

# Raman analysis of paintings: comparison between different excitation wavelengths in mobile systems

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## INTRODUCTION

Mobile Raman spectrometers can be a very powerful tools for the non-destructive *in situ* investigation of artworks that cannot be moved to laboratories, because of their size or their value. A major limitation of most portable instruments is the use of a single laser line, usually chosen between the very common 532 nm generated by a doubled Nd:YAG laser and the 785 nm line of a diode laser. The presence of a second laser line could help in case a strong fluorescence overwhelms the Raman signal.



**We studied important paintings present in Sicily (Italy):**

- 1) Wall paintings of Sala Vaccarini at the Libraries "Civica and A. Ursino Recupero", 16th century monumental complex of Benedictine Monastery in Catania.
- 2) A group a few paintings from the Italian master Caravaggio (1571-1610) and from his disciples, Regional Museum of Messina.

**Instruments:**

A) dual laser mobile Raman spectrometer, EZRAMAN-I-DUAL Raman system (TSI Inc., Irvine CA, USA), equipped with a 785 nm and a 532 nm excitation source,

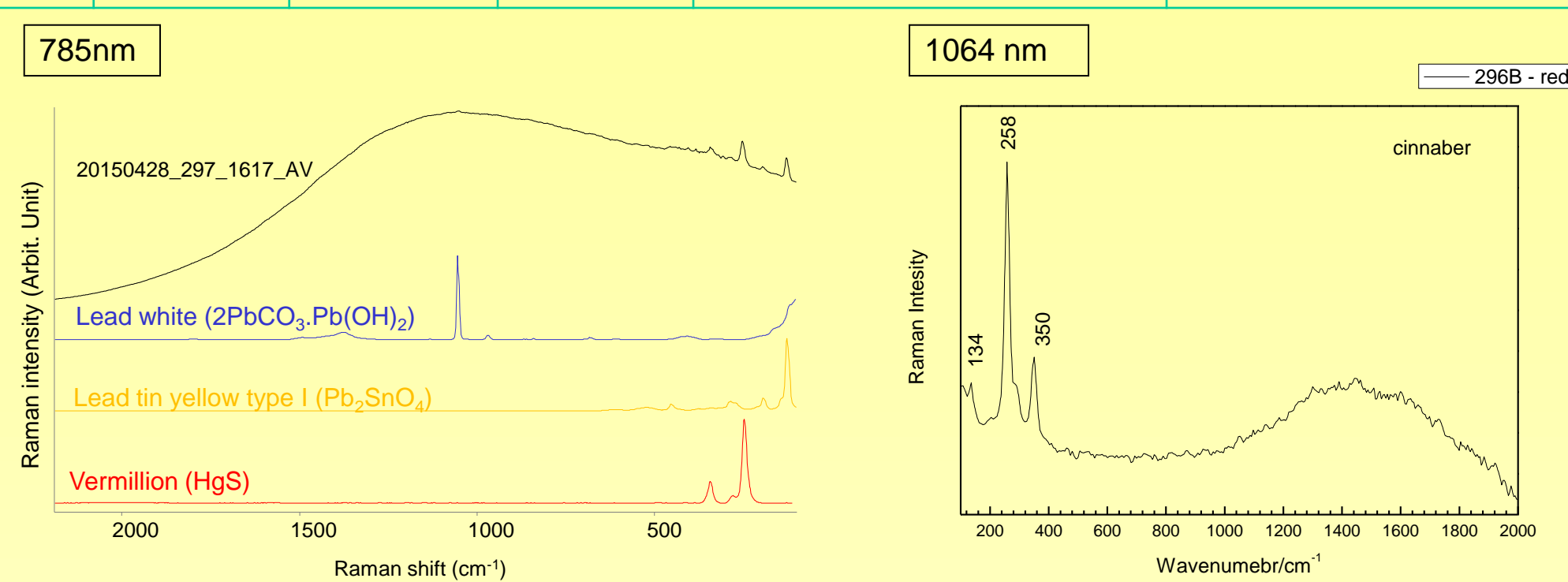
B) mobile Raman spectrometer from B&W Tek Inc. (i-Raman EX) with a NIR source, at 1064 nm.



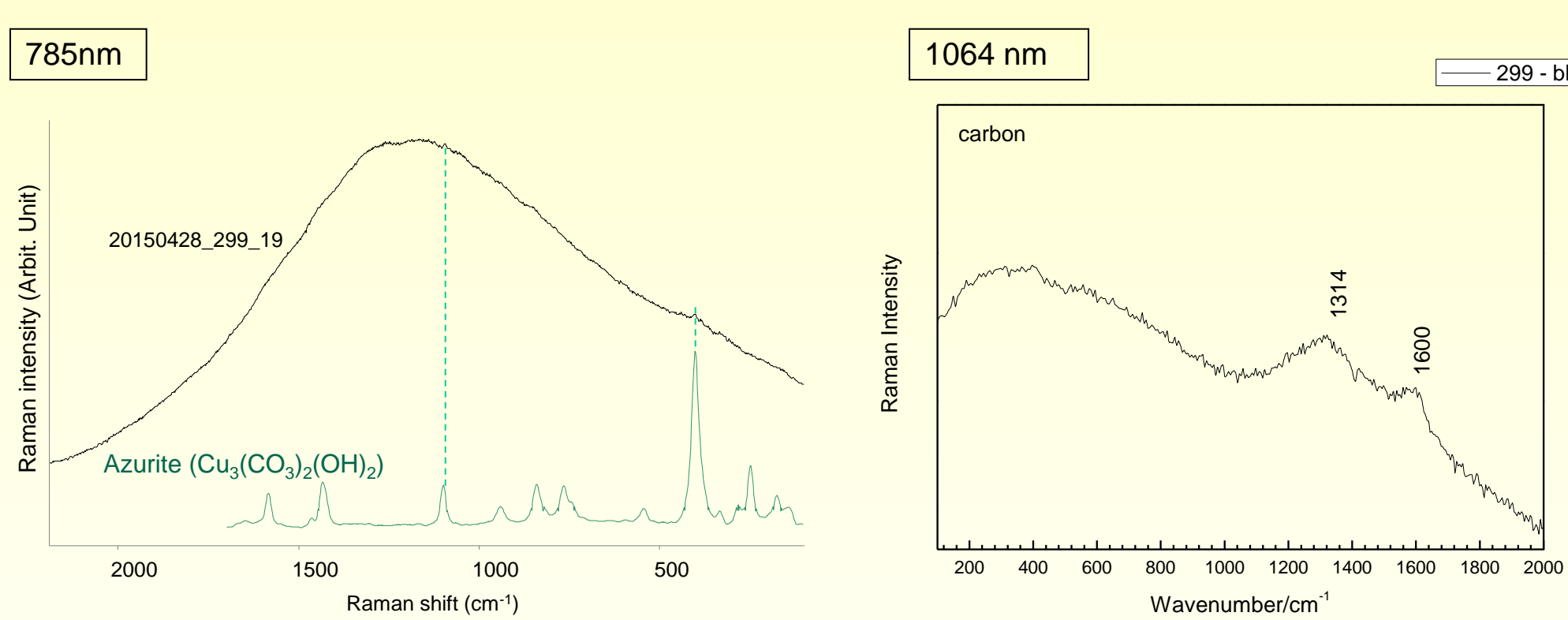
## CARAVAGGIO

### Resurrezione di Lazzaro (Caravaggio)

| Point | Area          | Colour  | XRF results     | Raman results 785 nm  | Raman results 1064 nm |
|-------|---------------|---------|-----------------|---|-----------------------|
| 296   | Vest of Marta | Orange  | Sn, Pb<br>Hg, S | Vermillion (HgS)<br>Lead tin yellow type I (Pb <sub>2</sub> SnO <sub>4</sub> )<br>Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> ) | Vermillion (HgS)      |
| 297   | Vest of Marta | Arancio | Sn, Pb<br>Hg, S | Vermillion (HgS)<br>Lead tin yellow type I (Pb <sub>2</sub> SnO <sub>4</sub> )<br>Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> ) | Vermillion (HgS)      |

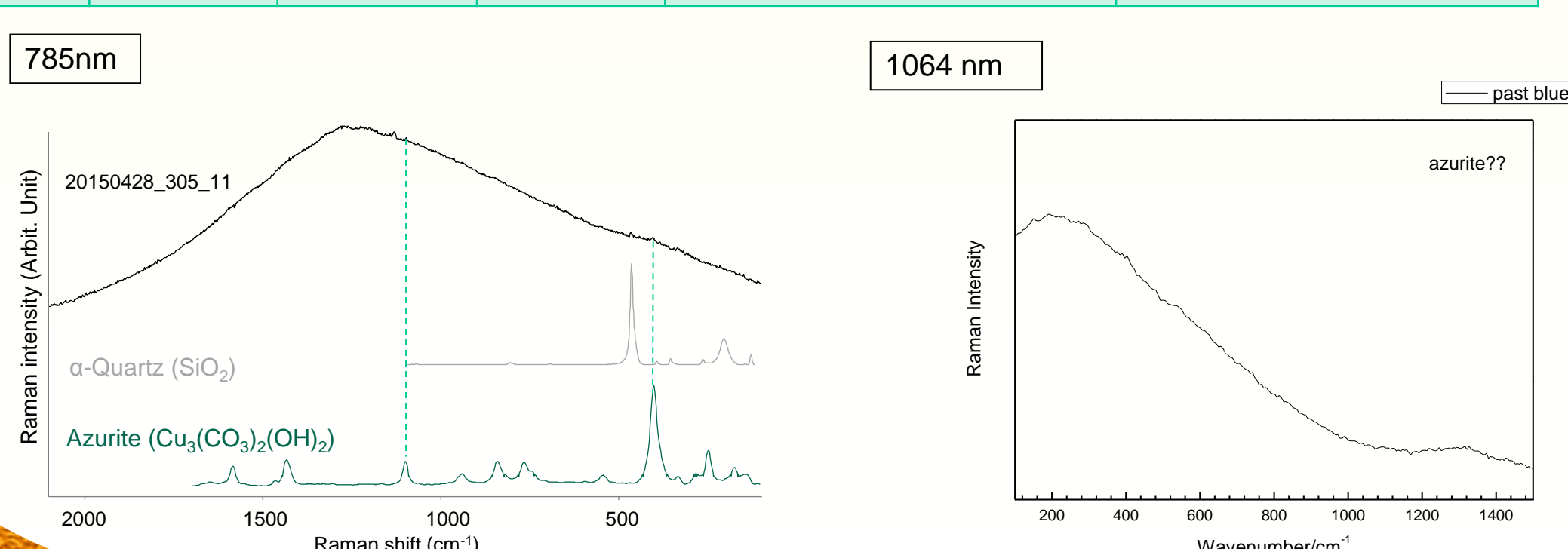


| Point | Area             | Colour | XRF results | Raman results 785 nm                                  | Raman results 1064 nm                                 |
|-------|------------------|--------|-------------|---|---|
| 299   | Vest of Christ   | Blue   | Cu          | Azurite (CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> )     | Carbon black  |
| 300   | Cloth of Lazzaro | Blue   | Cu          | Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> ) | Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> ) |



### Adorazione dei Pastori (Caravaggio)

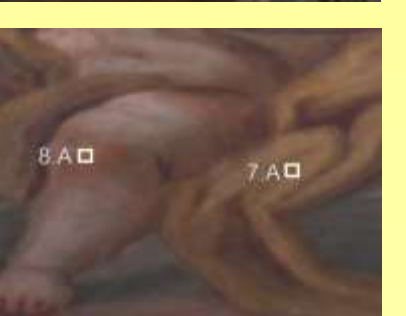
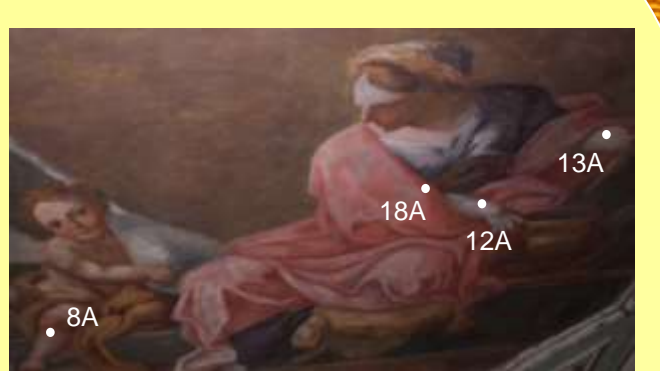
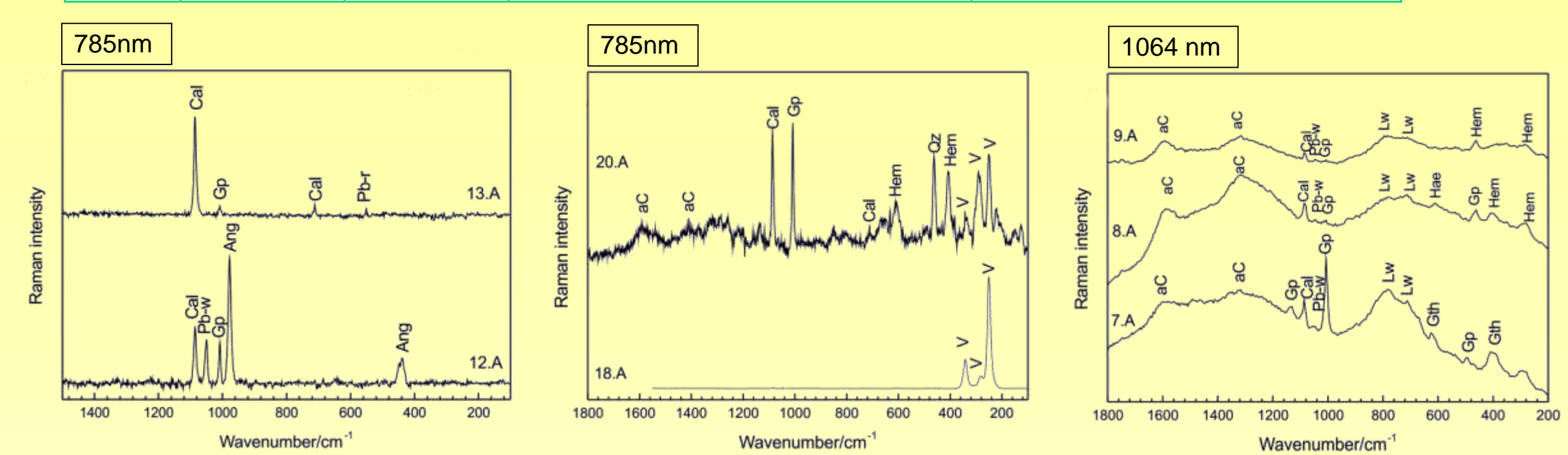
| Point | Area          | Colour    | XRF results | Raman results 785 nm  | Raman results 1064 nm |
|-------|---------------|-----------|-------------|---|-----------------------|
| 305   | Robe of Maria | Dark Blue | Cu, Fe, Si  | Azurite (CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> )<br>A-Quartz (SiO <sub>2</sub> ) | Carbon black          |



## WALL PAINTINGS SALA VACCARINI

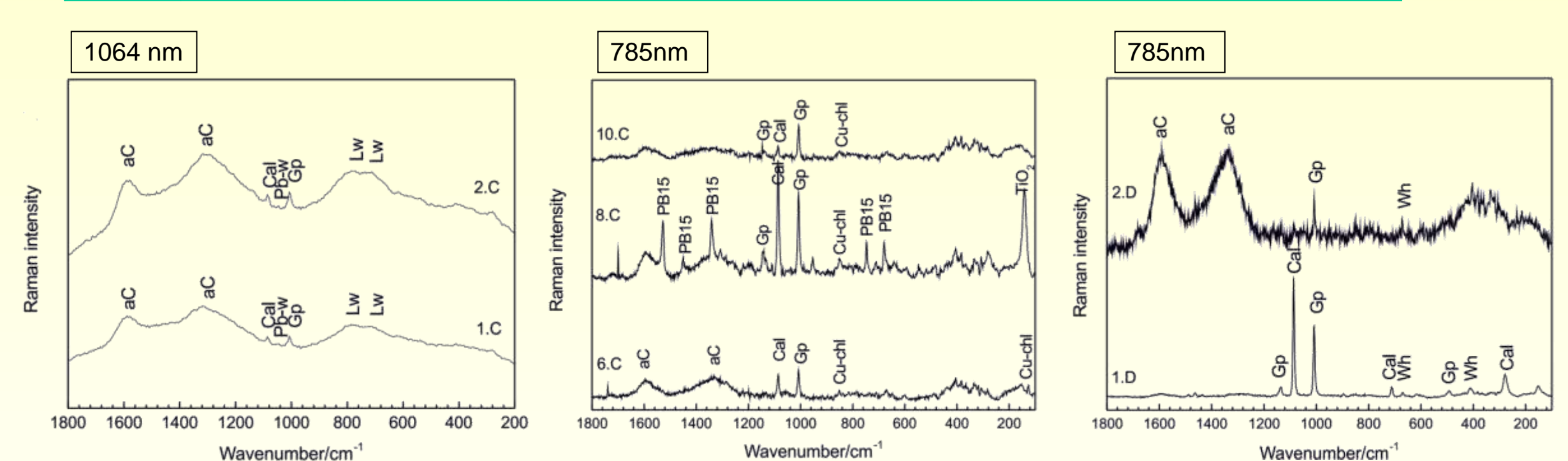
### The Alchemy

| Point        | Area         | Colour  | Raman results 785 nm   | Raman results 1064 nm   |
|--------------|--------------|---------|--|---|
| 8A, 12A, 13A | Skin         | Pinkish | Anglesite (PbSO <sub>4</sub> )<br>Gypsum (CaSO <sub>4</sub> )<br>Calcite (CaCO <sub>3</sub> )<br>Red lead (Pb <sub>3</sub> O <sub>4</sub> )<br>Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> ) | Carbon black (CaCO <sub>3</sub> )<br>Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> )<br>Gypsum (CaSO <sub>4</sub> )<br>Limewash (Ca hydroxides) |
| 18A          | Women's Vest | Red     | Vermillion (HgS)<br>Calcite (CaCO <sub>3</sub> )   | /   |



### The Medicine

| Point           | Area      | Colour         | Raman results 785 nm   | Raman results 1064 nm   |
|-----------------|-----------|----------------|--|---|
| 2C, 1C, 6C, 10C | Landscape | Blue and Green | Carbon black<br>Gypsum (CaSO <sub>4</sub> )<br>Calcite (CaCO <sub>3</sub> )<br>Copper Chloride | Carbon black (CaCO <sub>3</sub> )<br>Calcite (CaCO <sub>3</sub> )<br>Lead white (2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub> )<br>Gypsum (CaSO <sub>4</sub> )<br>Limewash (Ca hydroxides) |



## Conclusions

Despite the very strong fluorescence, probably related to the presence of varnish, the use of different laser lines allowed to identify most of the main pigments in the oil paintings of Caravaggio and disciples.

A larger number of pigments were identified in the wall paintings of Sala Vaccarini, with both instruments. Different sources identified different pigments.

The various laser lines showed different behavior during the analysis: lower fluorescence was induced by the source with the longest wavelength (at 1064 nm) but the measurements required a slightly longer time due to low scattering efficiency at high wavelengths. The highest efficiency can normally be reached with the lowest wavelength (532 nm), but in this work the induced fluorescence was too high to produce useful results. A good compromise was represented by the 785 nm line, whose increase in efficiency respect to the 1064 line is balanced by a worse fluorescence background. Even the different cut-off at low wavenumbers should be considered (i.e. for some inorganic pigments).

As final conclusion, it can be said that both instruments have their advantages and disadvantages. Depending on the research question the one is preferred above the other.

