

How do we know what they used?

Spectroscopic techniques for identifying artists' materials

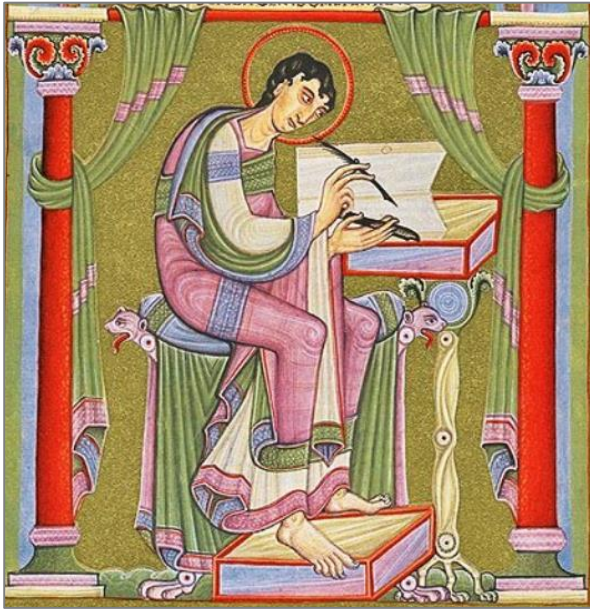
Melissa Vigil (Mysie)
KWHSS, June 24, 2023



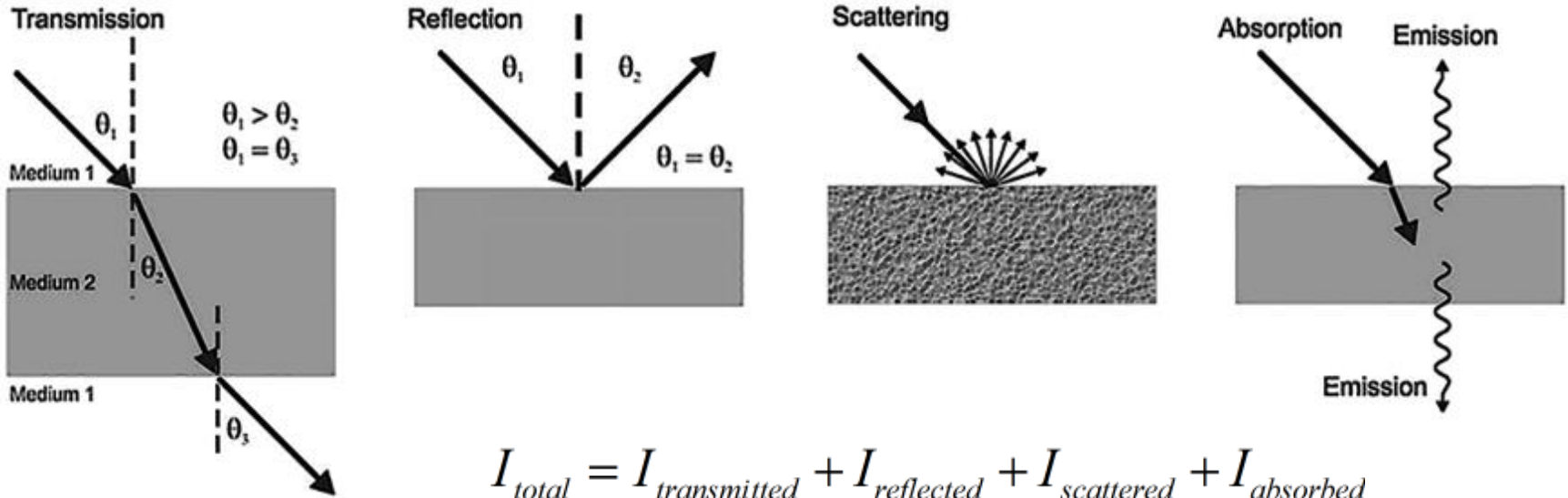
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What evidence do we have concerning the scribal process from manuscript images?

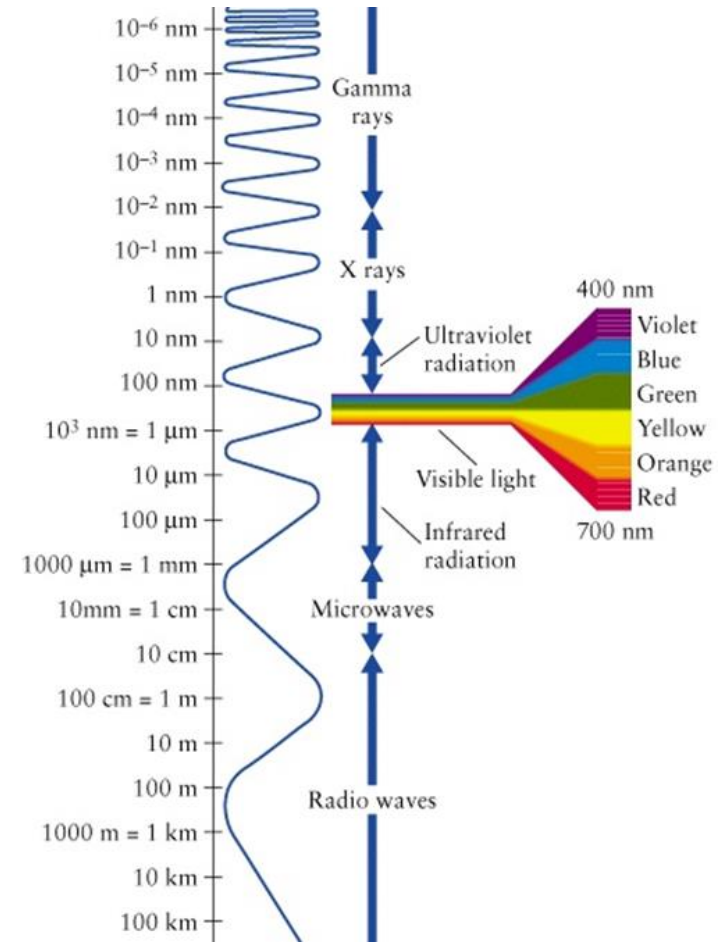
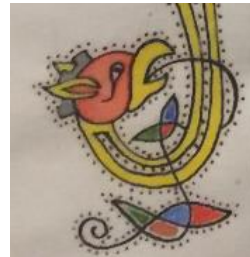
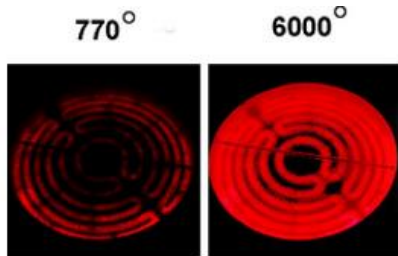


Optics can help us learn more because electromagnetic waves carry information about the materials they encounter



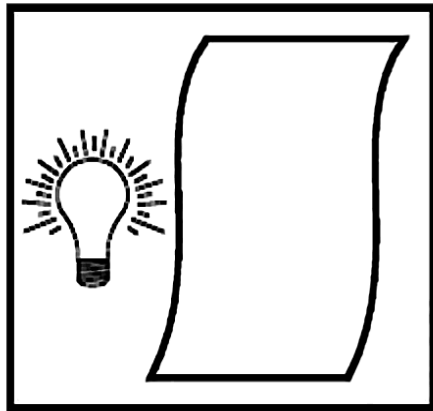
Why do things have color?

- **Temperature** – blackbody radiation
- **Physical structure** – constructive and destructive interference from films, grooves, or holes in the object structure
- **Selective absorption** – atoms, molecules, and crystal structures absorb some energy from some wavelengths than others

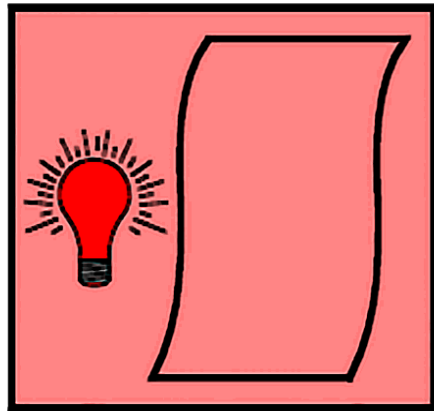


“White” objects reflect all visible wavelengths.

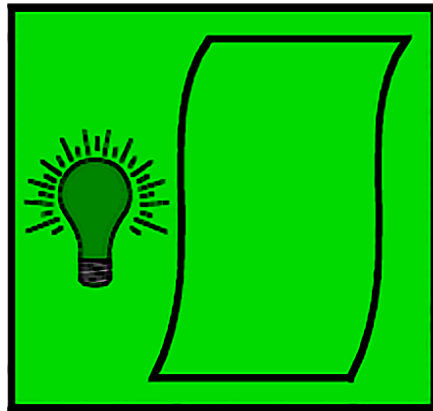
If monochromatic light is used, the “white” object will now match the color of the incident light.



White Light

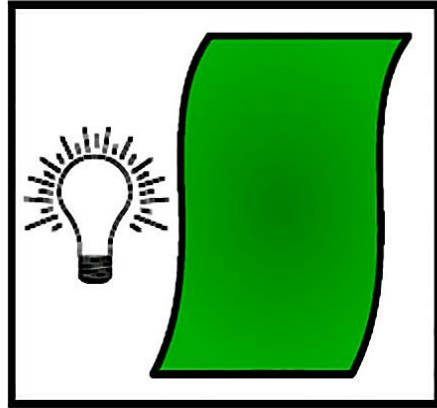


Red Light

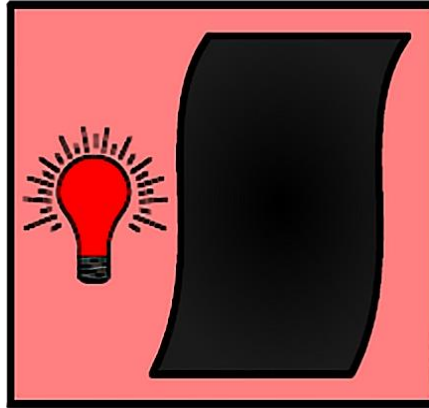


Green Light

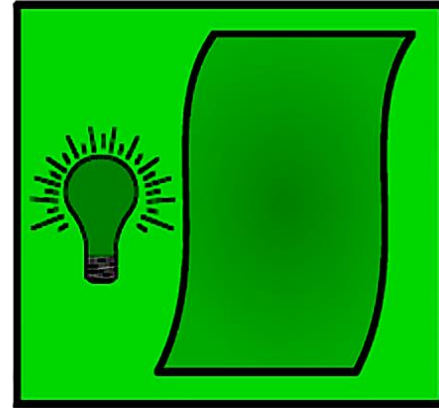
“Colored” objects appear black if the incident light does not include the wavelengths they reflect.



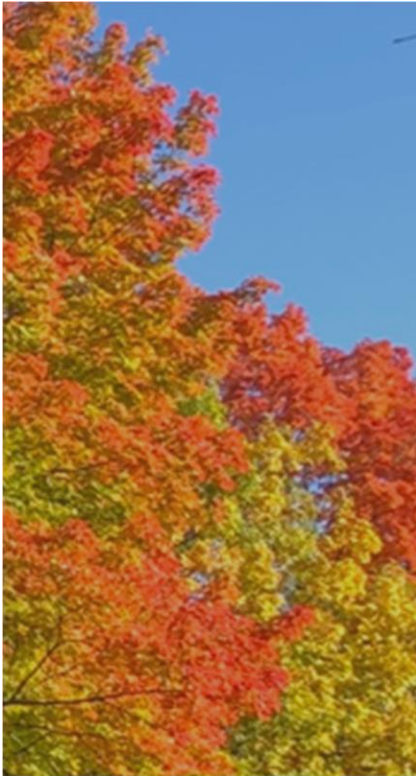
White Light



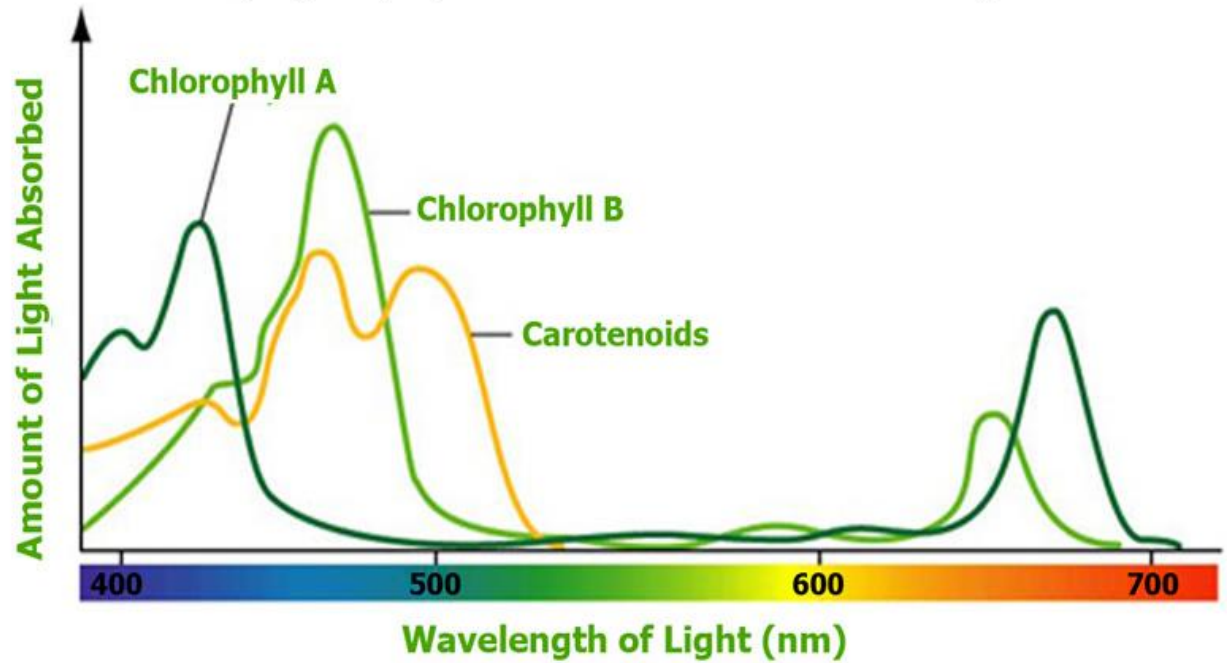
Red Light



Green Light



Chlorophyll A, B, Carotenoid Absorbance Spectra:



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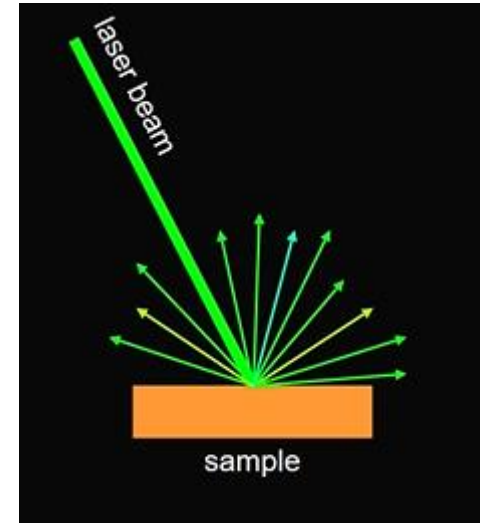
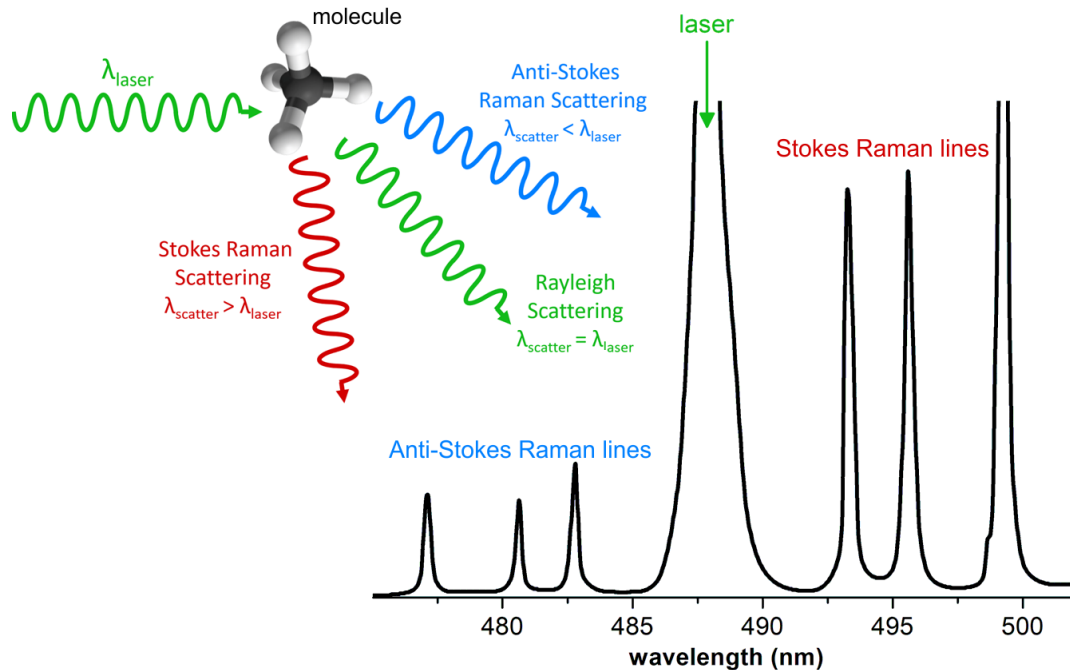
Imaging an object using different light sources gives information about the materials present.



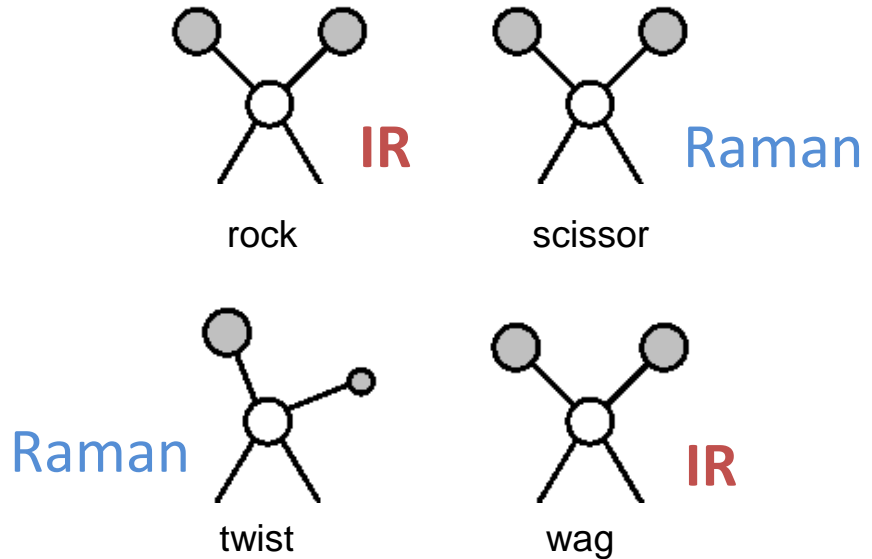
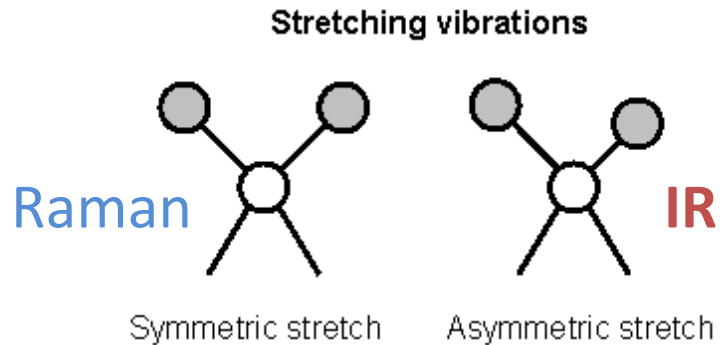
IR imaging can reveal what lies beneath the paint layers.



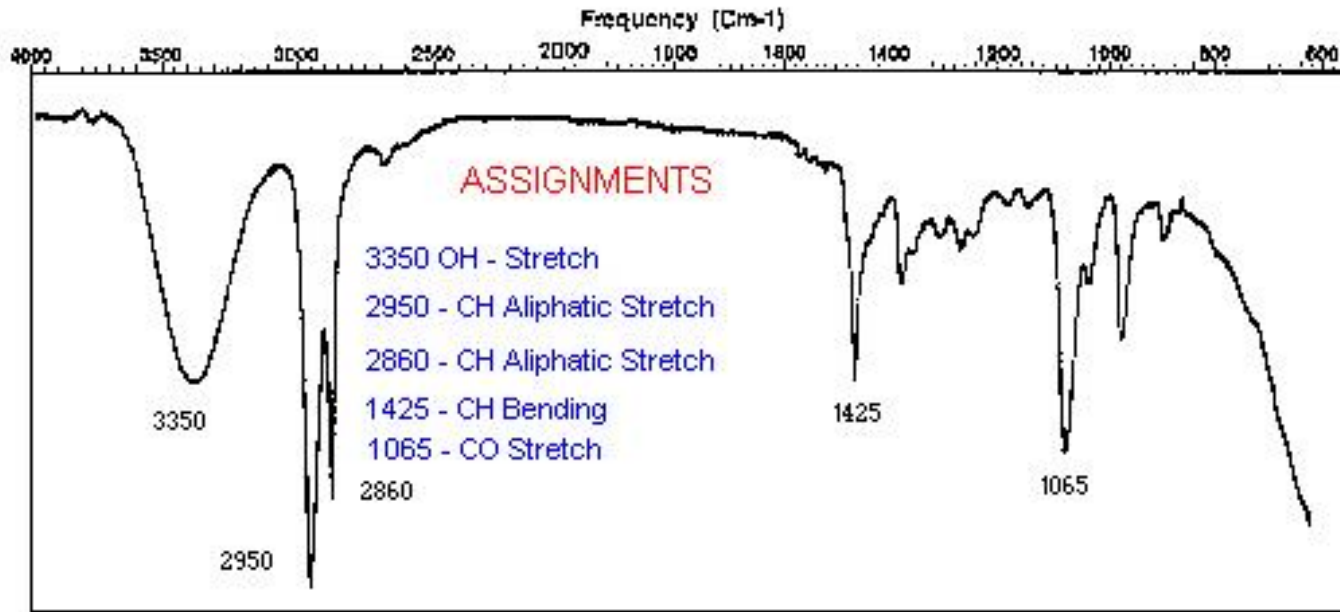
Raman spectroscopy looks for the frequencies of the molecular vibrations.



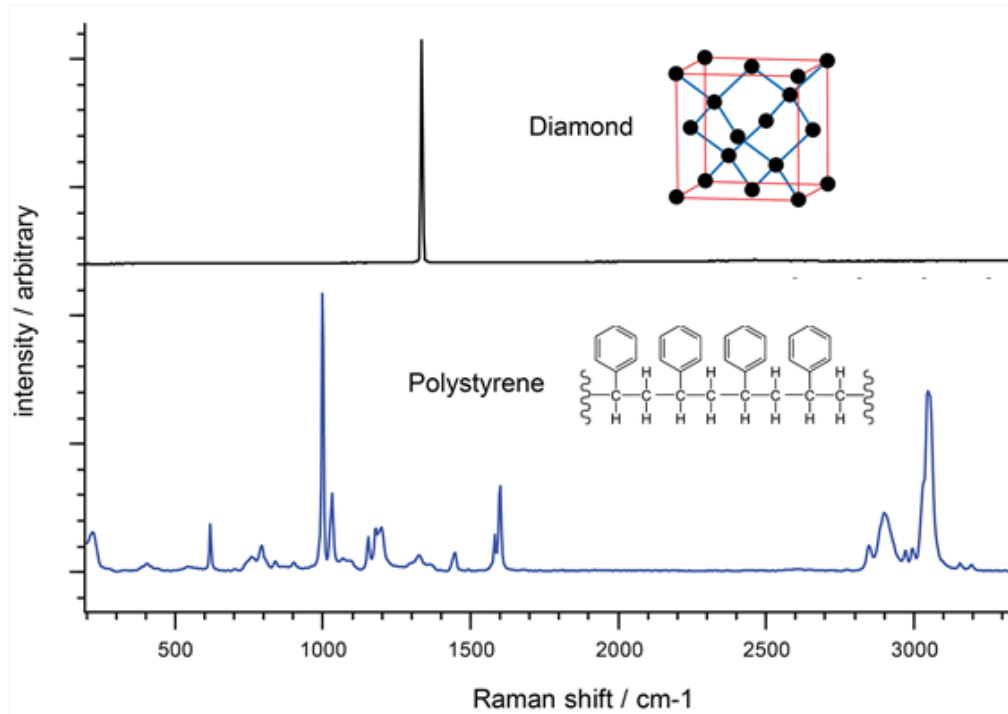
When the light frequency matches the material vibrations, light is absorbed. Others are reflected or transmitted.



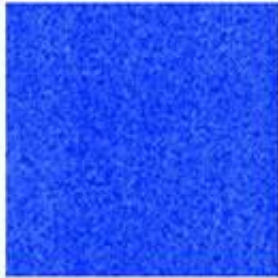
When the light frequency matches the material vibrations, light is absorbed. Others are reflected or transmitted.



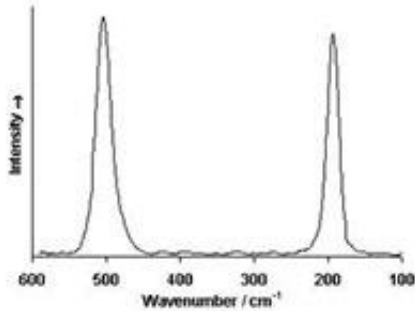
When the light frequency matches the material vibrations, light is absorbed. Others are reflected or transmitted.



<http://colourlex.com/project/raman-spectroscopy/>



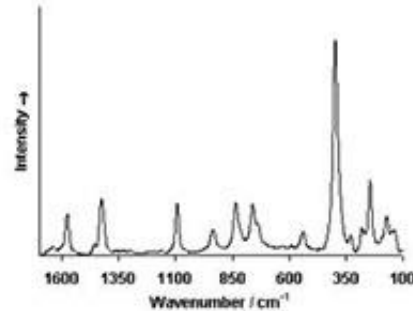
Cobalt blue



Raman spectrum of cobalt blue



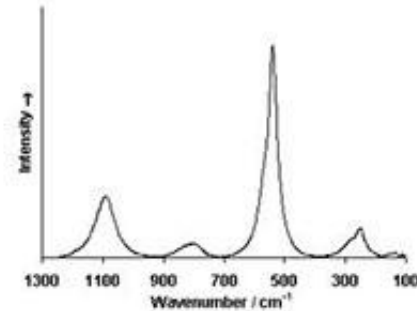
Azurite



Raman spectrum of azurite



Ultramarine



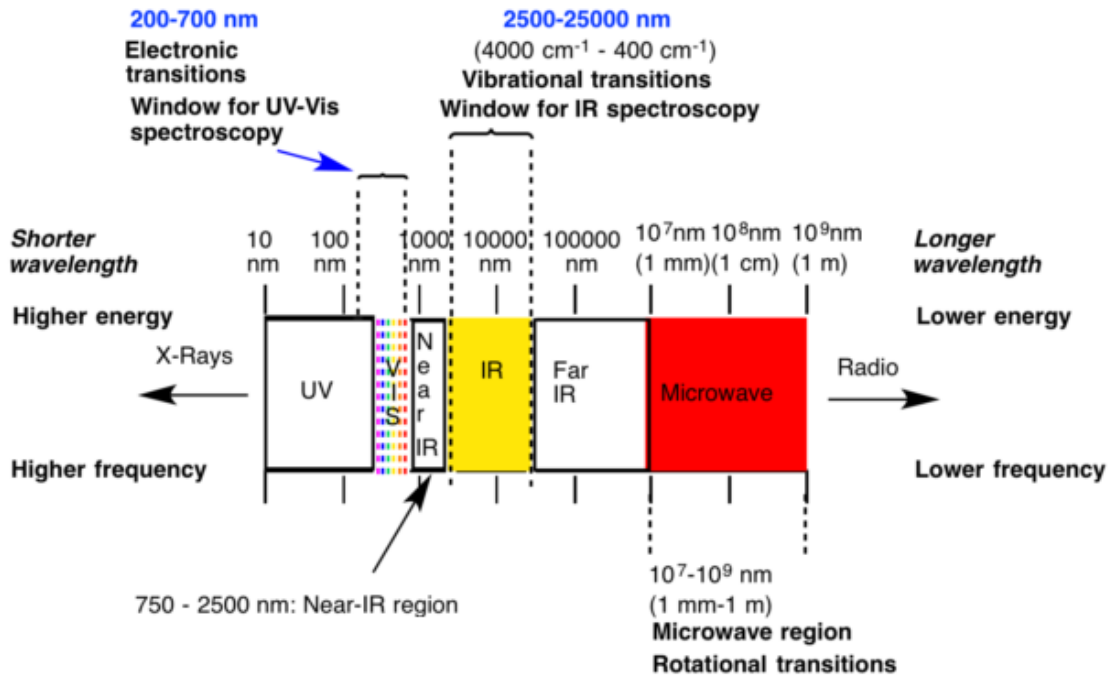
Raman spectrum of ultramarine

<https://www.masterorganicchemistry.com/2016/11/11/bond-vibrations-ir-spectroscopy/>

$$v = f\lambda$$

$$\frac{1}{\lambda} = \frac{c}{f}$$

$$c = 2.998 \times 10^8 \text{ m/s}$$

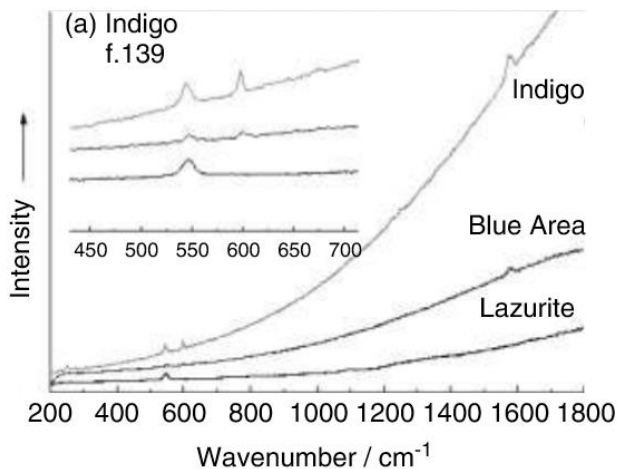


Results from Various Studies

The Lindisfarne Gospels and two other 8th century Anglo-Saxon/Insular manuscripts: pigment identification by Raman microscopy

Katherine L. Brown and Robin J. H. Clark*

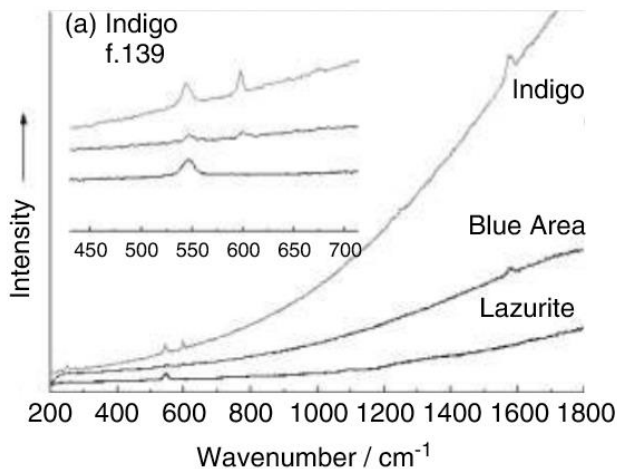
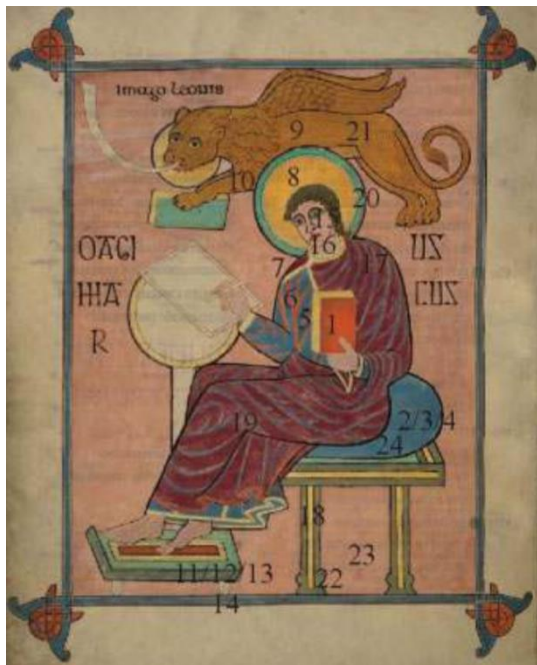
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The Lindisfarne Gospels and two other 8th century Anglo-Saxon/Insular manuscripts: pigment identification by Raman microscopy

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Table 2. The pigments identified on the evangelist portrait of St. Mark — Cotton MS Nero D iv f. 93v

Area	Colour	Pigment	Area	Colour	Pigment
1	Orange	Red lead	13	Green	Possibly verdigris
2	Blue	Indigo	14	Blue	Indigo
3	Blue	Indigo	15	Pink	—
4	Blue	—	16	Red	Red lead
5	Blue	Indigo	17	Dark red	—
6	Red	Red lead	18	Yellow	Orpiment
7	Pink	—	19	Black	Probably iron gall, Trace carbon
8	Yellow	Orpiment	20	Green	Verdigris
9	Yellow	—	21	Yellow	—
10	Yellow	—	22	Green	Indigo/orpiment
11	Dark green	Indigo, Trace orpiment	23	Pink	—
12	White	Plain parchment	24	Black	Probably iron gall

<https://onlinelibrary.wiley.com/doi/epdf/10.1002/jrs.1110>



Anal. Chem. 1996, 68, 1755–1761

Characterization of Pararealgar and Other Light-Induced Transformation Products from Realgar by Raman Microspectroscopy

Karen Trentelman* and Leon Stodulski

Mark Pavlosky

<https://pubs.acs.org/doi/pdfplus/10.1021/ac951097o>



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<http://marinmineral.com/mixed289.html>

<https://www.dakotamatrix.com/mineralpedia/7020/orpiment>

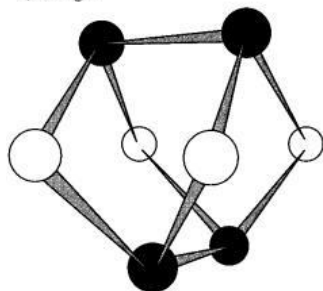
<https://www.dia.org/art/collection/object/dreams-men-63568>

Characterization of Pararealgar and Other Light-Induced Transformation Products from Realgar by Raman Microspectroscopy

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<https://pubs.acs.org/doi/pdfplus/10.1021/ac951097o>

a) Realgar



b) Pararealgar

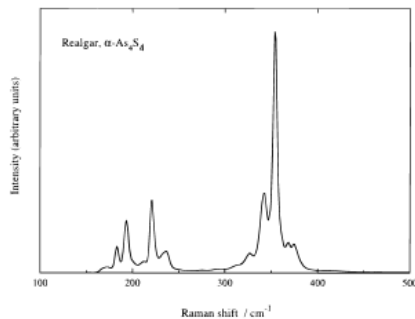
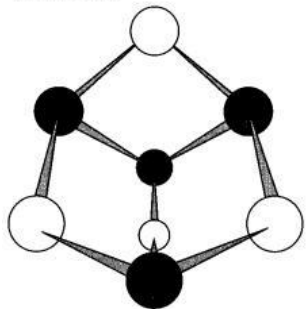


Figure 2. Raman spectrum of red crystals from realgar sample. This spectrum is identified as that of the low-temperature phase of realgar, α -As₄S₆.

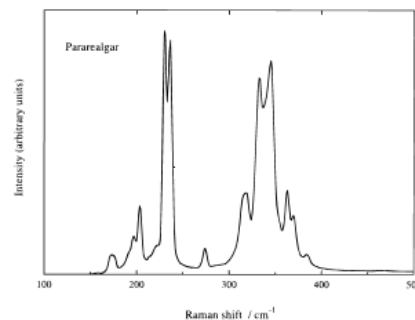


Figure 3. Raman spectrum of yellow material removed from surface of light-irradiated realgar sample. The material is identified as pararealgar.

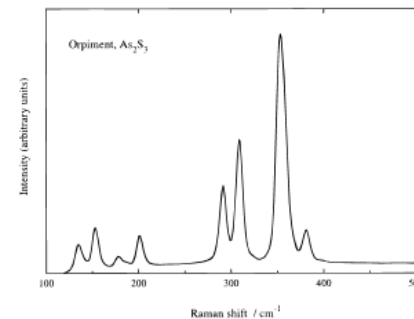


Figure 4. Raman spectrum of orpiment.

Raman microscopy and x-ray fluorescence analysis of pigments on medieval and Renaissance Italian manuscript cuttings

Lucia Burgio^{ab}, Robin J. H. Clark^{b1}, and Richard R. Hark^c

5726–5731 | PNAS | March 30, 2010 | vol. 107 | no. 13

Pigment	A	B	C
Lead white	✓	✓	✓
Gypsum			✓
Azurite	✓	✓	✓
Lazurite	✓	✓	✓
Indigo	✓	✓	✓
Malachite	✓	✓	✓
Vermilion	✓	✓	✓
Red lead	✓	✓	✓
Lead tin yellow (I)	✓	✓	✓
Goethite		✓	✓
Carbon	✓	✓	✓
Iron gall ink	✓	✓	✓
Mosaic gold		Impurity	✓
Shell gold		✓	✓
Shell silver	✓		✓

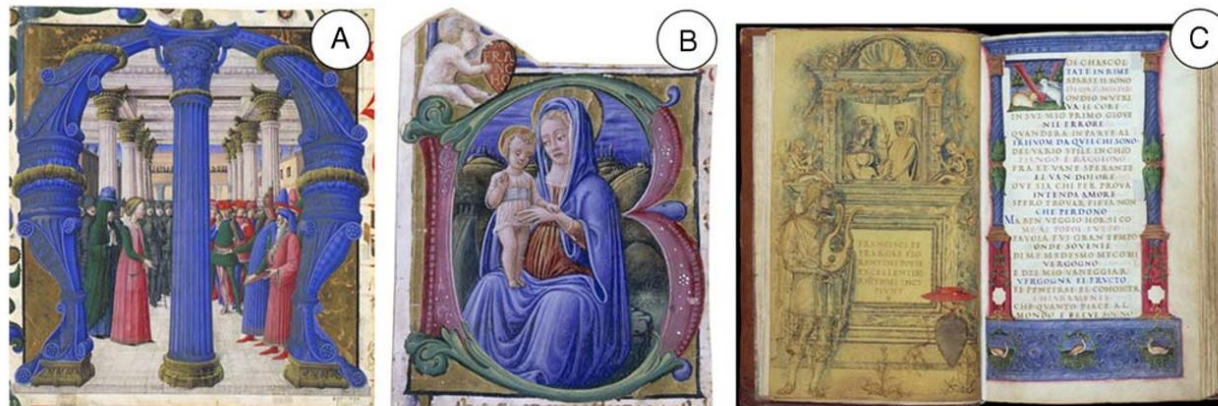


Fig. 1. Some of the cuttings analyzed in this study: (A) St. Giustina of Padua disputing with the Emperor Massimian, by Gerolamo da Cremona (V&A accession number 817-1894); (B) Madonna and Child, by Franco de' Russi (V&A accession number E.1275-1991); (C) two pages from the *Sonnets and Triumphs* by Francesco Petrarca, painted by Bartolomeo Sanvito (V&A accession number L.101-1947). Copyright Victoria and Albert Museum, London.

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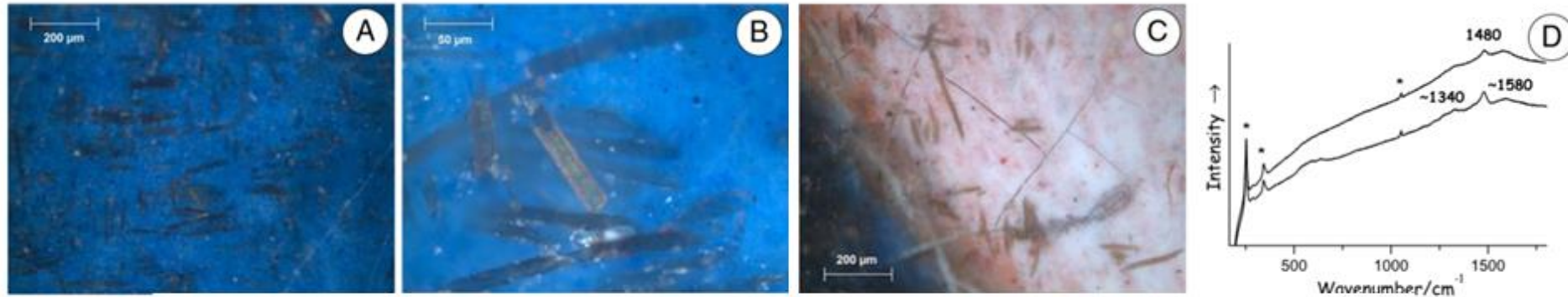


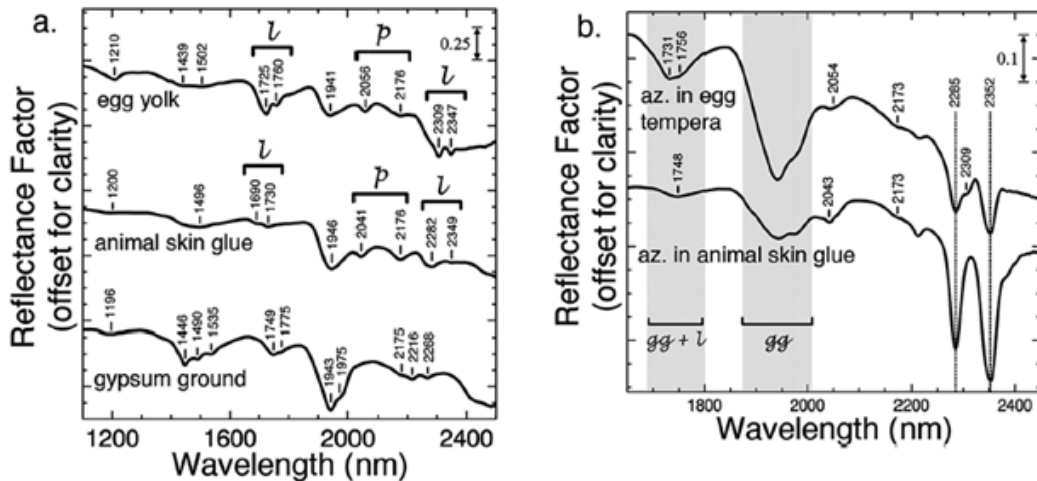
Fig. 3. Microscopy images of areas rich in needle-shaped crystals of iron gall ink: *dark blue shadow* area on the Virgin's mantle, $\times 100$ magnification (A) and $\times 400$ magnification (B); proper right side of mouth of the Virgin, $\times 100$ magnification (C); Raman spectra from the needle-shaped crystals of iron gall ink (signature band at $1,480\text{ cm}^{-1}$) in the Child's flesh tones. The asterisks mark the peaks due to vermilion and lead white in the carnation mixture (D).

Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy

Kathryn A. Dooley,^{ab} Suzanne Lomax,^a Jason G. Zeibel,^c Costanza Miliani,^d Paola Ricciardi,^{†a} Ann Hoenigswald,^a Murray Loew^b and John K. Delaney^{*ab}



Fig. 4 Visible image and endmember map for Gabriel. (Left) Colour image. (Right) False-colour image showing the locations to which the endmembers map in the panel. Egg yolk binder (red EM) maps mainly to Gabriel's red robe. Glue binder (blue EM) maps to areas of the face and feet. Azurite in a glue binder (green EM) and malachite in an egg yolk binder (yellow EM) map to the sky and dark green tunic and wings, respectively.



https://www.researchgate.net/publication/242015258_Mapping_of_egg_yolk_and_animal_skin_glue_paint_binders_in_Early_Renaissance_paintings_using_near_infrared_reflectance_imaging_spectroscopy

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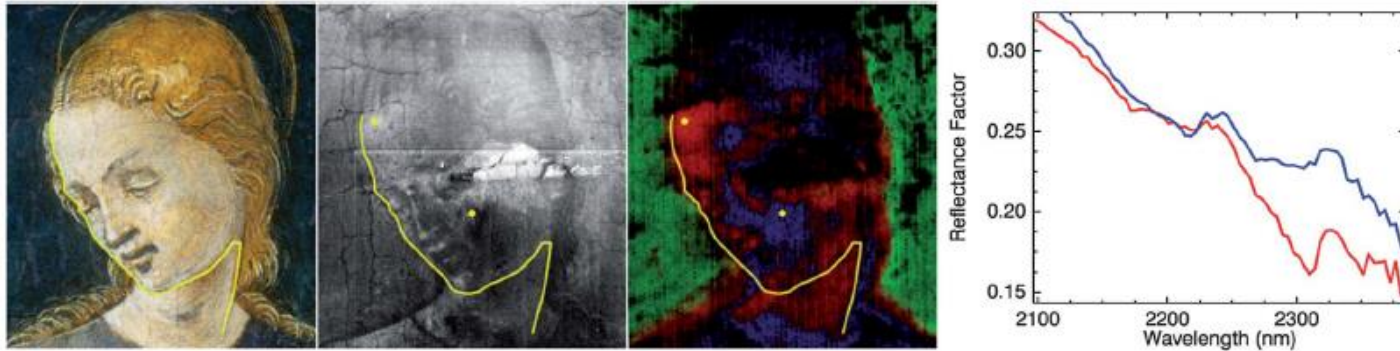


Fig. 9 Detail images for head region of the Virgin. (Left) Colour image. (Middle left) X-ray photograph showing areas of lead white highlights and the loss on her proper left cheek and ear. (Middle right) Endmember map in which red regions have stronger lipid absorbance and blue regions have little-to-no lipid absorbance. The yellow trace is a line of reference. (Right) Average spectra from a 2×2 pixel region (denoted by yellow dots in the middle images) from the Virgin's forehead and cheek.



Spectroscopic analysis of pigments and inks in manuscripts. III. Old-Slavonic manuscripts with multicolored rubrication

Irena Nastova^a, Orhideja Grupče^{a,*}, Biljana Minčeva-Šukarova^a, Maja Kostadinovska^b,
Melih Ozcatal^c

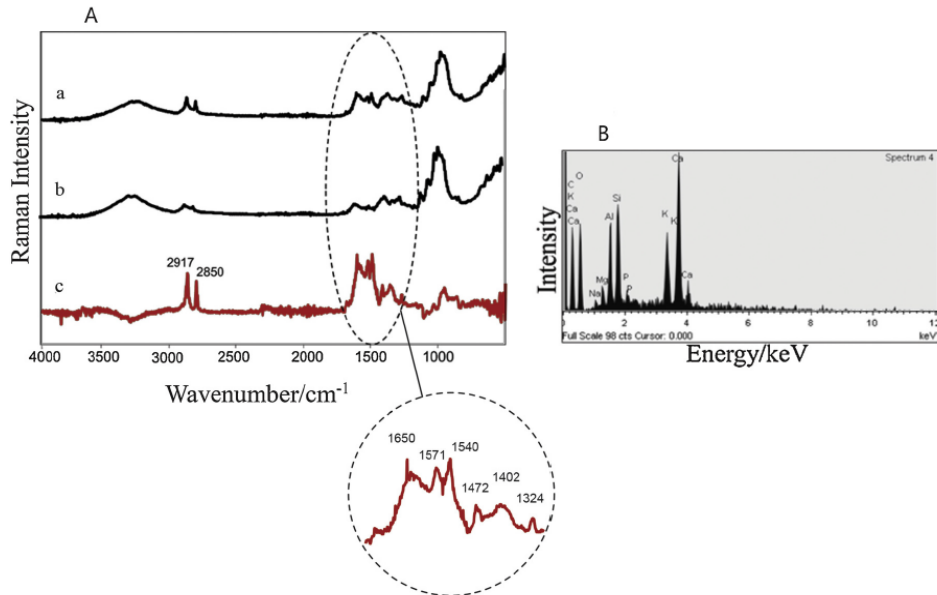


Fig. 5. K₂O manuscript: (A) Representative FTIR spectra of the purple-red pigment (a) pigment and paper (b) clean paper (c) subtraction with enlarged section; (B) Representative SEM-EDX spectrum of the purple-red pigment.

Spectroscopic analysis of pigments and inks in manuscripts. III. Old-Slavonic manuscripts with multicolored rubrication

Irena Nastova^a, Orhideja Grupče^{a,*}, Biljana Minčeva-Šukarova^a, Maja Kostadinovska^b,
Melih Ozcatal^c

Color	Z_FG (End of 16th/beginning of 17th c.)	K_FG (End of 16th/beginning of 17th c.)	S_FG (Beginning of 17th c.)	P_R (First half of 16th c.)	K_O (Second half of 15th c.)
Illumination					
Yellow	n/a	Orpiment	Orpiment	Orpiment	n/a
Gold	Gold	n/a	Gold	n/a	n/a
Bright-red	Vermilion + red lead	Vermilion	Vermilion	Vermilion + red lead	Vermilion
Purple-red	Organic purple-red,vermilion + red lead	n/a	n/a	Organic purple-red	n/a
Blue	Indigo, azurite	Azurite	Indigo, azurite	Azurite	Azurite
Green	n/a	n/a	Organo-Cu complex	n/a	n/a
Brown	Gall ink	Gall ink	Gall ink	Gall ink	Gall ink
Inks					
Red	Vermilion + Red lead	Vermilion	Vermilion	Vermilion	Vermilion
Purple-red	Madder	Madder	n/a	n/a	Madder
Blue	Indigo, azurite	Azurite	Indigo, azurite	n/a	
Brown/Black	Gall ink	Gall ink	Gall ink	Gall ink, carbon	Gall ink, carbon, logwood

Identification of iron-gall inks in historical drawings by Fibre Optics Reflection Spectroscopy – Extension to the NIR spectral range

Milena Reháková^{a,*}, Lukáš Gál^a, Michaela Belovičová^a, Michal Oravec^a, Vladimír Dvonka^a, Danica Stojkovičová^b, Michal Čeppan^a

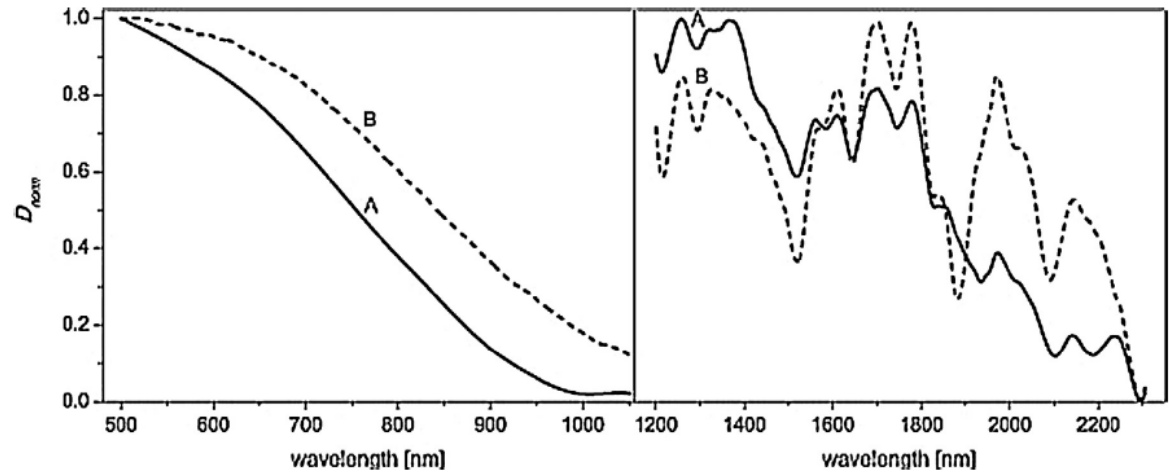


Fig. 4. Vis-NIR (left) and NIR (right) spectra of the drawing in Fig. 3.

Identification of iron-gall inks in historical drawings by Fibre Optics Reflection Spectroscopy – Extension to the NIR spectral range

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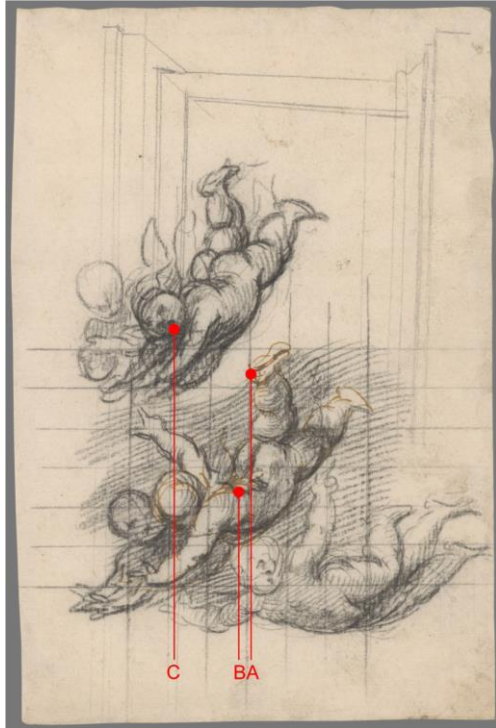


Table 2

The results of TFA and XRF analysis of three drawings from the collections of the Slovak National Gallery.

Drawing		AET (Vis–NIR)	SPOIL (Vis–NIR)	AET (NIR)	SPOIL (NIR)	XRF
K1473	A	0.006	3.9	0.021	6.9	No Fe
	B	0.007	4.1	0.016	6.5	No Fe
K1063	A	0.004	3.1	0.008	2.5	Fe
	B	0.004	3.5	0.008	2.4	Fe, Cu
K1510	A	0.004	4.1	0.007	2.6	Fe
	B	0.032	7.2	0.016	9.4	No Fe
	C	0.032	7.5	0.027	8.1	No Fe

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