Andrew Meek*

QUALITATIVE COMPOSITIONAL ANALYSIS OF A LATE 16TH CENTURY ENAMELLED GLASS GOBLET

[a] Introduction

The goblet shown in Fig. 1 is thought to have been produced in either Venice or the Tyrol in the late sixteenth century (for a detailed discussion of this object see Thornton, this volume). It is enamelled with an image of a lady holding a fan on one side, and on the other side with an as yet unidentified coat of arms. Gold decorates the goblet on the rim, knop and throughout the enamelled areas. The aim of this study was to use compositional analysis to provide more information about the raw materials used to produce the goblet. The analysis focussed on the enamels, but the glass body itself and the gold were also analysed.

[a] Methodology

[b] X-ray fluorescence (XRF)

A Bruker ARTAX X-ray spectrometer was used with a helium atmosphere, 50 kV voltage, 0-50 keV spectral range, 0.5 mA current, 0.65 mm diameter collimator and 100 seconds live time.

The type of analysis carried out is entirely non-destructive and does not even require contact with the surface of an object. In the case of this study it has been used to provide qualitative data about the elements present. Even though measurements were made in a

* Department of Conservation and Scientific Research, The British Museum, Great Russell Street, London, WC1B 3DG, UK.

helium atmosphere, it has not been possible to obtain any data for elements lighter than silicon, including aluminium, magnesium, sodium etc.

[b] Visible light microscopy

Macro images were taken using a Leica MZ APO microscope with attached Leica DFC 500 digital camera at magnifications of 8-32x.

[a] Results

Tab. 1: XRF results summary.

Analysis	Colour	Significant elements
Woman's Hair	Yellow	Pb, Sn, Fe
Woman's Forehead	Pink	Pb, Sn, Fe
Rim Circle	Blue	Co, Ni, As, Bi, Pb, Sn
Woman's Fan	Black	Co, Ni, As, Bi, Mn, Pb, Sn
Woman's Sleeve	Light Blue	Pb, Sn, Co, Ni, As, Bi
Woman's Bodice	White	Pb, Sn
Woman's Bodice	Gold	Au (+elements from underlying enamel)
Woman's Chest	Brown	Pb, Sn, Fe
Woman's Neck	Dark Pink	Pb, Sn, Fe
Grass	Green	Cu, Zn, Pb, Sn
Woman's Chest	Black	Co, Ni, As, Bi, Fe, Pb, Sn
Crest: Lion's Tongue	Red	Fe, Pb, Cu
Shield	Black	Co, Ni, As, Bi, Mn, Pb, Sn
Shield	Red	Fe, Pb, Cu
Mantling	Black and Gold	Fe, Pb, Au
Helmet	Black	Fe, Co, Ni, As, Bi, Pb, Sn
Vessel Body	n/a	Si, K, Ca, Mn, Fe (Ti, S, Cl, Pb, Br, Sr)

[b] Enamels

[c] Blue

The blue enamel is coloured by the addition of cobalt (Tab. 1). The opacity results from the presence of lead and tin, either in the form of lead stannate or tin oxide (cassiterite) crystals. There have been many sources of cobalt exploited by glassmakers since glass was first produced[1]. It is often possible to suggest the source used by studying other elements in the glass which are suspected to have been added unintentionally along with the cobalt as impurities in the source.

In the case of this goblet, the cobalt added appears to be from minerals associated with nickel, arsenic and bismuth (Tab. 1). This cobalt type was used in the sixteenth to eighteenth centuries. Geochemical and historical sources suggest it came from the Erzegibirge Mountains, on the German-Czech border[2]. The associated elements are not only linked with the geological source, but also the method of processing. Gratuze *et al.*[3] suggest that the geological source was either smaltite ($(Co,Fe,Ni)As_2$) or erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$). They suggest that these minerals were roasted to produce a colourant. In earlier periods this roasting was more intense, resulting in a lower level, or absence, of volatile arsenic.

[c] Yellow and white

These two colours of enamels both contain significant levels of lead and tin, which suggests the use of a lead-tin calx (a residue formed when metals are heated together[4]. It is possible to produce both white and yellow enamels by the addition of varying levels of lead and tin alone[5].The yellow enamels of the goblet contain higher lead and lower tin levels than the white. The yellow enamel

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1 Henderson 2000: 30-32.
2 Zucchiatti *et al.* 2006: 134-5.
3 Gratuze *et al.* 1999: 125-6.
4 See Biron and Verità 2012: 2711.
5 Ibid.; Henderson 2000: 36.

also contains significant levels of iron (Tab. 1). Due to the size of the XRF beam some ‘black’ enamel was also included in the yellow enamel analysis. It is therefore suggested that the iron detected in the yellow enamel was caused by the accidental analysis of some black enamel also present in the hair.

The Erzgebirge Mountains, Cornwall or Brittany were the sources of tin exploited in Europe at this time. It is therefore suggested that the tin used in the enamels on the goblet is likely to have come from one of these regions. Sources of lead are more widespread, and as such it is much harder to suggest a provenance for this raw material.

[c] Black

The ‘black’ colours found on the goblet were created using different combinations of colourants. The ‘blacks’ of the fan and on a quarter of the crest are actually very dark blue enamels produced with the addition of cobalt from the same source as the blue enamels discussed above (Tab. 1). These enamels have a slightly elevated level of manganese, but not sufficient to suggest that this is the reason for the colouring.

The ‘blacks’ on the woman’s chest and the helmet are also produced using cobalt, but with the addition of iron. This may be the result of a mixing of a dark blue enamel with a brown iron-rich enamel to produce this colour.

Finally, the analysis of the mantling enamel, which is a dark decoration underlying gold, does not contain any cobalt. This analysis appears to show that a brown, high iron, high lead enamel was used. However, the possibility that a cold painted pigment containing a brown-coloured iron compound mixed with lead white was added in place of enamel later cannot be excluded.

[c] Red, pink and dark pink

The red enamels are characterised by elevated levels of iron and lead (Tab. 1). It appears that the red colouration is formed by particles of iron oxide (hematite) within the enamel[6] . The pink and dark pink enamels appear to have been produced by mixing red enamel with varying quantities of white enamel (see above).

[c] Green

The green colour of this enamel is produced by the addition of copper (Tab. 1). Zinc is also present, suggesting that the copper may have been added as brass (copper and zinc) rather than simply as pure metallic copper. The opacity of this enamel is caused by the presence of lead and tin (see section on white enamels above).

[c] Brown

The brown enamel on the woman's chest is coloured with the addition of iron (Tab. 1). Lead and tin are also found in this analysis and may be part of the brown enamel or from the white enamel underneath.

[b] Gilding

The gilding on the goblet was also analysed and was confirmed as gold. It was also possible to observe that the gold on the goblet was applied as leaf around the rim and inside the knop, and painted on as powder, probably suspended in a liquid medium, around the enamelling on the body[7].

[b] Body Glass

As noted above it is not possible to identify elements with a lower atomic number than silicon with the XRF methodology employed in this study. It is therefore not possible to comment on some of the most important elements contained in this glass, i.e. sodium, magnesium and aluminium. However, it is possible to

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[6] See Verità 1998: 132.

[7] Eastaugh *et al.* 2004: 171.

show that this glass contains many of the elements expected for a glass type known as *vitrum blanchum* (Tab. 1)[8].

Vitrum blanchum is an almost colourless glass produced from the 14th to 18th century[9]. It can be differentiated from *cristallo*, a glass of higher clarity produced from the 15th to 17th century, by its slight grey colour and increased iron and calcium levels. Excavated examples of c*ristallo* glass have been found to contain *c*.4-6 wt% calcium oxide, whereas *vitrum blanchum* glasses contain *c*.8-12 wt%[10]. By comparison with XRF analyses of glass standards of known composition it is possible to suggest that the levels of calcium in the goblet are around 8%.

Many examples of sixteenth century glass vessels have suffered because of their unstable composition due to a deficiency in calcium[11]. However, the levels of calcium in the goblet must be high enough to produce a stable glass as the body glass shows no signs of deterioration.

[b] Macroscopic examination

Low magnification images were taken of portions of the enamelled decoration. Fig. 2 shows the woman's head and illustrates how the enamel was applied to the cheek. Clearly the temperatures achieved in the furnace were high enough to vitrify the enamel, but not to melt it entirely, leaving ridges where it was applied (Fig. 2). From this investigation it was possible to see how the decoration was built up. A series of firings must have been carried out to produce the layering of enamels seen on the goblet.

[a] Conclusions

The compositional analysis of the enamels allowed the use of various colouring agents to be identified. Of particular note is

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8 See McCray 1999; Biron and Verità 2012.

9 Verità and Zecchin 2009.

10 Ibid.: 607.

11 Newton and Davison 1989: 143.

the use of a cobalt-based blue colourant which it can be suggested came from the Erzgebirge Mountains. The analysis of the glass itself suggests that it was produced from a glass type known as *vitrum blanchum*.

By examining the enamels and gold decoration under magnification it was possible to observe how they may have been applied, and also the order in which each of the colours was added.

While the data collected during this study allows a greater understanding of the processes employed to produce this goblet it does not provide enough information to suggest whether it was made in Venice or the Tyrol. Further scientific investigation of similar vessels of more secure provenance and date will be necessary to establish criteria for differentiating between the two manufacturing areas[12].

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Fig. 1 - Late 16th century enamelled glass goblet. London, British Museum, Prehistory and Europe S.853, width of rim is 11.5 cm (© Trustees of the British Museum).

Fig. 2 - Enamelling of the woman's face (width of field of view is approximately 2.5 cm; © Trustees of the British Museum).