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Ancient Monuments Laboratory
Report 1/92

EXAMINATION OF COLOURED TIN GLAZES ON EARLY POST-MEDIEVAL DELFTWARE FROM THE CITY OF LONDON

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Summary

Fourteen samples of early delftware pottery sherds from several Museum of London sites were analysed using XRF. The purpose of the analysis was to confirm the elements used to provide coloured glazes. The samples came with several specific questions, which have been reproduced in the report and answered where possible.

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Introduction

Delftware is the name given to English-made pottery with an opaque, white tin oxide glaze. It is also referred to as 'maiolica' or 'majolica', although this term is strictly used for wares of the same type made elsewhere, especially from Italy. The pottery is fired twice, firstly without glaze (bisque firing) and then, at a higher temperature, the glaze is fired (glost firing). This double firing means that the object is easier to glaze and decorate, shrinkage after glazing is reduced and a more porous surface for the glaze to adhere to is provided. A good summary of the origins and methods of manufacture of delftware pottery can be found in Garner and Archer (1972).

The glaze itself was produced from powdered glass mixed with litharge (lead oxide) which acted as a flux, to which was added tin oxide to produce the opaque white colour. A variety of metal oxides were used to produce different colours. The principal oxides used at this time were cobalt (blue), manganese (purple), copper (green), antimony (yellow) and iron (red).

The glazed surfaces of a number of sherds found during recent excavations in the City of London were analysed by X-ray Fluorescence (XRF). The purpose of these analyses was to investigate the various coloured glazes and record qualitatively their constituent elements. The samples were presented for analysis as a single group and the results are listed in site order below (Table 2). The results have been interpreted in two forms, firstly as a general discussion including quick reference tables and secondly, for each individual sherd along with any specific questions that were asked. Many glaze samples were found to be of a similar nature. Therefore, in the latter section, where no written comment appears after the analytical results, the sample had a standard delftware appearance with composition similar to others already discussed. A brief summary of all the sites mentioned in this report can be found in the Museum of London Department of Urban Archaeology's Archive Catalogue (Schofield 1987).

SECTION 1. GENERAL ANALYSIS AND DISCUSSION

Introduction

The coloured glazes under examination were generally found to be as expected from the literature, that is, cobalt blue, manganese purple et cetera. The variations in appearance, however, were less easy to account for. The difference in shades of, for instance, the white glazes may have been due to slight variations in the composition of the glaze mixture but this cannot be judged from a qualitative analysis. Firing conditions were also suggested as a possible reason for colour variation and although this is quite possible, XRF analysis cannot confirm this. It is also possible that burial conditions may alter the appearance of glazes, that is, they may be 'stained' or altered by the surrounding soil. Many of the samples were from different contexts and sites and this range of environmental conditions may explain the visual differences noted. The presence of iron in some of the glazes and not in others is not necessarily significant. This is because iron is abundant in soil and traces of it are likely to be found on the surfaces of excavated objects. Iron is also present in the clay used to make the object and so a small crack or chip in the glaze would reveal iron under XRF.

White (Tin Only)

All of the white glazes examined were typical lead-based delftware glazes with tin oxide producing the white colour. Many of them also contained copper, presumably at low levels, but this did not seem to have any visible effect. Iron was also detected in some samples but, as with copper, it did not seem to be responsible for any major visible differences. However, some of the white glazes were noted to have had a distinct pink tinge to them. This could be explained by the presence of iron which is known to have been used to produce a red colour in some delftware pottery glazes. Indeed, all the 'pink' glazes did appear to contain iron, but so did one of the 'white' glazes. However, as mentioned above, the iron detected may not be an original component of the glaze. Firing conditions may be another explanation of the pink colouration. (See 'Firing Conditions' section below).

Blue (Cobalt Colours)

All the blue glazes under analysis were found to contain cobalt. Many of the samples also contained nickel. This is not unexpected, as cobalt and nickel sources often occur together. The fact that some cobalt glazes have no trace of nickel at all would suggest that there are at least two different sources for cobalt in use during the period that this pottery was made. This type of glaze is often referred to as Sevrès Blue or Mazarin Blue.

Green and Turquoise (Copper Colours)

The green and turquoise glazes were all copper based and one of the greens was compositionally indistinguishable from one of the turquoises. Zinc was detected in the turquoise samples but it was also found in one of the green samples. Therefore, both green and turquoise are often compositionally identical at a qualitative level. The reason for the distinct colour difference is therefore more complicated than the addition of some particular element. Weyl (1986) says that the "variation of the copper colour with new constituents in a glass is most striking in the field of ceramic glazes, for they are subject to greater variation in composition than any other glasses." Weyl quotes the work of Hecht (1895) on turquoise glazes who found that a blue glass becomes more green when boric oxide is added or the alkali is replaced by CaO, BaO or MgO (aluminium oxide has a similar effect). Furthermore, work carried out by Granger (1914) on porcelain frits shows that just increasing the copper concentration can affect the blue-green colour. The amount of lead in glazes/glasses also seems to have the effect of turning copper colours from blue to green.

To summarise, we can see that small variations in composition of copper coloured glazes can radically affect their colour. Very small additions of oxides and quantitative variations are difficult to detect using XRF unless a full quantitative analysis is done, preferably with mounted samples in a scanning electron microscope. Note that cuprous oxide (Cu_2O) can give a red colour to glass but for these green colours the more oxidised cupric oxide (CuO) is needed. (See Firing Conditions below).

Yellow and Brown (Antimony Colours)

The yellow coloured glazes were all obtained from antimony, which produces a colour known as Florentine Yellow. However, other colours produced by antimony, that is, orange and brown, were present, sometimes side-by-side on the same sample. Turner and Rooksby (1959), looking at coloured glass found that the compound lead pyroantimonate ($Pb_2Sb_2O_7$) was responsible for a yellow colour and the compound $Pb_2Sb_2O_7$-$Pb_2Sn_2O_6$ produced an orange colour. In the glazes, the yellow colours are due to the formation of crystals of antimony-lead or antimony-lead-tin oxides. It is likely that the mixtures of these and intermediate compounds and the effects of different crystal sizes would produce the range of antimony based colours noted. This could be investigated using X-ray diffraction.

Purple (Manganese Colours)

The two examples of purple glazes were both of lead/tin/manganese composition. According to Weyl (1986), the conditions of the melt should be as oxidising as possible to achieve a good manganese purple colour. This fact is interesting as it gives some insight into the firing conditions used with this pottery (see below).

Firing Conditions

The furnace conditions under which glass is melted affects the colours produced by colourants. Figure 1 below shows the range of temperatures and oxidising/reducing conditions used for most ancient high temperature processes. The conditions are more oxidising at the top of the graph than at the bottom. The slightly curved diagonal lines represent the boundaries where certain compounds change form. For example, the PbO/Pb line divides the conditions in which lead exists as lead oxide (PbO) or in its metallic form (Pb).

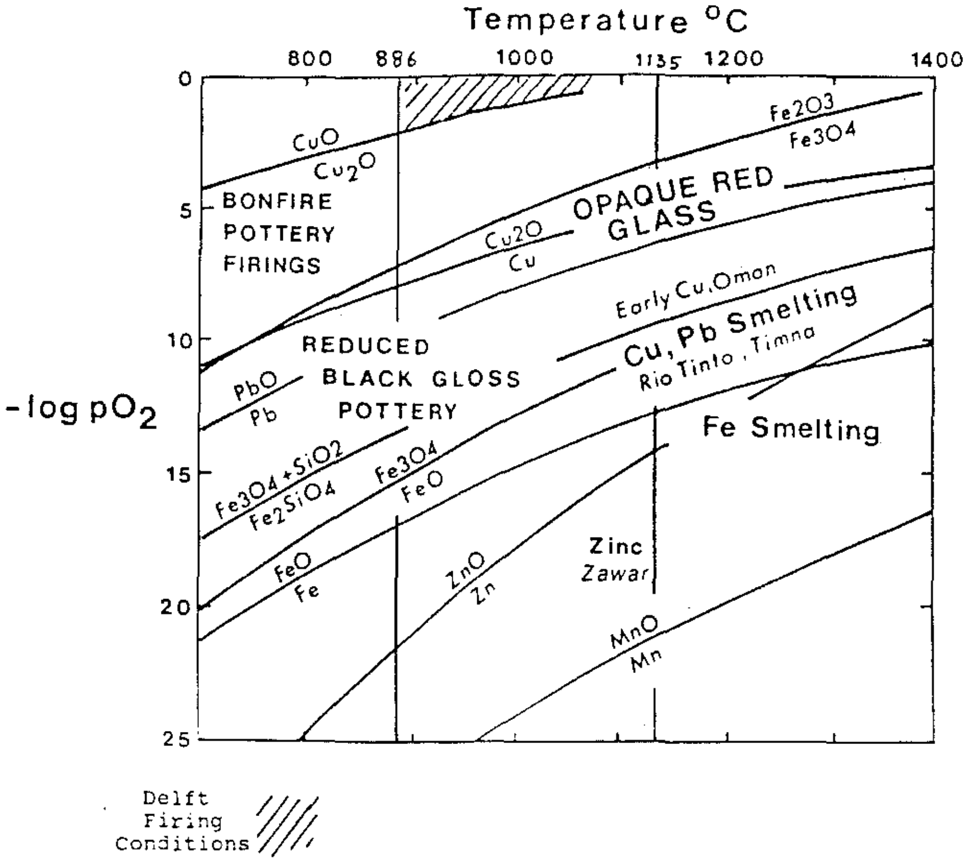

Figure 1. Graph of temperature against partial oxygen pressure showing the range of conditions suitable for delftware glaze. (After Freestone (1987)).

The upper temperature limit of suitable firing conditions can be defined by several factors. Firstly, colourants added to the glaze deteriorate at the temperatures shown below.

Element	Max. Temp. °C	Effect of Excess Temperature
Cobalt	1250	Blotchy Colours
Copper	1225	Volatises
Antimony	1135	Unstable
Manganese	1200	Gives Brown Colour

The nature of the glaze itself must also be taken into consideration. The lowest possible maturing temperature (melting point) of the glaze will be at some point around the melting point of the flux, lead oxide. Lead oxide melts at 886°C. This is confirmed by Hodges (1964), who states that maiolica glazes mature within the temperature range 900-1050°C. Rice (1987) says that "earthenwares are fired at from 900°C to approximately 1200°C" and Garner and Archer (1972) confirm that the "second [glaze] firing was at a higher temperature" than the first biscuit firing and that "too low a temperature gave poor colours and discoloured glaze".

The reducing/oxidising conditions (partial oxygen pressure) necessary for glazed delftware pottery must be strongly oxidising, that is, right at the top of figure 1. It has already been noted that the conditions should be as oxidising as possible to achieve a good manganese purple colour (Weyl 1986). Also, there is a need to keep copper pigments in the cupric form for the green or turquoise colours, that is, above the CuO/Cu_2O line on figure 1. Pinkish iron colours that were noted on some of the samples would only occur with iron in the ferric form and the formation of the yellow colour lead-antimony-tin oxide crystals (see above) also required oxidising conditions. Therefore, the range of redox conditions for delftware glost firing must lie at the top of the figure 1. in the the shaded area.

The firing conditions may also be responsible for some of the unusual effects seen on individual sherds. Sample E had distinct pink coloured areas on its rear surface glaze. It also showed areas which appeared as a clear glaze containing white flecks. There were also signs of bubbling on the rear surface. These effects could not be explained by XRF as all areas were compositionally identical. The distribution of the pink colour suggests a possible explanation. Red colouration is produced by ferric ions (Fe^{3+}). Microscopic examination showed that the pink colouration often occurred around tiny black inclusions in the glaze. This suggests that iron-rich particles in the fabric of the ceramic came into contact with the glaze, colouring it red. This argument also applies to some of the other samples noted to have a pink tinge (for example, Sample A). The flecked area is likely to be a separation or precipitation of one or more of the constituents. These white particles are most likely to be white tin oxide which has not been ground finely enough.

Sample M had a distinct matt appearance over much of its surface and the white glaze had a distinct 'purple' shade. The most likely explanation for the matt surface is abrasion in use combined with aggressive burial conditions. This piece also differed from the others in being the only example of a charger with a lead-glazed (that is, not tin opacified) back and its white glaze was of similar appearance to the flecked area of sample E, suggesting a poorer quality manufacture. The composition of the glaze may have been slightly different to that of the majority of the pieces which may explain its poorer survival.

Table 1. List of Samples by Site and Context.

Sample	Context	Description
Apothecaries Hall and 22-6 Blackfriars Lane, EC4 (APO81)		
A	[8]	Small albarello (Ointment Pot).
Capel House, 54-62 New Broad Street, EC2 (CAP86)		
B	[29]	Charger/dish (cn26562).
C	[29]	Dish.
D	[27]	Tankard.
E	[27]	Dish/charger (cn26244).
F	[520]+[563]	Saucer/small dish.
PLA Warehouse, Cutler Street, E1 (CUT78)		
G	[344]	Dish (cn25488).
H	[337]	Albarello.
Mitre Square, 11-12 Mitre Street, EC3 (HTP79)		
I	[220]	Biscuit ware dish.
J	[220]	Dish/charger (naa32159u).
K	[220]	Dish Fragments.
L	[220]	Dish (naa32160x = 221).
5 Pilgrim St, EC4 (PIL75)		
M	[1]	Dish.
10 St Swithin's Lane, EC4 (SL75)		
N	[10]	Albarello (cn26271).

Table 2. Comparative Elemental Analysis.

			Pb	Sn	Cu	Fe	Co	Ni	Sb	Mn	Zn
	AP081										
A	[8]	White	X	X		X					
	CAP86										
B	[29]	White	X	X	X	X					
		Blue	X	X	X	?	X	X			
		Dk Blue	X	X	X	X	X	X			
C	[29]	Blue	X	X	X	X	X				
		Green	X	X	X	X					
		Orange	X	X	X	X			X		
D	[27]	White	X	X	X	X					
E	[27]	F White	X	X	X	X					
		B White	X	X	X	X					
		B Pink	X	X	X	X					
F	[520]										
	+[563]	Glaze(Area)	X	X	X	X	X	X			
	CUT78										
G	[344]	White	X	X							
		Blue	X	X		X	X				
		Brown	X	X					X		
H	[337]	Blue	X	X			X	X			
		Purple	X	X						X	
	HTP79										
I	[220]	Powder	X	X							
J	[220]	White	X	X							
		Green	X	X	X						X
		Brown	X	X	X	X			X		
		Yellow	X	X	X	X			X		
		Purple	X	X						X	
K	[220]	Turqu.	X	X	X						X
L	[220]	White	X	X							
		Blue	X	X			X				
		Green	X	X	X	X					
		Yellow	X	X					X		
	PIL75										
M	[1]	White	X	X							
		Blue	X	X		X	X	X			X
		Yellow	X	X		X			X		X
		Reverse	X								
	SL75										
N	[10]	Orange	X	X					X		
		Turqu.	X	X	X	X					X

KEY: X=element detected
?=element possibly present

SECTION 2. INDIVIDUAL SHERD ANALYSIS

Apothecaries Hall and 22-6 Blackfriars Lane, EC4 (APO81)

Sample A
[8] Small albarello (Ointment Pot). White glaze with pink tinge.

White - Lead/Tin/Iron

This is a typical delftware glaze of lead oxide with tin oxide producing the white colour. Iron was also detected which may account for the pink tinge as iron oxide can produce a red colour. (See Section 1. Firing Conditions)

Capel House, 54-62 New Broad Street, EC2 (CAP86)

Sample B
[29] Charger/dish (cn26562).

Is there any way of identifying the black dots in the tin glaze?

White - Lead/Tin/Copper/Iron

Blue - Lead/Tin/Cobalt/Nickel/Copper

Dark Blue - Lead/Tin/Cobalt/Nickel/Copper/Iron

The charger has a standard tin/lead white glaze with cobalt providing the blue colour. Nickel is often found with cobalt and the lack of it in some of the other samples suggests the possibility of more than one source. The copper and nickel are probably impurities in the cobalt. Microscopic examination of the black 'dots' reveals them to be inclusions just under the surface of the glaze. Therefore XRF analysis, being a surface analysis technique, cannot reveal their chemical nature. It is quite likely that they are simply ash/charcoal particles or some other unreactive 'dirt' accidentally introduced during firing, as they have not reacted with the glaze.

Sample C
[29] Dish.

Orange and green are of interest. How does this green differ from the turquoise colour found on some vessels?

Green - Lead/Tin/Copper/Iron.

Orange - Lead/Tin/Antimony/Iron/Copper

Blue - Lead/Tin/Cobalt/Copper/Iron

The green colour was found to contain copper and iron. The results for the more turquoise colours on some of the other samples (see below) also contained zinc. The copper colours tend to vary a great deal depending on the presence of other elements. Zinc is unlikely to produce a bluer colour by itself, but in conjunction with other trace elements it may. For a fuller discussion on copper colours see Section 1. The orange colour is obtained from antimony oxide, which produces a yellow colour (known as Florentine Yellow). The darker orange shade may be produced by a lead/antimony/tin oxide compound (see Section 1. Yellow and Brown (Antimony Colours)) but this has not been verified. Once again, cobalt produced the blue colour.

Sample D
[27] Tankard.

The exterior is a creamy white. This vessel is from an earlier group than most of the plain white glazed wares. Are the glaze components different or were perhaps the firing conditions the cause of the glaze colour?

White - Lead/Tin/Iron/Copper

XRF analysis of this glaze was unable to show any major compositional difference between it and any of the other white glazes which are noted to be of a different shade. It is, therefore, impossible to judge the cause of the glaze colour using XRF.

Sample E
[27] Dish/charger (cn26244).

Are the pink areas on the reverse due to something in the glaze or firing conditions?

Front White - Lead/Tin/Copper/Iron

Back White - Lead/Tin/Copper/Iron

Back Pink - Lead/Tin/Copper/Iron

Analysis of the three 'white' areas on this sample was unable to differentiate between them compositionally. The rear surface had two distinct areas when examined under the microscope. The 'pink' area appeared to be a distinct pink glaze, whereas the white area consisted of a clear glaze containing many white particles of tin oxide. The pink colour is likely to have been due to the prescence of ferric ions. (See also Section 1. Firing Conditions).

Sample F
[520]+[563] Saucer/small dish.

The glaze has an odd devitrifying type of appearance. Is this due to the glaze content?

An area analysis of the glaze showed that it was compositionally no different from any of the other blue and white wares analysed.

PLA Warehouse, Cutler Street, E1 (CUT78)

Sample G
[344] Dish (cn25488).

Brown - Lead/Tin/Antimony

White - Lead/Tin

Blue - Lead/Tin/Cobalt/Iron

Colourants as already discussed.

Sample H
[337] Albarello.

Purple - Lead/Tin/Manganese

Blue - Lead/Tin/Nickel/Cobalt

Again, nickel traces appear in the cobalt blue colour. This is likely to be an impurity stemming from the cobalt source.

Mitre Square, 11-12 Mitre Street, EC3 (HTP79)

The wares from Mitre Square are the earliest group of tin-glazed wares in the City. They may be products of the late 16th Century pottery documented to be at Holy Trinity Priory, Aldgate. A potter has commented that their glazes appear more alkaline than those from later tin-glazed wares - is this detectable by XRF?

Assuming that the term "more alkaline" refers to a glaze with higher levels of soda or potash, then an XRF analysis for sodium or potassium is possible. Sodium is difficult to detect with XRF and so an analysis of potassium levels was attempted. Potassium was detected in higher proportions in the Mitre Square example naa32160x than in the Capel House tankard from context 27. However, similar high amounts were detected in another Capel House sample, cn26562.

Sample I
[220] Biscuit ware dish.

Is the powdery substance on the surface unfired tin glaze?

Powder - Lead/Tin

Analysis of the powdery surface of this sample revealed lead and tin, which was not detected on the unpowdered surfaces. Microscopic investigation showed a very rough covering of white powder which showed no signs of ever having been fired. This suggests that the powder could indeed be an unfired delftware glaze. This is also backed up by the shape and clay type of the dish, which is identical to some of the other chargers under analysis.

Sample J
[220] Dish/charger (naa32159u).

Yellow - Lead/Tin/Antimony/copper/iron

Brown - Lead/Tin/Antimony/copper/iron

Green - Lead/Tin/Copper/zinc

Dark Purple - Lead/Tin/Manganese

White - Lead/Tin

This sample had a floral decoration involving five different colours. The white was a standard lead/tin oxide glaze with no other significant elements present. The yellow and brown colours both contained antimony, copper and iron. The green is a copper colour and the purplish-black is a manganese colour.

Sample K
[220] Dish Fragments.

Turquoise - Lead/Tin/Copper/zinc

This turquoise colour is a copper/zinc mix.

Sample L
[220] Dish (naa32160x = 221).

Green - Lead/Tin/Copper/iron

Blue - Lead/Tin/Cobalt

White - Lead/Tin

Yellow - Lead/Tin/Antimony

Colours similar to those already discussed.

5 Pilgrim St, EC4 (PIL75)

Sample M
[1] Dish.

Yellow and blue and reverse glaze.

Yellow - Lead/Tin/Antimony/zinc/iron

Blue - Lead/Tin/Cobalt/nickel/zinc/iron

White - Lead/Tin

Reverse - Lead

(See also Section 1. Firing Conditions). This sample had a different appearance to the others. The 'white' had a distinct 'purple' shade, and the whole piece was less bright and had a matt appearance. The yellow and blue glazes were found to be standard antimony and cobalt respectively, although zinc was detected in both. The reverse glaze, interestingly, showed no trace of tin. This however is not unusual and it is mentioned in Garner and Archer (1972) that "almost all seventeenth century chargers have lead-glazed backs, possibly as a measure of economy". The odd appearance of this specimen may be due to environmental or technological effects. The matt surface could be due to heavy weathering effects of the soil, or more simply, it could be attributed to different (possibly inferior) sources of raw materials or differences in composition or manufacture. The fact that it has a lead glazed reverse in itself would suggest a different technology to the other samples. Microscopic examination revealed a heavily weathered and knife marked glaze with only patches of glassy surface remaining. The white glaze appeared similar to sample E, that is, a clear glaze with large white particles near the surface. It is likely, therefore, that this is an example of inferior quality delftware which could not stand up to environmental effects as well as the other samples.

10 St Swithin's Lane, EC4 (SL75)

Sample N
[10] Albarello (cn26271).

Orange yellow and turquoise are the main colours of interest.

Orange Yellow - Lead/Tin/Antimony

Turquoise - Lead/Tin/Copper/zinc/iron

Colours similar to those already discussed.

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