

CHARACTERIZATION OF 18TH-CENTURY MEISSEN PORCELAIN USING SEM-EDS*

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Analytical investigations of fragmented Meissen porcelains well dated to between 1725 and 1763 have been carried out using SEM-EDS. The aim of the analysis was to characterize elements in bodies, glazes and overglaze enamels in order to create a baseline data set of materials used in the manufacture of porcelain at the Meissen factory, Saxony, during the 18th century. Analyses indicate body and glaze compositions to be consistent with a post c.1720–30 date, when a change from a lime-rich flux to a potassium-rich flux is documented to have occurred. Overglaze enamel compositions are shown to be consistent with contemporary accounts of enamel preparations at Meissen. Overglaze enamel compositions show that mixtures of pigments, in addition to documented enamel 18th-century preparations, were in use at Meissen between c. 1725 and 1763.

KEYWORDS: SEM-EDS, PORCELAIN, OVERGLAZE ENAMEL, MEISSEN, 18TH CENTURY

INTRODUCTION

The manufacture of hard-paste porcelain was first achieved in Europe in 1708 in Dresden, by a group led by Johann Friedrich Böttger (1682–1719) under Augustus the Strong, Elector of Saxony and King of Poland. The breakthrough followed over 200 years of documented experimentation instigated by Royal courts throughout Europe to discover a formula for ‘white gold’ that rivalled Chinese and Japanese wares (Kingery 1986; Emerson *et al.* 2000). Production of porcelain soon followed, with the establishment of the first European porcelain factory in Meissen, Saxony in 1710.

Under Böttger (1708–19) a limited range of cold enamel paints and gilding were used to decorate porcelain. Cold paints were soon replaced by fired enamel colours with superior lustre, brilliance and adherence (Weiss 1971; Menzhausen 1990; Cassidy-Geiger 2008; Pietsch 2010). The new palette of fired enamels and the formation of fine painting in miniature-like style mark a period of artistic brilliance that established the factory’s world reputation (Weiss 1971; Walcha 1981).

The exceptional quality, popularity and commercial value associated with early Meissen led to the production of imitations by other European porcelain factories in the 19th century (Lang 1986). For the art-historian, distinguishing these later pieces from early 18th-century originals has proved to be problematic, necessitating the need for scientific investigation to help determine the century in which an object was made (e.g., Neelmeijer *et al.* 2000; Halfpenny and Mass 2009).

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Technological investigation of Meissen porcelain and its decorative components has been the focus of a number of analytical studies in recent decades (Schulle and Ullrich 1982; Hornig-Sutter 1984a,b, 1985a,b; Schulle and Ullrich 1985; Stiegelschmitt and Tomandl 1985; Uda *et al.* 1999; Neelmeijer *et al.* 2000; Page and Chilton 2001; Casadio 2004; Colomban and Milande 2006; Lee *et al.* 2008; Bezur and Casadio 2009; Halfpenny and Mass 2009; Ullrich *et al.* 2010). The majority of these studies have been restricted to non-invasive surface analysis using air-path instruments such as XRF and Raman spectroscopy due to the complete nature of porcelains under analysis. Of the fragmented Meissen porcelains investigated in published studies, only a small number have undergone SEM-EDS analysis, largely due to the lack of available samples for destructive analysis, and these have focused on glaze and body compositions only (Schulle and Ullrich 1982, 1985).

In this study, fragments from six Meissen porcelains well dated to between 1725 and 1763 have been analysed using SEM-EDS (Fig. 1). The porcelains belong to one of the most important private collections of 18th-century Meissen formed in Dresden from the mid-1890s until c.1926 by Gustav and Charlotte von Klemperer (Loesch 2001, 2004; Kuhn 2008, 2010). A catalogue of the collection, published in 1928, comprises over 800 objects and provides an almost complete survey of production at the factory from its founding up until the end of the Seven Years War in 1763 (Schnorr von Carolsfeld 1928). The collection suffered loss and irreparable damage in February 1945, during the Allied bombing raids of the Second World War (Kuhn 2008). The six objects used in this study were broken as a result. A small group from the surviving collection, including the objects in this study, were recently auctioned at Bonhams, London, in December 2010 (Bonhams 2010).

The broken nature of the group provided a rare opportunity to sample and analyse whole Meissen sherds in an SEM chamber prior to auction. By accurately characterizing the body, glaze and overglaze enamel colours of each individual object, this study aims to establish a baseline compositional data set of materials used in the manufacture of porcelain at Meissen between 1725 and 1763. The compositional data are discussed with reference to recipes and raw materials documented in contemporary accounts published by Berling (1910), Heintze (1910), Seyffarth (1957), Weiss (1971), Walcha (1981) Menzhausen (1990), Sterba (1991), Schärer (1996) and Lübke (2000), in order to help to refine the dates for technological development during this period of manufacture.

The investigation has been conducted as part of a larger-scale collaborative research project between Cranfield University and Bonhams, London, which aims to characterize changes in porcelain technology at Meissen via a systematic non-destructive analytical survey of securely dated objects primarily using handheld X-ray fluorescence spectrometry (HH-XRF) in order to help date objects with insecure provenance.

SAMPLES

The samples consist of fragments from six objects: two Augustus Rex bottle vases (AR1; AR2) dating to 1725–33, two armorial plates (GG; MH) dating to 1740 and 1745, a plate with an ornithological design (BS) dating to 1755–63, and a plate from the ‘Japanese Service’ (JS) dating to 1763. The armorial plates and the plate from the ‘Japanese Service’ can be securely dated by supporting archival evidence, including factory inventories and diplomatic correspondence, and the vases and the plate with an ornithological design are well dated stylistically (S. Kuhn 2010, pers. comm., 14 July). The collection also comprises several pieces of the same services for comparison. A description of the objects is given in Table 1. Sample names are given



Figure 1 The Meissen porcelain analysed in this study: (a) AR1; (b) AR2; (c) GG; (d) MH; (e) BS; (f) JS. Figures 1 (a) and 1 (b) are published courtesy of Bonhams.

Table 1 Description of samples

<i>Object</i>	<i>Date</i>	<i>Description</i>	<i>Enamel colours analysed</i>
AR1	1725–33	Fragments of a bottle vase with 'Augustus Rex' manufacturing mark	Yellow, green, turquoise, purple, red, orange, black, bronze, gold
AR2	1725–33	Fragments of a bottle vase with 'Augustus Rex' manufacturing mark	Turquoise, blue, purple, red, gold
GG	1740	Fragments of an armorial plate from the Götzensdorf–Grabowski service	Yellow, green, turquoise, blue, purple, red, brown, black
MH	1745	Fragments of an armorial plate from the Münchhausen service	Purple, gold
BS	1755–63	Fragments of a plate from a complete service with a bird design	Yellow, green, blue, purple, orange, gold, brown
JS	1763	Fragments of a plate from the Japanese Service for the Chinese House at Sanoussi	Yellow, green, blue, pink, orange, brown, black, gold

Each object consists of several fragments. The fragment numbers are listed after 'Object' in the overglaze enamel results in Table 4.

by a two-letter prefix (representing the object name), followed by the fragment number (numerical or alphabetical).

METHODOLOGY

A LEO 435VP scanning electron microscope fitted with an energy-dispersive spectrometer, based at Cranfield University, was used for all analyses. The instrument allowed analysis of elements with an atomic number 6 (C) and above and has detection limits typically in the range of 0.05–0.26 wt%, depending on element (Pollard *et al.* 2007, 111). In practice here, a detection limit of 0.1% was applied to all elements. Three different sample preparation procedures were used. To determine body composition, fragments of porcelain were prepared by embedding in epoxy resin, ground flat, polished with diamond paste to 1 µm and carbon coated. Flat surface chips of glaze and individual enamel colours measuring approximately 0.5–1.0 mm in diameter were stub mounted and carbon coated. Flatness and perpendicularity to the beam was checked by scanning across the surface of the glaze and checking that it remained in focus. Carbon-coated samples were analysed under high vacuum with an accelerating voltage of 20 kV and a beam current of 200 µA. Larger fragments with overglaze enamel decoration that were intended for reconstruction were analysed under variable-pressure mode under the same voltage and current. All samples were measured for 50 000 counts on the highest peak, and glass standard Corning 'B' was used to monitor analytical drift. At least two analyses were conducted on each sample, giving a high degree of consistency, and the mean composition was calculated. The body and glaze compositions were compared against individual enamel colours in order to identify colouring agents.

In order to validate the results obtained from polished sections, fragments and surface chips, samples of glass standard Corning 'C' (the closest to the enamel compositions) were prepared in exactly the same manner as the porcelain samples. At least three analyses were carried out on each sample and the results averaged. As shown in Table 2, the results of the three preparation techniques are virtually identical and very consistent with the published values.

Table 2 Average analyses by SEM-EDS of glass standard Corning C prepared as polished sections, fragments and chips (results given as wt% oxides normalized to 100%; n, number of individual analyses in the average for each preparation; target composition after Vincenzi et al. 2002)

	n	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	TiO ₂	Sb ₂ O ₅	CuO	PbO	CoO	BaO	SrO ₂	SO ₃	Cl	SiO	ZnO	NiO
Target Corning C		34.87*	0.87	0.34	5.07	2.76	1.07	2.84	0.82*	0.14	0.79	0.03	1.13	36.7	0.18	11.4	0.19	0.10	0.10	0.29	0.052	0.02
Polished section, coated, HV	3	35.6	1.0	0.3	4.8	2.3	1.0	2.8	0.0	0.0	1.5	0.0	1.1	37.5	0.2	11.0	0.3	0.3	0.0	0.1	0.0	0.0
Fragment, uncoated, VP	3	36.6	1.1	0.3	4.8	2.4	1.1	2.6	0.1	0.0	1.8	0.0	1.2	36.2	0.2	10.9	0.0	0.3	0.1	0.2	0.1	0.1
Surface chips, coated, HV	4	35.9	1.0	0.3	4.8	2.4	1.0	2.7	0.1	0.0	1.6	0.0	1.2	37.3	0.2	11.1	0.0	0.2	0.0	0.3	0.1	0.0
Overall average	10	36.0	1.1	0.3	4.8	2.4	1.1	2.7	0.0	0.0	1.6	0.0	1.1	37.0	0.2	11.0	0.1	0.3	0.0	0.2	0.0	0.0
Overall standard deviation	10	1.1	0.0	0.0	0.1	0.2	0.1	0.1	0.0	0.0	0.1	0.0	0.1	1.1	0.0	0.2	0.2	0.2	0.1	0.3	0.0	0.0

*Unpublished data (from Brill, cited in Vincenzi et al. 2002); Mn not found in replicate analyses of Corning C by Unipire and Control Services Inc. using LiBO²/ICP (Brill 1999, 541).

Enamel colours were recorded visually by matching with colour standards in the *Munsell book of color* (glossy edition) as recommended practice (Orton *et al.* 1993, 136–8; Umland 1999). Descriptions of colours are based on visual interpretation, and hues and tones are documented using the Munsell recording system. Systematic documentation of hues and tones enabled the full range of colours to be evaluated and provided a baseline for comparison with future studies.

RESULTS

Porcelain body

The chemical compositions of the bodies are very consistent, with 60–62% silica (SiO₂), 33–36% alumina (Al₂O₃) and 2.7–3.6% potash (K₂O). As shown in Table 3, these compositions are

Table 3 Comparison of average body and glaze compositions with 'Böttger' and early 'Meissen' porcelain (*n*, number of individual analyses in the average results; –, below detection limit; n.q., not quoted)

Sample	Date	<i>n</i>	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂	PbO
<i>Porcelain bodies</i>											
AR1 ¹	1725–33	6	62.1	33.1	0.5	0.1	0.4	3.4	0.3	–	–
AR2 ¹	1725–33	4	59.9	34.6	1.2	0.1	0.5	3.3	0.4	–	–
GG ¹	1740	4	60.0	35.5	0.5	0.1	0.6	2.9	0.4	–	–
MH ¹	1745	4	59.9	35.8	0.5	–	0.5	2.7	0.4	–	–
BS ¹	1755–63	4	60.5	34.3	0.4	0.1	0.5	3.6	0.5	–	–
JS ¹	1763	4	61.2	33.7	0.3	0.1	0.4	3.5	0.6	–	–
<i>Previous body analyses</i>											
Böttger ^{3a}	c.1712	n.q.	61.5	30.1	6.3	1.1	0.1	0.3	n.q.	n.q.	n.q.
Böttger ^{3b}	c.1715	n.q.	57.6	35.8	4.3	1.2	0.2	0.2	n.q.	n.q.	n.q.
Böttger ⁴	1710–20	n.q.	n.q.	n.q.	8.7	n.q.	n.q.	0.7	n.q.	n.q.	n.q.
Meissen ^{3c}	c.1731	n.q.	59.0	35.2	0.3	0.2	0.8	3.9	n.q.	n.q.	n.q.
Meissen ⁵	c.1782	n.q.	56.6	39.8	0.5	0.2	1.1	1.4	0.4	n.q.	n.q.
<i>Glazes</i>											
AR1 ²	1725–33	4	68.9	15.1	6.9	0.1	0.4	3.7	1.0	0.9	2.6
AR2 ²	1725–33	4	73.0	17.4	3.9	0.1	0.8	3.9	0.5	–	0.3
GG ²	1740	4	72.0	16.2	2.8	0.1	0.8	4.5	1.0	0.1	2.2
MH ²	1745	2	72.6	16.1	4.2	0.1	0.9	3.3	0.8	0.1	1.3
BS ²	1755–63	2	73.9	17.4	3.6	0.1	1.4	2.5	0.3	–	–
JS ²	1763	4	73.7	14.4	4.1	0.1	1.0	3.8	1.1	–	1.1
<i>Previous glaze analyses</i>											
Böttger ^{3a}	c.1712	n.q.	71.6	19.2	5.7	1.1	0.9	0.6	n.q.	n.q.	n.q.
Böttger ^{3b}	c.1715	n.q.	74.0	17.2	5.8	0.8	0.9	0.5	n.q.	n.q.	n.q.
Böttger ⁴	1710–20	n.q.	n.q.	n.q.	13.0	n.q.	n.q.	1.3	n.q.	n.q.	n.q.
Meissen ^{3c}	c.1731	n.q.	72.2	18.1	3.4	0.5	1.3	4.1	n.q.	n.q.	n.q.
Meissen ⁵	c.1782	n.q.	73.9	17.9	3.5	0.4	1.8	2.1	0.5	n.q.	n.q.

¹Average results of bodies analysed in this study: all samples prepared as polished cross-sections, carbon-coated and analysed using HV SEM–EDS at 20 kV and 200 μA; wt% oxides normalized to 100%. ²Average results of glazes analysed in this study: all samples consist of stub-mounted glaze chips, carbon-coated and analysed using HV SEM–EDS at 20 kV and 200 μA; wt% oxides normalized to 100%. ³After Schulle and Ullrich (1982): ^afragments of a vase cover; ^bfragments of a lid from a Kendi bottle; ^cfragments of a Kirschner vase—samples prepared as polished sections and analysed using SEM–EDS, 20 kV, 2–5 nA. ⁴After Hornig-Sutter (1985a): pagoda figure, method of analysis not quoted. ⁵After Ullrich *et al.* (2010); fragments of a Meissen dish prepared as polished sections using EPMA, 20 kV.

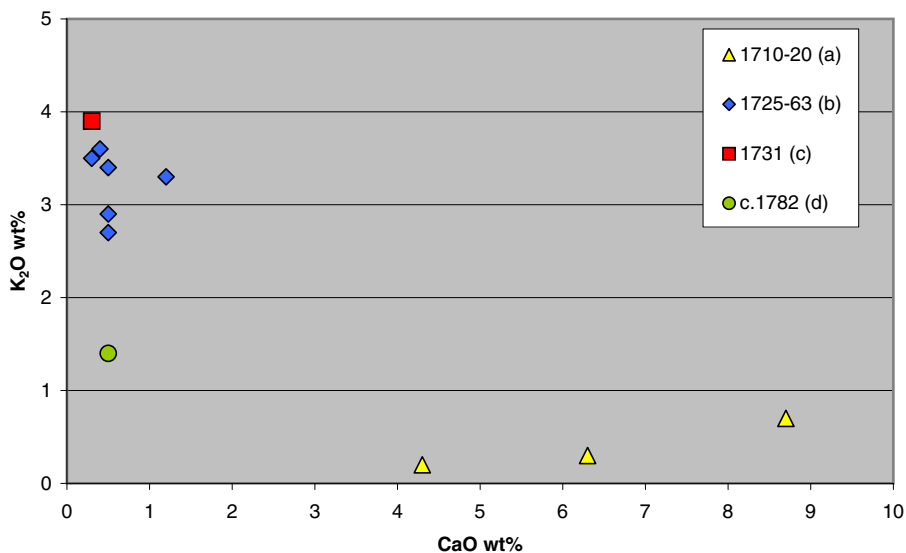


Figure 2 A plot of the SEM–EDS analyses of K_2O against CaO for porcelain bodies produced at Meissen between 1710 and c.1782: (a) after Hornig-Sutter (1985a) and Schulle and Ullrich (1982); (b) objects analysed in this study; (c) after Schulle and Ullrich (1982); (d) after Ullrich *et al.* (2010).

consistent with analyses of a Meissen body dating to c.1731 that has 3.9% potash (Schulle and Ullrich 1982, 1985). As Figure 2 shows, the high potash and low lime content distinguish the bodies from lime-rich ‘Böttger’ porcelain produced at the factory from 1709 until c.1725, which has potash levels from 0.2% to 0.7% and lime from 4.3% to 13% (Schulle and Ullrich 1982, 1985; Hornig-Sutter 1985a; Stiegelschmitt and Tomandl 1985). The composition of the group differs slightly from a later Meissen body dating to c.1782, which has 1.4% potash (Ullrich *et al.* 2010).

Glazes

The chemical composition of the clear glazes of the von Klemperer porcelains are also very consistent as a group, with 69–74% silica (SiO_2), 15–17% alumina (Al_2O_3) and 2.5–4.5% potash (K_2O). As shown in Table 3 and Figure 3, these results are consistent with SEM–EDS analyses of a Meissen glaze dating to c.1731 (Schulle and Ullrich 1985). The higher potash content differentiates the von Klemperer glazes from earlier Böttger glazes, which have potash in the region of 0.5–1.3%. The potash and lime composition of the group is very similar to a late 18th-century Meissen glaze dating to c.1782 (Ullrich *et al.* 2010).

Overglaze enamels

All of the overglaze enamels (excluding the gold and copper-pink colours) consist predominantly of lead oxide and silica. As Table 4 shows, the composition of the lead–silica matrix exhibits a high degree of heterogeneity. Silica (SiO_2) varies from 14% to 65% and lead (PbO) from 10% to 75%. Alumina, lime and potash are also present, in addition to metallic oxides acting as colourants. The types of metallic oxides present are dependent on the enamel colour desired. As overglaze enamels were analysed *in situ*, elements from the glaze and porcelain body

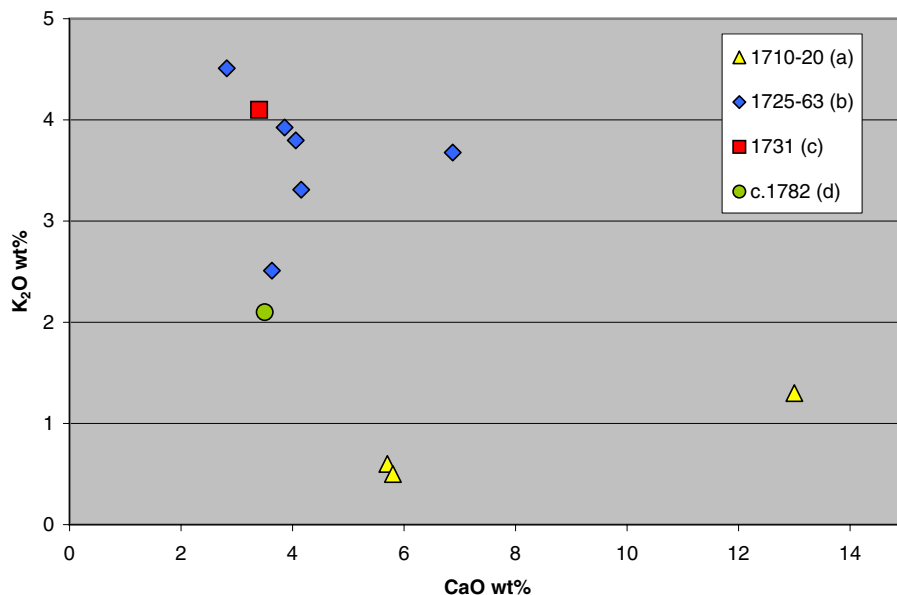


Figure 3 A plot of the SEM–EDS analyses of K_2O against CaO for porcelain glazes produced at Meissen between 1710 and c.1782: (a) after Hornig-Sutter (1985a) and Schulle and Ullrich (1982); (b) objects analysed in this study; (c) after Schulle and Ullrich (1982); (d) after Ullrich et al. (2010).

substrates—that is, silica, alumina, lime, magnesia and iron oxide—will also be reflected in the results (the interaction volume being dependent on the thickness and composition of the enamel and accelerating voltage and current). The majority of the metallic oxides are, however, not common to all three components and can be considered specific to the enamel.

Yellow-coloured enamels are present on four of the objects studied: AR1, GG, BS and JS. The results indicate that each of the yellow enamels is rich in lead oxide (34–75% PbO) and antimony (4.2–7.2% Sb_2O_3). Yellow enamels on AR1, BS and JS contain traces of tin (<0.3% SnO_2) and the two later objects (BS [1755–63] and JS [1763]) contain traces of zinc (<0.2% ZnO). Iron (Fe_2O_3) in the region of 1% is present in all yellow enamel areas investigated.

Two main hues of green have been used to decorate the six objects; green with a yellow hue—green (yellow)—and green with a blue hue—green (blue). Green (yellow) enamels all comprise copper and antimony and may be subdivided into two groups: copper-rich and antimony-rich. Vase AR1, dating to 1725–33, has two areas of copper-rich green (yellow) enamels of the same Munsell hue and shade (7.5 GY4/6). The ratios of copper (CuO) to antimony (Sb_2O_3) are 1.8 and 3.6, respectively. Objects dating from 1740 to 1763 are decorated with antimony-rich green (yellow) enamels, with different shades of the same Munsell hue (5GY) and with a ratio of copper (CuO) to antimony (Sb_2O_3) in the range of 0.4–0.9. The plate from the ornithological service dating to 1755–63 is also decorated with a green (blue) enamel that is coloured by copper, cobalt and antimony. Some arsenic and nickel are also present. The ratio of cobalt to copper in green (blue) enamels is around 0.5. Tin is present (0.1–2.9% SnO_2) in all green areas investigated except in the green (yellow) enamel on plate GG dating to 1740.

Two hues of turquoise are represented in the von Klemperer objects, turquoise with a green hue (10G) and turquoise with a blue hue (5BG). Each colour is copper-rich with varying levels of cobalt. The lightest shade of turquoise on bottle vase AR2 has a pastel tone with a CoO/CuO ratio

Table 4 Average analyses of overglaze enamels by SEM-EDS: wt% oxides normalized to 100% (n, number of individual analyses in the average results; –, below detection limit)

Object Fragment	Date	Colour	Munsell	HV/NP	n	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂	CoO	CuO	MnO	NiO	ZnO	As ₂ O ₃	SnO ₂	Sb ₂ O ₃	BaO	PbO	P ₂ O ₅	Au ₂ O ₃	Ag ₂ O	
Yellow																											
ARI C	1725–33	Yellow	10 Y 8.5/8	VP	2	13.5	1.8	2.1	–	0.1	0.3	0.9	0.4	–	0.2	–	–	–	–	0.2	5.7	–	74.5	–	–	–	–
GG G1	1740	Yellow	10 Y 8/8	VP	2	38.1	5.8	4.1	0.2	0.2	0.5	1.0	–	–	–	–	–	–	–	–	7.2	–	42.7	–	–	–	–
BS 8	1755–63	Yellow	5 Y 8/8	VP	2	21.7	2.8	1.8	0.2	0.3	1.1	1.0	0.1	–	–	–	0.1	–	–	0.3	7.1	–	63.3	–	–	–	–
JS 2	1763	Yellow	7.5 Y 8/8	VP	2	35.8	4.0	3.8	0.2	0.3	1.8	1.0	0.1	–	–	–	0.5	–	–	–	7.1	–	45.2	–	–	–	–
JS 7, 9b	1763	Yellow	7.5 Y 8/8	HV	3	46.0	5.9	4.5	0.3	1.1	1.3	1.0	1.0	–	0.2	0.4	–	0.2	–	0.3	4.2	–	33.5	–	–	–	–
Green																											
ARI D	1725–33	Green (yellow)	7.5 GY 4/6	VP	2	31.5	4.5	2.9	0.1	0.6	1.2	0.6	0.36	–	8.3	–	–	–	–	2.3	4.7	–	42.9	–	–	–	–
ARI 2	1725–33	Green (yellow)	7.5 GY 4/6	HV	3	36.7	5.1	2.9	0.1	0.2	0.6	0.5	0.24	–	6.2	0.5	–	–	0.1	1.1	1.7	–	43.7	–	–	–	–
GG G1	1740	Green (yellow)	5 GY 5/6	VP	2	25.9	4.0	2.6	0.2	0.4	1.2	–	–	0.1	4.9	–	–	–	–	0.1	10.9	–	49.3	–	–	–	–
GG 2	1740	Green (yellow)	5 GY 5/6	HV	3	27.3	3.9	3.0	0.1	0.2	0.3	0.9	–	–	6.1	–	–	–	–	–	6.5	–	51.3	–	–	–	–
BS 1, 2	1755–63	Green (blue)	2.5 G 5/4	HV	4	43.8	6.4	2.1	0.2	0.1	1.0	0.6	–	2.4	5.9	–	1.6	–	0.3	2.9	0.6	–	31.2	–	0.9	–	–
BS 6, 7	1755–63	Green (yellow)	5 GY 5/6	VP	3	29.4	4.5	2.5	0.1	0.2	0.9	0.8	–	–	6.0	–	–	–	–	0.4	7.2	–	47.7	–	–	–	–
BS 8	1755–63	Green (blue)	2.5 G 5/4	VP	2	36.0	5.0	1.8	0.2	0.02	1.0	0.5	–	4.0	8.1	–	2.7	–	0.2	0.2	0.6	–	39.5	–	–	–	–
JS 10	1763	Green (yellow)	5 GY 5/2	VP	2	38.8	4.8	3.7	0.2	0.3	1.4	1.1	–	–	3.8	–	–	0.3	–	0.1	6.8	–	38.5	–	–	–	–
Turquoise																											
ARI D	1725–33	Turquoise	10 GY 6/4	VP	2	27.9	2.9	3.1	–	0.2	0.4	0.6	0.1	1.1	5.3	–	0.1	–	2.8	3.2	0.9	–	51.3	–	–	–	–
AR2 B	1725–33	Turquoise (green, mid)	5 BG 7/4	VP	2	38.5	1.9	1.8	0.1	0.9	2.1	0.5	–	0.3	5.2	–	0.2	–	0.1	11.2	–	–	37.0	–	–	–	–
GG B6	1740	Turquoise (blue, light)	10 GY 4/6	VP	2	39.6	6.3	3.4	0.2	–	0.5	0.5	–	5.0	7.3	–	1.2	–	0.6	0.4	–	–	35.0	–	–	–	–
Blue																											
AR2 B	1725–33	Blue (purple)	7.5 PB 6/4	VP	2	31.9	1.4	1.8	–	0.6	1.5	0.7	–	1.8	0.3	0.1	0.6	–	0.4	4.6	–	–	54.1	–	–	–	–
GG B6	1740	Blue (purple)	7.5 PB 3/8	VP	2	38.1	2.5	3.3	0.1	1.0	1.6	0.7	–	2.7	–	–	0.3	–	0.4	8.3	–	–	40.9	–	–	–	–
BS 7	1755–63	Blue (purple)	5 PB 6/6	VP	2	15.9	2.5	1.3	–	0.1	0.5	1.1	–	6.1	0.4	0.3	1.4	–	0.2	0.1	–	0.1	69.9	–	–	–	–
JS 6	1763	Blue (purple)	5 PB 5/6	VP	2	41.2	4.7	4.9	0.3	0.4	1.7	1.1	0.1	3.8	–	–	0.5	–	1.1	1.4	–	0.1	38.7	–	–	–	–
JS 2, 3	1763	Blue (purple)	5 PB 3/10	HV	3	47.3	4.1	3.1	0.1	1.2	1.9	0.7	–	0.7	0.2	0.1	0.2	–	0.2	12.7	–	–	27.4	–	–	–	–
JS 10a	1763	Blue (grey)	5 B 5/2	VP	3	46.1	6.1	4.2	0.3	0.2	1.6	0.8	–	3.1	3.6	–	1.2	–	0.4	0.4	–	–	31.8	–	–	–	–
JS 10b	1763	Blue (grey, dark)	5 B 5/2	VP	2	51.7	4.7	10.2	0.8	0.3	1.3	1.1	–	6.4	3.8	0.1	3.9	–	0.4	0.2	–	0.1	15.0	–	–	–	–
Purple/pink																											
ARI D	1725–33	Purple (red, dark)	2.5 RP 2/8	VP	2	43.5	6.3	3.9	0.3	0.2	0.6	0.9	–	0.1	0.3	0.1	0.1	0.1	–	10.8	–	–	27.4	0.1	5.1	–	–
AR2 B	1725–33	Purple (red, dark)	2.5 RP 2/8	VP	2	46.1	6.3	3.5	0.2	0.2	0.8	0.8	–	0.1	0.2	0.1	0.1	0.2	–	9.0	–	–	24.8	0.1	7.4	–	–
GG L	1740	Purple (mid-)	10 P 3/10	VP	2	50.0	8.5	4.2	0.4	0.4	0.7	0.9	–	0.1	–	0.1	0.1	0.2	–	5.2	–	–	25.9	0.1	3.0	–	–

Table 4 (Continued)

Object Fragment	Date	Colour	Munsell	HV/VP	n	SiO ₂	Al ₂ O ₃	CaO	MgO	Ni ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂	CoO	CuO	MnO	NiO	ZnO	As ₂ O ₃	SnO ₂	Sb ₂ O ₃	BaO	PbO	P ₂ O ₅	Au ₂ O ₃	Ag ₂ O		
MH 3	1745	Purple (red dark)	7.5 RP 2/6	HV	2	58.6	9.2	3.6	0.4	0.4	1.2	0.6	-	-	-	-	-	-	-	8.2	-	0.1	15.3	0.1	1.9	-		
BS 6	1755-63	Purple (red, dark)	5 RP 2/8	VP	2	40.0	5.0	2.5	0.2	0.2	0.4	1.0	-	0.1	0.2	0.1	0.2	0.2	-	11.3	-	-	35.2	-	3.3	-		
BS 2	1755-63	Purple (red, dark)	5 RP 2/8	HV	2	49.1	7.9	2.9	0.3	0.3	1.2	1.1	-	-	0.1	0.1	0.1	0.1	-	6.6	-	-	27.8	-	2.1	-		
JS 2	1763	Pink (light)	10 P 7/2	VP	2	58.3	10.0	5.0	0.3	0.4	1.2	1.7	-	0.1	-	0.5	-	-	-	2.3	-	0.2	19.0	-	0.6	-		
<i>Red/orange</i>																												
ARI D	1725-33	Red (brick)	10 R 3/8	VP	2	41.4	6.0	3.3	0.2	0.2	0.6	19.4	0.4	-	-	-	-	-	-	-	-	-	-	28.2	-	-	-	
ARI D	1725-33	Orange (peach, dark)	10 R 5/6	VP	2	55.6	10.2	5.1	0.2	0.4	1.4	8.0	0.4	-	-	0.1	-	-	-	-	-	-	-	18.3	-	-	-	
AR2 B	1725-33	Red (orange)	8.75 R 4/12	VP	2	56.2	8.8	5.2	0.1	0.4	1.4	16.2	0.1	-	-	-	-	-	-	-	-	-	-	11.5	-	-	-	
GG C	1740	Red (brick)	10 R 3/10	VP	2	52.6	10.0	4.1	0.2	0.4	0.9	13.3	0.1	-	-	-	-	-	-	-	-	-	0.1	18.1	-	-	-	
BS 6	1755-63	Orange (red)	2.5 YR 4/10	VP	2	49.2	7.8	3.1	0.1	0.3	1.2	15.2	-	-	-	-	-	-	-	0.2	-	-	22.7	-	-	-	-	
JS 6	1763	Orange (peach, light)	2.5 YR 8/6	VP	2	65.1	11.0	4.4	0.2	0.9	3.2	3.9	-	-	0.1	-	-	0.2	-	0.4	-	-	10.2	-	-	-	-	
<i>Brown</i>																												
GG 4	1740	Brown (yellow, dark)	5 YR 2/4	HV	2	39.1	5.2	2.4	0.3	0.4	1.0	12.5	-	-	-	0.6	-	-	0.2	-	2.0	-	35.9	-	-	-	-	
BS 7	1755-63	Brown (mid-, dark)	2.5 YR 2/4	VP	2	39.8	5.7	2.8	0.2	0.5	0.9	13.3	-	-	-	0.3	-	0.5	-	0.2	-	-	35.7	-	-	-	-	
JS 6	1763	Brown (mid-)	2.5 YR 3/2	VP	2	53.3	6.4	3.6	0.3	0.5	1.8	7.7	-	0.8	0.1	2.5	0.3	0.2	-	2.0	-	-	20.2	-	-	-	-	
<i>Black</i>																												
ARI C	1725-33	Black	N 5	VP	2	31.8	3.8	2.4	0.2	0.3	0.5	0.7	0.3	-	0.3	17.2	-	-	-	-	-	-	0.2	42.2	-	-	-	-
GG C	1740	Black	N 1.75	VP	2	40.0	5.6	2.9	0.4	0.3	0.3	6.0	-	1.4	0.2	5.7	0.3	-	-	-	-	-	-	36.7	-	-	-	-
JS 6	1763	Black	N 1.5	VP	1	43.1	5.2	4.6	0.3	0.5	2.1	1.9	-	5.4	0.6	1.5	0.5	0.3	-	0.7	4.6	-	28.3	-	-	-	-	-
<i>Copper/pink</i>																												
ARI C	1725-33	Copper (pink)	2.5 YR 5/4	VP	2	32.7	4.9	3.7	0.2	0.4	0.9	0.8	0.3	-	-	-	-	-	0.3	-	-	-	8.4	1.9	45.4	-	-	
<i>Gold</i>																												
ARI C	1725-33	Gold	n/a	VP	2	3.2	0.4	0.3	-	0.2	0.2	0.3	0.1	-	-	0.1	-	-	-	-	-	-	0.2	1.0	0.2	93.6	0.1	
AR2 B	1725-33	Gold	n/a	VP	2	7.0	0.9	0.6	0.1	0.4	0.2	0.5	-	-	-	-	-	-	-	-	-	-	0.1	2.6	1.8	85.5	-	
MH 3	1745	Gold	n/a	HV	2	6.6	0.5	0.5	0.1	0.3	0.2	0.8	0.1	-	-	-	-	0.1	-	-	-	-	2.9	0.3	87.3	-	-	
BS 4	1755-63	Gold	n/a	HV	2	3.6	0.3	0.3	0.1	0.6	0.2	0.3	-	-	-	-	-	-	0.1	-	-	-	0.9	2.4	90.9	0.2	-	
JS 5	1763	Gold	n/a	HV	2	8.4	1.3	0.6	0.1	1.0	0.9	0.5	0.3	-	-	-	-	0.7	-	-	0.2	-	4.9	0.1	80.4	0.2	-	

Where two fragments are listed, analysis has been conducted on two adjoining fragments where the enamel decoration is divided by a break in the porcelain.

of 0.1, elevated potash (2.1% K_2O) and high tin (11.2% SnO_2). A darker shade of turquoise present on plate GG is coloured by cobalt and copper with a CoO/CuO ratio of 0.7 and contains 1.2% NiO. Antimony is not present in either of these colours. The third turquoise colour analysed, on bottle vase AR1, has a more varied formulation, with a CoO/CuO ratio of 0.2, 0.9% Sb_2O_3 , 2.8% As_2O_3 and 3.2% SnO_2 .

Two main hues of blue of varying shades are represented: blues with a delicate purple tone—blue (purple) (5PB–7.5PB)—and blue with a grey tone—blue (grey) (5B). Cobalt is present in all blue (purple) enamels (0.7–6.1% CoO) in addition to traces of copper (<0.4% CuO) on AR2, BS and JS. The blue (grey) enamel decorated on plate JS has cobalt with elevated copper (3.6–3.8% CuO) with a CoO/CuO ratio of 0.9–1.7. High tin (4.6–12.7% SnO_2) occurs in three of the five blue (purple) enamels and high nickel (3.9%) occurs in the darkest blue (grey) enamel on plate JS. Potash (K_2O) occurs between 1% and 2% in three of the four objects analysed (AR2, GG and JS).

Purple- and pink-coloured enamels are decorated on all six objects and range in hue and shade from light pink to deep purple (10P–2.5RP). Tin and gold occur in all areas analysed, with a SnO_2/Au_2O_3 ratio between 1.2 and 4.3.

Iron oxide (Fe_2O_3) is present in all orange and red enamels, with levels in the range of 3.9–19.4%. No other colouring agents are present above the detection limits. The shades represented range from peach (2.5YR) to brick red (10R).

Two brown hues, 2.5YR and 5YR, are represented in three objects dating between 1740 and 1763 (GG, BS and JS). Each are coloured by iron (7.7–13.3% Fe_2O_3) and manganese (0.3–2.5% MnO), with the addition of antimony (~2.0 Sb_2O_3), cobalt (~0.8% CoO), copper (~0.2% CuO) and/or tin (<2.0% SnO_2).

Three black areas were examined, each with different compositions. The black enamel on the earliest object (AR1), dating to 1725–33, is manganese-rich (17.2% MnO) and contains traces of iron and copper (<0.7% Fe_2O_3 and CuO). The black enamel on the plate dating to 1740 (GG) is composed of roughly equal levels of iron and manganese (around 6% Fe_2O_3 and MnO), along with cobalt (1.4% CoO). In contrast, the black decoration on plate JS dating to 1763 is cobalt- and antimony-rich (5.4% CoO and 4.6% Sb_2O_3), with lesser amounts of iron and manganese (around 2% Fe_2O_3 and MnO).

A copper-coloured enamel with a pink tone—copper (pink) (2.5YR)—occurs on bottle vase AR1, dating to 1725–33. The enamel consists of 45.4% Au_2O_3 , 8.4% PbO_2 and 32.7% SiO_2 . The pinkish tone and high lead and silica differentiates this enamel from the gilt areas.

Analyses of the gilt areas on five objects indicate a small number of elements occurring with gold. All have phosphorus (0.1–2.4% P_2O_5), and traces of silver (<0.2% Ag_2O) occur in the earliest and later objects (AR1, BS and JS). Lead occurs in all gold enamels at 1.0–4.9% PbO , and zinc is present at <0.7% ZnO in the gilding on plates MH, BS and JS. No mercury is present in any of the areas analysed.

DISCUSSION

Porcelain body

The increased potash and lower lime content of the von Klemperer bodies versus the pre-1720 ‘Böttger’ bodies support evidence from contemporary accounts for a change in the paste formula at some time between 1719 and 1725, to a preparation using a potassium-rich feldspar. Laboratory notes and factory records dating to the developmental period in 1708–9 indicate that the first hard-paste wares were produced from a mixture of white clay from Colditz and calcined alabaster

(calcium sulphate) from Nordhausen; the clay was quickly supplanted by kaolin from Aue and lime introduced used as a flux (Heintze 1910; Kingery 1986; Kingery and Vandiver 1986). The paste formula was modified sometime after Böttger's death in 1719, when potassium-rich feldspar (*Siebenlehner gestein*) replaced lime, producing a whiter shade of porcelain more equivalent to Chinese wares (Heintze 1910). The exact date of this change is uncertain; however, in 1720 the Meissen paste compounder David Köhler noted that a change in body and glaze technology was required to prevent underglaze blue decoration from running (Pietsch 2010). Substitution of lime for feldspar also has the additional benefit of decreasing the firing temperature from around 1400°C to 1300°C, as shown by replication experiments conducted at the Massachusetts Institute of Technology (Kingery 1986; Kingery and Vandiver 1986). Results show a further change in paste recipe may have occurred sometime between 1763 and c.1782, which utilized a lower concentration of feldspar. Further analyses of late 18th-century samples would be required to confirm this.

Trace elements in the clay such as zirconium and rubidium have been shown to indicate further subgroups for dating (Hornig-Sutter 1985a; Stiegelschmitt and Tomandl 1985), but the recorded levels of these elements, <120 ppm, are below the detection limits of the SEM. A comparative study of trace element levels with contemporary factory records may help secure dates for the change in clay sources and provide further compositional markers for dating.

Glaze

The increased levels of potash in the von Klemperer glazes are also consistent with the use of potassium-rich feldspar. The composition differs from early glazes dating from 1709 to c.1720, which are documented to consist of a mixture of quartz, kaolin and lime (Heintze 1910). As a study by Kingery and Vandiver (1986) using ultraviolet light has shown, feldspar may have been utilized as a flux in glaze technology at Meissen prior to its introduction to the paste recipe. The study found variable levels of purple fluorescence associated with the use of feldspar in the glazes of three samples dating to the Böttger period (before 1720). Records indicate that the factory was certainly experimenting with feldspar by this period, as 750 pounds of '*Flemmingscher Stein*' containing feldspar was delivered to the factory in 1720 (Walcha 1981, 52).

The requirement for a high-temperature glaze to suit the high-fired body is reflected in the results; the glazes have the same components as the porcelain bodies, but with higher levels of feldspar to increase fluidity (Kingery 1986). AR1 has a higher lime content than the rest of the group, which may reflect the use of mixed flux, as was the practice at the du Paquier factory (Bezur and Casadio 2009). At Sèvres, calcareous fluxes were added to feldspathic glazes in order to reduce the problem of colour peeling resulting from potassium and sodium oxides being volatilized during repeated firing (Brongniart 1844, 678; Shaw 1968, 7). AR1 is highly decorated with rich metallic enamel colours that would benefit from a softer glaze by permeating sufficiently during repeated firing. A higher flux content would also have increased the fluidity of the glaze; extra thin coats were known to be used on Irminger's finely sculpted Böttger porcelain, so as not to mask the delicate detail (Heintze 1910; d'Albis 1986). Analysis of further pieces dating to 1710–30 would be useful to determine whether mixed fluxes were commonly employed during this period at Meissen and therefore represent an intermediate stage in glaze technology.

Overglaze enamels

The results indicate that metallic oxides are acting as pigments or opacifiers suspended within a lead silicate glass matrix, which is fused in place on the glaze substrate. The results correspond

Table 5 Fired enamel colours available to Meissen painters in 1731, as recorded in an enamel preparation book attributed to Johann Gregorius Höroldt, dated to 24 December 1731 (after Heintze 1910; Seyffarth 1957; Weiss 1971; Sterba 1991; Schärer 1996)

Colour	Base materials
'Iron red'	Iron ore, steel filings, rust
'Yellow'	Naples yellow pigment
'Yellow in the Japanese manner'	Iron compounds
'Green'	Copper or brass ash
'Yellow green'	Mixing yellow and green
'Blue green'	Mixing green and lightly alkaline cobalt pigment
'Blue'	Cobalt carbonate
'Brown'	Umber
'Good black'*	Cobalt carbonate, umber and manganese ore
'Silver'	Silver dust obtained by precipitation from melted-down coins
'Purple'	Precipitate from gold and tin solution
'Mother of pearl or copper colour'	Gold lustre
'Gold'	Gold dust from melted ducats, ground with flux of red lead
'Sea green in the Japanese manner'	Indian blue and brass ash
'Indian blue'	Cobalt carbonate and potassium bitartrate, rich in alkali
'Old Japanese purple'	Purple and flux
'Contour brown'	Umber, Naples yellow and iron red

*The same black preparation is used for painting outlines, but without mixing with flux.

to enamel recipes described in a notebook dated to 1731, attributed to Johann Gregorius Höroldt, Master Painter and Court Commissioner at the factory, entitled '*True and correct description of the enamel paints, which I invented with God's help and will be used by the Royal Porcelain Manufactory here as well as gold and silver and how they must be treated*' (Heintze 1910; Seyffarth 1957; Schärer 1996; Lübke 2000). The book details the preparations and raw materials for a range of overglaze enamel colours, including gold, silver and copper-coloured gold lustre, listed in Table 5. The colourless lead fluxes for the colours are described as composing of lead ashes, *lapis sillicis*, potash and tin ashes (Heintze 1910). Detection of tin and potash may therefore be attributed to the colourless flux as well as the pigment and/or opacifying agent. Potash occurs in all enamels analysed; however, tin is detected intermittently. If tin was present as an opacifier within the lead–silica matrix, SnO₂ would be present as discrete crystals. To establish this, further work using BSE–EDS on polished sections of overglaze enamels would be required.

Yellow The presence of lead oxide (PbO) and antimony (Sb₂O₃) corresponds to the first 'yellow' documented in Höroldt's enamel recipe book described as being produced from the pigment 'Naples yellow' (lead antimonate) bought from apothecaries (Seyffarth 1957). Records indicate that after 1769, yellow enamels at Meissen were manufactured in house from antimony *regulus* and iron ore (Heintze 1910). The presence of iron may be attributed to the glaze or as a deliberate addition as a tone enhancer, rather than Höroldt's second 'yellow', which is described as being 'in the Japanese manner' and manufactured from 'iron compounds' (Weiss 1971, 201; Miels and Lauschke 1965, 81; Sterba 1991, 22). Iron was the colouring agent for translucent yellow enamels on contemporary Japanese Kakeimon porcelain (1680–1725) and Chinese Kangxi (1662–1722)

famille verte porcelain. Iron yellow was gradually replaced by opaque tin- and antimony-based pigments from the late Kangxi period onwards, as a study by Miao *et al.* (2010), using Raman spectroscopy, XRF and XRD, demonstrates.

The low concentrations of tin (SnO_2) in three of the enamels suggest that it is dissolved in the lead–silica matrix rather than being present as an opacifier: studies have shown that tin is usually present in concentrations of around 5–20% when used as an opacifier in lead glazes (e.g., Maggetti and Neururer 2009) and enamels (Wypyski 2002). Both tin and or zinc may have been deliberately added to the Naples yellow pigment before arrival at the factory, prior to its conversion into a vitrifiable pigment. The Mariani manuscript dating to the 17th century describes one of three preparation of Naples yellow (also termed *giallo de'vasari* or 'potter's yellow') as having the addition of 'Alexandrine Tutti' (commonly associated with tin or zinc oxide) to lead antimonate (Dik *et al.* 2005). While the presence of zinc in potter's yellow has not yet been detected on securely dated pigment samples from paintings (Dik *et al.* 2005), recent investigations of du Paquier porcelain by Bezur and Casadio (2009) have detected zinc in addition to lead and antimony in yellow overglaze enamel decoration (Bezur and Casadio 2009). Zinc is also documented in eight contemporary Venetian lead–antimony–tin yellow glass recipes, as a study by Moretti and Hreglich (1984) has shown. Brongniart (1844, 529) notes that a range of yellow tones for porcelain painting was achieved at Sèvres by adding zinc oxide or iron oxide to antimony yellow enamels, from light yellow to golden yellow, respectively. The du Paquier zinc-containing yellow enamels are characterized by a luminous lemon colour (Bezur and Casadio 2009), while Moretti and Hreglich (1984) found that the addition of around 6.5% ZnO to Venetian yellow glasses moves the colour towards ochre or orange. The zinc-containing yellows on the objects analysed in this study have a slightly warmer hue than the yellows without zinc; however, the zinc contents are very low (<0.2%). A greater sample size of zinc-containing yellows is needed to make a direct comparison between tone and composition.

Green The green (yellow) enamels analysed appear to represent the 'grass green' documented in Höroldt's enamel colour book as being prepared by mixing 'yellow' ('Naples yellow') and 'green' ('copper or brass ash') (Seyffarth 1957; Weiss 1971, 201; Sterba 1991, 22). The absence of zinc in the green decoration on objects dating to 1725–63 suggests that copper was used, rather than brass ash. The green (blue) enamels decorated on object BS equates with Höroldt's 'blue green', which is documented as being prepared from 'lightly alkaline cobalt' and 'green' ('copper or brass ash'). However, the presence of antimony in the green (blue) enamel suggests that the colour may have been prepared by mixing Höroldt's 'grass green' with 'lightly alkaline cobalt' rather than 'green'.

Elevated tin (1.1–2.9% SnO_2) in three of the areas studied may indicate the deliberate addition of a tin opacifier. While the levels are low in comparison to tin-opacified lead glazes (e.g., Maggetti and Neururer 2009), SnO_2 has been found in concentrations as low as 1.8% in opaque yellow and green enamels on jewellery when present in association with antimony (Wypyski 2002). Further work using BSE imaging of polished sections of yellow and green enamels would be useful to confirm the nature of the tin.

Turquoise The copper-rich turquoise enamels most closely compare to Höroldt's 'blue green', prepared from mixing 'green' and 'cobalt pigment'. However, elevated potash on AR2 may indicate the presence of potassium bitartrate, as used in the 'sea green' listed in Höroldt's colour preparation book. 'Sea green' is documented as being prepared using 'brass ash, cobalt carbonate and potassium bitartrate'; however, the absence of zinc in this colour once again indicates that

copper was used, rather than brass ash. The opacity in the pastel tones of turquoise enamels on AR1 and AR2 is most likely produced by the high tin content.

Blue Three of Höroldt's documented colours—'blue', 'Indian blue' and 'blue green'—appear to be represented in the areas analysed. Cobalt and low potash on plate BS indicate Höroldt's 'blue', recorded as being prepared using 'cobalt carbonate'. Elevated potash in combination with cobalt in the blue (purple) enamels on AR2, GG and JS may indicate the presence of 'Indian blue', which is documented as being prepared using 'cobalt carbonate and highly alkaline potassium bitartrate flux'. High copper in the blue (grey) enamels on plate JS is indicative of 'blue green', but with a higher cobalt content than the green (blue) shades attributed to the 'blue green' preparation in this study.

The association of arsenic and nickel with cobalt-blue pigment in the blue enamels can be used to infer the geographical origin of the cobalt ore. As several studies have shown (e.g., Gratuze *et al.* 1992, 1995; Soulier *et al.* 1996), such an association is characteristic of cobalt ores mined from the Schneeberg (Erzgebirge) district of Saxony. Contemporary factory records dating to 1709 show that cobalt was obtained from the Schneeberg cobalt works (Heintze 1910). Gratuze *et al.* (1995) suggest that high nickel and arsenic contents associated with cobalt confirm the use of smaltite and erythrite ores, which are both present at Schneeberg.

The blue (grey) enamels on plate JS have a higher NiO/CoO ratio than the blue (purple) enamels: 0.4–0.6 compared to 0.1–0.3. The difference may be indicative of the contemporaneous use of two cobalt ores or a deliberate addition of nickel as a shading agent, as was common in Persian cobalt blue decoration (Shaw 1968, 5). However, a similar high nickel to cobalt ratio occurring in the green (blue) enamels on object BS dating to 1755–63, compared with the low nickel to cobalt ratios in the earlier enamels, may suggest that a nickel-rich cobalt ore was exploited sometime between 1740 and c.1755.

Purple/pink The tin and gold components are consistent with the raw materials used in the preparation of 'purple' recorded in Höroldt's colour book, which documents the base materials to consist of a 'precipitate from gold and tin solution' (Sterba 1991, 22). A page from a notebook in the Meissen factory archive attributed to Samuel Stötzel, and dated to 1731 (Carbert 1980), describes the preparation of the 'finest purple' as using English tin and a gold ducat dissolved separately in *aqua regia*. This preparation is indicative of the pigment Purple of Cassius, developed in the late 17th century by Andreas Cassius, and prepared from a precipitation of a mixture of gold trichloride and stannous chloride solutions (Shaw 1968, 37). The hue and shade of purple is dependent on the colloidal size of the gold. Copper and cobalt were used with Purple of Cassius in contemporary du Paquier purples to create more nuanced tones (Bezur and Casadio 2009); however, neither of these elements was detected here.

Red/orange The presence of iron (Fe_2O_3) indicates that both red and orange enamels represent Höroldt's 'iron red', manufactured from 'iron ore, steel filings and rust' (Weiss 1971, 201). An undated factory recipe published by Heintze (1910) states that 'various materials could be used to give a red colour but they are not equal to calamine and vitriol, I therefore find it unnecessary to use them'. Vitriol and calamine were common names for iron sulphate and zinc ore in the 18th and 19th centuries, zinc being added to brighten the tone (Shaw 1968, 29). Zinc is absent from the red and orange enamels on objects dating to before c. 1755–63, which are likely to predate the recipe. Heintze (1910) notes that purity of the red shades was soon recognized as being affected by copper in the iron sulphate ore. Trace amounts of copper are present in the orange

enamel on plate JS, dating to 1763. At some point between the date of the recipe and Heintze's publication in 1910, copper is precipitated from vitriol to obtain pure iron sulphate. On the basis of these documents, there are three potential compositional markers for dating iron red colours: iron with trace levels of copper; iron with trace levels of copper and zinc; and iron with zinc.

Brown The presence of iron and manganese in each of the brown enamels are representative of the calcinated pigment, Burnt Umber. Höroldt documents browns as being prepared from 'the best English Umber' (Seyffarth 1957). Three preparations of brown are apparent in the results. The first preparation, on plate GG, contains iron, manganese and antimony and probably represents Höroldt's 'Contour Brown'; the second preparation, on plate BS, contains iron, manganese and low zinc; and the third preparation, on plate JS, contains iron, manganese, tin and cobalt. Elevated manganese in the third preparation (2.5% MnO) indicates that the shade was produced from a mixture of umber and manganese-black, with tin added to lighten or opacify the shade.

Black The results here suggest that at least three recipes for black were in use: a manganese, iron and cobalt black; a manganese-rich black; and a combinational black that utilized a range of pigments depending on the required hue. The manganese, iron and cobalt pigment is consistent with Höroldt's 'good black' preparation, which consisted of well-mixed precipitates of cobalt, umber and manganese ore (Heintze 1910; Seyffarth 1957). Although Höroldt only mentions one recipe for black, Weiss (1971, 201) notes that prior to 1723, black was made from lead ash and manganese oxide. The manganese-rich black present on vase AR1, dating to 1725–33, is therefore consistent with this earlier factory recipe. Manganese-rich blacks were also utilized at du Paquier, alone or in combination with copper-oxide blacks (Bezur and Casadio 2009). However, no copper-rich pigments were identified in the black enamels investigated here.

Copper/pink The copper-pink colour present on vase AR1 is often referred to as 'Böttger lustre' and relates compositionally to the 'mother of pearl or copper colour' produced from fulminating gold listed in Höroldt's enamel preparation book (Seyffarth 1957). Fulminating gold had been known to alchemists since the medieval period (Steinhauser *et al.* 2008) and was first used at Meissen as an enamel colour under Böttger. The preparation is described by Höroldt as a precipitate of gold in a solution of *aqua regis* (nitro-hydrochloric acid) and oil of tartar (concentrated potassium carbonate solution) (Seyffarth 1957). Once dry, the pigment needed to be stored in a cool place to prevent it from exploding in the heat.

Stylistically, Kuhn (2011, pers. comm., 21 April) associates the use of the colour with the 1720s and 1730s, in particular to fill out elaborate gilt cartouches that are characteristic of the baroque-style decoration of the period. During this period, the lustre was used less commonly like a normal enamel colour in painted decoration, as is the case with its occurrence on vase AR1, dating to 1725–33.

Gold The variety in composition of the gold decoration may be representative of production by a number of different workshops. In the early 18th century, independent goldsmiths were commissioned by the factory to decorate enamelled and plain white wares (Honey 1954, 147ff.). Contemporary factory reports also note that by 1728 Meissen craftsmen had developed an in-house technique for painted gold decoration of a similar quality to that produced by the independent goldsmiths (Pietsch 2010). Despite this, large numbers of porcelains are recorded as being sent to the studios of George Funcke in Dresden, Conrad Christophe Hunger in Thuringia, and Abraham and Batholomäus Seuter in Augsburg (Walcha 1981; Rückert 1990; Pietsch 2010).

The in-house technique for the preparation of gold powder is described in Höroldt's recipe book as being produced from Dutch ducats, dissolved in *aqua regia* with the addition of 'Hungarian vitriol' (iron sulphate) (Schärer 1996). Dutch ducats were specifically recommended because they were 'easier to cut', a fact supported by Hunt (1979), who states that, at that time, Dutch ducats had the highest gold content of any other coinage in Europe, 98.6%. The low levels of silver and presence of zinc most probably represent impurities in the gold; however, a larger compositional study of gilt porcelain decorated by known goldsmiths may help to determine technical differences between studios.

In a study of contemporary porcelain from the du Paquier factory, Bezur and Casadio (2009) showed that the tone of the gold is indicative of both composition and application technique. They showed that red golds were achieved by the addition of copper oxide to gold powder, and by the application of gilding over an iron-rich bole, and a cool green tone was prepared by adding powdered silver. In comparison, the gilt areas on the Meissen objects have a red tone but lack notable levels of iron, silver or copper. The compositions are consistent with the application of gilding over an iron-red bole; the bole is not detected due to the thickness of the gilt layer and the excitation energy.

Summary This study has characterized 12 of the enamel paints documented by Höroldt to be in use at Meissen by 1731. These are summarized in Table 6, along with the range of elements that seem to act as markers for these colours. Two additional black preparations have been identified. Höroldt's 'green', 'yellow in the Japanese manner', 'sea green in the Japanese manner', 'old Japanese purple' and 'silver' are yet to be identified. More investigations by HH-XRF of securely dated objects are currently under way, with the aim of further characterizing the 18th-century Meissen palette and identifying the dates at which new colours were introduced.

CONCLUSIONS

This unique study of fragmented pieces of well-dated 18th-century Meissen porcelains has permitted compositional analysis of bodies, glaze and fired enamels, which can now be used as a baseline data set for comparative studies and further non-invasive investigation. Both body and glaze compositions are consistent with a date later than *c.*1725–30, when the change from a lime-based flux to a potassium-rich feldspar flux is documented to have occurred. Overglaze enamels are consistent with 18th-century technologies described by contemporary documents, and comprise 12 of the enamel preparations documented to have been developed by 1731. The results have shown that mixtures of pigments, in addition to documented enamel preparations, were in use between *c.*1725 and 1763. Analyses also indicate the potential for cobalt/nickel ratios and other minor and trace elements to further demarcate the chronology of the Meissen palette. The next stage of this project is to conduct a systematic characterization survey of Meissen technology by extending the sample set of 18th-century porcelain through non-destructive analysis of complete objects using handheld HH-XRF.

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Table 6 The characterization of enamels in Höroldt's enamel formula book dating to 1731 (after Heintze 1910; Seyffarth 1957; Weiss 1971; Sterba 1991; Schärer 1996), using results from this study

Höroldt's enamels, 1731							
Colour	Base materials	Objects	Date present	Colouring oxides	Munsell hue	Colour description	
'Iron red'	Iron ore, steel filings, rust	AR1, AR2, GG, BS, JS	1725–33, 1740, 1755–63	4–19%	Fe ₂ O ₃	2.5 YR, 8.75 R, 10 R	Orange (peach), orange (red), red (orange), red (brick)
'Yellow'	Naples yellow pigment	AR1, GG, BS, JS	1725–33, 1740, 1755–63	4–7% 33–75%	Sb ₂ O ₃ PbO	5 Y, 7.5 Y, 10 Y	Yellow
'Grass green'	Mixing yellow and green (copper or brass ash)	AR1, GG, BS, JS	1725–33, 1740, 1755–63	4–8% 2–11%	CuO Sb ₂ O ₃	5 GY, 7.5 GY	Green (yellow)
'Blue green'	Mixing green and slightly alkaline cobalt pigment	BS, JS	1755–63	39–51% 4–8% 2–6%	PbO CuO CoO	2.5 G, 5 B	Green (blue), blue (grey)
'Blue'	Cobalt carbonate	BS	1755–63	<1%	Sb ₂ O ₃	5 PB	Blue (purple)
'Indian blue'	Cobalt carbonate and potassium bitartrate, rich in alkali	AR2, GG, JS	1725–33, 1740, 1763	–6% –4%	CoO	5 PB, 7.5 PB	Blue (purple)
'Purple'	Precipitate from gold and tin solution	AR1, AR2, GG, MH, BS, JS	1725–33, 1740, 1743, 1755–63	–2% 2–11%	K ₂ O SnO ₂	2.5 RP, 5 RP, 7.5 RP, 10 P	Pink (light), purple (mid), purple (red)
'Brown'	Umber	BS, JS	1755–63	<7% 7–13%	Au ₂ O ₃ Fe ₂ O ₃	2.5 YR	Brown (mid)
'Contour brown'	Umber, Naples yellow and iron red	GG	1740	<3% <1% –13%	MnO CoO Fe ₂ O ₃	5 YR	Brown (yellow)
–	–	AR1	1725–33	–1% –2% –17%	MnO Sb ₂ O ₃ MnO	N.5	Black preparation 1
'Good black'	Cobalt carbonate, umber and manganese ore	GG	1740	–0.7% –0.3% –6% –1%	Fe ₂ O ₃ CuO MnO Fe ₂ O ₃	N 1.75	Black preparation 2
–	–	JS	1763	–0.2% –2% –5% –1%	CoO CuO MnO Fe ₂ O ₃	N 1.5	Black preparation 3
'Mother of pearl or copper colour'	Gold lustre	AR1	1725–33	–45%	CuO Au ₂ O ₃	2.5YR	Copper (pink)
'Gold'	Gold dust from melted ducats, ground with flux of red lead	AR1, AR2, MH, BS, JS	1725–33, 1745, 1755–63	80–94% <2% <0.2% <0.7%	Au ₂ O ₃ P ₂ O ₅ Ag ₂ O ZnO	n/a	Gold

For details of Munsell shade and tone, see Table 4. Höroldt's enamel colours 'yellow in the Japanese manner', 'green', 'sea green', 'old Japanese purple' and 'silver' are not present on these objects.

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