

Article

Assessing the Condition of Complex Poly-Material Artworks by Py-GC-MS: The Study of Cellulose Acetate-Based Animation Cels

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Abstract: The material composition of a group of Rodovetri, hand-painted animation cels, made in the 1950s and 1960s for Italian television, has been determined by Flash Py-GC-MS, Thermally assisted Hydrolysis and Methylation-(Py-)GC-MS and GC-MS investigations, where, for the pyrolysis applications, the pyrolyzer is connected septum-less to the GC inlet. The condition of the selected animation cels was generally poor (yellowing, exudation, warping, cracking). The cels are made of plasticized cellulose acetate (CA) and decorated with alkyd paint. Exuding plasticizers from the CA support migrated into the paint; this has softened the paint layers and made the cels stick together. CA is known to be very unstable and easily subjected to degradation, which cannot be reversed, only slowed down by preventive conservation. Most of the cels are plasticized with bis(2-methoxyethyl) phthalate (DMEP) and triphenyl phosphate (TPP). The research shows a relationship between the degradation of CA and the presence of TPP and DMEP.

Keywords: pyrolysis; GC-MS; cellulose acetate; animation cels; Rodovetri; alkyd paints; ESCAPE



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1. Introduction

Carosello 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 major studios of film production and animation of the 20th century, active in Milan from the late 1930s to the 1980s. In particular, Gamma film, founded by the Gavioli Brothers, was an important growth point for many young Italian designers and talents. The Gavioli Brothers have chosen to keep and store all this material and, later, to entrust all to the Micheletti Foundation and the Musil-Museum of Industry and Labor, located in Brescia (Italy). In the Musil Collection, more than 700,000 Rodovetri are now conserved [1]. The Rodovetri are transparent plastic sheets on which the animator painted the single frame of the animated sequence of a cartoon. Usually, the inkers transferred the lines of the initial paper drawing on the recto of the cel, and then the painters painted on the verso; only the finishes or the corrections were painted using colors on the front of the cel. The transparent surface allowed for creating the character to animate by applying multiple overlapping layers. The cels were then photographed on the motion picture film; each cel corresponds to a "position" of the animation of the character. For each second of animation, at least 12 frames were used to create the illusion of movement. Their use ended after the photo was taken; sometimes, the painted character/image was erased to reuse the transparent sheet. This is to say that the archiving and the conservation of the animated cels over time has never been considered as a crucial point: the cels were simply stored in cardboard boxes, superimposing one on top of the other, sometimes interspersed with

the paper sheets that had been used initially to separate the new sheets of acetate in their original box.

Over the last decade, the importance of these cels (which represent a remarkably interesting cross-section of the Italian animation art and of the “Made in Italy” advertising) was revisited and nowadays this issue is undeniable; the cels are actually small works of art and are the evidence of the birth of Italian Animation. The main illustrators worked in the cel-producing companies, and in the period after World War II and the advent of television in all households, Carosello was a well-known daily appointment for children, and not only for them. Like the previously studied animation cels from the Disney Animation Research Library [2–4] and the German Institute for Animated Film [5], Rodovetri were created both on cellulose nitrate and acetate.

While a first article by the present authors reported a particular case study of a Rodovetro made of cellulose nitrate [6], this paper focuses on Cellulose Acetate (CA) based sheets.

Cellulose acetate (CA), synthesized for the first time in 1865 by Paul Schützenberger through a reaction between cellulose with acetic anhydride, has been widely employed in the productions of films, membranes, textiles, coatings, and plastics [7].

Being less flammable and cheaper than cellulose nitrate, CA simply replaced the latter in the film industry [2]. Nevertheless, CA is an unstable plastic material too, since it may easily undergo chemical, physical, mechanical, and biological degradation [2,8,9].

CA degradation is associated with deacetylation steps, generally known as “the vinegar syndrome” [10], due to chemical hydrolysis and the emission of acetic acid, which can rapidly affect, often in a deleterious way, the materials that are in contact with it. Exudation and surface stickiness are generally reported, considering that, at the same time, the presence of plasticizers (such as phthalates-based compounds), their migration and subsequent loss play an important role in the degradation of CA sheets [2,3,11].

This paper deals with CA sheets used for the production of animation cels. The cels present the typical degradation phenomena of plastic supports and, in addition, all the problematics which may arise from migration of plasticizers and additives from the support into the paint and vice versa. To study these phenomena and elucidate the conditions of CA-based animation cels, Pyrolysis-Gas chromatography, coupled to Mass Spectrometry (Py-GC-MS) and Thermally assisted Hydrolysis and Methylation-(Py-)GC-MS, can provide crucial information both in terms of CA plastics supports [2,12,13] and painted layers, based on natural and synthetic binding media [6,14]. The aim of the research is to gain more insight into the composition of cellulose acetate-based animation cels and to highlight their degradation in complex systems (CA sheets + paint layers).

Furthermore, the paper presents, for the first time, a septum-less pyrolyzer connection, developed in the Cultural Heritage Agency of the Netherlands (RCE) laboratories. The septum-less connection prevents inconveniences that can arise from connecting a pyrolyzer to the standard split/splitless inlet of the GC.

2. Materials and Methods

2.1. Selected Animation Cels

In consultation with the staff of the Musil, it was decided to base the selection on: the complexity of the drawings, the special colors, the important cultural value and the worst overall condition. Some of the Rodovetri studied are shown in Figure 1.

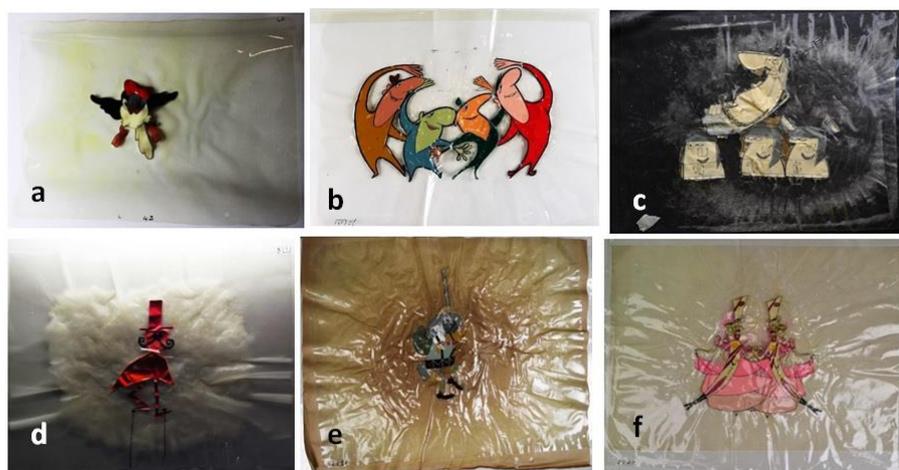


Figure 1. Visible light images of the analyzed Rodovetri: (a) La Rosa di Bagdad (1949), (b) Vegetalumina (1959), (c) Caio Gregorio (1960), (d) Brandy Gran Senior (1974), (e,f) Serie Stock (nd). The animation cells exhibit several degradation phenomena which compromise in many cases the stability of the plastic support and the readability of the characters.

Table 1 lists the samples of the animation cells selected for research, taken from both the plastic supports (cellulose acetate sheets) and from painted layers. These Rodovetri were created between 1949 and 1972 and represented the main characters of short, animated advertising spots.

Table 1. Cel, description, visual inspected condition, condition by Py-GC/MS results, plasticizers added, paint composition formulation. DMEP = bis(2-methoxyethyl) phthalate; TPP = triphenyl phosphate; DMP = Dimethyl phthalate; DEP = Diethyl phthalate.

Rodovetro/CA from the Series (Name, Year)	Typology of Sample	Samples Names	Optical Microscopy Picture (Where Available) — = 1 mm	Visual Condition through Macro and Micro-Observations	CA Condition According to Py-GC/MS Results	(Main) Detected Plasticizers	Composition of Painted Layers
"Brandy Gran Senior" Fabbri (1974)	Plastic support	A5a		Partially yellowed CA with the presence of exudates.	Degraded	DMEP + TPP	/
	Painted layer	C5a		Red painted film with surface whitening	/	/	Alkyd-pentaerythritol, drying oil, PR4, PR49, sulphide/sulphate, plasticiser-compounds
"Vita" Stock (nd)	plastic support	A13		Very yellowed, sticky and fragile CA fragments with the presence of exudates	Degraded	DMEP + TPP	/
"Stock Brandy Grand Senior"—series 2 (nd)	Plastic support	A15		Yellowed, sticky and fragile CA fragments with the presence of exudates	Degraded	DMEP + TPP	/
	Painted layer	C12a		Black paint fragments with exudation	/	/	Alkyd-pentaerythritol, heat bodied oil, stearate, pine resin, sulphide, plasticiser-compounds

Table 1. Cont.

Rodovetro/CA from the Series (Name, Year)	Typology of Sample	Samples Names	Optical Microscopy Picture (Where Available) — = 1 mm	Visual Condition through Macro and Micro-Observations	CA Condition According to Py-GC/MS Results	(Main) Detected Plasticizers	Composition of Painted Layers
“Derby” (1962)	Plastic support	A16		Partially yellowed surface, exudated and sticky	Minor Degradation	DMEP + TPP	/
“RHO” (nd)	Plastic support	A18b		Presence of black spots on the surface (biological attack?)	Good	DMEP + TPP	/
“Crepuscolo Veneziano—Sfinge Veneziana” (1970)	Plastic support	A20		Slightly yellowed CA fragment	Good	DMEP + TPP	/
	Painted layer	C20a		Opaque black paint sample	/	/	Acrylics, alkyd-pentaerythritol, drying oil, pine resin, carbohydrates, sulphide, plasticiser-compounds
	Painted layer	C22		Yellow paint sample	/	/	Alkyd-pentaerythritol, brassica oil, drying oil, sulphide, plasticiser-compounds
“Caio Gregorio” (1960)		ROD5-C12		Very yellowed and fragile CA fragment	Degraded	DMEP + TPP	/
“La Rosa di Bagdad” (1949)	Plastic support	ROD9-31		Very yellowed and fragile CA fragments	Degraded	DMEP + TPP	/
“Pasta Scarpe Drago” (nd)	Painted layer	C4b		Yellow paint fragments	/	/	Alkyd-glycerol, drying oil, pine resin, sulphide, plasticiser compounds.
“Ballo” Stock (nd)	Painted layer	C10d		Pink paint	/	/	Alkyd-pentaerythritol, castor oil, cenwax, pine resin, sulphide, plasticiser-compounds
“Recoaro” (1965)	Painted layer	C23a		White paint samples	/	/	Alkyd-pentaerythritol, drying oil, cenwax, starch, pine resin, plasticiser-compounds
	Painted layer	C23c		Light blue painted layer	/	/	Alkyd-pentaerythritol, drying oil, pine resin, starch, sulphide, plasticiser compounds.
“Vegetallumina” (1959)	Figure silhouette from the recto	RodA-3C22		Greyish paint film	/	/	Alkyd-pentaerythritol, drying oil, pine resin, starch, sulphide, plasticiser-compounds

Table 1. Cont.

Rodovetro/CA from the Series (Name, Year)	Typology of Sample	Samples Names	Optical Microscopy Picture (Where Available) — = 1 mm	Visual Condition through Macro and Micro-Observations	CA Condition According to Py-GC/MS Results	(Main) Detected Plasticizers	Composition of Painted Layers
Cellulose acetate sheet from Gamma film (1969)	Plastic support	VR11-V-AC	/	Slightly yellowed CA fragment	Good	DMP + DEP	/
Lourdes Castro, Ombres transparentes (1960s)	Plastic support	D 3,4,5,6		Warped CA sheet with the presence of exudates	Good	DEP + TPP	/

Fragments of the painted layers peeling off the plastic sheets have been used to characterize the composition of the paint.

For comparison purposes, a cellulose acetate sheet from the same animation studio (Gamma film), dated 1969, slightly yellowed but far less degraded than the selected Rodovetri, was studied.

For comparison, a sheet from a plastic book, made in the 1960s by Lourdes Castro, was also examined. Castro is a Portuguese artist that frequently uses plastic materials in her pieces. The artist's book, entitled *Ombres transparentes* (transparent shadows), belong to a series of 30 equal pieces made in the artist's studio in Paris, in 1967. Each book measures 30 × 28.5 × 2 cm and contains 25 CA sheets. Two of the books, stored in Museu de Serralves, Oporto, were studied by Van Oosten et al. in 2011 [15]. The sheet studied, (D 3,4,5,6), shows severe warping and crystalline exudation.

2.2. Flash Pyrolysis-GC-MS Investigation of Plastic

Flash Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) was used to characterize the material of the cels. The pyrolyzer used was a Frontier Lab 3030D, micro furnace pyrolyzer, septum-less mounted onto a Thermo Scientific Focus GC/ISQ-7000 mass spectrometer combination. Separation took place on a SLB5 ms (Supelco, Bellefonte, PA, USA) column with a length of 20 m, an internal diameter of 0.18 mm, and a film thickness of 0.18 µm. Helium with a constant flow of 0.9 mL/min was used as carrier. The split ratio was set to 1:30. The temperature program used was 35 °C stable for one minute, subsequently heated with a rate 16 °C per minute until 220 °C and with a rate of 10 °C per minute until 315 °C, held stable for 2 min. The temperature of the GC inlet was 290 °C, the temperature of the MS interface was 250 °C, and the temperature of the ion source was 220 °C. Mass spectra were recorded from 20 amu until 600 amu with a speed of 5 scans per second. Xcalibur 2.1 software was used to process the mass spectral data.

Samples obtained from the cels were placed in steel pyrolysis cups; the cups were transferred into the pyrolyzer, and the sample material was pyrolyzed at 600 °C. The sample size was approximately 20 µg.

2.3. Septum-Less Pyrolyzer Connection Novelty

Generally, a pyrolyzer is connected to the split/splitless inlet of the GC, for instance with a hypodermic needle passing the silicone injector septum. To avoid overloading the GC-MS system, and to facilitate rapid transfer of the pyrolysate to the GC inlet and column, a large portion of the pyrolysate is split off, by the GC inlet, before it enters the GC column. To avoid a cold spot in connecting the pyrolyzer, both the interface of the pyrolyzer and the GC inlet are set at a high temperature, and usually fitted with insulation.

The foregoing ignores the fact that the septum cap is designed to cool the septum, and, by that, reduce bleeding of silicones and prolong its life. Another aspect is the well-thought-out design of carrier flow paths in the GC inlet. By connecting the pyrolyzer, the carrier enters halfway up the inlet and disrupts these well-thought-out carrier flows. Shutting off the septum purge during sample introduction may help, but increases the chance of the

introduction of silicones and air from the hot and pierced septum. Mounting a pyrolyzer with a needle through a septum can cause carrier leakage, loss of sample information, introduction of air, accelerated aging of the silicone septum, and reduced column life.

In the RCE laboratory, a pyrolyzer is seen and adapted as the GC injector rather than a sample introduction device coupled to the GC inlet. Shortly after delivery and installation of the Frontier Laboratories 3030D pyrolyzer (in 2012), a split exit was constructed directly at the base of the (heated) interface of the pyrolyzer. The column passes the GC inlet, which now functions as a heated interface between pyrolyzer and GC oven, and is coupled to the pyrolyzer via this constructed split exit. The constructed split exit replaces the standard split exit of the GC inlet. The split flow is regulated by the GC digital pressure and flow controller. A schematic drawing of the pyrolyzer and the septum less coupling to the GC column is depicted in Figure 2.

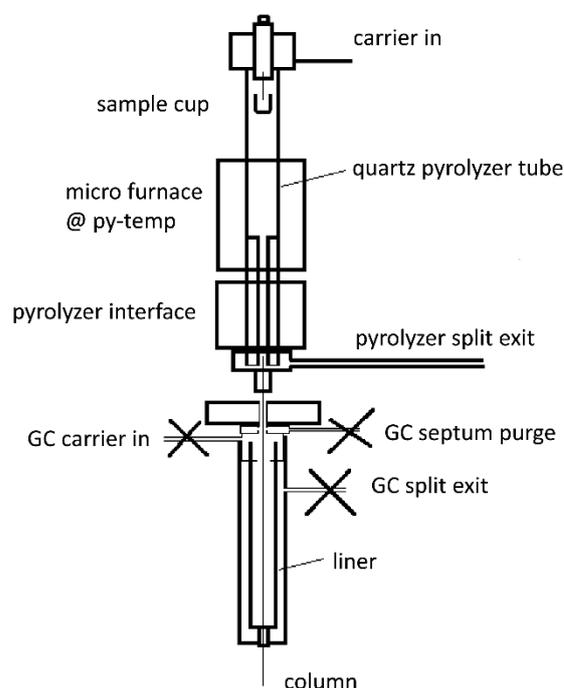


Figure 2. Septum-less connection of the pyrolyzer to the GC column, as developed at the RCE laboratory.

2.4. GC-MS Identification of Exudation and Plasticizer Content

The Lourdes Castro D 3,4,5,6 cellulose acetate sheet shows a significant amount of crystals on the surface. For determining the identity of the crystalline exudation on the sheet and the plasticizer content of the sheet, a small quantity of the crystals, scraped off of the surface using a scalpel knife, was dissolved in toluene; a section of the sheet, app. $0.5 \times 2 \text{ cm}^2$, was extracted with toluene in a Soxhlet setup. The dissolved and extracted materials were analyzed on a SLB5 ms (Supelco, Bellefonte, Pennsylvania, USA column with a length of 20 m, an internal diameter of 0.18 mm and a film thickness of 0.18 μm). The temperature program used had an initial temperature 80 °C, raised with 15 °C/min to 290 °C, and was stable for 2 min. The split ratio was 1:30. The injector temperature was set to 220 °C to avoid thermal degradation of the triphenyl phosphate (TPP) [16], used as flame retardant in the main part of the studied cels.

2.5. Analysis of Paint Samples by Thermally Assisted Hydrolysis and Methylation-(Py-)GC-MS

The composition of the binder of the painted layers was analyzed using Thermally assisted Hydrolysis and Methylation, pyrolysis Gas Chromatography-Mass Spectrometry (THM-(Py-)GC-MS), using the same instruments, settings, and column as mentioned in

paragraph 2.2. The temperature program used was 35 °C, stable for 1 min, subsequently raised with 60 °C per minute to 110 °C, raised with 14 °C per minute until 240 °C and with 5 °C per minute until 315 °C, stable for 2 min.

Sample material was made into a suspension with a few drops of a 5% solution of tetra methyl ammonium hydroxide (TMAH) in methanol and transferred to a steel pyrolysis cup. The pyrolyzer was set to a (high-speed) temperature range starting at 360 °C, raised to 700 °C with a rate of 500 °C/min, total time of one minute. The used method is a combination of thermal desorption and thermal degradation. By combination of the heat and the reagent, evaporation, hydrolysis and/or methylation, and pyrolytic conversion takes the place of the ester bonds, lipids and fatty acids, natural resins and natural and synthetic polymers present in the sample material. The interpretation of the result is done using the ESCAPE system, an expert system for characterization of (THM-)Py-GC-MS data using AMDIS & Excel [17]. The ESCAPE AMDIS library is firmly based on reference material analyses, spectra from the National Institute of Standards and Technology (NIST) library [18], on shared spectra recorded by experts in the conservation science field, and on retention index (RI). The system is tested by the experts on their instrumentation for the match quality and retention index of the collected spectra. The sample size was approximately 20 µg.

3. Results and Discussion

3.1. Plastic Substrate

Overall, the cels are warped, stiff and yellowed and show bloom and crystalline exudation, both in the CA portion and in the paint layers. In most cases, the deformations are due to the shrinkage of the plastic sheets, causing small fractions of the paint layers to come off. Furthermore, plasticizers migration was observed, as also highlighted in research on similar animation cels [5,19]. The selected cels presents different visual types of degradation and alterations, as illustrated in Figure 3.

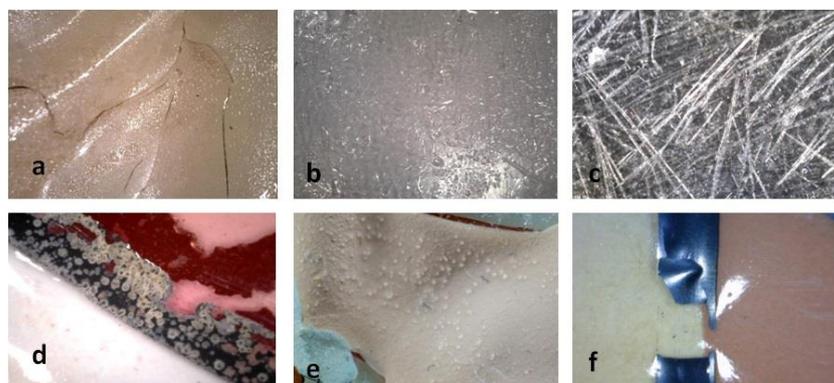


Figure 3. Optical microscopical images (— = 1 mm) illustrating degradation of the CA sheets: (a) yellowing and cracking, (b) exudation, (c) crystalline exudates; and on painted layers: (d,e) plasticizers migration and crystallization, (f) paint loss.

Table 1 presents a description, the visual observed condition, the condition by the interpretation of the Py-GC-MS data and the added plasticizers of the cels selected for research. The condition, according to the Py-GC-MS result, is based on the presence of acetic acid, typical for a pyrolysis analysis of cellulose acetate [20], and the presence of levoglucosan, a typical marker for the pyrolysis of cellulose [20]. The results suggest a relationship between the degradation of CA and the combination of TPP and DMEP. The main part of the cels plasticized with TPP and DMEP are yellowed and fragile, and the CA sheets from Gamma film and Lourdes Castro are both the same age as the Rodovetri, plasticized with, respectively, DMP and DEP, DEP and TPP, are in good condition.

The rationale for the state of degradation is explained by the results of the Py-GC-MS analysis of cel A5a on the basis of the pyrolysis products characterized as Cellulose Acetate (CA). The pyrogram is presented in Figure 4, and the identity of the pyrolysis products used in characterization is given in Table 2.

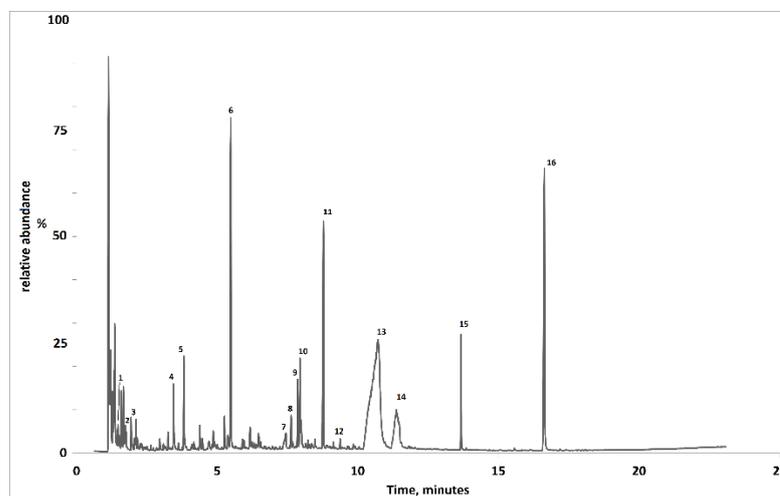


Figure 4. Pyrogram of cel A5a, identified as Cellulose Acetate (CA). Indicated identified compounds are listed in Table 2.

Table 2. Indicative pyrolysis products identified in cel A5a. Presented are the peak label, the retention time in minutes, the identity of the compound and the characteristic mass ions (AMU) and the molecular ion between brackets.

Peak #	Retention Time (min)	Identified Compound	<i>m/z</i> (M^+)
1	1.48	cyclopentadiene	39/(66)
2	1.76	acetic acid	43/45/(60)
3	1.94	methoxyethanol	45/(76)
4	3.45	2(5H)-furanose	55/(84)
5	3.81	furfural	39/95/(96)
6	5.48	phenol	66/(94)
7	7.45	benzoic acid	77/105/(122)
8	7.63	1,2-naphthalenedione	102/130/(158)
9	7.86	1,4:3,6-dianhydro- α -D-glucopyranose	69/(144)
10	7.95	5-hydroxy methylfurfural	41/79/(126)
11	8.78	phthalic anhydride	76/104/(148)
12	9.37	2-methoxyethylbenzoate	58/105/(180)
13	10.72	levoglucosan	60/(180)
14	11.33	1,6-Anhydro- β -D-glucofuranose	73/(162)
15	13.67	bis(2-methoxyethyl) phthalate (DMEP)	59/149/(282)
16	16.63	triphenyl phosphate (TPP)	77/(326)

The pyrogram is dominated by several large, as well as two oddly shaped peaks. Remarkably, only a minor amount of acetic acid is identified (compound #2). The presence of abundant peaks for levoglucosan, 1,6-Anhydro- β -D-glucofuranose, 2(5H)-furanose (#4) and furfural (#5) is an indication for cellulose rather than of cellulose acetate [20]. Cellulose acetate is recognizable by a clear and abundant acetic acid peak in the pyrogram [20]. The

minor amount of acetic acid detected and the presence of cellulose pyrolysis products indicate a deacetylation of the cellulose acetate polymer.

Cel A5a is plasticized with bis(2-methoxyethyl) phthalate (DMEP) and TPP; both plasticizers are suspected to cause degradation of the cellulose acetate polymer [21,22]. DMEP is a solvent plasticizer; if added in a large amount, it will solve the cellulose acetate. TPP, a bulky non-solvent plasticizer, is often applied as flame retardant.

CA consists of (acetylated) glucose-units linked together through B-glycosidic linkage to form long polymer chains. Hydrogen bonding between the polymer chains results in poor flexibility. Plasticizer of the solvent type, adsorbed to the polar groups of the polymer, will space the chains, lower the softening point and increase flexibility. Non-solvent plasticizers have little solvent action, and they decrease the interchain attraction by increasing the spacing between the chains. This is only possible after reduction of the hydrogen bonds by the solvent plasticizer [23].

It is believed that the applied pyrolysis temperature also fragments the plasticizer DMEP into methoxyethanol and phthalic anhydride, evidence for the presence of these compounds in the cel, by hydrolysis of DMEP, cannot be proved from the analysis results.

The significant amount of phenol is a result of the breakdown of TPP. Shinagawa and colleagues [21] observed a relation between TPP and the degradation of CA. Due to moisture, TPP is hydrolyzed into diphenyl phosphate (DPP) and phenol. DPP is a strong acid and causes rapid degradation of CA.

Phosphate esters are also used as aviation lubricants. ExxonMobil describes in a Technical Bulletin the mechanisms of degradation of phosphate esters: thermal degradation, oxidation, and hydrolysis [17]. All three pathways produce phosphoric acid derivatives as a harmful degradation product. Thermal degradation becomes an issue at temperatures of above 150 °C. Phosphate esters are quite resistant to oxidation; the most significant degradation path is hydrolysis, which will even occur at moderate temperatures.

The explanation for the presence of phenol in the pyrogram is not unambiguous. The pyrolysis temperature used for the analysis will certainly thermally degrade the TPP. The state of degradation of cel A5a refers to a moisture-induced hydrolysis of the TPP. Both pathways produce DPP in the first step. DPP was not detected in the analysis. A reasonable explanation could be that, once the TPP is hydrolyzed, or thermally degraded to DPP, the DPP is readily thermally degraded during pyrolysis to phenol and phosphoric acid. The GC-method and column used for the analysis of the material of the cels is not set-up, or suitable, to detect phosphoric acid; Shinagawa and colleagues used HPLC to indicate phosphoric acid [21]. In summary, it cannot be explained whether the detected phenol was already present in the cel material by the hydrolysis of TPP, or was formed during pyrolysis by thermal conversion.

The solvent plasticizer used to plasticize the cel A5a is bis(2-methoxyethyl) phthalate. Wilson and Forshee concluded in their research that the degradation of CA was principally oxidative in nature and moisture did not considerably affect the degradation [22]. They also observed that TPP can act like a stabilizer; ether esters plasticizers, like ethoxy ethyl phthalate, bis(2-(2-ethoxyethoxy)ethyl) phthalate, and also bis(2-methoxyethyl) phthalate (DMEP), can cause serious degradation.

A cellulose acetate sheet used by Lourdes Castro in 1962 and showing crystalline exudation was examined to determine exudation and the plasticizer content. The GC runs, combined in Figure 5, show that the sheet is plasticized with diethyl phthalate and triphenyl phosphate, and a minor amount of diethyl hexyl phthalate. The crystal exudation on the surface consists mainly of TPP (and some diethyl hexyl phthalate). DPP and phenol are not detected. The sheet examined shows exudation and warping due to the loss of the bulky TPP but no degradation of the CA.

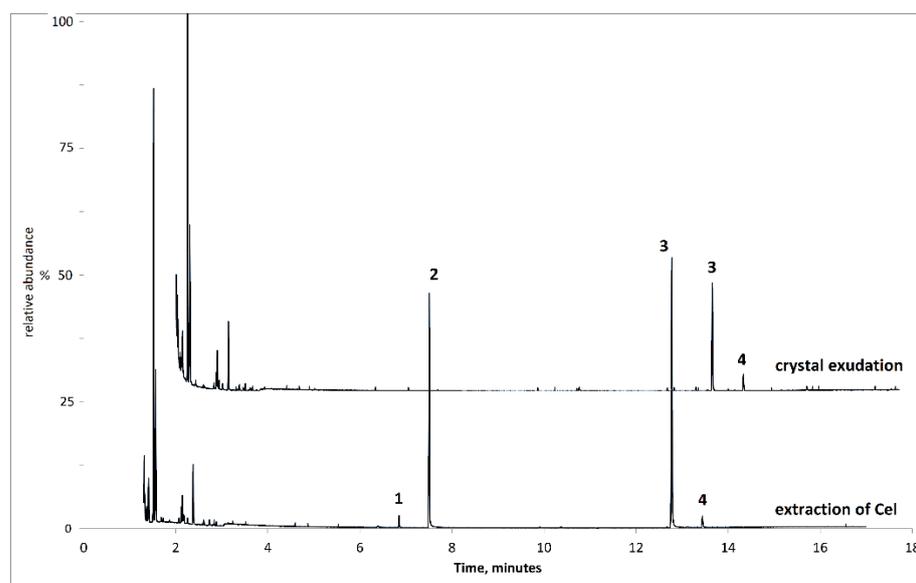


Figure 5. GC analysis of toluene extraction of a CA sheet, and that of solved crystals taken from the surface of the sheet. Peaks labelled, 1: butylated hydroxy toluene, 2: diethyl phthalate, 3: triphenyl phosphate, 4: diethyl hexyl phthalate.

3.2. Painted Layers

Cel A5a is one of the cels whose initial drawing is not on the recto of the original paper drawing; this cel is directly painted with red and pink colors on the verso, and finally retouched on the front of the acetate sheet using the black color. This cel shows an elegant mustachioed man, who then represented Stock Brandy Grand Senior's ideal client (Figure 1d). A sample of the red paint is analyzed using THM-(Py-)GC-MS. The GC run is depicted in Figure 6, the numbered, and by AMDIS identified, compounds are presented in Table 3.

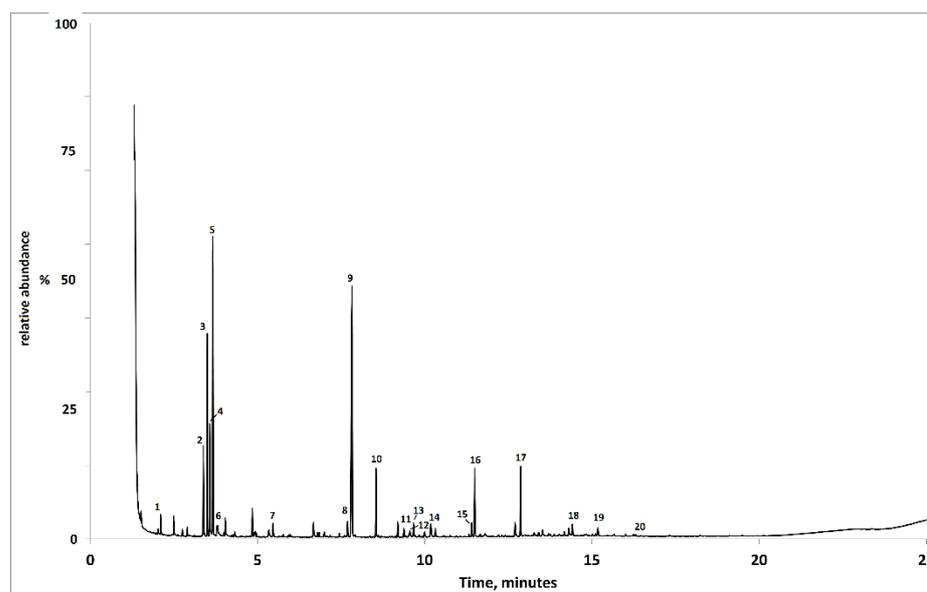


Figure 6. THM-Py-GC/MS analysis of paint sample C5a. The labelled compounds are presented in Table 3.

Table 3. THM-pyrolysis products identified in the red paint of cel A5a. Presented are the peak label, retention time, the identity of the compound and their typical, characteristic mass ions (AMU), the molecular ion between brackets.

Peak #	Retention Time (min)	Identified Compound	<i>m/z</i> (M ⁺)
1	2.10	1,2 dimethoxy ethane	45/60/(90)
2	3.38	glycerol, 1,3-dimethyl ether	45/75/(120)
3	3.51	glycerol, 1,2,3-trimethyl ether	59/89/(134)
4	3.58	glycerol, 2,3-dimethyl ether	45/75/89/(120)
5	3.67	Anisole	65/78/(108)
6	3.81	trimethyl phosphate	79/110/(140)
7	5.47	pentaerythritol, trimethyl ether	45/75/(178)
8	7.70	octanedioic acid, dimethyl ester	74/129/(202)
9	7.83	dimethyl phthalate	163/(194)
10	8.55	nonanedioic acid, dimethyl ester	74/152/(216)
11	9.38	decanedioic acid, dimethyl ester	74/125/(230)
12	9.57	2-naphthylamine, N-methyl	115/128/(157)
13	9.67	1-naphthylamine, N,N-dimethyl	128/154/(171)
14	10.18	1-naphthylamine, 2-methoxy	130/158/(173)
15	11.41	diphenyl-methyl phosphate (MDPP)	77/170/(264)
16	11.49	hexadecanoic acid, methyl ester	74/(270)
17	12.87	octadecanoic acid, methyl ester	74/(298)
18	14.42	dehydroabietic acid, methyl ester	239/(314)
19	15.18	7-methoxy dehydroabietic acid, methyl ester	227/267/(342)
20	16.91	7,15-dimethoxy tetrahydroabietic acid, methyl ester	73/340/(372)

To use ESCAPE, the identification report produced by AMDIS is copied to the ESCAPE Excel template. Syntaxes in template sort the identified compounds into materials, and confirmation of the presence of a material is based on expert knowledge present in the template. Peak areas are used for semi-quantification; ratios, if appropriate, are calculated.

The interpretation of the composition of binder and additives to the paint is complicated as the paint has absorbed the exuding plasticizers from the cellulose acetate substrate. Due to the THM reaction, the plasticizers DMEP and TPP are hydrolyzed and methylated into 1,2 dimethoxy ethane (#1) and dimethyl phthalate (#9), and anisole (#5), trimethyl phosphate (#6) and diphenyl-methyl phosphate (MDPP) (#15). Glycerol (#2, #3 and #4), fatty diacids (#8, #9 and #11), hexadecanoic acid (#16), and octadecanoic acid (#17) indicate the presence of a drying oil [24]. Pentaerythritol (#7) is a proof for the presence of an alkyd resin [25], indicating that part of the detected dimethyl phthalate is related to the alkyd resin.

The ESCAPE system identifies compounds #18, #19 and #20 as markers for an aged pine resin [26]. ESCAPE calculated the ratio of hexadecanoic acid to octadecanoic acid (P:S ratio) as 0.97. Commonly used vegetable oils used in paint formulations, like linseed, nut, and safflower, have ratios in the range of 1.2 to 2.5 [27]. Stearates, often added to paint formulations [28], contain mainly stearic and only a little palmitic acid. If a stearate is added to a linseed oil paint, the P:S ratio will lower to, for instance, 0.8 or 1.0, depending on the amount of stearate added. ESCAPE also detected sulfide and sulphate compounds, and recombined the naphthylamine compounds (#12, #13 and #14)

into Naphthol red, (2-Naphthalenol, 1-[(2-chloro-4-nitrophenyl) azo], (PR4), and Lithol red (1-Naphthalenesulfonic acid, 2-[(2-hydroxy-1-naphthalenyl)azo]-), (PR 49).

By the compounds identified and information presented in ESCAPE, the binder and additives to the red paint are characterized as a pentaerythritol based alkyd resin, modified with a drying oil, with additions of a stearate and some pine resin. The organic pigments are identified as Naphthol red (PR4) and Lithol red (PR 49). Sulfide and sulphate might be related to the synthetic pigments or may indicate the presence of a filler, for instance lithopone, a mixture of barium sulphate and zinc sulfide.

4. Conclusions and Further Perspectives

Pyrolysis in combination with GC-MS represents a powerful combination for the identification of polymers and additives to the polymer. The investigation on the selected group of Rodovetri (animation cels made for Italian television between the 1950s and 1970s) made it possible to gain more insight into the composition of CA sheets and their degradation phenomenon, with a focus on the role of plasticizers.

Follow-up research on this topic will include double-shot Py-GC-MS. A double shot type analysis, where a polymer sample is first desorbed at moderate temperature with attention to the thermal instability of TPP, followed by a high temperature flash pyrolysis of the desorbed polymer. The data collected in two separate GC-MS runs could provide a more precise information about the nature of the additives and the state and cause of degradation of cellulose acetate plasticized with DMEP and TPP.

The binding medium analyses of the paints show that the exuding plasticizers migrated into the (alkyd) paint with which the sheets are decorated. This will soften the paint layers and can cause the sheets to stick together, or to the paper sheet used to separate the decorated cels.

Degradation and deacetylation of cellulose acetate cannot be reversed, only slowed down by preventive conservation. To preserve the Rodovetri, cold, dark storage, low humidity, and reduced oxygen are advised. Ventilation is recommended, as is a non-stick plastic sheet to separate the decorated cels from each other.

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