Surface Analysis of Hard-Paste Porcelain Treated with Biotex® Enzymatic Stain Removing Powder

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KEYWORDS

Biotex · Ceramic · Porcelain · Conservation · Enzymes · Stain removal · XRF · FTIR

INTRODUCTION

Biotex is a household enzymatic stain removing powder (ESRP) originally designed for use on clothing; however, it is commonly repurposed by conservators for stain reduction of ceramics. Although cleaning treatments have been successful on many objects, insoluble, difficult-to-remove "tideline" residues have occasionally been reported after treatment.

Previous research focused on the effect of soaking treatments with ESRPs on porous ceramic body types (Green 1992; Hogan 1998; Hogan 2004). Little is known about this described phenomenon found on high-fired surfaces, although a questionnaire developed and circulated as part of this study showed that, in current practice, ESRPs are most commonly used on hard-paste porcelain. Therefore, this study concentrated on the residues produced after treatment with Biotex on porcelain. A list of components can be found via Unilever's Dutch language page (Anonymous 2015). See also the materials list below. While visible residues are not a common occurrence, it is unsettling when it does happen, and it would be helpful to understand if and how this can be avoided. Conservators have effectively removed residues with abrasives such as Micro-Mesh® (cushioned abrasive cloths) and acids, although both solutions risk causing damage to the glaze.

METHODOLOGY

The project aimed to further characterize the described phenomenon and identify circumstances in which it would be most likely to occur. Testing focused on methods of applying Biotex to hard-paste porcelain. The experimental methodology was created based on research conducted at the British Museum, UK, on the use of enzymatic stain removing powders in soaking treatments (Green1988; Green, Fisher and Bradley 1988; Green 1992; Lee 1996), and an internal report produced by Winterthur Museum, USA, on the contents of rinse water residues after a Biotex soaking treatment (Matsen 2013).

The study intended to relate to working practice as closely as possible, designing the methodology around responses from the international conservation community.

Sherds of 18th-century Chinese underglaze blue hard-paste porcelain were sourced. Thirty-six samples were made and treated in the following way: nine were used with room-temperature deionised water as a control, and 27 with warm (40°C) tap water, as is most commonly used in practice. Table 1 shows how each sample was treated with Biotex either by soaking (1 g Biotex in 200 ml water), poulticing (thumb sizes piece of cotton wool dipped in a 0.5% solution of Biotex in water), or by paste application (1 g Biotex in 10 drops of water) and the corresponding duration for each method.

INITIAL OBSERVATIONS

A visible residue was observed on samples 5 (Figure 1a) and 23 (Figure 1b), both of which were treated by poultice, but one with deionised water and the other with tap water. Residues were not observed on each of the other two samples

SAMPLE	WATER TYPE	TREATMENT	TREATMENT DURATION
1	Deionised	Soak	30 minutes
2	Deionised	Soak	6 hours
3	Deionised	Soak	24 hours
4	Deionised	Poultice	30 minutes
5	Deionised	Poultice	6 hours
6	Deionised	Poultice	24 hours
7	Deionised	Paste	30 minutes
8	Deionised	Paste	6 hours
9	Deionised	Paste	24 hours
10, 11 & 12	Tap	Soak	30 minutes
13, 14 & 15	Tap	Soak	6 hours
16, 17 & 18	Tap	Soak	24 hours
19, 20 & 21	Tap	Poultice	30 minutes
22, 23 & 24	Tap	Poultice	6 hours
25, 26 & 27	Tap	Poultice	24 hours
28, 29 & 30	Tap	Paste	30 minutes
31, 32 & 33	Tap	Paste	6 hours
34, 35 & 36	Tap	Paste	24 hours

Table 1. *Test sample categories*

treated in the same way and so the result did not conclusively indicate that the residues would always occur in those particular circumstances.

The residues appeared at the edge of the treatment area and could be described as a tideline, which may be indicative of the accumulation of material wicked to the edges during the drying process. In addition, after the soaking treatments, residues were observed on the sides of the glass beakers.

ANALYSIS

X-ray fluorescence spectroscopy (XRF)[i] was used to measure any elemental change at the surface and analyse residues. Though there was not enough material on the affected sample sherds to remove for analysis, there was enough residue material on the glass beakers used for the Biotex soaking treatments to collect for analysis. The XRF spectrum was compared to a Biotex powder reference spectrum (Figure 2).

Most of the elements detected in the residues could be explained as residual Biotex products; however, calcium was more strongly observed in the residues. Calcium carbonate and calcium sodium ethylenediamine tetra (methylene phosphonic acid) (EDTMP) are components of Biotex and could have contributed to this result. Biotex also includes calcium binders (sodium carbonate, sodium silicate, zeolite, sodium bicarbonate) that reduce the hardness of the water. Calcium may have been precipitated from the Biotex and tap water solution at the surface by these components, although residues were also observed on the deionsed water sample. Without sufficient material for analysis to compare the

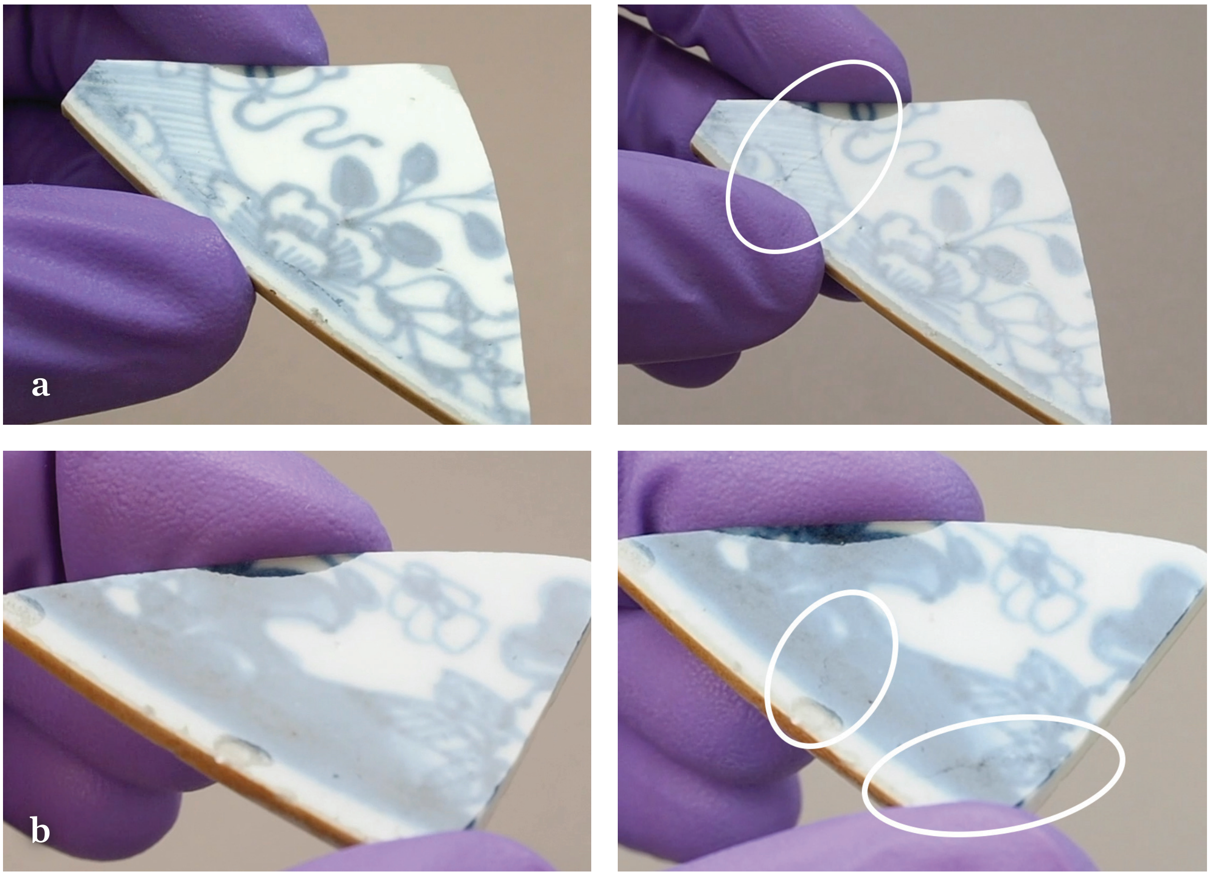

Figure 1. *Chinese underglaze blue hard-paste porcelain, 18th-century: a) video stills of sample 5 before treatment (left) and after treatment, with residues circled in white (right); b) video stills of sample 23 before treatment (left) and after treatment, with residues circled in white (right)*

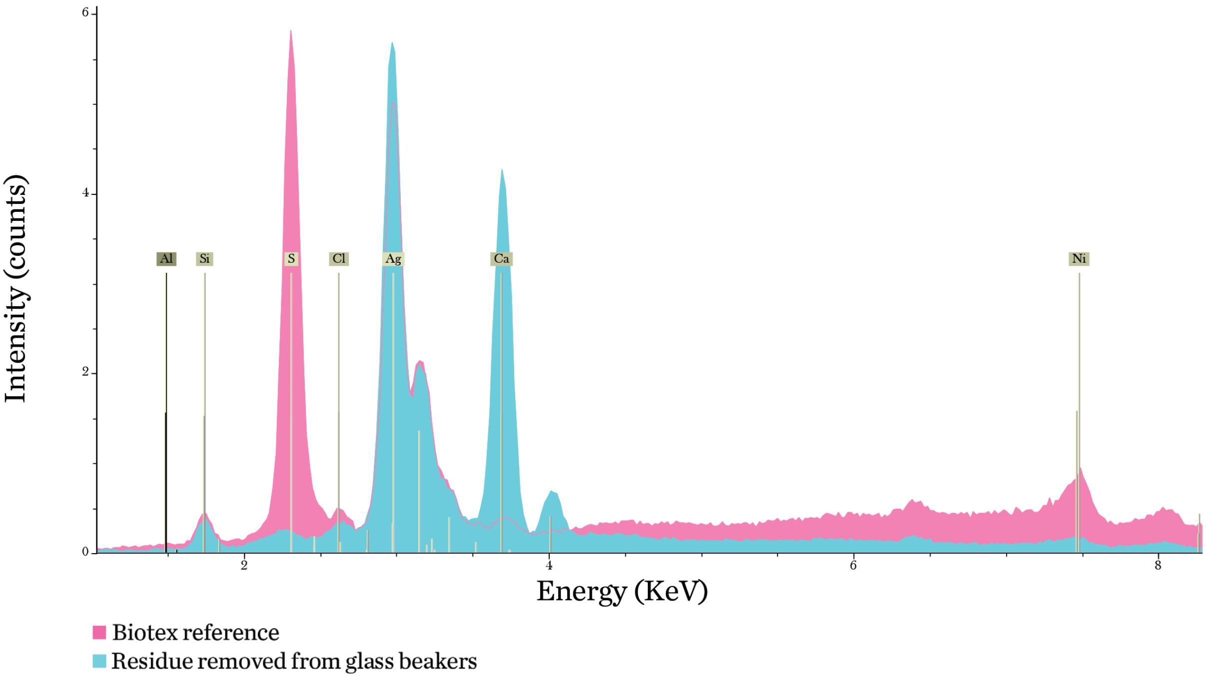

Figure 2. *XRF spectral overlay of Biotex (pink) and the first rinse residues (blue), removed from beakers that were used for soaking treatments*

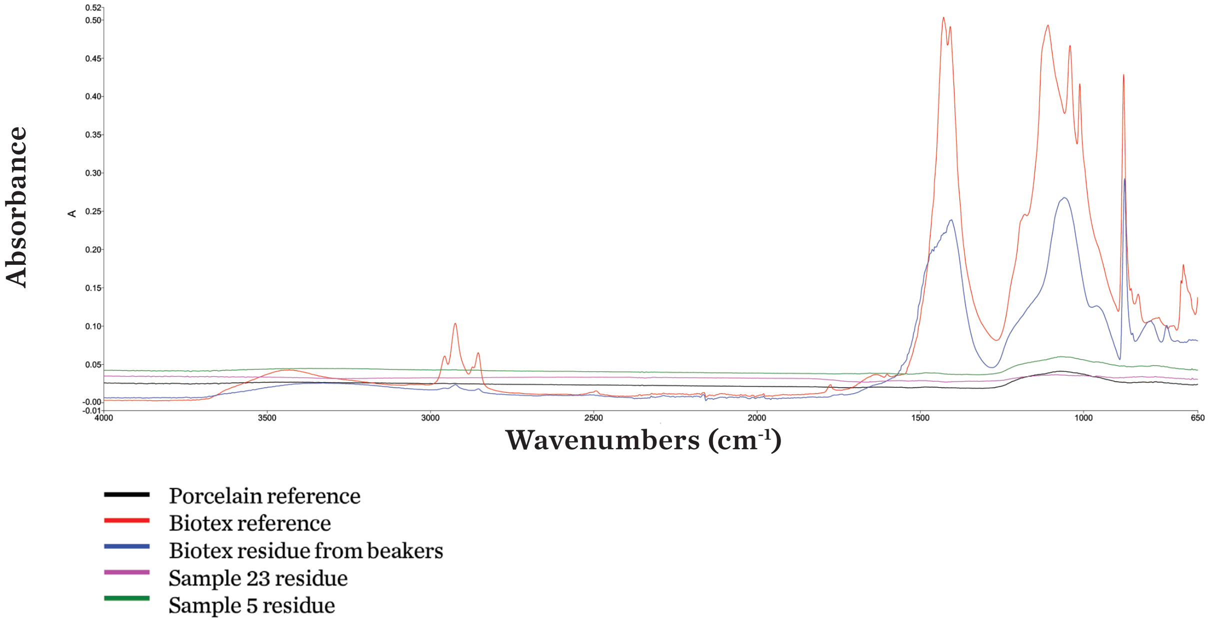

Figure 3. *FTIR spectral overlay of Biotex (red) and residues from test beakers (blue)*

tap water or deionised water residues, this theory cannot be confirmed. There is also a concern that the calcium could have been leached from the glaze by ion exchange due to the increased alkaline environment created by the Biotex, although no damage could be seen on the surface.

Fourier transform infrared (FTIR) spectroscopy[ii] was also used to analyse residues. The Biotex reference spectra was also compared with residue from the glass beakers (Figure 3). There was enough residue available from the glass beakers to be removed for FTIR analysis with the attenuated total reflectance (ATR) mode.

The FTIR results corroborate the conclusions drawn from the XRF findings: an aluminosilicate peak was found at 1059 cm^{-1} and a sharp O-C-O bending band at 874 cm^{-1}, indicating that the material removed from the glass beaker was primarily composed of residual Biotex components, namely zeolites and calcium carbonate.

CONCLUSION

The presence of aluminosiliates in residues from Biotex treatments was detected with XRF and FTIR, indicating zeolites are present in the residues. The source of calcium carbonate is difficult to determine. Both calcium carbonate and zeolites are insoluble in water, which may make them difficult to remove.

The analysis outlined in this study could be improved by the introduction of Secondary Ion Mass Spectroscopy (SIMS) depth profile analysis. The technique would allow for identification of the residues without removal, and observation of alkali attack, if that were happening.

ACKNOWLEDGEMENTS

I would like to express great appreciation to Lorna Calcutt, David Dorning, Professor Norman Billingham, Eric Nordgren, and Dr. John Agger for their assistance with analytical aspects of the project. Lauren Fair and Catherine Matsen from Winterthur Museum, and the Conservation team at the British Museum must also be thanked for kindly providing unpublished reports essential in forming the methodology of this project.

This project would not have been possible without the support of the Anna Plowden Trust, Edward James Foundation, Ernest Cook Charitable Trust, and Skinners Company.

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SELECTED MATERIALS

Biotex®: Unilever. Contains: Sodium sulfate, Sodium carbonate, Sodium Dodecylbenzenesulfonate, Sodium Silicate, Zeolite, Carboxylic Acid (C12-15 Pareth-7), Stearic Acid, Sodium Acrylic Acid/MA Copolymer, Perfume, Sodium chloride, Cellulose Gum, Sodium bicarbonate, Tetrasodium Etidronate, Calcium sodium EDTMP, Cellulose, Calcium carbonate, PEG-75, Kaolin, Titanium dioxide, Dextrin, Subtilisin, Sucrose, Sorbitol, Corn Starch Modified, Lipase, Amylase, Hydroxypropyl methyl cellulose, Disodium Distyrylbiphenyl Disulfonate, Sodium Thiosulfate, Mannanase. https://www.unilever.nl/merken/home-care/biotex.html (accessed 05 July 2019).

NOTES

[i] Bruker S1 Turbo Por X-Ray Fluorescence Spectrometer at 55 µA, 15kV, 60 seconds to detect lighter elements aluminium and silicon.

[ii] The attenuated total reflectance (ATR) attachment of a Perkin Elmer Frontier Spectrometer was preferred although the diffuse reflectance (DRIFTS) attachments were also used when there was not enough residual material to remove for ATR analysis.