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The Gutenberg Bibles: Analysis of the Illuminations and Inks Using Raman Spectroscopy

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The King George III copy of the Gutenberg Bible, held at the British Library, has been analyzed using Raman spectroscopy to determine the palette of pigments used in the illuminations on this work. The palette is found to comprise cinnabar/vermilion, lead tin yellow (type 1), carbon-based black, azurite, malachite, an organo−copper complex (a "verdigris"), calcium carbonate (chalk), gypsum, gold leaf, and basic lead carbonate ("lead white"). This is in agreement with contemporary descriptions of the pigments used for the illuminations. One pigment could not be identified, specifically the organic dark red/purple color used for the foliage. The palette of this copy of the Gutenberg Bible has been compared with those used for six other copies, held at Eton College and Lambeth Palace, England, the Bibliothèque Mazarine and the Bibliothèque nationale de France, and the Staatsbibliothek zu Berlin and the Niedersächsische Staats- und Universitätsbibliothek (SUB) Göttingen, Germany. The palettes are shown to be similar to one another, even though the styles of the primary illuminations differ. The two Gutenberg Bibles held in Germany, printed on vellum, have the more expensive palettes, which include lazurite. The SUB Göttingen copy has the most extensive palette with 16 pigment-related materials having been identified.

It is generally accepted that Johann Gutenberg was responsible, around the middle of the 15th century, for the invention of European printing using movable metal type, a technological development with a profound impact on Western culture. The printing of the Bible, a major financial and practical undertaking of approximately three years, was completed in 1455 in Gutenberg's workshop in Mainz, Germany.[1,2] Of the ∼180 copies thought to have been produced, it has been estimated that ∼135 were printed on paper and ∼45 on vellum. Substantial remains of 48 copies survive. The surviving copies and fragments are held at academic institutions and libraries throughout the world or in private collections.

After printing and prior to selling, the Gutenberg Bibles (as they have become known) required headlines, rubrics, and major capitals to be supplied by hand. Variations between surviving copies indicate that this was probably not coordinated by the printer's workshop but done locally to the specification of the buyer. Some copies were also illuminated to varying specifications, depending on the geographical location, taste, and wealth of the owner. The copies that have been examined are believed, on stylistic grounds, not all to have been decorated in the same part of Europe, although all in northern Europe, including one copy in England. It is therefore of interest to determine the palettes used on the illuminated copies of Gutenberg Bibles, to establish whether the palettes differ from one part of Europe to another, whether Europe in effect constituted a fairly coherent cultural unit in terms of the use of pigments and other materials for the creation of major book art or whether local tastes and resources are reflected in this material. In some cases, model books for the illuminations, such as the Göttingen model book,[3] were available to provide detailed guidance on the style and pigments to be used, although these guidelines were not always followed; later works[4,5] provide an understanding of the practical aspects of the illuminator's work.

Previous analyses of the Gutenberg Bibles have focused on the compositions of the printing inks and paper used. For example, the copy of the Bible held at the Doheny Library (University of Southern California) has been examined using an analytical procedure based upon particle-induced X-ray emission (PIXE analysis).[6,7,8] The analyses showed a significant variation between the Cu/Pb ratios of the printing inks on different pages and were argued to reinforce the view, based on paper analysis, that Gutenberg printed the Bible in six units concurrently. However, it has been suggested that the PIXE analyses were too few to draw such conclusions.[9]

This paper presents the results of the first identifications of the pigments used for selected illustrations on seven copies of

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† University College London.
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(1) Bechtel, G. *Gutenberg et l'invention de l'imprimerie: Une ènquete*; Paris, 1992.
(2) Davies, M. *The Gutenberg Bible*; British Library: London, 1996.
(3) Lehmann-Haupt, H. *The Göttingen Model Book*; University of Missouri; 1978.
(4) Boltz von Rufach, V. *Illuminier Buch, wie man allerly Farben bereitte, mischen, schattieren, und ufftragen soll, allen jungen angehenden Malern und Illuministen nützlich und fürderlich*; Basel; 1549; Verlag Geor Callwey: Munich; 1913.
(5) Borradaile, V.; Borradaile, R. *The Strasbourg Manuscript: A Medieval Painters' Handbook*; Munich, 1966.
(6) Cahill, T. A.; Kusko, B. H.; Eldred, R. A.; Schwab, R. N. *Archaeometry* **1984**, *26*, 3−14.
(7) Kusko, B. H.; Cahill, T. A.; Eldred, R. A.; Schwab, R. N. *Nucl. Instrum. Methods Phys. Res.* **1984**, *B3*, 689−694.
(8) Schwab, R. N.; Cahill, T. A.; Eldred, R. A.; Kusko, B. H.; Wick, D. L. *Pap. Bib. Soc. Am.* **1985**, *79*, 375−410.
(9) Tiegen, P. M. *Pap. Bib. Soc. Am.* **1993**, *45*, 1−10.

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Table 1. European Location, Pages Examined, and Page Materials of the Seven Gutenberg Bibles Studied

institution	pages examined	page material	example illustration
The British Library (King George III copy), London, England	Prologue page (Vol. I)	paper	Figure 1a
	p 1, Genesis (Vol. I)		Figure 1b
	p 1, Proverbs (Vol. II)		
Eton College, Eton, Berkshire, England	Prologue page (Vol. I)	paper	Figure 1c
	p 1, Genesis (Vol. I)		Figure 1d
	p 1, Proverbs (Vol. II)		
Lambeth Palace, London, England	John 46r (Vol. I)	vellum	
	Timothy I 87r (Vol. I)		Figure 2a
	90v, 91r (Vol. I)		Figure 2b
Bibliothèque Mazarine, Paris, France	three primary illuminated pages 4r, 5r (Vol. I)	paper	Figure 2c,d
Bibliothèque nationale, Paris, France	primary illuminated pages	vellum	Figure 3a,b
Staatsbibliothek, Berlin, Germany	4v−5r	vellum	-
	28v−29r		
	303v−304r		
	317v−318r		
Niedersächsische Staats- und Universitätsbibliothek (SUB) Göttingen, Germany	46v−47r (Vol. I)	vellum	-
	83v−84r (Vol. I)		
	1r (Vol. II)		

the Gutenberg Bible located in Europe. The Bibles used in the analysis are held at the following locations: the British Library (King George III copy), Eton College, and Lambeth Palace, England; the Bibliothèque Mazarine and the Bibliothèque nationale de France, Paris, France; the Staatsbibliothek zu Berlin and the Niedersächsische Staats- und Universitätsbibliothek (SUB) Göttingen, Germany.

Selected pages from the immensely valuable King George III copy of the Gutenberg Bible printed on paper and now held at the British Library, have been extensively examined (Table 1). In particular, the Prologue page (containing St. Jerome's introductory letter) and the first pages of the books of Genesis and Proverbs have been analyzed in detail. The pages, now bound in two volumes, consist of two columns of printed text which are surrounded by elaborate illustrations of flowers, foliage, animals, and fruit decorated in green, red, purple, yellow, blue, white, and black pigments (Figure 1a,b). The illuminations have been stated to have been painted in Erfurt, Germany[10] but this seems to have been based on the assumption that the binding was made in Erfurt, whereas it was in fact made in London, in Buckingham House around 1800 and thus provides no indication as to the early life of the volume. A southern German origin seems more likely, as the earliest known owners were based in Würzburg, in Franconia. The Bible was acquired by George III (1738−1820) at an unknown date but probably around 1800 and was transferred as part of the King's Library to the British Museum in 1828.

The Gutenberg Bible held at Eton College is also printed on paper and bound in two volumes; it truly has an Erfurt binding and is also presumed to have been illuminated in Erfurt, prior to binding. The decoration in this copy is comparable in style and use of colors to that of the King George III copy; the basic use of foliage, flowers, fruit, and animals is generically similar although the exact depictions of the fruit, flowers, and animals are different (Figure 1c,d). Three pages from the Eton College copy (the Prologue page, the first page of Genesis, and the first page of Proverbs) have been examined to provide close correlation with the King George III copy (Table 1).

(10) Weber, R. *Johannes Gutenbergs zweiundvierzigzeilige Bibel, Faksimile-Ausgabe nach dem Exemplar der Staatsbibliothek Preussischer Kulturbesitz Berlin: Kommentarband*; Schmidt, W., Schmidt-Künsemüller, F. A., Eds.; Munich, 1979; pp 9−31.

The historic library of the archbishops of Canterbury and the principal library for the Church of England, in Lambeth Palace, holds one of the copies of the Gutenberg Bible printed on vellum. The illuminations in this copy are considerably different from those on the King George III and Eton College copies. This decoration has been ascribed to England and consists of more elaborate patterns in a limited number of colors. The illuminated pages John 46r, Timothy I 87r, and 90v−91r (Vol. I) have been examined in this copy (Table 1; Figure 2a,b).

The Bibliothèque Mazarine, France's first public library, holds a copy of the Gutenberg Bible bound in two volumes and printed on paper. It is the least elaborately decorated of the bibles that have been examined as part of this study, the decoration not amounting to much more than calligraphical initials (Figure 2c,d). The pigments from three different illuminated pages of this copy were examined. The copy held at the Bibliothèque nationale de France is also bound in two volumes but is printed on vellum; stylistically, this volume has also been associated with the Göttingen model book. Again the pigments used on the primary illuminated pages of this Bible were examined (Figure 3a,b).

The copy of the Bible held at the Staatsbibliothek zu Berlin is also printed on vellum and bound in two volumes. The generic style of illumination in this Bible is similar to that observed on the King George III and Eton College copies, with twisting foliage, flowers, and birds (including a peacock) depicted around the two columns of text; but stylistic differences are also evident, and this decoration has been ascribed to Leipzig. It is more lavishly decorated than either the King George III or the Eton College copies. Four illuminated pages from this copy have been examined: 4v−5r, 28v−29r, 303v−304r, and 317v−318r (Table 1). The Gutenberg Bible held at SUB Göttingen is also printed on vellum and bound in two volumes. Pages 46v−47r, 83v−84r (Vol. I), and 1r (Vol. II) from this copy have been examined (Table 1). This copy is decorated by an artist using the so-called Göttingen model book, which has been associated with Mainz itself, the place where the Bibles were printed.

EXPERIMENTAL SECTION

The illuminations and inks used on the seven copies of the Gutenberg Bible were analyzed using a Renishaw System 1000 Raman spectrometer equipped with three laser sources (632.8-

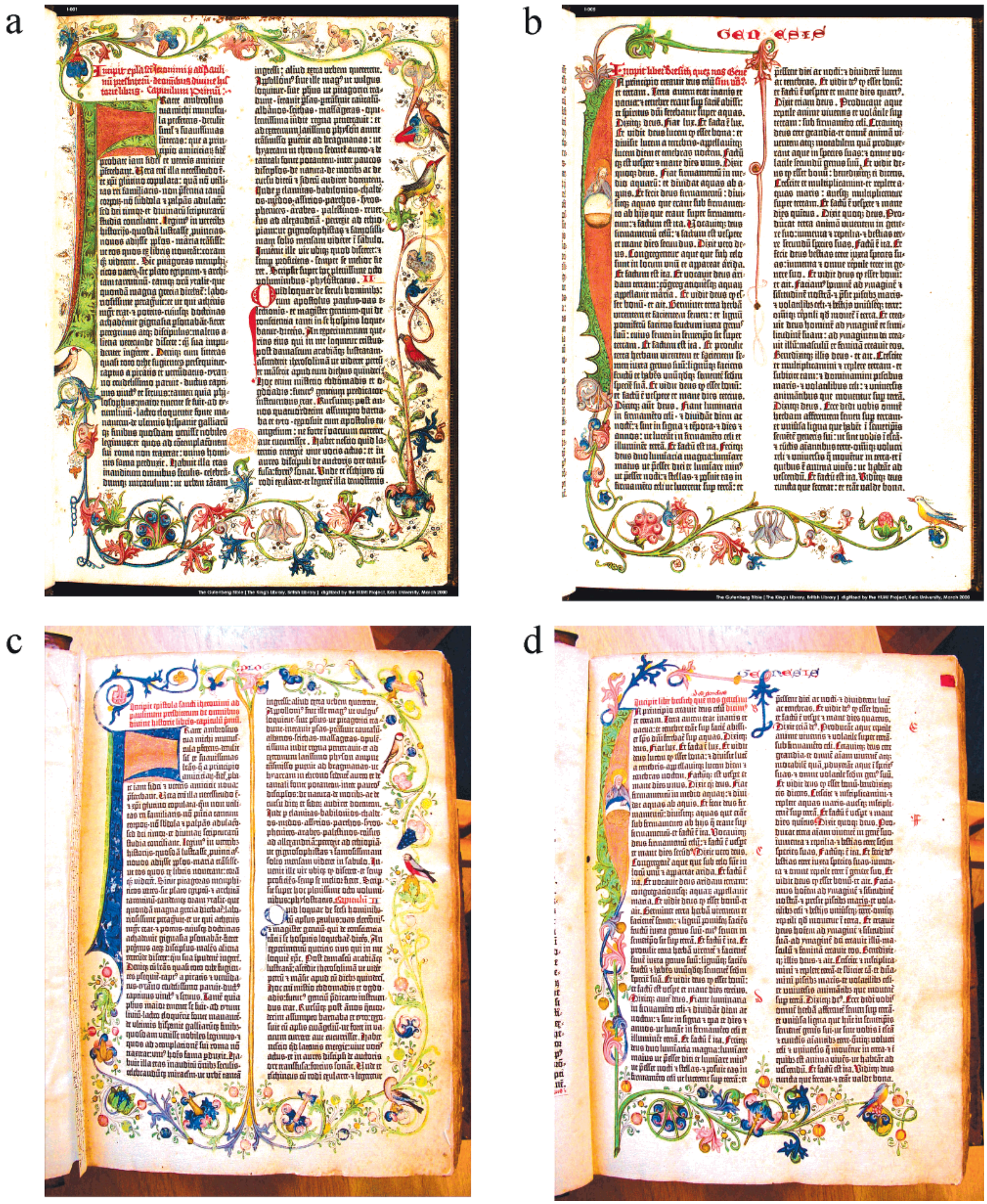

Figure 1. Illuminated pages from the Gutenberg Bibles held at (a) the British Library (Prologue page, King George III copy, Vol. I), (b) the British Library (page 1 of Genesis, King George III copy, Vol. I), both reproduced with permission of the British Library. (c) Eton College (Prologue page, Vol. I), and (d) Eton College (page 1 of Genesis, Vol. I); both reproduced courtesy of the Provost & Fellows of Eton College.

nm HeNe, 514.5-nm Ar^+ ion, and 783-nm diode lasers). The analysis of the pigments and inks was performed using two different methods. At the British Library, the illuminations in the King George III copy of the Gutenberg Bible were analyzed in situ, with the book held supported either on a unique book cradle[11] or on an extended microscope stage, which prevented the book from being opened out flat. Using the book cradle, the laser light was directed onto the page through the 10× objective on the

(11) Clark, R. J. H. *C. R. Chimie* **2004**, *5*, 7−20.

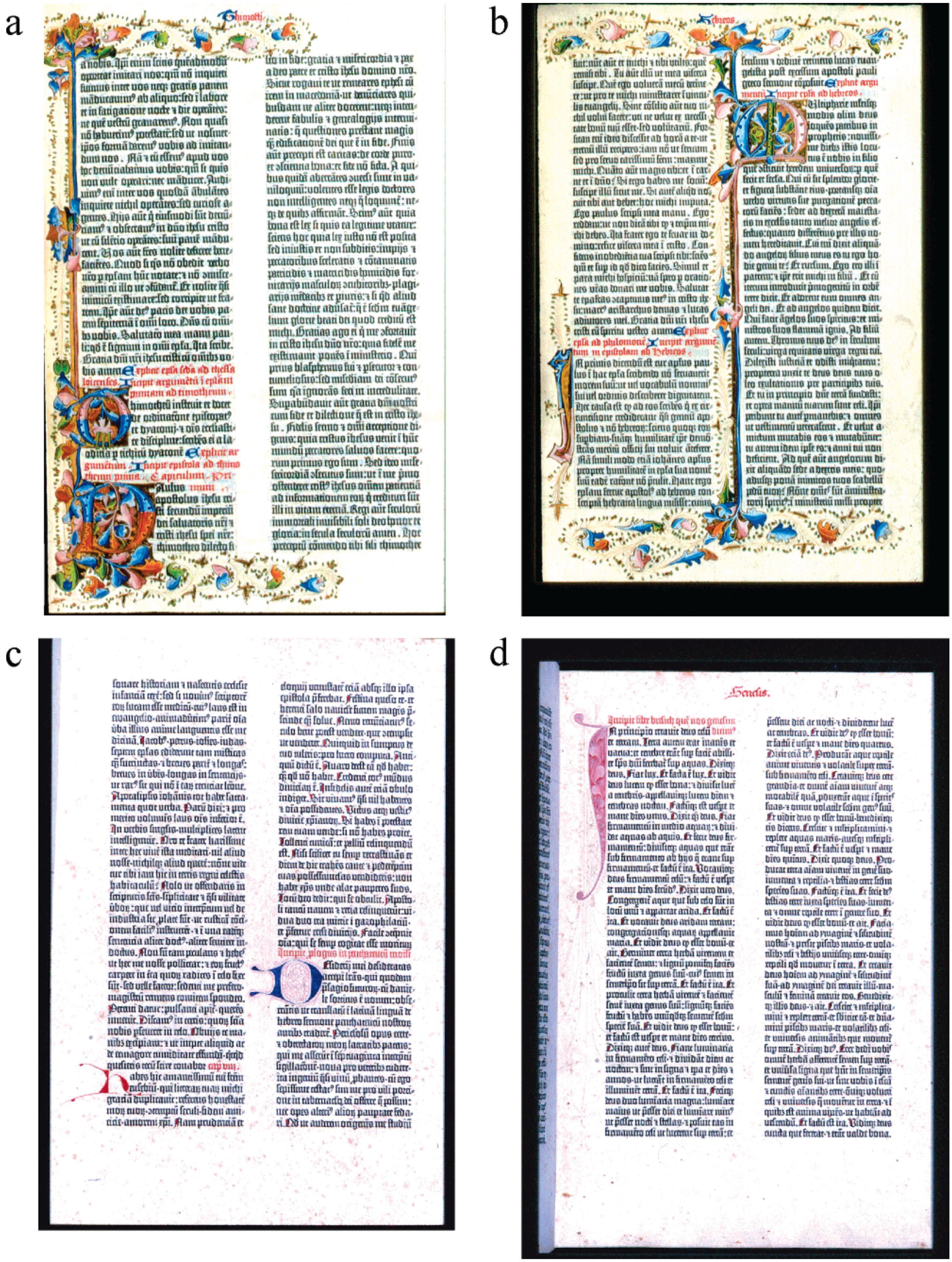

Figure 2. Illuminated pages from the Gutenberg Bible held at (a) Lambeth Palace (page 87r, Timothy I, Vol. I) and (b) Lambeth Palace (pages 90v−91r, Vol. I), both reproduced with permission of Lambeth Palace; (c) the Bibliothèque Mazarine (page 4r, Vol. I) and (d) the Bibliothèque Mazarine (page 5r, Vol. I), both reproduced with permission of the Bibliothèque Mazarine.

Figure 3. Illuminated pages from the Gutenberg Bible held at the Bibliothèque nationale de France: (a) Prologue page, Vol. I, (b) Page 1 of Genesis, Vol. I; both reproduced with permission of the Bibliothèque nationale de France.

remote probe head of either the HeNe or the near-IR diode lasers. The probes were mounted over the cradle and connected to the spectrometer via optic fiber cables. The Raman scattered light was collected through the same objective and transmitted to the spectrometer and onto a thermoelectrically cooled CCD detector operating at −70 °C. Similarly, with the book positioned on the extended microscope stage, the laser (either 632.8- or 514.5-nm excitation) was directed onto the pigment using the microscope objective, with the Raman light being collected back through the same objective and transmitted through a holographic notch filter onto the CCD detector. The microscope system has the advantage of allowing the use of higher powered objectives (up to 100×) so that focus onto individual pigment grains is possible.

The second method via which data were collected was by analysis of debris material collected using a fine brush from the gutters between each of the primary illuminated pages of the Bibles. In this way, material that has been lost from the illuminations is collected (together with any other material that may have collected in this area) and no direct sampling from the pages is required. The material from each page was stored on a glass slide and protected from contamination with a sealed glass coverslip. This method also allows copies of the Bible to which access is limited to be examined in great detail. In this ex situ method, glass slides containing the material from each page were analyzed under the Raman microscope as described previously. The Raman spectra obtained by these methods were compared with those in libraries of spectra obtained from reference samples.[12,13] The in situ method was applied to the King George III Gutenberg Bible only. The ex situ method was also applied to this copy to establish the extent to which this procedure is appropriate. The latter method was then used to analyze the pigments in six other copies of the Gutenberg Bible.

RESULTS AND DISCUSSION

King George III Copy. Visual inspection of the King George III copy of the Gutenberg Bible demonstrates that the palette consists of nine main colors: bright red, red/purple, purple, blue, green, yellow, white (or yellowish-white), black, and gold. In situ Raman analysis of the bright red pigment, as used for the rubrics, birds' plumage, flowers, and the area surrounding the male figure (page one of Proverbs), yields the spectrum of cinnabar, HgS (or its synthetic equivalent, vermilion). The Raman spectrum of this material has characteristic bands at 252, 284, and 342 cm^{-1} (Figure 4a). The naturally occurring mineral cinnabar has been used as a pigment since antiquity, with the synthetic form being produced in the western world since the 8th century A.D.

Analysis of the blue pigments, which occur as two different shades (a light shade for the flowers, buds, and birds, and a darker shade for the foliage), shows that the blue colorant is azurite, a basic copper carbonate mineral ($2CuCO_3 \cdot Cu(OH)_2$) or its synthetic form, blue verditer.[14] Both of these materials yield intense bands in the Raman spectrum at 403, 767, 1096, 1432, and 1578 cm^{-1} (Figure 4b). Although the natural form has been used as a pigment since antiquity, the synthetic form, distinguishable under a polarizing microscope by its spherulitic habit, has only been in

(12) Bell, I. M.; Clark, R. J. H.; Gibbs, P. *Spectrochim. Acta, Part A* **1997**, *53*, 2159−2179.

(13) Burgio, L.; Clark, R. J. H. *Spectrochim. Acta, Part A* **2001**, *57*, 1491−1521.

(14) Gettens, R. J.; FitzHugh, E. W. In *Artists' Pigments. A Handbook of their History and Characteristics*; Roy, A., Ed.; National Gallery of Art: Washington, and Oxford University Press: Oxford, 1993; Vol. 2, pp 23−36.

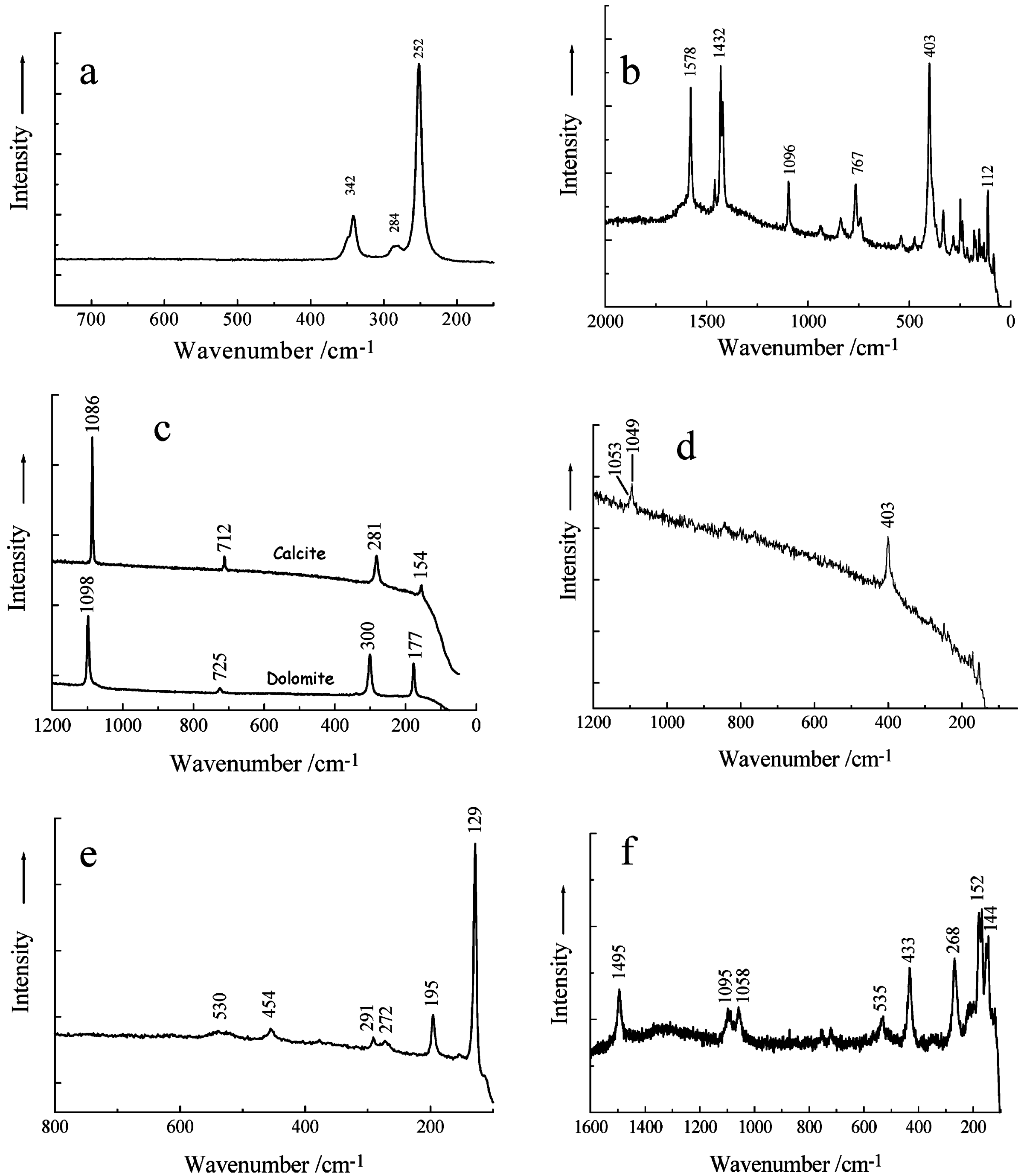

Figure 4. Raman spectra of pigments used on the illuminations on the King George III copy of the Gutenberg Bible: (a) vermilion from the rubrics, bird's feathers, and buds ($\lambda = 632.8$ nm), (b) azurite from the dark blue foliage ($\lambda = 514.5$ nm), (c) calcite and dolomite (from the copy held at the Bibliothèque nationale de France; $\lambda = 632.8$ nm), (d) basic lead carbonate (lead white) from the white highlights, with azurite ($\lambda = 632.8$ nm), (e) lead tin yellow (type 1) from the yellow/green foliage ($\lambda = 632.8$ nm), and (f) malachite from the light green foliage ($\lambda = 783$ nm).

production since the early 19th century;[14,15] it would therefore be anachronous on a 15th century manuscript. The analysis also shows that the azurite is mixed with calcite, $CaCO_3$ (probably in the form of chalk), to form the lighter blue paint, as identified by the presence of an additional intense band in some of the Raman spectra at 1086 cm^{-1}. Calcite was also identified as the white pigment used for the highlights in the foliage, flowers, and birds' plumage, yielding a Raman spectrum with bands at 154, 281, 712, and 1086 cm^{-1} (Figure 4c). It was also identified in association with gypsum (calcium sulfate, $CaSO_4{\cdot}2H_2O$), in which case an additional intense band was observed in the Raman spectrum at 1007 cm^{-1}. Analysis of the yellow/white pigment, which had also been used for highlights, shows that it is basic lead carbonate, $2PbCO_3{\cdot}Pb(OH)_2$, the most common of the "lead white" pigments.[15] This material yields a Raman spectrum with medium-strong bands at 1049 and 1053 cm^{-1} (Figure 4d). Lead white was also identified as having been used admixed with other pigments, notably vermilion and azurite, to produce the purple used for selected

(15) Eastaugh, N.; Walsh, V.; Chaplin, T. D.; Siddall, R. *The Pigment Compendium*; Elsevier: New York, 2004.

birds' plumage. These mixtures yield more complex spectra, with bands from each pigment component present, effectively combinations of Figure 4a, b, and d. For example, the spectrum shown in Figure 4d, contains bands at 403, 767, and 839 cm^{-1} associated with azurite (cf. Figure 4b), in addition to the bands at 1049 and 1053 cm^{-1} attributable to lead white.

Analysis of the yellow pigment used for illuminated letters within the printed text, for highlighted areas in the foliage, and for the heads of selected birds, shows that it is lead tin yellow (type 1), Pb_2SnO_4. This material yields a Raman spectrum with a characteristically intense band at 129 cm^{-1} and weaker bands at 195, 272, 291, 454, and 530 cm^{-1} (Figure 4e).[16]

Two main shades of green are observable on the illuminated pages—an olive green and a darker green, which are used to annotate certain capitals and to illustrate the vines and selected birds' plumage. The lighter green, as used for the foliage, was determined to be malachite (basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$), or its synthetic equivalent, green verditer. This material yields bands in its Raman spectrum at 144, 152, 268, 347, 433, 535, 720, 754, 1058, 1095, and 1495 cm^{-1} (Figure 4f). Analysis of the dark green pigment, as also used for the foliage, shows that this material is an organo–copper complex, with the Raman spectrum (Figure 5a) most closely matching that of a basic copper(II) ethanoate (a "verdigris", $Cu(CH_3COO)_2 \cdot Cu(OH)_2$).[12]

Raman analysis of the black printing ink and the black pigment used for the birds' plumage and to provide the outlines and fine details of the animals, fruit, and foliage, has been identified as a carbon-based black, yielding two characteristic broad bands in the Raman spectrum at 1340 and 1590 cm^{-1} (Figure 5b).

No Raman spectrum could be obtained from the gold material present in rounded areas of the foliage or in selected capitals. The low background to the spectra may indicate that this material is gold metal, which has no first-order Raman spectrum. Similarly the composition of the darker red/purple pigment that has been used to illustrate the flora and foliage could not be determined directly. Any Raman bands from this material are obscured by the high fluorescent background afforded by the paint. This response to the laser illumination may suggest that the red pigment is of organic origin. The contemporary model books suggest that lac (a dyestuff derived from various species of Coccoidea—scale insects) or brazilwood (dyestuffs derived from several closely related species of hard, brown-red wood)[15] should be used to give a dark red paint. Analysis by Scott et al.[17] of the red colorant on a 15th century German manuscript identified the use of rhubarb root mordanted with alum; this analysis also identified the presence of calcite, vermilion, azurite, and verdigris, the same pigments as found in this study on the contemporaneous King George III Bible.

The material collected from the gutters (ex situ method) of the pages of the King George III copy examined in situ was also analyzed in order to establish whether it could be related to the illuminations and whether this method of data collection could be applied to other illuminated books. The material obtained consists of small (3–45 μm) bright red/orange aggregates and anhedral crystals, larger anhedral blue crystals, yellow/white finely crystalline aggregates and subhedral crystals, black fragments, yellow/green particles, gold flakes, pale and bright green aggregates and crystals, larger white/colorless masses and euhedral crystals, dark red vitreous crystals, dark yellow aggregates, and blue, red, and green fibers. Raman analysis of the bright red/orange aggregates and crystals shows that they are cinnabar/vermilion, yielding spectra identical to that shown in Figure 4a. Examination of their particle morphology provides no indication as to source (natural or synthetic) because crystals produced by grinding the natural material or by "dry process" manufacture have similar morphologies. The bright blue crystals are azurite, yielding spectra identical to that shown in Figure 4b. In this case, examination of the particle morphology of the blue crystals (subhedral–euhedral grains rather than spherulitic grains) indicates that the blue material is natural azurite rather than synthetic blue verditer. Similarly, the bright green euhedral crystals obtained from the gutters are malachite, as determined by Raman analysis (yielding spectra identical to Figure 4f), with the particle morphology (again euhedral rather than spherulitic grains) indicative of the natural rather than the synthetic material. The pale green fragments yield weak Raman spectra dominated by fluorescence from which bands associated with verdigris (cf. Figure 5a) can be identified. Raman analysis of the yellow/white finely crystalline aggregates and crystals shows that they are calcite, resulting in spectra with band wavenumbers identical to those shown in Figure 4c. The black fragments were determined to be a carbon-based black, yielding Raman spectra as illustrated in Figure 5b. Analysis of the yellow/green particles present in the debris material shows that they are lead tin yellow (type 1), yielding spectra identical to that shown in Figure 4e. The gold flakes observed in the collected material give no Raman spectrum, and it is likely that these are fragments from the gold leaf used on the illuminations.

No Raman spectrum could be obtained from the dark red vitreous crystals or the dark yellow vitreous particles. These materials provide a fluorescent response under laser illumination so that no Raman bands could be identified. A few colored clothing fibers unrelated to the illuminations were also detected, indicating that caution must be exercised when endeavoring to relate material found in gutters to that on decorations.

The palette established here for the King George III copy of the Gutenberg Bible by the in situ method and confirmed by the ex situ method therefore consists of cinnabar/vermilion, azurite, chalk, "lead white", lead tin yellow type 1, malachite, an organo–copper complex (a verdigris), carbon-based black, gold leaf, and an organic red pigment (Table 2).

Six Further Copies of the Gutenberg Bible. Visual analysis of the material collected from the other six copies of the Gutenberg Bible identified a similar wide range of small, colored and colorless particles. Red/orange, blue, and black particles with similar appearance were common to the sets of material obtained from each of the Bibles. Raman analysis shows that the red/orange particles are cinnabar/vermilion (cf. Figure 4a), the blue crystals are azurite (cf. Figure 4b), and the black fragments are a carbon-based black (cf. Figure 5b), as found on the King George III copy (Table 2). Colorless aggregates and crystals of calcite were identified by Raman analysis (cf. Figure 4c) in the debris collected from all copies of the Bibles studied except for that from

(16) Clark, R. J. H.; Cridland, L.; Kariuki, B. M.; Harris, K. D. M.; Withnall, R. *J. Chem. Soc., Dalton Trans.* **1995**, 2577–2582.

(17) Scott, D. A.; Khandekar, N.; Schilling, M. R.; Turner, N.; Taniguchi, Y.; Khanjian, H. *Stud, Conserv.* **2001**, *46*, 93–108.

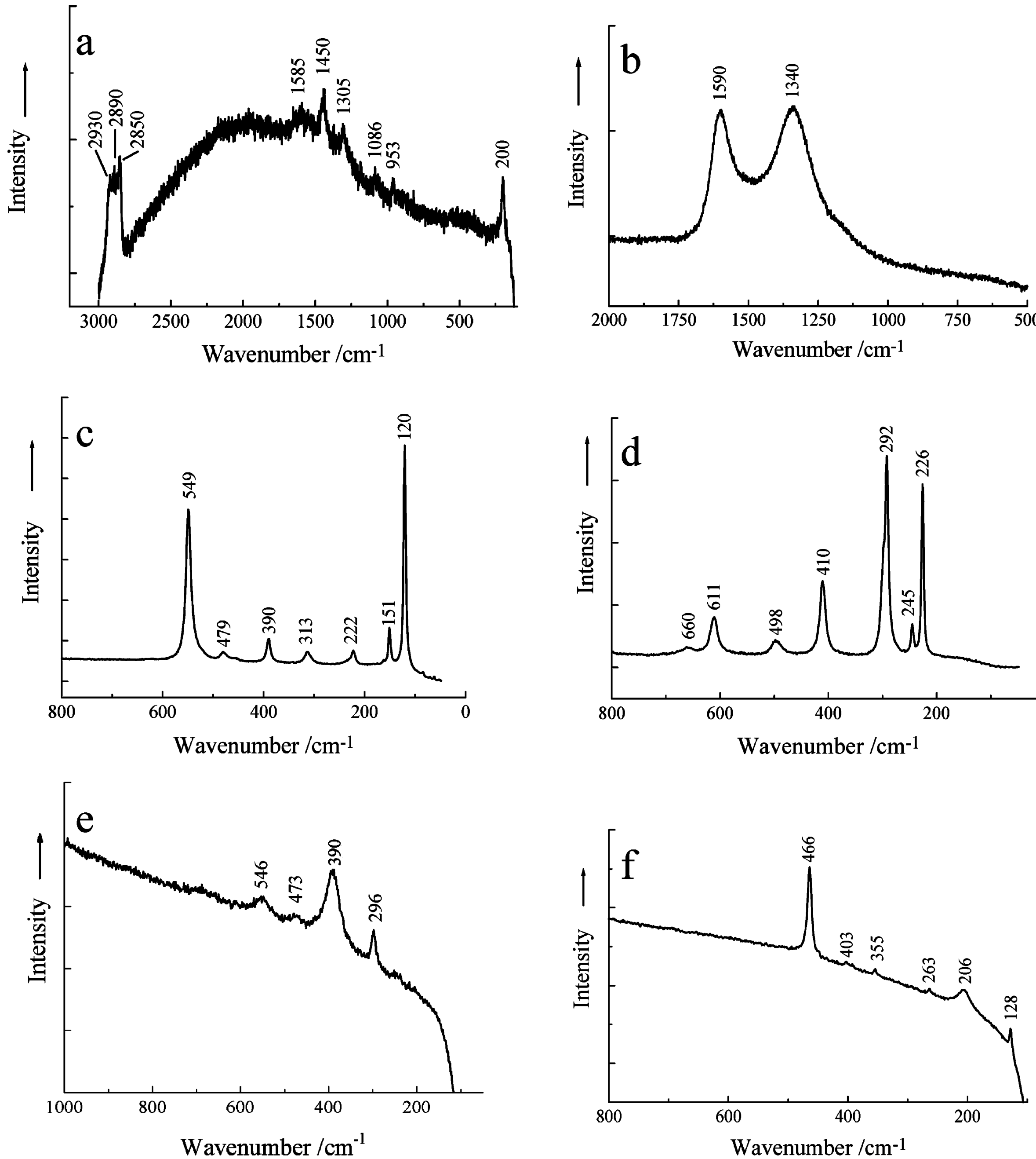

Figure 5. Raman spectra of pigments used for the illuminations in the Gutenberg Bibles: (a) verdigris from the dark green foliage (King George III copy), (b) carbon-based black from the ink and black outlines (King George III copy), (c) lead(II,IV) oxide (Lambeth Place copy), (d) red ochre (Eton College copy), (e) yellow ochre (Göttingen copy), and (f) quartz (Eton College copy). All spectra were collected using 632.8-nm excitation.

Eton College. A related colorless material with similar morphology was found in addition to the calcite in the material collected from the copy at the Bibliothèque nationale de France. This material yields a Raman spectrum with a profile similar to that of calcite, but with the Raman bands shifted by 12−20 cm^{-1} to higher wavenumbers as compared with those of calcite (Figure 4c). The band wavenumbers indicate that this material is dolomite, $MgCa(CO_3)_2$, isostructural with calcite but containing lighter magnesium cations in the crystal lattice. The presence of this Mg-rich material in addition to calcite may indicate a different source of the chalk pigment used for the illuminations in the Gutenberg Bible at the Bibliothèque nationale de France.

Fragments of metallic gold were found in the material from all copies of the Bibles except that from Eton College. However, visual analysis of this copy shows that gold leaf has been used for these illuminations. This result shows that material obtained from the gutters of the pages may not represent the complete palette for the illuminations. Yellow/green particles were identified in the gutter material collected from all copies of the Bibles except that from Lambeth Palace. Raman analysis of these particles shows that they are lead tin yellow (type 1), yielding Raman spectra identical to that shown in Figure 4e. Bright green anhedral particles were present in the material collected from all copies of the Bible examined except those held at Eton College, the

Table 2. Pigments and Related Materials Identified from Seven Copies of the Gutenberg Bible

	British Library	Eton College	Lambeth Palace	Bibliothèque Mazarine	Bibliothèque nationale	Göttingen	Staatsbibliothek, Berlin
red pigments:							
vermilion	X	X	X	X	X	X	X
lead(II,IV) oxide			X	X		X	
Fe_2O_3/red ochre		X	X				X
organic red	X	X				X	X
hansa red					X		
blue pigments:							
azurite	X	X	X	X	X	X	X
lazurite						X	X
indigo			X		X		X
green pigments:							
malachite	X		X		X	X	
verdigris	X		X			X	
phthalocyanine green			X				
yellow pigments:							
lead tin yellow (type i)	X	X		X	X	X	X
yellow ochre						X	
rutile						X	X
massicot						X	
white pigments:							
calcite	X		X	X	X	X	X
lead white	X	X					
anatase						X	
black pigments:							
carbon black	X	X	X	X	X	X	X
miscellaneous:							
gold leaf	X		X	X	X	X	X
quartz		X				X	
dolomite					X		
gypsum	X						
beeswax				X			X
realgar						X	

Bibliothèque Mazarine, and Berlin. Raman analysis of these grains shows that they are malachite, yielding spectra as shown in Figure 4f. Darker green fragments were only found in material from two copies of the Bibles in addition to the King George III copy—those from Lambeth Palace and Göttingen. Analysis of these grains shows that they are organo−copper complexes (verdigris compounds), yielding weak spectra similar to that shown in Figure 5a. White particles of basic lead carbonate, as found on the King George III copy of the Gutenberg Bible, were only found in one other copy of the Bibles analyzed here, that held at Eton College. The white material found in this copy yields spectra identical to that illustrated in Figure 4d.

Dark red particles were found in the material from three other copies of the Bibles examined (from the Eton College, Göttingen, and Berlin copies). Again, these gave a highly fluorescent response to the laser illumination and may perhaps be organic materials, similar to that found on the King George III copy.

Further pigments, not encountered on the King George III copy were identified within the debris materials collected from the other copies the Gutenberg Bibles (Table 1). From the Lambeth Palace, Bibliothèque Mazarine, and Göttingen copies, small orange-red crystals were collected. Raman analysis of these grains shows that they are lead(II,IV) oxide, Pb_3O_4, a strong Raman scatterer, which yields bands in the spectrum at 120, 151, 222, 313, 390, 479, and 549 cm^{-1} (Figure 5c). This material, more commonly known as minium or red lead, has been used as a pigment since antiquity. A further red pigment was identified in the material collected from the Eton College, Lambeth Palace, and Berlin copies. Analysis of these red-orange particles yields Raman spectra with bands at 226, 245, 292, 410, 498, 611, and 660 cm^{-1} (Figure 5d), characteristic of iron(III) oxide (Fe_2O_3), which may be present as a pure haematite pigment or as part of red ochre, for which haematite is the main colorant. A related natural earth material, yellow ochre, was identified as the yellow-orange particles in the material retrieved from the Göttingen copy. This material yields spectra with bands at 248, 296, 390, 473, and 546 cm^{-1} (Figure 5e), the principal colorant and component of which is the iron oxide hydroxide, goethite (α-FeOOH). Quartz (SiO_2), a common constituent of ochres, was also identified as a component of the colorless particles derived from the gutters of the Göttingen and Eton College copies. This mineral yields a Raman spectrum with bands at 128, 206, 263, 355, 403, and 466 cm^{-1} (Figure 5f). However, it should be noted that quartz, an inert and hence robust material, is a common component of dust and may be present in the gutters of the Bibles for this reason rather than because it is part of a pigment.

Two further blue pigments were detected in the material collected from three of the Bibles examined other than the King George III copy. Dark blue anhedral crystals were present in the debris accumulated in the copies held at Göttingen and Berlin, in addition to the paler blue azurite crystals. Raman analysis of this material yields spectra with bands at 258, 546, 805, 1096, 1360, and 1649 cm^{-1} (Figure 6a). These are characteristic of lazurite, a sodium aluminosilicate mineral, $Na_8[(Al,Si)_{12}O_{24}](S_n)$, in which the blue coloration is caused by the presence of the sulfur radical anions S_3^- and S_2^- in the aluminosilicate structure.[18] The identi-

(18) Clark, R. J. H.; Franks, M. L. *Chem. Phys. Lett.* **1975**, *34*, 69−72.

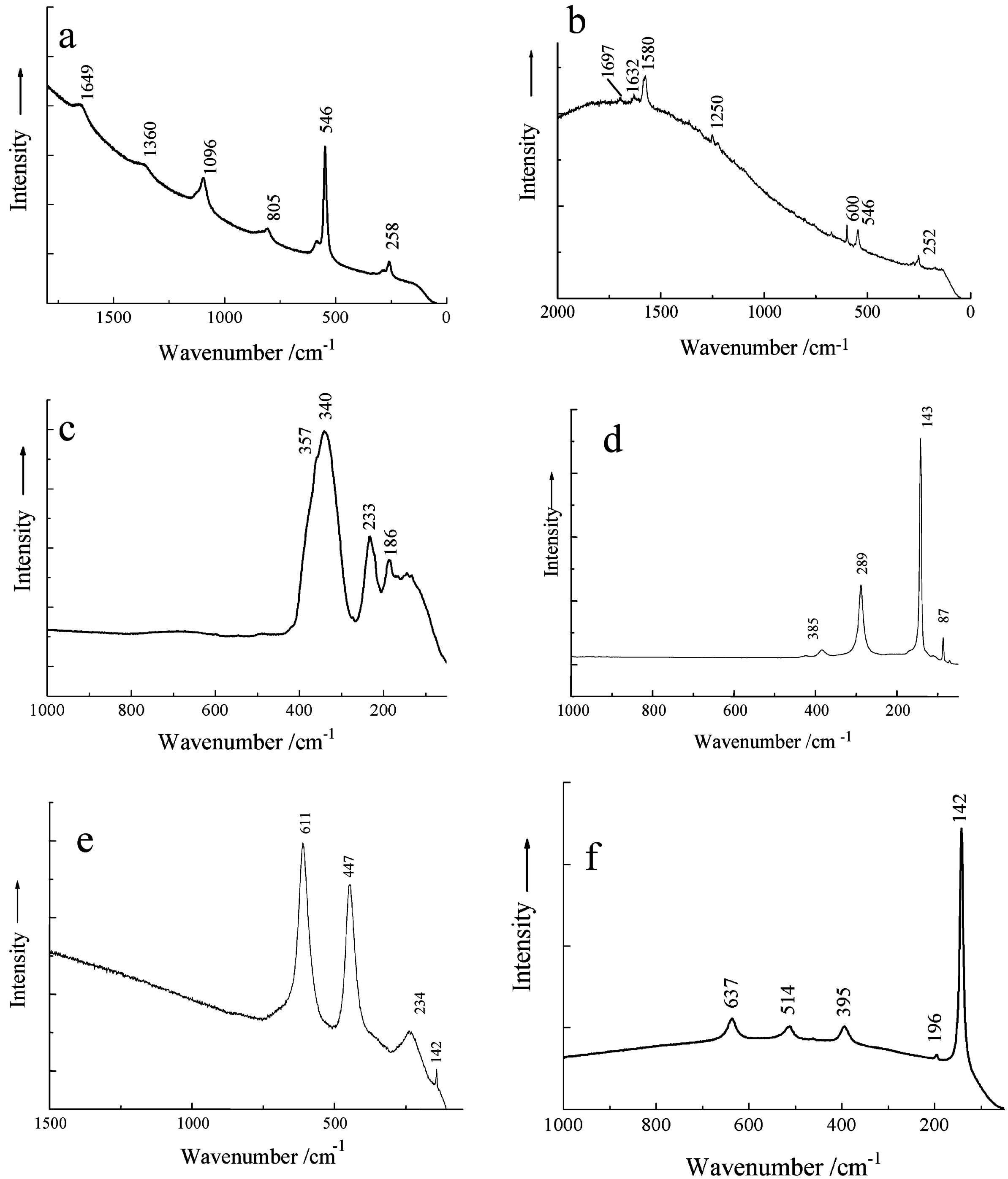

Figure 6. Raman spectra of pigments used for the illuminations in the Gutenberg Bibles: (a) lazurite (Berlin copy), (b) indigo (Bibliothèque nationale copy), (c) realgar (Göttingen copy), (d) massicot (Göttingen copy), (e) rutile (Göttingen copy), and (f) anatase (Göttingen copy). All spectra were collected using 632.8-nm excitation.

fication of lazurite as a palette component is of importance as this pigment is known to have been the most expensive. The presence of this material, combined with fact that both the Göttingen- and Berlin-held Gutenberg Bibles are printed on vellum, the expensive option, suggests that these copies were originally purchased by very wealthy owners.

The third blue pigment identified occurs as blue-green particles in the debris material collected from the Lambeth Palace, Bibliothèque nationale, and Berlin copies of the Bible. Raman analysis of these grains shows that they are indigo, a dyestuff derived from the leaves of various *Indigofera* species.[13,15,19−21] This material yields a spectrum with characteristic bands at 252, 546, 600, 1250, 1580, 1632, and 1697 cm^{-1} (Figure 6b).

Four further pigments were identified in the material from the Göttingen copy of the Gutenberg Bible but not observed on any of the other Bibles. As a result, the palette determined for this copy of the Gutenberg Bible is far wider than those of the other

(19) Burgio, L.; Clark, R. J. H. *J. Raman Spectrosc.* **1999**, *30*, 181−184.
(20) Vandenabeele, P.; Moens, L. *Analyst* **2003**, *128*, 187−193.
(21) Brown, K. L.; Clark, R. J. H. *J. Raman Spectrosc.* **2004**, *35*, 4−12.

Bibles examined here, with 16 pigment-related materials being identified (Table 2). The first of these additional pigments occurs as orange anhedral particles, which were shown by the Raman analysis to be realgar, As_4S_4, a naturally occurring mineral, which may also be synthesized by heating the arsenic sulfide mineral orpiment (As_2S_3). The orange particles yield a Raman spectrum with a broad doublet at 340 and 357 cm^{-1}, with weaker bands at 186 and 233 cm^{-1} (Figure 6c), indicative of the amorphous form of realgar. Identifications of realgar (amorphous or crystalline) in a pigment context are relatively few, particularly in western art,[22] with orpiment being much the more commonly encountered arsenic sulfide. Realgar has been identified as a component in orpiment-based pigments[23] although it is known as a pigment in its own right in Mesopotamian[24] palettes.

Yellow-orange particles of massicot, a lead(II) oxide (PbO), were also identified in the material obtained from pages 46v–47r and page 1r (Vol. II) of the Göttingen copy. These particles yield a Raman spectrum with bands at 87, 143, 289, and 385 cm^{-1} (Figure 6d). These bands are characteristic of massicot, an orthorhombic lead(II) oxide mineral with composition PbO. Massicot has been used in artwork since antiquity and is often found in association with lead(II,IV) oxide. The latter pigment was identified in the material collected from pages 46v–47r of the Göttingen copy, and hence, it is unclear whether the particles of massicot have fragmented from illuminations decorated with an original yellow massicot pigment or from the lead(II,IV) oxide pigment.

The other two materials observed in the debris from the Göttingen copy are TiO_2 polymorphs, found to occur as pale yellow anhedral aggregates and particles. The yellow particles retrieved from pages 46v–47r were determined by Raman analysis to be rutile, which yields a spectrum with bands at 142, 234, 447, and 611 cm^{-1} (Figure 6e). Rutile was also found in the material collected from pages 317v–318r of the Berlin copy. Rutile may occur as a component of natural earth pigments,[25,26] and thus the rutile grains identified here may be part of the red and yellow ochres already found in these Bibles. Natural rutile is not known to have been used as an artist's pigment, but its synthetic analogue has been used very extensively as an industrial pigment since its first production in the early 20th century.[27]

The second TiO_2 polymorph to be identified from the Göttingen copy is anatase, which yields bands in the Raman spectrum at 142, 196, 395, 514, and 637 cm^{-1} (Figure 6f). As in the case of rutile, anatase is rarely if ever encountered in a pigment context prior to the early 20th century when it was first made synthetically. Initial syntheses of anatase produced a yellow pigment (due to iron impurities, as found in natural samples), with later production methods (post ca. 1920) resulting in a pure white pigment. It is likely that the presence of rutile and anatase in the gutters of the pages is a result of fragmentation of recent conservation treatment or contamination from modern paint sources in the locality of the storage or exhibition areas for the Bibles.

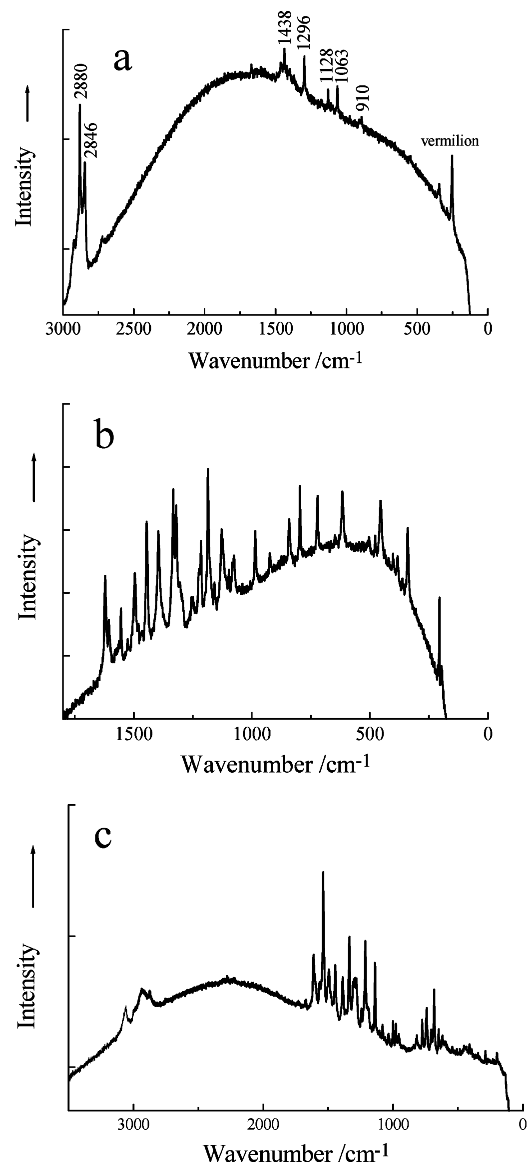

Figure 7. Raman spectra of materials found in the gutters of the Gutenberg Bibles: (a) beeswax (Bibliothèque Mazarine copy), (b) Hansa red (Bibliothèque nationale copy), and (c) phthalocyanine green (Lambeth Palace copy). All spectra were collected using 632.8-nm excitation.

Large white anhedral masses with a greasy appearance containing smaller red and blue grains were found in the material collected from the Bibliothèque Mazarine and Berlin copies. Raman analysis of this material yields a complex spectrum with intense bands at 500, 703, 910, 1063, 1128, 1296, 1356, 1430, 1438, 1466, 2846, and 2880 cm^{-1} and many further weaker bands, characteristic of beeswax (Figure 7a); Raman bands associated with azurite or vermilion are also often present in the spectra obtained from this material. The volume of the aggregates suggests that the latter are unlikely to be related to any pigment binder materials; they may be derived from dripping beeswax candles used historically close to the Bibles.

(22) FitzHugh, E. W. In *Artists' Pigments. A Handbook of their History and Characteristics*; FitzHugh, E. W., Ed.; National Gallery of Art: Washington, and Oxford University Press: Oxford, 1997; Vol. 3, pp 47–79.

(23) Barbet, A.; Fuchs, M.; Tuffreau-Libre, M. *Roman Wall Painting. Materials, Techniques, Analysis and Conservation. Proceedings of the International Workshop Fribourg*, 7–9 March 1996; Institute of Mineralogy and Petrography: Fribourg, 1997; pp 35–62.

(24) Clark, R. J. H.; Gibbs, P. J. *Chem. Commun.* **1997**, 1003–1004.

(25) Yü, F.-A. *Chinese Painting Colors. Studies of Their Preparation and Application in Traditional and Modern Times*; Hong Kong University Press: Hong Kong, and University of Washington Press: Seattle, WA, 1988.

(26) Duval, A. R. *Stud. Conserv.* **1992**, *37*, 239–258.

(27) Laver, M. In *Artists' Pigments. A Handbook of their History and Characteristics*; FitzHugh, E. W., Ed.; National Gallery of Art: Washington, and Oxford University Press: Oxford, 1997; Vol. 3, pp 295–355.

Two unambiguously anachronistic pigments were encountered on two of the Bibles examined. The first was observed as bright red particles or aggregates collected from the Bibliothèque nationale copy. These grains yield a complex Raman spectrum with intense bands at 1186, 1320, 1333, 1396, 1445, 1496, and 1623 cm^{-1} and weaker features at 196, 339, 455, 617, 723, 796.5, 843, 924, 986, 1126, 1216, 1224, and 1607 cm^{-1} (Figure 7b). These bands are characteristic of the azo group pigment marketed under the tradename Hansa red. The second anachronistic pigment encountered occurs as pale green aggregates collected from pages 90v–91r of the Lambeth Palace copy of the Gutenberg Bible. Raman analysis of these grains also results in a complex spectrum being obtained with many intense bands at 174, 200, 221, 233, 290, 412, 510, 544, 619, 643, 649, 684, 706, 740, 746, 775, 816, 838, 956, 978, 1001, 1034, 1081, 1105, 1139, 1197, 1214, 1244, 1282, 1301, 1337, 1387.5, 1445.5, 1466, 1481, 1502, 1537, 1566, 1612, 1672, 1729, 2276, 2875, 2928, 2992, and 3062 cm^{-1}, Figure 7c). The wavenumbers of these bands indicate that the particles are phthalocyanine green, $Cu(C_{32}H_{16-n}Cl_nN_8)$. Both Hansa red and phthalocyanine green are modern synthetic organic pigments produced for the first time in the early 20th century and are therefore out of place on a 15th century manuscript. Particles of these pigments may be present in the page gutters of the Bibles studied as fragments from recent restoration work or as contamination from other sources such as modern printed matter or inks used in pens or modern catalog marks.

CONCLUSIONS

Raman analysis of the primary illuminations of the King George III copy of the Gutenberg Bible held at the British Library shows that the palette consists of cinnabar/vermilion, azurite, calcite (chalk), basic lead carbonate (lead white), lead tin yellow type 1, malachite, an organo–copper complex (a verdigris), carbon-based black, gold leaf, and an organic red pigment.

Comparison with the palettes established for six further copies of the Gutenberg Bible (held at Eton College, Lambeth Palace, the Bibliothèques Mazarine and nationale, the Staatsbibliothek, Berlin, and the SUB Göttingen) by an ex situ method shows that the palettes have many similarities even though the styles of illumination vary considerably. This may be expected in terms of the comparatively limited number of pigments that were available for use in the 15th century across Europe, throughout which a high level of cultural integration of artistic practices had by then taken place. Azurite, cinnabar/vermilion and carbon-based black were identified in all copies of the Bibles examined, with lead tin yellow (type 1), calcite, and gold leaf identified on six out of seven of the Bibles.

Various pigments not found on the King George III copy were identified on the other Bibles. These pigments include lead(II,IV) oxide (Lambeth Palace, Bibliothèque Mazarine, and Göttingen copies), red and yellow ochres (Eton College, Lambeth Palace, Berlin, and Göttingen copies), indigo (Lambeth Palace, Bibliothèque nationale, and Berlin copies), and lazurite (Göttingen and Berlin copies). The presence of lazurite on the German-held Bibles, both printed on vellum, suggests that they were originally purchased by wealthy owners; vellum was undoubtedly more expensive than paper and therefore potentially is a sign of luxury. However, it was also considered to be more durable and therefore also used for nonluxury books, such as elementary school books. The British Library's second copy of the Gutenberg Bible is, in fact, on vellum and is undecorated, indicating perhaps that it was acquired on vellum for durability, rather than for added luxury. The significance as to the choice of vellum rather than paper is thus complex.

The Göttingen copy of the Gutenberg Bible appears to have the most extensive palette, with 16 pigment-related materials identified. Two of these materials (anatase and rutile) may however be present from modern sources. Similarly, examples of two modern 20th pigments (phthalocyanine green and Hansa red) were identified as brightly colored aggregates on two of the Gutenberg Bibles (Lambeth Palace and Bibliothèque nationale, respectively). The presence of these particles may be due to recent restoration work or contamination from other sources (such as inks from modern printed matter, pens, or catalog marks), as opposed to fragmentation from original artwork. This observation is useful from the point of view of the history of collections and the importance of this for using objects as historic evidence. There is no record of the decoration of these volumes having been restored during the 20th century, and this finding highlights the importance of interpreting the present visual appearance of an historic object jointly with its more recent history as part of institutional or private collections.

The ex situ method of analyzing the pigments used for illuminations has been successful in allowing the palettes to be determined of those books to which access is limited by time, equipment availability, etc. However this method is reliant on fragmentation from all pigments in the decoration, and for this reason, only incomplete palettes may potentially be established. Moreover, despite all possible curatorial care having been taken, material from page gutters remains potentially subject to possible contamination.

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