Chapter 6
Analytical Pyrolysis of Organic Paint Materials for Authentication and Attribution

A. Andreotti, J. La Nasa, F. Modugno, and I. Bonaduce

Abstract The chemical analysis of organic paint material is still one of our most important tools for understanding an object, planning its conservation, and supporting speculations on the object's identity and history. Analytical pyrolysis is a micro-destructive analytical technique that chemically characterizes organic materials in a large range of molecular weights, directly in the solid state, without the need for any pretreatment. This makes the technique particularly useful when dealing with samples from a work of art and archaeological object, where typically the composition in terms of significant analytes and the matrix is not known before the analysis, and natural and synthetic materials may be expected simultaneously.

In this chapter the use of analytical pyrolysis for the molecular characterisation of organic materials in case studies from archaeological objects and works of art, spanning from the fourth century BC to the 1980s, is presented. The aim is to discuss how analytical pyrolysis can contribute to issues related to the identification of artistic techniques, to reconstruct the history of an object through the study of its chemical signature, and to differentiate between original and non-original materials in paintings.

Keywords Chemical analysis · Cultural heritage · Natural binders · Synthetic binders · Restoration materials

6.1 Introduction

Radiocarbon dating represents one of the greatest advances in the authentication of works of art. Accelerator mass spectrometry (AMS) (Hendriks et al. 2018) has enabled even just 20–30 micrograms of carbon to be analysed, opening the way to

---

A. Andreotti (✉) · J. La Nasa · F. Modugno · I. Bonaduce
Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, via Moruzzi, Italy
e-mail: alessia.andreotti@unipi.it

M. P. Colombini et al. (eds.), *Analytical Chemistry for the Study of Paintings and the Detection of Forgeries*, Cultural Heritage Science,
https://doi.org/10.1007/978-3-030-86865-9_6

the applications of radiocarbon dating to the study of paint forgeries (Hendriks et al. 2019b; Hodgins 2019). (^{14}C) AMS is capable to detect post-1955 imitations of pre-1955 works (Hodgins 2019), and it can also date materials in paintings more ancient than 500 years produced with natural binders (Fiorillo et al. 2021), as well as with lead white (Hendriks et al. 2019a). However, (^{14}C) AMS is not suitable for dating paintings produced in the past 500 years, because in these last centuries artists' materials have calibrated radiocarbon dates that span centuries (Hodgins 2019). Another issue is the frequent presence of restoration materials, that needs to be excluded to achieve accurate radiocarbon dating.

Analysing the materials that make up a work of art is thus still one of our most important tools for authentication purposes. In some cases, for example, a forgery can be identified based on the detection of anachronistic materials. For instance, some natural pigments have specific patterns of appearance and use, and in other cases, particle morphologies can help distinguish between hand versus machine-ground pigments. Finally, there are synthetic pigments with known dates of invention and adoption (Hodgins 2019).

In the case of organic materials used as paint media and varnishes, things are significantly more complex. Proteins have been detected in Neolithic paintings – possibly as paint binders (Roldán et al. 2018). Proteins and polysaccharides have been identified as paint binders in Bronze Age paintings (Brecoulaki et al. 2008, 2012, 2017; Linn et al. 2018). Oils were introduced as artistic media, possibly originally in a mixture with proteins, in the course of the fourteenth/fifteenth century, although the first documented artistic painting with a drying oil as a paint binder dates back to the seventh century (Cotte et al. 2008). Terpenoid resins are commonly found in paintings, mostly as ingredients of varnishes, and some of them have documented periods of appearance and use, such as dammar and shellac resin. Synthetic materials were introduced as paint materials or for conservation in the late nineteenth century.

Although there are a limited number of classes of organic materials in a painting, their identification in a work of art is a useful starting point in understanding an object, in planning its conservation, and, in supporting speculations on the object's identity and history.

The analytical techniques for identifying materials in an art object include analytical pyrolysis coupled to (gas chromatography-) mass spectrometry. This is an extremely versatile technique that allows a rapid molecular characterisation of an organic sample. The technique is used in heritage science and has evolved considerably for over 30 years (Bocchini and Traldi 1998; Degano et al. 2018).

Analytical pyrolysis is a fast micro-destructive analytical technique that chemically characterizes organic materials in a large range of molecular weights, directly in the solid state, without the need for any pretreatment. In pyrolysis, the sample is heated up for few seconds in anoxic conditions: volatile molecules evolve during the sample heating, thermally unstable compounds are degraded, and high molecular weight components are fragmented into reproducible molecular patterns. In a typical pyrolysis gas chromatography mass spectrometry (Py-GC-MS) experiment, the pool of molecules produced upon thermal degradation are transferred into the gas chromatograph to be chromatographically separated and then analysed by a mass spectrometric detector. The molecular pattern that is obtained can be linked to the original chemical composition of the material. Molecular pattern recognition, semiquantitative analyses, or marker recognition are the main processes involved in data interpretation and in identifying a material (Degano et al. 2018).

Unlike all the other mass spectrometric based techniques, analytical pyrolysis characterizes the entire the organic fraction of a sample. While HPLC-MS and GC-MS based approaches can be used to characterise only the soluble/hydrolysable/volatile/thermally stable components of a sample, analytical pyrolysis also provides molecular insights into the highly insoluble, cross-linked and non-hydrolysable fractions of a material, including natural and synthetic macromolecules.

When HPLC-MS and GC-MS are used, several analytical protocols and experimental/instrumental conditions are required for different analytes. For example, for GC-MS analysis, lipids are best hydrolysed in alkaline conditions, proteins require acidic hydrolysis, and polysaccharides also require acidic hydrolysis, but with milder conditions (Bonaduce et al. 2016; Degano and La Nasa 2016). Derivatisation procedures are also often necessary in GC-MS, and again, different analytical conditions and reagents are used to maximise derivatisation yields for the different analytes (Andreotti et al. 2008b).

With analytical pyrolysis, all materials are the analysed at the same time. A paint sample can be introduced directly in its solid state, and no previous and customised wet-chemical pre-treatment is necessary. Thermally assisted reactions – e.g. hydrolysis and methylation as well as silylation – are commonly adopted as in-situ and on-line sample treatment in the analysis of hydrolysable and polar materials (Bonaduce and Andreotti 2009).

Analytical pyrolysis is thus ideal for the molecular characterisation of a micro sample from a work of art, where typically the composition in terms of significant analytes and the matrix is not known before the analysis. The constituent organic materials, both natural and synthetic, expected and unexpected, can be targeted simultaneously. This approach reduces the amount of sample required for the characterisation of different classes of organic materials, at the same time massively reducing the analytical workout.

The aim of this chapter is not to provide a comprehensive collection of all the work performed in the field, but rather to discuss mostly our experience in the use of analytical pyrolysis for the molecular characterisation of organic materials in case studies related to archaeological objects and works of art, which span from the fourth century BC to the 1980s.

We highlight how analytical pyrolysis can positively contribute to issues related to the identification of artistic techniques, to reconstruct the history of an artwork through the study of its chemical signature, and to differentiate between original and non-original materials in paintings. We aim to show the huge potential of the technique, and at the same time the challenges of reconstructing the chemical nature of the original artistic materials based on the recognition of its pyrolysis products.

6.2 The Analysis of Original and Restoration Materials in Ancient Polychromies and Paintings

6.2.1 An Etruscan Sarcophagus from the Fourth Century BC: "Sarcofago delle Amazzoni"

Our first case-study is an Etruscan masterpiece held in the Archaeological Museum of Florence. It is the fourth century BC architectural marble sarcophagus, known as the "Sarcofago delle Amazzoni" (Bottini and Setari 2007). For a detailed chemical characterization of the original and restoration materials, over twenty samples were taken from the *case* and *lid* of the sarcophagus (Andreotti et al. 2007). The analysis based on analytical pyrolysis with hexamethyldisilazane (Py(HMDS)-GC-MS) revealed the presence of alkyl pyrroles, pyrolysis products characteristic of animal glue proteins, and in lower amounts, hexadecanenitrile and octadecanenitrile, which are pyrolytic markers of egg yolk (Orsini et al. 2017). The uniform distribution of these materials in all the samples analysed suggests that these proteinaceous binders were used for the pictorial layers.

The presence of a lipid material was also evident in all the samples, as shown in the extract ion chromatogram relating to the fragment ion with *m/z* 117, (Fig. 6.1), common to all the trimethylsilyl esters of carboxylic acids, formed upon pyrolysis of lipids in the presence of HMDS.

However, the profile of the carboxylic acids was not the same in all the samples examined. In some of them, only monocarboxylic acids with 8–18 carbon atoms were present, while dicarboxylic acids such as azelaic acid were almost absent. For this set of samples, the profile showed that the lipids do not derive from a siccative oil: the observed molecular profile is indicative of a lipid with a low content of polyunsaturated fatty acids, such as egg yolk lipids. In other samples, in addition to monocarboxylic acids, the dicarboxylic acids suberic, azelaic and sebacic were observed in significant amounts, suggesting the presence of lipids deriving from a drying oil.

Interestingly, all the samples containing drying oil also contained traces of butolic acid, a pyrolytic marker of shellac. Shellac is a resinous substance produced by the glandular secretion of some insects of the Cochineal family (Coccus lacca, Lakshadia indica Madhihassan, etc.) in the forests of India and Thailand, which was widely imported in Europe from 1500 and used as a varnish. The combined presence of drying oil and shellac present in several areas of the sarcophagus point to a varnish likely used in a past restoration.

In two of the samples collected from the lid, a triterpenoid material was detected, but not in any of the other samples examined. The terpenoid resin was identified as mastic resin (a resin exudated from the trees of *Pistacia genus*) based on the detection of, among others, 29-orlean-17en-3one (Fig. 6.2). Mastic was only identified on the lid, again possibly due to a past restoration.

Finally, the analyses revealed a synthetic polymer in all the samples examined. The trimethylsilyl ester of acetic acid, benzene and other aromatic compounds, such

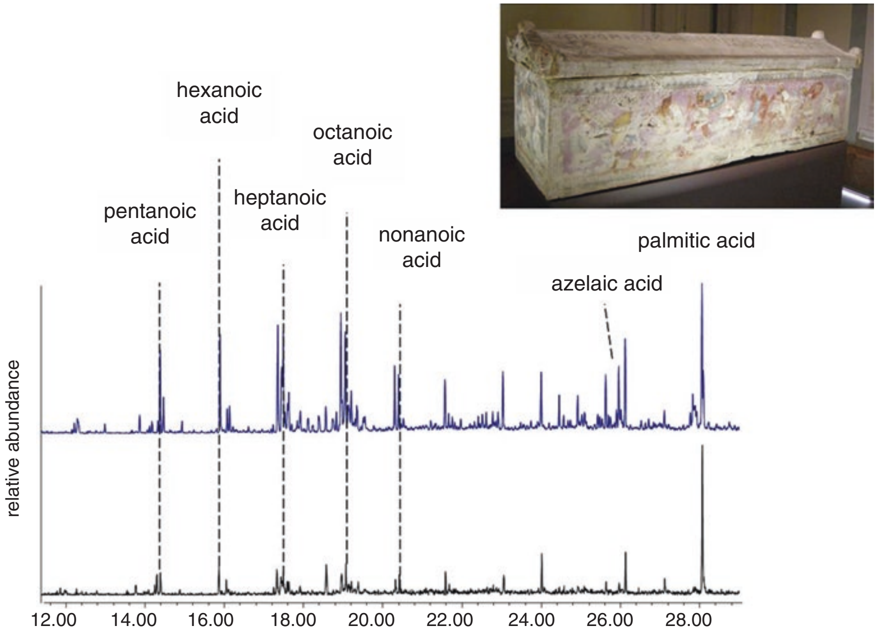

Fig. 6.1 Extract ion chromatogram of ion m/z 129, characteristic of the trimethylsilyl esters of carboxylic acids in two samples from Sarcofago delle Amazzoni. (Sarcofago delle Amazzoni picture from: I, Sailko, CC BY-SA 3.0 http://creativecommons.org/licenses/by-sa/3.0/, via Wikimedia Commons) Top: pyrolytic profile of a drying oil; bottom: pyrolytic profile of egg lipids

as styrene and alkylbenzenes are a characteristic signature of polyvinyl acetate (Bonaduce and Colombini 2003). This material was likely used since the early 1960s as to consolidate or protect pictorial surfaces. The protective based on polyvinyl acetate appeared to be evenly distributed over the polychromy.

6.2.2 *Mural Painting in a Roman Villa Dated 10 BC–5 AD: The Casa del Bicentenario in Herculaneum*

The *Casa del Bicentenario* was built during the Julio-Claudian period (from 27 BC to 68 AD), which was one of the most flourishing of the Imperial ages of Roman history. The *Casa del Bicentenario* in Herculaneum is one of the most magnificent houses in the forum area of Hercolaneum (Campania, Italy). The city was destroyed by the eruption of Vesuvius in 79 AD. After the eruption, all the buildings of the town were buried under approximately 20 meters of mud and ash. The *Casa del Bicentenario* has a large central *atrium*, two *alae*, the *tablinum*, and the *triclinium*, along the central axis. The walls are decorated with murals depicting architectural

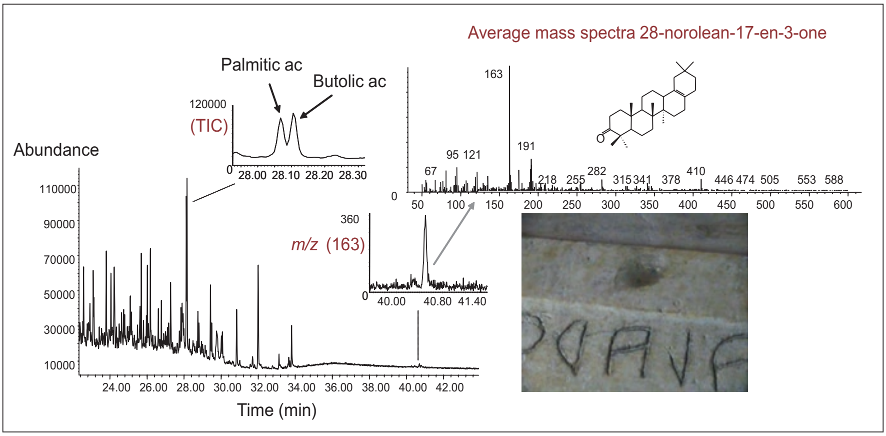

Fig. 6.2 Pyrogram of one of the Sarcophagus sample collected from the lid, with magnification of the peaks around 28 min (palmitic acid and butolic acid, shellac marker) and partial extract ion chromatogram of *m/z* 163, characteristic of the mass spectrum of 29-orlean-17en-3one (marker of mastic resin)

motives and animals, typical of the so-called artistic "Fourth Style" (50–62 AD) (Piqué et al. 2010, 2015).

A long national and international diagnostic campaign began in 2008 as part of a collaboration between the Getty Conservation Institute, the Herculaneum Conservation Project and the Parco Archeologico di Ercolano. The main aims were to identify the painting technique and compare the literature on Roman mural paintings (Andreotti et al. 2014; Casoli et al. 2006; Duran et al. 2010; Rainer et al. 2017; Berzioli and Casoli 2012; Chiantore et al. 2012), to study the plaster layering, identify the conservation issues, and develop environmental control strategies. In order to characterise the organic components of the pictorial layers, more than 20 microsamples from the mural paintings from the West and East Wall of the Tablinum were analysed by chromatographic – mass spectrometric techniques in our laboratory,

Two types of samples were analysed: raised flakes of pictorial film, and fragments that included the complete stratigraphy of the painting. An optical microscope revealed that all the samples had a translucent and brownish film on the surface – see Fig. 6.3 (layer E). The brownish film was mechanically separated from the paint fragments, and analysed by Py-GC-MS. Figure 6.3 (top) shows the extracted ion chromatogram of *m/z* 57 – characteristic mass fragment of aliphatic chains and is from the sample from the Medallion of the West Wall Tablinum. The chromatogram also highlights the presence of 15-hydroxy-hexadecanoic acid, tetracosanoic acid, long chain alcohols, and hydrocarbons. This molecular pattern is typical of beeswax (Riedo and Chiantore 2012). The wax is likely the superficial brownish layer in the cross sections, which is common to all the samples.

Since no other fixative or consolidating materials, either natural or synthetic, were detected, we hypothesized that beeswax was used as a protective layer, and that it penetrated the layers underneath through the paint layer and/or surface cracks.

The wax might have been applied to the wall paintings in undocumented restoration processes to consolidate the wall paintings and to make them shinier. In the pyrograms of all the samples collected from the decorated areas there were hexadecanenitrile and octadecanenitrile indicating the presence of egg (Orsini et al. 2017) probably used as a paint binder. Glycerol, levoglucosan, and other anhydro-sugars, which are typical pyrolysis products of a saccharide material, were also detected in all the samples (Fig. 6.3 bottom), with a chromatographic profile compatible with that of a fruit tree gum (Andreotti et al. 2009). The widespread presence of this gum might be due to its use as paint binder together with egg, or as a coating to protect the paintings. It is thus difficult to assert whether or not the saccharide material was part of the original paint layer.

The data interpretation is supported by investigations carried out on another villa in Hercolaneum, *Villa dei Papiri* (Amadori et al. 2015; Duran et al. 2010), which was discovered in 1750. What makes the wall paintings unique is that the villa was recently excavated (in 1991) and has not been restored, thus enabling the pictorial technique to be determined and the original paint materials to be investigated. The cross sections of the samples of the *Villa dei Papiri* wall painting showed a significantly less complex stratigraphy than the *Casa del Bicentenario samples*. Most interestingly, in the paintings of *Villa dei Papiri,* the brownish surface film was not

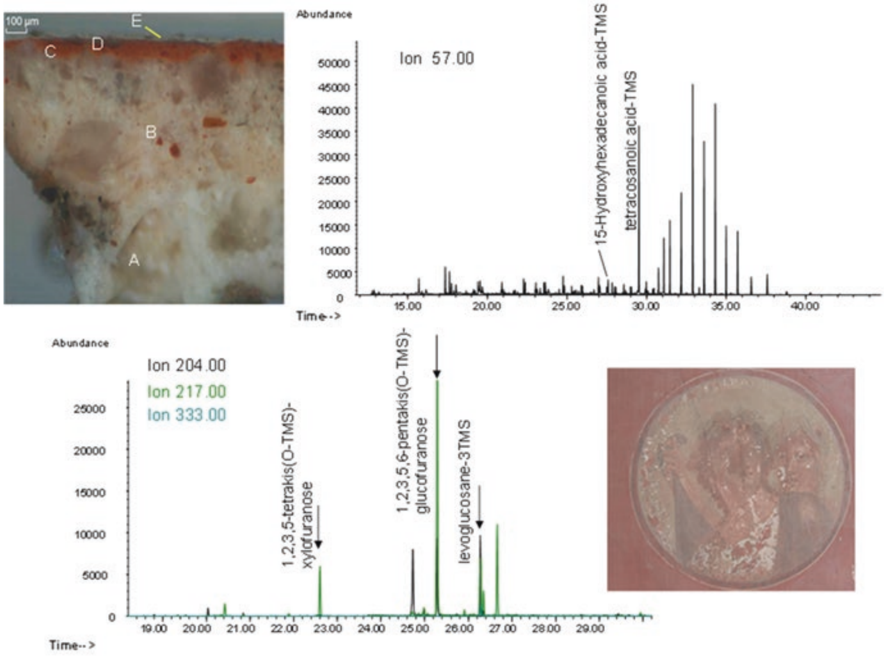

Fig. 6.3 Tablinum, West Wall – West Medallion 1 (South): cross section and extract ion chromatograms highlighting the typical beeswax (upper part, m/z 57) and saccharide (lower part, m/z 204, 217, 333) profiles

observed. Py-GC-MS evidenced the absence of beeswax. This strongly indicates that the wax layer found on the wall paintings of *Casa del Bicentenario* belongs to conservation work carried out after the excavations, which took place in the 1930s.

On the other hand, egg and a saccharide material were also detected in the paint samples from *Villa dei Papiri*, suggesting that the decorations in the two houses were painted with the same materials, and that the polysaccharides found in *Casa del Bicentenario* are original materials.

6.2.3 Hierapolis of Phrygia First-Third Century AD (Pamukkale, Denizli, Turkey)

During an archaeological campaign from 2014 to 2015 at the Hierapolis of Phrygia (Denizli, Turkey), evidence emerged of an ancient and extensive architectural restoration intervention of the Roman Imperial-era buildings. Determining the chronology of past restorations can be very difficult, and only rarely are epigraphic or stratigraphic data available. In the Hierapolis of Phrygia**,** the Corinthian portico was built in the Flavian age (68–96 AD) on the upper terrace of the Apollo Sanctuary, and the restoration work that followed the original construction consisted in a partial disassembly and reassembly of the columns and the repair and reinsertion of the capitals and decorative parts. The study of this restoration suggests that it was performed in the second or third century AD at the latest, likely following a seismic event, as suggested by the large number of interventions. The architectural blocks and the materials sampled were in an excellent state of conservation and have not been subject to any modern interventions. The type of architectural structures and the good state of these past conservation materials provided a unique opportunity to investigate the use of organic binders in ancient bonding mortars. Brocken blocks were reattached when possible, using metal cramps and dowels. In other cases, the damaged areas were mechanically removed, and replacements (in Greek *emblema*) were inserted. The composition of the adhesives used in these types of interventions was investigated, both for the large replacement parts and the small wedge-shaped *emblema.*

The mortars were investigated in the Sanctuary of Apollo, the Theatre, Temple B, the North Agora and the Ploutonion, dating back to the first to the third century AD. The analytical investigation together with the parallel archaeometric study of architectural blocks, revealed that different materials had been used simultaneously in the same monument, as in the case of the Corinthian Portico of the Apollo Sanctuary**.**

Py-GC-MS and/or EGA-MS analyses were performed on more than 20 samples (Cantisani et al. 2018). A large variety of materials was detected, above all plant oils, natural resins, beeswax, casein, egg and animal glue. In a few samples, the glues were made of a proteinaceous binder alone (egg-based or casein-based) where limited bonding was required, such as for a small section of a ‘gravity assisted position' or for small decorations even held in place by a small dowel. The analytical results of the Hierapolis' samples, however, show that the use of one single organic material as a glue was not common at the time. Materials such as beeswax, resin or animal glue, which are reported as being used often alone in ancient texts, as in the *Historia animalium* III, 10, 5, Hesychius (sv. Κόλλεα), and Pliny (H.N., 33, 30, *resina plumbo et marmori* "resin is for lead and marble"), have been mainly detected in a mixture with one or more other materials.

In most cases, in fact, many organic ingredients were combined into mixtures containing up to four different components. As an exhample, the pyrogram for one sample collected from the Sanctuary of Apollo had pyrolysis products ascribable to a lipid, and proteinaceous materials, namely a mixture of casein and smaller amounts of egg and animal glue, as well as small amounts of beeswax. The complex pyrogram with numerous olefins and aromatic compounds, is reported in extracted ion mode (Fig. 6.4). It highlights the pyrolytic maker compounds of casein (benzeneacetonitrile and indole) (Bonaduce and Colombini 2003).

The absence of diketopiperazines, and the presence of aromatic compounds can be ascribed to the fact that the proteinaceous materials are very aged, and thus extremely cross-linked (Ho and Shahidi 2005).

In summary, the following combinations were found:

- plant oil and egg;
- plant oil, egg and animal glue;
- plant oil, plant resin and egg;
- plant oil, beeswax, egg, animal glue;
- beeswax, plant resin, egg and animal glue;
- plant oil, beeswax, plant resin, egg and animal glue;
- plant oil, beeswax, plant resin, proteinaceous material.

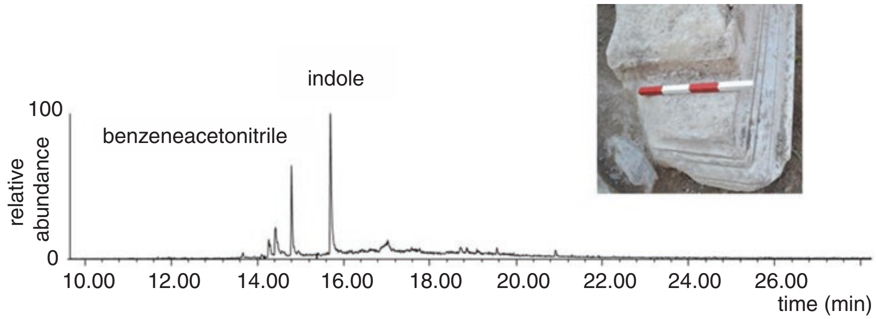

Fig. 6.4 Py-GC-MS extract ion chromatogram of m/z 90 to highlight the presence of benzeneacetonitrile and indole, markers of casein of a sample from the Sanctuary of Apollo

6.2.4 1385 AD ca – Annunciation and Saints by Giovanni del Biondo

The large polyptych *Annunciation and Saints* (406 cm × 377 cm) painted by Giovanni del Biondo (1356–1398 ca) around 1385 AD, was originally located in the sacristy of Santa Maria Novella (Florence, Italy) is now exhibited in the Galleria dell'Accademia in Florence. This masterpiece was painted in a period when egg yolk or *tempera grassa* (a mixture of oil and egg) were most commonly used as binders in panel paintings (Serefidou et al. 2016).

Although Giovanni del Biondo tended to follow the recipes provided by Cennino Cennini in his *Libro dell'Arte* (Brunello 1971) and other technical literature of his time (Brunello 1975), the surface of the panel looks unusually glossy, and is similar to the particular effects of medieval illumination and mural paintings, rather than traditional egg yolk tempera paints.

Analytical pyrolysis revealed the co-presence of different materials and identified the organic materials in the different paint layers.

The results showed that animal glue and a triterpene resin are the main constituents of those samples containing all the stratigraphy (preparation, paint layer and superficial brownish layer). Figure 6.5 shows the extracted ion pyrogram, highlighting the markers corresponding to animal glue and the plant resin. The peaks detected in the pyrogram are associated with characteristic dammar compounds: dammaredienol, ursonic acid, dammaradienone and oleanonic acid. In addition, smaller peaks, ascribable to egg yolk (Brunello 1975) and a saccharide material (Andreotti et al. 2009) were detected.

GC-MS analyses on the same samples showed that the saccharide material is honey. The pyrolysis of the material scraped from the surface containing mainly the brownish glossy layer, showed a low content of dicarboxylic acids, suggesting the absence of a lipid material, and detected the natural resin, animal glue and saccharide material. Analysis of the samples from an area that was cleaned before the sampling, showed only egg yolk and animal glue, based on the detection of hexadecanetrile and octadecanenitrile, pyrrole and alkylpyrroles (Brunello 1975). Analysis of the sample from the same cleaned area, after the preparation layer had been removed, revealed only egg.

It thus seems that del Biondo used an egg-tempera for the paint layers, applied on a ground made of using animal glue as binder. The stratigraphy is not complex, which highlights the high level of the egg-tempera technique at the turn of the fourteenth century. Lastly, the glossy surface was created using a coating made of a mixture of dammar resin, honey, and animal glue. Given that dammar resin was first introduced in Europe in around the seventeenth century, the darkened coating is likely due to past conservation work, known as a "beverone" which was commonly used to make the paint surface shinier. This interpretation is also corroborated by the absence of the coating over the areas protected by the twisted columns.

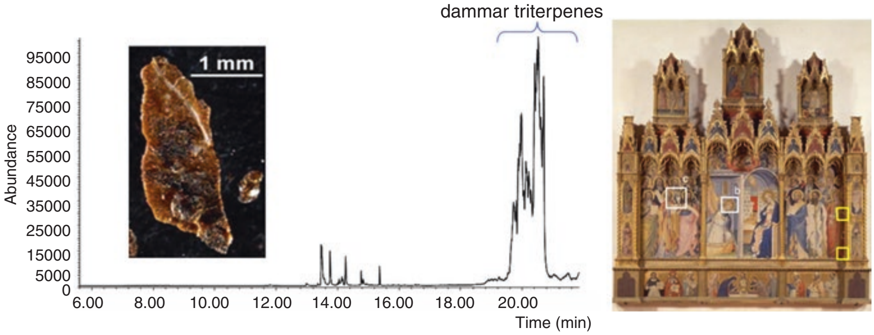

Fig. 6.5 Py-GC-MS extract ion chromatogram of m/z 189 of a sample taken from the central panel of the polyptych. The intense peaks are due to the presence of a triterpenoid resin, based on the identification of the mass spectra of oleanonic acid, ursonic acid, dammaradienol, and dammaradienone

6.2.5 Fourteenth–Seventeenth Century – Wall Paintings of the Monumental Cemetery of Pisa

The construction of the gothic cloister of the Monumental Cemetery in Pisa, also known as the *Campo Santo*, was begun in 1278 by the architect Giovanni di Simone. The walls were covered in over 2600 square meters of mural paintings (Fig. 6.6) created by an impressive number of famous artists including Francesco Traini, Buonamico di Martino da Firenze (Buonamico Buffalmacco), Spinello Aretino, Benozzo Gozzoli, Andrea Bonaiuti, Antonio Veneziano, Taddeo Gaddi, and Piero di Puccio. Due to their semi-outdoor position, the wall paintings have been subject to restorations since the fifteenth century, which became even more frequent during the eighteenth and nineteenth centuries. During the Second World War, an bomb exploded in the cemetery, burning the wood and melting the lead of the roof, thus damaging the paintings underneath. The recovery of these paintings began immediately and is still ongoing.

In 1945 the mural paintings were detached from the walls and relocated on asbestos cement supports, using a glue based on a mixture of casein and calcium hydroxide. A variety of materials were used in the post-war restorations, and already in the 1980s, the restored mural paintings had darkened, covered with efflorescence and flaking (Andreotti et al. 2008a, b). A new conservation campaign started, which is almost concluded (2021, the year of publication of the present volume). During these recent restorations, several paintings presented unexpected challenges that needed diagnostic campaigns to support conservation decisions.

An example of this complexity is the 'Giudizio Universale' by Bonamico Buffalmacco (Andreotti et al. 2008a; Bonaduce and Colombini 2003). The paint surface of a section of this mural was completely waterproof, preventing any restoration attempt using traditional approaches. Py-GC-MS analyses revealed the simultaneous presence of several materials. An example of the complexity of the

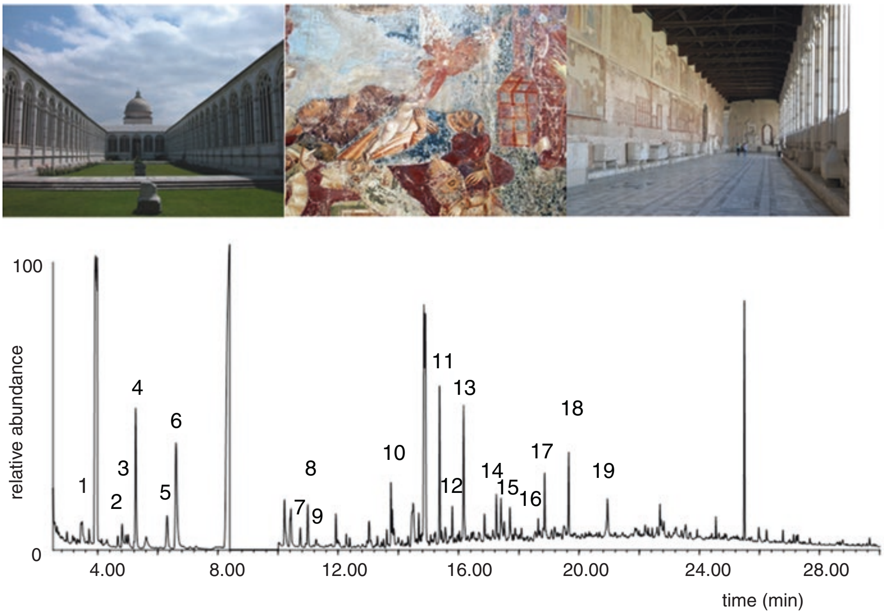

Fig. 6.6 Py-GC-MS chromatogram of one sample from the ‘Giudizio Universale’ by Bonamico Buffalmacco, Monumental Cemetery in Pisa. The TMS derivatives compounds identified are: 1: Benzene, 2: Ethyl acrylate, 3: Methyl methacrylate, 4: Acetic acid, 5: Pyrrole, 6: Toluene, 7: 2-Methylpyrrole, 8: 3-Methylpyrrole, 9: Benzaldehyde, 10: Phenol, 11: 2-Methylphenol, 12: 4-Methylphenol, 13: 2,4-Dimethylphenol, 14: benzene acetonitrile, 15: 3-Phenylpropionitrile, 16: Indole, 17: Phthalate, 18: Phthalate, 19: Benzyl benzoate

pyrograms obtained is shown in Fig. 6.6. Ethyl acrylate, methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, and butyl methacrylate were detected, unevenly distributed on the surface of the ‘Giudizio Universale’, and ascribable to Primal and Elvacite, two acrylic resins used in an attempt to detach the painting from the support.

Pyrolysis products derived from egg yolk, casein, and animal glue were also detected in the chromatograms. Hexadecanenitrile, octadecanenitrile, cholesterol derivatives, and carboxylic acids are the characteristic pyrolysis products used for egg yolk, indole for casein, whereas pyrrole, alkyl pyrroles, benzyl nitrile and 3-phenylpropionitrile are used for animal glue (Andreotti et al. 2008a, b). Egg yolk had been used possibly as a paint binder, or in a past conservation treatment. Casein and animal glue belong to post-war conservation interventions. Polyvinylacetate was also detected, based on the detection of high relative amounts of acetic acid trimethylsilyl ester, benzene and other aromatic compounds. This synthetic material also belongs to the post-war restoration. The presence in the pyrogram of high amounts of phenols, pointed to the presence of a phenol-formaldehyde resin. This material is not documented and it is not a conservation material. The hypothesis is that copolymerisation occurred between the casein (the glue between the paint layer and the canvas) and polyvinyl acetate (the glue placed between the canvas and the asbestos support), producing a phenol-formaldehyde-like material. Copolymerisation probably occurred due to the addition of formaldehyde to the casein glue, as an antimicrobial agent, which explains the high hydrophobicity of the paint surface.

6.2.6 *Sixteenth Century Madonna con Bambino, Giovanni Pietro Rizzoli*

The range of synthetic materials used by restorers over the last few decades has expanded significantly. A variety of modern materials have been tested based on different optical properties and durability, as well as solubility and performance, and their identification in an artwork contributes to reconstruct its history. In particular, modern varnishes include low molecular weight resins, and the two most common classes in conservation practice are hydrogenated hydrocarbon resins and urea-aldehyde resins.

Regalrez 1094 is a hydrocarbon resin synthesized from vinyl-toluene and α-methyl-styrene and subsequent hydrogenation of the unsaturated polymer. The Py-GC-MS profile of this resin is characterized by three different peak clusters, the first associated with the monomers of cyclohexane and cyclohexene, and another two at a higher retention time associated with cyclohexane dimers and trimers. Figure 6.7 reports the profile of a sample from a restored sixteenth century painting by Giovanni Pietro Rizzoli, part of the The Sander Collection, in which the three clusters of pyrolysis products of Regalrez 1094 are clearly visible.

6.3 Py-GC-MS Analysing Modern Paint Materials

In the twentieth century a wide range of synthetic materials were introduced as artists' media. The first commercial formulation of acrylic resin was marketed in the 1950s, and consisted of acrylic polymers dissolved in organic solvents, such as toluene and xylene. The evolution of the formulations and synthetic processes used to produce acrylic resins led to the introduction in the 1970s to copolymers based on different acrylic monomers, together with other monomeric species, such as styrene. This enabled producers to formulate acrylic resins for use as aqueous emulsions, which are still in use today.

Analysing the chemical structure of the acrylic resins, in order to clarify whether they were applied as emulsions or as solvent resins, and identifying specific additives, such as modern plasticizers or surfactants, is extremely useful in dating modern paints and detecting possible forgeries.

Py-GC-MS is the preferred method in the analysis of synthetic paints (Learner 2004).

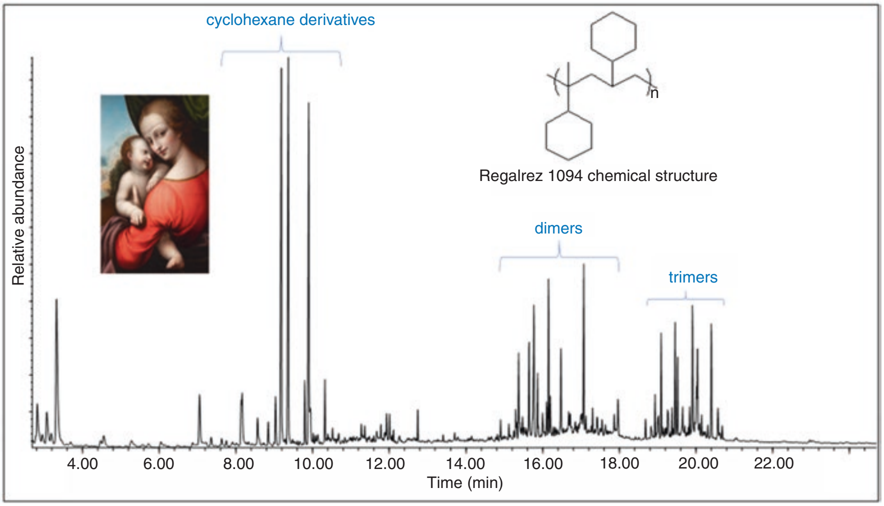

Fig. 6.7 Py-GC-MS profile of a sample from a sixteenth century painting by Giovanni Pietro Rizzoli (The Sander Collection) showing the presence of the modern varnish Regalrez 1094

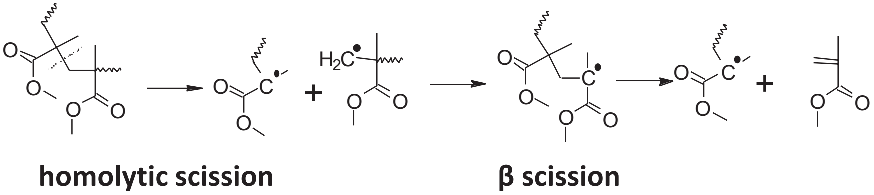

Fig. 6.8 Example of the unzipping pyrolysis mechanism of a generic acrylic resin

Acrylic resins undergo unzipping mechanism upon pyrolysis, which is a radical mechanism of thermal cleavage whereby the polymer is converted into the respective monomers. As an example, Fig. 6.8 reports the unzipping of a generic acrylic resin.

Acrylic resins with formulations compatible with the use of solvent paints have been detected in the works of several Italian artists. For example, Py-GC-MS analyses of *Superficie 207* (1957), a painting by Giuseppe Capogrossi (Galleria Nazionale di Arte Moderna, Rome), showed the presence of a resin based on ethyl acrylate (Fig. 6.9). Ethylacrylate was commonly used in the first formulations of acrylic resins dissolved in solvents (La Nasa et al. 2020).

Examples of acrylic formulations compatible as emulsions were detected in Anselm Kiefer’s “Cette Obscure Clarté qui Tombe des Etoiles” dated 1996 (Fig. 6.10), which contained styrene-acrylic copolymers typically used in these formulations (Bartolozzi et al. 2016; Pellegrini et al. 2013). This type of resin was identified due to the presence in the pyrolysis profile of both the monomers, n-butyl acrylate and styrene, together with the corresponding dimers and trimers. This was confirmed by the absence of the characteristic homo-oligomers, which are instead associated with polystyrene and n-butyl acrylate homopolymers. This formulation is one of the most common acrylic copolymers produced as an aqueous emulsion and used in several other applications as well as painting.

The same formulation based on *n*-butyl acrylate modified with styrene has also been detected as a paint binder in outdoor murals such as Tuttomondo (1989) in Pisa (La Nasa et al. 2016, 2021). Other common acrylic emulsions are produced by the copolymerization of different monomers, such as methyl acrylate, methyl methacrylate and ethyl acrylate, which have different commercial names, such as the families of Paraloid, Plextol and Primal (Osete-Cortina and Doménech-Carbó 2006). This type of resin is identified by both the pyrolysis markers characteristic of the monomers and their relative combined oligomers. Interestingly, acrylic emulsions are not only produced using copolymers. The analysis of the work of art "*The Italian Flag*" by Fernando Melani (1955–1960) revealed an ethylhexyl-acrylate homopolymer, identified by the monomer together with 2-hexanol, and 2-ethyl hexanol (Carlesi et al. 2016). This type of resin is generally applied as an aqueous emulsion. Polyvinlylacetate, when subject to pyrolysis, undergoes a two-step elimination process. The cleavage starts with a concerted mechanism that involves two adjacent carbon atoms to produce a double bond. The second step in the reaction leads to chain scission and aromatization reactions. Figure 6.11 shows the elimination reaction characteristic of polyvinyl resins.

Pure PVAc is too hard to form a film from an emulsion, thus the paint formulations contain massive amounts of plasticizers. These plasticizers are usually the most abundant in the pyrolysis profile of PVAc and can be divided into: external plasticizers, such as phthalate esters, and internal plasticizers, such as VeoVa (vinylversatate esters), copolymerized with the PVAc monomer (Learner 2001; Silva et al. 2010).

Polyvinyl acetate used as a paint binder has been detected in several works of art. For example, PVAc was detected in the paint samples from the "*La Caverna*

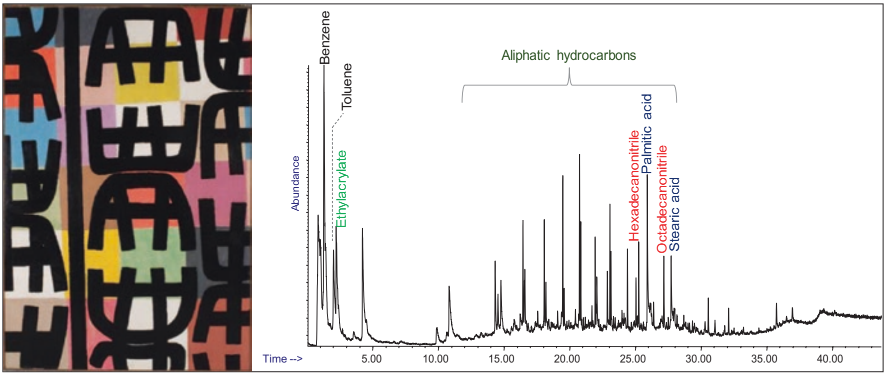

Fig. 6.9 Py-GC-MS chromatogram for a paint sample from "Superficie 207" (1957) by Giuseppe Capogrossi (La Nasa et al. 2020)

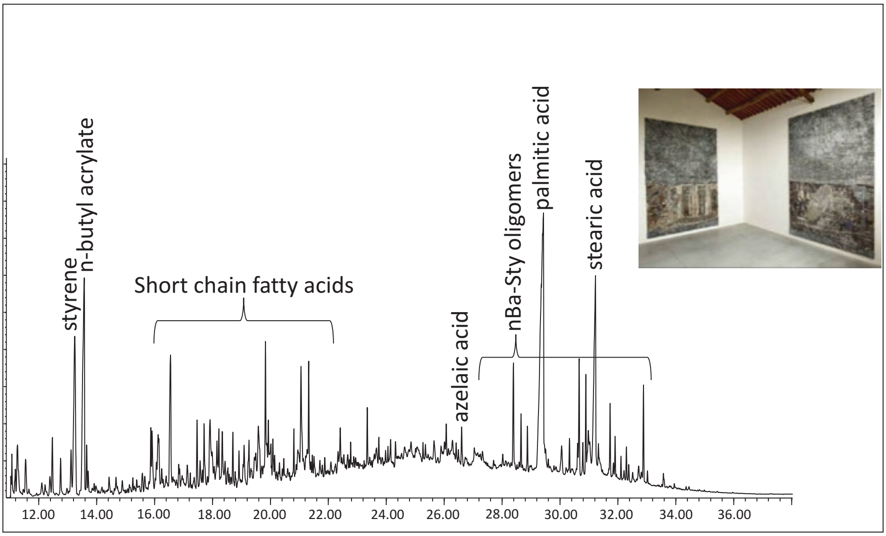

Fig. 6.10 Py-GC-MS profile of a paint sample from "Cette Obscure Clarté qui Tombe des Etoiles"(1996) by Anselm Kiefer (Pellegrini et al. 2013)

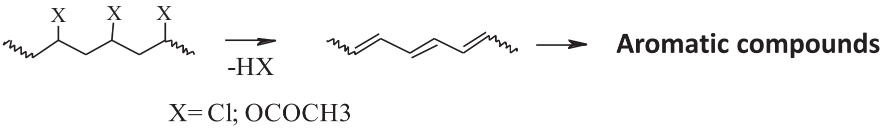

Fig. 6.11 The elimination reaction characteristic of the pyrolysis of polyvinyl resins

dell'Antimateria" (1958–1959) by Pinot Gallizzio (Bartolozzi et al. 2014). The pyrolytic profiles of the samples were characterized by the presence of acetic acid, benzene, and the aromatic species characteristic of the pyrolysis of this material (indene, naphthalene, fluorene and, anthracene), which were generally found with relatively high amounts of external plasticizers (phthalates) (Fig. 6.12). Several commercial materials containing PVAc were identified in the painting materials stored in two of the artist's former studios (Gottschaller et al. 2012).

Py-GC-MS can also be used to detect PVAc mixed with other synthetic polymers. Multi-shot analytical pyrolysis on the samples from the artworks Disgelo (Piero Gilardi, 1968) and Superficie Lunare (Giulio Turcato, 1969) showed how powerful this approach is in differentiating between different types of polymers: the polyurethane used in the 3D structure, from the paint binder on the surface, based on PVAc (Fig. 6.13) (Zuena et al. 2020).

PVAc is also often encountered as a paint binder in outdoor murals, such as those produced by Keith Haring in the Necker Hospital mural in Paris painted in 1987. Py-GC-MS analyses showed that Haring used a PVAc paint binder with VeoVa as an internal plasticizer (La Nasa et al. 2016, 2021).

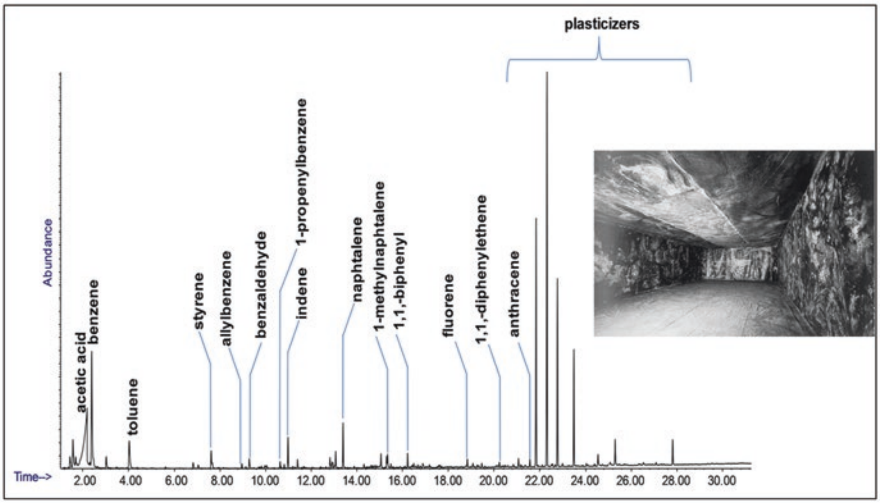

Fig. 6.12 Py-GC-MS profile of a paint sample from “La Caverna dell’Antimateria” (1958–1959) by Pinto Gallizio (Bartolozzi et al. 2014)

Another important class of resins is **alkyd resins**. These resins, often referred to as “smalts” when used in art, consist of oil-modified polyesters synthesized from polyols, aromatic polybasic acids, with different oil contents (or a source of fatty acids) (Fig. 6.14). They have been used as commercial binders for paints and coatings since the 1940s (Ploeger et al. 2008).

The pyrolysis profiles of alkyd paints are similar to drying oils, due to the acylglycerol/fatty acid portion in the polymer network. However, the presence of pyrolysis products related to the polyols and aromatic polybasic acid portion of the resin distinguishes them from drying oils.

Given that the formulation of alkyd resins has been modified over the years, their characterization by analytical pyrolysis is key to understanding painting techniques and to identifying forgeries (La Nasa et al. 2021). More recent alkyd formulations are characterized by specific components, such as styrene, which distinguish them from the first alkyds based mainly on lipids.

Pablo Picasso and Jackson Pollock are good examples of painters who used alkyd paints. The analysis of Pablo Picasso’s *Nude Woman in a Red Armchair* (1932) showed the presence of fatty acids, dicarboxylic acids, glycerol, and phthalic anhydride, which are characteristic markers of alkyds (Cappitelli and Koussiaki 2006). The same pyrolysis markers associated with the use of alkyd resin were detected in a paint sample from Pollock’s *Yellow Island* (1952).

Alkyd resins have also been detected in *Superficie 207* (1957) by Giuseppe Capogrossi (La Nasa et al. 2020), amongst other Italian artists, where an alkyd resin was used in a mixture with a styrene resin (Figs. 6.14 and 6.15), thus highlighting the use of analytical pyrolysis to detect more than one paint binder in the same

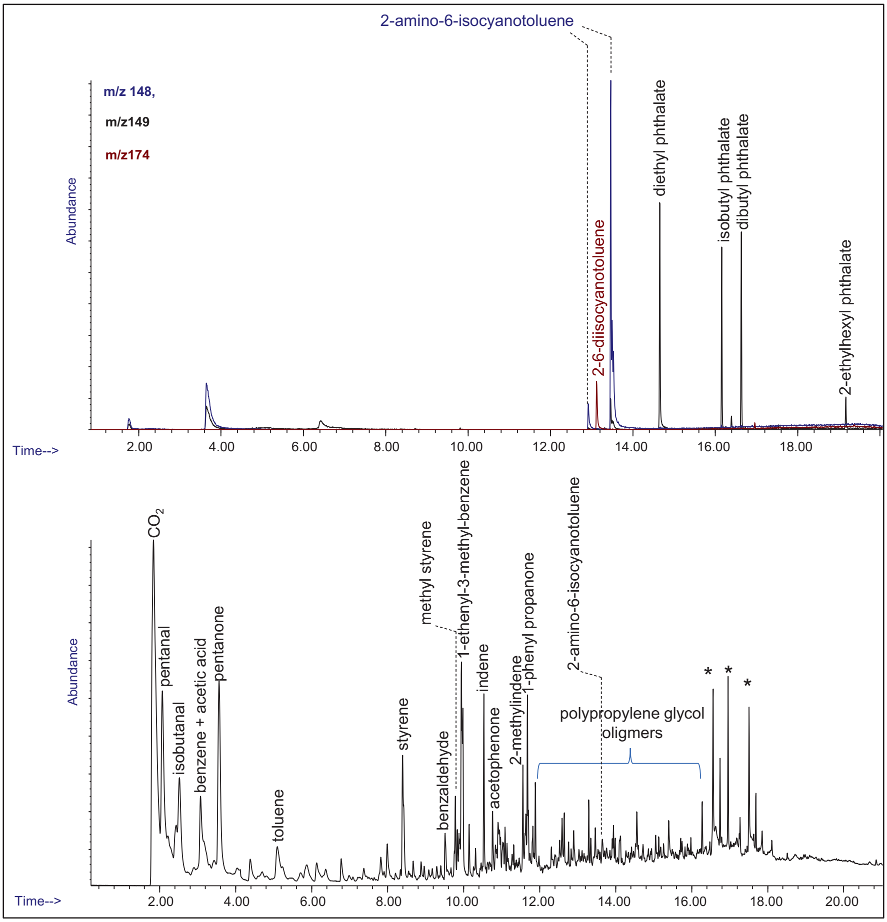

Fig. 6.13 Py-GC-MS chromatograms obtained at 350 °C and 600 °C by a double shot approach on a paint sample from “Superficie Lunare” (1969) by Giulio Turcato (Zuena et al. 2020)

sample. Finally, several alkyd resins have been identified in the commercial painting materials stored in Lucio Fontana’s former studios (Cappitelli 2004).

As with the other classes of paint binders mentioned in this chapter, alkyds have also been used in outdoor murals. For example, an alkyd resin paint binder was detected in the samples from Keith Haring’s mural in Collingwood (1984), Melbourne (La Nasa et al. 2016, 2021).

In the last few years, low molecular weight urea-aldehyde resins have been introduced as paint binders in retouch paints. Although the nature of the monomers used in synthesizing these classes of resins is generally known, the specific synthetic pathways and the final chemical composition of the materials are patented and thus such information is not publicly available. Tentative structure elucidations together with their relative mass spectra have been published in the literature for Laropal

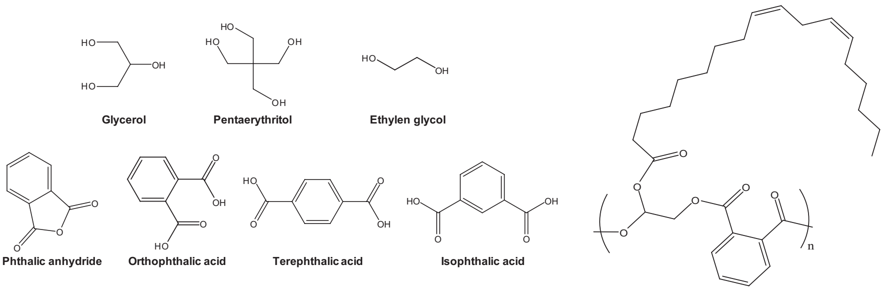

Fig. 6.14 Polyols and polybasic acids used in artistic alkyd paint formulations, and model structure of alkyd resin containing phthalic anhydride, glycerol, and linoleic acid

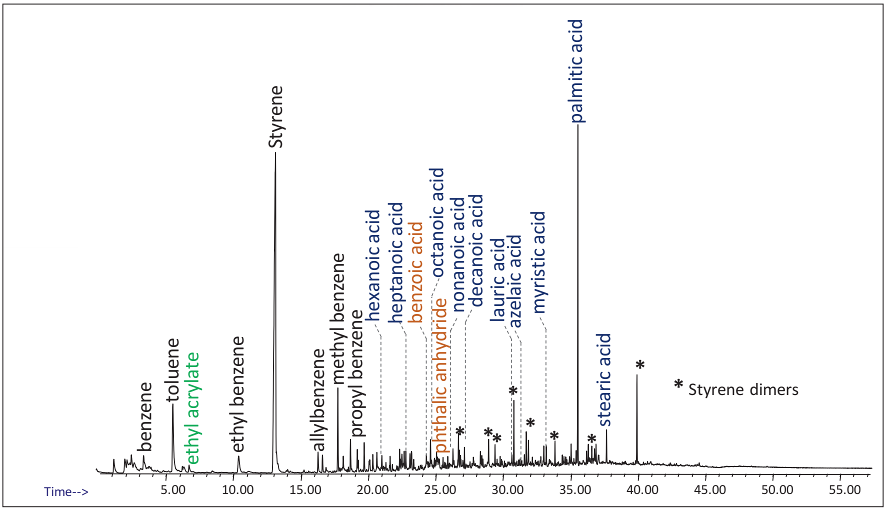

Fig. 6.15 Py-GC-MS chromatogram of a paint sample from "Superficie 207" (1957) by Giuseppe Capogrossi (La Nasa et al. 2020)

A81 (Bonaduce et al. 2013) (Fig. 6.16). This information can be used to detect these polymers in paint samples, highlighting retouches in the paintings.

6.4 Characterization of Organic Pigments

Besides the characterization of the paint binders, analytical pyrolysis can also be used to characterize organic pigments. Identifying pigments is crucial to improve the knowledge of an artwork, its historical context, and painting technique. In the nineteenth century organic pigments were continuously being developed, each characterized by a specific synthesis and commercialization year. Knowing the type of

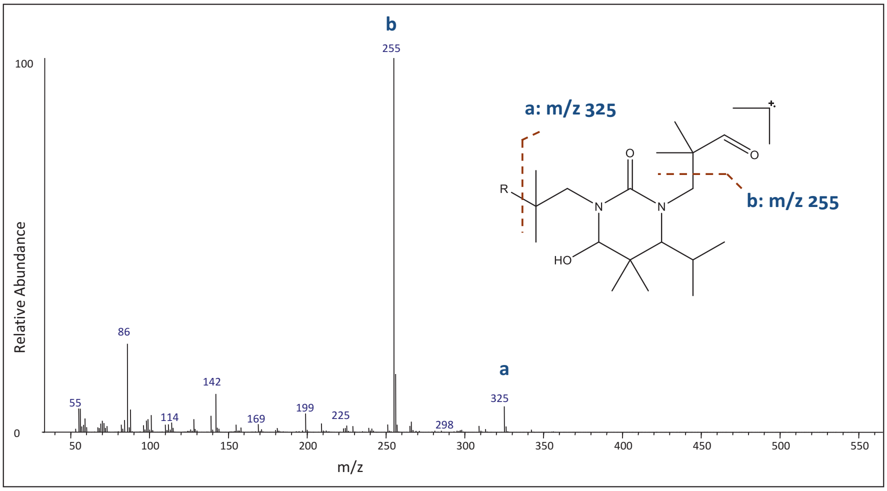

Fig. 6.16 Mass spectra (EI) of the most abundant pyrolysis products of the resin Laropal A81 (Bonaduce et al. 2013)

organic pigment may also help to solve authenticity, attribution, and conservation problems.

Py-GC-MS has been applied for the characterization and ageing of several classes of organic pigments: β-naphthol pigment lakes, BONA pigment lakes, disazopyrazolone, triarylcarbonium, dioxazine, anthraquinone, indanthrone, isoindoline, and thioindigo (Ghelardi et al. 2015; Russell et al. 2011). Each pigment has specific pyrolysis markers that can be used to identify these chemical species in paint samples.

Good examples of analytical pyrolysis are the results obtained for the identification of the organic pigments used by Francis Bacon, Clyfford Still, and Jackson Pollock in their paintings (Ghelardi et al. 2015; Russell et al. 2011).

A list of all the organic pigments that can currently be identified by Py-GC-MS is reported in Table 6.1 (Ghelardi et al. 2015; Russell et al. 2011).

6.5 Conclusions

The case studies illustrated in this chapter demonstrate how Py-GC-MS is extremely efficient at identifying both natural and synthetic artistic materials, in a wide range of molecular weights, including synthetic resins that are not suitable for investigation by conventional GC-MS.

The material analysis of an artwork constitutes a complementary and fundamental tool in the authentication of an artwork. This is because the chemical analysis and identification of paint materials provide important information on the artistic technique, which is essential in relation to attribution and dating issues.

Table 6.1 The organic pigments that can currently be identified by Py-GC-MS (Ghelardi et al. 2015; Russell et al. 2011)

Red	PR1, PR3, PR4, PR5, PR6, PR7, PR9, PR12, PR14, PR17, PR22, PR23, PR31, PR41, PR48:1, PR48:2, PR49:1, PR49:2, PR52:1, PR53:1, PR57:1, PR63:1, PR83, PR90, PR112, PR123, PR144, PR147, PR149, PR166, PR170, PR175, PR176, PR178, PR179, PR185, PR188, PR190, PR208, PR214, PR221, PR254, PR255, PR264
Orange	PO16, PO36, PO46, PO61, PO62, PO73
Violet	PV1, PV3, PV19, PV23, PV27, PV32, PV37, PV39, PV42, PV44, PV51, PV52, PV53
Green	PG7, PG8, PG10, PG13, PG36
Brown	PBr23, PBr25, PBr38, PBr41
Blue	PB1, PB15:0, PB15:1, PB15:2, PB15:3, PB15:4, PB15:6, PB17, PB60, PB62, PB76
Yellow	PY1, PY2, PY3, PY6, PY12, PY13, PY14, PY17, PY55, PY65, PY73, PY74, PY75, PY81, PY87, PY97, PY109, PY110, PY120, PY126, PY127, PY151, PY154, PY173, PY175

Cross-checking the information obtained from the chemical analysis of paint materials with knowledge on the history and evolution of artistic techniques – not only over centuries but also decades as in the twentieth century – helps to date a painting or identify a forgery if any anachronistic materials are detected. When the object of study concerns modern and contemporary art, the chemical analysis of the materials used in an artist's workshop also provides a valuable source of additional information for cross-reference in order to reinforce or confirm possible attributions.

Acknowledgements The authors are grateful to all the conservators, curators and conservation scientists that collaborated to the researches described in the chapter, and contributed to the publication of the results in the cited references. The Sander Collection, the restorer Stefano Ticci, and Adarte (Florence) are kindly acknowledged for providing the varnish sample from the Madonna con Bambino by Giovanni Pietro Rizzoli, and for allowing us to include the analytical results in this contribution.

References

Amadori, M.L., Barcelli, S., Poldi, G., Ferrucci, F., Andreotti, A., Baraldi, P., Colombini, M.: Invasive and non-invasive analyses for knowledge and conservation of Roman wall paintings of the Villa of the Papyri in Herculaneum. Microchem. J. **118**, 183–192 (2015)

Andreotti, A., Bonaduce, I., Colombini, M., Modugno, F.: in Sarcofago delle Amazzoni. In: Bottini, A., Setari, E. (eds.) Le componenti organiche della pittura, pp. 157–162. Mondatori Electa, Milano (2007)

Andreotti, A., Baracchini, C., Bonaduce, I., Caleca, A., Colombini, M., Paolucci, A.: *Saving the Medieval Paintings by the Master Painter of the Triumph of Death in Pisa*. Paper presented at the Proceedings of 2008 ICOM-CC Triennial Conference (2008a)

Andreotti, A., Bonaduce, I., Colombini, M.P., Modugno, F., Ribechini, E.: Characterisation of natural organic materials in paintings by GC/MS analytical procedures. In: New Trends in Analytical, Environmental and Cultural Heritage Chemistry, pp. 389–423 (2008b)

Andreotti, A., Bonaduce, I., Colombini, M.P., Modugno, F., Ribechini, E.: A diagnosis of the yellowing of the marble high reliefs and the black decorations in the chapel of the tomb of Saint Anthony (Padua, Italy). Int. J. Mass Spectrom. **284**(1–3), 123–130 (2009)

Andreotti, A., Bonaduce, I., Colombini, M.P., Degano, I., Lluveras, A., Modugno, F., Ribechini, E.: Characterisation of natural substances in ancient polychromies. In: Liverani, P., Santamaria, U. (eds.) Diversamente bianco-La policromia della scultura romana, pp. 191–206. Edizioni Quasar, Roma (2014)

Bartolozzi, G., Cucci, C., Marchiafava, V., Masi, S., Picollo, M., Grifoni, E., et al.: A multidisciplinary approach to the investigation of “La Caverna dell’Antimateria” (1958–1959) by Pinot Gallizio. Herit. Sci. **2**(1), 29 (2014). https://doi.org/10.1186/s40494-014-0029-7

Bartolozzi, G., Picollo, M., Marchiafava, V., Centeno, S.A., Duvernois, I., Di Girolamo, F., et al.: Anselm Kiefer: a study of his artistic materials. Archaeol. Anthropol. Sci. **8**(3), 563–574 (2016). https://doi.org/10.1007/s12520-015-0238-3

Berzioli, M., Casoli, A.: FTIR spectroscopy as a fingerprint for waxes. In: Omarini, S. (ed.) Encaustic. History, Technique and Research, pp. 154–155. Nardini Ed (2012)

Bocchini, P., Traldi, P.: Organic mass spectrometry in our cultural heritage. J. Mass Spectrom. **33**(11), 1053–1062 (1998)

Bonaduce, I., Andreotti, A.: Py-GC/MS of organic paint binders. In: Organic Mass Spectrometry in Art and Archaeology, pp. 304–326. Wiley (2009)

Bonaduce, I., Colombini, M.P.: Gas chromatography/mass spectrometry for the characterization of organic materials in frescoes of the Momumental Cemetery of Pisa (Italy). Rapid Commun. Mass Spectrom. **17**(22), 2523–2527 (2003)

Bonaduce, I., Colombini, M.P., Degano, I., Di Girolamo, F., La Nasa, J., Modugno, F., Orsini, S.: Mass spectrometric techniques for characterizing low-molecular-weight resins used as paint varnishes. Anal. Bioanal. Chem. **405**(2), 1047–1065 (2013). https://doi.org/10.1007/s00216-012-6502-9

Bonaduce, I., Ribechini, E., Modugno, F., Colombini, M.P.: Analytical approaches based on gas chromatography mass spectrometry (GC/MS) to study organic materials in artworks and archaeological objects. Top. Curr. Chem. **374**(1), 6 (2016)

Bottini, A., Setari, E.: Il sarcofago delle Amazzoni. Electa, Milano (2007)

Brecoulaki, H., Zaitoun, C., Stocker, S.R., Davis, J.L., Karydas, A.G., Colombini, M.P., Bartolucci, U.: An Archer from the Palace of Nestor: a new wall-painting fragment in the Chora Museum. Hesperia. **77**(3), 363–397 (2008)

Brecoulaki, H., Andreotti, A., Bonaduce, I., Colombini, M.P., Lluveras, A.: Characterization of organic media in the wall-paintings of the “Palace of Nestor” at Pylos, Greece: evidence for a Secco painting techniques in the Bronze Age. J. Archaeol. Sci. **39**(9), 2866–2876 (2012)

Brecoulaki, H., Sotiropoulou, S., Perdikatsis, V., Lluveras-Tenorio, A., Bonaduce, I., Colombini, M.P., Tournavitou, I.: Appendix A: a technological investigation of the painting materials. In: The Wall Paintings of the West House at Mycenae, vol. 54, pp. 147–158. INSTAP Academic Press (2017)

Brunello, F.: Il Libro dell’Arte di C. Cennini, p. 589. Neri Pozza Editore, Vicenza (1971)

Brunello, F.: De arte illuminandi e altri trattati sulla tecnica della miniatura medievale. N. Pozza, Vicenza (1975)

Cantisani, E., Vettori, S., Andreotti, A., Ismaelli, T.: Ancient restorations at Hierapolis: research on the artificial binders. In: Ismaelli, T., Scardozzi, G. (eds.) Ancient Quarries and Building Sites in Asia Minor: Research on Hierapolis in Phrygia and Other Cities in South-Western Anatolia: Archaeology, Archaeometry, Conservation. Bari Edipuglia (2018)

Cappitelli, F.: THM-GCMS and FTIR for the study of binding media in Yellow Islands by Jackson Pollock and Break Point by Fiona Banner. J. Anal. Appl. Pyrolysis. **71**(1), 405–415 (2004). https://doi.org/10.1016/S0165-2370(03)00128-1

Cappitelli, F., Koussiaki, F.: THM-GCMS and FTIR for the investigation of paints in Picasso’s still life, weeping woman and nude woman in a Red Armchair from the Tate Collection, London. J. Anal. Appl. Pyrolysis. **75**(2), 200–204 (2006). https://doi.org/10.1016/j.jaap.2005.05.008

Carlesi, S., Bartolozzi, G., Cucci, C., Marchiafava, V., Picollo, M., La Nasa, J., et al.: Discovering "The Italian Flag" by Fernando Melani (1907–1985). Spectrochim. Acta A Mol. Biomol. Spectrosc. **168**, 52–59 (2016). https://doi.org/10.1016/j.saa.2016.05.027

Casoli, A., Violante, C., Mastrobattista, E., Santoro, S.: Le pitture dell'Insula del Centenario a Pompei: Le indagini sulle sostanze organiche. Paper presented at the IV Congresso nazionale di Archeometria, Pisa (2006)

Chiantore, O., Riedo, C., Andreotti, A., Colombini, M.P., Lluveras, A., Tenorio, et al.: Organic materials in the wall paintings of the Vesuvian area. In: Omarini, S. (ed.) Encaustic. History, Technique and Research, pp. 41–122. Nardini Ed (2012)

Cotte, M., Susini, J., Solé, V.A., Taniguchi, Y., Chillida, J., Checroun, E., Walter, P.: Applications of synchrotron-based micro-imaging techniques to the chemical analysis of ancient paintings. J. Anal. At. Spectrom. **23**(6), 820–828 (2008)

Degano, I., La Nasa, J.: Trends in high performance liquid chromatography for cultural heritage. Top. Curr. Chem. **374**(2), 20 (2016)

Degano, I., Modugno, F., Bonaduce, I., Ribechini, E., Colombini, M.P.: Recent advances in analytical pyrolysis to investigate organic materials in heritage science. Angew. Chem. Int. Ed. **57**(25), 7313–7323 (2018)

Duran, A., Jimenez De Haro, M., Perez-Rodriguez, J., Franquelo, M., Herrera, L., Justo, A.: Determination of pigments and binders in Pompeian wall paintings using synchrotron radiation–high-resolution X-ray powder diffraction and conventional spectroscopy–chromatography. Archaeometry. **52**(2), 286–307 (2010)

Fiorillo, F., Hendriks, L., Hajdas, I., Vandini, M., Huysecom, E.: The rediscovery of Jan Ruyscher and its consequence. J. Am. Inst. Conserv., 1–9 (2021). https://doi.org/10.1080/01971360.2020.1822702

Ghelardi, E., Degano, I., Colombini, M.P., Mazurek, J., Schilling, M., Learner, T.: Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples. Anal. Bioanal. Chem. **407**(5), 1415–1431 (2015)

Gottschaller, P., Khandekar, N., Lee, L.F., Kirby, D.P.: The evolution of Lucio Fontana's painting materials. Stud. Conserv. **57**(2), 76–91 (2012). https://doi.org/10.1179/2047058411Y.0000000002

Hendriks, L., Hajdas, I., Ferreira, E.S., Scherrer, N.C., Zumbühl, S., Küffner, M., et al.: Combined 14 C analysis of canvas and organic binder for dating a painting. Radiocarbon. **60**(1), 207–218 (2018)

Hendriks, L., Hajdas, I., Ferreira, E.S., Scherrer, N.C., Zumbühl, S., Küffner, M., et al.: Selective dating of paint components: radiocarbon dating of lead white pigment. Radiocarbon. **61**(2), 473–493 (2019a)

Hendriks, L., Hajdas, I., Ferreira, E.S., Scherrer, N.C., Zumbühl, S., Smith, G.D., et al.: Uncovering modern paint forgeries by radiocarbon dating. Proc. Natl. Acad. Sci. **116**(27), 13210–13214 (2019b)

Ho, C.-T., Shahidi, F.: Flavor components of fats and oils. In: Bailey's Industrial Oil and Fat Products (2005). https://doi.org/10.1002/047167849X.bio009

Hodgins, G.W.L.: Identifying art forgeries by radiocarbon dating microgram quantities of artists' paints. Proc. Natl. Acad. Sci. **116**(27), 13158–13160 (2019). https://doi.org/10.1073/pnas.1907933116

La Nasa, J., Orsini, S., Degano, I., Rava, A., Modugno, F., Colombini, M.P.: A chemical study of organic materials in three murals by Keith Haring: a comparison of painting techniques. Microchem. J. **124**, 940–948 (2016). https://doi.org/10.1016/j.microc.2015.06.003

La Nasa, J., Moretti, P., Maniccia, E., Pizzimenti, S., Colombini, M.P., Miliani, C., et al.: Discovering Giuseppe Capogrossi: study of the painting materials in three works of art stored at Galleria Nazionale (Rome). Heritage. **3**(3) (2020). https://doi.org/10.3390/heritage3030052

La Nasa, J., Campanella, B., Sabatini, F., Rava, A., Shank, W., Lucero-Gomez, P., et al.: 60 years of street art: a comparative study of the artists' materials through spectroscopic and mass spectrometric approaches. J. Cult. Herit. **48**, 129–140 (2021). https://doi.org/10.1016/j.culher.2020.11.016

Learner, T.: The analysis of synthetic paints by pyrolysis-gas chromatography-mass spectrometry (PyGCMS). Stud. Conserv. **46**(4), 225–241 (2001). https://doi.org/10.1179/sic.2001.46.4.225

Learner, T.: Analysis of Modern Paints. Getty Publications (2004)

Linn, R., Bonaduce, I., Ntasi, G., Birolo, L., Yasur-Landau, A., Cline, E.H., et al.: Evolved gas analysis-mass spectrometry to identify the earliest organic binder in Aegean style wall paintings. Angew. Chem. **130**(40), 13441–13444 (2018)

Orsini, S., Parlanti, F., Bonaduce, I.: Analytical pyrolysis of proteins in samples from artistic and archaeological objects. J. Anal. Appl. Pyrolysis. **124**, 643–657 (2017). https://doi.org/10.1016/j.jaap.2016.12.017

Osete-Cortina, L., Doménech-Carbó, M.T.: Characterization of acrylic resins used for restoration of artworks by pyrolysis-silylation-gas chromatography/mass spectrometry with hexamethyldisilazane. J. Chromatogr. A. **1127**(1–2), 228–236 (2006)

Pellegrini, D., Modugno, J.L.N.F., di Girolamo, F., Colombini, M.P.: Indagini scientifiche su Cette obscure clartè qui tombe des étoiles di Anselm Kiefer. EDIFIR, Florence (2013)

Piqué, F., Chiari, G., Colombini, M.P., Torraca, G.: I dipinti murali della Casa del Bicentenario ad Ercolano: Degrado e prevenzione. In: Driussi, G.B.A.G. (ed.) Scienza e Beni Culturali, vol. 26, pp. 837–847. Arcadia Ricerche, Marghera (2010)

Piqué, F., Macdonald-Korth, E., Rainer, L.: Observations on materials and techniques used in Roman wall paintings of the tablinum, House of the Bicentenary at Herculaneum. In: Beyond Iconography: Materials, Methods, and Meaning in Ancient Surface Decoration. Selected Papers on Ancient Art and Architecture, pp. 57–76. Archaeological Institute of America, Boston (2015)

Ploeger, R., Scalarone, D., Chiantore, O.: The characterization of commercial artists' alkyd paints. J. Cult. Herit. **9**(4), 412–419 (2008)

Rainer, L., Graves, K., Maekawa, S., Gittins, M., Piqué, F.: Conservation of the Architectural Surfaces in the Tablinum of the House of the Bicentenary, Herculaneum Phase I: Examination, Investigations, and Condition Assessment. Getty Conservation Institute, Los Angeles (2017)

Riedo, B., Chiantore, O.: Py-GC/MS to evaluate waxy materials. In: Omarini, S. (ed.) Encaustic. History, Technique and Research, pp. 156–158. Nardini Ed (2012)

Roldán, C., Murcia-Mascarós, S., López-Montalvo, E., Vilanova, C., Porcar, M.: Proteomic and metagenomic insights into prehistoric Spanish Levantine Rock Art. Sci. Rep. **8**(1), 1–10 (2018)

Russell, J., Singer, B.W., Perry, J.J., Bacon, A.: The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography–mass spectrometry. Anal. Bioanal. Chem. **400**(5), 1473 (2011). https://doi.org/10.1007/s00216-011-4822-9

Serefidou, M., Bracci, S., Tapete, D., Andreotti, A., Biondi, L., Colombini, M.P., et al.: Microchemical and microscopic characterization of the pictorial quality of egg-tempera polyptych, late 14th century, Florence, Italy. Microchem. J. **127**, 187–198 (2016)

Silva, M.F., Doménech-Carbó, M.T., Fuster-López, L., Mecklenburg, M.F., Martin-Rey, S.: Identification of additives in poly(vinylacetate) artist's paints using PY-GC-MS. Anal. Bioanal. Chem. **397**(1), 357–367 (2010). https://doi.org/10.1007/s00216-010-3505-2

Zuena, M., Legnaioli, S., Campanella, B., Palleschi, V., Tomasin, P., Tufano, M.K., et al.: Landing on the moon 50 years later: a multi-analytical investigation on Superficie Lunare (1969) by Giulio Turcato. Microchem. J. **157**, 105045 (2020). https://doi.org/10.1016/j.microc.2020.105045