Lavinia de Ferri
l.de.ferri@khm.uio.no

[1]Lavnia de Ferri, [2]Beatrice Campanella, [3]Davide Vallotto, [3]Alice Martignon, [2]Stefano Legnaioli, [3]Benedetta Tomaini, [3]Giulio Pojana

1 Museum of Cultural History, University of Oslo, Oslo, Norway
2 Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of CNR, Pisa, Italy
3 Department of Philosophy and Cultural Heritage, Ca' Foscari University of Venice, Venice, Italy

Application of spectroscopic and imaging techniques for the study of historical natural dyes.

The collection

Moisè Michelangelo Guggeneheim was the greatest antique dealer of Venice in the second half of the 19th century, other than a designer and a consultant for museum collectors and other dealers.
The textile collection was originally composed of about 800 fragments ranging from the 4th to the 19th century. The collection is currently divided among 4 owners: 2 museums, the heirs and **140 fragments** were donated to the ***Venetian School of Art Applied to Industry***, that he co-funded in 1872. The school has become the *Liceo Artistico Statale «Michelangelo Guggenheim»* that still owns this part of the collection.

Portrait of M. Michelangelo Guggenheim

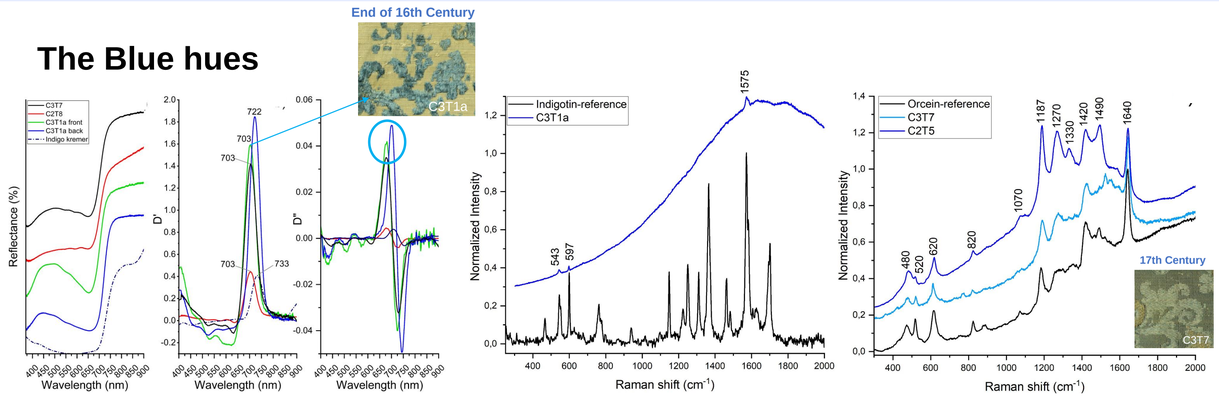
Methods

VIS images:
Nikon D800e digital camera; Zeiss lens Makroplanar 100mmf/2.8; ISO100; f8 aperture; shutter speed 1/2 -1/16 s; White and color calibrations by a ColorChecker Passport panel and X-Rite software.
UVR-images:
Modified Samsung NX1100 digital camera (removal of low-pass filter); Olympus Zuiko 28-mm f/2.8 lens; 50-mm Macro f/3.5; Badeer-U filter for the 320–380 nm range. Light source at 365 nm.
IRR-Images:
Modified Samsung NX1100 digital camera (removal of low-pass filter); Olympus Zuiko 28-mm f/2.8 lens; 50-mm Macro f/3.5; Hoya (Kenko Tokina Ltd., Tokyo, Japan) RM90 IR pass filter for the 900-1150 nm range. Tungsten light source
Elaboration:
Adobe lightroom + Adobe Photoshop CS6. Methods adapted by [1]
VIS-Reflectance Spectroscopy (VRS)
Portable fiber optic spectrophotometer Quest U (B&W Tek Inc); Y-shaped silica glass fiber bundle; 0.28 mm^2 collecting spot; Optical resolution of~ 1.5 nm; 2048 pixel linear silicon CCD array detector; Tungsten light source; Spectral range.370–950 nm; 250 cycles of 12–42 ms each; incident and acquisition angles at 45° from the surface normal; Calibration: 99% Teflon diffuse reflectance metrological Labsphere.
SERSS-Surface Enhanced Raman Scattering Spectroscopy
Dyes extraction: ~1 mg of textile sample in 50 µL of 0.5 M oxalic acid/ methanol/ acetone/ water (1: 30: 40: 40 v/v/v/v) solution; Ultrasound: 30 minutes at 60 °C.
Silver colloid: Lee and Meisel synthesis procedure
Raman Measurements: 5 µL of Ag colloid + 1 µL of extract; Renishaw InVia spectrometer + optical Leica DLML microscope; NPLAN objective 20×; NdYAG laser at 532 nm; laser power output 1-5 mW; 1200 lines mm^{-1} grating monochromator; Spectral range: 350 and 2000 cm^{-1}; 3 accumulations and an exposure time of 10 s; Spectral intensities normalised by scaling their values between 0 and 1; No smoothing or baseline correction.

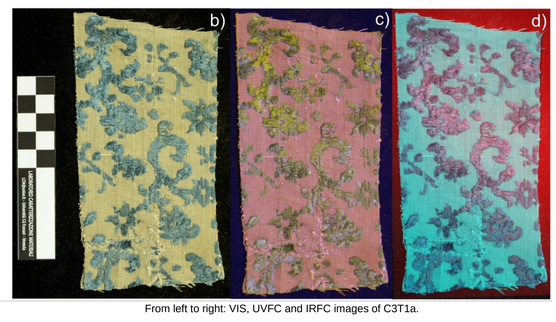
Sample	Color	Date (century)	Sample	Color	Date (century)
C1T2a	red	16th	**C2T7**	dark red	16th-second half
C1T2b	yellow/gold	16th	**C2T8**	red	/
C1T3	green	16th	**C2T9**	red	/
C1T4	Purple, blue	16th-last quarter	**C3T1a**	blue	16th-end of
C1T5	red	16th-17th	**C3T1b**	green	16th
C2T1	purple	/	**C3T2**	red	18th
C2T2	red	15th-16th	**C3T4**	brown	15th
C2T3	Green, yellow, brown/orange	15th-16th	**C3T6a**	green	16th
C2T4	blue	/	**C3T6b**	green	16th
C2T5	Blue, gray	/	**C3T7**	blue	17th-last quarter
C2T6	Blue, brown/orange	/	**C3T9**	Dark and light pink	/
			C3T12	Red, light and dark brown	18th-last quarter

List of the analyzed fragments, samples threads and dates.

The Blue hues



VRS
- Only indigotin in all the blue areas
- Spectral differences between the front and the back side: conservation condition of the dye



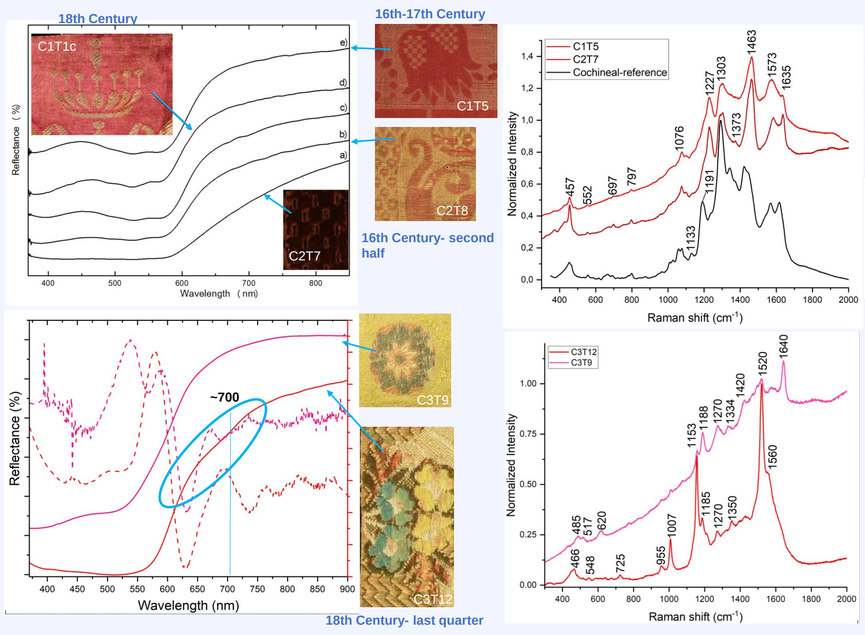
From left to right: VIS, UVFC and IRFC images of C3T1a.

SERSS
- **Indigotin**: exclusivly only in a couple of fragments (a)
- 4 fragments contained also **orcein**, not revealed by VRS

FC imaging
- UV and IR-FC images confirm the presence of indigotin
- Images don't show differences when orcein is present (c,d)

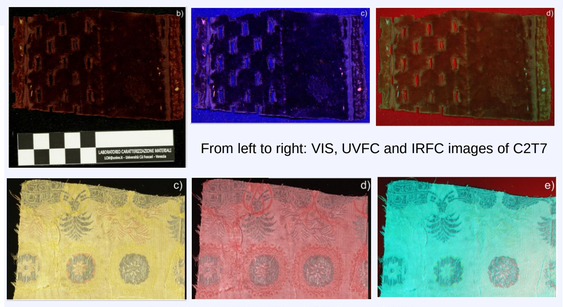
- Combination of indigotin and orcein: since the end of the 13th century.
- *Indigo* as source of indigotin was introduced in the 16th century and became prevalent in the 17th century.
- Both *Indigo* and *Woad* are possible sources for **C1T4** dated back to the beginning of the 16th century.

The Red & Pink hues



VRS
- Anthraquinones, mostly of animal origin
- Flat shape of C2T7: high concentration of the dye
- Slope change in C3T12: second component

SERS
- **Cochineal** (Carminic acid)
- **Annatto** (bixin/norbixin) in C3T12
- **Orcein** and **Annatto** in C3T9



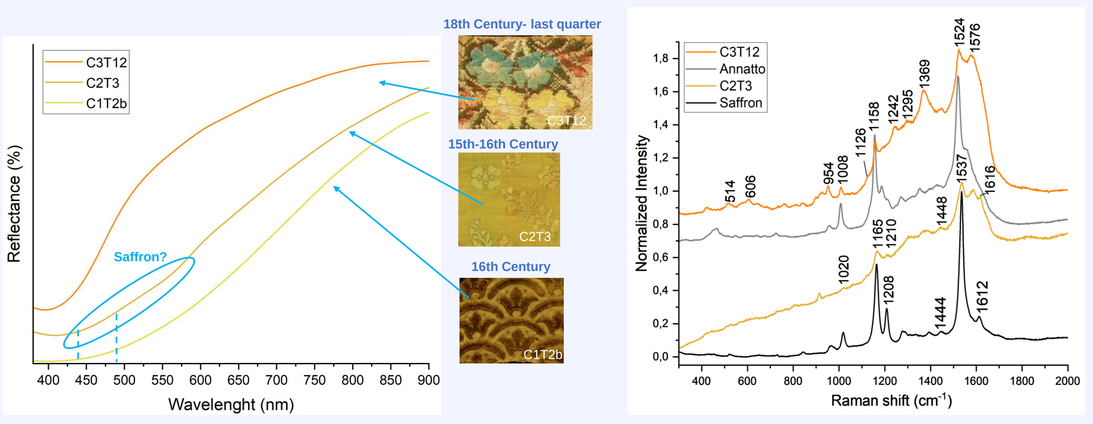
From left to right: VIS, UVFC and IRFC images of C2T7

From left to right: VIS, UVFC and IRFC images of C3T9

FC Imaging
- Colors of cochineal containg fragments not consistent with the literature: e.g., high concentration on a velvet.
- Yellow hue in the IRFC image of C3T9: anthraquinones.
- No information about Orcein

- Most of the fragments are dated to after the 16th century: *American cochineal* imported from 1518
- Dutch recipes (17th-18th century): Annatto as a brightening agent on cochineal
- The combination anthraquinone + Annatto + Orcein was never found in the literature.

The yellow hues

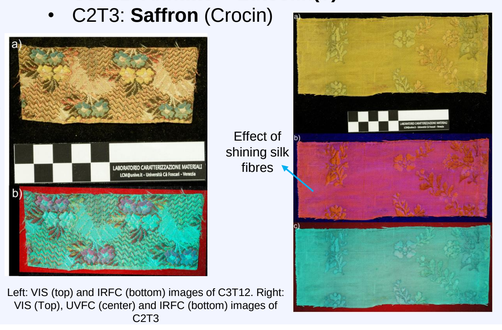


VRS
- **Flavonoid:** extremely common
- Spectral modification in C2T3: presence of a second component.

FC Imaging
- IRFC: white color in C3T12 compatible with flavonoids (luteolin)
- Carotenoids (crocin) appear white in IRFC and red in UVFC as in C2T3.

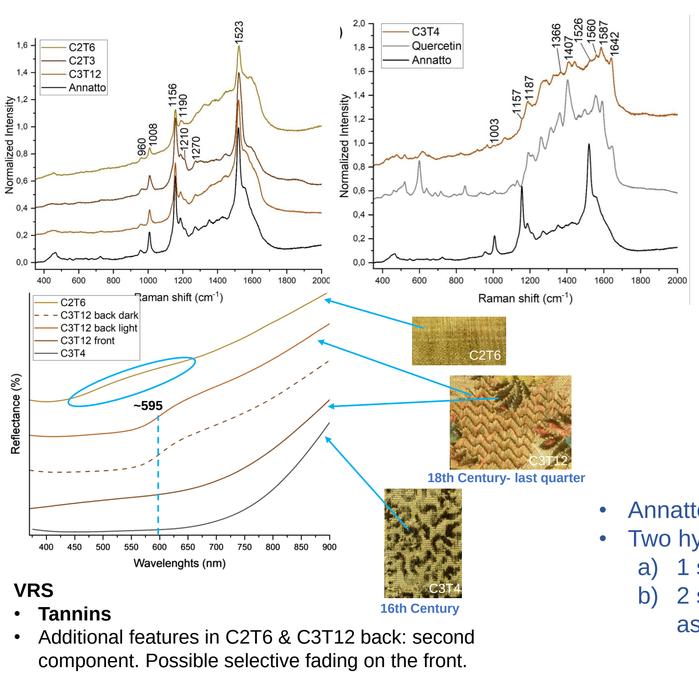
- *Weld* (luteolin) and *Dyer's broom* were the most used yellow dye in Europe between the early Middle Ages and 1492. Only after 1775 Quercitron became easily available.

SERSS
- C3T12: **Annatto + Luteolin(?)**
- C2T3: **Saffron** (Crocin)



Left: VIS (top) and IRFC (bottom) images of C3T12. Right: VIS (Top), UVFC (center) and IRFC (bottom) images of C2T3

The brown hues



VRS
- **Tannins**
- Additional features in C2T6 & C3T12 back: second component. Possible selective fading on the front.

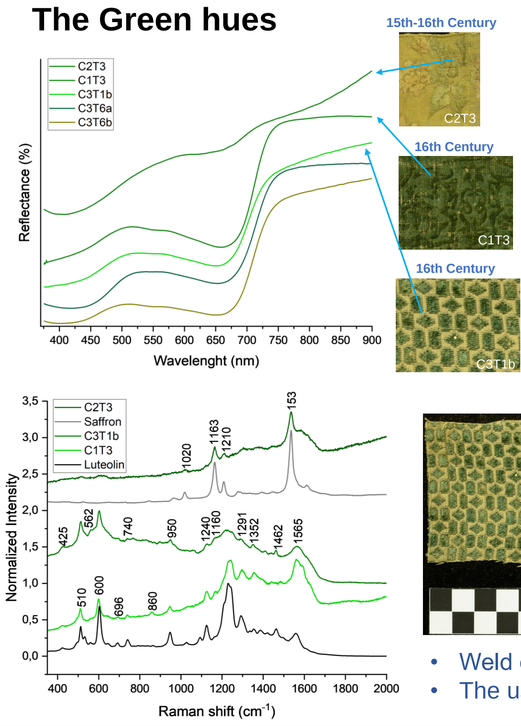
SERSS
- **Annatto** in C2T6 and C3T12
- **Quercetin +Annatto+ Tannin** (ellagic acid?) in C3T4

From left to right: VIS, UVFC and IRFC images of C2T6

FC Imaging
- Carotenoids (Annatto) are reddish in UVFC (C2T6)
- Tannins appear dark in UVFC and red-orange in IRFC

- Annatto was also used to obtain brown shades
- Two hypothesis for C3T4:
  a) 1 source for quercetin & tannins
  b) 2 sources: Persian berries from South-Central Europe as source of quercitin.

The Green hues



VRS
- Features of indigotin dominate the profiles
- C2T3: the yellow dye affects the spectrum
- Not possible to identify the yellow dye.

SERSS
- Only **indigotin** in C3T6a & b: low amount of the yellow dye. Intentional or faded (high light fastness)
- C1T3 & C3T1b: **Luteolin**
- C2T3: **Saffron**

FC Imaging
- Dominant greenesh (UVFC) and reddish (IRFC) hues of indigotin
- C2T3: the pinkish color of saffron in UVFC may be responsible of the brownish hue of the light green embroidery.

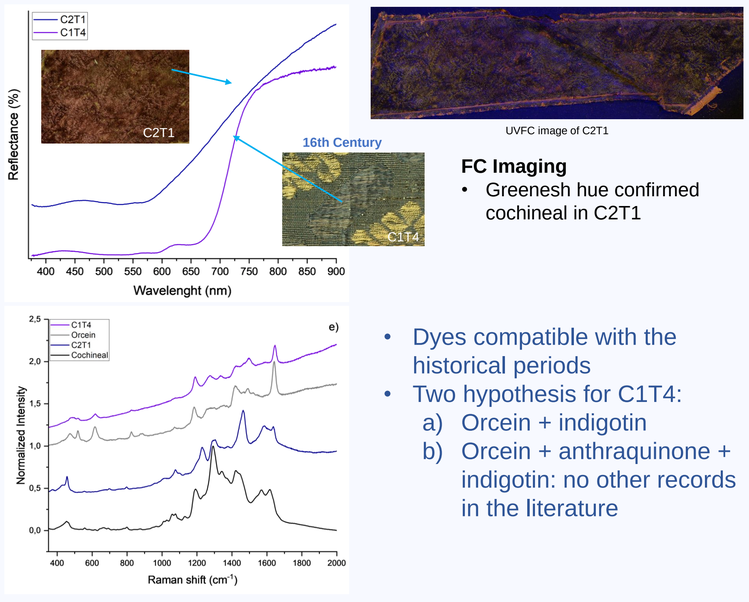
Clockwise: VIS, UVFC and IRFC images of C3T1b

- Weld or Dyer's broom are the most probable sources of luteolin
- The use of saffron and Indigo is compatible with the historical periods.

The Purple hues

VRS
- C2T1**:** Cochineal mordanted with alum
- C1T4: i) anthraquinone + indigotin or ii) orcein+ indigotin

SERSS
- C2T1**: Cochineal**
- C1T4: **Orcein**



FC Imaging
- Greenesh hue confirmed cochineal in C2T1

- Dyes compatible with the historical periods
- Two hypothesis for C1T4:
  a) Orcein + indigotin
  b) Orcein + anthraquinone + indigotin: no other records in the literature

Conclusions

- A selection of textile fragments belonging to the M.M. Guggenheim collection has been studied through a multitechnique approach involving VRS, SERSS and FC imaging.
- **VRS and Raman** spectroscopy demostrated their **complementarity** in the study of historical dying mateirals highlighting the complexity of **mixtures** used in the past centuries. Such a situation is normally not evident when using only one these technique since each of them can restitute only a part of the composition.
- In many cases **FC imaging** results supported the spectroscopic findings even if the **lack of a complete database** of substrates, dyes and application methods represent a strong limit for the interpretation of images.

Acknowledgments

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References

[1] D. Tamburini, J. Dyer, Dyes and Pigments. 162, 494–511 (2019)