

# Polychrome Decoration on Staffordshire Figures: Identification of a New Enamel Colourant and Underglaze Oxide

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## Keywords

Staffordshire; enamel; underglaze; earthenware polychromy

## Abstract

*Thanks to a generous donation in 2002, Winterthur's collection of Staffordshire figures is now the largest of its kind in an American museum, with about 270 earthenware sculptures that represent the full range of manufacture and decoration techniques known to English potters at the time. Dating from 1740 to 1900, they span the rise and fall of figure production in Staffordshire. Research, survey, and analysis were conducted to identify manufacture technologies and chemical compositions of the polychrome decoration. Underglaze and overglaze techniques are discussed. Several analytical techniques (X-ray fluorescence spectroscopy, Raman spectroscopy, and scanning electron microscopy equipped with energy-dispersive X-ray microanalysis) were employed, making important discoveries, including the identification of an orange enamel colourant unique to Staffordshire earthenwares, new compositional information on high-temperature underglaze oxides, and the technology of a mysterious blue overglaze colour.*

## Introduction

The Staffordshire figure, produced in Staffordshire (West Midlands, England), was a popular collectible in eighteenth and nineteenth century England and in the colonial and new United States (Grigsby 1990, p. 271; Halfpenny 1991; Schkolne 2006); the figures represented subjects from characters of allegory, poetry, and mythology, to contemporary English royalty and politicians. Figures in lead-glazed earthenware (pearlware) afforded middle classes the chance to showcase luxury items in their homes, upon mantelpieces and dining tables. In many ways, English factories were capitalising on the public esteem held for Chinese and Continental European porcelain prototypes, producing strikingly similar replications in a more affordable material (Sandon 2009, p. 33). Highly decorative, Staffordshire figures exhibited a range of painting techniques, including coloured slips, glazes, underglaze oxides, and overglaze enamels. The decorating techniques examined in-depth in this paper focus on those under and over the glaze, including high-temperature underglaze oxides (Pratt colours), overglaze enamels, and a second blue overglaze.

## Staffordshire Figures at Winterthur

Winterthur has a representative collection of over 270 Staffordshire figures, the largest of its kind in an American museum. A detailed survey carried out as part of this research identified three distinct time periods: Early (1780–1820), Middle (1820–1860), and Late (1860–1900); as well as all decoration techniques listed above. Table 1 provides a breakdown of the figures in each category.

## Underglaze and Overglaze

Known as Pratt colours, high temperature underglazes were developed in Staffordshire in the 1790s to expand the decorating colour palette; the 'new' colours could withstand high gloss-firing temperatures (Lewis and Lewis 2006, p. 18). Although the Pratt factory is known to have made only a few ceramics with this type of decoration, contemporary collectors now refer to this class of pottery as Pratt ware (Halfpenny 1991, p. 100).

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Period	Date range	Total # recorded	Slips	Coloured glazes	Underglaze oxides	Enamels	Second blue overglaze
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
<b>Totals</b>		<b>232</b>	<b>14</b>	<b>35</b>	<b>16</b>	<b>192</b>	<b>26</b>

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

Technique, with example at Winterthur	Application	Visual	Chemical
<p><b>Underglaze Pratt colours</b></p>  <p>Shepherd with lost sheep, c.1795–1810 (02.30.14) H 22 cm W 8.25 cm</p>	<ul style="list-style-type: none"> <li>Concentrated metal oxides ground with a medium (oil or water)</li> <li>Applied to a bisque body by brush</li> <li>Painted figure dipped in lead glaze and glost-fired at 1050°C</li> </ul>	<ul style="list-style-type: none"> <li>Glossy surfaces</li> <li>Mixtures of colour particles often visible under the glaze</li> <li>Total glaze coverage from dipping</li> <li>Palette contains blue, olive greens and browns, muted oranges and yellows</li> </ul>	<ul style="list-style-type: none"> <li>Mixtures of concentrated pigments create colour</li> <li>Pigments are dispersed colour compounds (not dissolved)</li> </ul>
<p><b>Overglaze enamels</b></p>  <p>Shepherd and shepherdess bocage group c.1800–1820 (02.30.57.1) H 29 cm W 18.6 cm</p>	<ul style="list-style-type: none"> <li>Low-fired coloured glasses consisting of metal oxides ground with fluxes in a medium</li> <li>Applied to an already glost-fired ceramic</li> <li>Fired again in smaller kilns at successive firings between 700 and 900°C</li> </ul>	<ul style="list-style-type: none"> <li>Textures vary from matte to glossy</li> <li>Bubbling from firing is common</li> <li>Always occurs over the glaze</li> <li>More susceptible to surface abrasions, delamination, and flaking</li> <li>Great variety of colours including brilliant pinks, reds, turquoise, oranges</li> </ul>	<ul style="list-style-type: none"> <li>Mixtures of metal oxides and lead or borax fluxes</li> <li>Pigments can be dissolved or dispersed</li> </ul>
<p><b>Second blue overglaze</b></p>  <p>John Brown and the Prince of Wales, c. 1850–1860 (02.30.130) H 20 cm W 10.6 cm</p>	<ul style="list-style-type: none"> <li>Hypothesis: painted on a glazed ceramic (like an enamel) but then 'passed a second time through the glost oven, when the colour combines and sinks into the glaze, producing a magnificent effect' (Sandeman 1901, p. 318)</li> </ul>	<ul style="list-style-type: none"> <li>Glossy, rich blue colour that appears to be in glaze matrix</li> </ul>	<ul style="list-style-type: none"> <li>Colourant is cobalt (Co<sup>2+</sup>)</li> </ul>

Table 2. Key characteristics of underglaze and overglaze decoration (Photos: Winterthur Museum).

Overglaze enamels, developed slightly later, allowed for an even greater colour variety by lowering the required firing temperature, and thus the range of colourants on English ceramic figures expanded throughout the nineteenth century. A second type of blue overglaze decoration, deep and rich in colour, appears in the mid-nineteenth century, and is primarily used to decorate the jackets on figures. These three decorating techniques are defined in more detail in table 2. Colour recipes were often highly guarded, leaving enamelling shops to explore their own colour-making chemistry and most painters to purchase enamels from independent vendors. This culture of secrecy yielded a wide variety of materials and much experimentation to achieve the brightest and best colours. Potters and craftsmen searched for new colours to keep up with consumer demands (Lowengard 2002, p. 102; Keefe 2000, p. 10).

Dossie's *Handmaid to the Arts* (1758) discusses enamel production with listed enamel recipes, and a workbook of Mr Thomas Lakin (of Lakin & Poole, then Lakin, Poole & Shrigley of Burslem, 1795) was published posthumously by his wife in 1824 that contains recipes for enamels, coloured glazes, and underglazes (Baines 1824).

Until now, knowledge of Staffordshire colour recipes has come from these limited sources. While Chinese, Continental European, and a few select English porcelain glazes and enamels have been characterised chemically, this study is the first to systematically analyse Staffordshire earthenware decoration. This study establishes a database of enamel and glaze compositions present on Staffordshire earthenware figures, determining how they evolved over time and providing a baseline of information that can be used for future research.

## Technical Study

A representative group of 32 figures was selected for technical study of the polychrome decoration (table 3).

Elemental analysis with X-ray fluorescence spectroscopy (XRF) established colourants and fluxes present in the glazes, underglazes, and enamels. A laboratory-based spectrometer with ~70  $\mu\text{m}$  beam size was used for finely painted areas.

Although XRF is a surface analysis technique, it penetrates several layers of ceramic decoration, presenting challenges for distinguishing between elements detected from different layers. Where possible, spectra were compared to those of glaze and body (or body alone) to determine which elements

belong to coloured decorations and which belong to underlying layers. Elements located in underlying layers could also be identified by detecting the inversion of high-energy and low-energy X-ray line intensities (for example, the ratios of the  $L\alpha$  and  $L\beta$  lines), since the lower energy lines are more highly attenuated for buried elements.

Four figures were selected for microsampling and were analysed with scanning electron microscopy equipped with energy-dispersive X-ray microanalysis to help understand body–glaze and glaze–enamel interaction zones and changes in compositions as a function of depth. These samples were also studied with micro-Raman spectroscopy. When pigments or opacifying agents such as cassiterite ( $\text{SnO}_2$ ) are dispersed within the glass matrix, identification of these oxides is possible by micro-Raman spectroscopy. Appendix I details all experimental methodologies.

The authors are unaware of previous comprehensive technical studies of decoration techniques on eighteenth and nineteenth century Staffordshire ceramics, but studies of Meissen, Sèvres, and Du Paquier polychrome porcelain are numerous. For a summary of comparable analytical studies, see Fair and Mass (*Ars Ceramica* publication forthcoming).

## Results and Discussion

All analysis data are in table 4, Appendix II. Further discussion below is organised by colour.

### Blues

Cobalt is the main colourant for most blue decoration on Staffordshire figures and is the only blue underglaze colourant. When present, cobalt is detected along with varying degrees of nickel and arsenic, suggesting that Staffordshire craftsmen used cobalt minerals from Erzgebirge mines in Saxony, which also supplied Meissen and Du Paquier (Gratuze and others 1995; Bezur and Casadio 2009, p. 1189).

Blue enamel shades are light blue, dark blue, turquoise, and blue–green. Light and dark blues contain cobalt, and occasionally have copper, tin, manganese, and iron. Turquoise enamel consists primarily of copper and arsenic; four figures with turquoise enamel in the Early Period also contain cobalt, along with arsenic, tin, and antimony. Arsenic could be present as opacifying lead arsenate or as a residual component of the cobalt ore. Blue–green enamel is unique to the Middle and Late Periods and consists primarily of cobalt and chromium.

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AL number	Accession number	Description	Decoration type	Date range
5411	2002.30.5	Faith	coloured 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 overglaze and enamel	1860–1900
5426	2002.30.11	Iphigenia	coloured 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
5439	2002.30.139	Lighthouse with boaters (Grace Darling)	enamel	1820–1860
5440	2002.30.80	Guiseppe Garibaldi and horse (equestrian)	enamel	1860–1900
5441	2002.30.101	Tam O'Shanter and Sooter 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	coloured glaze and slip	1780–1820
5458	2002.30.15.2	Sportsman's companion	coloured glaze and underglaze oxide	1780–1820
5461	2003.13.63	St George and the Dragon (equestrian)	coloured glaze	1780–1820
5463	2003.13.63.1	Vase (male gardener)	coloured 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 overglaze and enamel	1820–1860
5483	2002.30.129	Vase or spill vase (dog and child)	enamel	1860–1900

Table 3. List of 32 figures in Wintertbur collection analysed in this study. Museum accession numbers with corresponding Analytical Lab (AL) numbers.

The data suggest that zinc as a flux with cobalt oxide was popular in Staffordshire significantly later than the 1760s date attributed to Meissen. No Early Period blue enamels contain zinc as a major component; however, after 1820, zinc is often a major component, with roughly equivalent concentrations in the Middle and Late Periods. Zinc may also be intentionally added to enhance the colour; at Meissen, Höroldt noted that adding zinc to cobalt blue precipitate soft-

ened the harsh blue tone (Casadio and others 2012, p. 62). In both the Middle and Late Periods, the other blue overglaze technology contains cobalt as the colourant. A similar dark blue/black in the Late Period was found to contain cobalt and iron, as well as copper, chromium, manganese, and arsenic as minor components. Zinc is not detected with cobalt on areas with this particular overglaze technique.

## Greens

Green underglaze Pratt colours contain cobalt, tin, and antimony, achieving the colour by mixing blue and yellow pigments. This confirms that the high-temperature underglaze oxides are mixtures of concentrated pigments, and proves a different colouring technology from polychrome glazes or early underglazes, a fact not always well understood in the literature. All of the Early Period green enamels are copper-based. Chromium green enamels first appear on Winterthur's figures in the Middle Period, nearly 20 years after the introduction of chromium green at Sèvres in 1802 (Préud 1997, pp. 57–58). At both Staffordshire and Meissen, copper as a green colourant does not cease once chromium is introduced. In the Middle Period, there are two enamel greens: one with chromium, and one with copper. Chromium and copper were used together 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). Lakin's Grass Green formulation is the same recipe for 'grass green' documented by Höroldt at Meissen (Casadio and others 2012, p. 67; Domoney, Shortland, and Kuhn 2012). Darker greens come from mixing cobalt with copper or chromium, and sometimes manganese and iron. This is similar to Du Paquier dark greens; however, 'subtractive colour mixing' using Naples yellow and cobalt blue was also found there and at Meissen (Bezur and Casadio 2006, p. 1192).

## Yellow

Yellow enamels and underglazes contain lead, tin, and antimony. Antimony comes from lead antimonate (Naples yellow,  $\text{Pb}_2\text{Sb}_2\text{O}_7$ ), but tin can be present as the opacifier cassiterite (tin oxide,  $\text{SnO}_2$ ) or as the yellow pigment, lead–tin yellow (type I,  $\text{Pb}_2\text{SnO}_4$  or type II,  $\text{Pb}(\text{Sn},\text{Si})\text{O}_3$ ). Historic recipes suggest tin oxide is added for opacity: Lakin includes 'oxide of tin' in recipes for orange, yellow, and green underglaze colours (Baines 1824). Dossie mentions using tin compounds for pigmentation of yellow and green enamels, but where transparency is desired, the tin is omitted (Dossie 1758, pp. 291–296). Research from Meissen, Sèvres, and Du Paquier explain the presence of tin by cassiterite (Colomban, Sagan, and Faurel 2001, p. 356; Casadio 2004, p. 181; Bezur and Casadio 2006, p. 1186), and small amounts of tin oxide have been found in English porcelain glazes (Owen and Hillis 2003, p. 867; Owen 2001, pp. 112–113).

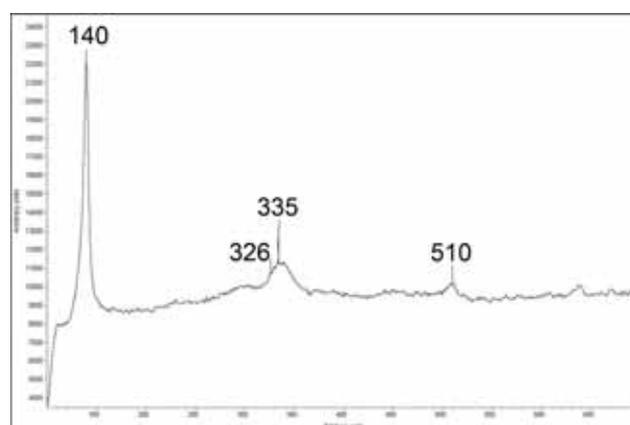


Fig. 1. (top) *Lion*, c. 1825–1840 (1967.900.1) H 21.4 cm W 13.3 cm (Photo: Winterthur Museum), with sample location starred; (bottom) Raman spectrum from yellow enamel indicating peaks for Naples yellow and lead–tin yellow type II.

As yet, cassiterite is absent in all Raman spectra of Staffordshire enamels. Raman spectroscopy of yellow enamel on the base of the *Lion* (figure 1) clearly identified lead–tin yellow type II (silicon-substituted lead (II) stannate,  $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ) with two peaks ( $140, 326\text{ cm}^{-1}$ ). Naples yellow was also confirmed with three peaks ( $140, 335, 510\text{ cm}^{-1}$ ). There is evidence that lead–tin yellow was adapted for use in enamelling on Chinese porcelain in the eighteenth century (Kerr and Wood 2004, p. 634; Miao, Yang, and Mu 2010). Raman spectroscopy investigation of an olive brown underglaze sample from the *Sportsman's Companion* (figure 2) also identified a mixture of Naples yellow and two peaks to confirm lead–tin yellow type I ( $123, 303\text{ cm}^{-1}$ ). The cross-section of this sample shows clearly that underglaze Pratt colours consist of mixtures of pigments that remain undissolved in the overlying glaze.

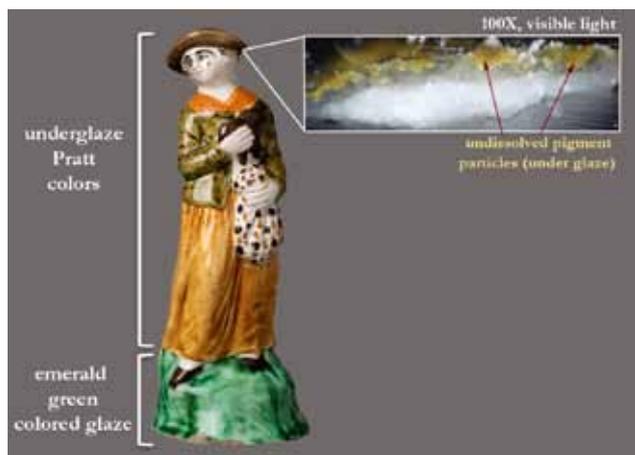


Fig. 2. (left) *Sportsman's Companion*, c. 1790–1820 (2002.30.15.2) H 18.4 cm W 7.6 cm (Photo: Winterthur Museum), with sample location indicated; (right) cross-section image of underglaze brown.

Zinc as a flux in green and yellow enamels was used at Meissen after 1800 (with the exception of one *hausmaler* ware), but at Du Paquier there are documented cases of zinc-fluxed green and yellow enamels as early as 1725 (Page and Chilton 2001, p. 234; Bezur and Casadio 2009, p. 1187). Only one Staffordshire figure from the Early Period contains zinc as a minor component, while in the Middle and Late Periods, zinc is present as a major component in green enamel compositions only.

### Orange

In the Early Period, orange enamel was achieved mostly with dissolved iron oxide ( $\text{Fe}_2\text{O}_3$ ), while orange underglaze colours contain Naples yellow and iron oxide. In the Late Period, copper and antimony are added to these iron-based orange enamels.

In the Middle Period, a bright, vibrant orange that seems entirely unique to Staffordshire decoration was added to the enamel palette, observable in the figure of the Queen (Victoria) and the King (Victor Emmanuel II) of Sardinia (figure 3). Raman spectroscopy confirmed the presence of lead (II) chromate, as mixtures of chrome yellow ( $\text{PbCrO}_4$ , peaks at 340, 407, 842  $\text{cm}^{-1}$ ) and chrome yellow–orange ( $\text{PbCrO}_4\text{-PbO}$ , peaks at 355, 378, 825, 832  $\text{cm}^{-1}$ ). Massicot (lead (II) oxide,  $\text{PbO}$ ) is also detected, with peaks at 143 and 289  $\text{cm}^{-1}$ .

Lead chromate as an orange enamel colourant has, to our knowledge, no precedent in Continental European or Chinese enamelled porcelain wares from the nineteenth cen-

tury. At Sèvres, lead uranate ( $\text{PbUO}_4$ ) was used for golden-yellow enamels (Colomban, Sagon, and Faurel 2001), but uranium was not identified here. Furthermore, chromium in orange enamel recipes is discussed by neither Lakin nor Dossie.

### Red, Pink, and Purple

Red, pink, and purple enamels can be divided into three groups: (1) deep rustic reds and brownish-pink shades where iron oxide is the colourant; (2) deep reds and brownish-pinks where iron, but also iron chromate and colloidal gold (with tin) are the colourants; and finally, (3) pink, magenta, and purple colours that contain mainly gold and tin. The use of gold and tin (purple of Cassius) as a red, pink, and purple enamel colourant was common practice in Staffordshire from the Early Period onward, and was documented by both Dossie and Lakin (Dossie 1758, pp. 284–285, 298; Baines 1824, pp. 55–57).

In addition to gold, Staffordshire purple and magenta colours 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 Du Paquier to create deeper tones; while at Meissen, the purple shade is dependent on the colloidal size of the gold (ratio of gold-to-tin) (Domoney, Shortland, and Kuhn 2012, p. 468).

Dossie describes how to obtain a 'cheaper' red colour with iron oxide, which can be 'enlivened by mixing one part of glass of antimony...' (Dossie 1758, p. 286). Iron oxide-based reds were found on seventeenth century English porcelain jars at the British Museum (Spataro and others 2009). The Early Period Staffordshire figures analysed 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 colourant for Cornelian Red enamel (Baines 1824, pp. 50–51). Chromium in red and purple enamel is identified only on one figure from the Middle Period.

### Browns

Brown underglaze colours contain mixtures of cobalt and/or manganese, with Naples yellow, lead–tin yellow, and iron oxide. Brown enamels are based primarily on iron oxide, with varying additional components including copper, manganese,

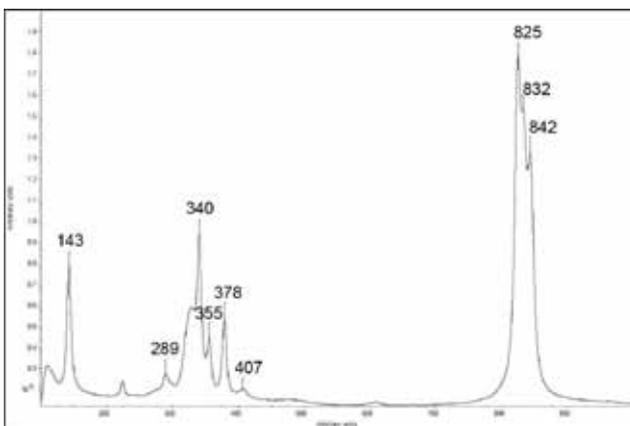


Fig. 3. (top) *Queen and King of Sardinia*, c. 1855 (2002.30.142) H 34.3 cm W 21.3 cm (Photo: Winterthur Museum), with sample location starred; (bottom) Raman spectrum from orange enamel indicating peaks for massicot, chrome yellow, and chrome yellow–orange.

cobalt, and occasionally gold, tin, antimony, and chromium. Gold and tin are detected together, suggesting that the pigmentation involves colloidal gold reduced with tin chlorides. Du Paquier brown enamels also contain gold and tin (Bezur and Casadio 2006, p. 1200). In the Middle Period, colloidal gold as a brown colourant is replaced by chromium. In the Late Period, chromium and iron are the major colourants in the brown enamels. Chromium is 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 (Casadio and others 2012, p. 70). Colomban found black/brown enamels at Sèvres to contain mixtures of magnesium oxide, iron oxide, and iron (II) dichromate (Colomban, Sagon, and Faurel 2001, p. 354).

### Grey and Black

Grey enamels and black underglazes are coloured with iron, manganese, and cobalt.

In the Early Period, two black enamels are 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 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 (Casadio and others 2012, p. 70), 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

This study has shed new light on polychrome decoration of Staffordshire earthenware figures. In many cases, the techniques closely follow trends established at the leading European porcelain production centres. However, several significant differences are noted, demonstrating the scientific progress made at Staffordshire during the period 1780–1900. Previously, scholars believed underglaze colourants were the same metal oxides used in glaze technologies. Instead, Pratt colours are made by mixtures of concentrated metal oxides. For example, where copper is the sole colouring oxide in green glazes, Pratt green underglaze consists of concentrated mixtures of cobalt blue and Naples yellow/lead tin yellow pigments.

Detection of nickel and arsenic with cobalt in both underglaze and overglaze technology suggests that a Saxony cobalt ore source was used at Staffordshire.

While exact application methods of the second blue overglaze could not be definitively determined with non-destructive analytical techniques, the results of this study suggest that the deep blue colour was applied in a second process of overglaze enamelling. This contradicts the hitherto-accepted idea that this impressive deep blue used to colour coats and jackets of many mid-nineteenth century Staffordshire figures was applied under the glaze.

Use of a zinc flux with blue, yellow, and green enamels appears to be a post-1820 technology in Staffordshire, later than at porcelain factories in Continental Europe.

An apparently new orange enamel colour based on dispersed lead chromate was 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 colourant in those cases.

Yellow underglaze and overglaze in Staffordshire contain tin and antimony colourants. Based on Raman spectroscopic findings, 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.

The survey and analysis of Winterthur's Staffordshire figure collection has amassed a body of knowledge that contributes to the understanding and appreciation of Staffordshire ceramic glaze and enamel technology and of these important, yet understudied figures.

## Appendix I. Analysis Details

### X-ray Fluorescence Spectroscopy (XRF)

An ArtTAX  $\mu$ XRF spectrometer with Si PIN diode detector and both molybdenum (Mo) tube and tungsten (W) tube was employed for qualitative and semi-quantitative elemental analysis of glaze, slip, underglaze, and enamel compositions. Both the Mo and W tube operate at 600  $\mu$ A current and 50 kV, detecting elements with energies as low as potassium ( $Z \geq 19$ ) and as high as uranium ( $Z = 92$ ) (Bronk and others 2001). With Mo tube, collection time averaged 100 seconds (no filter); with W tube, collection time averaged 300 seconds (Ni 50  $\mu$ m filter).

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 of 17 to  $\sim 5$  keV. This is highly useful for ceramic bodies, glazes, and enamels because pigments and glaze colourants are typically transition metals with 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  $\sim 20$  and 30 keV. This enables the W tube to have high sensitivity detecting elements such as tin, antimony, and barium, 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 common enamel colourants. 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.

### Scanning Electron Microscopy With Energy-dispersive X-ray Microanalysis

Samples were removed from edges of prior loss using SPI Supplies diamond scribe or #15 scalpels. Samples analysed with SEM were prepared in one of two ways: powder samples were mounted directly onto SPI Supplies 10X15 mm carbon stub using double-sided carbon tape. Intact fragments were prepared as cross-sections by casting in Epo-Kwick epoxy resin (Buehler) and polishing with series of silicon carbide papers (240-, 400-, and 1200-grit) and Buehler diamond suspensions (6-, 1-, and ¼-µm) on Texmet 2000 polishing cloths. Once polished, cross-sections were mounted onto carbon stubs with carbon tape adhesive.

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 20° sample tilt. EDS data were analysed with Bruker XFlash detector and Quantax model 200 EDS detector with Esprit 1.8 software.

### Micro-Raman Spectroscopy

A Renishaw inVia dispersive Raman microscope with 785 nm laser was the source used for qualitative phase identification. The laser operates in 3200–100 cm<sup>-1</sup> spectral range with 3 cm<sup>-1</sup> resolution and 30-second scan time at varying powers from 1 to 5% laser power. Generated spectra were interpreted with Galactic Grams and OMNIC software and compared to reference spectra published in the literature and available online (Burgio and Clark 2000; Colomban, Sagon, and Faurel 2001; Casadio 2004; Colomban and Milande 2006; Casadio and others 2012; RRUFF Project and online database of Raman spectroscopy, <http://rruff.info>; UCL Raman Spectroscopic Library of Natural and Synthetic Pigments, [www.chem.ucl.ac.uk/resources/raman/index.html](http://www.chem.ucl.ac.uk/resources/raman/index.html)).

## Appendix II.

### XRF Data of Underglaze and Overglaze

Colour	Time period	#	Major elements	Minor elements	Possible colourants
<b>Underglaze Pratt Colours</b>					
Medium green	Early	2	Pb, Co	Sn, Sb, Ni, As*	Ground cobalt oxide; lead antimonate; lead stannate**
Olive green	Early	2	Pb, Co, Sn, Sb	Ni, As*, Zn(tr)*	Ground lead antimonate; cobalt oxide; lead stannate**
Blue	Early	2	Pb, Co	Ni, As	Ground cobalt oxide
Medium brown	Early	1	Pb, Co, Mn	Ni	Ground cobalt oxide and manganese oxide
Dark brown	Early	1	Pb, Mn	Sb, Sn, Fe	Ground manganese oxide; iron oxide; lead antimonate; lead stannate**
Olive brown	Early	1	Pb, Co, Sb, Mn	Sn*, Ni(tr)*, As(tr)*	Ground cobalt oxide; lead antimonate; manganese oxide; also with lead stannate
Orange	Early	4	Pb, Sb, Fe	Sn	Ground iron oxide; lead antimonate; lead stannate**
Yellow orange	Early	1	Pb, Sb, Sn	Co, Zn*	Ground lead antimonate; lead stannate**; cobalt oxide
Yellow	Early	3	Pb, Sb, Sn	Cu(tr)*	Ground lead antimonate and lead stannate**
Black	Early	1	Pb, Mn, Co, Ni, Fe*	Cu(tr)	Ground manganese oxide; cobalt oxide; copper oxide; also with iron oxide
<b>Overglaze Enamels</b>					
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

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Colour	Time period	#	Major elements	Minor elements	Possible colourants
<b>Overglaze Enamels</b>					
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
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
Grey 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?

Colour	Time period	#	Major elements	Minor elements	Possible colourants
<b>Overglaze Enamels</b>					
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
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
Grey	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
<b>Second Blue Overglaze</b>					
Blue	Middle	1	Co		Dissolved cobalt
	Late	1	Co		Dissolved cobalt
Dark blue/black	Late	1	Co, Fe	Cu, Cr, Mn, As	Dissolved cobalt; dissolved iron, copper, chromium, manganese

Table 4. XRF data of underglaze and overglaze decoration on Wintertbur figures. \* Detected only once. \*\* Presence of tin may indicate tin oxide opacifier, rather than lead–tin yellow pigment.

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