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The application of Raman spectroscopy to investigate and characterize cementitious materials from a fresco of San Giuseppe’s church in Cagliari

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Chapter 0

Dedica
Abstract

This thesis presents some of the newest possible applications of Raman spectroscopy. Raman spectroscopy is a spectroscopic technique known to be non-invasive and non-destructive. It has evolved from a static technique to a dynamic one thanks to the equipment that can be used "in situ". This is why in this thesis project we decided to explore the application potential to cultural goods, in particular in the field of diagnostic and preservation of them.

Thanks to Raman microscopy, in fact, we are able to identify:
- molecules and compounds present in the surface examined (a painting surface in this specific case);
- the technique used by the author to make the work of art, and also possible works of restoration or eventual alteration caused by the environment or atmospheric conditions.

All these informations can help understand the state of conservation of the artifact and the best way to prevent, avoid or even arrest the degradation process. The artifact studied is a sample of a mural painting from San Giuseppe’s church in Cagliari. Using Raman spectroscopy it has been examined with the aims of identifying:
- the pigments and the compounds used by the author;
- the mural painting technique used to create the painting and the changes made during time.

Moreover we focus our attention on a new application that can help to measure the dimension of calcite’s grains found in the sample and to understand the stratigraphy of the painting. These techniques are meant to be used in addition to archeological and chemical techniques already used in the field of preservation of cultural goods.
Chapter 1

Raman spectroscopy

Raman spectroscopy is a spectroscopic technique whose aim is to observe vibrational, rotational, and other lower frequency modes in a system [1]. It is used in chemistry and in condensed matter physics to identify molecules, determine the crystal structure and the orientation of a crystal on a micrometer scale.

Raman spectra take place when a photon from an incident beam of monochromatic light, hits the molecule studied. At this point, the photon can give the molecule part of its energy or take it. The laser light interacts with molecular vibrations so that the final frequency of the scattered photon is shifted up or down. In fact Raman spectra have lines of higher or lower frequencies. The remaining part of the light is deflected after an elastic collision, called Rayleigh scattering.

Figure 1.1: C.V. Raman.

Raman scattering takes its name from the physicist C.V. Raman that discovered it;
discovery for which he had the Nobel in 1930 [2].

Generally, and in this case too, a sample is illuminated with a laser beam. The reflected radiation is collected with a lens that sends it through a monochromator. The radiation from Rayleigh scattering is filtered out by a notch filter (edge pass filter, or a band pass filter), while the one from Raman scattering is sent onto a detector. This is how Raman spectra are obtained.

1.1 Laser

To analyze the sample the laser is essential. A laser is a device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation. LASER is in fact an acronym for "Light Amplification by Stimulated Emission of Radiation". The first one was built in 1960 by Theodore H. Maiman at Hughes Research Laboratories, based on theoretical work by Charles Hard Townes and Arthur Leonard Schawlow.

The main characteristic of a laser is that it emits light coherently, spatially and temporally. Thanks to the spatial coherence a laser can focus to a tight spot. This is the reason why laser can be applied in cutting with high precision and in lithography. Moreover thanks to spatial coherence the laser beam stays narrow even over great distances. This property is called collimation and allows the laser to be used as a pointer. On the other hand lasers can have a high temporal coherence which allows them to emit light with a very narrow spectrum so that they can emit a single color of light.

For all this properties a laser can be used as an excitation source. It is used to obtain Raman spectra even in small areas, as the sample here analyzed, and even without damaging it, thanks to the possibility to control its intensity.

Laser physics  We know from quantum mechanics that electrons orbit around the nucleus on discrete orbitals, i.e. they are found only in specific energy levels. When the system absorbs energy from the outside (light or heat) electrons can be excited from one energy level to a higher energy level. This is an electronic transition and it is called a quantum leap. Electronic transitions cause emission and absorption lines, respectively when an electron jumps on a lower energy level and on a higher energy level, which can
be seen in the spectrum.

Figure 1.2: Principle of amplification of light in a laser.

An electron cannot stay in an excited state forever. In fact, in figure 1.2 we see, on the right, that the electron decays to a lower energy state and it emits a photon of the same energy of the incident one. This process causes the amplification of light. The emission of a photon can happen spontaneously or it can be stimulated. When the emission is spontaneous the photon is emitted randomly in phase and direction. When the emission is stimulated it is possible to control direction, frequency and phase. An ideal laser should have only stimulated emission, but the spontaneous emission cannot be completely eliminated.

Different things are needed to built a laser. An active laser medium is necessary: certain crystals properly doped, for example, with rare-earth ions; glasses; gases (HeNe, N, ect.); semiconductors; liquids (dye lasers). Moreover it is necessary to have electric current or light (usually another laser) to pump the energy into the system in a process called *pumping*.

For the laser to work, the condition of **population inversion** needs to be reached. There have to be more electrons in the excited states than in lower states. This is possible in systems with at least three or four energy levels: most lasers are four-level lasers.
Once a laser has the active medium and it has reached the population inversion condition it needs an optical feedback. Generally the laser consists in an optical cavity (optical rasonator) in which there are two mirrors one at each extreme. Only light that is reflected hundreds of times from one mirror to another and only light of a specific wavelength will be amplified at the end of the process.

### 1.2 Raman theory

Raman spectroscopy can be described as follows. A photon collides with a molecule in a level $E_i$. Once the collision has taken place it can transfer a fraction of its energy to the internal energy of the molecule, which is excited to a final level $E_f$ [3]. For the law of conservation of energy, the total energy of the system has to remain constant after the molecule moves. It is for this reason that the scattered photon has less (or more) energy, i.e. its frequency has decreased (or increased):

$$\hbar(\omega_0 - \omega_s) = E_f - E_i > 0.$$ \hspace{1cm} (1.1)

The energy difference $\Delta E = E_f - E_i$ can be vibrational, rotational or electronic energy [3]. The inelastic radiation is called *Stokes radiation*. The final energy, shifted up or down, can be related, respectively, to *anti-Stokes radiation* and to *Stokes radiation*. So that in a Raman spectrum one can find the elastically scattered radiation (Rayleigh scattering), the inelastic Stokes and anti-Stokes radiation.

Raman scattering is usually extremely weak: the order is of 1 in 10 millions photons that collide with the sample is scattered with loss or gain of energy, caused by a change in the vibrational energy of the molecules in the sample. For this reason, sometimes, the incident laser frequency is chosen close to the energy of an electronic transition of the molecules or crystal studied. The resonance can enhance intensity of the Raman scattering so that the study results facilitated. This is a particular case of Raman spectroscopy, called Resonance Raman spectroscopy (RR) [4]. Raman spectroscopy and RR spectroscopy can give information about the molecules vibrational modes so that they can be used to identify unknown substances. Usually these techniques and infrared (IR) spectroscopy are complementary.
To explain the Raman effect, describing the electric dipole is unavoidable. It can be written, as follows, as the sum of an eventual permanent moment $\mathbf{p}_0$ and a field-dependent contribution $\mathbf{p}_{\text{ind}} = \tilde{\alpha} \mathbf{E}$, where $\tilde{\alpha}$ is the electric polarizability, a tensor with components $\alpha_{ij}$ [3]:

$$\mathbf{p}(E) = \mathbf{p}_0 + \tilde{\alpha} \mathbf{E}. \quad (1.2)$$

Both the dipole moment and the polarizability can depend on the nuclear displacements $q_n$ of the vibrating molecule. It is possible to expand the two quantities into Taylor series for small displacements:

$$\mathbf{p}(q) = \mathbf{p}(0) + \sum_{n=1}^{Q} \left( \frac{\partial \mathbf{p}}{\partial q} \right)_0 q_n + \ldots \quad (1.3)$$

$$\alpha_{ij}(q) = \alpha_{ij}(0) + \sum_{n=1}^{Q} \left( \frac{\partial \alpha_{ij}}{\partial q} \right)_0 q_n, \quad (1.4)$$

where $Q = 3N - 6$ (or $Q = 3N - 5$ for linear molecules) is the number of normal vibration modes and $\mathbf{p}(0)$ and $\alpha(0)$ are, respectively, the dipole moment and polarizability at the equilibrium position $q = 0$ [3].

From the Maxwell-Boltzmann statistics, it can be said that the ground state level has a higher population compared to the one in the excited states. It means that Stokes lines are more intense than those anti-Stokes:
Figure 1.4: Raman transition.

\[ \frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \frac{(\nu_0 + \nu_m)^4}{(\nu_0 - \nu_m)^4} e^{\frac{(E_1 - E_0)}{kT}}. \]  

(1.5)

In classical physics it can be explained if we associate to a laser beam a periodic electric field of amplitude \( E_0 \) and frequency \( \nu_0 \) related as follows:

\[ E = E_0 \cos(2\pi \nu_0 t). \]  

(1.6)

The laser beam hits the molecule that starts vibrating inducing, in this way, a dipole moment \( P \). The dipole moment can be calculated through the product of the electric field associated to the laser beam and the polarizability. This last one is linked to the second derivative of the dipole energy:

\[ \alpha_{i,j} = -\frac{\partial^2 E_{\text{dip}}}{\partial E_i \partial E_j}. \]  

(1.7)

There are two different cases:
- the molecule is symmetrical (i.e. \( i=j \)) so that the polarizability will have the same value in all directions;
- the molecule is antisymmetric so that the polarizability tensor will have different value in different directions.
The nuclear displacement \( q \) can be represented by:

\[
q = q_0 \cos(2\pi \nu_m t).
\]  

(1.8)

Once the first equations and the last ones are combined:

\[
P = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos(2\pi \nu_0 t) \cos(2\pi \nu_m t).
\]  

(1.9)

The external field causes an elastic scattering, due to the first term depending on the frequency of the incident beam, and a second effect linked to two frequencies. Using Werner’s formula:

\[
\frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 E_0 \left[ \cos 2\pi (\nu_0 + \nu_m) t + \cos 2\pi (\nu_0 - \nu_m) t \right].
\]  

(1.10)

Respectively anti-Stokes and Stokes Raman scattering are represented through the dipole term depending on the frequency \( \nu_0 + \nu_m \) and the term depending on the frequency \( \nu_0 - \nu_m \). In this case, only when \( \left( \frac{\partial \alpha}{\partial q} \right)_0 \neq 0 \), the Raman vibration is called Raman-active.

In quantum mechanics perturbation theory can describe the Raman effect. Using time-dependent perturbation theory \[5\], we consider the laser beam as a periodic perturbation

\[
H' = \mu E.
\]  

(1.11)

Eigenfunctions and the time-independent Hamiltonian represent the molecule in the original state:

\[
H(t) = H_0 + \lambda H'(t),
\]  

(1.12)

so that the time-dependent Schrödinger equation will be:

\[
i\hbar \frac{\partial \Psi_n(t)}{\partial t} = H(t) \Psi_n(t).
\]  

(1.13)

If an external field perturbs the system, the wave function at the first order of correction for the perturbation theory becomes:

\[
\Psi = \Psi_n^0 + \Psi_n^1.
\]  

(1.14)
Combining the two of these last equations [6], first order correction for the wave function is given by:

\[
\Psi_n^1 = \frac{1}{2\hbar} \sum_r \Psi_0^0 \left( \frac{\mu_{rn}E_0}{\omega_{rn} - \omega} e^{i(\omega_n + \omega)t} + \frac{\mu_{rn}E_0}{\omega_{rn} + \omega} e^{i(\omega_n - \omega)t} \right)
\]  

(1.15)

where \(\omega_{rn} = \omega_r - \omega_n\).

The expectation value of the induced dipole moment is represented by the transition from the initial state \(\Psi_i\) to the final state \(\Psi_f\):

\[
M_{fi}(t) = \langle \Psi_f | \mu | \Psi_i \rangle \approx \langle \Psi_f^0 + \Psi_f^1 | \mu | \Psi_i^0 + \Psi_i^1 \rangle = M_{fi}^0 + M_{fi}^1.
\]  

(1.16)

The term \(M_{fi}^0\) can be ignored because it does not represent a Raman transition:

\[
M_{fi}(t) = M_{fi}^1 = \frac{e^{i(\omega_f - \omega)t}}{2\hbar} \sum_r \left( \frac{\mu_{fr}\mu_{ri}E_0}{\omega_{ri} - \omega} + \frac{\mu_{ir}\mu_{fr}E_0}{\omega_{rf} + \omega} \right) + \frac{e^{i(\omega_f + \omega)t}}{2\hbar} \sum_r \left( \frac{\mu_{fr}\mu_{ri}E_0}{\omega_{ri} + \omega} + \frac{\mu_{ir}\mu_{fr}E_0}{\omega_{rf} - \omega} \right).
\]  

(1.17)

We can distinguish Stokes and anti-Stokes radiation respectively by the positive or negative value of \(\omega_{fi}\). Rayleigh scattering is found when final and initial state are the same and it is proportional to \(|M_{ii}|^2\) [2]:

\[
M_{ii}(t) = M_{ii}^1 = \frac{e^{i(\omega) t}}{2\hbar} \sum_r \left( \frac{\mu_{ir}\mu_{ri}E_0}{\omega_{ri} - \omega} + \frac{\mu_{ri}\mu_{ir}E_0}{\omega_{rf} + \omega} \right) + \frac{e^{i(\omega) t}}{2\hbar} \sum_r \left( \frac{\mu_{ir}\mu_{ri}E_0}{\omega_{ri} + \omega} + \frac{\mu_{ri}\mu_{ir}E_0}{\omega_{rf} - \omega} \right).
\]  

(1.18)

1.3 Raman spectroscopy and calcite crystals sizes.

This thesis project wanted to apply Raman spectroscopy to the study of a sample from San Giuseppe’s Church, in Cagliari (fig. 2.3) to investigate the help that Raman spectroscopy could give to archeology and art. In fact this technique is an important instrument in the arsenal of art conservators and archeologists. The latest technologies have made possible to analyze different types of cultural property \textit{in loco}, i.e. on-site.

We demonstrated the actual potential of Raman spectroscopy in two different ways:
- identifying the different pigments and binders in the sample;
- determining the sizes of calcite crystals formed.

The Raman theory summarised in chapter 1.1 and in the subsection below (1.3.1) explain how to identify molecules. We referred to a spanish study, "Micro-Raman spectroscopy applied to depth profiles of carbonates formed in lime mortar"[7] to determine the sizes of calcite crystals.

1.3.1 Vibrational frequencies

When the atoms in a molecule are in periodic motion the molecule vibrates while, as a whole, has constant translational and rotational motion. This molecular vibration has its own frequency, called vibrational frequency, and the typical frequencies of molecular vibrations cover a range from less than $10^{13}$ to approximately $10^{14}$, corresponding to wavenumbers of about 300 to 3000 cm$^{-1}$. A molecular vibration is excited when a molecule absorbs a quantum of energy, $E$, corresponding to the vibrational frequency, $\nu$, according to Plank’s relation $E = h\nu$, where $h$ is Plank’s constant.

The motion in a normal vibration can be described, in first approximation, as a kind of simple harmonic motion. For example, studying a diatomic molecule, which has one normal mode of vibration, as a two body problem, in first harmonic approximation [8] we have:

$$
\nu_m = \frac{1}{2\pi c} \sqrt{\frac{K}{m}} \quad \text{(1.19)}
$$

where $K$ is a constant. Hence vibrational frequencies depend on the atoms masses and on the bonding intensity between them. When light atoms are strongly bound the Raman frequencies are high, when heavy atoms are weakly bound the Raman frequencies are low. For example, C-H bonds in polystyrene vibrate about 3000 cm$^{-1}$, while C-C have bonds at 800 cm$^{-1}$[2]. This difference is due to the different masses of the two atoms. Moreover, if we consider a double bond as $C = C$, stronger then C-C bond, Raman frequencies will be about 1600 cm$^{-1}$ [2].

All the differences depend on several aspects: on the molecule structure, local conditions as the symmetry, crystaline phase, morphology, etc. A molecule can vibrate in
two different vibrational normal modes. The first is the *stretching*, which is linked to a change in the bond length. The second one is the *bending*, linked instead to a change in the angle between two bonds. Stretching needs more energy compared to bending. In fact in a molecule the vibrational mode of stretching requires more energy than changing the angle between two bonds.

More in detail we have:

- Symmetric stretching, in which two atoms move away or get close simultaneously;
- Antisymmetric, in which one atom move away from the other while the other one gets close;
- Scissoring, in which there is a symmetric change in the angle between two bonds as it happens when we use scissors;
- Rocking, in which there is a symmetric change in the angle between a group of atoms and the rest of the molecule;
- Twisting, in which there is a change in angle between the planes of two groups of atoms;
- Wagging, in which there is a change in angle between the plane of a group of atoms and a plane through the rest of the molecule.

**Classification of normal modes** Molecular symmetry is a concept that help understand the molecule’s chemical properties and the spectroscopic transitions allowed. The main study of molecular symmetry is found in the group theory. Some geometric operations can be applied to a molecule in its original configuration. If the starting configuration it is equivalent to the final one, the operation applied is called a symmetry operation and this means that the system have symmetry elements [8].

The symmetry operations which can be applied to a molecule form a *symmetry group*. Symmetry elements and their associated symmetry operations are classified down below:

- **Identity** $E$ is the element that every molecule has: it consists of no change. The operation leave the configuration indistinguishable from the starting state;

- **Plane of symmetry** $\sigma$ is the plane of reflection that cuts the molecule in two identical parts, also called mirror plane;
- Centre of symmetry or inversion center is the centre of symmetry of the molecule, i.e. the midpoint of the lines that link every atom in the molecule. This point can correspond to an atom or not;

- Symmetry axis or rotation axis $C_n$ is the axis around which after an operation of rotation by $\frac{360^\circ}{n}$ the molecule is indistinguishable from the starting configuration, both with counter-clockwise and clockwise;

- Rotation-reflection axis is the axis around which, after an operation of rotation by $\frac{360^\circ}{n}$ and a following operation of reflection in a plane perpendicular to it, the molecule stays unchanged. In fact, even after the rotation there is an axis that cuts the molecule into two identical parts.

All the symmetry operations discussed leave at least one point fixed. For this reason this group is called a point group. Point groups are not all the same: they are different in the combination of elements present in the molecule. For example the position in space of
a three dimensional object is linked to the concept of spatial group. Combining all point groups with translation operations simple and complex we have 230 spatial groups [2].

The operation applied to a molecule can be identified in the form of matrices called representations. They can be of two types: reducible, if they are diagonalizable in submatrices; irreducible if they are not. The sub-matrices of a reducible matrix are irreducible and their trace is called characters of a matrix. This trace help describing the point group inside the character table. Character tables (fig. 1.5) are used to classify vibrational normal modes because some of the characteristic of a molecule (vibrational states and modes, electronic state, ect.) can be different depending on symmetry operations of the point group of the molecule.

Starting from the left, the first column is formed by the types of symmetry operations. Conventionally, in nonlinear molecules, $A_1$, $A_2$, $B_1$, $B_2$ denote non-degenerate vibrations, while E denotes vibrations doubly degenerate. More specifically $A_1$ and $A_2$ represent symmetric rotations around the principal axis, respectively symmetric stretching and bending, and twisting. $B_1$ and $B_2$ represent asymmetric rotations around the principal axis respectively the asymmetric bending and the wagging. The last two column on the right give informations about IR and Raman activities.

The analysis of all these vibration modes helps studying molecular symmetries and the consequent state of degradation of the sample examined.
1.3.2 Size of crystals.

We focused our attention on the chemical process of carbonation. This chemical reaction starts when a calcium hydroxide reacts with a carbon dioxide and forms insoluble calcium carbonate:

\[ Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \]  \hspace{1cm} (1.20)

It is a slow process that occurs in concrete, for example, where lime (calcium hydroxide) in the cement reacts with carbon dioxide from the air and form calcium carbonate. There are three different types of calcium carbonate: calcite, vaterite and aragonite. The crystallized form most thermodynamically stable is calcite, aragonite and vaterite in that order [7]. For this reason calcite is usually the primary polymorph formed during carbonation, while aragonite and vaterite are secondary products.

In lime mortars carbonation may differ on the outer layers of the sample from the process inside the mortar. This difference in the carbonation process generally is caused by the presence of a rather thick material and by the fact that CO$_2$ diffusion coefficient and steric hindrance may impact crystal growth [7]. This explains the difference in size among all the calcite spectra found in the sample. Moreover the peaks at wavenumber below 400 cm$^{-1}$ are related to the lattice mode, and this is the main reason for which this method to measure calcite crystal size was proposed. The $A_{280}/A_{712}$ ratio between the areas under the respective Raman frequency (280 cm$^{-1}$, 712 cm$^{-1}$) in calcite can be used to determine the crystal size of this calcium carbonate polymorph [7]. This technique can determine the length of the side of the rhombus which constitutes the calcite crystal.

<table>
<thead>
<tr>
<th>Calcite size ($\mu$m)</th>
<th>$A_{280}/A_{712}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>18.8</td>
</tr>
<tr>
<td>15</td>
<td>11.5</td>
</tr>
<tr>
<td>20</td>
<td>15.4</td>
</tr>
<tr>
<td>25</td>
<td>10.2</td>
</tr>
<tr>
<td>30</td>
<td>3.4</td>
</tr>
<tr>
<td>agglomerate</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 1.1: $A_{280}/A_{712}$ ratio for calcite crystals with different sizes; Tab.3 [7].
As shown in Tab. 1.1, as calcite size increases the ratio of areas $A_{280}/A_{712}$ decreases, with a sharp decline for sizes lower than 25 µm [7]. The amount of every polymorphic phase of calcium in lime mortar is closely related to band intensity, but this is not the only factor that affects the intensity of the band [7]. To avoid these other factors two bands relative to calcite are used. If bands are not observed or if they overlap with bands of other compounds that constitute the sample, this technique cannot be used.

1.4 Equipment

Raman spectroscopy generally requires the equipment shown in fig. 1.5-1.6 and described below (technical characteristics are shown at the end of the section):
- laser source;
- a system to focus on the incident laser beam and to gather the scattered light;
- filters or a monochromator;
- a spectrograph;
- a detector;
- CCD.

For this thesis the equipment was similar to the one in scheme. A spectrograph has replaced the monochromator: the entire spectrum is sent to the CCD, not only light of one wavelength.

As said before, working with Raman scattering needs an excitation source of monochromatic light for which we used a laser beam. Since the laser could have some secondary lines, there is usually a filter to eliminate them.

One of the characteristics of Raman spectroscopy is its application to reduced areas of the sample. Using a laser, the small diameter of the incident beam (1-2 mm) can be reduced even more with the help of a system of lenses [2], so that it can be used also with very tiny samples. The laser used in this particular case was Nd:YAG (neodymium-doped yttrium aluminium garnet; Y$_3$Al$_5$O$_{12}$). It is a crystal used as a lasing medium (the source of optical gain within a laser) for solid-state lasers. A flashtube or some laser diodes optically pump Nd:YAG lasers. This type of laser is one of the most used. It typically emits light with a wavelength of 1064 nm, in the infrared [9]. Lasers at a higher frequency (UV, visible) can activate some electronic transitions that cause unwanted fluorescence
As seen in Ch.1, sec. 1.2, Raman scattering is a weak phenomenon; in fact the incident laser beam has to be properly focused on the sample, with the help of the microscope, and scattered light gathered. It is possible to gather it thanks to the system of lenses, one for the focus and one for the gathering. The best configuration is the one at 180°, so that the incident beam and the scattered light have opposite directions.

The quantity of light that a lens can gather is connected with the ratio between its focal length and its diameter:

$$F = \frac{f}{D} \quad (1.21)$$

$F$ is a number which indicates the lens capacity to gather light: if $F$ is small, its capacity is big.

Once the light is scattered, the intense Rayleigh scattering has to be removed with a filter, because otherwise it would hide Raman scattering. The filter doesn’t let all the frequencies pass.

In the second place there is the spectrograph which has a slit from which the light gets in and a second one to let it out. Moreover it is equipped with a diffraction grating. Once the light gets in it is sent onto a concave mirror that reflects the light in parallel beams.
onto the diffraction grating. It is this last one optical component that splits and diffract light into several monochromatic beams and in different directions. The monochromatic light beams are sent onto another mirror that directs them into the exit slit.

The spectrograph, along with the diffraction grating, has its own resolution, called spectral resolution. It is the ability to resolve features in the electromagnetic spectrum. Usually it is denoted by \( \Delta \lambda \), and is closely related to the resolving power defined as:

\[
R = \frac{\lambda}{\Delta \lambda} \tag{1.22}
\]

where \( \Delta \lambda \) is the smallest difference in wavelengths that can be distinguished at a
wavelength of \( \lambda \). This means that spectral resolution depends on the resolving power of the diffractional grating, on the optical path of the light inside the spectrograph, and on the slits opening.

If the opening gets bigger the spectrum gets wider: \( \Delta \lambda \) increases and resolution decreases. Hence R is inversely proportional to the slit width. To detect all wavelengths, diffraction grating rotates. Increasing the distance between diffraction grating and slits improves the spectrograph, because the number of light beams that could get out decreases.

![Figure 1.10: Spectral answer of two different diffraction gratings.](image)

It is important to notice what happened to the light into the spectrograph because as we just said its intensity decreases. This happens, above all, because of the diffraction grating, even if there are other factors decreasing light intensity.

The wavelength at which the diffraction grating works with more efficiency is called *blaze*. It can be deduced that the efficiency of diffraction gratings working in reflection is closely dependent on the wavelength: if the wavelength used is far from the *blaze*, intensity will be weak and results with many uncertainties. Moreover the blaze wavelength depends on the density of grooves in the diffraction grating, as we can see in the fig. 1.8. To enhance the efficiency blazed gratings, also called echelette grating, are used (1.9). Blaze angle is relative to the reflecting surface of the grating. To reach the highest reflectivity the diffraction angle and the incidence angle must be identical [10]. This means that the diffracted beam is back-reflected into the direction of the incident beam. The beams are
perpendicular to the step and therefore parallel to the step normal. Hence it holds in a particular configuration called Littrow configuration: \( \alpha = \beta = \theta_B \). Diffraction angles at the grating are not influenced by the step structure. They are determined by the line spacing and can be calculated according to the grating equation:

\[
d (\sin \alpha + \sin \beta) = m \lambda \quad (1.23)
\]

For the Littrow configuration, this becomes:

\[
2 d \sin \theta_B = m \lambda. \quad (1.24)
\]

By solving for \( \theta_B \) the blaze angle can be calculated for arbitrary combinations of diffraction order, wavelength and line spacing:

\[
\theta_B = \arcsin \frac{m \lambda}{2d}. \quad (1.25)
\]

Figure 1.11: An example of blazed grating.

Once the light has passed through the monochromator a device detects it. There are different types of detectors, but most of them uses the photoelectric effect, as the photomultiplier. Usually they consist in a photocathode, several dynodes, and an anode. Incident photons strike the photocathode material, which is usually a thin vapor-deposited conducting layer on the inside of the entry of the device. The workfunction (i.e. the minimum energy needed to remove an electron from a solid to outside the solid) characterising
these materials should be low. In fact, semiconductors as gallium arsenide (GaAs) and indium gallium arsenide (InGaAs) are often used [11].

Generally in Raman spectroscopy detectors with a photodiode array detection are used. They can detect Raman spectra in every frequency on the whole range available. In this case, as shown in table 1.3, the detector type is InGaAs and it is usually used to work near IR region.

Detectors have different characteristics depending on several parameters. Some of them, for example, consider also the background noise caused by the detector itself. The parameters used to describe them are:

- the spectral working range, limited by the dependence in the relation between the intensity of the incident light, i.e. its energy, and the electrical response;
- the responsiveness, i.e. the ratio between the electrical signal outgoing and the incident power;
- the time constant, ideally close to zero, defined as the time interval during which the electrical signal outgoing is the 63% of the constant outgoing signal $V_0$;
- the Noise equivalent power (NEP or $P_N$), i.e. the incident power of light needed to produce an outgoing signal equal to the noise caused by the detector. The NEP depends largely on the type of detector and on the detector’s geometry;
- the capability to detect, defined as the $P_N$’s reciprocal, called $D$;
- the special capacity, used to compare different types of detector.

**CCD**  The whole spectrum is sent to the CCD and recorded. CCD stays for charge-coupled device. It is used to transfer electrical charge to device that can manipulate it. For example a CCD can help converting electrical charge into digital values.

A CCD is an integrated circuit that can accumulate electrical charge thanks to the presence of semiconductors. The electrical charge accumulated is proportional to the electromagnetic radiation intensity that hits the semiconductors. These semiconductor elements in the CCD are called photosites and are the ones that convert light into electrical charges. All these elements are coupled so that they can transfer the electrical charge between them. At the end the CCD can read the charges and build the image on the CCD surface itself.

The image processed is analogue or digital. It can be used immediately or recorded in a digital format.
It’s thanks to the CCD that we can see on the computer display the Raman spectra studied.

<table>
<thead>
<tr>
<th><strong>Laser</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Source</td>
<td>1064 nm</td>
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<tr>
<td>Laser Power</td>
<td>450 mW</td>
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<table>
<thead>
<tr>
<th><strong>Spectrometer</strong></th>
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<tbody>
<tr>
<td>Model</td>
<td>i-Raman EX-1064S</td>
</tr>
<tr>
<td>Range</td>
<td>(175-2500) cm$^{-1}$</td>
</tr>
<tr>
<td>Resolution</td>
<td>$\sim$ 9.5 cm$^{-1}$</td>
</tr>
</tbody>
</table>

**Table 1.2:** Technical features of the equipment [12]

<table>
<thead>
<tr>
<th><strong>Detector</strong></th>
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</thead>
<tbody>
<tr>
<td>Detector type</td>
<td>InGaAs Array</td>
</tr>
<tr>
<td>Digitizer Resolution</td>
<td>16 bit</td>
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<tr>
<td>Integration time</td>
<td>200 $\mu$ 20 min.</td>
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</table>

<table>
<thead>
<tr>
<th><strong>Electronics</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer interface</td>
<td>USB 3.0/2.0/1.1</td>
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<tr>
<td>Trigger mode</td>
<td>5V TTL</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Specifications</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension</td>
<td>17x34x23.4</td>
</tr>
<tr>
<td>Operating temperatures</td>
<td>0 - 35°</td>
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</table>

<table>
<thead>
<tr>
<th><strong>Microscope</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscope type</td>
<td>BWTEK BAC 151B</td>
</tr>
<tr>
<td>Wavelength</td>
<td>532, 785, 1064 nm</td>
</tr>
<tr>
<td>Power Input</td>
<td>5V DC, 300mA</td>
</tr>
<tr>
<td>Dimensions</td>
<td>24.3x20.8x37.8 cm</td>
</tr>
</tbody>
</table>

**Table 1.3:** Specifications of the Detector and the microscope [12].
Chapter 2

Raman applications and cementitious materials

The Raman technique has different applications. As we have seen, Raman spectroscopy is used in chemistry and in condensed matter physics to identify molecules, to study chemical bonding and characterize crystals. For instance, both Raman and IR spectra were used to determine the vibrational frequencies of SiO, Si_2O_2 and Si_3O_3 on the basis of normal coordinate analyses [13].

In solid-state physics it is used:
- to characterize materials; in fact as we have identified single molecules, it is possible to identify solid materials by characteristic phonon modes: information on the population of a phonon mode is given by ratio of the Stokes and anti-Stokes intensity of the spontaneous Raman signal.

Raman spectroscopy can also be used to observe other low frequency excitations of a solid, such as plasmons, magnons, and superconducting gap excitations. Both plasmons and magnons are quasiparticles. Plasmon is defined as a quantum of plasma oscillation. Magnon, called also wave spin, is a perturbation in the electrons spin structure in a crystal lattice;
- to measure temperatures; distributed temperature sensing (DTS) uses the Raman-shifted backscatter from laser pulses to determine the temperature along optical fibers;
- to find the crystallographic orientation of a sample studying the polarization of Raman-scattered light with respect to the crystal and the polarization of the laser light,
knowing the crystal structure’s point group.

Also nanotechnology can benefit from Raman spectroscopy: it can be used to study nanowires and understand their structures. Raman active fibers (aramid and carbon) have vibrational modes that show a shift in Raman frequency with applied stress: polypropylene fibers exhibit similar shift. Aramid synthetic fibers are known to be heat-resistant (melting point > 500°) and strong. For these properties they find applications in the aerospace and military field, in building bicycle tires, marine cordage, etc.. These fibers are formed by chain molecules highly oriented along the fiber axis. It is this characteristic that gives them the distinctive strength.

Carbon fibers are formed by carbon atoms. They are heat-resistant and strong too. Moreover they have low weight, high chemical resistance, all properties that allow them to be used in a lot of engineering applications.

Aside from all these applications Raman spectroscopy can also be used in the biopharmaceutical industry to identify active pharmaceutical ingredients and their polymorphic forms, if they exist. These polymorphic forms have indeed different physical properties, like solubility and melting point.

Raman spectroscopy has a wide variety of applications, not only in the biopharmaceutical industry but in all biology and medicine. It has helped to confirm the existence of low frequency phonons in proteins and DNA [14] and promoting studies about their biological functions [25]; it has also used as a noninvasive technique for real-time, in situ biochemical characterization of wounds. Thanks to a new technique, Spatially offset Raman spectroscopy (SORS), less sensitive to surface layers than conventional Raman, it can be possible to discover counterfeit drugs without opening their packaging, and to non-invasively study biological tissue.

The Raman application utilised in this thesis project is, instead, that on works of history and art: paintings, historical documents, etc. Raman spectroscopy allows to study the working method of an artist, identifying both individual pigments in paintings and their degradation products. Moreover this application can give informations about the original state of the sample in cases where the pigments degraded with age [16] and about the social and economic conditions when they were created. This application can be indeed combined with archeology and history to better understand the several characteristics describing a more or less ancient object or a work of art and, together they
can be of great help in understanding when and how it needs restoring.

Before starting we did a search about the historical period in which San Giuseppe’s church was built, about all materials and compounds usually employed in these kind of works and about the technique of the affresco applied in that historical period.

### 2.1 San Giuseppe’s church.

San Giuseppe’s Church is located in the main neighborhood of Cagliari, Castello (Castéddu ’e susu in Sardinian) next to the tower of the Elephant.

The events that led to the construction of the church were many and troubled. The building works of San Giuseppe’s church started in 1663 and ended in 1735. In that period Sardinia was under Spain’s rule, but in the early 1700s, after the death of Carlos II, a war of succession started which led to a long time of bombing carried out by English, Dutch and Austrain militia. In one of these bomb attacks, the church of San Giuseppe itself was affected: there is still a bomb stuck in one of the church’s walls, with a brief epigraph to remember that day of the bombing, 12th August 1708, as it shows figure 2.2 [2].

Subsequently, in 1718 Sardinia was under Savoia’s rule. It was during this time that the works of the church of San Giuseppe continued, untill 1735 [2]. Also the work of decorating the interior of the church lasted years: it ended only in the 1800s, stopped many times for economic reasons.

Unfortunately the church was bombed again in 1943, during the Second World War, when it took heavy damage (see fig. 2.3 on the right). It didn’t remain this way too long. In fact in the years post-war the church was restored and opened. The damages caused by the IIWW bombing led to a reintegration of all parts involved, to give back to the city
Figure 2.2: The bomb stuck in the church after 1700s bombing.

Figure 2.3: The figures show the interior of San Giuseppe’s church in Cagliari: the one on the right after the bombing in 1943.

the monument [17]. Part of the restoring work was carried out with the remains themself of the church, but for economic and pratical reasons other materials were also used. For example also reinforced concrete can be found, used above all for structural changes [17]. The church was closed again in the '70s and still is.

San Giuseppe’s church is still plenty of works of art, even though lots of them were destroyed during the bombing. The frescos located in the sacristy still remain, a part of
them is shown in figure 2.4 [18].

![Image](image.jpg)

**Figure 2.4:** Here is possible to see a detail of the fresco in the sacristy of San Giuseppe Church.

### 2.2 Common compounds.

To better understand the work of construction that led to San Giuseppe’s church, we did a search on the processes of constructing a building, during the relative construction period, along with one about all cementitious materials used in that time in these same processes, among which there are cement, lime plaster, sand, chalk, and some of the coloured pigments used in paintings. Right down below we are going to describe some of these materials in detail.

#### 2.2.1 Cementitious materials and coloured pigments.

We focused our attention on binders, like cement, that have the characteristic of binding materials together. Cement is used for construction with the aim of binding together all materials used. Before that it sets, hardens and adheres to the other materials. It is used also solely, but generally it is used to bind sand and gravel together.

Cement is usually inorganic, but often it is lime or calcium silicate based. It can be characterized as being either hydraulic or non-hydraulic, according to the ability of the cement to set in the presence of water.
Already in 18th century some French and British engineers formalized a technique for making hydraulic cement [19], i.e. cement that sets in the presence of water. When there is not water we talk about non-hydraulic cement, such as slaked lime (calcium oxide mixed with water). It hardens by carbonation in the presence of carbon dioxide which is naturally present in the atmosphere. Initially calcium carbonate (limestone or chalk) produces calcium oxide (lime) by calcination at temperatures above 825°C for about 10 hours at atmospheric pressure:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2. \] (2.1)

The calcium oxide is then mixed with water to make slaked lime (calcium hydroxide):

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2. \] (2.2)

Once the excess water is completely evaporated (process technically called setting), the carbonation starts:

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}. \] (2.3)

It is important to consider that in the air the partial pressure of carbon dioxide is low. This means that the reaction takes a significant amount of time to be completed.

The carbonation reaction requires the dry cement to be exposed to air, and for this reason the slaked lime is a non-hydraulic cement and cannot be used under water. This whole process is called the lime cycle. On the contrary, hydraulic cement hardens by hydration when water is added. This type of cement (such as Portland cement) is made of a mixture of silicates and oxides; their four main components are:
- Belite (2CaO·SiO₂);
- Alite (3CaO·SiO₂)
- Tricalcium aluminate (celite; 3CaO·Al₂O₃))
- Brownmillerite (4CaO·Al₂O₃·Fe₂O₃).

All the mechanical properties of the cement are the results of the elements listed above. Moreover, as we said, cement can be aggregated with sand to produce concrete. Conventionally all the materials consisting in grains of size between 2 mm and 40 µm form the sand. Under 40 µm they form silt [20]. Considering that every rock can start a
process of disintegration, both sands and silts can contain every type of minerals. But as
time goes by, the ones that prevail are only the strongest and the hardest of them, as the
more chemically stable [20]

Among the common compounds building up sands and silts there are:
- quartz, as it will be confirmed in chapter 3;
- feldspars, a groupe of rock-forming tectosilicate minerals that make up about 41 %
of the Earth’s continental crust by weight. They crystallize from magma as veins in both
intrusive and extrusive igneous rocks and are also present in many types of metamorphic
rock (i.e. rocks that arise from the transformation of existing rock types caused by heat
and pressure changes);
- garnets, a group of silicate minerals with similar physical properties and crystal forms,
but with different chemical composition. There are different species: pyrope, almandine,
spessartine, grossular;
- micas, a groupe of sheet silicate minerals;
- magnetite, a rock mineral, one of the main irone ores; it’s one of the oxides of iron,
in fact its chemical formula is Fe₃O₄.

Moreover, we can find minerls more common like dolomite (CaMg(CO₃)₂, otherwise
called calcium magnesium carbonate,and calcium carbonate CaCO₃, both of them rela-
tively softer and chemically not so stable, only in ”younger” sands [20].

Figure 2.5: Feldspar (18x21x8.5 cm), garnet and quartz crystal.
2.3 Quantitative and qualitative stratigraphy: painting a fresco and a secco.

The sample studied in this thesis comes from a fresco in the church of San Giuseppe. The fresco, from the Italian word fresco that means fresh, is a technique of mural painting executed in a distinctive way upon freshly laid, or wet lime plaster. Water is used as the vehicle for the dry-powder pigment to merge with the plaster, and with the setting of the plaster, the painting becomes an integral part of the wall. It has been employed since antiquity and is closely associated with Italian Renaissance painting (late 13th century to late 16th century). This technique may be considered in contrast with fresco-secco or secco mural painting techniques.

Fresco-secco (or a secco or fresco-finto) is a wall painting technique where pigments mixed with an organic binder and/or lime are applied onto a dry plaster. This technique contrasts with the fresco technique, in which the layer is wet, as said above. In this type of painting, pigments do not become part of the wall, as in buon fresco. For this reason fresco - secco paintings are less durable: the colors may flake off the painting as time goes by. But it has also some advantages: the working time is longer and the painting is retouchable.

In the affresco technique, buon fresco pigment is mixed with room temperature water and is used on a thin layer of wet, fresh plaster, called the intonaco. Because of the makeup of the plaster, a binder is not required, as the pigment mixed solely with the water will sink into the intonaco, which itself becomes the medium holding the pigment. After that, the pigment is absorbed by the wet plaster and after hours, the plaster dries in
reaction to air. This is the chemical reaction which fixes the pigment particles in the plaster. Chemically, the reactions are those seen at 2.1; 2.2; 2.3, in which respectively we have:

- calcination of limestone;
- slaking of quicklime;
- setting of the lime plaster;

As we can see, the reaction is the same seen in pages 21 - 22. In buon fresco paintings we find different layers. The base is called rinzaffo made of a mixture of sand with big grains and a layer of mortar [2]. After that we find the arriccio, a rough underlayer added to the whole area to be painted that is let to dry for some days before painting. Many artists sketched their compositions on this underlayer in a red pigment called sinopia that would never be seen. The name sinopia is also used to refer to these under-paintings.

On the day of painting, the intonaco, a thinner, smooth layer of fine plaster was added to the amount of wall that was expected to be completed that day, sometimes matching the contours of the figures or the landscape, but more often starting from the top of the composition. This area is called the giornata, and the different day stages can usually be seen in a large fresco, by a sort of seam that separates one from the next.

Fresco presents a main difficulty in its painting: generally a layer of plaster requires ten to twelve hours to dry and the artist has to paint between one hour after the plaster has been added and two hours before the drying time. The artist has from seven to nine hours to work. Once a giornata is dried, no more buon fresco can be done, while the
unpainted intonaco must be removed with a tool before starting again the next day. It is possible, if the artist makes a mistake, to remove the whole intonaco area or to change it later, a secco. After the fresco has been painted the process of carbonatation of the lime is fundamental. It fixes the colour in the plaster ensuring durability of the fresco for future generations.

As one can imagine in a well-sized fresco it is possible to find maybe ten to twenty or even more giornate, or separate areas of plaster. After several centuries, the giornate, which were initially nearly invisible, can sometimes become visible: in some frescos they may be seen even from the ground. Additionally, the border between them was often covered by a secco painting. This kind of painting can easily fall.
Chapter 3

Data analysis

3.1 Samples

In the present work a cross section of a 18th-century fresco from San Giuseppe’s church, in Cagliari, is studied by means of Raman spectroscopy. The sample was prepared to be studied in its different layers, from the top to the bottom, until its roughest layer, the arriccio. The two aims of this thesis project are:
- to identify and investigate the different cementitious materials that constitute the sample;
- to evaluate the different sizes of calcite grains in function of their depth in the sample.

For the first aim, the sample used was the one shown in figure 3.1. For the second one, six samples of calcite were prepared in lab.

3.2 Experimental

All the Raman spectra were measured with a BWSpace4 equipped with a BKTEK microscope (x20) and a laser of wavelength 1064 nm, all at room temperature.

Spectra were taken starting from the upper layer to the deepest. For each layer three points were studied, chosen by their different structure displayed on the computer (above all by their different colours compared to those around them). In particular, Raman spectroscopy was performed from the surface of the sample to collect spectra at the following depths: 0, 0.1, 0.2, 0.3 cm. In the deepest layers was difficult to find
three different points for each layer, so, to map in the most complete way all the sample, from 0.4 until 1 cm in depth, the points were chosen without regular range between them. Spectra were taken in a range from 150 cm\(^{-1}\) until 2000 cm\(^{-1}\).

Through the spectra it was possible to know the different materials that constitute the sample. Once obtained these data from the affresco sample, six different samples of calcite were prepared in lab. From a piece of calcite (marble), six different sizes of grains where obtained, grinding it by hand, with the help of a hammer and a mortar. The different sizes were obtained using several sieves: one for sizes smaller respectively than 149, 74, 44, 37 and 1 \(\mu m\).

At the end we produced calcite grains of the following sizes:

\[
\begin{align*}
&> 149 \, \mu m; \\
&(149 - 74) \, \mu m; \\
&(74 - 44) \, \mu m; \\
&(44 - 37) \, \mu m; \\
&(37 - 1) \, \mu m; \\
&< 1 \, \mu m.
\end{align*}
\]

Once we had all the sample prepared we analyzed them with Raman spectroscopy.
Chapter 3

In the first place we studied the Raman spectra obtained from the affresco. In every spectra the most pronounced and clearest peaks were compared with the peaks in scientific literature. Every peak or group of peaks is, in fact, characteristic of a molecule or a crystal. So that with all the peaks found we could go back to the pigments present in the sample or the binder used. After that we focused on calcite spectra and, in particular, on its peaks $279 \text{ cm}^{-1}$ and $711 \text{ cm}^{-1}$, to reproduce the technique used in [7]. With a data analysis and graphing software we measured the areas under the peaks $279 \text{ cm}^{-1}$ and $711 \text{ cm}^{-1}$ and we calculated the ratio between them. At the end we compared them to the results of the study replicated ([7]) finding the size of calcite grains in function of their depth in the sample.

In the second place we followed the exact same process with the spectra from the calcite prepared in lab. Then we compared the results obtained from the affresco and those obtained from the calcite that we prepared.

3.3 Results and discussion

Several materials were found in this work, studying 22 different spectra. From the cross section it was possible to know with the naked eye, the upper layer from the others. Results, obtained from the shifts measured, were in agreement with what it was expected. In fact, from the fresco technique we expected to find at least some coloured pigments in the first layers, calcite ($\text{CaCO}_3$), plaster, and a binder, in the deepest ones.

In the first layers calcite, hematite and gypsum are found. In particular, calcite is found in almost all the spectra, through different strong peaks among which that centered at $1087 \text{ cm}^{-1}$. The region about $1450 \text{ cm}^{-1}$ is a sign of C - H bond [2], that suggests the presence of organic elements. These two peaks are reproducible throughout the entire sample either with high intensity, most of the time, or low. This underlines, in particular with peaks of high intensity, the abundance of calcite respect to the others elements found, and as we will see, also the different size oh its grains through the sample.

Gypsum is found in his characteristic frequency at $1007 \text{ cm}^{-1}$, a peak of medium intensity, and at $495 \text{ cm}^{-1}$ which is less intense. It is found only in spectra 1, 3 and 8, as shown in fig. 3.3 and 3.4. This means that gypsum was used only in the first millimeters of the fresco. In fact, according to the fresco thecnique it is usual to use it,
along with calcium carbonate and water, in the upper layer before starting to paint. The same can be said for the hematite, probably used for the working drawings. It has been found in spectra 1, 3 and 8. Peaks at 282, 404, 495, and 643 cm$^{-1}$ are typical of amorphous compounds, found in almost every spectra. In particular they show the presence of quartz that can be linked to the sand grains used in the plaster mixture. Moreover this presence is underlined by the wide band, also typical of amorphous elements, as shown in spectra 2, 6, 8, and to a lesser extent in spectrum 9. Another peak at 515 cm$^{-1}$ is found in spectra 2, 5, 6 and 9, from which it is possible to assume the presence of moganite along quartz. That mixture of minerals is know as chalcedony, with the chemical structure SiO$_2$, a silicon dioxide [21]. A strong peak is found at 785 cm$^{-1}$ in spectra 7, 8 and 9, all corresponding to the depth 0.3 mm from the first layer. This peak is a hint of calcium hydroxide, characterised by the O - H bond. Calcium hydroxide is obtained when calcium oxide is mixed with water, as it is in the fresco technique. This element may suggest that the chemical reaction of carbonatation has not been completed yet [22].

In the deepest layers some differences were found. Every spectrum, from 10 to 22, will be described in detail below.

*Spectrum 10.* This spectrum shows a very strong peak at 463 cm$^{-1}$. It is a sign
of a strong presence of quartz in this region, above all the others. Since the peak intensity is very strong, it leads to assume that the point analysed was a mixture of sand grains.
Figure 3.4: Raman spectra of the 3rd mm of the plaster.

Spectrum 11. In spectrum 11 two peaks, 220 and 263 cm$^{-1}$, can be seen to be very strong, as in spectrum 10. A smaller peak is found at 330 cm$^{-1}$, next to a wide band around 417 cm$^{-1}$, as it has been said before, typical of amorphous elements [2], as quartz, along the frequencies 521, 579 and 630 cm$^{-1}$. The intense peak at about 712 cm$^{-1}$ is the sign of a strong presence of calcite, as the ones at 275 and 1087 cm$^{-1}$. Two more peaks are found at 1245 and 1617 cm$^{-1}$, that will be found in other spectra below.

Spectrum 12. In spectrum 12 an intense peak at 463 cm$^{-1}$ is found. Along with peaks less intense, as 201 and 540 cm$^{-1}$, it confirms again the presence of quartz. A band of medium width is found at 1087 cm$^{-1}$. Through this frequency and those at 275 and 712 cm$^{-1}$ the presence of calcite is still confirmed. Moreover, a little amount of graphite is underlined by the peaks of weak intensity about 1393 and 1571 cm$^{-1}$. The band at 798
Figure 3.5: Raman spectra of the deepest layers of the sample, from 0.4 until 0.6 cm.

\[ \text{cm}^{-1} \] is instead associated with the vibration mode of calcium hydroxide.

*Spectrum 13.* In this case it can be noted a strong presence of calcite shown through
the peaks of high intensity 279, 712 and 1087 cm\(^{-1}\). For the first time also calcium solphate is found: two bands suggest its presence, the one at 1036 cm\(^{-1}\) and the other one about 1169 cm\(^{-1}\), both of them of weak intensity.

Spectrum 14. Moving forward in depth, a stronger presence of calcite is underlined by the fact that all its bands, or just some of them, reach a higher intensity [2]. The two bands at 1360 cm\(^{-1}\) and 1607-1677 cm\(^{-1}\) may suggest the presence of calcium oxalate in a particular crystalline state: coxoite CaC\(_2\)O\(_4\) \(\cdot\) 3H\(_2\)O) [23]. In this region, in contrast with the two following spectra, there is just one weak peak at 465 cm\(^{-1}\), that gives us a hint about the presence of quartz. At the same time, even at this depth (4 mm about), there are two peaks, the one at 410 cm\(^{-1}\) and the one at about 614 cm\(^{-1}\), that still confirm the presence of hematite.

Spectrum 15. The main aspect about this spectrum is the sign of quartz revealed by the intense peak at 463 cm\(^{-1}\). While calcite is found in his frequencies only at very weak intensity.

Spectrum 16. Spectrum 16 has several bands of medium intensity and three strong peaks well defined. These last ones are 194, 263 and 463 cm\(^{-1}\), respectively from Pb\(_2\)SnO\(_4\), called giallo di piombo [2], calcite (see also peaks 699, 1082 and 1462 cm\(^{-1}\)) and quartz. The presence of a coloured pigment as Pb\(_2\)SnO\(_4\) can be explained considering that spectrum 16 is still around the first 5 mm (in depth) of the fresco. In this way, a small amount of it could be passed among the first grains of cementitious materials and stopped there. It can be noted that the pigment is an oxide. In fact, in the fresco technique, pigments have to be oxides so that they do not interfere in the carbonation [24].

Spectrum 17. Calcite can be noted immediately: it has its three characteristic peaks of medium intensity (711, 1462, 1607 cm\(^{-1}\)) and of very strong intensity (276, 1088 cm\(^{-1}\)). This means that, in this region, calcite presence has increased [2]. The largest band in this spectrum is the one at 773 cm\(^{-1}\), typical of calcium hydroxide (O - H bond [2]). All the other bands are too weak and they can be confused with background noise.

Spectrum 18. Spectrum 18 is very similar to spectrum 17. The main difference is the
large weak band at 508 cm\(^{-1}\), sign of an amorphous compound. As it can be seen in almost all the spectra there is a weak peak at 1042 cm\(^{-1}\) (often 1030 cm\(^{-1}\)). This peak is associated with calcium sulphate anhydrous (anhydrite), for which, the absence of H\(_2\)O causes a shift from the characteristic 1006 cm\(^{-1}\) of calcium sulphate dihydrate towards greater Raman frequencies [25].

*Spectrum 19.* Compared to the others spectra, in this case there is a large band at 822 cm\(^{-1}\). Undoubtedly, it is sign of an amorphous compound found in small quantities in almost all the spectra: probably an organic binder. Calcite still confirms its presence.

*Spectrum 20.* Spectrum 20 shows a strong presence of quartz, through its characteristic peak at 462 cm\(^{-1}\). A peak of medium intensity is found at 201 cm\(^{-1}\) and 390 cm\(^{-1}\), sign of a well defined crystalline structure. The other peak at 785 cm\(^{-1}\) is instead associated with the vibration mode of calcium hydroxide.

*Spectrum 21.* Calcite, quartz and calcium hydroxide are still present until the deepest layers of the sample. The peaks here are well defined, of strong or medium intensity. The largest band is the one at 1234 cm\(^{-1}\) and the two frequencies always found together at 773 cm\(^{-1}\) (calcium hydroxide) and 822 cm\(^{-1}\).

*Spectrum 22.* This spectrum is the first that we found with just two peaks of strong
Figure 3.7: Raman spectra of the deepest layers of the sample, from 0.8 until 1 cm.

intensity, at 693 and 785 cm\(^{-1}\). The first one can be linked to the characteristic 711 cm\(^{-1}\) of calcite, while the second one is associated with calcium hydroxide and is a sign of an uncompleted process of carbonation [22].

Once the match between the spectra and their chemical and physical meaning has completed, it was possible to proceed comparing sizes from calcite spectra found in the sample and the ones found in the six samples prepared in lab. This study is based mainly on the work [7], in which, thanks to Raman spectroscopy, a relation between two peaks of calcite spectrum (276 and 711 cm\(^{-1}\)) and the size of the grains analysed was found. In fact this study proposed a new model to determine the crystal size of calcium carbonate polymorphs, using the \(A_{280}/A_{712}\) ratio in calcite [7]. The size to which they referred is to the length of the size of the rhombus [7]. The main point on which this study is based is
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<thead>
<tr>
<th>Depth</th>
<th>Spectrum</th>
<th>Peaks (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mm</td>
<td>1</td>
<td>282, 404, 816, 1007, 1082, 1456, 1607</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>643, 822, 1007, 1184, 1229, 1456, 1612</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>611, 822, 1007, 1462, 1612</td>
</tr>
<tr>
<td>0.1 mm</td>
<td>4</td>
<td>269, 643, 822, 1082, 1234, 1451, 1607</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>290, 404, 711, 822, 1082, 1229, 1456, 1607</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>269, 515, 705, 785, 1082, 1234</td>
</tr>
<tr>
<td>0.2 mm</td>
<td>7</td>
<td>711, 785, 1082, 1234, 1344, 1462</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>611, 711, 785, 956, 1082, 1234, 1344, 1462</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>276, 463, 643, 711, 785, 1082</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>10</td>
<td>201, 463</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>263, 417, 705, 1082</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>201, 463, 1082</td>
</tr>
<tr>
<td>&gt; 0.3 mm</td>
<td>13</td>
<td>279, 785, 1082, 1462, 1607</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>276, 711, 1082, 1234, 1456, 1607</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>201, 463, 1082</td>
</tr>
<tr>
<td>&gt; 0.5 mm</td>
<td>16</td>
<td>194, 263, 463, 699</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>276, 711, 773, 1088, 1607</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>276, 508, 767, 1082</td>
</tr>
<tr>
<td>&gt; 0.7 mm</td>
<td>19</td>
<td>276, 785 - 822, 1082, 1234, 1462</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>201, 390, 462, 785</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>276, 463, 785, 1082, 1234, 1456, 1607</td>
</tr>
<tr>
<td>1 cm</td>
<td>22</td>
<td>279, 693, 785, 1088, 1456</td>
</tr>
</tbody>
</table>

Table 3.1: Peaks of spectra obtained from the fresco sample at their respective depth.

that carbonation on the outer surface may differ from the inside process, since the CO<sub>2</sub> diffusion coefficient and steric hindrance could impact crystal growth [7]. So that the calcite crystals through the sample have different sizes.

It is possible to see, in the figure below, a little difference between the two areas under the peaks at 279 cm<sup>-1</sup>. The ratios between these areas and those under 711 cm<sup>-1</sup> were studied. We expected to distinguish at least two parts of the fresco: the first layer, on which drawings were painted, and the *arriccio*, the roughest layer. The first layer should
Figure 3.8: Calcite spectra in two different sizes: less than 1 \( \mu \text{m} \) and more than 149 \( \mu \text{m} \).

have smaller grains while the second one should be rougher, i.e. it should have bigger grains.

Using the relations from the work [7] we noticed that under the ratio 3.6, it is not possible to determine the size of crystals precisely. In fact, in the table showed in [7], next a ratio
of 3.6, the word "agglomerate" is found. This may suggest that this technique is not precise enough with calcite grains bigger than 30 µm or with calcite agglomerate with other materials. However it was possible to find the order of magnitude corresponding to what we expected: 10-30 µm. Moreover with the six samples of calcite, as the following table shows, ratios $A_{279}/A_{711}$ are bigger than those found in the sample from the fresco and sizes are smaller, as we expected. To find the profile of the sample from the fresco, i.e. to distinguish the first layer from the arriccio, we studied the presence of different elements along with the fresco technique. In particular: finding gypsum in spectra 1, 3 and 8, means that the first layer ends at 3 mm about, because gypsum was used only for the outer layer, and the arriccio starts from 3 mm to 1 cm.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Calcite size (µm)</th>
<th>$A_{279}/A_{711}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.4</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>9.6</td>
<td>19.0</td>
</tr>
<tr>
<td>4</td>
<td>32.4</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>31.2</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>31.7</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>32.7</td>
<td>0.6</td>
</tr>
<tr>
<td>8</td>
<td>32.9</td>
<td>0.4</td>
</tr>
<tr>
<td>9</td>
<td>32.4</td>
<td>0.9</td>
</tr>
<tr>
<td>11</td>
<td>31.9</td>
<td>1.3</td>
</tr>
<tr>
<td>12</td>
<td>30.6</td>
<td>2.5</td>
</tr>
<tr>
<td>13</td>
<td>31.5</td>
<td>1.7</td>
</tr>
<tr>
<td>14</td>
<td>31.5</td>
<td>1.7</td>
</tr>
<tr>
<td>16</td>
<td>31.4</td>
<td>1.7</td>
</tr>
<tr>
<td>17</td>
<td>30.8</td>
<td>2.3</td>
</tr>
<tr>
<td>18</td>
<td>29.2</td>
<td>3.6</td>
</tr>
<tr>
<td>19</td>
<td>30.8</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>32.3</td>
<td>1.0</td>
</tr>
<tr>
<td>21</td>
<td>30.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 3.2: $A_{279}/A_{711}$ ratio for calcite crystals with different sizes from the fresco of San Giuseppe.
<table>
<thead>
<tr>
<th>Calcite size (µm)</th>
<th>$A_{279}/A_{711}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.0</td>
<td>9.0</td>
</tr>
<tr>
<td>25.2</td>
<td>7.1</td>
</tr>
<tr>
<td>25.8</td>
<td>6.5</td>
</tr>
<tr>
<td>23.9</td>
<td>8.1</td>
</tr>
<tr>
<td>25.1</td>
<td>7.1</td>
</tr>
<tr>
<td>26.0</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 3.3: $A_{279}/A_{711}$ ratio for calcite crystals with different sizes prepared in lab.
Chapter 4

Conclusions.

This thesis project wanted to investigate the potential of the Raman technique in the field of cultural goods: in both art and archeology. To do this, the Raman spectra of a sample from a fresco of San Giuseppe church in Cagliari and of six calcite samples prepared in lab were analysed. For every spectrum in the sample from the fresco we found pigments and binders present on it. After that we focus on calcite spectra, both those of the sample and those prepared in lab. We studied the ratio between the areas under the peaks $279 \text{ cm}^{-1}$ and $711 \text{ cm}^{-1}$ and get back to the size of calcite grains.

In the first layers we found, as expected, hematite (404 $\text{ cm}^{-1}$, Fe - O stretching) and gypsum (495 $\text{ cm}^{-1}$ and 1007 $\text{ cm}^{-1}$). The hematite is a sign of a preparatory drawing before the fresco was painted. The gypsum is usually used in the upper layers to cover the roughest ones. This means that the first layer, the arriccio, covers less than 1 mm.

In almost all the spectra we found calcite - calcium carbonate ($275, 715, 1082 \text{ cm}^{-1}$) and calcium hydroxide (O - H bond) with a characteristic peak at 785 $\text{ cm}^{-1}$. Calcium hydroxide is obtained from calcium oxide mixed with water. This means that the mural painting was made a fresco and that the carbonatation process has not ended yet. Different studies confirmed the affresco technique with subsequently works a secco [17]. In fact we found a peak around 1450 $\text{ cm}^{-1}$ (C - H bond) that suggest the presence of organic material, like oil, usually mixed with calcite in paintings a secco.

In spectra 2, 5, 6 and 9 we found also moganite and quartz (chalcedony) which confirms the presence of sand usually mixed with the cement.
Chapter 4

We calculated the size of calcite grains with the technique proposed in [7] to study the stratigraphy of the mural painting. The range of sizes found in the sample goes from $32.9 \, \mu m$ to $29.2 \, \mu m$, except for spectrum 3, which presents a size of $9.6 \, \mu m$. Spectrum 3 is in the first layer of the sample. This means that the upper layer is made by thinner materials. On the contrary the *rinzaffo* is composed by roughest, i.e. bigger grains, as expected.

From the spectra of the six samples prepared in lab we got six sizes, from $23.0 \, \mu m$ to $26 \, \mu m$. Except for the size from the range $(149 - 74) \mu m$, all sizes were in order from the smaller to the bigger one. This confirms the potential of Raman spectroscopy in measurements of the order of micrometer. The fact that all sizes are found from $23.0 \, \mu m$ to $26 \, \mu m$ is because calcite grains of smaller sizes are found in all ranges prepared.

In conclusion Raman spectroscopy can be applied with success in the field of diagnostic and preservation of cultural goods both in the identification of materials and in the measurement of crystal grains.
Chapter 5

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Acknowledgements