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Case study

20th century artists' oil paints: The case of the *Olii* by Lucio Fontana

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ABSTRACT

During the 20th century, many innovative binders have been rapidly introduced to the art world and soon became popular as artists' paints and pictorial media. However, despite the advantages that new synthetic materials presented, oil paints have never been entirely substituted. Indeed, this paper focuses on the results provided by the scientific analysis of a group works from the oeuvre of Lucio Fontana (1899–1968), all of which created between 1960 and 1964 using oil-based media, and aims to illustrate how oils contained in the pictorial media have influenced these works' respective ageing and degradation processes. Despite the apparent coherence in the behaviour of many of Fontana's creations, some artworks revealed discrepancies in terms of the physical and mechanical behaviour of the pictorial films and in alterations resulting from degradation processes. Samples taken from case studies belonging to the *Olii* and *Fine di Dio* series were analysed using optical microscopy, X-Ray Fluorescence (XRF), Fourier-Transform Infrared Spectroscopy in attenuated total reflectance (FTIR-ATR) and Gas Chromatography-Mass Spectrometry (GC-MS) in order to study and identify the materials employed by the artist and the products of their degradation processes. These analyses gave unexpected but useful results (such as the presence of non-drying or slow-drying oils in the paint formulations) which not only provided us with new insight into the nature of the constituent materials, but also facilitated the elaboration of correct conservation measures and suitable restoration interventions.

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1. Introduction and aims of the research

During the first decades of the 20th century, many innovative binders were introduced to the art world and soon became popular as artists' paints and painting media [1–3]. As a direct consequence, the composition and nature of many artistic and pictorial binders were thus subjected to radical changes. However, despite the advantages that these new synthetic materials presented, oils continued to dominate as the most versatile binding medium, and have never been entirely substituted [4,5].

This research, part of a larger research project dedicated to the nature of 20th Century artists' oil paints (namely the *20th Century oil paints Project*), deals with a group of works by one

of the most important Italian artists of the 20th century, Lucio Fontana (1899–1968). Even though previous studies have shown that Fontana had started to use new synthetic binders as substitutes for traditional oils [6–9], this survey focused specifically on the analysis of works from the *Olii* and the *Fine di Dio* series created between 1960 and 1964, in which, the artist used the classical pictorial medium of oils with new expressive aims. In these series, Fontana usually applied monochromatic pictorial layers to the canvas, then, while the medium was drying, he pierced, engraved and manipulated the paint, which soaked into and around the edges of the holes and even leaked onto the rear of the canvas. The artist applied the oil media in a thick *impasto* using brushes, spatulas and his fingers in order to achieve a sculptural effect, and sometimes glued shaped elements such as small pieces of coloured glass or sequins onto the surface. The paint layers of the works belonging to these series are normally compact and rigid, and seldom present conservative problems. However, with time some of the pictorial surfaces have begun to show the effects of the drying process and the movement of the support (which generally manifest in the form of craquelures), but rarely actual losses in the paint layer or its detachment from the canvas have been noticed. Despite the apparent coherence in the behaviour of many of Fontana's

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Table 1
A short description of the analysed paintings by Lucio Fontana and the observations about their state of conservation before restoration.

Paintings ^a	Description	State of conservation
<i>Concetto Spaziale. Notte d'amore a Venezia</i> , 1960, Fondazione Lucio Fontana (60 O 81), 80 × 100 cm	This rectangular canvas, belonging to the <i>Concetto Spaziale (Olii)</i> series, is covered in monochromatic red-brown paint; the pictorial surface presents punctures, cuts and scratched incisions	The reddish-brown pictorial layer was wrinkled and widespread craquelure has created 'islands' which tend to detach from the fabric support (Fig. 1a). In some places, this phenomenon was so advanced that it has caused losses in the paint layer. In some parts, the paint layer appears to be extremely brittle and fragile, while in others, it is still sticky and only partially dry
<i>Concetto Spaziale</i> , 1962, Fondazione Lucio Fontana (62 O 66), 145 × 115 cm	This rectangular canvas, belonging to the <i>Concetto Spaziale (Olii)</i> series, is covered in monochromatic pink paint with slashes, cuts and graffiti	These three pink <i>Concetto spaziale</i> artworks presented all the same type of deterioration: strange, lighter yellow stains in the form of drops and puddles were noted on the painted surfaces (Fig. 1b)
<i>Concetto Spaziale</i> , 1962, Fondazione Lucio Fontana (17 37/92), 100 × 80.5 cm	This rectangular canvas, belonging to the <i>Concetto Spaziale</i> series, is covered in monochromatic pink paint with slashes, cuts and graffiti	
<i>Concetto Spaziale. Fine di Dio</i> , 1963, Fondazione Lucio Fontana (63 FD 14), 178 × 123 cm	This oval painting, belonging to the <i>Concetto Spaziale (Fine di Dio)</i> series, is characterized by a monochromatic pink paint with punctures, cuts and scratched incisions	
<i>Concetto Spaziale. Fine di Dio</i> , 1963, Fondazione Lucio Fontana (63 FD 23), 178 × 123 cm	This monochromatic black oval work, belonging to the <i>Concetto Spaziale (Fine di Dio)</i> series, presents punctures, slashes and sequins glued to the surface	In this black <i>Concetto Spaziale</i> , the edges of the slashes appeared to be deformed and instead of protruding onto the rear, they appeared to have contracted and had pushed through onto the front of the canvas (Fig. 1c)
<i>Concetto spaziale. Fine di Dio</i> , 1964, Fondazione Lucio Fontana (64 FD 5), 178 × 123 cm	This monochromatic yellow painting on an oval canvas with punctures, slashes and scratches belongs to the <i>Concetto Spaziale (Fine di Dio)</i> series	It did not present any unusual alterations and therefore represented an ideal reference standard (Fig. 1d)

^a Fontana's works are classified in the general catalogue by year, the initial letter of the series and the number of the work within its respective series – hence 60 O 81 should be read as a work dated to 1960, belonging to the *Olii* series and the 81st work catalogued in this series, and so on for the other paintings analysed.

creations, some works belonging to the abovementioned series have revealed discrepancies in terms of both the physical-mechanical behaviour of the pictorial film and in terms of alterations resulting from degradation processes. A short description of the six works of art and the observations about their state of conservation before the restoration treatments are listed in Table 1. These anomalies could have been interpreted as the results of ageing, humidity, heat, radiation or previous restoration processes, but with the aim of better understanding their conservation conditions and ageing behavior, it was decided to investigate the possibility that these anomalies resulted from the nature of the paint composition itself.

2. Experimental

2.1. Samples

The opportunity of investigating the aforementioned artworks by Fontana was presented when these paintings required restoration, and samples were provided thanks to the generosity of the works' owners and the Fondazione Lucio Fontana in Milan, Italy. Micro-fragments of the respective pictorial layers were taken from the back sections or lateral margins of the paintings, some of which also contained the ground layer of the canvas. These samples were found to be composed of different layers of monochromatic paints and in some cases contained glass fragments or sequins, glued by the artist on the paint.

2.2. Instrumental details

Samples were observed both in visible and UV light with an Olympus SZX16 optical microscope equipped for microphotography.

XRF was carried out using a Bruker Tracer III-V portable XRF instrument, equipped with a low power Rh-tube operating at 40 kV and 2.2 μ A and a peltier cooled Si-PIN detector.

FTIR-ATR was performed using a Perkin Elmer Spectrum 1000 FTIR combined with a Graseby Specac Golden Gate Single Reflection Diamond ATR, from 4000 to 600 cm^{-1} for 64 scans and a resolution of 4 cm^{-1} .

GC-MS analysis was performed using a Thermo Quest GC-8000 instrument with a Supelco Column equity 5, 30 m, 0.25 mm, 0.5 μ m interfaced with MS MD-800. The inlet temperature was 300 °C, the MS interface was at 270 °C. The temperature program was set from 120 °C to 300 °C with a ramp of 10 °C/min, 3 min. The MS was run in Full Scan mode (m/z 40–600), 1.9 scans/s. Solvent delay was set at 4.5 min. The transfer line was at 240 °C and the source temperature was 220 °C. Electron Ionisation energy was 70 eV. Samples were prepared using (trifluoromethylphenyl) trimethylammonium hydroxide, overnight reaction: fatty acids were transesterified into their correspondent methyl esters, while the glycerol reacted forming different (trifluoromethyl)phenyl ethers [10,11].

3. Results and discussion

Table 2 fully reports the typology of the examined samples and the analytical results obtained by XRF, FTIR-ATR and GC-MS on the six Fontana's paintings.

The *Concetto spaziale. Notte d'amore a Venezia* (60 O 81) (detail shown in Fig. 1a) was analysed as both ground and pictorial layers. The white ground layer is composed of a mixture of linseed oil and lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), with zinc oxide (ZnO), calcium carbonate (CaCO_3) and barium sulphate (BaSO_4) as whiteners and/or fillers. The presence of a lead soap was observed thanks to the FTIR absorption peak at around 1530 cm^{-1} : this was most likely due to the absorption of lead carboxylates formed as products after the reaction of the oil binder with the lead pigment

Table 2

Samples analysed and analytical results obtained by XRF, FTIR-ATR and GC-MS on the six Fontana's paintings.

Paintings	Samples	XRF results	FTIR ATR results	GC-MS results ^a	Considerations
<i>Concetto Spaziale. Notte d'amore a Venezia</i> (60 O 81)	White ground layer	S, Ba, Ca, Zn, Pb	Drying oil Carbonates Calcium sulphate Lead carboxylates	Saturated monocarboxylic (lauric, myristic, palmitic, stearic) and dicarboxylic (suberic, azelaic, sebacic) acids; unsaturated (oleic) acids; glycerol P/S = 1.4 A/P = 5.6 Alizarin	The ground layer is composed of a mixture of linseed oil and lead white (2PbCO ₃ *Pb(OH) ₂) with zinc oxide (ZnO), calcium carbonate (CaCO ₃) and barium sulphate (BaSO ₄) as whiteners/fillers. It shows the presence of lead soaps
	Red-brown paint	Traces of S, Ba, Ca, Zn (probably contamination from the ground layer)	Oil-based paint Organic red dyestuff (1,2-dihydroxyanthraquinone, also known as alizarin, Mordant Red 11 or Turkey Red)	Saturated monocarboxylic (palmitic, stearic, arachidic, behenic) and dicarboxylic (suberic, azelaic, sebacic) acids; unsaturated (oleic, linoleic) acids; glycerol; ricinoleic acid P/S = 1 A/P = 3.2	The red-brown layer is composed of a modified linseed oil paint with the addition of ricinoleic acid, mixed with alizarin
<i>Concetto Spaziale</i> (62 O 66)	Pink paint	Zn	Oil-based paint Zinc carboxylates Organic red dyestuff Calcium carbonate	Antinolo Red B also known as Thioindigo Red B ((2Z)-2-(3-oxo-1-benzothiophen-2-ylidene)-1-benzothiophen-3-one) Saturated monocarboxylic (lauric, myristic, palmitic, stearic) and dicarboxylic (suberic, azelaic, sebacic) acids; unsaturated (oleic) acids; glycerol; special unsaturated fatty acids (erucic and gondoic and their oxidation products 13,14-dihydroxydocosanoic and 11,12-dihydroxyeicosanoic acids) P/S = 3.5 A/P = 1.6	The pink coloration is given by an organic red dyestuff (Antinolo Red B) whitened with zinc oxide (ZnO). Calcium carbonate (CaCO ₃) was added as filler/extender. Zinc soaps were detected The paint is an oil-based paint containing rapeseed oil
<i>Concetto Spaziale</i> (1737/92)	Pink paint	As for <i>Concetto Spaziale</i> (62 O 66)	As for <i>Concetto Spaziale</i> (62 O 66)	As for <i>Concetto Spaziale</i> (62 O 66) but P/S = 3.4 A/P = 1.8	
<i>Concetto Spaziale. Fine di Dio</i> (63 FD 14)	Pink paint	As for <i>Concetto Spaziale</i> (62 O 66)	As for <i>Concetto Spaziale</i> (62 O 66)	As for <i>Concetto Spaziale</i> (62 O 66) but P/S = 3.4 A/P = 1.7	
<i>Concetto Spaziale. Fine di Dio</i> (63 FD 23)	Black paint	Ca, P, Fe, Pb, Zn	Drying oil Prussian blue/black silicates	Saturated monocarboxylic (lauric, myristic, palmitic, stearic) and dicarboxylic (suberic, azelaic, sebacic) acids; unsaturated (oleic) acid; glycerol P/S = 1.3 A/P = 3.1	The black coloration is due to the presence of pigments such as bone black or ivory black (Ca ₃ (PO ₄) ₂) and Prussian blue (Fe ₄ (Fe(CN) ₃) ₃). The presence of quartz and silicates is linked to the use of sequins, which were applied on the painted surface using a poly-vinyl-acetate-based glue The paint medium is a drying oil (linseed oil?)
	Adhesive for sequins	–	Poly-vinyl-acetate (PVAc)	–	
<i>Concetto spaziale. Fine di Dio</i> (64 FD 5)	Yellow paint	K, Cr, Zn	Drying oil Zinc carboxylates Calcium carbonate	Saturated monocarboxylic (lauric, myristic, palmitic, stearic) and dicarboxylic (suberic, azelaic, sebacic) acids; unsaturated (oleic) acids; glycerol; special unsaturated fatty acids (erucic and gondoic and their oxidation products 13,14-dihydroxydocosanoic and 11,12-dihydroxyeicosanoic acids) P/S = 1.7 A/P = 1	The painted layers are composed of zinc yellow (ZnCrO ₄ + K ₂ CrO ₄) and an oil-based paint containing rapeseed oil probably mixed with linseed oil Calcium carbonate (CaCO ₃) was added as filler/extender. Zinc soaps were detected

P/S: palmitic to stearic acid ratio (suggesting the kind of oil); A/P: azelaic to palmitic acid ratio (indicating the degree of oxidation/polymerization of an oil).

^a Fatty acid are intended as their correspondent methyl esters, while glycerol reacted forming (trifluoromethyl)phenyl ethers.

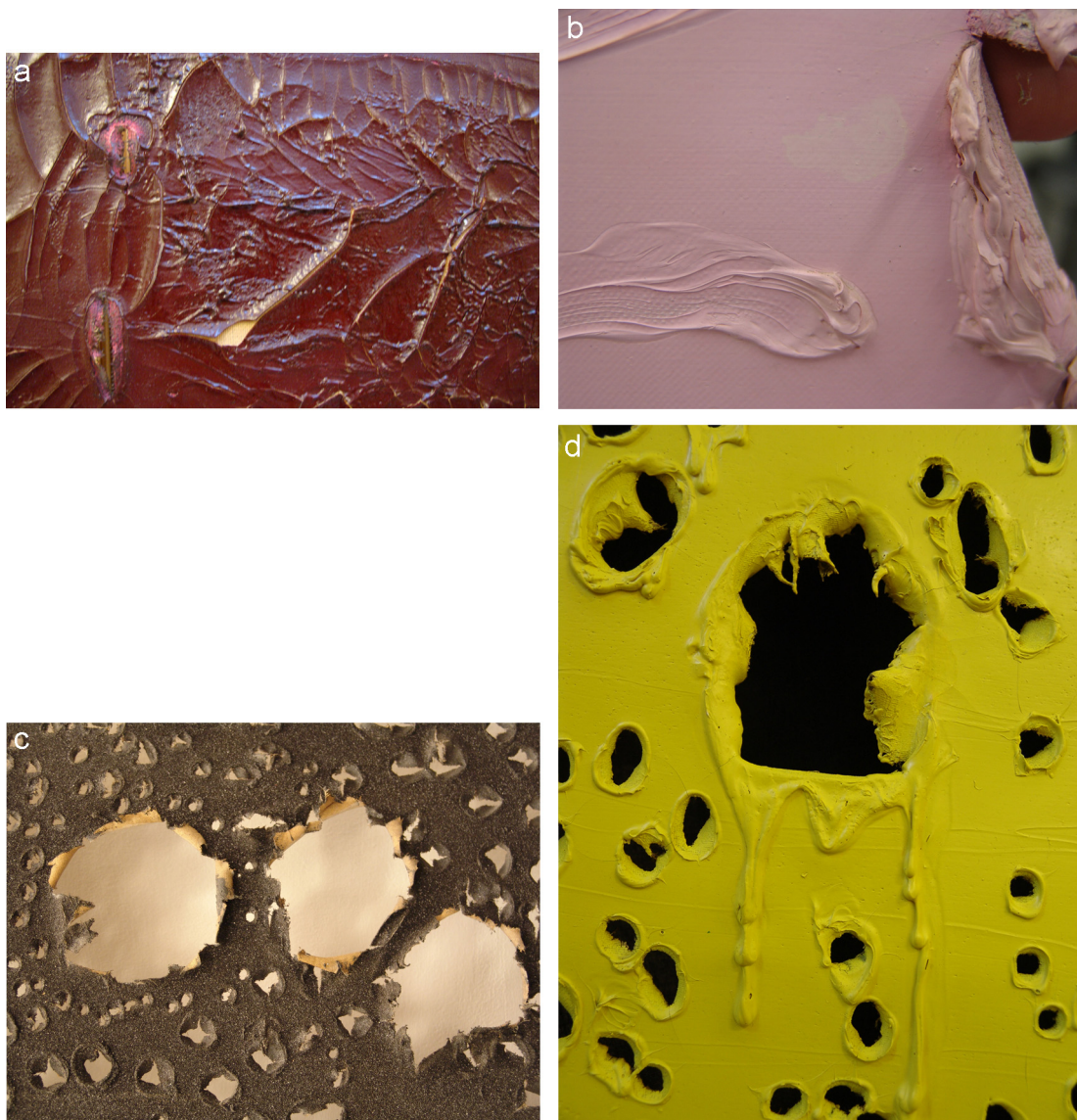


Fig. 1. Details of Lucio Fontana's paintings showing the degradation phenomena and the peculiarity of the artist's technique: a: *Concetto spaziale-Notte d'amore a Venezia* (60 O 81); detail of the widespread craquelure and paint losses; b: *Concetto spaziale* (62 O 66); detail of the whitish spot on the painted surface; c: *Concetto spaziale-La Fine di Dio* (63 FD 23); detail of the deformation of the edges of the slashes; d: *Concetto spaziale-La Fine di Dio* (64 FD 5); detail of the cuts and slashes on the painted canvas.

[12–14]. The coloration of the red-brown paint is attributable to the presence of alizarin, an organic red dyestuff mainly composed of 1,2-dihydroxyanthraquinone [15], while the medium was identified as an oil. In addition to the usual saturated and unsaturated fatty acids, the presence of ricinoleic acid, formally called 12-hydroxy-9-cis-octadecenoic, was detected by GC-MS analysis (Fig. 2a). This monounsaturated fatty acid is the main constituent (up to 95%) of castor oil, which is a non-drying oil obtained from castor seeds. It is likely that the red paint in this painting contained modified linseed oil, that is linseed oil with the addition of castor oil, as suggested also by the fact that after 50 years, the painting does not appear to have dried completely. The presence of this oil binder may explain some of the signs of degradation evident in the pictorial layers (both hard fractured and sticky areas), and the wrinkles that have formed on the surface might be linked to this use of castor oil in the thick, bodied pictorial layer. Over time, the evaporation of volatile compounds (such as alcohols, aldehydes and ketones) from the oxidative cross-linking reactions occurred, leading to weight losses [16]. As the drying speed is slowed by the

presence of a non-drying oil, it is possible that the evaporation rate also occurred slowly, causing the formation of more visible, deeper wrinkles [17].

Then three 'pink' *Concetto spaziale* (a detail of the painting labelled 62 O 66 is depicted in Fig. 1b) were studied, since they demonstrated similarities regarding the degradation phenomena (see Table 1) and the formulation of the paints, the results are hereinafter treated together. The pink colour was found to be the result of a mixture of an organic red dyestuff (likely Antinolo Red B also known as Thioindigo Red) with zinc white (ZnO) as whitener. The binding media were identified as drying oils; moreover, all the FTIR-ATR spectra reported a clear, broad carboxylate absorption around $1570\text{--}1540\text{ cm}^{-1}$ (see the spectrum depicted in Fig. 3a). These peaks are possibly the result of the influence of zinc white in the drying and ageing of the oil as they could refer to the formation of metal carboxylates (soaps) with the carboxylic acids present [12,18]. Metal soaps can be formed after hydrolysis of the fatty acid molecules in the triglycerides of drying oils with metal-based pigments; however, the presence of added stearates as dispersion

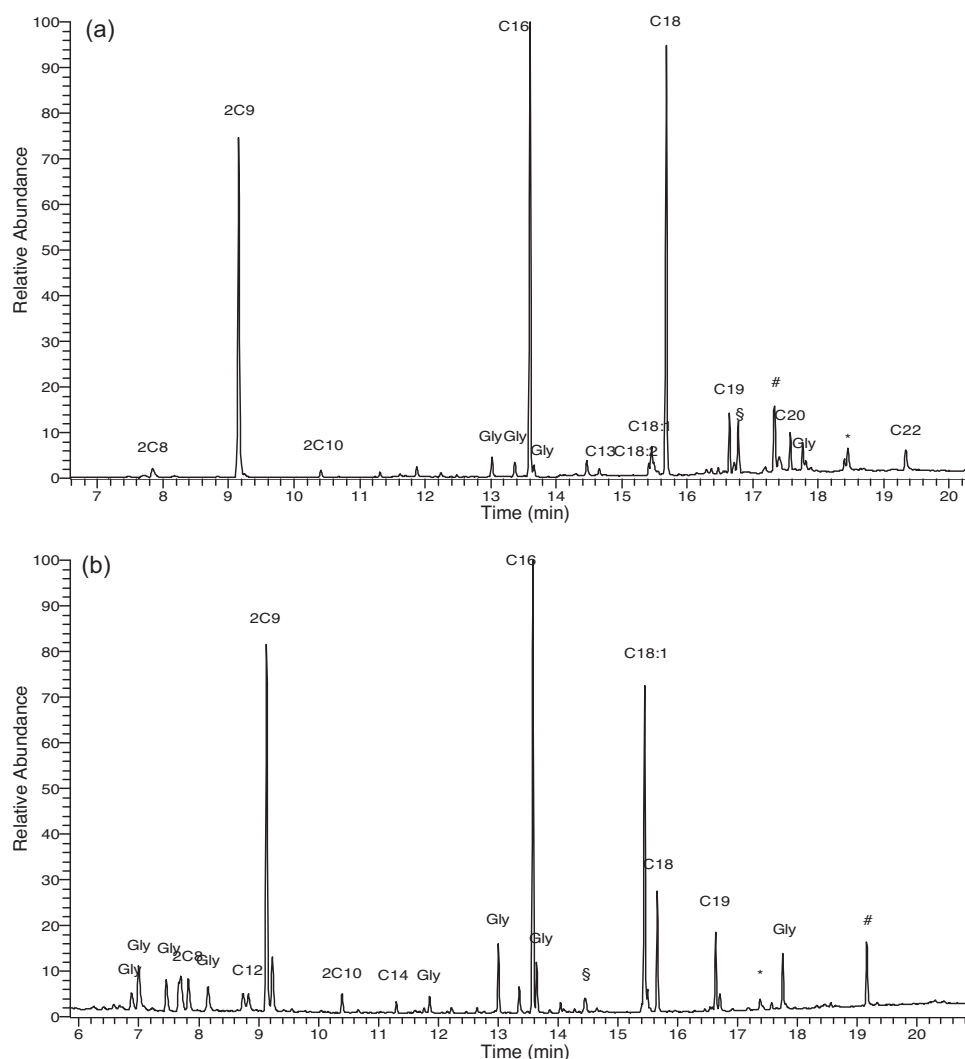


Fig. 2. Total ion current chromatograms of a red sample from *Concetto spaziale. Notte d'amore a Venezia* (a) and a pink paint sample from *Concetto spaziale–Fine di Dio* (63 FD 14) (b): a: TIC of red sample from *Concetto spaziale. Notte d'amore a Venezia*, after transesterification and GC-MS analysis (Gly = glycerol, 2C8 = suberic acid, 2C9 = azelaic acid, 2C10 = sebatic acid, C16 = palmitic acid, C18:1 = oleic acid, C18 = stearic acid, C19 = nonadecanoic acid, internal standard, C20 = arachidic acid, C22 = behenic acid, # = ricinoleic acid, § = ricinoleic acid, methoxy, * = 9,10-dihydroxy octadecanoic acid); b: TIC of pink paint from *Concetto spaziale–Fine di Dio* (63 FD 14), after transesterification and GC-MS analysis (Gly = glycerol, 2C8 = suberic acid, C12 = lauric acid, 2C9 = azelaic acid, 2C10 = sebatic acid, C14 = myristic acid, C16 = palmitic acid, C18:1 = oleic acid, C18 = stearic acid, C19 = nonadecanoic acid, internal standard, * = gondoic acid, # = erucic acid).

agents in the paint formulation [19,20] cannot be excluded. A minor addition of calcium carbonate as a filler or extender is suggested by carbonatic absorption peaks at 1413 and 873 cm^{-1} . Amongst the characteristic drying oil compounds, two uncommon fatty acids were detected by GC-MS analysis (Fig. 2b): erucic (13-docosenoic) and gondoic (11-eicosenoic) acids and their oxidation products (13,14-dihydroxydocosanoic acid and 11,12-dihydroxyeicosanoic acid respectively). These unsaturated fatty acids are considered to be bio-markers as they are present only in oils obtained from the seeds of *Brassicaceae*, such as rapeseed oil [21]. Moreover, the P/S ratios for the pink works are around 3.6 and may refer to the use of rapeseed oil (whose P/S is around 3.5–3.8) as binding media. This is a semi-drying oil which was introduced in the 20th century according to modern artists' handbooks [4,5]. The high content of oleic acid and the consequentially high degree of unsaturation is most likely to be a consequence of the presence of a slow-drying oil, but this phenomena could also be explained in another way – in fact, the significant amounts of oleic acid may be linked to the presence of zinc oxide, which have also been noted in other artworks. It would thus appear that in an oil-based medium, zinc oxide forms a packed structure which is able to trap oleic acid in

the pictorial layer: this effect can also occur years after the oxidation process ends [22–24]. The unusual degradation phenomena observed in all of these paintings might be the result of the presence of a slow-drying oil (rapeseed oil) containing a large amount of unsaturated acids (oleic, erucic and gondoic were detected after almost 50 years) whose triglycerides reacted with zinc white from the painted layers to form metal soaps. As FTIR analyses suggest, metal soaps are present in the form of zinc carboxylates, and hence it is probable that zinc soaps are present as formed and/or added soaps (as dispersion agents) and that they migrated and conglomerated on the surface, forming the light yellow spots.

Although it did not show any evident degradation phenomena on the surface (Fig. 1d), similar results were found for the artwork named *Concetto spaziale. Fine di Dio*, (64 FD 5). The yellow coloration is due to the use of zinc yellow ($\text{ZnCrO}_4 + \text{K}_2\text{CrO}_4$) (see XRF reported in Fig. 4), while the medium is an oil. GC-MS results are comparable with the pink series: besides the presence of common fatty acids, the yellow paint exhibits high amounts of unsaturated oleic, gondoic and erucic acids. The presence of rapeseed oil is also suggested in this case, although the P/S ratio is

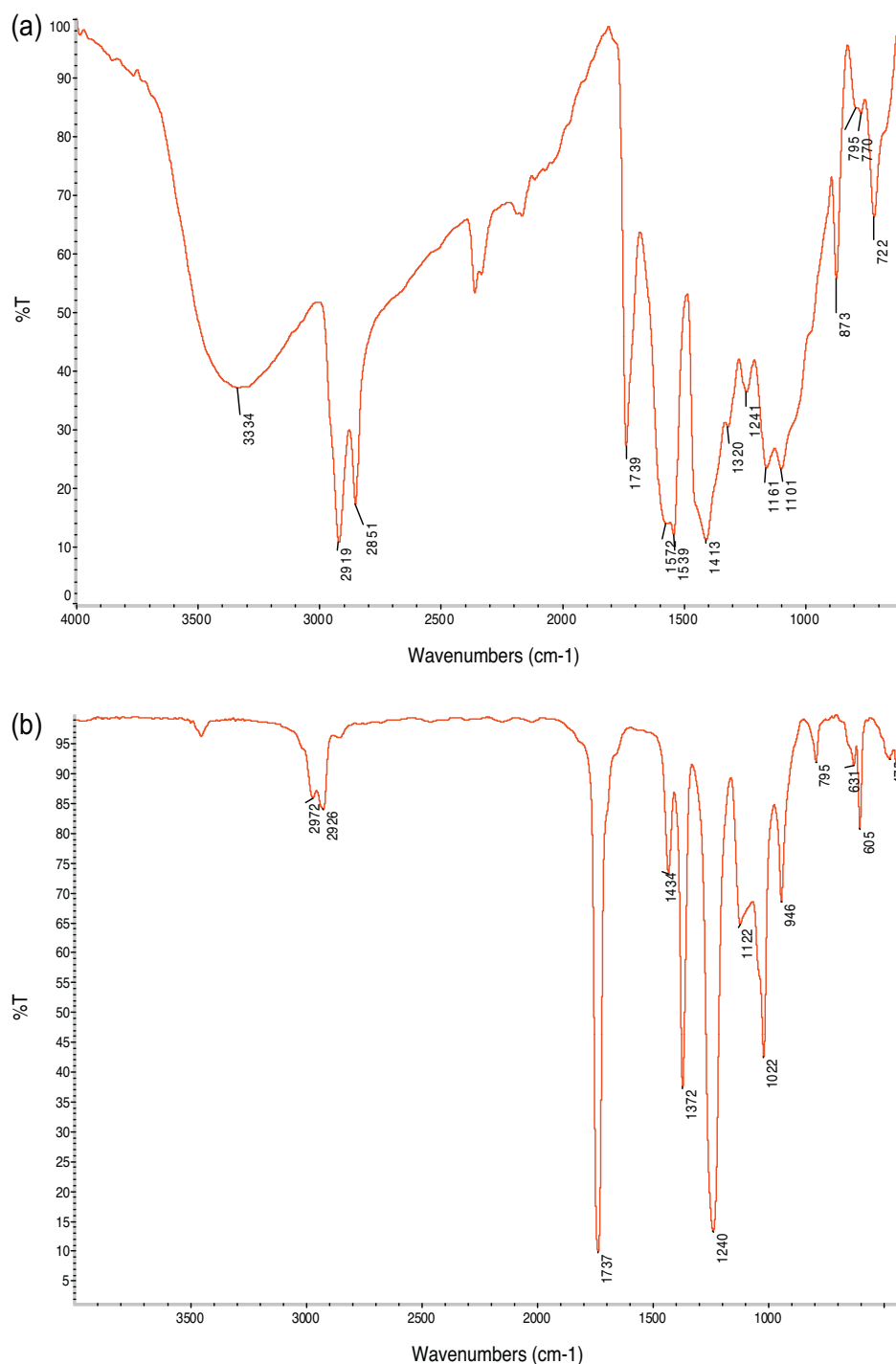


Fig. 3. FTIR-ATR spectra of the pink paint in *Concetto spaziale-La Fine di Dio*, (63 FD 14) (a) and of the adhesive used to glue sequins in *Concetto spaziale-La Fine di Dio*, (63 FD 23) (b); a: FTIR-ATR spectrum of the pink paint in *Concetto spaziale-La Fine di Dio*, (63 FD 14); b: FTIR-ATR spectrum of the adhesive used to glue sequins in *Concetto spaziale-La Fine di Dio*, (63 FD 23).

1,7- this value suggests the mixture with other oil media (such as the traditional linseed oil). As observed in the pink *Olii*, the abundant oleic acid content might be related to the action of zinc pigments and the broad FTIR peak at 1574 cm^{-1} can be explained by the presence of zinc soaps, formed and/or added in the paint formulation.

The last analysed painting is a black *Concetto spaziale-Fine di Dio* (63 FD 23) (Fig. 1c), whose coloration is due to the presence of pigments such as bone black or ivory black ($\text{Ca}_3(\text{PO}_4)_2$) and Prussian blue ($\text{Fe}_4(\text{Fe}(\text{CN}_6)_3$). From samples taken from the pictorial layer

(including areas in which the sequins were present), it was ascertained that it was an oil-based paint. The high degree of unsaturation associated with the high content of oleic acid suggests that the paint, even 50 years after its application to the canvas, is still immature or that a non-drying oil was added to the paint. The P/S ratio is 1.3, value which is conventionally referred to linseed oil [25]; nevertheless, the use of this traditional binder is rather improbable, due to the different behavior shown by the pictorial layer under examination. It is likely that other lipidic binders, exhibiting similar P/S ratio, were employed [4,5,11,21]. In this sample, the

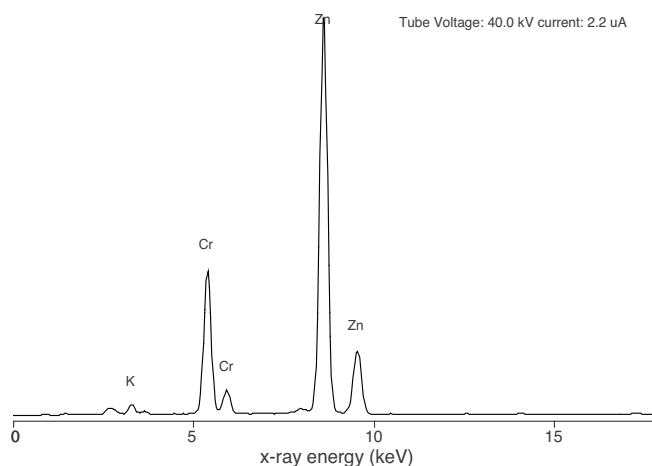


Fig. 4. XRF spectrum of a yellow paint sample from *Concetto spaziale-La Fine di Dio* (64 FD 5).

sequins appeared not only to be embedded in the pictorial film, but in some places were also embedded in a superficial layer of polyvinyl acetate (PVA)-based adhesive (most likely to be Vinavil[®], produced by the Italian company Montecatini) (Fig. 3b). This glue could have played a role in the creation of tensions and the deformation of the pictorial layers, however there is also the possibility that this alteration could be caused by the extreme thinness of the pictorial film.

4. Conclusions

The results obtained by this study have provided us with important information regarding the works of the *Olii* series created by Lucio Fontana between 1960 and 1964. During the same period, the artist experimented with several different and innovative pictorial binders, but still tended towards more traditional binding materials. Fontana himself was known to be an experimental artist and he used to mix house paints with manufactured oil paints [7–9]. Nevertheless, as we have proven, Fontana used oil paints containing different lipidic binders: a non-drying oil such as castor oil, a semi-drying oil such as rapeseed oil and the traditional drying binder, linseed oil. It is not clear if Fontana wished to experiment with different kinds of oils in order to achieve different effects or if he simply used readymade paints without knowing their composition, however, the materials and the techniques that he used are now proven to be closely linked to the conservation problems exhibited by the pictorial layers and observed during conservation treatments. Furthermore, these analyses gave unexpected, but useful results which not only provided us with new insight into the nature of the constituent materials, but also facilitated the identification of suitable conservation methods.

From an analytical point of view, this study has reinforced previously stated conclusions that maintain that modern and contemporary artists used and still use varying forms of this traditional medium – which are often generically labelled as ‘oils’ – without any specific regard to their binding properties. The uninformed use of these oils demands that each case study be analysed separately in order to develop suitable treatment methods for each and every work and avoid detrimental generalisations.

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