Table S1. Detailed description of the spectral library assembled, with indications of the dye molecular classes and of the experimental conditions used to acquire the spectra. Abbreviations: MW colloid = colloid prepared by microwave-assisted reduction of silver sulfate; LM colloid = colloid produced according to the Lee-Meisel procedure.

Colorant	Molecular class	Technique	λ_{exc}	Experimental conditions
Acid Orange 7	Monoazo	SERS	488 nm	MW colloid, extract from dyed fiber
Alizarin	Anthraquinone	Raman	488 nm	Analysis of the powder
Alizarin	Anthraquinone	FT-Raman	1064 nm	Analysis of the powder
Alizarin	Anthraquinone	SERS	488 nm	MW colloid
Alizarin	Anthraquinone	SERS	488 nm	MW colloid, pH=2
Alizarin	Anthraquinone	SERS	488 nm	MW colloid, pH=4.5
Alizarin	Anthraquinone	SERS	488 nm	MW colloid, pH=7
Alizarin	Anthraquinone	SERS	488 nm	MW colloid, pH=9
Alizarin	Anthraquinone	SERS	488 nm	MW colloid, pH=12
Alizarin/Purpurin	Anthraquinone	SERS	488 nm	1:1 mixture, MW colloid
Alizarin/Purpurin	Anthraquinone	SERS	488 nm	1:3 mixture, MW colloid
Alizarin/Purpurin	Anthraquinone	SERS	488 nm	3:1 mixture, MW colloid
Aniline Blue	Tryphenylmethane	SERS	488 nm	LM colloid
Aniline Blue	Tryphenylmethane	SERS	633 nm	LM colloid
Aniline Blue	Tryphenylmethane	SERS	785 nm	LM colloid
Bixin	Carotenoid	Raman	488 nm	Analysis of the powder
Bixin	Carotenoid	Raman	633 nm	Analysis of the powder
Bixin	Carotenoid	Raman	785 nm	Analysis of the powder
Brilliant Blue R	Tryphenylmethane	SERS	633 nm	LM colloid
Brilliant Blue R	Tryphenylmethane	SERS	785 nm	LM colloid
Brilliant Cresyl Blue	Oxazin	SERS	633 nm	LM colloid
Brilliant Cresyl Blue	Oxazin	SERS	785 nm	LM colloid
Cabbage	Anthocyanin	SERS	488 nm	MW colloid, extract from the plant
Carminic Acid	Anthraquinone	Raman	488 nm	Analysis of the powder
Carminic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=2
Carminic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=4.5
Carminic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=7
Carminic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=9
Carminic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=12
Carmine	Anthraquinone	Raman	488 nm	Analysis of the powder
Carmine	Anthraquinone	SERS	488 nm	MW colloid
Carmine	Anthraquinone	SERS	488 nm	MW colloid, HF hydrolysis
Celestine Blue B	Oxazin	SERS	633 nm	LM colloid
Celestine Blue B	Oxazin	SERS	785 nm	LM colloid

Cresyl Violet A	Oxazin	SERS	633 nm	LM colloid
Cresyl Violet A	Oxazin	SERS	785 nm	LM colloid
Crystal Violet	Tryphenylmethane	SERS	488 nm	LM colloid
Crystal Violet	Tryphenylmethane	SERS	633 nm	LM colloid
Crystal Violet	Tryphenylmethane	SERS	785 nm	LM colloid
Eosin Y disodium	Fluorone	SERS	488 nm	LM colloid
Eosin Y disodium	Fluorone	SERS	633 nm	LM colloid
Eosin Y disodium	Fluorone	SERS	785 nm	LM colloid
Erythrosin B	Fluorone	SERS	488 nm	LM colloid
Erythrosin B	Fluorone	SERS	633 nm	LM colloid
Erythrosin B	Fluorone	SERS	785 nm	LM colloid
Gallocyanine	Oxazin	SERS	633 nm	LM colloid
Gallocyanine	Oxazin	SERS	785 nm	LM colloid
Harmaline	Alkaloid	Raman	488 nm	Analysis of the powder
Harmaline	Alkaloid	Raman	633 nm	Analysis of the powder
Harmaline	Alkaloid	Raman	785 nm	Analysis of the powder
Harmaline	Alkaloid	FT-Raman	1064 nm	Analysis of the powder
Harmaline	Alkaloid	SERS	488 nm	MW colloid
Harmane	Alkaloid	Raman	488 nm	Analysis of the powder
Harmane	Alkaloid	Raman	633 nm	Analysis of the powder
Harmane	Alkaloid	Raman	785 nm	Analysis of the powder
Harmane	Alkaloid	FT-Raman	1064 nm	Analysis of the powder
Harmane	Alkaloid	SERS	488 nm	MW colloid
Harmalol	Alkaloid	FT-Raman	1064 nm	Analysis of the powder
Harmalol	Alkaloid	SERS	488 nm	MW colloid
Indigo	Indigoid	Raman	488 nm	Analysis of the powder
Indigo	Indigoid	Raman	785 nm	Analysis of the powder
Indigo	Indigoid	FT-Raman	1064 nm	Analysis of the powder
Indigo	Indigoid	SERS	488 nm	MW colloid
Laccaic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=2
Laccaic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=4.5
Laccaic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=7
Laccaic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=9
Laccaic Acid	Anthraquinone	SERS	488 nm	MW colloid, pH=12
Madder	Anthraquinone	Raman	488 nm	Analysis of the powder
Madder	Anthraquinone	FT-Raman	1064 nm	Analysis of the powder
Madder	Anthraquinone	SERS	488 nm	MW colloid
Madder	Anthraquinone	SERS	488 nm	MW colloid, HF hydrolysis
Methyl Violet	Triphenylmethane	SERS	633 nm	LM colloid
Methyl Violet	Triphenylmethane	SERS	785 nm	LM colloid
Monobromoindigo	Indigoid	Raman	488 nm	Analysis of the powder

Monobromoindigo	Indigoid	Raman	785 nm	Analysis of the powder
Monobromoindigo	Indigoid	FT-Raman	1064 nm	Analysis of the powder
Monobromoindigo	Indigoid	SERS	488 nm	MW colloid
Patent Blue	Triphenylmethane	SERS	633 nm	LM colloid
Patent Blue	Triphenylmethane	SERS	785 nm	LM colloid
Purpurin	Anthraquinone	Raman	488 nm	Analysis of the powder
Purpurin	Anthraquinone	SERS	488 nm	MW colloid
Purpurin	Anthraquinone	SERS	488 nm	MW colloid, pH=2
Purpurin	Anthraquinone	SERS	488 nm	MW colloid, pH=4.5
Purpurin	Anthraquinone	SERS	488 nm	MW colloid, pH=7
Purpurin	Anthraquinone	SERS	488 nm	MW colloid, pH=9
Purpurin	Anthraquinone	SERS	488 nm	MW colloid, pH=12
Rhodamine 6G	Triphenylmethane	SERS	488 nm	LM colloid
Rhodamine 6G	Triphenylmethane	SERS	633 nm	LM colloid
Rhodamine 6G	Triphenylmethane	SERS	785 nm	LM colloid
Rhubarb	Anthocyanin	SERS	488 nm	MW colloid, extract from the plant
Sandal	Biflavonoid	SERS	488 nm	MW colloid, extract from the plant
Sappan	Neoflavonoid	SERS	633 nm	MW colloid, extract from the plant
Sulforhodamine B	Triphenylmethane	SERS	488 nm	LM colloid
Sulforhodamine B	Triphenylmethane	SERS	633 nm	LM colloid
Sulforhodamine B	Triphenylmethane	SERS	785 nm	LM colloid
Sunset Yellow FCF	Monoazo	SERS	488 nm	LM colloid
Syrian Rue	Alkaloid	SERS	488 nm	MW colloid, extract from the plant
Victoria Blue	Triphenylmethane	SERS	633 nm	LM colloid
Victoria Blue	Triphenylmethane	SERS	785 nm	LM colloid

Table S2. Detailed results of the classification tests of query spectra from works of art using PCA and CC algorithm combined with those series of spectral trasformations which led to the best classification rate. Misclassifications are marked with an asterisk.

Query SERS spectra	Colorant	PCA match BCC/Scaling	CC match BCC/Smoothing/Scaling/IIDer.
Lake pigment from Corinth, Greece	Madder	Madder SERS488nm_HF	Madder SERS488nm_HF
Alizarin crimson (Winsor & Newton)	Alizarin	Alizarin SERS488nm_pH=2	Alizarin SERS488nm_pH=2
Carmine (Winsor & Newton)	Carmine	**Laccaic acid*** SERS488nm_pH=2	Carmine SERS488nm_HF
Mauve (Winsor & Newton)	Crystal violet	Crystal violet SERS488nm	Crystal violet SERS488nm
Feathered bag from Peru	Madder	Purpurin SERS488nm_pH=2	Madder SERS488nm_HF
Cap with feathers from Chile	Madder	Purpurin SERS488nm_pH=2	Madder SERS488nm_HF
Tunic from Peru	Madder	Madder SERS488nm	Madder SERS488nm_HF
Tasseled tunic from Peru	Carmine	Carmine SERS488nm_HF	Carmine SERS488nm_HF
Crucifix from Spain	Lac dye	Laccaic acid SERS488nm_pH=9	Laccaic acid SERS488nm_pH=2
Bust of Saint Barbara	Madder	Madder SERS488nm_HF	Madder SERS488nm_HF
Statue of Caligula	Madder	Madder SERS488nm_HF	Madder SERS488nm_HF
Mandolin by Vinaccia	Carmine	Carmine SERS488nm_HF	Carmine SERS488nm_HF
Nur al-Din panel, red	Carmine	Carminic acid SERS488nm_pH=2	Carminic acid SERS488nm_pH=2
Nur al-Din panel, violet	Lac dye	Laccaic acid SERS488nm_pH=9	Laccaic acid SERS488nm_pH=12
Painted cloth from India	Lac dye	Laccaic acid SERS488nm_pH=4.5	Laccaic acid SERS488nm_pH=2
Silver ball, barge, and trees by Dove	Madder	Purpurin SERS488nm_pH=2	Madder SERS488nm_HF
The card players by Lievens, red 1	Madder	Madder SERS488nm	Madder SERS488nm_HF
The card players by Lievens, red 2	Madder	**Carmine*** SERS488nm_HF	Madder SERS488nm_HF
The card players by Lievens, red 3	Madder	Madder SERS488nm_HF	Madder SERS488nm_HF
The card players by Cézanne	Madder	Madder SERS488nm_HF	Madder SERS488nm_HF