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Elucidating the composition and the state of conservation of nitrocellulose-based animation cells by means of non-invasive and micro-destructive techniques

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ABSTRACT

This paper presents the first study on *Rodovetri*, animation cels produced between the 1950s and the 1970s for the Italian television and conserved at the Museum of Industry and Labour "Musil" (Italy). Although these cels are considered as works of art and witnesses of Italian animation design, they have never been studied before. The study of one of the most endangered cel groups of the Musil collection is presented here. The main aims were to investigate the composition of these animation cels, to identify the materials used for painting the characters, and to assess the state of conservation of the cels. The results, which were obtained by means of a multi-analytical non-invasive and micro-destructive approach, underline the composition of the plastic substrate as nitrocellulose, while the painted layers – which contain a variety of pigments and dyes – were found to be bound with a mixture of plant gum and animal glue. This study also provides information on their state of conservation, in particular in relation to the de-nitration of plastic sheets. Important issues on the preventive conservation are also raised.

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1. Introduction

This research focuses on the study of *Rodovetri*, animation cels produced for *Carosello*, which was the most important advertising space shown on Italian television from 1957 to 1977.

These animation drawings were created by Gamma Film and Cinestabilimento Fratelli Donato, two important studios for film production and animation, active in Milan ever since the late 1930s and up to the 1980s. In particular, Gamma film, founded by the Gavioli Brothers, was a significant growth point for many young Italian designers and talents, such as Paolo Piffarerio, Adelchi Galoni, Carlo Peroni, and screenwriters, such as Cesare Zavattini.

The Gavioli Brothers conserved and stored all the animation cells produced by Gamma film and, later on, entrusted the Micheletti

Foundation and the "Musil" Museum of Industry and Labour, located in Brescia (Italy), for their storage and conservation. More than 700,000 animation cels are now conserved in the Musil Collection [1].

The *Rodovetri* are transparent plastic sheets on which the animator painted the single frame of the animated sequence of a cartoon. Generally, the inkers transferred the lines of the drawing on the verso of the cel, and then the painters painted on the recto. The transparent surface made it possible to create characters that could be animated by applying multiple overlapping layers. The cels were then photographed on the motion picture film: each cel corresponded to a "position" of the animation of the character, and 12 frames were needed for each second of animation in order to recreate the illusion of movement.

After their use (which ended with the photograph), their archiving and their conservation over time was never considered as a crucial point: the cels were stacked one on top of the other,

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Fig. 1. a: a cel with the animation of Little Red Riding Hood; b: a cel with the animation of The Big Bad Wolf; c: superimposed cels in the cardboard box; d: detail of degradation of the cel.

sometimes interspersed with sheets of acid paper, and were usually placed in cardboard boxes.

The absolute importance of these cels, which represent a very interesting cross-section of the Italian art of animation (recognised as such, in fact, by Walt Disney himself) and of the “Made in Italy” advertising, is undeniable: they are indeed small works of art. Nevertheless, to the best of the authors’ knowledge, these Italian animation cels have never been analysed before from the point of view of their constitutive materials. In fact, no documentation is available on the type of plastic substrate employed, nor on the materials used to paint the animation characters.

Worldwide, in fact, the study and conservation of animation cels have not yet received appropriate attention up to now, with the exception of a few research projects carried out on American and German animation cels by The Getty Conservation Institute (GCI) and the German Institute for Animated Film (Deutsches Institut für Animationsfilm, DIAF).

In 2009 GCI, in collaboration with the Disney Animation Research Library, started a research project aimed at studying Disney animation cels dating from 1929 to 2000. The multi-analytical research pointed out that these animation cels were generally created on nitrocellulose or cellulose acetate supports [2,3]. In particular, it was found that cellulose nitrate was used until 1942, while the use of acetate supports began as early as 1929 [4]. As concerns the painted layers, plant gum binding media were identified in some paints. An extensive condition survey was also performed, and reported on the damages made by the plastic substrate and the paint layers [5,6].

The animation cells from the film “Plaste Color” (1968), which is conserved on DIAF premises, were found to be drawn on cellulose acetate sheets and the characters, painted with a mixture of alkyd resin and polyvinyl acetate. These cels, which are among the most endangered of the collection, exhibited deformations in the acetates and problems in the paint adhesion [7].

The present paper, which is contextualised in the research on animation cels, is aimed at defining the materials used for

making the Rodovetri and their conservation status. At the same time, this study is intended to evaluate the effectiveness of some non-invasive spectroscopic techniques, implemented by portable devices, on such materials. Indeed, some of these techniques, such as Fibre Optic Reflectance Spectroscopy (FTIR) and Total Reflectance FT-IR, have not been used previously for analysing animated cels. The data obtained on the Rodovetri will complement and extend the results reached by the GCI and DIAF on similar materials.

1.1. The case study and the conservation issues

From the numerous animation cels conserved at the Musil, the sequence entitled “Cappuccetto Rosso” (*Little Red Riding Hood*), which dates back to post-World War II, exhibited the most problematic situation.

The series consists of dozens of cels representing a modern version of the famous fairy tale, in which the young girl is depicted riding an animated scooter (Fig. 1a), which enables her to escape from the scatter-brained wolf that is running after her (Fig. 1b). This group of cels presents different types of degradation and alterations. The plastic sheets, which are kept inside plasticized cardboard boxes, appeared to be damp and emitted acidic vapours. They had a very yellowed appearance, and were stiff and glued together, sometimes in groups of ten. Besides evident deformations due to shrinkage and expansion, fragments of the sheets were present on the adjacent cel: all things considered, they looked very fragile and very degraded (Figs. 1c–d). For some groups of sheets, self-combustion was evident: this was the cause of the blackening and the crumbling of the layers adhering to each other, and led to the complete loss of the pieces. These groups were immediately separated from cels in better conditions, so as to avoid the interaction of acids and the consequent chemical reactions that could further compromise their conservation.

The shrinkage of the sheets had caused accentuated and sometimes local deformations, and these did prevent both a suitable

positioning of the detached fragments and a correct reading of the image.

In addition to grazing, crosslinking, warping and weeping, the formation of blooming was detected on both the support and the pictorial film. These rigid, crystalline and dried efflorescences lead to alterations in the stability of the coloured areas. In some parts, due to the total loss of the sheet, the pictorial film was “free floating”.

These observations as to appearance and transparency, together with the acidic odour and the observed deterioration, tended to the assumption that these cels were made on nitrocellulose sheets.

Nitrocellulose, or cellulose nitrate (CN), was the first semi-synthetic plastic. It was initially produced by Alexander Parker in 1862 by nitrating cellulose with a mixture of nitric acid and sulphuric acid [8]. It is a very versatile polymer that is used in numerous applications [9], and for this reason are often present in museum artefacts, modern and contemporary art and design objects [10,11]. Celluloid, i.e. CN with camphor as a plasticizer, was used for the production of movie films [12,13] and transparent sheets for animations [4,5]. This material proved to be rather unstable because it is sensitive to light, heat and humidity [14–17]. It has a tendency to turn yellow and to wrinkle over time, and generates hazardous gases while ageing [18].

Fig. 1

1.2. Aims of the research

This is the first time that a scientific research project has been performed on Italian animation cels. All pieces of information obtained from a direct observation of the evidence of significant deterioration and the knowledge of the materials used provided important data on Rodovetri.

The research was aimed at:

- investigating the composition of the plastic substrate of the selected animation cels;
- defining the state of conservation and the degradation phenomena that occurred;
- identifying binders, pigments, dyes and fillers used to paint the animation characters.

A multi-analytical approach was performed, using both non-invasive and micro-destructive techniques. Information was gathered by means of direct analysis of the Rodovetri and of detached samples from the cels and the painted areas.

Special focus on preventive conservation strategies for Rodovetri and recommendations to the MUSIL for optimal storage and conservation treatments were given that were based on the above-mentioned observations and by considering the potential sensitivity of cellulose nitrate to heat, light and humidity.

2. Materials and methods

2.1. Optical microscopy

The samples were observed both in visible and UV light, using an Olympus SZX16 optical microscope equipped for microphotography.

2.2. FORS – fibre optic reflectance spectroscopy

This spectroscopic technique was applied mainly for the identification of both pigments and dyes, and in recent years has also been applied to analyses of contemporary artworks [19–22]. An analysis of absorption bands in the UV-Vis-NIR range can

provide important data for the identification of pigments/dyes present in the Rodovetri analysed. The device consists of two Zeiss spectro-analysers mounted on a single chassis, models MCS601 UV-NIR and MCS611 NIR 2.2 WR. They have an acquisition step of 0.8 nm/pixel with a linear detector of 1024 silicon photodiodes and of 0.6 nm/pixel, with a linear detector of 256 Indium Gallium Arsenide (InGaAs) photodiodes, respectively. Measurements were acquired in the 350–2200 nm range. The light source was a tungsten lamp (model CLH600), with a colour temperature of about 3000 K and an emission interval of between 320 and 2500 nm. An optical-fibre-fused anhydrous quartz band was used to send and receive electromagnetic radiation from the analysed area. The data acquired were processed using Aspect Plus software.

2.3. Raman Spectroscopy

This technique is well known as an important tool in the study of pigments, dyes and fillers in classic and modern paintings. Its use, in combination with FORS and TR-FT-IR, led to the certain identification of materials present in the painted areas of the Rodovetri. A BWTEK Raman spectrometer equipped with a 785 nm laser and operating in the 80–3200 cm^{-1} spectral range was used. Spectra were acquired with a resolution of 3 cm^{-1} by employing an intensity of the Raman signal in the 3.5–35 mW range with a measuring time of four frames of 60 seconds each. Dark measurement was subtracted from each measurement. The measuring head was connected to the laser and to the spectrometer by means of two fibres, and was internally equipped with a notch filter to allow for collinear laser and spectrum collection. A 5 mm NIR lens focused the radiation on the sample, thus resulting in a 150-micron beam spot.

2.4. FT-IR spectroscopy

This technique was used to identify the polymeric materials of the cels, pigments, dyes and fillers in painted areas.

2.4.1. FT-IR – ATR

FT-IR-ATR analyses were performed on detached samples by using a Thermo Nicolet Nexus 670 FT-IR spectrophotometer combined with a Smart Orbit Single Reflection Diamond ATR accessory, which operated from 4000 to 400 cm^{-1} for 64 scans with a 4 cm^{-1} resolution. Spectra were elaborated with the use of Omnic 9.0 and Origin 9.0 software.

2.4.2. Total Reflectance (TR) FT-IR

This non-invasive technique was applied directly on the studied cels. A portable Bruker Optics Inc. model FT-IR ALPHA spectrometer with a total-reflectance module was used. Spectra were acquired in the 7500–375 cm^{-1} range with a 4 cm^{-1} resolution and 256 scans for each spectrum. The probe head was positioned at a distance of 1.5 cm from the investigated surface. EZ OMNIC 7.3 and OPUS 7.0 software were used for processing the data.

2.5. Pyrolysis GCMS analysis of polymers

A Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Focus GC / ISQ mass spectrometer combination was used to identify the polymeric material of the cels and the additives. Separation took place on a Supelco SLB5 MS column (20 m, 0.18 mm, 0.18 μm). Helium with a constant flow of 0.9 mL/min was used as a carrier. The temperature program used was: 35 °C (1 min)–16 °C/min–220 °C–10 °C/min–315 °C (2 min). The temperature of the interface was 250 °C, while that of the ion source was 220 °C. Mass spectra were recorded from 20 amu up to 600 amu with a speed of 5 scans/sec. Xcalibur 2.1 software was used for processing the mass spectral data.

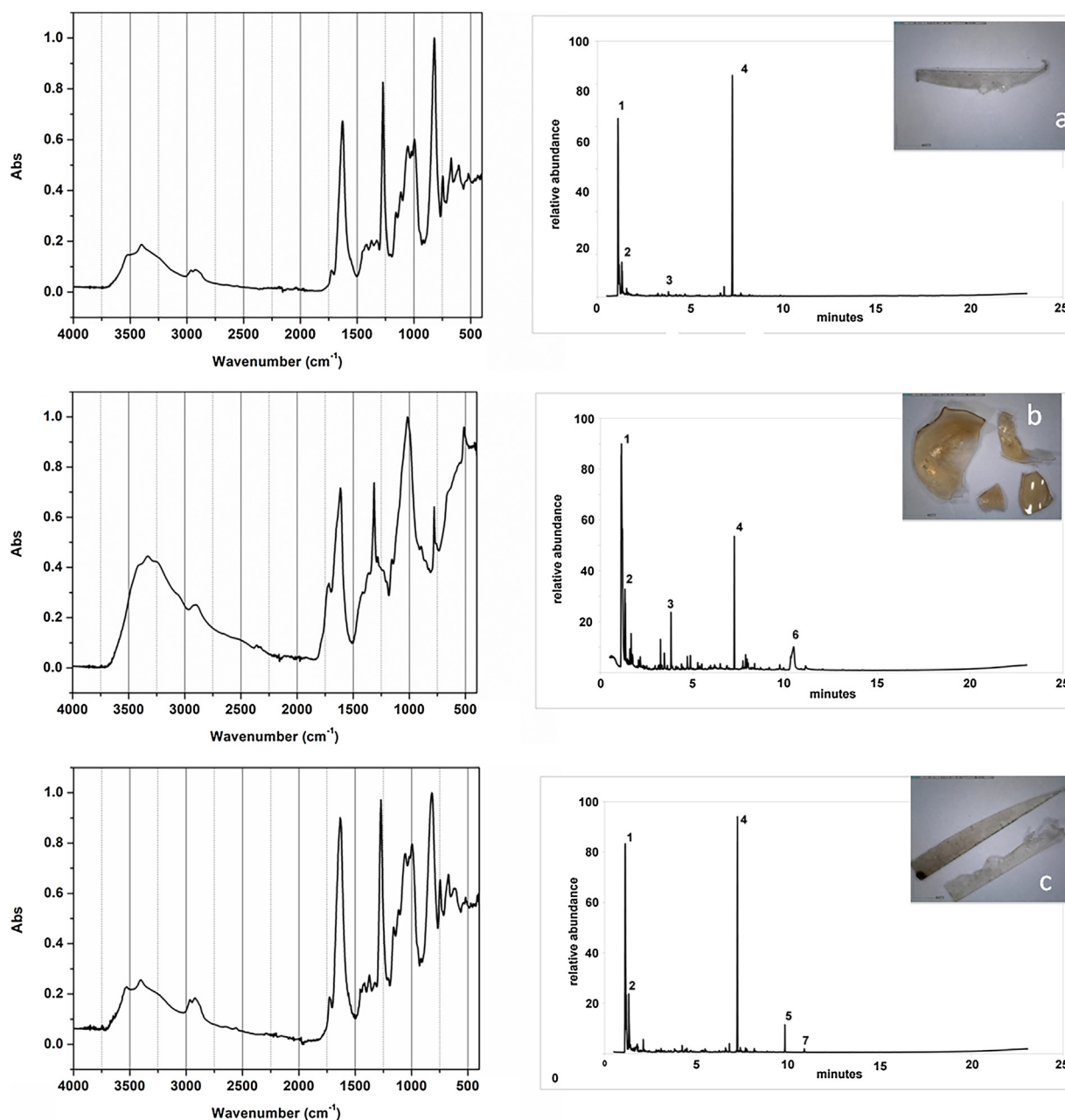


Fig. 2. FT-IR-ATR spectra (left) and TIC chromatograms (right) of a: greyish and opaque plastic sample; b: yellowed plastic sample; c: greyish and opaque plastic sample with exudates.

Samples obtained from the cels were placed in steel pyrolysis cups. The cups were then transferred into the pyrolyser, and the sample material was pyrolysed at 600 °C.

2.6. Thermally-assisted Hydrolysis and Methylation-(py)-GCMS analysis of paint samples

The composition of the binder of the painted layers was analysed using Thermally-Assisted Hydrolysis and Methylation, pyrolysis Gas Chromatography-Mass Spectrometry (THM-py-GCMS) [23–24].

The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Focus GC / ISQ mass spectrometer combination. Separation took place on a Supelco SLB5 MS column (20 m, 0.18 mm, 0.18 μm). Helium was used as the carrier

with a constant flow of 0.9 mL/min. The temperature program used was: 35 °C (1 min)–60 °C/min–110 °C – 14 °C/min–240 °C–5 °C/min – 315 °C (2 min). The temperature of the interface was 250 °C, while that of the ion source was 220 °C. Mass spectra were recorded from 20 up to 600 amu with a speed of 7 scans/sec. Xcalibur 2.1 software was used for collecting and processing the mass spectral data.

Sample material was made into a suspension with a few drops of a 5% solution of tetra methyl ammonium hydroxide (TMAH) in methanol, and the solvent/suspension was then transferred to a pyrolysis cup. The sample was pyrolysed using a high-speed temperature range starting at 360 °C, raised to 700 °C with a rate of 500 °C/min, with a final time of 0.3 minute.

Interpretation of the GCMS results was made using the ESCAPE system, an expert system for characterizing py-GCMS data using AMDIS & Excel [25].

Table 1
Major pyrolysis products after Py-GCMS of detached samples from the plastic substrate (Fig. 2).

Label	Identified compound	Retention time (min)
1	Nitrous oxide (N ₂ O) and carbon dioxide (CO ₂)	1.12
2	Acrolein	1.31
3	Furfural	3.81
4	Camphor	7.25
5	Dimethyl phthalate	9.84
6	Levoglucosan	10.45
7	Diethyl Phthalate	10.90

3. Results and discussion

3.1. Plastic substrate

FT-IR-ATR and Py-GCMS enabled identification of the composition of the animation cels and the presence of degradation products. Fig. 2 shows the IR spectra and the pyrograms obtained from detached samples of the plastic substrate, coming from three different cels and having a different appearance: (a) a greyish and opaque plastic sample, (b) a yellowed and brittle plastic specimen, and (c) a greyish and opaque sample similar to (a) but with a surface that is rich in exudates.

For the three samples, the characteristic IR absorption features of a cellulose-based polymer are visible in the broad band centred at 3400 cm⁻¹ (linked to the stretching of OH bound) and in the strong bands in the 1150–1000 cm⁻¹ range (due to the C–O stretching vibrations). The typical features for cellulose nitrate (CN) are also present, and consist of sharp absorption bands at 1650 and 1281 cm⁻¹ which are associated with the asymmetric and symmetric stretching of NO₂, respectively. Moreover, NO stretching (840 cm⁻¹), O–NO₂ asymmetric and symmetric deformations (750 and 690 cm⁻¹, respectively) were observed [14,17].

Py-GCMS results corroborated the IR findings. In fact, the CN typical main products, formed upon pyrolysis, were detected in all the samples, as depicted in the total ion chromatograms (TIC) of Fig. 2: nitrous oxide (N₂O) and carbon dioxide (CO₂), acrolein and furfural (Table 1) [26].

The presence of camphor as a plasticiser was found as a major compound in all the samples, by means of Py/GCMS analysis (peak #4, Table 1). This terpenoid substance, which has been used since the early formulation of celluloid [10,14], was also identified thanks to its characteristic IR bands at 1733, 2963 and 2874 cm⁻¹ due, in turn, to the carbonyl group and the –CH₂ stretching absorption bands, respectively.

Other plasticisers were detected only in sample (c), namely, dimethyl phthalate and diethyl phthalate (peak #5 and 6, Table 1). These additives are known to migrate to the plastic surface and to

form exudations and crystals [27]. In this case, their presence could be associated with the blooming observed in the condition survey of the Cappuccetto cels.

In the same way, camphor is known to have been slowly lost from nitrocellulose by means of evaporation, thus causing the CN to become brittle. This loss could be accelerated if the nitrocellulose decomposed, thus producing nitrous and nitric acids [28]. Indications of these degradation processes, which occurred in sample (b), are given by IR and Py/GCMS results: the loss of the plasticiser is suggested by the decrease in the camphor peak (#4) in the Py/GCMS, while the decrease in the IR intensities of the nitro groups at 1650, 1280 and 840 cm⁻¹ suggested a partial de-nitration of NC (Fig. 2 b). Nevertheless, in the IR spectra of sample (b), the absorption at 1733 cm⁻¹ (associated with camphor) was intense: some studies have suggested that this band can be also linked to the carbonyl impurities formed during ageing and degradation processes, and that the ratio 1650 cm⁻¹ can be used: 1733 cm⁻¹ to monitor the degradation of NC [12,16]. This ratio is not useful for nitrocellulose containing camphor, as is the case of the animation cels studied.

Another indication of the degradation of the CN (b) is linked to the broadening of the characteristic IR band of the cellulosic compounds in the 1150–1000 cm⁻¹ range and to the identification of levoglucosan (peak #6, Table 1). The latter is usually a minor pyrolysis compound from cellulose and starch [26,29], but an intense and broad peak is formed only in degraded de-nitrated CN.

3.2. Painted layers

3.2.1. Binding media

To assess the composition of the binding media, two paint film fragments were analysed by means of THM-py-GCMS, namely a blue paint fragment from the Wolf's pants and a brownish-orange sample from the Wolf's tail.

The binder of blue paint was characterised as a mixture of about 60 parts plant gum and 40 parts animal glue. Glycerol was identified, together with a minor amount of pine resin.

Similarly, the binding media of the other sample were identified as a mixture of 75:20 animal glue and plant gum; some glycerol and camphor were also present.

Except for camphor (which is the CN plasticizer, as pointed out above), the detected organic compounds may be associated with the use of a homemade paint mixture and/or a commercial tempera.

3.2.2. Pigments and dyes

All the pigments, dyes and fillers were identified using non-invasive portable spectroscopic techniques, by comparing the acquired data with reference spectra from public and proprietary databases (Table 2).

Table 2
Résumé of the results obtained by using non-invasive techniques on Cappuccetto Rosso cel.

Analysed area	Colour	FORS	TR-FT-IR	RAMAN
Red cap	red	–	PR4, barite	PR4
Yellow hair	dark yellow	Rutile, lithopone	Rutile, barite	Lead(II) chromate, rutile, barite
Face near the mouth	pink	Rutile, lithopone	Rutile, barite, PR4	PR4, rutile, barite
Pants	White	Rutile, lithopone	Rutile, barite (lithopone)	
White eyes of the motorbike	white			Rutile, barite
Motorbike	blue	Ultramarine blue, rutile	Rutile, Barite, ultramarine blue	Ultramarine blue, rutile, barite
front tire	grey	Rutile	Rutile, barite, bone black	Carbon black, rutile, barite
Motorbike	yellow	Rutile, lithopone	Rutile, barite	Lead(II) chromate, rutile, barite
Shoe sole	Dark brown	Ox/ldrox Fe	Kaolinite, barite, goethite, hematite	Hematite, barite
Shoe	Light brown	Ox/ldrox Fe		
Sock	Dark blue	Ultramarine blue, rutile		Ultramarine blue, rutile
Motorbike shadow	black		Bone black	
Motorbike eye pupil	black			carbon black
Substrate			Cellulose nitrate	

Naphthol red (2-Naphthalenol, 1-[(2-chloro-4-nitrophenyl) azo] PR4) dye was found in the red and pink areas. Its identification was achieved by comparing the FT-IR spectra, after being processed with the Kramers–Kroenig correction, with the IOD00228 spectrum in the Infrared and Raman users group (IRUG) 2007 spectral database [30,31] (Fig. 3). This result was also confirmed, using Raman spectra, by the presence of the peaks at 1337 and 1587 cm^{-1} [32]. In addition, in the FT-IR and Raman spectra acquired on the red areas the filler material barite (barium sulphate, BaSO_4) was detected by the absorption bands at 1185, 1120, 1080 cm^{-1} (SO_4^{2-} asymmetric stretching), 635 and 612 cm^{-1} (SO_4^{2-} out of plane and in plane bending) in IR, and at 988 cm^{-1} (symmetric stretching) in Raman spectrum [33,34].

In the case of pink areas, rutile (titanium white, TiO_2) and lithopone, a composite pigment consisting of zinc sulphide (ZnS) and barium sulphate, were mixed with the PR4 dye to obtain the desired shade (Fig. 4). The semiconductor rutile presents a typical S-type band shape in its UV-Vis reflectance spectrum, with the characteristic inflection point at around 400 nm [35,36] that corresponds to the electromagnetic energy necessary for making electrons overcome their characteristic band gaps. Also the Raman spectra showed the presence of rutile due to peaks at 143, 443 and 610 cm^{-1} deriving from Ti-O stretching [37,38]. The presence of rutile was further con-

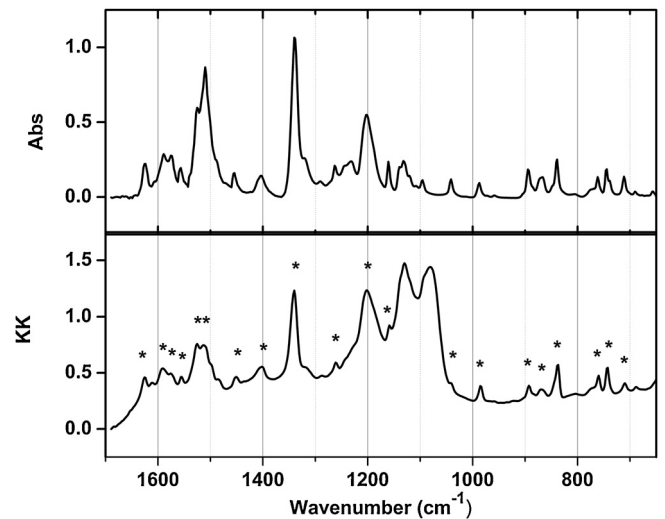


Fig. 3. a: reference FT-IR spectrum of PR4 (IOD00228) from IRUG 2007 database; b: reflectance spectrum of the red area processed with the Kramers–Kroenig correction, * (stars) point out bands due to PR4.

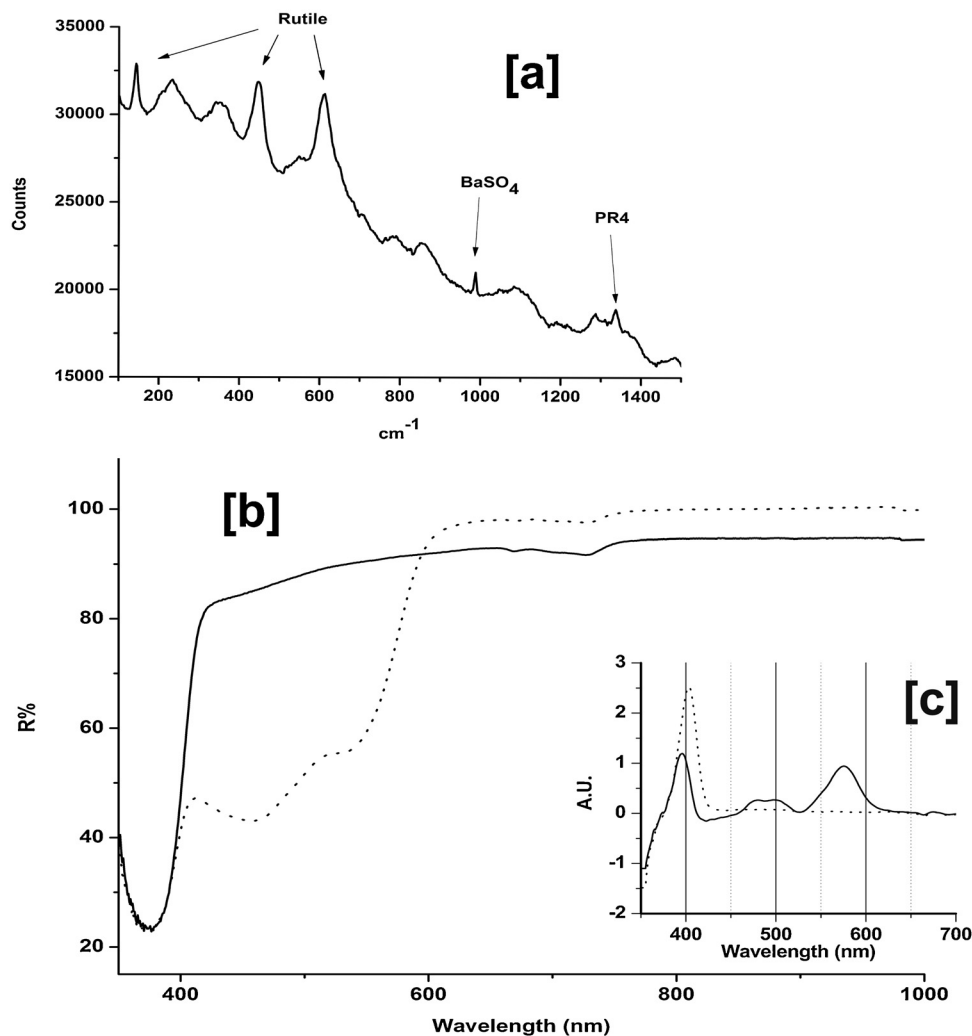


Fig. 4. a: Raman spectrum acquired on a pink area; b: comparison of FORS spectra acquired on a white area (black line) and on a pink area (dotted line), both of which showing the presence of Co(II) absorption bands at 650–750 nm (lithopone pigment); c: comparison of first derivative spectra of b: spectra, both showing an inflection point at about 400 nm that was attributable to rutile.

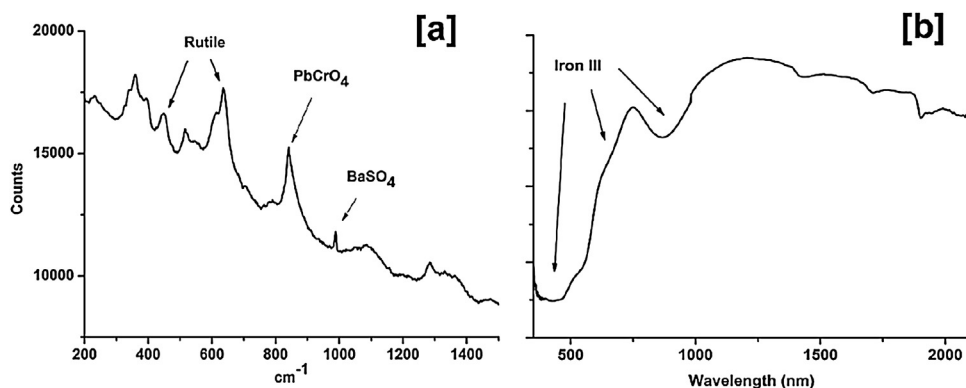


Fig. 5. a: Raman spectrum of a yellow area showing the absorption band at 841 cm^{-1} due to lead chromate; b: FORS spectrum of a brown area showing the absorption bands of an iron (III)-base pigment.

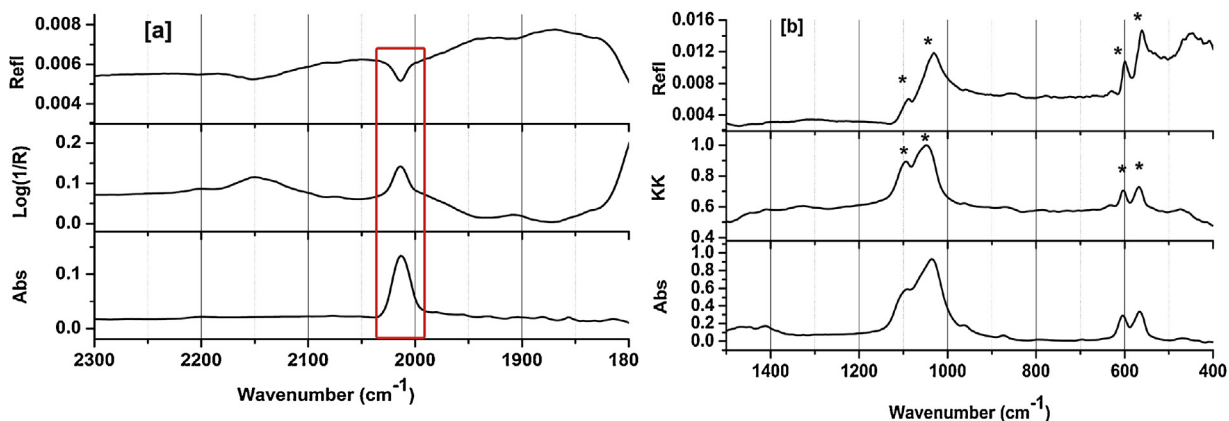


Fig. 6. a: comparison of a reflectance FT-IR spectrum acquired on a black area (top), of the same spectrum, shown as $\text{Log}(1/R)$ (middle), and of an ATR FT-IR reference one of bone black pigment from IRUG 2007 database (IMP00342) (bottom) showing the absorption band at 2013 cm^{-1} (red square); b: comparison of a reflectance FT-IR spectrum acquired on a black area (top, * (stars) point out bands due to bone black), the reflectance spectrum processed with the Kramers–Kroenig correction (middle, * (stars) point out bands due to bone black), and an ATR FT-IR reference one of bone black pigment from IRUG database (IMP00342) (bottom).

firming by the broad absorption bands in the $800\text{--}450\text{ cm}^{-1}$ range, in the FT-IR spectra, attributable to Ti-O stretching [33].

The presence of lithopone was hypothesised by the weak composite absorption band in the $650\text{--}750\text{ nm}$ range, due to the presence of a very low cobalt(II) content in the ZnS lattice (Fig. 4 b) [39]. Starting from the mid-1920s, cobalt(II) was added to the sulphide in order to improve the pigment's light-fastness as well as its brightness and whiteness [40]. FT-IR and Raman data revealed the presence of barite, which is part of lithopone. As for the yellow areas, no information about the pigment was obtained from either FT-IR and FORS spectra. They showed only the presence of rutile and lithopone. The yellow pigment was identified as lead chromate (PbCrO_4) by Raman, due to the characteristic absorption band at 841 cm^{-1} that corresponds to CrO_4^{2-} ion stretching (Fig. 5a) [37,38].

Blue ultramarine was the pigment responsible for the hue of the pants and the motorbike. It was identified by its characteristic FORS spectral shape and by the strong absorption band centered at 600 nm . This is due to the charge transfer transition inside the S_3^- group that is present in the lattice of the complex aluminosilicate, the strong FT-IR band at 1025 cm^{-1} and the Raman band at 548 cm^{-1} . Rutile and barite were added in order to obtain different shades of blue.

Brown shoes were painted using an iron(III)-based pigment. FORS spectra (Fig. 5b) showed the typical shape of a mixture of iron oxide and hydroxide, with the typical absorption bands of hematite ($\alpha\text{-Fe}_2\text{O}_3$) not only at around 445 nm , to be attributed to the charge transfer transition of the Fe-O bond, but also at 649 nm and 870 nm ,

due to ligand field transitions of the iron(III) ion. Goethite, $\alpha\text{-FeO(OH)}$, presents charge transfer transitions absorption bands at 400 and 480 nm , as well as those at about 649 and 917 nm , due to ligand field transitions (Fig. 5b).

The use of iron(III)-based pigments was confirmed by both Raman and TR-FT-IR spectra showing the typical absorption bands of hematite (220 and 286 cm^{-1} , Raman spectrum) and goethite (800 and 895 cm^{-1} , OH in plane and out plane bending, IR spectrum). FT-IR spectrum also showed two bands at 3695 and 3620 cm^{-1} attributable to the OH stretching of kaolinite, which was possibly used as a filler [33,41].

No useful information was obtained from FORS data for the identification of the black pigment used in this rodovetro. Raman spectrum showed the absorption bands characteristic of carbon black, at 1330 and 1590 cm^{-1} , due respectively to sp^3 (diamond) and sp^2 (graphite) orbitals hybridization. A complete identification of the black pigment was achieved thanks to FT-IR data. As reported in Fig. 6b, the IR spectrum showed the typical features of a bone black pigment with bands at 1035 (PO_4^{3-} -stretching), 605 and 565 cm^{-1} (PO_4^{3-} - out of plane and in plane bending). In addition, the absorption band at 2013 cm^{-1} was observed in the FT-IR spectrum: this band is characteristic of the particular class of black pigments, but its assignment still remained unclear (Fig. 6a) [42].

Grey areas were obtained using rutile, barite and a very small amount of bone black.

Lastly, white zones were obtained with a mixture of rutile and lithopone. Indeed, all the techniques used showed the presence of rutile and barite, but only FORS spectra allowed the certain identi-

fication of lithopone due to the presence of Co(II) absorption bands at 670 and 730 nm (Fig. 4b).

4. Conclusions and further perspectives

This study provided the first pieces of information regarding the materials used for the production of a group of Italian animation cels that depict *Little Red Riding Hood and the Big Bad Wolf*. The condition survey reported a very endangered conservative situation.

The multi-analytical approach by means of micro-invasive and non-invasive techniques was successfully applied for elucidating the composition of the plastic substrate and the painted layers and in assessing the state of conservation of the cels.

The plastic sheets were found to be composed of nitrocellulose (NC), plasticised with camphor and phthalates. According to visual observations and the detection of specific degradation markers, it was noted that some cels were in good conditions; others were affected by the de-nitration of NC, with a subsequent yellowing and brittleness of the plastic substrate; in some others, the migration of phthalates caused exudations and blooming on the plastic surface.

As regards the binding media, this analysis revealed that the animation characters were painted with a tempera paint composed of a mixture of animal glue and plant gum. Non-invasive analyses made it possible to identify the pigments and dyes used in the painting of the selected animation cels. It was possible to obtain their definite identification, along with the recognition of an extensive use of barite as filler. A different filler was found only in the case of brown areas, and this was identified as kaolinite.

The information acquired was then transferred to conservators at the MUSIL. This then made it possible to design specific preventive actions for conservation of the animation cels studied. As is well-known, nitrocellulose-based cels need to be conserved in a controlled environment, preferably at 15–18 °C and 30–35% RH. Since these animation cels needed to be located in a neutral pH environment, it was decided to store them in a structure made of acid-free paper, together with an alkaline reserve, where they could remain without modifications while being protected from dust, polluting substances and possible chafing. It was also highly recommended to insert between the paper and the painted nitrate sheet, a transparent plastic film free of plasticizers, chlorinated and nitrified substances and residual solvents. It was suggested to avoid any exposure to direct light by keeping the sheets possibly inside showcases, where they would be protected from UV irradiation.

Only in this way these small works of art can survive and only thus it will be possible to pass on these artworks and heritage objects to future generations, in order to show them the birth and development of Italian animation before the digital era.

Nevertheless, the results so far obtained will be implemented in coming years, when the information on other series of *Rodovetri* will be available. In fact, the systematic investigation of significant amount of cels and their materials would increase the awareness on their artistic values and their best conservation and restoration procedures. In addition, the desirable interaction with the other two Institutions, GCI and DIAF, on this matter will make it possible to substantially improve the knowledge of those objects and the record on their degradation phenomena and effects.

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