

CHAPTER X

IN SITU METHODOLOGY FOR COMPOSITIONAL GROUPING OF MEDIEVAL STAINED GLASS WINDOWS: INTRODUCING THE “WINDOLYZER” FOR pXRF

L. W. ADLINGTON, I. C. FREESTONE, L. SELIGER,
M. MARTINÓN-TORRES, F. BROCK, A. SHORTLAND

Abstract

A materials science approach can illuminate our understanding of the life history of medieval stained glass windows; however, chemical analysis has been inhibited by their architectural context, preventing the removal of samples. Non-invasive techniques that can be used *in situ*, such as handheld/portable X-ray fluorescence spectrometry (pXRF), are thus very important to this field of study, yet this technique is also impeded by significant obstacles: the presence of deterioration and painted detail (subject of a previous paper) and the protrusion of the lead comes which hold the individual pieces together. In the present paper, we address the obstacle that lead comes present for *in situ* analysis and offer a simple, inexpensive and adaptable solution in the form of a 3D-printed attachment (a window analyzer, or “WindoLyzer”) that allows control over the working distance between spectrometer and sample. This simple modification to the standard pXRF system combined with empirical calibrations allows precise, reproducible results with a level of accuracy sufficient to distinguish compositional groups. We then present a case study in which this development is put to practice to answer important questions related to the history of conservation of a medieval panel from Canterbury Cathedral. This technique has allowed the recognition of previously unidentified repairs to the original panel, and shown that late eighteenth century craftsmen were recycling medieval glass to execute their work. Particularly promising is the ability to distinguish different groups of glass which are clearly of medieval origin, opening the way for future studies on the movement of glass in the medieval period.

Introduction

The later medieval period saw a tremendous rise in the construction of cathedrals and churches, underpinning an immense industry and resulting in a sharp increase in the demand for glass to fill the windows. Stained glass windows were increasingly important to medieval culture as symbols of iconography and prestige, and they represent a complex *chaîne opératoire*. A materials science approach can illuminate our understanding of the life history of medieval windows, including the identification of different sources of glass and their provenance¹, the investigation of glass-making technology including the generation of different colors², and the identification and dating of infill glass used in later repairs³.

The study of medieval stained glass windows by chemical analysis has been inhibited by their architectural context; their position embedded in the walls of cathedrals and churches makes the removal of samples impossible unless the window is dismantled, an expensive and intensive undertaking. Therefore, the removal of samples is generally only feasible when a conservation program demands the dismantling of the window as well as the removal of the lead strips, called comes, that hold the glass pieces together. Non-invasive techniques that can be used *in situ*, such as handheld

¹ Laura W. Adlington et al., “Regional Patterns in Medieval European Glass Composition as a Provenancing Tool,” *Journal of Archaeological Science* 110 (2019): 104991, <https://doi.org/10.1016/j.jas.2019.104991>.

² Laura W. Adlington and Ian C. Freestone, “Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements,” *MRS Advances* 2, no. 33–34 (2017): 1785–1800, <https://doi.org/10.1557/adv.2017>.

³ David Dungworth, “The Value of Historic Window Glass,” *The Historic Environment* 2, no. 1 (2011): 21–48, <https://doi.org/10.1179/175675011X12943261434567>.

(portable) X-ray fluorescence spectrometry (pXRF), are of utmost importance in instances where sampling is impossible, and the technique has been used successfully for the chemical characterization of post-medieval window glass⁴. However, the use of handheld pXRF to analyze medieval stained glass is impeded by two significant obstacles: (1) the presence of deterioration and painted detail, which for the purpose of analysis creates a layer of modified composition and means the results will not accurately reflect the bulk glass, and (2) the presence of the lead comes, which prevents the placement of the spectrometer directly on the surface of the glass and results in reduced measured X-ray intensity.

In our recent work on dismantled windows⁵, we addressed the problem of deterioration and poor surface conditions affecting analysis by handheld pXRF. The chemical composition of medieval glass, with characteristically low silicon and high potassium and calcium, makes it one of the least durable glasses of pre-modern times. Several environmental factors drive the deterioration of medieval stained glass windows, the most compelling of which is rainwater⁶, which reacts with the glass in such a way that results in leaching; the formation of corrosion crusts, cracks and pits; and the dissolution of the silica network⁷. Leaching is the process by which modifying ions are drawn out from the surface layer of the glass and replaced by the diffusion of hydrogen-containing species from the rainwater⁸. Compounds in the rainwater, absorbed from atmospheric gases, form hard crusts of sulfates, carbonates, chlorides and nitrates of the modifiers as well as organic compounds⁹. Corrosion crusts commonly identified on medieval stained glass include gypsum and syngenite, though a wide range of crystalline phases have been identified¹⁰. Furthermore, medieval stained glass pieces often have decorative details, including a grey-, black- or brown-monochrome pigment called grisaille, which is often rich in lead and iron¹¹, and yellow stain, composed of a silver compound and sometimes copper¹². Some metals, in particular lead, have been found to diffuse into the surrounding glass, suggesting that even

⁴ David Dungworth, "Historic Windows: Investigation of Composition Groups with Nondestructive pXRF," *Glass Technology: European Journal of Glass Science and Technology Part A* 53, no. 5 (2012): 192–97; Rebecca B. Scott et al., "In Situ Analysis of Ancient Glass: 17th Century Painted Glass from Christ Church Cathedral, Oxford and Roman Glass Vessels," *Glass Technology: European Journal of Glass Science and Technology Part A* 53, no. 2 (2012): 65–73.

⁵ Adlington and Freestone, "Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements."

⁶ Lucile Gentaz et al., "Early Stage of Weathering of Medieval-like Potash – Lime Model Glass: Evaluation of Key Factors," *Environmental Science and Pollution Research* 18 (2011): 291–300, <https://doi.org/10.1007/s11356-010-0370-7>.

⁷ Sandra Davison and Roy G. Newton, *Conservation and Restoration of Glass* (Oxford: Butterworth-Heinemann, 2008).

⁸ Noemí Carmona, "Corrosion of Stained Glass Windows: Applied Study of Spanish Monuments of Different Periods," in *Modern Methods for Analysing Archaeological and Historical Glass*, ed. Koen Janssens (Chichester, UK: John Wiley & Sons, 2013); José-María Fernández-Navarro and María-Ángeles Villegas, "What Is Glass? An Introduction to the Physics and Chemistry of Silicate Glasses," in *Modern Methods for Analysing Archaeological and Historical Glass*, ed. Koen Janssens (Chichester, UK: John Wiley & Sons, 2013), 1–22, <http://onlinelibrary.wiley.com/book/10.1002/9781118314234>; Michael Melcher, Rita Wiesinger, and Manfred R. Schreiner, "Degradation of Glass Artifacts: Application of Modern Surface Analytical Techniques," *Accounts of Chemical Research* 43, no. 6 (2010): 916–26, <https://doi.org/10.1021/ar9002009>.

⁹ Michael Melcher and Manfred R. Schreiner, "Leaching Studies on Naturally Weathered Potash-Lime-Silica Glasses," *Journal of Non-Crystalline Solids* 352, no. 5 (May 2006): 368–79, <https://doi.org/10.1016/j.jnoncrysol.2006.01.017>; Roy G. Newton, *The Deterioration and Conservation of Painted Glass: A Critical Bibliography*, Corpus Vitrearum Medii Aevi Great Britain Occasional Papers II (Oxford: Oxford University Press, 1982); Jérôme Sterpenich and Guy Libourel, "Les Vitraux Médiévaux: Caractérisation Physico-Chimique de l'altération," *Technique* 6 (1997): 70–78; Gebhard Woisetschläger et al., "Weathering Phenomena on Naturally Weathered Potash-Lime-Silica-Glass with Medieval Composition Studied by Secondary Electron Microscopy and Energy Dispersive Microanalysis," *Mikrochimica Acta* 135 (2000): 121–30.

¹⁰ N. Carmona et al., "Analysis of Corroded Glasses by Laser Induced Breakdown Spectroscopy," *Spectrochimica Acta - Part B Atomic Spectroscopy* 60, no. 7–8 (2005): 1155–62, <https://doi.org/10.1016/j.sab.2005.05.016>; Tiziana Lombardo et al., "Characterisation of Complex Alteration Layers in Medieval Glasses," *Corrosion Science* 72 (2013): 10–19, <https://doi.org/10.1016/j.corsci.2013.02.004>; Melcher and Schreiner, "Leaching Studies on Naturally Weathered Potash-Lime-Silica Glasses."

¹¹ N. Carmona et al., "Study of Glasses with Grisailles from Historic Stained Glass Windows of the Cathedral of León (Spain)," *Applied Surface Science* 252, no. 16 (2006): 5936–45, <https://doi.org/10.1016/j.apsusc.2005.08.023>; Andreia Machado et al., "Swiss Stained-Glass Panels: An Analytical Study," *Microscopy and Microanalysis*, 2017, <https://doi.org/10.1017/S1431927617000629>; Trinitat Pradell et al., "Materials, Techniques, and Conservation of Historic Stained Glass 'Grisailles,'" *International Journal of Applied Glass Science* 7, no. 1 (2016): 41–58, <https://doi.org/10.1111/ijag.12125>; L. Van Wersch et al., "Analyses of Early Medieval Stained Window Glass From the Monastery of Baume-Les-Messieurs (Jura, France)," *Archaeometry* 58, no. 6 (2016): 930–46, <https://doi.org/10.1111/arcm.12207>.

¹² An Yu Zhang, Tatsuya Suetsugu, and Kohei Kadono, "Incorporation of Silver into Soda-Lime Silicate Glass by a Classical Staining Process," *Journal of Non-Crystalline Solids* 353 (January 2007): 44–50, <https://doi.org/10.1016/j.jnoncrysol.2006.09.033>; D. Jembrih-Simbürger et al., "The Colour of Silver Stained Glass-Analytical Investigations Carried out with XRF, SEM/EDX, TEM, and IBA," *Journal of Analytical Atomic Spectrometry* 17 (April 4, 2002): 321–28, <https://doi.org/10.1039/b111024c>; J.

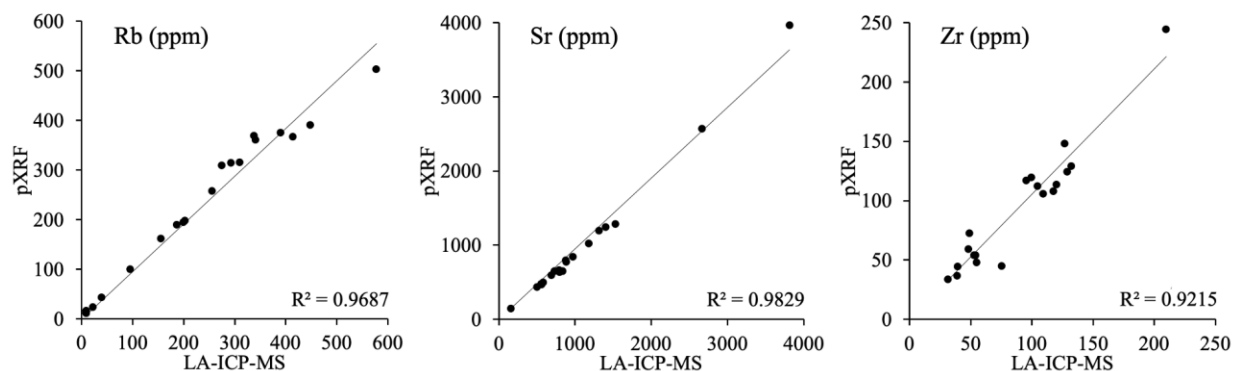


Figure X-1 Analysis of medieval and post-medieval window glass from the Great East Window of York Minster¹⁶, comparing LA-ICP-MS¹⁷ and pXRF¹⁸ measurements of Rb, Sr and Zr. Trendlines are forced through zero.

if an area of glass that appears to be free of grisaille is selected for analysis, there may be some migration of certain elements affecting the analysis¹³. These phenomena affect the analysis of several elements, in particular lower Z elements (including K, Ca and above) that are measured from more shallow depths within the glass¹⁴. We have attempted to minimize the effects of these surface compositional changes in our work by analyzing windows which have been cleaned for conservation and/or restoration. In these circumstances, any surface deposits which interfere with light transmission through the window and are not firmly bound are removed. Furthermore, many of the windows of interest were “cleaned” prior to WWII, when they were subjected to relatively rigorous surface abrasion. With these points in mind, we have shown that in principle it should be possible to use a pXRF spectrometer to analyze medieval windows using a few, well-measured heavy trace elements, which had previously been used to classify post-medieval glass types by David Dungworth¹⁵. Rb and Sr were used as proxies for major elements K and Ca respectively, which are related to the potash- and lime-rich vegetal ash in the glassmaking recipe, while Zr is related to the heavy minerals in the glassmaking sand. These may be used to distinguish different production groups in the supply to the window as well as identifying non-original glass used in repairs. Since then, we have analyzed a subset of medieval and post-medieval window glass by both LA-ICP-MS and handheld pXRF^{16,17,18}, showing good agreement between the methods and allowing tailored empirical calibration (**Figure X-1**).

In the present paper, we address the obstacle that lead comes present for *in situ* analysis. Lead comes used in medieval windows can protrude some 4-5mm, increasing the distance between the spectrometer and glass that varies unsystematically from sample to sample (**Figure X-2**). We evaluate the effect this has on analysis of medieval window glass and present a simple, inexpensive and adaptable solution in the form of a 3D-printed attachment, which maintains

Delgado et al., “Characterisation of Medieval Yellow Silver Stained Glass from Convento de Cristo in Tomar, Portugal,” *Nuclear Instruments and Methods in Physics Research B* 269, no. 20 (2011): 2383–88, <https://doi.org/10.1016/j.nimb.2011.02.059>.

¹³ Márcia Vilarigues and R. C. da Silva, “Ion Beam and Infrared Analysis of Medieval Stained Glass,” *Applied Physics A: Materials Science & Processing* 79 (2004): 373–78, <https://doi.org/10.1007/s00339-004-2538-9>.

¹⁴ Adlington and Freestone, “Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements”; Bruce Kaiser and Aaron N. Shugar, “Glass Analysis Utilizing Handheld X-Ray Fluorescence,” in *Handheld XRF for Art and Archaeology*, ed. Aaron N. Shugar and Jennifer L. Mass, Studies in Archaeological Sciences (Leuven, Belgium: Leuven University Press, 2012), 449–70.

¹⁵ Dungworth, “Historic Windows: Investigation of Composition Groups with Nondestructive pXRF.”

¹⁶ 19 glass pieces from the Great East Window of York Minster (early 15th century) were analysed by both methods. This group includes multiple medieval colours and compositions, as well as post-medieval high lime low alkali glass (HLLA), kelp ash glass, and synthetic soda glass. Analyses by pXRF were carried out on the surface of the glass, while the LA-ICP-MS analyses were carried out on samples removed from the glass pieces, which were embedded in epoxy resin with the cross-section exposed and polished to 1µm.

¹⁷ The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses were carried out at the Rutherford Laboratory at the Cranfield Forensic Institute using a New Wave 213 laser attached to a Thermo Series II ICP-MS using the parameters reported in: Rita Giannini, Ian C. Freestone, and Andrew J. Shortland, “European Cobalt Sources Identified in the Production of Chinese Famille Rose Porcelain,” *Journal of Archaeological Science* 80 (2017): 27–36, <https://doi.org/10.1016/j.jas.2017.01.011>, with a few variations: RF power: 1350-1450W, nebulizer gas flow rate: 0.65-0.8 L/min, extraction -610 to -630V, dwell time 20ms, 18-20 sweeps, fluence >15 J/cm, carrier gas flow rate (He): 500-550 L/min.

¹⁸ The pXRF analyses were conducted using the parameters reported in: Adlington and Freestone, “Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements.”



Figure X-2 Lead comes can protrude multiple millimeters, and together with the use of small pieces of glass, prohibit the placement of the pXRF spectrometer directly on the surface of the glass for analysis. The panel in this image has been recently conserved and releaded, and the modern lead comes in these panels protrude by about 2-4mm.

a constant distance between spectrometer and sample. This simple modification to the standard pXRF system allows precise, reproducible results with a level of accuracy sufficient to distinguish compositional groups. We then present a case study in which this development is put to practice, allowing the identification of original and non-original glass in a 12th century panel from Canterbury Cathedral.

The interference of lead comes on *in situ* analysis

The interference of lead comes on the analysis of windows is a problem with particular relevance to medieval stained glass, though it is not limited to windows of this period. Color in medieval stained glass windows was achieved through the use of differently colored glass pieces (with the exception of yellow stain¹⁹) rather than the use of enamels on the surface of a glass pane, which was an approach widely used in the post-medieval period. The glass pieces were cut into shapes joined together with lead strips, or comes, which have an H-shaped cross-section. The pieces of glass held by the comes are often too narrow or otherwise incompatible to accommodate the dimensions of the face of a commercially available handheld pXRF²⁰. The lead comes can therefore prevent the placement of the spectrometer flush against the surface of the glass material for analysis for all but the largest pieces of glass.

The problem of distance between sample and detector is not a new one for pXRF analysis, and has been previously addressed in the context of materials that do not have completely flat surfaces, creating distance between the detector and (parts of) the sample, and thereby resulting in reduced intensity. The lost intensity is attributed both to the absorption of the X-rays (both incident and characteristic) in air, and to the changed angle of detection affecting the

¹⁹ A cementation technology used on window glass from the early 14th century, in which a silver compound dispersed in a carrier medium such as clay or ochre was fired onto the surface of the glass at a temperature below the softening point, in order to apply a yellow colour to the surface of window glass pieces. Gloria Molina et al., “Color and Dichroism of Silver Stained Glasses,” *Journal of Nanoparticle Research* 15, no. 9 (2013): 1–13; Delgado et al., “Characterisation of Medieval Yellow Silver Stained Glass from Convento de Cristo in Tomar, Portugal”; Jembrih-Simbürger et al., “The Colour of Silver Stained Glass-Analytical Investigations Carried out with XRF, SEM/EDX, TEM, and IBA”; Zhang, Suetsugu, and Kadono, “Incorporation of Silver into Soda-Lime Silicate Glass by a Classical Staining Process”; W. A. Weyl, *Coloured Glasses* (Sheffield: The Society of Glass Technology, 1951).

²⁰ For example, the spectrometer used in this study (the Innov-X/Olympus Delta Premium DP-6000CC) has a face with the dimensions 7.5 x 2.7cm.

relative intensity of the scatter peaks²¹ as well as the absorption path of the X-rays through the sample. The lost intensity caused by irregular surfaces can be corrected by normalizing the intensity of characteristic peaks to the intensity of scatter peaks (Rayleigh scatter is preferred for this purpose, although Compton scatter is also sufficient); however, this correction is considered suitable only for distances of up to 1 mm to mid-Z elements and up to 3 mm for heavy elements²².

The likelihood that the distance between spectrometer and sample will frequently exceed 3 mm in medieval windows encased in lead comes is a key obstacle for the analysis by handheld pXRF. The results of tests on dismantled medieval window glass pieces, in which analyses were conducted at increasing distance (or added working distance, AWD), show that some elements (Fe, Cu and Pb) do not behave predictably due to the presence of grisaille and yellow stain and an inability to aim the spectrometer's beam at increased distances (**Figure X-3**). However, for the heavy elements of interest (Rb, Sr, and Zr), the increased distance results in reduced apparent concentrations despite normalization to the Compton scattering (**Figure X-3**). In theory, this problem may be corrected through the application of empirical calibrations developed by analyzing matrix-matched standards. However, a further complication stemming from *in situ* conditions is the variation in the distance between spectrometer and sample for each sample, severely disrupting the precision of the data. This is illustrated in **Figure X-4**, which shows the analysis of the same medieval window glass pieces²³ first using a test stand on a dismantled panel (**Figure X-4**, left) and then

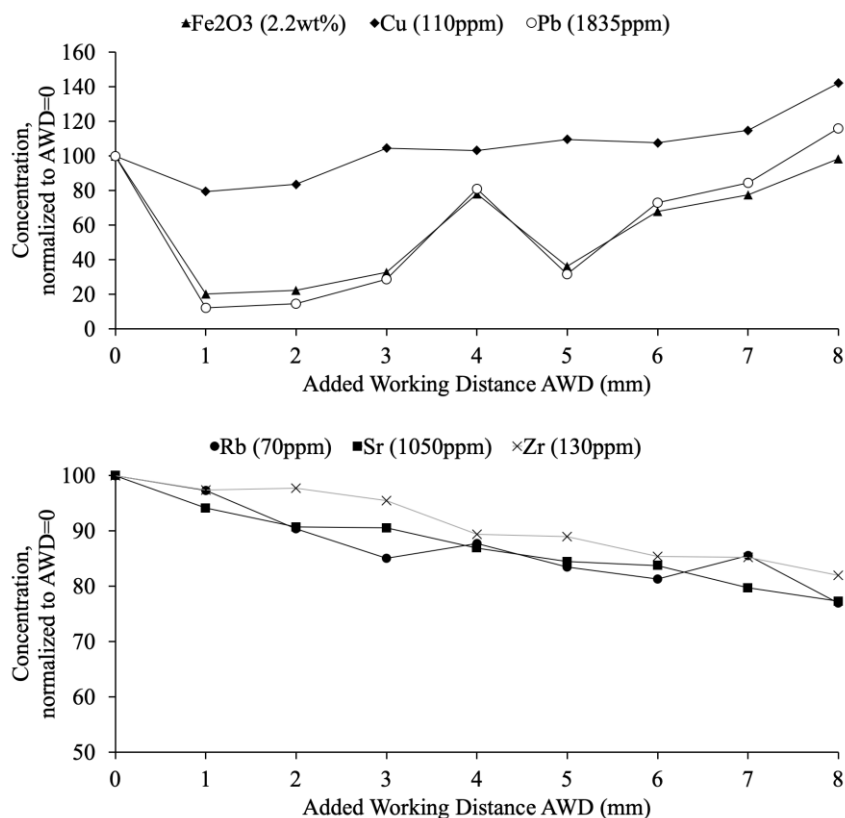


Figure X-3 Tests analyzing medieval window glass pieces at increasing distances to show the behavior of different elements; concentrations at each AWD are normalized to the measurement taken at AWD=0 (i.e., directly on the surface of the glass). Measured concentrations of Fe, Cu and Pb are influenced by the presence of grisaille and yellow stain, and the difficulty in aiming the spectrometer at clean areas of the glass. However, Rb, Sr and Zr show a steady decrease in the measured concentrations with increasing distance, despite normalization to the Compton scattering.

²¹ Philip J Potts, Peter C Webb, and Olwen Williams-Thorpe, "Investigation of a Correction Procedure for Surface Irregularity Effects Based on Scatter Peak Intensities in the Field Analysis of Geological and Archaeological Rock Samples by Portable X-Ray Fluorescence Spectrometry," *Journal of Analytical Atomic Spectrometry* 12, no. July (1997): 769–76.

²² Potts, Webb, and Williams-Thorpe; Detlef Wilke, Dagmar Rauch, and Patrick Rauch, "Is Non-Destructive Provenancing of Pottery Possible With Just a Few Discriminative Trace Elements?," *STAR: Science & Technology of Archaeological Research* 0, no. 0 (2016): 1–18, <https://doi.org/10.1080/20548923.2016.1209030>.

²³ Adlington and Freestone, "Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements."

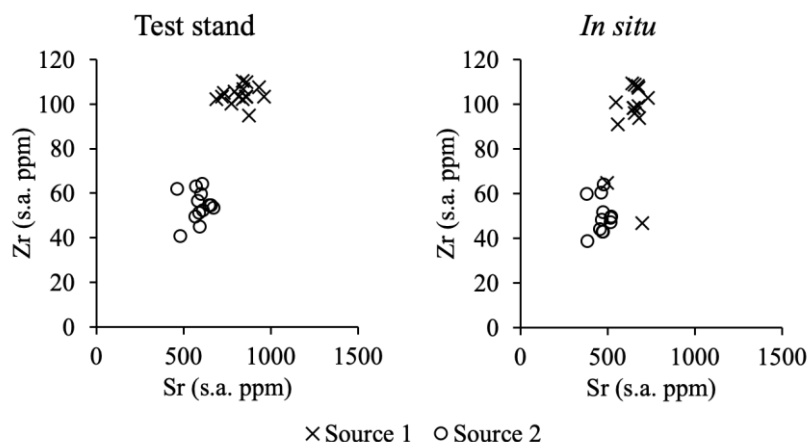


Figure X-4 Analysis of the same medieval panel using handheld pXRF with a test stand (left) and again under *in situ* conditions (i.e., after the panel had been reinstated within lead came; right). The concentrations are reported as “s.a. ppm” or surface analysis ppm, to emphasize that the data is semi-quantitative (see later section). The two groups observed in the test stand analyses (as well as in major elements characterized by electron microprobe) reflect two production groups that have been connected to different sources, one in England and in continental Europe²³. In the *in situ* analyses, there is an overall decrease in the concentrations, particularly in the Sr contents; variable degrees of interference by the lead came has resulted in the misidentification of two samples.

in situ, after the panel had been conserved and releaded (**Figure X-4**, right). Two of the samples could not be analyzed *in situ* because they were too small and too close to the edge of the panel, where the encasing frame became a large obstacle. For the glass pieces that could be analyzed *in situ* measured concentrations of the elements of interest were typically 10-20% lower than the analyses of the same pieces removed from the window. Furthermore, analyses of some samples were affected so severely that they were apparently assigned to the wrong compositional group (**Figure X-4**, right).

Our solution is based upon the premise that if the AWD can be controlled and kept constant during *in situ* analyses, the results may be corrected through empirical calibration based on matrix-matched standards. Calibration curves (forced through 0) based on the analysis of up to 25 glass standards (dependent on the element analyzed, as some standards do not have certified concentrations for all elements) were developed for analyses carried out on the surface of the glass (AWD=0) and at a 5mm distance (AWD=5). **Table X-1** reports the coefficient of determination (R^2) of the calibration curve for several elements at both AWD=0 and AWD=5; R^2 is used here to quantify how well the analyzed data are in agreement with the known compositions of the standards (not as a measure of accuracy, but how well the data can be corrected through linear calibration). These numbers compare favorably, supporting the idea that if the distance is held constant during the *in situ* analysis of medieval windows, the reduced intensity resulting from a higher AWD can be corrected through empirical calibration while maintaining good precision.

Adaptation of instrumentation

An attachment for the Innov-X/Olympus DP6000CC was designed and 3D-printed with the purpose of bypassing the lead came and maintaining a constant distance from the glass surfaces. The window analyzer attachment, nicknamed the WindoLyzer 5 (referring to the 5 mm AWD), was designed using a freely available, simple to use, browser-based program called Tinkercad (tinkercad.com, **Figure X-5**). Since most lead came in the case study only protrude 3-4 mm, an AWD of 5 mm was chosen, with accommodation up to 4 mm for lead came protrusion; however, this distance could be easily adjusted on Tinkercad and reprinted. The design was imported to the Cura software for selection of printing parameters (100% fill density, print speed 80m/s, layer height 0.1mm, shell thickness 1.2mm and bottom/top thickness 0.8mm) and creation of the gcode file for input into the printer. The WindoLyzer 5 was printed in polylactic acid (PLA) using the Ultimaker2 3D printer with a 0.4mm nozzle at the UCL Institute of Making with a printing time of 3-4 hours. The supports on the printed WindoLyzer 5 were then removed with a scalpel and where needed, it was sanded with 2500 grit sand paper to smooth any jagged edges that might damage the glass surface. A fabric strap with Velcro was devised to securely fix the attachment to the spectrometer for analysis (**Figure X-5**).

Table X-1 The coefficient of determination (R^2) of the calibration curves (forced through zero) for several elements for analyses undertaken directly on the surface of the standards (i.e., with no added working distance, AWD=0mm) and with AWD=5mm. The calibration curves are based on the pXRF analysis of up to 25 glass standards. R^2 is used here to quantify how well the analyzed data can be corrected through linear calibration, with values approaching 1 indicating a good fit.

	R^2 (0mm)	R^2 (5mm)
K	0.988	0.989
Ca	0.988	0.988
Ti	0.992	0.989
Mn	0.995	0.993
Fe	0.999	0.998
Co	0.954	0.976
Ni	0.983	0.993
Cu	0.994	0.995
Zn	0.996	0.996
Rb	0.999	0.999
Sr	0.989	0.991
Zr	0.982	0.981
Pb	0.962	0.967

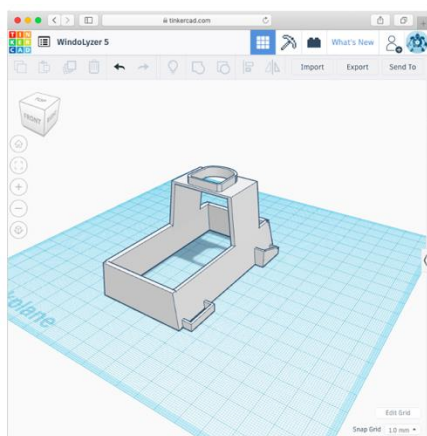


Figure X-5 A window analyzer attachment nicknamed the WindoLyzer 5 was designed using tinkercad.com (top left) and 3D printed at the Institute of Making at UCL. The attachment is secured to the spectrometer using Velcro on a fabric strap (bottom left) and used to analyze the Methuselah panel from Canterbury Cathedral (right).

The handheld pXRF analyses were carried out using an Innov-X/Olympus Delta Premium DP6000CC spectrometer, which has a Rh anode, a silicon drift detector and a spot size of 10mm. The built-in program called the “Soils” mode was chosen for analysis, as this mode is optimized for oxygen-rich matrices and uses normalization to the Compton scatter peak rather than fundamental parameters for quantification. The Soils mode uses three so-called “beams”, or settings with different combinations of primary radiation voltage, current and filters. Beam 1 operates with a 40kV accelerating voltage, 89 μ A tube current, and a 1.5mm copper filter (optimized for heavier elements with higher energy characteristic X-rays); Beam 2 uses a 40kV accelerating voltage, 52 μ A tube current, and a 2.0mm aluminum filter (targeting mid-Z elements); and Beam 3 runs with a 15kV accelerating voltage, 68 μ A tube current, and a 0.1mm aluminum filter (for the analysis of lighter elements with lower energy characteristic X-rays). The three beams were run sequentially for 10s, 5s and 5s respectively for a total of 20s in real time. The pXRF data is transformed into element concentrations by the Innov-X/Olympus algorithm, proprietary information which includes Compton normalization as well as other necessary corrections. The concentrations were further corrected using empirical calibrations based on the analysis of matrix-matched standards, with the WindoLyzer 5 in position. Corning D was used as a secondary standard to measure accuracy²⁴ and precision with satisfactory results (**Table X-2**).

As the WindoLyzer 5 was printed in a material composed of very light elements (polylactic acid, C₃H₄O₂), it will not interfere with analysis but also will not stop scattered X-rays, potentially increasing radiation risks to the user. Tests using a Geiger counter showed negligible increase in the radiation dose rate to the analyst when standing behind the spectrometer (for *in situ* analyses or using a vertical lightbox or stand). If, however, the analyst is standing to the side of the spectrometer (for example, for tabletop analyses), there is an increase in the dose rate and therefore in such instances, a lead shield should be used for personal protection, which is already standard practice at the UCL Institute of Archaeology.²⁵

Table X-2 The mean of repeated analyses ($n=39$) of Corning D compared to the accepted concentrations²⁴, with accuracy and precision (RSD) reported. Oxide concentrations are given in weight percent, and elemental concentrations are reported as parts per million. The elements of interest for this paper are Rb, Sr and Zr.

	Mean	Accepted	Accuracy	RSD
K₂O	10.88	11.3	-3.7	3.8
CaO	14.35	14.8	-3.1	3.1
TiO₂	0.39	0.38	2.5	4.8
MnO	0.56	0.55	0.9	3.5
Fe₂O₃	0.52	0.52	-0.9	5.1
Co	176	181	-2.6	19.1
Ni	366	393	-6.8	8.8
Cu	2950	3036	-2.8	2.7
Zn	852	803	6.1	4.4
Rb	44	46	-4.2	9.9
Sr	489	482	1.5	2.8
Zr	94	93	1.3	7.0
Sn	789	788	0.2	4.2
Sb	7053	7302	-3.4	2.1
Ba	2736	2606	5.0	23.2
Pb	1959	2088	-6.2	2.5

²⁴ Accepted concentrations taken from Laura W. Adlington, “The Corning Archaeological Reference Glasses: New Values for ‘Old’ Compositions,” *Papers from the Institute of Archaeology* 27, no. 1 (2017): 1–8., and references therein.

²⁵ The maximum dose rate measured 50cm behind the spectrometer during operation was 0.5 μ Sv/h with a whole body dose equivalent of 13.1 μ Sv based on 260 hours of use annually (1 hour per working day). The maximum dose rate measured 20cm to the side of the spectrometer used together with a lead shield was 2.6 μ Sv/h with a whole body dose equivalent of 67.7 μ Sv based

Semi-quantitative data from surface analyses by pXRF

One of the referees of this paper cogently argued that XRF data generated on complete objects should not be quantified. They note, and we agree, that in the case of stained glass windows there will always be uncertainties associated with the inclusion of some corroded material in the analysis, possible attenuation due to surface deposits, and issues due to geometry. Thus the data cannot be considered fully quantitative and our groupings should be carried out using uncorrected, relative X-ray counts. There is strength to this argument, as there is a danger that readers unfamiliar with the analytical method might attempt to use the data to test hypotheses which require a much closer accuracy and precision than is possible. This is especially the case in art history and archaeology, where researchers come from a wide range of disciplinary specialisms.

In spite of the foregoing, we consider the quantification correction performed by our instrument, which produces data in a format that is readily comparable with other studies, to be an essential aspect of the present work, in spite of the uncertainties. In dealing with heritage materials, where access is expensive in terms of staff time in underfunded institutions, we have a duty to extract the maximum amount of information that we can from our analyses. Furthermore, this is the only accessible method at present which allows the analysis of in situ stained glass windows. The use of even approximate quantified data allows a far more useful interpretation than the use of (for example) peak areas. For example, an estimation of the actual concentrations of Rb and Sr can provide an indication of the amounts of K₂O and CaO, thus allowing the samples to be related to broad compositional categories of medieval glass, even although they cannot be closely compared with specific production sources. In the investigation of archaeological materials, including glass, there is a long history of using “quantified” XRF data obtained from the surface of whole artefacts²⁶ but these data are carefully interpreted by the authors who are typically aware of the potential problems. We acknowledge that use of these data as truly quantitative could lead to serious misinterpretations in cases where unanticipated errors are large. Therefore we label our data in graphs “s.a. ppm” (surface analysis ppm) to warn any potential user that they may be subject to errors which we cannot determine.

Case study: 12th century panel from Canterbury Cathedral

The focus of the case study is a figurative panel dated to the 12th century from Canterbury Cathedral, depicting the figure of Methuselah (**Figure X-6**), which is one of a series of panels depicting the ancestors of Christ. This series has been studied in detail through an art historical approach²⁷ and has a relatively well-documented conservation history. The ancestors were originally portrayed in pairs, one over the other, in the upper windows (clerestory) circling the choir, northeast and southeast transepts, presbytery and the Trinity Chapel at the eastern end of the cathedral. The original glazing and construction of the Methuselah panel has been dated to the late 1170s²⁸, as part of the earliest phase of construction during rebuilding works after a devastating fire in 1174. In the 1790s, the extant ancestor figures were removed from their original positions in the clerestory, adapted into their current rectangular form, and used to

on 260 hours of use annually. Both dosages are well within the annual dose limits dictated by the Ionising Radiation Regulations of 2017, which are set at 20mSv (20,000 µSv) for employees who work with radiation and 1mSv (1000 µSv) for the public. Calculations for converting measured dose rate to annual whole body equivalents, and the example annual number of hours of pXRF use, is based on: Marek Rouillon, Louise J. Kristensen, and Damian B. Gore, “Handheld X-Ray Fluorescence Spectrometers: Radiation Exposure Risks of Matrix-Specific Measurement Scenarios,” *Applied Spectroscopy* 69, no. 7 (2015): 815–22, <https://doi.org/10.1366/14-07809>.

²⁶ M. J. Hughes and J. A. Hall, “X-Ray Fluorescence Analysis of Late Roman and Sassanian Silver Plate,” *Journal of Archaeological Science* 6, no. 4 (1979): 321–44, [https://doi.org/10.1016/0305-4403\(79\)90017-7](https://doi.org/10.1016/0305-4403(79)90017-7); I. Nakai et al., “Development of a Portable X-Ray Fluorescence Spectrometer Equipped with Two Monochromatic x-Ray Sources and Silicon Drift Detector and Field Analysis of Islamic Glasses at an Excavation Site in Egypt,” *X-Ray Spectrometry* 34, no. 1 (2005): 46–51, <https://doi.org/10.1002/xrs.752>; S. Röhrs and H. Stege, “Analysis of Limoges Painted Enamels from the 16th to 19th Centuries by Using a Portable Micro X-Ray Fluorescence Spectrometer,” *X-Ray Spectrometry* 33, no. 6 (2004): 396–401, <https://doi.org/10.1002/xrs.713>; Olwen Williams-Thorpe, Philip J. Potts, and Peter C. Webb, “Field-Portable Non-Destructive Analysis of Lithic Archaeological Samples by X-Ray Fluorescence Instrumentation Using a Mercury Iodide Detector: Comparison with Wavelength-Dispersive XRF and a Case Study in British Stone Axe Provenancing,” *Journal of Archaeological Science* 26, no. 2 (1999): 215–37, <https://doi.org/10.1006/jasc.1998.0323>.

²⁷ Madeline H. Caviness, “Canterbury Cathedral Clerestory: The Glazing Programme in Relation to the Campaigns of Construction,” in *British Archaeological Association Conference Transactions, Vol 5: Medieval Art and Architecture at Canterbury before 1220*, vol. 5, 1982, 46–55; Madeline H. Caviness, *The Windows of Christ Church Cathedral Canterbury* (London: CVMA (GB) II, 1981).

²⁸ Richard Marks, *Stained Glass in England during the Middle Ages* (London: Routledge, 1993); Caviness, “Canterbury Cathedral Clerestory: The Glazing Programme in Relation to the Campaigns of Construction”; Caviness, *The Windows of Christ Church Cathedral Canterbury*.



Figure X-6 The figurative panel depicting Methuselah was once part of a series depicting the ancestors of Christ, originally decorating the windows of the clerestory at Canterbury Cathedral. The Methuselah figure and the other surviving ancestors were removed in the 1790s to large windows in the southwest transept and the west end. *Panels 2,3e from window SXXVIII at Canterbury Cathedral* © Dean and Chapter of Canterbury

glaze the great perpendicular windows in the cathedral's southwest transept and west end. The figure of Methuselah, which has since had its home in the Great South Window (GSW) of the Cathedral, was thus adapted through the addition of the arched frame above the figure's head; this glass, depicting *rincaux* (foliage decoration) on a red ground, is also medieval in appearance. Conservation records and close study have led to the identification of several other pieces of non-original glass within the panel, although the identification of some of the glass pieces as infills by Madeline Caviness²⁹ has been revisited during the most recent conservation.

The stonework of the GSW recently underwent seven years of restoration culminating in November 2016, providing a rare opportunity for both specialists and the public to examine the stained glass panels more closely. While the panels were removed from the window and cleaned by the conservators at The Cathedral Studios (such that no substantial corrosion crusts remain), they were not removed from their lead comes, providing an opportunity to test the use of the WindoLyzer against the identified areas of conservation.

²⁹ Caviness, *The Windows of Christ Church Cathedral Canterbury*.

Results

Eighty-nine pieces of glass from across the panel were analyzed by handheld pXRF using the WindoLyzer 5 with the instrument parameters reported above. The glasses comprise blue (dark and light shades), green, purple (or murry), red, white, yellow, and a pale flesh-toned color. The majority of the glasses have trace element compositions consistent with medieval glass made from relatively unrefined raw materials. The exceptions are three glass pieces with low trace element concentrations (<30ppm Rb, <200ppm Sr and <30ppm Zr), which are consistent with compositions of glass made with synthetic soda (produced in England post-1835)³⁰.

Several distinctive categories of medieval glass were detected, with varying concentrations of Rb, Sr and Zr (**Figure X-7**). For the purposes of this paper, these have been grouped by Sr contents, with Type A containing about 250ppm Sr, Type B containing about 530ppm Sr, and Type C containing about 1000ppm Sr.

The figurative part of the panel, comprising Methuselah, his throne and footstool, the blue background, the banner bearing his name, and the red band forming the arch above him, is considered largely original on historical and stylistic grounds and contains mostly the Type A glass ($n=63$). Type A glass is therefore considered to be the composition representing the glass used to make the original window. Nine samples have higher Sr (Type B), predominantly blue glass pieces. An exception is a yellow piece that also has higher Rb (374ppm), which may indicate this is a different glass type or may reflect the addition of potash in order to adjust the basicity and lower the melting temperature of the melt, assisting in the creation of yellow color by oxidized iron. This technique has been detected elsewhere³¹.

The glass pieces used in the area above the archway (added during the 1790s) are marked in **Figure X-7**, and comprise both Type A and Type C glass. Four of the five red glass pieces from the background are Type C with high Sr, while the majority (including one red glass piece from the background and nine variously colored pieces from the rinceaux of the foreground) are composed of the lower Sr Type A glass (**Figure X-8**). These Type A glasses in the frame, with similar Sr concentrations to the majority of the original glass from the figurative parts of the panel, nonetheless tend to have higher Rb (all but two samples contain 179-220ppm Rb, while the original glass contains 100-175ppm Rb and somewhat lower Zr (ranging 86-156ppm Zr in the non-original frame, and 108-177ppm in the original figure).

Discussion

The arched frame, which was added to the figure during the 1790s, has at least two types of medieval glass within it, and appears to have been made from glass amassed from different periods/windows. The areas above the archway

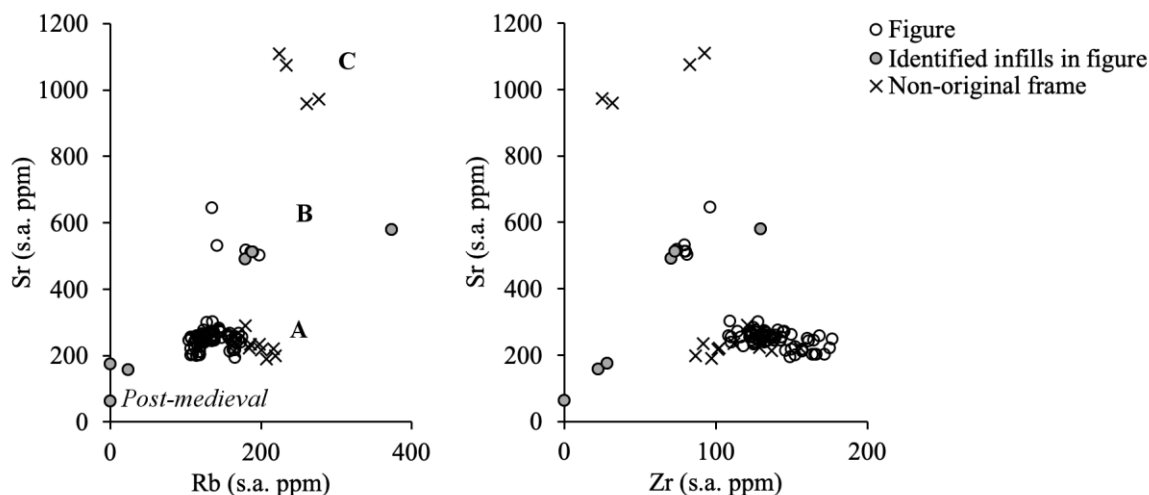


Figure X-7 Rb, Sr and Zr concentrations for the analyzed glass in the Methuselah panel. The concentrations are reported as “s.a. ppm” or surface analysis ppm, to emphasize that the data is semi-quantitative. Three glass pieces with low trace element concentrations are consistent with compositions of glass made with synthetic soda, and therefore identified as post-medieval. The remaining are consistent with medieval compositions, and are discussed in this paper in groups based on their Sr content: Type A (low Sr, about 250ppm), Type B (about 530ppm Sr), and Type C (containing about 1000ppm Sr).

³⁰ Dungworth, “Historic Windows: Investigation of Composition Groups with Nondestructive pXRF”; Dungworth, “The Value of Historic Window Glass.”

³¹ Adlington and Freestone, “Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements.”

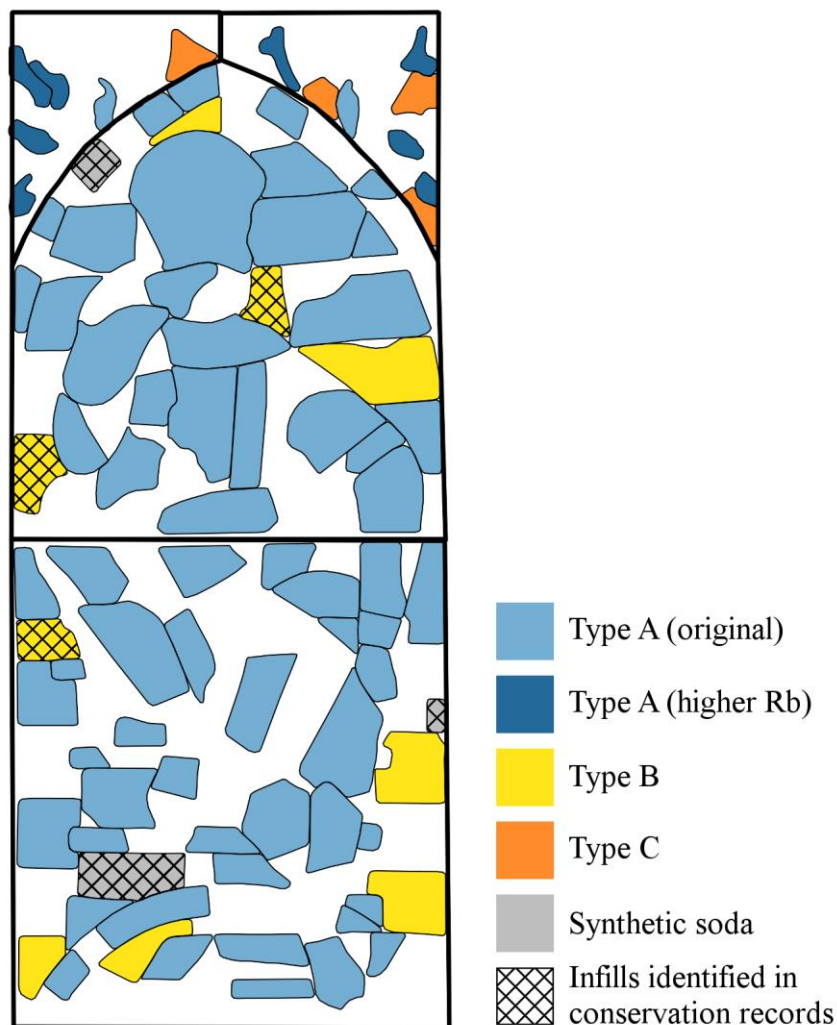


Figure X-8 Distribution of glass compositions within the Methuselah panel. Non-original infill glass identified in conservation records are also marked.

contain several pieces that are similar in composition to the original glass used to glaze the 1170s figure of Methuselah, although with some minor differences in their Rb, and to a lesser extent Zr, concentrations. This glass probably shares a source/origin with the original glass, but is possibly from a window that pre- or post-dates the ancestor series.

Six of the analyzed glass pieces from within the original, figurative part of the panel were previously identified as repairs or replacements in conservation records or through art historical study. Of these, three were identified as glass made with synthetic soda, dating them to sometime after 1835. The remainder are Type B glass pieces, including the high-Rb yellow and two blue pieces. During the most recent conservation intervention, however, the identification of those two blue glass pieces as replacement glass was revisited, as both the Type A and the Type B blue glass pieces are identical in color under transmitted light and both show typical corrosion patterns that indicate they have been the shape they are now for a long time. Visually, the only distinction seems to be that the Type B blues are more prone to deterioration on both the internal and external surface than the original Type A blue glass pieces, but this could indicate only minor differences in chemical composition resulting from unintentional variations of a recipe. The trace element data, however, shows a difference of about 300ppm Sr between the two groups, suggesting the Type B blue glass pieces have a distinct origin or source. Therefore, this group, along with six additional samples that were not previously identified, represent either a secondary source of blue glass that is original to the panel, or otherwise represent a very early repair.

It is interesting to note that no kelp ash glass, a glass type characterized by high Sr contents (in the range of 3000-4000ppm) was detected in the panel despite this being the dominant glass-making technology in England during the

1790s³². Rather the late eighteenth century work is represented by the use of glass which is likely to have been centuries old at the time it was implemented. The practice of reusing glass from dismantled windows to repair windows or create new designs is well-documented³³, including in an account from the 1770s which refers to windows containing “repaired mixed glass”³⁴, perhaps containing fragments salvaged after damage by iconoclasts. This practice has the potential to complicate identification of non-original glass through chemical analysis, by handheld pXRF as well as by other methods. However, in the present case, the areas of known intervention could be distinguished using handheld pXRF, excluding two glass pieces in the arched frame which were indistinguishable from the original glass in their trace element concentrations. The problem of identification of early repairs, however, is not unique to analysis by handheld pXRF³⁵.

Conclusions

Stained glass windows offer an important resource for the study not only of medieval art history but also issues such as trade, technology and craft organization. Furthermore, they have frequently undergone extensive modification and repair in the past, much of which is undocumented in contemporary sources, yet requires unravelling to allow informed understanding and conservation. These issues should be amenable to investigation using the approaches of archaeological science. However, the physical circumstances of medieval stained glass windows pose a significant obstacle to their analysis, necessitating the development of viable methodologies using *in situ* techniques such as handheld pXRF. In this paper, a simple, inexpensive and adaptable attachment allowed control over the working distance between spectrometer and sample as well as quantification of the data through empirical calibrations. Through careful selection of quantifiable heavy trace elements³⁶, a targeted methodology was employed to effectively bypass the inherent limitations of surface analysis by pXRF to address important questions related to the history of conservation of a medieval panel from Canterbury Cathedral. This has demonstrated the presence of a range of medieval and modern glass in the window. It has allowed the recognition of previously unidentified repairs to the original panel, and shown that late eighteenth century craftsmen were recycling medieval glass to execute their work. Particularly promising is the ability to distinguish different groups of glass which are clearly of medieval origin, opening the way for future studies on the movement of glass in the medieval period.

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³² Kelp ash production in England has been dated to c. 1700–1835. Dungworth, “The Value of Historic Window Glass.”

³³ E. Milner-White, “The Restoration of the East Window of York Minster,” *The Antiquaries Journal* 30, no. 3–4 (November 29, 1950): 180–84, <https://doi.org/10.1017/S0003581500087850>; Sarah Brown, *The Great East Window of York Minster: An English Masterpiece* (London: Third Millennium Publishing LTD, 2018); Charles Winston, *Memoirs Illustrative of the Art of Glass-Painting* (London: John Murray, 1865).

³⁴ William Gostling, *A Walk in and about the City of Canterbury: With Many Observations Not Hitherto Described in Any Text* (Canterbury: Simmons and Kirkby, 1779), 291; Caviness, *The Windows of Christ Church Cathedral Canterbury*, 10.

³⁵ Several glass pieces from the Great East Window of York Minster, which were analysed by electron microprobe (EPMA-WDS), were found to be chemically indistinguishable from the original glass despite clear stylistic characteristics that dated the painting to a different period. Laura W. Adlington, “Making a Medieval Stained Glass Window: An Archaeometric Study of Technology and Production” (Unpublished PhD thesis submitted to UCL Institute of Archaeology, 2019).

³⁶ Adlington and Freestone, “Using Handheld pXRF to Study Medieval Stained Glass: A Methodology Using Trace Elements”; Dungworth, “Historic Windows: Investigation of Composition Groups with Nondestructive pXRF.”

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