

## NOT JUST SIMPLE WATER DRIPS: THE CASE OF AN EARLY 1900s OIL PAINTING ON STONE

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### Abstract

*Water drips marks are commonly found on wall paintings as a result of water infiltration, often perceived as stains. Water drips can cause material migration and deposition while potentially interacting with water-soluble constituents. Peculiar features of water marks noticed during a conservation campaign on a dome painting in a church in Malta, generated a series of investigations. This study presented aim at gaining insight into the process involved in the deposition of material on the painted surface and its potential implications for the conservation of the painting. Painted in 1903 by Giuseppe Calì (1846-1930), a leading local artist, the oil-based painting on stone is characterized by a complex stratigraphy and material composition. The painting was left in critical condition after a long history of recurring heavy rainwater infiltration triggering extensive salt deterioration and water drips. Visual observations indicated that the water drips emerged from paint craquelure and along their path they reacted with the painted surface. Semi-transparent white-brownish material deposited by the drips were examined by means of digital microscopy and were characterized into three distinctive morphologies: cubic, needle-shaped and amorphous. Sampled drips were further studied by a multianalytical approach, involving IR and Raman spectroscopies and GC-MS with pyrolysis. In particular, the organic fraction of the deposited material mainly consisted of fatty acids from the oil medium, with dicarboxylic acids being consistently detected. This could indicate that a portion of the dried lipidic crosslinked network, especially the more hydrophilic fraction, and formed metal soap were segregated and separated from the oil-based painting and partially leached onto the surface of the painting. These results provide useful insights into the interaction of liquid water with oil paints, and on its detrimental effects on the stability of the oil-based paint system.*

**Keywords:** Water drips; Oil painting; Degradation; Wall painting; Oil on stone

### Introduction

Giuseppe Calì (1846-1930) is a renowned artist in the Maltese Islands who worked extensively in various local churches both on wall and canvas paintings. Calì earned a reputation for his rapid brushwork, ranging from smoothly to thickly applied, composing scenographic, romantic and naturalistic compositions. For his wide range of work Calì used oil-based paints, and in the case of wall paintings, the oil paints were applied directly on local limestone masonry [1-2].

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Despite their relatively young age, many of Cali's wall paintings have been found in a poor condition. In most cases, this degradation has been attributed to neglect and lack of maintenance of the stone masonry causing water infiltrations and triggering in turn salt activity [1-6]. Salt deterioration is effectively the main deterioration factor for stone masonry structures in Malta. A clear example of a wall painting by Cali found in appalling condition is the one in the dome of the Crucifix chapel in the church of the Immaculate Conception Church, in Bormla, Malta.

The dome of the Crucifix chapel is divided into four bays by four ribs decorated with carved gilded stone and is crowned by a lantern. Each of the four bays was painted in 1903 with a different episode of the early life of Christ. In 1963, only sixty years later, the painting was heavily restored after surviving the Second World War and recurrent water infiltrations. It is estimated that by that time about 45% of the original wall painting had already been lost.



**Fig. 1.** Context images shows the appearance of the long white drips running down the surface of the paintings, with a macro image on the right. The two sets of micrographs, at the bottom, show the same drip in diffuse and raking light showing the lack of colour and increase in texture in comparison with the surrounding, unaffected area.

By 1996 the condition of the interior of the dome was once again found in bad condition [7]. In 2004 a series of analytical studies was carried out to understand the causes of deterioration with the main emphasis being on the effects of salt activity, causing paint delamination and severe deterioration of the stone support [3-5]. Cross-section analysis revealed the complexity of the painting stratigraphy, encompassing at least 17 layers belonging to

different painting phases. The 1903 painting was found to consist of multiple white preparatory layers mainly composed of lead white and chalk, and one to two thin paint layers. The binder was found to be mainly linseed oil with traces of beeswax. The preparatory layer was applied over pre-existing paint layers, unrelated to Cali's painting scheme, some of which are composed of a combination of lead and zinc white. The stone masonry was also found to be a poor-quality limestone pointed and repaired in the past with lime-gypsum mortar [3-5].

In 2020 in view of a conservation project, a new condition assessment and a series of investigations were carried out. Compared to 2004, in 2020 the condition of the paintings was found to have considerably worsened, whilst several areas of the painting had collapsed. One of the aspects that was investigated over the last campaign was the presence of numerous long white drips, probably generated by rainwater infiltration. These drips marks, from now on referred to as "drips" in this contribution, were particularly interesting since along their trail the upper paint layer appeared thinner than in the unaffected areas, while white material was also found to have deposited along the edges and at the end of the drips (Fig. 1).

The manifested characteristics of the "drips" seemed to point to a possible interaction between water and oil paints causing material migration and deposition. Drips marks caused by rainwater infiltration are a relatively common phenomenon in wall paintings, but they are poorly investigated, especially in the context of oil-based wall paintings.

This paper presents the preliminary results obtained from the study of these white drips. It is argued that a better understanding of this phenomenon is likely to provide useful information on the properties and vulnerability of oil paintings, in particular to their exposure to liquid water – which is predominately relevant for oil paintings in an architectural context.

## Materials and methods

For this preliminary study, a multi-analytical approach was adopted, characterize the organic components of the "drips". Following the in-situ examination of the "drips" with a digital microscope, some of the whitish deposited material was scraped and analysed using FT-IR in ATR mode, Raman spectroscopy and Py-GC/MS.

Moreover, during the conservation works, it was noted that in spite of the recent repair work on the exterior, some rainwater was still seeping through the stone and the paint forming drips. The liquid (referred from now on as "liquid drips") was therefore sampled using a pipette and stored in a vial for analysis.

### *Onsite Microscopy*

The Dino-Lite Edge Digital Microscope AM7915 MZT was used in two different magnifications under diffuse and raking light. Such investigation allowed to observe the "drips" and to classify them in different groups of the bases of the morphology and texture.

### *FT-IR-ATR and Raman Spectroscopy*

Scraped samples from the "drips" were investigated by FT-IR in ATR mode and Raman Spectroscopy.

A Bruker ALPHA II Fourier Transform IR Spectrometer was used for FT-IR analysis in Attenuated Total Reflectance mode (FT-IR-ATR) using a synthetic diamond crystal for the compression of the samples. The spectra were recorded in the wavelength range from 4000 to 350 $\text{cm}^{-1}$ , with 4 $\text{cm}^{-1}$  resolution. The background was measured with 24 scans before each acquisition, while samples were investigated using 128 scans, 4 $\text{cm}^{-1}$  resolution. Spectra were elaborated with OPUS and Origin 9.0 software.

Raman spectra were collected with a Bravo Raman spectrometer by Bruker Optics, characterized by a dual laser excitation (two lasers at 758 and 852nm working simultaneously). The Raman spectra were collected in the spectral range between 3200–300 $\text{cm}^{-1}$  with 10 $\text{cm}^{-1}$  resolution, scan time from 1s to 60s.

### *Py-GC/MS*

The composition of the organic fraction of the painted layers and the scraped drips was analysed using Thermally assisted Hydrolysis and Methylation, pyrolysis Gas Chromatography-Mass Spectrometry (THM-Py-GC/MS).

The pyrolysis unit used was a Frontier Lab 3030D, micro furnace pyrolyzer mounted on a Thermo Scientific Focus GC/ISQ mass spectrometer combination. Separation took place on a SLB5 ms (Supelco) column with a length of 20 meters, an internal diameter of 0.18mm and a film thickness of 0.18 $\mu$ m. Helium was used as the carrier, with a constant flow of 0.9mL/min. The split ratio was 1:30. The temperature program used, was 35°C, stable for 1 minute, subsequently raised with 60°C per minute until 110°C, raised with 14°C per minute until 240°C and with 5°C per minute until 315°C, stable for 2 minutes. The temperature of the interface was set at 250°C, the temperature of the ion source at 220°C. Mass spectra were recorded from 29 until 600amu with a speed of 5 scans per second. XCalibur 2.1 software was used to collect and process the mass spectral data.

Samples were treated with 3 $\mu$ L of 25% solution of TMAH in methanol and transferred to steel eco-cups for pyrolysis, as reported in [8-10].

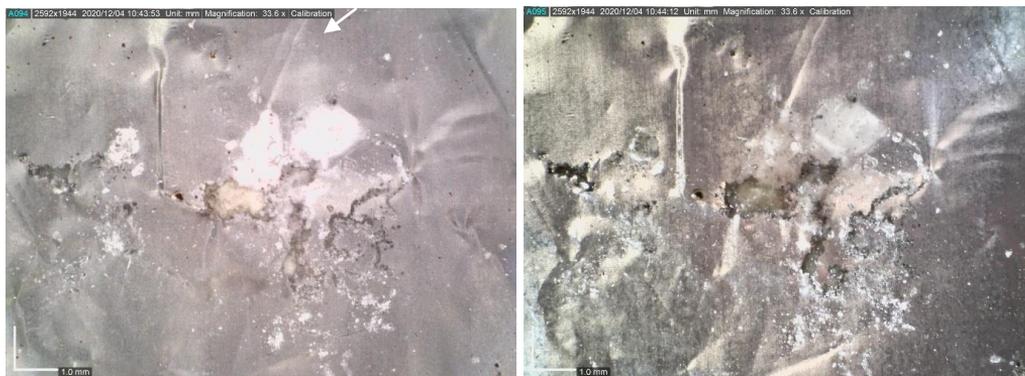
The interpretation of the results is done using the ESCAPE system, an expert system for characterization of (THM-)Py-GC/MS data using AMDIS & Excel. The ESCAPE AMDIS library is firmly based on spectra from the NIST library and data shared by experts in the conservation science field [11, 12].

## Results and discussion

### *Initial observations of samples*

The first few scrapings of the “drips” were collected and stored in aluminium foil then placed in a sealed plastic box. In less than a month, the samples were found to have reacted with the aluminium foil, which as a result, was found punctured and darkened at the edges (Fig. 2). In few cases upon the opening of the aluminium foil a faint, foul smell was perceived. On the spot, the pH of the liquid was tested. It gave a rough result of a neutral pH.

The pH of the “liquid drips” collected after rainwater infiltration, was also found to have roughly a neutral pH using the same method above.



**Fig. 2.** Micrographs in diffuse and raking light of the reacted aluminium foil.  
The arrow points at the droplet found within the aluminium foil

### *Morphology and description of the drips*

The “drips” were generally found to have a white colour, although in some instances they also appeared light brown. “Drips” were present on all four bays but were particularly evident and numerous on those two bays, that were reported to suffer the most from water infiltration. Visual observations indicated that the water drips emerged from paint craquelure and losses and ran down on the surface of the wall painting (Fig. 3). White material deposited on the edges of the drips’ path while the paint layer was missing or thinned, as well as rougher in texture in comparison with the unaffected adjacent areas.



**Fig. 3.** Micrograph of drip emerging from a paint loss

With the aid of digital microscopy, the deposited material at the end of the drip was characterized into three distinctive morphologies: “needle-shaped”, “cubic” and “amorphous” (Fig. 4). No specific pattern relating to the location of these diverse formations seemed to be apparent.

The “needle-shaped” formation was mainly found to be composed of multiple, thin micro-crystalline structures, usually spread out as a thin layer, more rarely as a thicker deposit. This formation was always found to be white, and while sampling, it was found to be powdery. The deposited material of the “cubic” and “amorphous” formation occasionally had a light brown-tinge. The former was often found to be transparent while the latter was composed of a white porous crust. With substantial deposition of the “cubic” material, a “wall”-like structure similar to the “amorphous” deposition forms at the tip of the drip (Fig. 4). While sampling, the “cubic” formation seemed to be tacky, while the “amorphous” drip was brittle.



**Fig. 4.** Micrographs in raking light showing the “needle-shaped”, “cubic” and “amorphous” formations respectively

#### ***Chemical composition of the drips***

FT-IR in ATR mode and Raman spectroscopy performed on scrapings representing all three morphology of the “drips” gave insights on their organic and inorganic composition. All samples were found to include gypsum and metal carboxylates, also known as metal soaps (Fig. 5). Research in the degradation of oil paintings implies that the metal soap formation within oil paintings is fairly common, however, this research is mostly carried out and aimed for easel painting conservation [13-20]. The characterization of the specific metal soaps, however, was not possible due to the similarities in the IR vibrations of the different metal carboxylates and considering the instrumental resolution ( $4\text{cm}^{-1}$ ).

According to Py-GC/MS, the majority of the “drips” was composed of a substantial amount of difatty acids (such as adipic, glutaric, pimelic, azelaic, suberic and sebacic acids, being azelaic the most abundant) (Fig. 6). In the chromatograms of the deposited drip material some differences were observed according to the drip morphology. In comparison, the amorphous formations had higher amounts of difatty acids than both the “cubic” formation and

the “needle-shaped” formation. All samples likewise included amounts of saturated monofatty acids, such as myristic, palmitic and stearic acids, demonstrating a typical fatty acid profile of a dried drying oil. The only exception was one sample of “cubic” deposited material (GC\_B1S3\_s\_7), which had myristic acid as the most abundant fatty acid. The “needle shaped” formation on the other hand was mainly composed of gypsum.

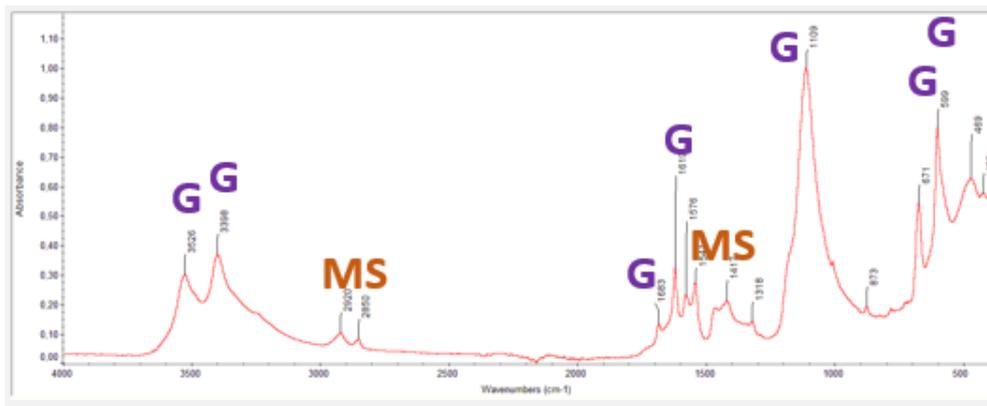


Fig. 5. FT-IR spectroscopy showing peaks for gypsum (G) and metal carboxylates (MS)

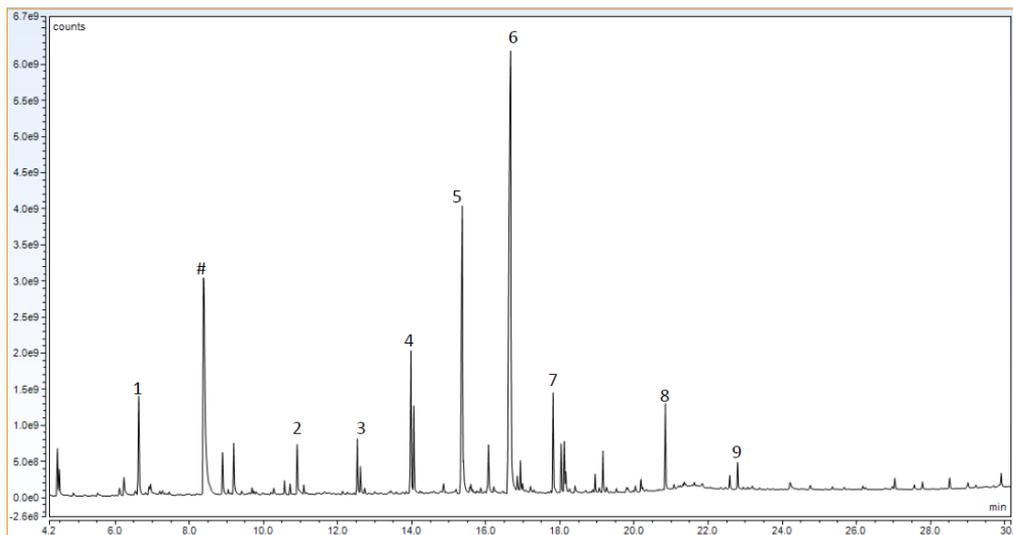


Fig. 6. Py-GC-MS results after thermal desorption and thermal degradation using TMAH. Difatty acids (2 = glutaric, 3 = adipic, 4 = pimelic, 5 = suberic, 6 = azelaic, 7 = sebacic acids as methyl esters) are mainly present, together with 1 = glycerol, 8 = palmitic and 9 = stearic acids as methyl esters. Peak labeled as # is due to TMAH

It almost seems that there has been leaching that, with percolating water, has conveyed the most hydrophilic part of the lipidic binder, specifically the difatty acids. Within the “liquid drip” samples only traces of fatty acids and alkenes were identified. This indicates high amounts of fatty acids found in the former solidified drips is likely to be a build up after recurrent water infiltrations. Meanwhile, the presence of the alkanes possibly relates to the traces of beeswax found in the painting mixture in the 2004 technical study [3-5]. However, beeswax is known to be insoluble in water hence this outcome of migration of the alkanes with the presence of water is not yet understood.

The white drips are, therefore, likely to be a result of the migration of oil paint components due to water infiltrations that have seeped through the external stone cracks and through the entire stratigraphy of the painting. Recurrent water infiltrations in this case have caused the unbound oil components out of the paint system. The gypsum, on the other hand, was instead probably leached out from old plaster repairs and mortar joints of the stone masonry.

At this stage of research, unfortunately, it has not been possible to explain the dissolution of the paint layer along the drip trail, and not even the corrosion of the aluminum foil used to store the samples. The pH results reported above did not give any indication to narrow down any possible causes.

## Conclusions

These preliminary results revealed that the more hydrophilic part of the oil paint network along with metal soaps can be leached out from oil-based wall paintings as a result of recurrent rainwater infiltrations. These leached components can then deposit on the surface of the painting together with soluble salts, in this case gypsum, more commonly found in masonry structures. This investigation on material deposited by water drips found on oil-based wall paintings demonstrates that white accretions on these paintings are not necessarily due to just soluble salts, as it is often believed. Their composition can actually be more complex and can also include organic components originating from the oil painting itself. So far, investigations into these “drips” have targeted the organic components of the deposited material. The next step will be to characterize the inorganic components.

This should allow gaining a better understanding on the combination of salts and metal soaps present within the deposited material, as well as on the possible presence of other materials inherent to the painting that may have been leached out by liquid water infiltrations. Such investigation may also provide insights into the reasons behind the different morphologies of the “drips” and help understand the thinning of the paint layer along the drip trail.

In spite of its limitations, this study pointed out the detrimental effects that prolonged exposure to liquid water can generate in oil-based wall paintings. Besides activating salt activity and related salt deterioration, water can also leach out oil paint components. This emphasises the need of strict preventive measures aiming to avoid rainwater infiltrations, and also of a cautious use of water during conservation treatments.

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