12	34	12	58	0
Middle	1820-1860	100	1	1	0	99	23
Late	1860-1900	35	1	0	4	35	3
Totals		232	14	35	16	192	26



Figure 7: (left) Benjamin Franklin, Staffordshire, 1780-1800, 13 1/10" (33.2 cm) h., Winterthur (02.30.010); (center) *Dr. Franklin* AL5444, Staffordshire, 1772-1795, 13" (33.2 cm) h., Winterthur (60.517); (right) *Dr. Franklin*, Staffordshire, 1785-1795, 13 1/8" (33.8 cm) h., Winterthur (60.518).

into each time period. The table also shows the number of figures (by date) that contain each form of decoration technique identified. The Winterthur collection of Staffordshire figures has roughly the same number from the Early and Middle periods, and two-thirds less from the Late period.

Slips and colored glazes were primarily used in the Early period; while enamels were the decoration technique chosen for the majority of the Middle and Late periods. The underglaze oxides known as “high temperature underglaze colors” or “Pratt colors” are also only found in the Early period. Finally, another form of overglaze blue decoration is identified in the Middle period. Each of the five decoration types identified on the figures in the

Winterthur collection is described in more detail below.

Slips

Slips are homogeneous mixtures of clay and water. They are applied to a clay body that has not yet been bisque fired. Typically, the colored slips used were brown (made with iron and manganese oxides), or orange (made with iron oxides).³⁰ The colored clay-water mixtures would be made into a slurry and applied to the figure with a brush. The figure would then be dipped into a vat of lead glaze and fired only once at glaze firing temperatures, roughly 1050°C.

The earliest Staffordshire earthenware figures made on any scale date to the first half of the eighteenth century and were

decorated with sparse additions of colored slips to pick out eyes or ornament costumes (*figure 8*). Slips continued to be used on figures throughout the eighteenth and nineteenth centuries, and in conjunction with other types of decoration, but only sparingly to decorate minor components such as shoes and hats.

Colored glazes

Early figures produced in the eighteenth century were prepared by bisque firing at 1150°C, painting with colored glazes, and then glaze firing at approximately 1050°C (*figure 9*). Colored glazes are made by grinding metal oxides and adding them as colorants to the lead glaze batch. According to one nineteenth-century recipe book,



Figure 8: Man with bottle and bone, brown slip decoration, Staffordshire, 1780-1800, 4 2/3" (11.9 cm) h., Winterthur (1973.503).



Figure 9: St. George and the Dragon, colored glaze decoration, Staffordshire, 1780-1800, 11" (27.9 cm) h., Winterthur (02.30.6).

lead glaze for earthenware typically consisted of Cornish stone,³¹ lead oxide (PbO), borax (Na₂B₄O₇), flint, and soda.³²

China blue is made by adding a very small amount (less than 0.1%) of cobalt oxide (CoO) to the glaze.³³ The main metal oxide colorants generally used for colored glazes are a more concentrated amount of cobalt (Co²⁺) for blues, copper (Cu²⁺) for greens, manganese (Mn²⁺) for browns, and iron (Fe³⁺) for yellows; purple is achieved by mixing manganese and cobalt, and black glaze is made by mixing manganese, iron (Fe²⁺), and

cobalt.³⁴ Just as with the colored slips, there is a limited palette possible for glazes because only those colors mentioned above were able to withstand the high temperature of the glost firing.

If the figure were to be glazed and left as undecorated pearlware, it would be dipped into a vat of china blue glaze. If it were to be colored, the glaze mixtures would be hand painted onto the biscuit earthenware body with brushes. With the glazes applied, the figure would then be glost fired at roughly 1050°C. In total, Staffordshire figures that were plain pearlware or

decorated with colored glazes were fired twice only (bisque + glost).

One indication that a figure is decorated with colored glazes is that there are often areas of exposed, undecorated biscuit body in the nooks and crannies. This is due to the colored glazes not requiring an overall dipped coating of a clear glaze on top of them; firing colored glazes in a glost firing will yield a glossy surface. Another indication that colored glazes were used is the presence of pooling in the recesses and folds of drapery, etc., where the color is more concentrated. This is due to the glaze's low viscosity and

tendency to run at these higher temperatures.

Underglaze oxides

While underglaze decoration techniques had been used on ceramics throughout Europe and Asia prior to the eighteenth century, the underglaze technique detailed here refers to a specific technology developed in England in the last decade of the eighteenth century, using “high temperature colors” under the glaze. Also known as Pratt colors,³⁵ the technique was created to produce a greater variety of hues that could withstand the high glost firing temperatures. This technique added to the palette olive greens and browns, and more brightly colored oranges and yellows (*figure 10*).³⁶

Underglaze Pratt colors consist of concentrated metal oxides ground with water, oil, or an extremely diluted slip that are applied by brush or with sponges directly to a bisque-fired body. If a medium other than water was used to grind and apply the metal oxides, the wares were subjected to an in-between firing called “hardening on” to evaporate off any excess medium.³⁷ Once decorated, the figure was dipped in glaze and fired at glost temperatures.

According to Thomas Lakin’s recipe book, a typical palette for “Colours under Glaze” included the following metal oxides ground with a lead-based flux: blue, made with cobalt; green, made by mixing *oxide of yellow* (likely lead antimonate) with cobalt (box 2); browns, made by mixing antimony, manganese, cobalt, and/or potassium nitrate; orange, made with iron, tin, and antimony; mustard yellows, made with antimony and possibly with the addition of tin; mulberry, made with manganese, cobalt and potassium nitrate; and black, which was made with a mixture of

antimony, manganese, cobalt, and tin.³⁸

Underglaze colors can sometimes be difficult to distinguish from colored glaze decoration, as they are often used together as complimentary techniques. Since underglaze oxides require an overlying coating of lead glaze, these pieces are always dipped in glaze as the final step, meaning that there will be no area of exposed, unglazed body remaining as there are with figures decorated in colored glazes only.

Another key characteristic of Prattware figures is the muted color palette of olive greens, browns and mustard yellows. In addition, there are no obvious areas of pooling in folds of draperies or recesses as there are on figures decorated with colored glazes; many times brushstrokes are still visible because the colors do not tend to run or blur in the lead glaze. The blue underglaze color is an exception to this – cobalt is known to run in lead glazes, whether it is applied under the glaze or whether it is mixed and dissolved in it.³⁹

Enamels

The decoration techniques described above have included a fairly limited range of colors available for use, since the methods require that the colorant be able to withstand glost firing temperatures above 1000°C. The technology of enameling glass and ceramics was applied in Europe during the eighteenth century, thus opening the door for a much wider range of colors to decorate Staffordshire figures (*figure 3*).

Enamels are similar to colored glazes and underglaze colors in that the colorants are metal oxides. Rather than being added to a glaze mixture, however, they are ground with fluxes (lead oxide and/or borax) and aluminosilicates.

Enamels are essentially low-fired colored glasses that when applied to a glazed surface and heated, become fused to the glassy substrate. Enamels will always be found over the glaze, and are sometimes called “overglaze colors” or “overglaze enamels” for this reason.

A flux is an oxide that disrupts the silicate network, lowering its melting temperature and promoting fusion with other oxides. The most common fluxes used in enamel recipes for Staffordshire figure decoration were lead and borax.⁴⁰ Enamels applied to Staffordshire figures were typically fired between 700 and 900°C. These low firing temperatures opened the



Figure 10: Shepherd with lost sheep, AL5414, underglaze (Pratt color) decoration, Staffordshire, 1795-1810, 8 7/10" (22.1 cm) h., Winterthur (02.30.14).

door for a much wider range of colors. Color combinations that require elements that volatilize at higher temperatures are stable at these lower, “onglaze” temperatures. For example, while iron was used at higher glaze firing temperatures to achieve a yellow glaze or underglaze color, at lower firing temperatures, iron oxides produce variations of red enamels, including reddish-brown, pink, or orange shades.

To make an enamel color, the first step was to calcine the fluxes in a special kiln called a muffle kiln, or in small bowls inside a glost oven. A muffle kiln has an inner box or lining (the muffle) that acts as a large saggard and protects the work from combustion gases and falling ashes during firing. After calcining, the fluxes were finely ground with water, mixed with the necessary proportions of the colored metal oxides, and ground again. Most sources state that the enamel colors were then mixed in oil and applied with a brush, similar to the method of underglaze colors.⁴¹ Once the enamel paint was applied, the wares would be fired in an enamel kiln, at temperatures ranging from 700 to 900°C.

Within this lower temperature range, obtaining a desired color or particular shade was temperature-specific. Some colors can be obtained at the higher end of this range, such as browns, greens, and blues, and would need to be applied and fired first; while other colors requiring lower temperatures, such as pinks, peaches, and reds, would need to be applied subsequently and fired last. These multiple firing sequences and highly temperature-specific color combinations meant two things: one, to produce a figure with many enamel colors was a longer and more costly endeavor than the other decoration techniques. Secondly, the kiln operator needed to be highly skilled

with the placement of the wares inside the kiln, ensuring that each piece would be fired at its required temperature and minimizing the number of firings necessary to limit mistakes and manufacturing flaws.

Enamelled ware is easy to identify, as the colored decoration is always sitting on top of the glazed surface. Unfortunately for this reason, these wares are prone to abrasion, flaking, and wear. The surface texture can vary from matte to glossy, and often exhibits bubbling; this can be due to a variety of factors, including enamel composition, pigment and flux preparation, firing conditions, etc.

A second overglaze blue decoration

A final type of decoration present on Staffordshire figures is a dark blue that is used primarily on jackets and coats of figures (*figure 4*). This decoration does not appear on figures until the mid-nineteenth century, but then its use becomes prevalent. In the past, this impressive color has usually been described by writers and collectors as “underglaze blue.” The colorant is cobalt oxide (Co^{2+}), and it almost always exhibits a glossy surface with a deep, rich blue color that blurs into the lead glaze around the edges where it is applied. The color appears to have a uniform concentration throughout, but it appears to be *in* the glaze matrix, rather than underneath or on top of it.

This blue decoration is largely not discussed in the literature. Sandeman’s work from 1901 discusses various methods of applying cobalt oxide as a colorant. It can be mixed with the lead glaze batch and applied as a colored glaze; however, the blue colored glazes tend to exhibit more pooling and greater variation of tone than these later blue applications in question. Concentrated cobalt oxide can also

be ground with a medium and applied to the bisque fired body underneath the glaze, as an underglaze color; however, the appearance again is slightly different from the blue found on the jackets of figures in the nineteenth century. Sandeman describes a third technique in the following passage:

[S]ome mention should be made of oxide of cobalt or oven blue. This blue is unaffected by great heat, and can be painted on the glaze, and may then be passed a second time through the glost oven, when the colour combines and sinks into the glaze, producing a magnificent effect. Oxide of cobalt is suited to most glazes, as it is unaffected in appearance by the presence of vitreous matter, and resists the greatest heat that is attained in ovens used for commercial purposes. Should the piece, however, to which it has been applied, be overglazed, it is likely to flow a little. It may also be used on biscuit and be hardened on and dipped in the same manner as under-glaze colours, but with proper treatment it seems to give even better results employed overglaze as described.⁴²

These “even better results” may be this overglaze technique that is similar to an enamel application, but “sinks into the glaze” to achieve the deep rich color seen on the brilliant blue jackets of many figures from the later period.

Technical Analysis

A technical study of the polychrome decoration was carried out on a representative group of thirty-two figures in the Winterthur collection (see Appendix I). This study reveals important information about the microstructural, elemental, and molecular compositions of the colored decoration and how the recipes evolved over time. Of greatest interest are the materials and techniques used for the enamels, which because of the range

of colors achieved, tend to be the most varied in the technologies used to produce them, and, because of their position above the glaze, the most prone to instability and flaking.

On each figure in the group of thirty-two selected for this study, elemental analysis of the clay body, glaze, and each colored surface decoration present was conducted using energy-dispersive x-ray fluorescence (XRF) spectroscopy. In addition, four figures were selected for microsampling, and these were further analyzed with scanning electron microscopy equipped with energy-dispersive x-ray microanalysis (SEM-EDS). These samples were also studied with micro-Raman spectroscopy. Based on these analyses, a body of information has been gathered that provides important information about the materials and techniques of manufacture of Staffordshire figures with polychrome decoration, and also about the evolution of these technologies.

Previous technical studies and analysis

While the authors are unaware of previous comprehensive technical studies published on the decoration techniques of ceramics from eighteenth- and nineteenth-century Staffordshire, studies have been done on the manufacture and enameling techniques of the leading European porcelain manufactories of the period, such as Meissen, Sèvres, and Du Paquier.⁴³

Page and Chilton analyzed green and blue overglaze enamels on Meissen figures in the collection at the Gardiner Museum of Ceramic Art, using XRF spectroscopy to identify major compositional components and to establish dates of manufacture based on records of when certain materials were first introduced and

incorporated in production.⁴⁴ At Meissen, for instance, copper was the only colorant used for green enamels until the early nineteenth century, when chromium was introduced and became more prevalent as a green enamel colorant. Chromium was first introduced at Sèvres in 1802, but its exact date of introduction at Meissen is not known.⁴⁵ Zinc oxide is thought not to have been used as a flux in blue enamels until after 1760, although it could be found earlier as a component of a brass ash-based colorant.⁴⁶ Zinc has been identified in Du Paquier enamel compositions from 1725-1740 and in a hausmaler-painted Meissen saucer dating from c. 1750-1760; however zinc was not consistently used as a flux in yellow and green Meissen enamels until the nineteenth century; and bismuth was used as a flux in gilding only after 1770-75.⁴⁷ Based on the detection of high proportions of chromium and low or nonexistent proportions of copper in green enameled areas on six of the objects analyzed, Page and Chilton concluded that these objects were manufactured after 1802. Detection of high amounts of zinc present in blue enameled areas on three objects further narrowed down possible dates of manufacture.

Similarly, Mass and Halfpenny conducted research and analysis on an enameled Meissen soup tureen with chinoiserie scenes in The Campbell Collection of Soup Tureens at Winterthur Museum that was initially thought to be eighteenth-century (c. 1740).⁴⁸ Elemental analysis with XRF identified chromium as the green enamel colorant, indicating that the tureen overglaze decoration in fact dates to the nineteenth century or later. Their analysis also detected bismuth and zinc as fluxes for the gilding and yellow enamels,

respectively, further confirming a later decoration date.

In 2009 Bezur and Casadio conducted XRF analysis of Du Paquier porcelain from the collections of the Art Institute of Chicago, the Metropolitan Museum of Art, the Sullivan Collection, and two other private collections.⁴⁹ The scientists sought to characterize the materials, including the underglaze and overglaze decoration, in order to “chart technological developments at the factory and potential transfers of knowledge and skill to or from the other European hard-paste porcelain producers in the first forty years of the eighteenth century”. In addition to characterizing components of the various porcelain bodies of Du Paquier porcelain, XRF analysis revealed the chemical makeup of the Du Paquier color palette, establishing that all the underglaze colors and overglaze enamels were based on “low-firing lead silicate glasses colored with metals and mineral oxides that are consistent with eighteenth-century production.”⁵⁰

As yet, Staffordshire enamels have not been systematically characterized with XRF or any other elemental or molecular analysis technique. The established dates for when certain materials were introduced at factories such as Meissen and Du Paquier can be useful guides for interpreting the compositional data of Staffordshire ceramics, helping to explain if and when information or materials were transferred to English pottery factories from their European counterparts.

Analysis by Casadio utilized micro-Raman spectroscopy coupled with XRF to identify specific phases of enamel components present on Meissen wares in the collection of the Art Institute of Chicago.⁵¹ Raman was

successfully used to characterize green, yellow, brown, black and red enameled areas. Casadio found that earlier pieces (1700-1770) with green enamel contained mixtures of copper and Naples yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7$), while later green shades (after 1802) contained chromium (III) oxide (Cr_2O_3), and one later piece showed evidence of uvarovite garnet (Victoria green, $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$); Naples yellow was identified as the sole colorant for yellow enamels on both early and later pieces; hematite ($\alpha\text{-Fe}_2\text{O}_3$) was identified as the colorant for red enamels; magnetite (Fe_3O_4) was identified in analyzed areas of black

enamel; and brown enamels were found to contain a mixture of magnetite and hematite.

In 2006 a study of Meissen porcelain and stoneware was conducted at the Musée National de Céramique in Sèvres, France, using on-site Raman spectroscopy.⁵² Raman analysis of a mid-eighteenth century figure of a harlequin with polychrome enamels showed the yellow, maroon and green enamels to contain Naples yellow; cassiterite (SnO_2) was added to the green to achieve the “*vert d'eau* pale color”; in other green areas, the colorant was found to be a mixture of blue (not specified) and Naples yellow

pigments; cassiterite was also observed in the blue enamels.

Colomban, et al. also carried out a comprehensive Raman spectroscopic investigation of the enamel colorants used at the Sèvres factory,⁵³ having access to some of the experimental batches and palettes, as well as pure oxides and pigment powders used and prepared there. Using back-scattering micro- and macro-Raman configurations, as well as x-ray diffraction to identify the phases of the reference pigment powders, the Sèvres enamel palette was characterized, and the suitability of Raman for the analysis of white,



Figure 11: Lauren Fair positioning a Staffordshire figure below the spectrometer for XRF analysis.

green, yellow, brown and red enamel colors was verified.

Other techniques for analyzing enamel and glass chemistries include SEM with both energy-dispersive (EDS) and wavelength-dispersive (WDS) x-ray spectroscopies. SEM-EDS has been used to study Renaissance-period enamels on metal substrates,⁵⁴ and early Venetian enameling on glass.⁵⁵ Both studies successfully characterized structures of opacifiers present in the enamel compositions and distinguished between groups that contain lead and those that are soda or mixed soda/potash fluxed glasses.

The analytical techniques utilized in this study, including XRF, Raman, and SEM-EDS, were chosen based on their appropriateness in studying the glazes, underglaze oxides, and enamels of the earthenware decoration. With this study, these analytical techniques have for the first time been applied to the polychrome decoration of Staffordshire figures, using the aforementioned results of the Meissen, Sèvres, and DuPaquier studies as points of reference to compare and contrast manufacturing techniques.

Energy Dispersive X-ray Fluorescence (XRF)

The use of XRF to study glaze decoration and overglaze enamels on ceramics is ideal, as it is relatively quick, noninvasive, and nondestructive. The results provide essential elemental information about the colorants and fluxes present in these materials.

A group of thirty-two figures was selected that represent the range of colors, decoration techniques, and time periods present in the Winterthur collection of Staffordshire figures. A full list can be found in Appendix I.

Elemental analysis with XRF was carried out on this group to establish the colorants and fluxes present in the glazes, slips, underglaze oxides, and enamels. A laboratory-based spectrometer was used, since the figures are portable and a ~70 micron x-ray beam size can be achieved for finely painted areas (*figure 11*).

On each figure, measurements were taken from two spots of each color present to obtain representative results and observe consistency of color composition. Although XRF is a surface analysis technique it will penetrate through several layers of the ceramic surface decoration, and the layered structure of the ceramic body, glaze, colored oxides, and/or overglaze enamel, presents challenges for distinguishing between elements detected from each layer. Therefore, where possible, all spectra are compared to a spectrum of the glaze and body (or the body alone) to determine which elements belong to the colored decorations and which belong to underlying layers. Appendix II provides a full description of the experimental methodologies used for XRF, SEM-EDS, and Raman spectroscopies.

Energy Dispersive Scanning Electron Microscopy with X-ray Microanalysis (SEM-EDS)

Of the group of thirty-two figures analyzed with XRF, four figures were chosen from which to take ~1 mm samples of the body, glaze, underglaze, and/or enamel layers to be examined using SEM-EDS. This was carried out to obtain more complete elemental data (the Artax spectrometer does not detect elements lighter than potassium when used in air-path mode). Back-scattered electron imaging and x-ray mapping were utilized to create an elemental map of the sample cross-sections to help understand

body-glaze and glaze-enamel interaction zones as well as changes in the compositions as a function of depth.

Dispersive Raman Microanalysis (Raman)

Raman spectroscopy is a useful tool for identifying the molecular components of ceramic bodies, glazes, and enamels. If the metal oxides are dissolved into the glassy matrix, Raman spectroscopy will not detect this; however, when pigments or opacifying agents such as cassiterite (SnO₂) are dispersed within the glass matrix, specific analysis of these oxides is possible by micro-Raman scattering. The same samples prepared for use with the SEM were also used for Raman analysis with no additional sample preparation necessary.

Results and Discussion

Slips

Three of the figures analyzed in this study contain instances of colored slip decoration (AL5411, AL5427, and AL5457), all from the Early Period. Of these, only two colors were noted: dark brown and orange.

With XRF, the dark brown slip was found to contain lead, iron, and manganese, suggesting the main colorants are iron oxides and manganese dioxide.

Orange slip was only identified once on the figure of Faith, AL5411 (*figure 12*), and was found to contain iron and also barium as a minor component. This detection of barium warrants further investigation. Staffordshire potter Josiah Wedgwood (1730-1795) created his strongly colored jasperware in the 1770s, based on the inclusion of barium sulfate in the body recipe. Although baryte was found in mines on the outskirts of Stoke-on-Trent, and Wedgwood

made use of its properties to yield colored stoneware clays, barium was otherwise not a typical clay additive during this period.⁵⁶

Colored glazes

Like the colored slips, the only instances of colored glaze decoration of the figures analyzed in this study occur in the Early Period. Sixteen Early Period figures were analyzed with XRF, and six of these are decorated with colored glazes (AL5411, AL5426, AL5457, AL5458, AL5461, and AL5463). Table 2 outlines the colorant elements and fluxes detected in the colored glazes, as well as various trace elements and their frequency of occurrence in figures from the Early Period.

The greens contain dissolved copper, with an olive green glaze having the addition of manganese. Medium blue glaze is made with cobalt, and varying degrees of nickel and arsenic were also detected (likely from the cobalt ore

employed), as well as manganese in two figures. The browns are made with manganese (Mn^{2+}) and the addition of iron (Fe^{3+}) gives a medium brown, while the addition of copper yields a grayer brown. Yellow glazes consist of dissolved iron (Fe^{3+}); purple glaze contains manganese and cobalt; and black glaze contains manganese, iron (Fe^{2+}), nickel, and cobalt.

The colorants used are, for the most part, consistent with eighteenth- and nineteenth-century European glaze technology; however, black glazes used at Meissen have been shown to contain copper, while the Staffordshire black glaze analyzed here does not. The association of nickel and arsenic with cobalt suggests

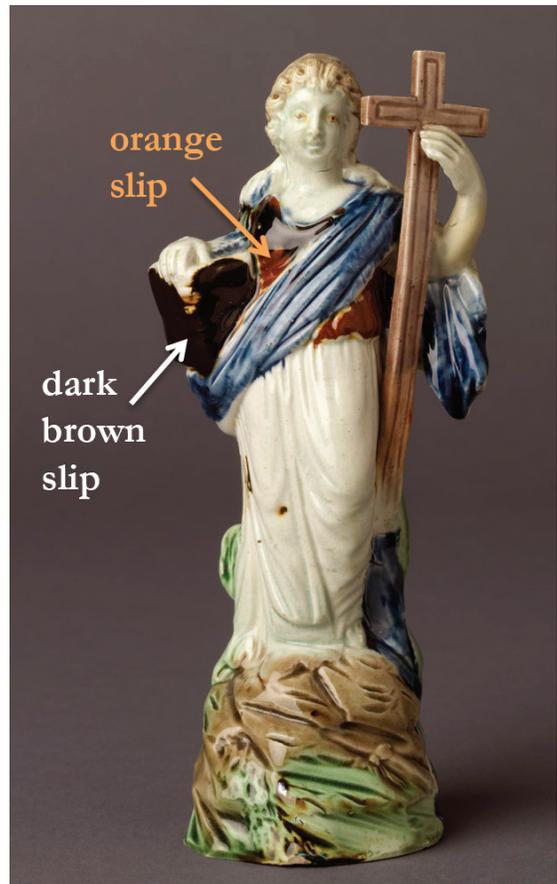


Figure 12: Faith, AL5411, indicating locations of orange and dark brown slip, Staffordshire, 1780-1800, 5¾" (14.6 cm) h., Winterthur (02.30.5).

Table 2 XRF data of colored glazes on Early Period (1780-1820) Staffordshire figures in Winterthur collection. Sixteen Early Period figures analyzed; six with colored glazes beyond china blue glaze

Glaze color	# ID'd	Major elements	Minor elements	Possible colorants
China blue	16	Pb	Co(tr), Ni, As, Cu*	Dissolved cobalt
Medium green	5	Pb, Cu		Dissolved copper
Emerald green	1	Pb, Cu	Sn(tr)*	Dissolved copper
Olive green	1	Pb, Cu	Mn	Dissolved copper and manganese
Medium blue	3	Pb, Co	Ni, Mn, As	Dissolved cobalt
Brown	2	Pb, Mn	Fe, Ni	Dissolved manganese and iron
Red-brown	2	Pb, Mn	As, Zn(tr)	Dissolved manganese
Gray-brown	2	Pb, Cu, Mn		Dissolved copper and manganese
Yellow	2	Pb, Fe		Dissolved iron
Purple	1	Pb, Mn	Co, As	Dissolved manganese and cobalt
Black	1	Pb, Mn, Fe, Ni, Co	As	Dissolved manganese, iron, nickel, cobalt

*detected only once

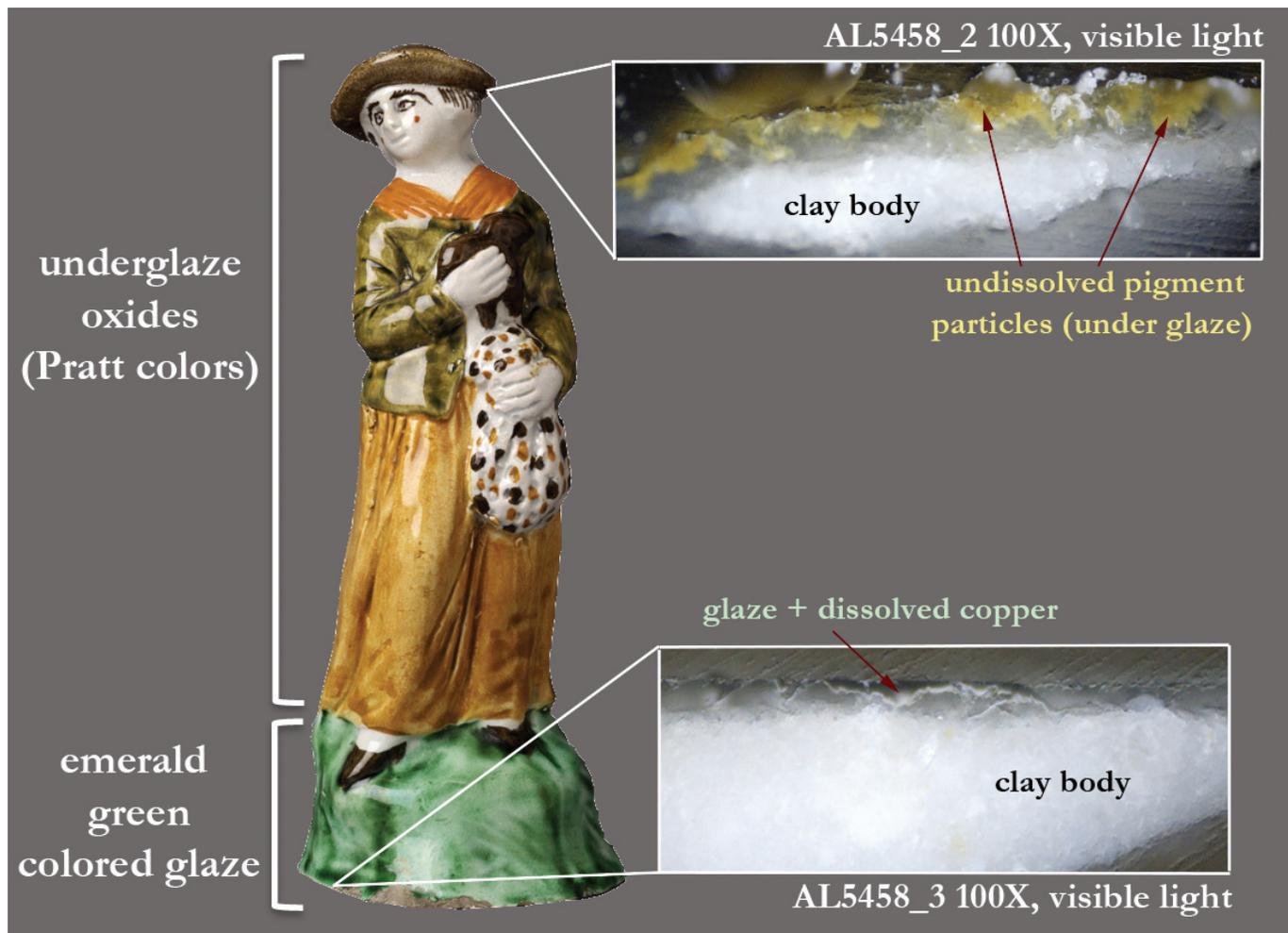


Figure 13: Sportsman's Companion, AL5458, with locations of glaze color and underglaze colors indicated, Staffordshire, 1790-1820, 7¼" (18.4 cm) h., Winterthur (02.30.15.2); sample location and cross-section image of AL5458_2 underglaze brown from figure's hat; sample location and cross-section image of AL5458_3 of emerald green glaze from figure's base.

that Staffordshire craftsmen obtained their supply of cobalt minerals from the Erzgebirge mines in Saxony, which also supplied Meissen and Du Paquier.⁵⁷

It is notable that china blue glaze is present on almost all figures from each time period. If the figures were enameled or underglaze-painted, they would have been dipped in china blue glaze; if the figures were decorated with colored glazes, the china blue glaze served as a white color in the decorative scheme. Because the concentration of cobalt in this glaze is so small, it is not consistently detected with XRF.

The figure of a Sportsman's Companion, AL5458, is decorated with an emerald green glaze on its

base (*figure 13*); the remainder of the figure contains underglaze decoration, which is discussed in more detail below. A sample of the colored glaze (AL5458_3, shown in cross-section in visible light in *figure 13*) was taken from the base near an area of loss and examined with the SEM. A back-scattered electron (BSE) image was obtained, and elemental analysis and x-ray mapping was conducted on this sample (*figure 14*). The aluminosilicate body is visible, with a copper green colorant dissolved into a lead-based glaze matrix. One interesting aspect is a potassium-enriched region at the interface of the glaze and the body. Further investigation into this

phenomenon, an interaction zone, is warranted.

Underglaze Pratt colors

The other type of decoration covering the majority of the Sportsman's Companion are high temperature underglaze oxides, commonly referred to as Pratt colors. Four of the sixteen Early Period figures analyzed contain this type of decoration (AL5414, AL5426, AL5437, and AL5458). Table 3 outlines the major elements and fluxes detected with XRF in the underglaze colors, as well as various minor elements and their frequency of occurrence, in figures from the Early Period.

For the most part, the XRF data is consistent with historic recipes of

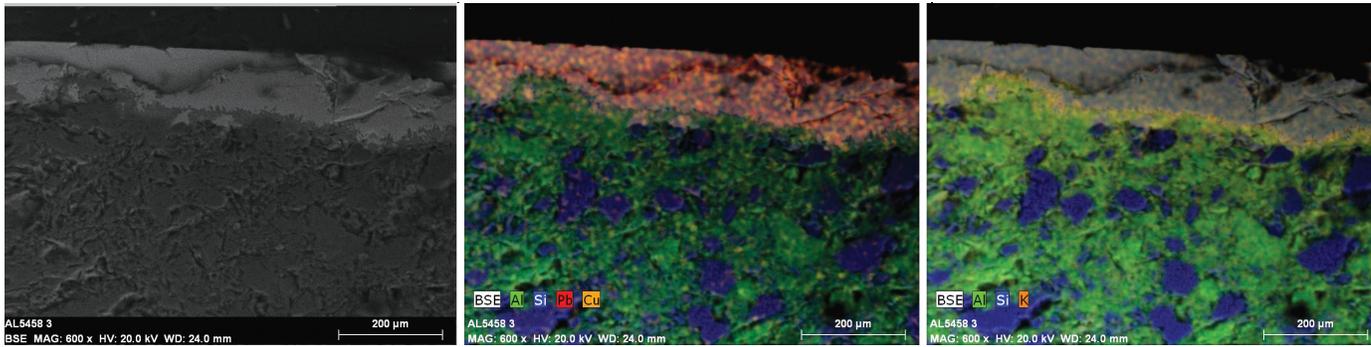


Figure 14: Cross-section images of sample of emerald green glaze (AL5458_3) from the figure of the Sportsman's Companion in figure 13: (left) BSE 600X showing glaze, body and interaction zone; (center) BSE 600X with map of Al, Si, Pb, Cu, showing copper dissolved into a lead glaze and an aluminosilicate body; (right) BSE 600X with map of Al, Si, K, showing a potassium-enriched line at the interaction zone between glaze and body.

underglaze Pratt colors, which must be formulated to withstand the relatively high temperature glaze firing. The results indicate that mixtures of various metal oxides were used to obtain each desired shade. This is a significant difference from colored glaze technology, which typically utilizes one metal oxide dissolved in the

glaze matrix per color. For instance, where copper is the sole colorant for the emerald green glaze in the Sportsman's Companion, XRF detects cobalt, tin, and antimony in areas of green underglaze decoration. The XRF spectrum from the emerald green glaze on the figure's base and the spectrum from the olive green underglaze on the

figure's jacket are shown for comparison, illustrating the differences in their elemental make-up (figure 15).

Since underglaze Pratt colors consist of concentrated amounts of the coloring metal oxides, they are not completely dissolved in the overlying glaze matrix.

Examination of a sample in cross-

Table 3 XRF data of underglaze Pratt colors on Early Period (1780-1820) Staffordshire figures in Winterthur collection. *Sixteen Early Period figures total analyzed; four with underglaze oxide colors*

Underglaze "Pratt" color	# ID'd	Major elements	Minor elements	Possible colorants
Medium green	2	Pb, Co	Sn, Sb, Ni, As*	Ground cobalt oxide; lead antimonate; lead stannate**
Olive green	2	Pb, Co, Sn, Sb	Ni, As*, Zn(tr)*	Ground lead antimonate; cobalt oxide; lead stannate**
Blue	2	Pb, Co	Ni, As	Ground cobalt oxide
Medium brown	1	Pb, Co, Mn	Ni	Ground cobalt oxide and manganese oxide
Dark brown	1	Pb, Mn	Sb, Sn, Fe	Ground manganese oxide; iron oxide; lead antimonate; lead stannate**
Olive brown	1	Pb, Co, Sb, Mn	Sn*, Ni(tr)*, As(tr)*	Ground cobalt oxide; lead antimonate; manganese oxide; also with lead stannate**
Orange	4	Pb, Sb, Fe	Sn	Ground iron oxide; lead antimonate; lead stannate**
Yellow orange	1	Pb, Sb, Sn	Co, Zn*	Ground lead antimonate; lead stannate**; cobalt oxide
Yellow	3	Pb, Sb, Sn	Cu(tr)*	Ground lead antimonate and lead stannate**
Black	1	Pb, Mn, Co, Ni, Fe*	Cu(tr)	Ground manganese oxide; cobalt oxide; copper oxide; also with iron oxide

*detected only once

**presence of tin may suggest tin oxide opacifier, rather than lead-tin yellow pigment (type I, Pb_2SnO_4 or type II, $Pb(Sn,Si)O_3$)

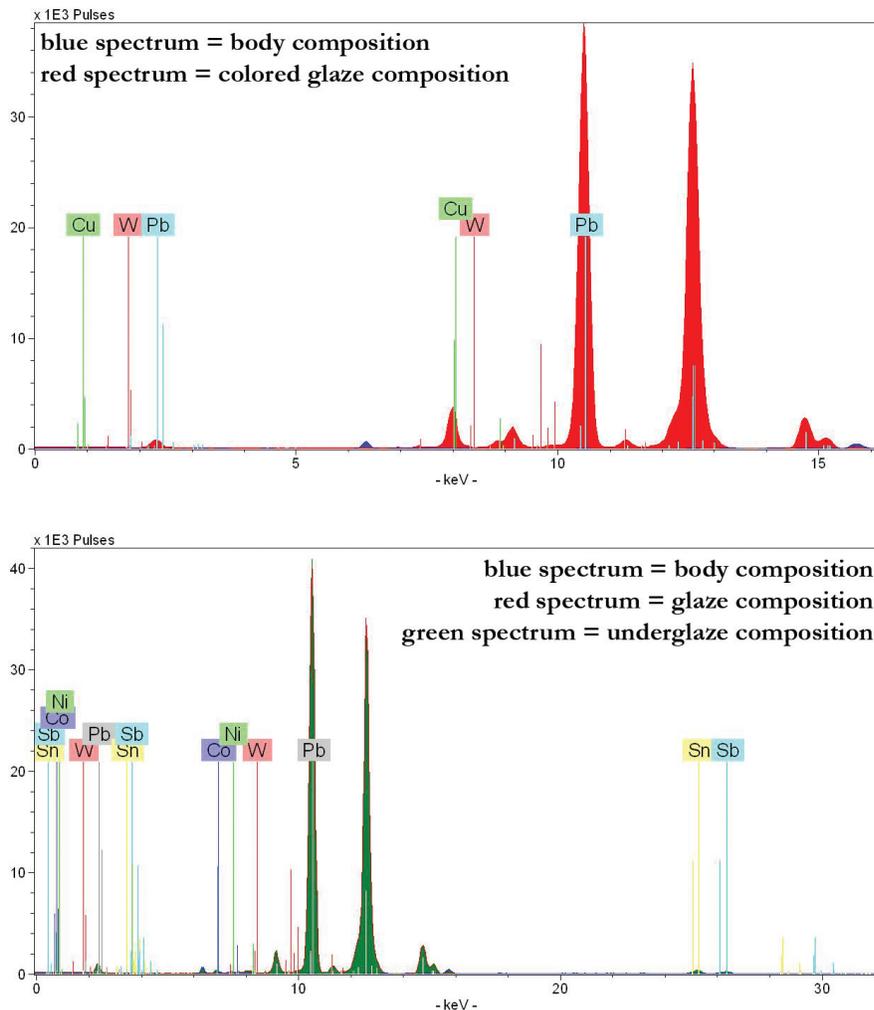


Figure 15: (top) XRF spectrum Sportsman’s Companion AL5458 area of emerald green glaze on base showing *copper* as the green coloring metal oxide (W tube); (bottom) XRF spectrum Sportsman’s Companion AL5458 area of olive green underglaze on figure’s jacket showing *cobalt, tin, and antimony* as the green coloring metal oxides (W tube).

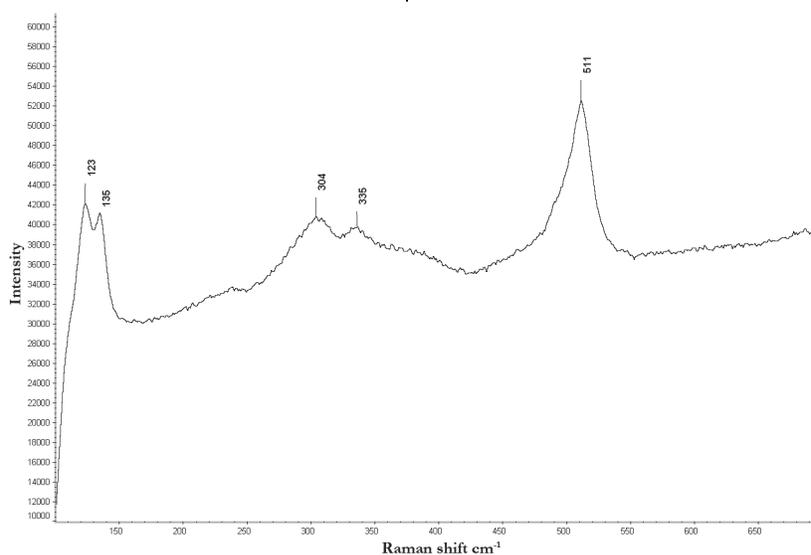


Figure 16: Raman spectrum from Sportsman’s Companion AL5458_2 olive brown underglaze pigment indicating peaks at 135, 335, 511 cm^{-1} for Naples yellow, and peaks at 123, 304 cm^{-1} for lead-tin yellow (type I).

section (AL5458_2, shown in visible light in figure 13) from the olive brown underglaze color from the Sportsman’s Companion demonstrates how the mixture of pigment particles is not dissolved in the glaze matrix.

XRF and SEM-EDS analysis of this area identified cobalt, antimony, and manganese, and this finding is consistent with Lakin’s recipe for “brown underglaze colours”.⁵⁸ Tin was also identified; this element is often present in glaze and enamel recipes as cassiterite (tin oxide, SnO_2) and used as an opacifier in accompaniment with Naples yellow.⁵⁹ Lakin lists recipes for orange, yellow, and green underglaze colors that include “oxide of tin” as a possible ingredient.

However, the tin could also be present as the yellow pigment lead-tin yellow (type I, Pb_2SnO_4 or type II, $\text{Pb}(\text{Sn},\text{Si})\text{O}_3$). Raman spectroscopy was therefore carried out on areas of concentrated pigment in the brown underglaze cross-section (AL5458_2) in order 1) to identify phases of the coloring oxides present, and 2) to determine the role of tin in the underglaze colorant sample.

The presence of lead antimonate particles (Naples yellow, $\text{Pb}_2\text{Sb}_2\text{O}_7$) was confirmed (134, 334, and 511 cm^{-1}),⁶⁰ and the resulting Raman spectrum is shown (figure 16). Tin is likely not present as cassiterite in this sample, as its characteristic peaks (630, 775 cm^{-1}) are missing from the Raman spectrum. Additional peaks at 123 cm^{-1} and 303 cm^{-1} likely correspond to lead-tin yellow type I.⁶¹ The data suggests that the underglaze green shades are achieved by mixing cobalt oxide for blue, and the yellow pigments Naples yellow and lead-tin yellow.

Blue underglaze colors contain cobalt oxide, and nickel and arsenic

are also detected to varying extents. Brown underglaze colors contain either mixtures of cobalt and manganese, or manganese, Naples yellow, lead-tin yellow, and iron oxide. Yellow underglaze colors contain mixtures of Naples yellow and lead-tin yellow. Orange underglaze colors consist of Naples yellow with the addition of iron oxide (Fe_2O_3) to shift an otherwise yellow underglaze to a golden orange color. Black underglaze colors consist of manganese, cobalt, and iron.

One figure of a Snuff Taker, AL5467, reportedly from the Middle Period, contains underglaze decoration (*figure 17*). The colors present on this figure differ greatly from the Pratt colors seen in the Early Period, as they do not exhibit the typical muted and olive-toned palette, but rather consist of brighter colors in unique shades, including blue-green, magenta, and gray. Table 4 lists the major elements and fluxes detected with XRF in the underglaze colors of this one figure, as well as various trace elements.

Figure 17: Snuff taker or Smell, AL5467, underglaze decoration, Staffordshire, 1820-1830, 8½" (21.5 cm) h., Winterthur (02.30.42).



Table 4 XRF data of underglaze oxides from the Snuff Taker, AL5467 (Middle Period) Staffordshire figure

Underglaze color	Major elements	Minor elements	Possible colorants
Green	Pb	Ni, Co(tr), Sn(tr), Sb(tr)	Ground cobalt oxide; lead antimonate; lead stannate**
Blue green	Pb, Ni, Co, Cu, As	Cr, Zn, Sn(tr), Sb(tr)	Ground cobalt oxide; copper oxide; chromium oxide; lead stannate**; also with lead antimonate
Blue	Pb, Co, Ni	As, Sn, Sb(tr)	Ground cobalt oxide; lead stannate**; also with lead antimonate
Dark blue	Pb, Co	As, Ni, Sn	Ground cobalt oxide; lead stannate**
Magenta	Pb, Sn	Au?	colloidal gold?
Yellow	Pb, Sb, Sn, Cu		Ground lead antimonate; lead stannate**; also copper oxide
Gray	Pb	Ni, Co, Mn, Cr, As	Ground cobalt oxide; manganese oxide; chromium oxide
Black	Pb, Ni, Co, Cu, As, Cr	Mn, Sn	Ground cobalt oxide; copper oxide; chromium oxide; manganese oxide

**presence of tin may suggest tin oxide opacifier, rather than lead-tin yellow pigment

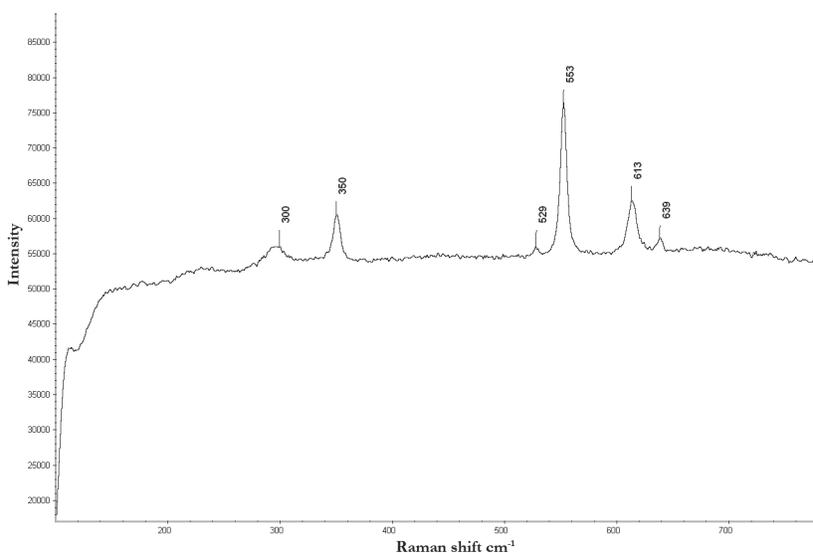


Figure 18: Raman spectrum from Snuff Taker AL5467_4 green underglaze pigment indicating peaks at 300, 350, 553, 613 cm^{-1} for eskolaite (UCL Raman Library, 2011).

The presence of chromium in the blue-green, gray, and black underglaze colors, as well as zinc in the blue-green, confirms a different pigment technology from the earlier period Pratt figures, and legitimizes the Middle Period date attribution. Raman microanalysis was carried out on sample AL5467_4 taken from an area of green underglaze on the grassy mound to further characterize this colorant. Although chromium was not identified with XRF in this area, the presence of eskolaite (chromium (III) oxide, Cr_2O_3) was confirmed with Raman, identifying four peaks consistent with this

compound (300, 350, 553, 613 cm^{-1})⁶² (figure 18).

A question that still remains about this figure is the colorant for the magenta underglaze. Using both molybdenum and tungsten excitation during XRF, gold was detected only inconclusively in one measurement.

Enamels

Enamel decoration characterizes the majority of the Staffordshire figures in the Winterthur collection. Table 5 provides the elemental data obtained through XRF, organized by color and time period. Of the

thirty-two figures analyzed in this study with XRF, nine from the Early Period have enameled decoration, while there are ten enameled figures in the Middle Period, and six in the Late Period. The table includes the number of times the particular color was identified (#), and lists the major and minor elements detected, as well as the possible colorants of the enamel that can be inferred from this data.

Blue Enamels:

The shades of blue enamel present on the Staffordshire figures consist of light blue, dark blue, turquoise, and blue green. The light and dark blues are obtained with cobalt oxide, associated with varying levels of nickel and arsenic, and occasionally contain copper, tin, manganese and iron. This is congruent with enamel technology from other European manufacturers of the eighteenth and nineteenth centuries.

The turquoise blue enamel consists primarily of copper and arsenic, with one instance of tin; four figures with turquoise enamel in the Early Period also contain cobalt, along with arsenic, tin, and antimony. The arsenic in this case could be present as lead arsenate opacifier or as a residual component of the cobalt ore used. Blue green enamel is unique to the

Table 5 XRF data of enamel colors on Staffordshire figures in the Winterthur collection

Enamel color	Time period	#	Major elements	Minor elements	Possible colorants
Medium green 1	Early	1	Pb, Cu	As, Sn, Sb, Ba(tr)*	Dissolved copper, dispersed lead stannate**, lead antimonate
	Middle	2	Pb, Cu	Sn(tr)	Dissolved copper; dispersed lead stannate**
Medium green 2	Middle	3	Pb, Co, Cr, Zn	Sn, Cu, Ni*	Dissolved cobalt, chromium; also with dissolved copper
	Late	2	Pb, Cr, Zn	Co, Cu*, Sn, Ni*, Sb*	Dissolved chromium, cobalt; dissolved copper, dispersed lead stannate** or lead antimonate

Enamel color	Time period	#	Major elements	Minor elements	Possible colorants
Yellow green 1	Early	4	Pb, Cu	Sn, Sb, Zn, Co, Fe*, Ni*, As*	Dissolved copper; dispersed lead stannate** and/or lead antimonate; and/or dissolved cobalt, iron
	Middle	3	Pb, Cu	Sn, Sb, Co, Mn	Dissolved copper, dispersed lead stannate**, lead antimonate; dissolved cobalt, manganese
Yellow green 2	Middle	2	Pb	Co, Cr, Sn, Sb, Zn	Dissolved cobalt, chromium, dispersed lead stannate**, lead antimonate
Lime green	Early	2	Pb, Sn	Cu	Dispersed lead stannate**; dissolved copper
	Middle	1	Pb	Sb	Dispersed lead antimonate
Olive green	Early	2	Pb, Cu, Fe*	Sn, Sb*, As*	Dissolved copper, dispersed lead stannate**; dissolved iron or dispersed lead antimonate
	Middle	1	Pb, Cu, Co, Mn	Sn, Sb(tr)*, Ni*	Dissolved copper, cobalt, manganese, dispersed lead stannate**; dispersed lead antimonate
Blue green	Middle	3	Pb, Zn, Cr	Co, Sb, Sn, Ni(tr)*, Mn(tr)*	Dissolved chromium, cobalt; dispersed lead stannate** and/or lead antimonate, dissolved manganese
	Late	3	Pb, Cr, Zn	Co, Cu, Sn(tr)*	Dissolved chromium, cobalt; dissolved copper
Blue 1 (lighter)	Early	1	Pb, Cu	Co, Sn, Fe*	Dissolved copper, cobalt, dispersed lead stannate**; dissolved iron
Blue 2 (darker)	Early	2	Pb, Co	Ni, As, Cu(tr)*	Dissolved cobalt; also with dissolved copper
	Middle	7	Pb, Co, Zn	Ni, As	Dissolved cobalt
	Late	2	Pb, Zn, Co	Ni, As*	Dissolved cobalt
Dark blue	Early	1	Pb, Co	Ni, As, Sn(tr)*	Dissolved cobalt
	Middle	1	Pb, Co	Mn, K, Ba?, Ni(tr)*	Dissolved cobalt, manganese
	Late	1	Pb, Zn, Co		Dissolved cobalt
Turquoise	Early	7	Pb, Cu	As, Sn, Sb, Co, Zn(tr)*	Dissolved copper; dispersed lead stannate**, calcium antimonate and/or antimony oxide, and/or dissolved cobalt
	Middle	1	Pb, Cu	As	Dissolved copper
	Late	1	Pb, Cu	As, Sn*	Dissolved copper; dispersed lead stannate**
Brown	Early	5	Pb, Fe, Cu	Mn, Au(tr), Sn(tr), As, Co(tr)*, Zn(tr)*	Dissolved iron, manganese, and/or copper; mixture of other trace elements
	Middle	6	Pb, Fe	Mn, Cr, Ni, Co, Cu, Ca*	Dissolved iron; dissolved manganese, chromium, cobalt, copper
	Late	1	Pb, Fe	Zn, Cr, Co, Mn*	Dissolved iron, chromium, cobalt; dissolved manganese

Enamel color	Time period	#	Major elements	Minor elements	Possible colorants
Red brown	Early	4	Pb, Fe	Cu*, As*, Mn*, Sn(tr)*, Au?*	Dissolved iron; mixture of other trace elements
	Middle	5	Pb, Fe, Cu, Co, Mn	Zn, Cr, Ni*, Sn(tr)*, Ca*	Dissolved iron; dissolved copper, cobalt, manganese, chromium
	Late	5	Pb, Fe, Co*	Zn, Cr, Mn, Sn(tr), Sb(tr), Cu*, Ni*, As(tr)*	Dissolved iron; chromium, manganese, dispersed lead stannate**, and/or lead antimonate, dissolved copper
Gray brown	Early	2	Pb, Fe	Mn, Cu, Co*, Sn(tr)*	Dissolved iron, manganese, copper; dissolved cobalt
	Middle	3	Pb, Fe, Mn	Co, Ni, Zn	Dissolved iron, manganese, cobalt
	Late	1	Pb, Cu	Zn, Mn, Co, Cr*, Fe*, Ni*	Dissolved copper, cobalt, manganese; also with chromium and iron
Red	Early	4	Pb, Fe	Au, Sn(tr)	Dissolved iron; colloidal gold
	Middle	6	Pb, Fe	Cr*, Zn(tr), Au?, Ca(tr)*	Dissolved iron; possibly dissolved chromium and/or colloidal gold
	Late	5	Pb, Fe	Sn(tr), Sb(tr), Cu, Zn, Au(tr)*	Dissolved iron; also with dispersed lead stannate** and lead antimonate, dissolved copper and colloidal gold?
Red orange	Early	2	Pb, Fe		Dissolved iron
	Middle	6	Pb, Fe	Ca, Cu(tr)*, As(tr)*	Dissolved iron; dissolved copper, calcium (for bleaching effect?)
	Late	1	Pb, Cr*, Fe*		Dissolved chromium and/or iron
Orange	Middle	5	Pb, Cr, Fe*	Cu, Sn(tr), Sb(tr)*	Dissolved chromium, copper; dispersed lead stannate**, lead antimonate and/or dissolved iron
	Late	5	Pb, Cr	Sn, Fe, Sb(tr), Cu*, Ca*, Au?*	Dissolved chromium; also with dispersed lead stannate** and/or lead antimonate, dissolved iron, calcium and colloidal gold?
Peach	Early	8	Pb, Fe	Au(tr)?, Ca	Dissolved iron and/or colloidal gold; calcium as bleaching agent?
	Middle	8	Pb, Fe, Ca	Cr(tr)*, Mn(tr)*, Cu(tr)*, Hg(tr)*	Dissolved iron with calcium as bleaching agent? And trace other elements
	Late	6	Pb	Fe, Ca, Zn, As(tr), Au?, Cu*	Dissolved iron; also with dissolved calcium, colloidal gold?
Pink 1	Early	2	Pb	Au, Sn(tr), Fe*, Sb*	Colloidal gold; dissolved iron or lead antimonate
	Middle	2	Pb, Au	Sn, Co, Ag(tr), Cu(tr)*	Colloidal gold; dissolved cobalt
	Late	3	Pb	Au(tr), Sn(tr), Zn(tr)*, Co(tr)*	Colloidal gold; also with dissolved cobalt
Brown pink 1 (darker)	Early	4	Pb, Fe, Cu*	Hg*, Zn*, Sb*	Dissolved iron; dissolved copper, lead antimonate

Enamel color	Time period	#	Major elements	Minor elements	Possible colorants
Brown pink 2 (lighter)	Early	1	Pb	Au(tr), Sn, Cu	Colloidal gold
	Middle	1	Pb, Fe*	Ca, Au(tr), Zn*	Colloidal gold; dissolved iron
	Late	2	Pb, Fe	Au(tr), Ni, Cu(tr)	Dissolved iron; also with colloidal gold and/or dissolved copper
Magenta	Early	1	Pb	Au, Sn(tr)	Colloidal gold
	Middle	3	Pb, Au	Sn, Co*, Mn*, Cu*	Colloidal gold; dissolved cobalt, manganese, copper
Purple	Early	4	Pb	Au, Sn, Sb(tr)	Colloidal gold; dispersed lead antimonate, and/or calcium antimonate
	Middle	1	Pb, Au, Co	Sn, Cr	Colloidal gold, dissolved cobalt, chromium
	Late	1	Pb, Co	Au, Sn, Zn(tr)*, Ni(tr)*	Dissolved cobalt, colloidal gold
Yellow	Early	7	Pb, Fe	Sb, Sn, Ni, As, Cu, Zn, Ba?*	Dispersed lead antimonate, and/or lead stannate**; dissolved iron and copper
	Middle	6	Pb, Zn*	Sn, Sb, Cr*, Cu(tr)*	Dispersed lead stannate**, lead antimonate; dissolved chromium or copper
	Late	5	Pb	Fe, Sn, Sb, Zn, Cr	Dissolved iron, dispersed lead stannate**, lead antimonate; dissolved chromium
Yellow orange	Early	4	Pb	Fe, Sb, Mn, Cu, Ba, Sn, As*, Au(tr)?*	Dissolved iron, dispersed lead antimonate
	Middle	3	Pb	Fe, Sb, Cu*, Sn*	Dissolved iron, dispersed lead antimonate; dissolved copper, dispersed lead stannate**
	Late	1	Pb, Sb, Sn		Dispersed lead stannate**, lead antimonate
Gray	Early	1	Pb	Fe, Co, Mn, Ni, Ca, As	Dissolved iron, cobalt, manganese
	Middle	1	Pb	Fe, Co, Mn, Ni*, As*	Dissolved iron, cobalt, manganese
	Late	2	Pb	Co, Fe, Mn, Ca	Dissolved cobalt; dissolved iron and manganese
Black 1	Early	5	Pb, Fe	Mn, Co, Ni, Cu	Dissolved iron, manganese, cobalt; dissolved copper
	Middle	9	Pb, Fe, Co, Cu, Mn	Ni, As, Cr, Ca, Ba	Dissolved iron, cobalt, copper, manganese; dissolved chromium
	Late	6	Pb, Fe, Co	Mn, Zn, Ni, Cr	Dissolved iron, cobalt, manganese; dissolved chromium
Black 2	Early	2	Pb, Cu	Co, Ni*, As*, Sn(tr)*	Dissolved copper, cobalt

*detected only once

**presence of tin may indicate tin oxide opacifier, rather than lead-tin yellow pigment

Middle and Late Periods and consists primarily of cobalt and chromium.

Of the Staffordshire figures analyzed from the Early Period, none of the blue enamels contain zinc as a major component; zinc is only detected in trace amounts in one area of an Early Period turquoise enamel. Half of the blue enamels from the Middle Period contain zinc as a major component, with cobalt; while all the Late Period blue enamel colors contain zinc and cobalt as major components. In both the Middle and Late Periods, the concentrations of zinc present are roughly equivalent (based on peak areas). This suggests that the use of zinc as a flux with cobalt oxide became popular at Staffordshire factories significantly later than the 1760s date attributed to Meissen. It is also possible the zinc is an intentional addition to the composition to enhance the blue color of the enamel; at Meissen, Höroldt noted that adding zinc to cobalt blue precipitate softened the harsh blue tone.⁶³

Dossie mentions ultramarine (lapis lazuli) as an adequate blue pigment for enamels;⁶⁴ however he warns against its reliability to achieve a consistent blue, and for most of the blue recipes listed in his treatise, cobalt oxide is an additional component. Colomban successfully identified lapis lazuli with Raman analysis at the glaze-body interface of a 1725 Meissen ewer stopper.⁶⁵ Raman analysis will be required on the blue enamels in



Figure 19: Dick Turpin on Black Bess AL5415, with blue overglaze decoration on figure's jacket and dark blue/black overglaze decoration on figure's hat and horse, Staffordshire, 1865-1875, 9 1/3" (23.5 cm) h., Winterthur (02.30.79.1).

the Winterthur collection of Staffordshire figures to determine if it was used in Stoke-on-Trent.

Though the application method differs, mention is made here of the other overglaze blue decoration prevalent during the Middle Period and used most frequently to color

figures' jackets. Of those figures analyzed with XRF in this study, one from the Middle Period (Highland Jessie, AL5479) and one from the Late Period (Dick Turpin, AL5415, figure 19) have this blue overglaze. Table 6 outlines the elemental data collected.

Table 6 XRF data of blue overglaze decoration on Staffordshire figures in the Winterthur collection

Overglaze color	Major elements	Minor elements	Possible colorants
Blue	Co		Dissolved cobalt
Dark blue/black	Co, Fe	Cu, Cr, Mn, As	Dissolved cobalt; dissolved iron, copper, chromium, manganese

The figure of Dick Turpin exhibits the characteristic dark blue color on the figure's jacket, as well as a darker blue/black on the figure's horse that appears to have the same method of application. In both the Middle and Late Periods, the blue overglaze contains cobalt as the colorant; while the Late Period dark blue/black overglaze consists of cobalt and iron as major components, as well as copper, chromium, manganese, and arsenic as minor components. It is interesting to note that while zinc is present with cobalt in blue enamels fairly regularly in the Middle and Late Periods, zinc is not detected with cobalt on areas with this particular overglaze decoration technique.

Unfortunately, it was not possible to sample from any area of this blue overglaze decoration for the purpose of studying the layers in cross-section; therefore, the method of application could not be further investigated.

Green Enamels:

In the Early Period figures analyzed with XRF, the green enamel colors are shown to be copper based. This is to be expected, since the use of chromium green enamels did not become commonplace in European porcelain decorating facilities until after 1802, when it was adopted as an overglaze enamel color at Sèvres. Chromium in the green enamels first appears on Staffordshire figures of the Winterthur collection in the Middle Period.

It is important to note that in both Staffordshire and Meissen, the use of copper as a green colorant does not cease once chromium is introduced. In the Middle Period, there are two groups of green enamel decoration: one with chromium based greens, and the other with copper based green



Figure 20: Lion AL5466, Staffordshire, 1825-1840, 11 2/3" (29.4 cm) w., Winterthur (67.900.1) with sample location starred.

enamels. Chromium and copper were also used together in recipes to make green enamels in the Late Period.

Lakin's recipe book lists two green enamel recipes: one Grass Green based on "Blue Vitrol [*sic*]" (copper (II) sulfate) mixed with Naples yellow; and another Pomona Green based on "Oxide of Green Chroma" (chromium (III) oxide, Cr_2O_3) (box 2).⁶⁶ It should be noted that Lakin's Grass Green formulation is the same as a recipe for "grass green" documented by Höroldt at Meissen.⁶⁷

Since the majority of decorators from the eighteenth and nineteenth centuries were purchasing enamel cakes from independent vendors, it is feasible that the artists would have a mixture of enamels at hand in their studios at any given time. Thus, the use of earlier technologies for green enamel could still prevail in a workshop well after chromium oxide pigments were introduced.

There is great interest among scholars to be able to distinguish by

eye the difference between chromium based and copper based green enamels. As yet, this does not seem to be possible. Enamel color can vary greatly depending on the atmosphere of the firing kiln, the pigment particle size and amount of grinding carried out, the use of different fluxes, as well as other factors such as the addition of other coloring oxides in the enamel mixture.

Shades of green on the Staffordshire figures include a medium green, yellow green, lime green, and olive green, as well as a blue green mentioned above.

Lighter (yellowish) green tones are produced by adding Naples yellow or lead-tin yellow, and commonly both tin and antimony are present together as additives. Tin is most likely present as lead-tin yellow, since this yellow pigment was detected with Raman analysis in samples from areas of yellow enamel (see further discussion of the role of tin in yellow enamels below), but it can also be present as

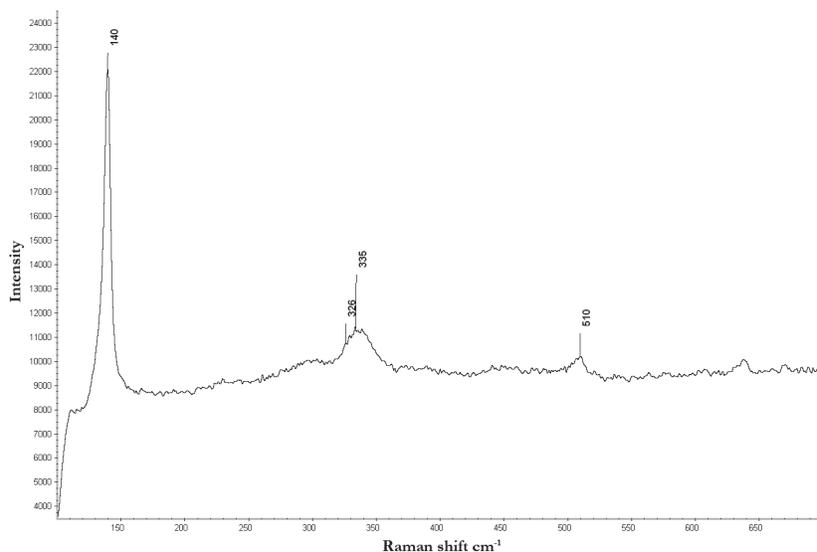


Figure 21: Raman spectrum from AL5466_1 yellow enamel indicating peaks at 140, 335, 510 cm^{-1} for Naples yellow, and peaks at 140, 326 cm^{-1} for lead-tin yellow type II.

the opacifying agent cassiterite (tin oxide, SnO_2).

Dossie mentions using tin and/or antimony compounds for pigmentation of yellow and green enamels, and since these are both opacifiers, where the recipe specifies a transparent color, the tin is omitted.⁶⁸ Lakin's recipe for Grass Green only calls for Naples yellow mixed with copper.⁶⁹ Investigation of green enamel samples with SEM or Raman is necessary to clarify the tin compounds present in each shade of green. Previous studies of green enamels from Meissen, Sèvres, and Du Paquier porcelain list cassiterite as an opacifier, rather than a tin-based yellow pigment.⁷⁰

The darker greens are obtained by mixing cobalt with either copper or chromium. Manganese and iron are also present as additives. This is similar to Du Paquier dark green compositions; however, a practice of "subtractive color mixing" using Naples yellow and cobalt blue enamels without the use of any copper has been found at both Meissen and Du Paquier.⁷¹ All Staffordshire green enamels analyzed in this study contain either copper, chromium, or both, as the main green colorants.

As stated above, zinc as a flux in green and yellow enamels was used at Meissen only after 1800 (with the exception of one piece of *hausmaler*⁷² ware), but at Du Paquier there are documented cases of zinc-fluxed green and yellow enamels as early as 1725. Of the enameled Staffordshire figures analyzed, only one from the Early Period (the Tithe Pig Group, AL5464) contains zinc as a minor component; while in the Middle and Late Periods, zinc is present as a major component in green enamel compositions.

Yellow Enamels:

As with the green, yellow, and brown underglazes and the lighter (yellowish) green enamels, the yellow enamels almost always contain both tin and antimony. Although published research on ceramics from Meissen, Sèvres, and Du Paquier explain the presence of tin in these colors by the compound cassiterite, it is equally likely that Staffordshire enamel makers used lead-tin yellow pigment. There is evidence that lead-tin yellow was used in China as a yellow glass colorant in cloisonné enameling on metal as early as the fifteenth

century, and that in the eighteenth century it was adapted for use in enameling on porcelain.⁷³

The use of lead-tin yellow in Staffordshire is demonstrated by the Raman analysis of a sample from the yellow faux marbling on the base pedestal on Middle Period figure of a Lion, AL5466 (*figures 20 and 21*). The sample was analyzed with SEM and Raman to better characterize the tin and antimony mixture. Raman analysis of the yellow enamel particles from the AL5466_1 cross-section confirmed the presence of lead antimonate (Naples yellow, $\text{Pb}_2\text{Sb}_2\text{O}_7$) with three peaks (140, 335, 510 cm^{-1}).⁷⁴ The presence of lead-tin yellow type II (silicon-substituted lead (II) stannate, $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$) is also suggested with two peaks (140, 326 cm^{-1}).⁷⁵

Orange Enamels:

In the Early Period, orange enamel was achieved mostly through the use of dissolved iron oxide. The resulting shade was a deep red-orange color. Use of this red-orange color based on iron oxide continued in the Middle, Late, and even Modern Periods, and in these later periods the addition of copper and also antimony is detected in the compositions.

Dossie lists a number of orange enamel recipes that call for mixing yellow glass from antimony with red glass from "gold by tin" (purple of Cassius).⁷⁶ On one figure from the Early Period (Purity, AL5447), XRF detected trace amounts of gold and tin in an area of yellow-orange enamel.

In the Middle and Late Periods, a very distinctive shade of orange was added to the Staffordshire enamel palette that consisted of a bright, vibrant orange. A sample of this enamel color was taken from the figure of Queen (Victoria) and the King (Victor Emmanuel II) of

Sardinia, AL5470 (figure 22). The sample, from the king's cloak (AL5470_2), was analyzed with Raman spectroscopy (figure 23). The analysis confirms the presence of lead (II) chromate as mixtures of chrome yellow (PbCrO_4), chrome yellow deep ($\text{PbCrO}_4 \cdot \text{PbO}$), and chrome yellow-orange ($\text{PbCrO}_4 \cdot \text{PbO}$). Strong peaks in the Raman spectrum demonstrate the presence of these three pigments: chrome yellow ($340, 407, 842 \text{ cm}^{-1}$); chrome yellow deep ($355, 378, 832 \text{ cm}^{-1}$); and chrome yellow-orange (825 cm^{-1}). Massicot (lead (II) oxide, PbO) is also detected with peaks at 143 and 289 cm^{-1} .⁷⁷

The use of lead chromate as an orange enamel colorant is an unexpected find, as there seems to be no precedent for it at any of the leading European porcelain factories, nor in discussions of Chinese enameled wares from the nineteenth century. At Sèvres, lead uranate (PbUO_4) was used for golden yellow enamels, but uranium was not identified here. An orange color was achieved in a ceramic glaze in the early twentieth century with a uranium-based colorant in Fiesta wares,⁷⁸ but the use of dispersed lead chromate to achieve this color seems to be unique to Staffordshire enameled earthenware.

The use of chromium in orange enamel recipes is not discussed by Lakin, even though he used chromium at his factory for the production of green, red, and black enamel colors. His recipe for orange enamel only specifies Naples yellow, iron (II) oxide, and tin oxide.⁷⁹

Brown Enamels:

There are three shades of brown enamels present on the Staffordshire figures: medium brown, red brown and gray brown. These brown shades from each time period are based primarily on iron



Figure 22: Queen and King of Sardinia AL5470, a group portraying Queen Victoria and Victor Emmanuel II, King of Sardinia, Staffordshire, c. 1855, $13\frac{1}{2}$ " (34.3 cm) h., Winterthur (02.30.142), with sample location starred (AL5470_2).

oxide, with varying additional metal oxides that include copper, manganese, cobalt, and occasionally gold, tin, antimony, and chromium.

When gold is present, tin is also detected, suggesting that the pigmentation involves colloidal gold reduced with tin chlorides (see further discussion of gold-tin coloration in red and purple enamels below). Brown enamels at

Du Paquier were also shown to contain gold and tin, though iron was not detected in these instances.⁸⁰ Gold is used as a coloring component of the brown enamels in the Early Period. However, in the Middle Period, colloidal gold as a colorant is replaced by the use of chromium.

In the Late Period, chromium is always detected in the brown enamels as a major component, in

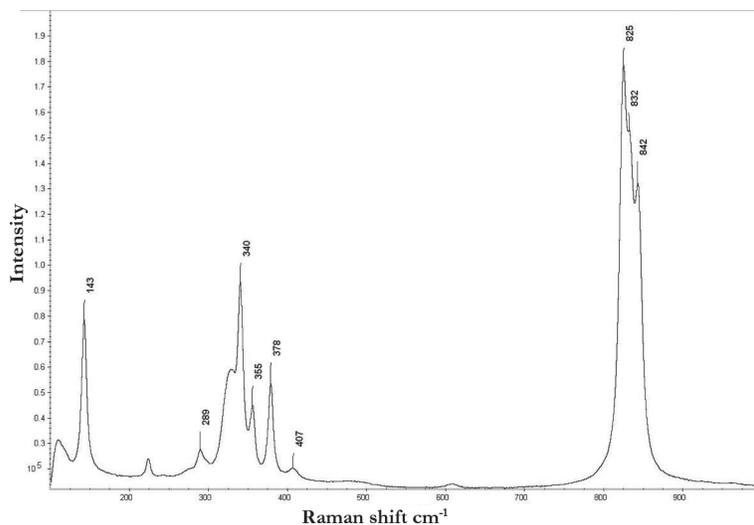


Figure 23: Raman spectrum from AL5470_2 orange enamel indicating bands 143, 289 cm^{-1} for massicot; 340, 407, 842 cm^{-1} for chrome yellow; 355, 378, 832 cm^{-1} for chrome yellow deep; and 825 cm^{-1} for chrome yellow-orange

addition to iron. The chromium is likely present either as dispersed lead (II) chromate or as an iron chromate compound. At Meissen, a nineteenth-century brown enamel was found to contain iron and manganese, but also chromium, cobalt, and nickel.⁸¹ Colomban found black/brown enamel at Sèvres to contain a mixture of magnesium oxide, iron oxide, and iron (II) dichromate.⁸²

Red, Pink, and Purple Enamels:

The red, pink, and purple enamel colors can be divided into three groups: 1) deep rustic reds and brownish pink shades where iron oxide is the main colorant; 2) deep reds and brownish pinks where iron is the main coloring oxide along with other red colorants such as iron chromate and colloidal gold (with tin); and finally, 3) pink, magenta, and purple colors that contain gold and tin as the main colorants.

The use of gold and tin (purple of Cassius) as a red, pink, and purple enamel colorant was common practice in Staffordshire from the Early Period onward, and documented both by Dossie and

Lakin.⁸³ Its use is also documented at Meissen,⁸⁴ the coloration occurring by the formation of colloidal gold during an oxidation/reduction reaction with tin salts.

In addition to colloidal gold, Staffordshire purple and magenta colors also contain instances of cobalt and manganese in both the Middle and Late Periods. Cobalt and also copper were added to gold-based purple enamels at DuPaquier in order to create deeper tones; while at Meissen the shade of the purple enamel is dependent on the colloidal size of the gold (the gold-to-tin ratio).⁸⁵

Dossie also describes how to obtain a “cheaper” red color by using iron oxide, which can be “enlivened by mixing one part of glass of antimony...”⁸⁶ The Early Period Staffordshire figures analyzed contain instances of both gold-based reds and iron oxide-based reds. Antimony is detected, along with iron and gold, on pink enamel from the Early Period and red enamel from the Late Period.

Lakin’s recipe lists *chromate of iron* as a colorant for Cornelian Red enamel.⁸⁷ Chromium in red and

purple enamels is only identified on one figure from the Middle Period (Highland Jessie, AL5479).

Gray and Black Enamels:

The gray enamels are colored with iron, manganese, and cobalt. Gray in the Modern Period additionally contains zinc and copper.

In the Early Period there are two types of black enamel detected: one with iron, manganese, copper, and cobalt with nickel; and the other with copper and cobalt with nickel and arsenic. In the Middle and Late Periods, black enamels are found to contain chromium, in addition to iron, cobalt (with varying degrees of nickel and arsenic), and manganese. In the Middle Period copper is also detected.

At Meissen, nineteenth century black enamels were found to contain chromium,⁸⁸ and as stated above, Colomban found that black/brown enamels at Sèvres contained a mixture of manganese oxide, iron oxide, and iron (II) dichromate.

Conclusions

The chief conclusions of this study are as follows:

(1) The colorants used for slip decoration and colored glazes in Staffordshire were, for the most part, congruent with the ceramic decorating technologies of the time period. However, the use of barium in an orange clay source warrants further study to determine if its inclusion was intentional.

(2) The study also yields important information about the colorants and technology of underglaze Pratt colors. Previously, scholars thought that underglaze colorants for the “high temperature oxides” were the same metal oxides used in colored glaze technology. The results of this study

demonstrate how most Pratt colors are made instead by mixtures of concentrated metal oxides.

Therefore, a green underglaze Pratt color is not made with copper oxide (as would a green glaze), but rather consists of a mixture of Naples yellow, and/or lead-tin yellow, and cobalt oxide blue pigments.

(3) The detection of nickel and arsenic with cobalt suggests a Saxony cobalt ore source, and this is consistent throughout the Staffordshire glaze, underglaze, and overglaze enamel technology.

(4) While the exact application method of the second overglaze blue decoration could not be definitively determined with non-destructive analytical techniques alone, the results of this study strongly suggest that the deep blue color was applied in a second process of overglaze enameling. This contradicts the hitherto-accepted idea that this impressive deep blue used to color the coats

and jackets of many mid-nineteenth century Staffordshire figures was applied under the glaze.

(5) The use of zinc as a flux with blue, yellow, and green enamels appears to be a post-1820 technology in Staffordshire, suggesting that its use there occurred later than at porcelain factories in continental Europe.

(6) An apparently new orange enamel color based on dispersed lead chromate was being used in Staffordshire that has not been documented elsewhere, either in Asian or European enamel recipes. Chromium was also detected in brown, black, red and purple enamels. Further investigation is needed to determine if iron chromate or lead chromate is the colorant.

(7) In yellow-tinted underglaze and enamels in Staffordshire, both tin and antimony were detected as colorants. Based on the few findings from Raman analysis of tin-

containing yellow compounds, tin is most likely present not as cassiterite as is documented at other European porcelain factories, but rather as lead-tin yellow, mixtures of which type I and II have been identified. This is in conjunction with Naples yellow, perhaps to prepare a cooler, less orange yellow than can be obtained with Naples yellow alone.

This study has thus shed new light on the technology of polychrome decoration in the manufacture of Staffordshire earthenware figures. In many cases, the techniques closely follow trends established at the leading European porcelain production centers. At the same time, however, several significant differences are noted, demonstrating the scientific progress made by Staffordshire potters and enamel makers during the period 1780-1900.

Appendix I: List of thirty-two figures in the Winterthur collection analyzed in this study.

Winterthur Museum accession numbers for each object are listed with their corresponding Analytical Lab (AL) numbers.

AL number	Accession number	Description	Decoration type	Date range
5411	2002.30.5	Faith	colored glaze and slip	1780-1820
5414	2002.30.14	Man with lost sheep	underglaze oxide	1780-1820
5415	2002.30.79.1	Dick Turpin on Black Bess (equestrian)	blue 'glaze' and enamel	1860-1900
5426	2002.30.11	Iphigenia	colored glaze and underglaze oxide	1780-1820
5427	2002.30.20	Falconer or sight or air	enamel and slip	1780-1820
5433	2002.30.96	Nicholas Ridley and Hugh Latimer	enamel	1820-1860
5434	2002.30.57.1	Shepherd and shepherdess or Sound	enamel	1780-1820
5436	2002.30.25	Demosthenes	enamel	1780-1820
5437	2002.30.26	Jupiter	underglaze oxide	1780-1820
5438	2002.30.78	Bull baiting dogs and man	enamel	1820-1860

AL number	Accession number	Description	Decoration type	Date range
5439	2002.30.139	Lighthouse with boaters (Grace Darling)	enamel	1820-1860
5440	2002.30.80	Guisepe Garibaldi and horse (equestrian)	enamel	1860-1900
5441	2002.30.101	Tam O'Shanter and Souter Johnny	enamel	1860-1900
5442	2002.30.82.1	Prince of Wales (equestrian)	enamel	1860-1900
5444	1959.579	George Washington	enamel	1780-1820
5445	1960.517	Benjamin Franklin	enamel	1780-1820
5447	2002.30.97	Purity	enamel	1780-1820
5452	2002.30.172	Vase or spill vase (the Rival)	enamel	1860-1900
5453	1960.518	Benjamin Franklin	enamel	1780-1820
5457	1958.3103	Shepherd and Shepherdess	colored glaze and slip	1780-1820
5458	2002.30.15.2	Sportsman's companion	colored glaze and underglaze oxide	1780-1820
5461	2003.13.63	St. George and the Dragon (equestrian)	colored glaze	1780-1820
5463	2003.13.63.1	Vase (male gardener)	colored glaze and enamel	1780-1820
5464	2003.13.64	Tithe (Tythe) Pig Group	enamel	1780-1820
5466	1967.900.1	Lion	enamel	1820-1860
5467	2002.30.42	Stuff Taker or Smell	underglaze oxide	1820-1860
5470	2002.30.142	Queen and King of Sardinia	enamel	1820-1860
5475	2002.30.47.1	Uncle Tom	enamel	1820-1860
5476	2002.30.68	Shepherd and dog	enamel	1820-1860
5478	2002.30.73.1	Tailor's Wife (on goat)	enamel	1820-1860
5479	2002.30.151	Highland Jessie (Jessie and Corporal Brown)	blue 'glaze' and enamel	1820-1860
5483	2002.30.129	Vase or spill vase (dog and child)	enamel	1860-1900

Appendix II: Details of each analytical technique used in this technical study.

XRF

An ArtTAX μ XRF spectrometer with a Si PIN diode detector and both a molybdenum (Mo) tube and a tungsten (W) tube was employed for qualitative and semi-quantitative elemental analysis of the glaze, slip, underglaze oxide, and enamel compositions. A portable Bruker Tracer III-V XRF with rhenium (Re) tube was also tested, but it was determined this instrument had no additional advantages over the laboratory-based equipment with W tube. This instrument has a spot size of approximately 70-100 microns (for the polycapillary focusing optic on the Mo tube) and both the Mo and W tube operate at a 600 μ A current, with a tube voltage of 50 kV, detecting elements with energies as low as potassium ($Z \geq 19$) and as high as uranium ($Z=92$).⁸⁹ With the Mo tube in use, collection time averaged around 100 seconds, and no filter was employed; when the W tube was in use, collection time averaged around 300 seconds, and a Ni 50 μ m filter was employed.

A W tube was used for the majority of XRF analyses. The primary excitation for molybdenum (Mo $K\alpha_1$, 17.480 keV) renders this tube most efficient at exciting elements with x-ray lines in the range of 17 to \sim 5 keV. This is highly useful for ceramic bodies, glazes, and enamels because pigments and glaze colorants are typically transition metals that have K lines in this energy range. The primary excitation line for tungsten (W $L\alpha_1$, 8.396 keV) renders this tube most efficient at exciting lighter elements with x-ray lines below this energy; the W $K\alpha_1$ occurs at 59.318 keV, and for this

reason, W tubes are also efficient at exciting heavier elements with x-ray lines between \sim 20-30 keV. This enables the W tube to have high sensitivity detecting elements such as tin, antimony, and barium, which are often seen in glazes and enamels. Disadvantages to using the W tube are that the $L\alpha_1$ line often interferes with the detection of copper (Cu $K\alpha_1$, 8.048 keV) or gold (Au $L\alpha_1$, 9.713 keV), two elements that are common enamel colorants. A nickel filter effectively absorbs the W $L\alpha_1$ lines, however and allows for improved identification of elements with x-ray lines in this region.

SEM

Samples were removed from the selected objects from edges of prior loss to the ceramic body and glaze or enameled decoration using a SPI Supplies diamond scribe or a #15 scalpel blade. Samples to be analyzed with the SEM were prepared in one of two ways: if the sample was powdery, it was mounted and adhered directly onto a SPI Supplies 10 X 15 mm carbon stub using double-sided carbon tape adhesive. If the sample consisted of an intact fragment, it was prepared as a cross-section by casting in Epo-Kwick epoxy resin (Buehler) and polishing with a series of silicon carbide papers (240-, 400-, and 1200-grit) and Buehler diamond suspensions (6-, 1-, and $\frac{1}{4}$ -micron) on Texmet 2000 polishing cloths. In between each polishing, samples were cleaned in an ultrasonic water bath. Once polished, the epoxy-embedded cross-sections were mounted onto the carbon stubs with carbon tape adhesive, and all sides of the epoxy cube were painted with SPI Supplies conductive carbon paint (colloidal graphite in a solvent mixture).

Samples were examined using a Topcon ABT-60 scanning electron

microscope with an accelerating voltage of 20 kV, a working distance of 24.0 mm, varying magnifications between 300 and 2000X, and a sample tilt of 20°. The EDS data was analyzed with a Bruker XFlash detector and Quantax model 200 EDS detector with Esprit 1.8 software. The EDS equipment is capable of detecting elements with energies as low as carbon ($Z=6$) and as high as bismuth ($Z=83$). Back-scattered electron (BSE) images, energy-dispersive x-ray (EDS) spectra, and elemental maps were gathered for all samples.

Raman

A Renishaw inVia dispersive Raman microscope with a 785 nm laser was the source used for qualitative phase identification. The laser operates in the 3200-100 cm^{-1} spectral range with a resolution of 3 cm^{-1} and a scan time of 30 seconds at varying powers from 1-5% laser power. The generated spectra were interpreted with Galactic Grams and OMNIC software and compared to reference spectra published in the literature by Colombari and Casadio,⁹⁰ and available online (the RRUFF Project and online database of Raman spectroscopy, <http://rruff.info>; UCL Raman Spectroscopic Library, <http://www.chem.ucl.ac.uk/resources/raman/index.html>, accessed 2011).

Notes

1. The authors gratefully acknowledge support by the Samuel H. Kress Foundation. They would also like to thank Winterthur Curator of Ceramics and Glass Leslie B. Grigsby, Winterthur Objects Conservator Bruno P. Pouliot, and Former Winterthur Director of Museum Collections Patricia Halfpenny for diligent advisement and significant contributions to this project. Additionally, the authors thank Winterthur Scientist Catherine Matsen and University of Delaware Associate

- Professor Chaoying Ni for their assistance and supervision of analyses.
2. Robert Harrison, "Staffordshire Figures and Aspects of the English Landscape," parts 1-5, *Ars Ceramica* 19 (2003): 5-23; 20 (2004): 5-29; 21 (2005): 46-77; 22 (2006): 40-51; 23 (2007): 40-70; Pat Halfpenny, *English Earthenware Figures 1740-1840* (Woodbridge, Suffolk: The Antique Collectors' Club Ltd, 1991); Myrna Schkolne, *People, Passions, Pastimes, and Pleasures: Staffordshire Figures 1810-1835* (Winston Salem, North Carolina: Hot Lane Press, 2006); Myrna Schkolne, "A Pearlware Puzzle: Walton Figures and Their Look-Alikes," *American Ceramic Circle Journal* 16 (2011): 57-77.
 3. Leslie Grigsby, personal communication with author, 2011.
 4. Halfpenny, *English Earthenware Figures*, 11; John Sandon, *British Porcelain* (New York: Shire Publications Ltd, 2009), 45.
 5. Schkolne, *People, Passions, Pastimes and Pleasures*, 24.
 6. Halfpenny, *English Earthenware Figures*, 132.
 7. Leslie Grigsby, *English Pottery: Stoneware and Earthenware 1650-1800: The Henry H. Weldon Collection* (London: Sotheby's Publications, 1990), 272-274.
 8. Sandon, *British Porcelain*, 33.
 9. Halfpenny, *English Earthenware Figures*, 132.
 10. Robert Sayer, *The Ladies Amusement; or, Whole Art of Japanning Made Easy* (London, 1760).
 11. Schkolne, *People, Passions, Pastimes and Pleasures*, 11.
 12. Grigsby, *English Pottery: Stoneware and Earthenware 1650-1800*, 271.
 13. Richard Owen Cambridge, *The Scribleriad: An Heroic Poem*, book 2, (London, 1751).
 14. "Quaint Mantel Ornaments," *Dallas Morning News*, (Dallas, TX), March 21, 1909.
 15. Sarah Lowengard, "Chemistry in colour: ceramics and glass in 18th-century Britain," *Endeavour* 26 (3) (2002): 102; J.W. Keefe, "A Concise History of the Staffordshire Figure," *Enduring Charm: Staffordshire Pottery Figures from the Collection of Mr. and Mrs. Thomas Norton Bernard* (New Orleans: New Orleans Museum of Art, 2000), 10.
 16. Halfpenny, *English Earthenware Figures*, 12.
 17. *Ibid.*, 130.
 18. Grigsby, *English Pottery: Stoneware and Earthenware 1650-1800*, 24.
 19. Sandon, *British Porcelain*, 55.
 20. Llewellynn Jewitt, *The Ceramic Art of Great Britain from Pre-historic Times Down to the Present Day*, vol. 2, (London: Virtue and Co. Ltd., 1878), 299.
 21. Simeon Shaw, *History of the Staffordshire Potteries* (Hanley, Staffordshire, 1829), 167.
 22. Robert Dossie, *The Handmaid to the Arts*, vol. 1, (London: Printed for J. Nourse at the Lamb opposite Katherine-Street in the Strand, 1758), 228-309.
 23. Zaffre is an impure form of cobaltous oxide obtained by roasting native cobalt ores such as cobaltite and smaltite.
 24. G. W. Elliot, compiler, *Some descriptions of Pottery Making and Working Conditions, 1557-1844*, (Stoke-on-Trent, Staffordshire: Albion Galleries, 1970).
 25. Thomas Lakin, of Lakin & Poole, then Lakin, Poole & Shrigley of Burslem (1795).
 26. E. Baines, ed., *The Valuable Receipts of the Late Mr. Thomas Lakin, with Proper and Necessary Directions for Their Preparation and Use in the Manufacture of Porcelain Earthenware, and Iron Stone China, Together with the Most Recent and Valuable Improvements in the Admired Art of Glass Staining and Painting* (Leeds: Edward Baines, 1824).
 27. E. A. Sandeman, *Notes on the Manufacture of Earthenware* (London: Virtue and Company Ltd., 1901), 320.
 28. Halfpenny, *English Earthenware Figures*, 318.
 29. Examination of glazed and enameled ceramics with an ultraviolet light source can sometimes aid in the identification of lead-based glazes (no fluorescence under long-wave UV, 400-315nm; bright fluorescence under short-wave UV, 180-280nm), as well as identification of the body composition (bone china fluoresces white), and previous repairs (e.g., epoxies fluoresce bright white; shellac fluoresces orange).
 30. Grigsby, *English Pottery; Stoneware and Earthenware 1650-1800*, 23.
 31. Cornish stone refers to the feldspar-rich granite that is obtained from an area in Cornwall, United Kingdom.
 32. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 23-26.
 33. Roy Newton and Sandra Davison, *Conservation of Glass* (Boston: Butterworths, 1989), 9.
 34. Halfpenny, *English Earthenware Figures*, 55.
 35. The class of pottery decorated with high temperature underglaze colors is often called Pratt ware by contemporary collectors; however there is record of only two jugs of this type marked by the Pratt factory, and there is no evidence that Pratt ever produced figures (Halfpenny, *English Earthenware Figures*, 100).
 36. J. and G. Lewis, *Pratt Ware: English and Scottish relief decorated and underglaze coloured earthenware, 1780-1840*, (Woodbridge, Suffolk: Antique Collectors' Club Ltd., 2006), 18.
 37. Sandeman, *Notes on the Manufacture of Earthenware*, 304.
 38. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 33-36.
 39. Cobaltous oxide acts as a flux in lead glazes; even though alone it has a high melting point (2860 °C), it readily dissolves and flows in glazes because of the fluxing interaction (Frank Hamer, *The Potter's Dictionary of Materials and Techniques* [New York: Watson-Guptill Publications, 1975], 66).
 40. Simeon Shaw, *The Chemistry of the Several Natural and Artificial Heterogeneous Compounds Used in Manufacturing Porcelain, Glass and Pottery* (London: W. Lewis and Son, 1837), 522; Sandeman, *Notes on the Manufacture of Earthenware*, 317-318.
 41. Dossie, *Handmaid to the Arts*, 231; Sandeman, *Notes on the Manufacture of Earthenware*, 319.
 42. Sandeman, *Notes on the Manufacture of Earthenware*, 318.
 43. The Du Paquier porcelain manufactory was established in Vienna by Claude Innocentius Du Paquier in 1718. During its 25 years of business, it was

- second only to Meissen for leading Europe in the production of hard-paste porcelain.
44. John Page and Meredith Chilton, "Scientific Analysis of Meissen Commedia Dell'Arte sculpture in the Gardiner Museum Collection," appendix to *Harlequin Unmasked: The Commedia Dell'Arte and Porcelain Sculpture*, by Meredith Chilton, (New Haven: Yale University Press, for The George R. Gardiner Museum of Ceramic Art, 2001), 322-326.
 45. T. Pr ud, *The S vres Porcelain Manufactory: Alexandre Brongniart and the Triumph of Art and Industry, 1800-1847*, (New York: The Bard Graduate Center for Studies in the Decorative Arts, 1997), 57-58.
 46. Francesca Casadio, Anik  Bezur, Kelly Domoney, Katherine Eremin, Lynn Lee, Jennifer L. Mass, Andrew Shortland, Nicholas Zumbulyadis, "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain In Central Europe," *Studies in Conservation* 57 (forthcoming); K. Domoney, A. Shortland, S. Kuhn, "Characterization of 18th-Century Meissen Porcelain Using SEM-EDS," *Archaeometry* 54 (3) (June 2012): 454-474.
 47. Page and Chilton, "Scientific Analysis of Meissen," 324; A. Bezur and F. Casadio, "Du Paquier Porcelain – Artistic Expression and Technological Mastery: A Scientific Evaluation of the Materials," in *Fired by Passion: Vienna Baroque Porcelain of Claudius Innocentius Du Paquier*, vol. 3, ed. Meredith Chilton, (Stuttgart: Melinda and Paul Sullivan Foundation for the Decorative Arts and Arnoldsche Art Publishers, 2009), 1201.
 48. Halfpenny and Mass, "Two Converging Perspectives on One Meissen Tureen," *American Ceramic Circle Journal* 15 (2009): 70-77.
 49. Bezur and Casadio, "Du Paquier Porcelain."
 50. *Ibid.*, 1186.
 51. F. Casadio, "Decoration of Meissen Porcelain: Raman Microscopy as an Aid for Authentication and Dating," in *Proceedings of the Sixth Infrared and Raman Users Group Conference*, ed. Marcello Picollo (Florence, 2004): 178-184.
 52. P. Colomban and V. Milande, "On Site Raman Analysis of the Earliest Known Meissen Porcelain and Stoneware," *Journal of Raman Spectroscopy* 37 (2006): 606-613.
 53. P. Colomban, G. Sagon, and X. Faurel, "Differentiation of Antique Ceramics from the Raman Spectra of their Coloured Glazes and Paintings," *Journal of Raman Spectroscopy* 32 (2001): 351-360.
 54. M.T. Wypyski, "Technical Appendix: Composition of Enamels on the George Watch," *Metropolitan Museum Journal* 35 (7): 150-152; M.T. Wypyski, "Renaissance Enameled Jewelry and 19th century Renaissance Revival: Characterization of Enamel Compositions," In *Materials Issues in Art and Archaeology VI, Proceedings of the Materials Research Society Symposium*, vol. 712, eds. Pamela B. Vandiver et al. (Boston, 2002): 223-233.
 55. I. C. Freestone and M. Bimson, "Early Venetian Enamelling on Glass: Technology and Origins," In *Materials Issues in Art and Archaeology IV, Proceedings of the Materials Research Society Symposium*, vol. 352, eds. Pamela B. Vandiver, et al., (Cancun, Mexico, 1995) 415-431.
 56. R. Kerr and N. Wood, "Chemistry and Chemical Technology, Part XII: Ceramic Technology," In *Science and Civilisation in China*, vol. 5, (Cambridge, 2004), 767.
 57. Bezur and Casadio, "Du Paquier Porcelain," 1189.
 58. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 33-34.
 59. Bezur and Casadio, "Du Paquier Porcelain," 1186.
 60. In their study, Colomban, et al. used pigment powders prepared at the S vres factory as references, and these are published with their corresponding Raman data in the 2001 paper, p. 356.
 61. Spectroscopic Library of Natural and Synthetic Pigments, <http://www.chem.ucl.ac.uk/resources/raman/index.html> (University College London; accessed Spring 2011).
 62. *Ibid.*
 63. Casadio et al., "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain."
 64. Dossie, *Handmaid to the Arts*, 288-289.
 65. Colomban and Milande, "On Site Raman Analysis," 6.
 66. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 49 and 51.
 67. Casadio et al., "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain"; Domoney et al., "Characterization of 18th-Century Meissen Porcelain," 454-474.
 68. Dossie, *Handmaid to the Arts*, 291-296.
 69. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 49.
 70. Colomban et al., "Differentiation of Antique Ceramics," 356; Casadio, "Decoration of Meissen Porcelain," 181; Bezur and Casadio, "Du Paquier Porcelain," 1186.
 71. Bezur and Casadio, "Du Paquier Porcelain," 1192.
 72. Wares painted in independent home workshops rather than at the Meissen factory.
 73. Kerr and Wood, "Chemistry and Chemical Technology," 634.
 74. Colomban, et al., "Differentiation of Antique Ceramics," 356.
 75. Spectroscopic Library of Natural and Synthetic Pigments, (University College London; accessed Spring 2011).
 76. Dossie, *Handmaid to the Arts*, 296-297.
 77. Library of Natural and Synthetic Pigments, (University College London; accessed Spring 2011).
 78. Art deco table wares produced by the Homer Laughlin China Company of Newell, West Virginia, in the first half of the 20th century.
 79. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 50.
 80. Bezur and Casadio, "Du Paquier Porcelain," 1200.
 81. Casadio et al., "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain."
 82. Colomban et al., "Differentiation of Antique Ceramics," 354.
 83. Dossie, *Handmaid to the Arts*, 284-285, 298; Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 55-57.

84. Casadio et al., "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain."
85. Domoney et al., "Characterization of 18th-Century Meissen Porcelain," 468.
86. Dossie, *Handmaid to the Arts*, 286.
87. Baines, *The Valuable Receipts of the Late Mr. Thomas Lakin*, 50-51.
88. Casadio et al., "Flames of Desire: Decorating Eighteenth and Nineteenth Century Porcelain."
89. H. Bronk, S. Rohrs, A. Bjeoumikhov, N. Langhoff, J. Schmalz, R. Wedell, HE Gorny, A. Herold, and U. Waldschlager, "ArtTAX - a new mobile spectrometer for energy-dispersive micro X-ray fluorescence spectrometry on art and archaeological objects," *Fresenius Journal of Analytical Chemistry* 371 (3) (2001): 307-316.
90. See notes 51-53.

Lauren Fair is the Assistant Conservator of Objects at Winterthur Museum, Garden & Library and Adjunct Assistant Faculty for the Winterthur/University of Delaware Program in Art Conservation. Specializing in objects conservation with a significant interest in decorative arts, she has worked extensively with gilded wooden objects, as well as silver, ceramics, and outdoor sculpture and monuments. A year-long internship at the Metropolitan Museum of Art exposed her to considerable treatment work and analysis of an early eighteenth-century Damascene interior, as well as a wide variety of ceramic and metal objects. In 2010-11, she completed a Kress-funded fellowship at Winterthur, focusing on the in-depth technical analysis of the enamels and other polychrome decoration found on Staffordshire figures in the museum collection. Lauren received her B.A. in art history from the University of Delaware in 2005 and her M.S. in art conservation in 2010 from the

Winterthur/University of Delaware Program in Art Conservation.

Dr. Jennifer Mass received her Ph.D. in inorganic chemistry from Cornell University, after which she was awarded an Andrew W. Mellon fellowship at the Sherman Fairchild Center for Objects Conservation at the Metropolitan Museum of Art. She is currently the Laboratory Director and Senior Scientist at the Winterthur Museum's Scientific Research and Analysis Laboratory and is also a faculty member in the Winterthur/University of Delaware M.S. Program in Art Conservation. While at Winterthur she has conducted research on the degradation mechanisms of artists' materials, and on the development of a confocal x-ray fluorescence microscope for the depth profiling of paintings. Jennifer has published numerous articles on her research in the art conservation, physics, and materials science literature, and she has received awards for her confocal XRF research from the Italian Society for Nondestructive Testing and from the American Materials Research Society. Jennifer has also co-edited a volume on handheld XRF applications in art and archaeology, and co-organized two symposia on the application of synchrotron-based methodologies to the study of cultural heritage. Her current research interests are focused on XRF methodologies for historic silver alloys, overglaze enamel technologies in porcelains and earthenwares, and pigment alterations in the works of the early modern painters.

In the Spring of 2012 a poster titled "Under, over, and in the mix of: A practical guide to telling the difference between types of polychrome decoration on English earthenware figures" was presented by Lauren Fair at the annual

conference of the American Institute for Conservation of Historic and Artistic Works (AIC). The poster summarizes the different decoration techniques explored more fully in this paper, and it serves as a reference for the quick identification of these decoration types, as well as offering a mode of exchange about the evolution of the pyrotechnologies of the eighteenth and nineteenth centuries. This poster can be viewed on the AIC website ([conservation-us.org](http://www.conservation-us.org)) where all posters and abstracts from the 2012 conference in Albuquerque are posted online.

http://www.conservation-us.org/data/n_0001/resources/live/43-UnderOverandintheMix.pdf