Metamerism and trace element investigations for optimal conservation and analysis of Dutch blue and white glazed tiles

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SUMMARY: This paper concerns two investigations of relevance, respectively, to the conservation and analysis of blue and white Dutch tiles: computer match pigment selection and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) applied to provenance studies.

Metamerism is one of the most troublesome issues for conservators dealing with blue and white tiles. The retouching of missing areas of blue glaze often results in a colour match which is imperceptible in the lighting of the conservation studio but very discordant in the different lighting set-ups used for museum display. Studies by the authors have demonstrated the potential of computer match pigment selection to provide non-metameric pigment combinations which match original glazes for all light sources.

Analysis of blue and white Dutch tile glazes has the potential to yield valuable new information for a better understanding of glaze recipes and, potentially, the geographical source of the cobalt mineral employed for depicting the glaze design. In view of the importance and diversity of tin-glazed earthenware in Dutch cultural history, reports of glaze composition, in particular those which quantify trace elements, are remarkably scanty. We present the results of 2-D LA-ICP-MS mapping of cobalt, iron, holmium and terbium. In these maps the concentration is colour coded, with warmer colours representing higher concentrations and cooler colours lower concentrations. The results demonstrate that this methodology, previously published for glass analysis, has great potential for interesting element relationships between those present in major/minor amounts and those present in trace/ultra-trace (parts-per-billion) concentrations. These relationships are clearly visualised by the colour-coded 2-D maps of 54 analysed elements. In addition to expected relationships between cobalt and minor elements such as arsenic, manganese and iron, correlations were found between cobalt and elements, such as holmium and terbium, at ultra-trace concentrations. This approach has therefore the power to discriminate different geological origins of cobalt ores used for blue and white ceramics as well as the potential to pinpoint regional variations in glaze recipes within the Netherlands.

KEY-WORDS: Dutch tiles; restoration of blue colour in ceramics; metamerism; computer-matching of colour; provenance of the cobalt pigment.

METAMERISM AND TRACE ELEMENT INVESTIGATIONS FOR OPTIMAL CONSERVATION AND ANALYSIS OF DUTCH BLUE AND WHITE GLAZED TILES

This paper concerns two investigations of relevance, respectively, to the conservation and analysis of blue and white Dutch tiles; computer match pigment selection and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). A previous communication by the authors addressed these related issues, metamerism and LA-ICP-MS analysis, with respect to blue and white Chinese ceramics [1].

Metamerism is one of the most troublesome issues for conservators dealing with blue and white tiles. The retouching of missing areas of blue glaze often results in a colour match which is imperceptible in the lighting of the conservation studio but very discordant in the different lighting set-ups used for museum display (Figure.1). Continuing studies by the authors are demonstrating the potential of computer match pigment selection to provide non-metameric pigment combinations which match original glazes for all light sources [2]. In particular, the colour variations of blue designs and the neutral ‘white’ background of a range of ten Dutch tiles have been recorded and recipes selected by means of a unique computer database for non-metameric glaze colour matching [3]. This paper tackles the practical issues involved with implementation of these colour matches for visually optimal reinstatement of missing tile glazes with pigment/polymer recipes. The tiles in question are illustrated in Figure 2 and the relevant computer-generated non-metameric pigment colour-matching recipes are given in Table 1.

Figure 1. Two areas of a non-metameric pigment retouching recipe which match the blue of the tile design perfectly in daylight but, in the lighting of this image, are very discordant

Tile 1 Tile 2 Tile 3

Tile 4 Tile 5

Figure 2. Dutch tiles whose corresponding non-metameric pigment colour-matching recipes are given in Table 1

	Chromophtal Blue A3R	Prussian Blue	Cobalt Blue	Anthraquinone	French Ultramarine Deep	Chromophtal Violet B	Orasol Red BL	Carbon Black	Burnt Umber	Terre Vert	CIE Lab dE*		
											D65	A	TL84
Tile1 mid				67.049				32.951			0.69	0.35	1.48
Tile1 mid		0.501	76.514					22.985			0.68	0.58	1.52
Tile1 neutral								16.542		83.458	0.27	0.05	0.35
Tile2 neutral								12.787	7.497	79.716	0.12	0.11	0.21
Tile3 neutral		0.189						12.739		87.072	0.19	0.19	0.28
Tile4 dark		0.247			55.34			44.413			0.76	1.32	1.53
Tile4 mid		0.605			45.346			54.05			0.57	1.02	1.41
Tile4 mid		0.128	78.993					20.879			0.68	1.16	1.58
Tile4 neutral								17.326	10.552	72.122	0.12	0.23	0.14
Tile5 dark					41.355	0.729		57.916			0.68	0.82	0.80
Tile5 mid		47.583					4.372	48.045			0.18	0.23	1.95
Tile5 mid	57.058						0.412	42.53			0.30	1.34	2.23
Tile5 neutral								12.409	3.354	84.236	0.12	0.24	0.27

Table 1. Computer pigment colour match predictions (%) from selected areas of the Dutch tiles illustrated in Figure 2

Analysis of blue and white Dutch tile glazes has the potential to yield valuable new information for a better understanding of glaze recipes and, potentially, the geographical source of the cobalt mineral employed for depicting the glaze design. In view of the importance and diversity of tin-glazed earthenware in Dutch cultural history, reports of glaze composition, in particular those which quantify trace elements, are remarkably scanty. Figure 3 depicts the results of 2-D LA-ICP-MS mapping of cobalt, iron, terbium and holmium. In these maps the concentration is colour coded, with warmer colours representing higher concentrations and cooler colours lower concentrations.

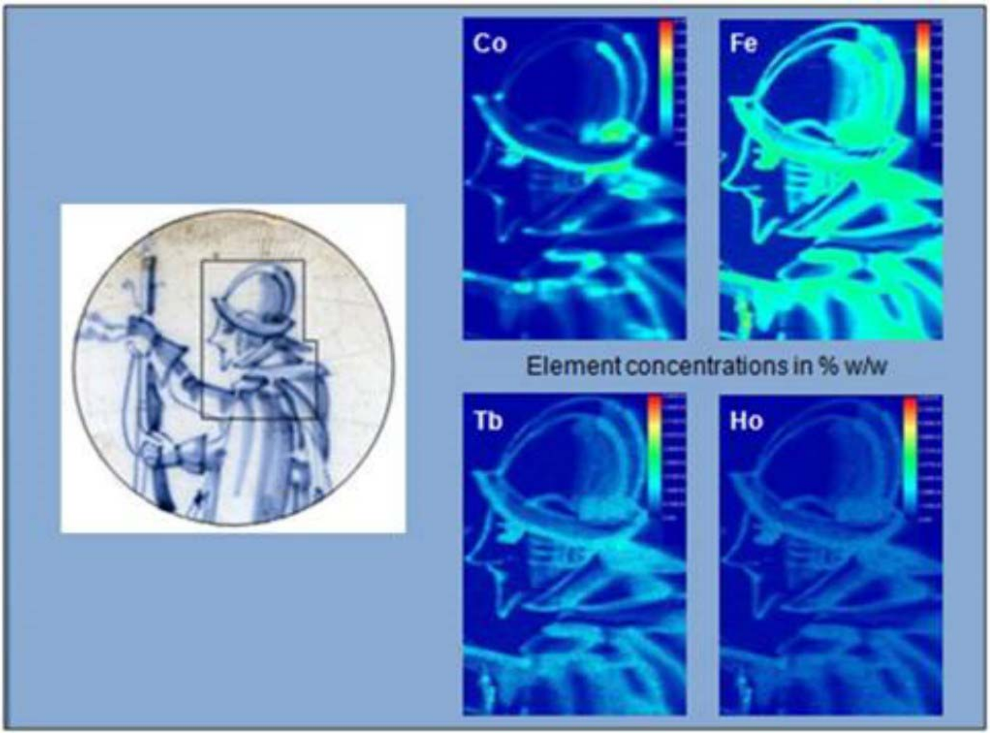

Figure 3. Colour-coded concentration maps for cobalt, iron, terbium and holmium corresponding to an area of Dutch tile glaze design

The 2-D maps, using a methodology previously validated [4,5] enable a correlation with cobalt of those trace and ultra-trace element impurities which are present in the cobalt ores and thus have the potential to be diagnostic fingerprinting elements for geological sources. Once these elements are associated with the elemental profiles of geological samples of ores, raw material sourcing can be definitive. At present, candidate ores have not been analysed but the potential of the approach is shown in Figure 3. The tile design depicted in blue is matched, as anticipated, by cobalt. The concentration maps for the exotic elements terbium and holmium also display this pictorial outline perfectly, indicating that these elements are associated only with the cobalt.

In a similar approach, by means of LA-ICP-MS line scans, a previous paper indicated the potential of cerium as an impurity element with finger-printing potential in cobalt-blue Chinese glazes [1]. Likewise, a recent report [6] has indicated the potential of LA-ICP-MS 2-D maps for the study of the glassy cobalt pigment smalt in paint cross-sections.

The element associations are clearly visualised at a glance by the colour-coded 2-D maps of 54 analysed elements. In the case of the blue in Dutch tiles, in addition to expected, long-established [7] relationships between cobalt and minor elements such as arsenic, manganese, nickel and iron, correlations were found between cobalt and several elements, of which holmium and terbium are very clear-cut examples, at ultra-trace concentrations. This approach has therefore the power to provide a signature for specific geological origins of the cobalt-containing raw material, as well as the potential to pinpoint regional variations in glaze recipes within the Netherlands.

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