

1 **Analytical approaches based on GC/MS to study organic materials in artworks and**
2 **archaeological objects**

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1 **Abstract**

2 Gas chromatography/mass spectrometry (GC/MS), after appropriate wet chemical sample pre-treatments or
3 pyrolysis, is one of most commonly adopted analytical technique in the study of organic materials from
4 cultural heritage objects. Organic materials in archaeological contexts, in classical art objects or in modern
5 and contemporary works of art may be the same or belong to the same classes, but can also vary
6 considerably, often presenting different ageing pathways and chemical environments. This paper provides
7 an overview of the literature published in the last ten years on the research based on the use of GC/MS for
8 the analysis of organic materials in artworks and archaeological objects. The latest progresses in advancing
9 analytical approaches, characterising materials and understanding their degradation, and developing
10 methods for monitoring their stability are discussed. Case studies from the literature are presented to
11 examine how the choice of the working conditions and the analytical approaches is driven by the analytical
12 and technical question to be answered, as well as the nature of the object from which the samples are
13 collected.

14

15 **Key words**

16 gas chromatography/mass spectrometry; wet chemical sample pre-treatment; analytical pyrolysis; organic
17 materials; paintings; archaeological objects

18

1 **1.Introduction**

2 Gas chromatographic techniques were first used in conservation science in the 1970s, and were driven by
3 the interest in identifying organic materials present as binders in paintings, or associated with archaeological
4 objects. Since the pioneering work of Mills and White in the laboratories of the National Gallery in London
5 [1-3] and of Michael Shilling at the Getty Conservation Institute in Los Angeles[4], gas chromatography
6 coupled with mass spectrometry (GC/MS) has become an established method for investigating organic
7 materials in art and archaeological objects.

8 Most organic materials encountered in cultural heritage are macromolecular. In some cases they are natural
9 or synthetic polymers (such as proteins, plant gums, vinyl and acrylic resins), others undergo oligomerisation
10 or cross-linking reactions as an effect of exposure to light and air (such as natural resins or drying oils). Organic
11 materials in the cultural heritage are also polar and have a low volatility. Their analysis by GC/MS thus entails
12 chemical or thermal treatments in order to reduce the original macromolecules into low polarity, low
13 molecular weight components, thus facilitating their volatilisation and subsequent separation onto a gas
14 chromatographic column. This can be achieved by coupling analytical pyrolysis with gas chromatography
15 mass spectrometry (Py-GC/MS), or by a wet-chemical treatment of the samples prior to GC/MS. Common
16 analytical approaches, method developments, advantages and drawbacks of the different methods, as well
17 as instrumental aspects have been discussed and overviewed in detail in the literature [5-12].

18 In the last ten years, analytical research involving GC/MS, and PY-GC/MS has tackled three related challenges:
19 advancing analytical approaches, characterising materials and understanding their degradation, and
20 developing methods for monitoring their stability. The choice of the working conditions and the analytical
21 approaches is firstly driven by analytical and technical questions, among which: what painting or
22 manufacturing technique has been applied? What is the object's state of conservation? Which chemical
23 markers or features allow to detect a specific material? Which analytical procedure detects a specific analyte?

24 The answers clearly depend on the classes of organic materials found in the sample and the nature of the
25 sample itself. Organic materials in archaeological contexts, in classical art objects or in modern and
26 contemporary works of art may be the same or belong to the same classes, but can also vary considerably,
27 often presenting different ageing pathways and chemical environments. thus requiring different analytical
28 approaches. Thus the following sections discuss the recent advances in GC/MS and Py-GC/MS for the
29 characterisation and identification of organic materials in archaeological contexts, classical art objects and
30 modern and contemporary works of art.

31

1 **2. Organic materials in archaeological contexts**

2 Archaeological organic samples involve a range of critical characteristics, making their study an analytical
3 challenge. Their investigation is complicated by the ageing and degradation of the molecules present in the
4 organic substances [13-18]. This means that in order to establish the origin of the natural substances in the
5 sample and to understand the alteration processes that have modified the materials it is essential to identify
6 the molecular composition as well as to reveal the presence of molecular markers . Gas
7 chromatography/mass spectrometry (GC/MS), after opportune wet-chemical pre-treatments of the sample
8 or using analytical pyrolysis, is thus the most commonly adopted technique.

9 The possibility of identifying unexpected compounds by MS detection on the basis of their mass spectra
10 makes GC/MS particularly suitable for studying unknown matrices and/or following ageing and degradation
11 pathways. In addition, given that gas chromatography combustion-isotope ratio mass spectrometry (GC-C-
12 IRMS) can be used to measure the carbon stable isotope ratios ($\delta^{13}\text{C}$) of palmitic and stearic acids, the exact
13 origin of lipid substances from archaeological findings can be identified, which is one of the greatest
14 challenges of organic residues analysis [19]. In fact, degraded lipid substances are mainly composed of
15 palmitic and stearic acids regardless of the original source, due to degradation processes that tend to make
16 the fatty acid profile of archaeological samples difficult or impossible to diagnose. Isotopic analysis has
17 proven to be a powerful tool in identifying the origin of lipid materials of a very similar composition, even in
18 mixtures. This analysis distinguishes between ruminant and porcine adipose fats and between lipids from C3
19 and C4 plants. In addition, ruminant adipose and dairy fats can also be distinguished by the $\delta^{13}\text{C}$ values along
20 with $\Delta^{13}\text{C}$ ($\delta^{13}\text{C}_{18}-\delta^{13}\text{C}_{16}$) of their fatty acids [19].

21 Since 2000, GC/MS, Py-GC/MS and GC-C-IRMS have been well established techniques for identifying organic
22 substances and materials linked to specific productions, daily-life and food activities, religious or ritual
23 practices, and cosmetic and medical activities [20-47]. In addition, the same techniques, particularly GC-C-
24 IRMS, have been used to address some key questions concerning animal husbandry in prehistoric phases [48-
25 52].

26 A particularly interesting study was recently carried out by GC/MS and GC-C-IRMS on organic residues
27 preserved in sieves/strainers from the region of Kuyavia (Poland) and dating back to 5,200–4,800 cal. BC, to
28 investigate the function of these ceramic vessels [50]. The chromatographic profile along with $\delta^{13}\text{C}$ values of
29 palmitic (C_{16}) and stearic (C_{18}) acids, and $\Delta^{13}\text{C}$ ($\delta^{13}\text{C}_{18}-\delta^{13}\text{C}_{16}$) values provided direct chemical evidence of their
30 use in milk processing (Figure 1). The chemical data obtained provided evidence of the high abundance of
31 dairy products and the specific features of the ceramic shreds, characterized by the presence of several holes,
32 led the authors to suggest that already 7000 years ago prehistoric people were able to make cheese.

1 **Figure 1. TAG distributions of total lipid extracts of sieves from the region of Kuyavia (a). The blue bars denote TAGs present in**
2 **both adipose and milk fats whereas those in red are only detectable in milk fat. Plots of the $\delta^{13}\text{C}$ values for the C16:0 and C18:0**
3 **fatty acids prepared from animal fat residues extracted from sieves(c). $\Delta^{13}\text{C}$ values of the extracts plotted against their $d^{13}\text{C}_{16:0}$**
4 **values from the same potsherds (e). Adapted from [50].**

5

6 The chemical study of organic materials from archaeological contexts is generally based on the knowledge of
7 the behaviour of the materials under ageing, and on comparisons with reference materials of a known origin.
8 Thus, collecting reference materials for testing analytical procedures and comparing analytical data, and
9 submitting them to artificial ageing treatments, are important preliminary steps in the research on ancient
10 materials [6, 17, 18]. Further considerations are required for the potential use of unexpected materials that
11 are not extensively used in modern society, such as the *Brassicaceae* oil used as an illuminant found in two
12 Roman ceramic lamps (lamps 718 and 809) discovered at the archaeological site of North Necropolis of
13 Antinoe (Egypt)[31]. The two lamps showed an adherent blackish residual deposit, which was submitted to
14 an analytical protocol based on GC/MS analysis. After alkaline hydrolysis, extraction and derivatisation
15 reaction with BSTFA, the samples produced the chromatographic patterns shown in Figure 2.

16

17 **Figure 2. GC/MS chromatogram of a) sample 718 and b) sample 809[31]**

18

19 The extracts consisted of a series of linear monocarboxylic saturated fatty acids ranging from 9 to 24 carbon
20 atoms with hexadecanoic acid (palmitic) and octadecanoic acid (stearic) as the most prominent, and a high
21 abundance of long chain acids ($\text{C}_{20}\text{-C}_{24}$), a series of α,ω -dicarboxylic acids ranging from 4 up to 14 carbon
22 atoms, with nonanedioic acid (azelaic) as the main constituent of this group, a series of ω -hydroxycarboxylic
23 acids ranging from 8 up to 14 carbon atoms, and three long chain dihydroxycarboxylic acids with 18, 20 and
24 22 carbon atoms, namely, 9,10-dihydroxyoctadecanoic acid, 11,12-dihydroxyeicosanoic acid and 13,14-
25 dihydroxydocosanoic acid; each of the dihydroxycarboxylic acids was present as a pair of threo-erythro
26 isomers. The predominance of C9 dicarboxylic acid (azelaic acid) together with the presence of 9,10-
27 dihydroxylated acids implied high amounts of oleic acid in the original lipid material. On the other hand, the
28 presence of 11,12-dihydroxyeicosanoic acid and 13,14-dihydroxydocosanoic acid was a very distinctive
29 feature of these samples and, the formation of 11,12-dihydroxyeicosanoic acid and 13,14-
30 dihydroxydocosanoic was ascribed to the oxidation of gondoic and erucic acids. Since the only seed oils that
31 contained high amounts of gondoic and erucic acids were those derived from *Brassicaceae* [31, 53, 54], the
32 results were interpreted as chemical evidence of the use of a seed oil derived from *Brassicaceae* species for
33 lighting purposes. It was impossible to detect the botanical species from which the seed oil used in the
34 examined lamps was actually produced, thus it is not known whether the oil came from radish as reported
35 by Pliny, or from another *Brassicaceae* plant such as rapeseed. In any case, detection of the characteristic

1 markers in lamps from Antinoe, one of the main urban centres of Roman Egypt, represents chemical
2 confirmation of the widespread use of cruciferous oil at that time, and is consistent with ancient documents
3 [55]. This was supported by the results obtained in the aging tests and analysis performed on *Brassica juncea*
4 oil and the pure gondoic and erucic acids. It was possible to demonstrate that 11,12-dihydroxyeicosanoic acid
5 and 13,14-dihydroxydocosanoic acid are markers for cruciferous seed oil in archaeological residues.

6 Lipids of animal and plant origin as well as plant resins are the most commonly encountered substances in
7 archaeological findings. In fact, owing to their lower susceptibility to structural modification and degradation
8 by chemical and microbiological attacks as well as hydrophobicity, they may survive better than
9 carbohydrates, proteins and nucleotides in archaeological environments [13-15, 18], A similar argument can
10 be made for the chemical components of alcoholic beverages and wines whose water-solubility limits their
11 persistence in archaeological environments. The detection of wine and other alcoholic beverage residues has
12 always been of great interest in the archaeological community and although some papers have appeared in
13 the literature [46, 56, 57], it still remains an analytical challenge. In this framework, a completely new
14 biomarker approach entailing the detection of bacterial lipids formed during the fermentation and ethanol
15 production, was recently published [58].Correa-Ascencio et al. used gas chromatography/mass spectrometry
16 in selected ion monitoring (m/z 191) of lipid extracts to reveal characteristic bacterio-hopanoids produced
17 by *Zymomonas mobilis* bacterium during the fermentation of maguey plants (*Agavaceae*) in order to identify
18 pulque residues in pottery vessels from Teotihuacan (150 B.C. to A.D.650, Mexico).

19 The chemical study of organic materials from archaeological contexts is also complicated by the fact that the
20 substances and materials used by ancient populations varied widely depending on their availability, which
21 was strictly related to geography. On the one hand, the study and identification of plant and animal residues
22 in European and Mediterranean artifacts are well represented and reported in the literature. On the other,
23 sources of the substances used in America, in eastern countries such as China as well as in Australia and
24 Africa, which could differ quite substantially from those used traditionally in Mediterranean/European areas,
25 have been studied less. In recent years, a number of papers dedicated to the GC/MS study of non-
26 European/Mediterranean objects have appeared in the literature [58-68]. Some of these papers aim to fill
27 the gap regarding the material composition of non-European/Mediterranean archaeological findings by
28 carrying out systematic GC/MS investigations of reference substances that had not previously been studied.

29 A recent trend in the characterisation of organic materials in archaeological objects is to perform non invasive
30 analyses of the volatile organic compounds (VOCs) released from the organic components. VOC emissions
31 can be characteristic of a given material, and can provide information on the material composition and its
32 state of degradation. According to the experimental asset, the analysis can provide qualitative,
33 semiquantitative or quantitative information. It is performed by exposing an adsorbing fiber to volatile
34 molecules released from a surface or from a solid sample enclosed in a closed vial, in some cases with the
35 assistance of heating to increase the concentrations of VOCs.

1 In the latter case, the technique is referred to as headspace solid phase microextraction (SPME) [69]. The
2 main advantage of this approach is that it is totally non invasive and non destructive for the sample. This
3 approach was used for example in the detection of phenolic derivatives and sesquiterpenoid isomers, which
4 were recognised as the volatile biomarkers of birch bark tar. Directly at the archaeological site, these and
5 other volatile compounds emitted were trapped as soon as the archaeological artefacts were discovered and
6 recovered from their sediment matrix, providing a non-destructive analytical method for investigating the
7 nature of the glues used in the past [70]. The same approach was used to determine the composition of a
8 mummy balm in samples from the tomb of Khnoumit at Dachour in Egypt, by recognising the VOC profiles of
9 volatile terpenes and phenols characteristic of conifer resin [69]. Another example is the investigation of the
10 different geological origins of amber from the volatile fraction. Romanian (romanite) and Baltic (succinite)
11 ambers were studied showing significant differences in the VOC profile[71].

12 Lignocellulosic polymers are a particular class of organic biomaterials in the cultural heritage. Preserved wood
13 archaeological objects are extremely rare, due to the fragility of wood towards fire, insects and biological
14 agents such as fungi. Wood survives for centuries only when degrading agents are less aggressive, as is the
15 case of waterlogged shipwrecks. In these cases, the determination of the chemical composition of wood is
16 key in assessing its preservation and evaluating the necessity for consolidation.

17 Analytical pyrolysis coupled with GC/MS is a powerful tool for this purpose, due to the difficulties in obtaining
18 information on the molecular structure of lignin and cellulose by other techniques using a limited amount of
19 sample [72]. Pyrolysis of wood produces a mixture of low molecular weight compounds derived from
20 polysaccharides, which also lead to the formation of levoglucosan, and of relatively simple phenols resulting
21 from the cleavage of ether and C-C bonds of lignin [73-75]. The phenols produced retain their substitution
22 patterns from the lignin polymer [76] thus it is possible to identify components from the p-
23 hydroxyphenylpropanoid (H), guaiacylpropanoid (G) and syringylpropanoid (S) lignin units. Pyrolysis products
24 of wood are polar, low volatile molecules. Consequently specific reagents are added to the sample before
25 pyrolysis in order to achieve the in situ thermally-assisted hydrolysis of specific bonds and the derivatisation
26 of polar groups present in the pyrolysis products, in order to improve the chromatographic separation and
27 analytical response of polar compounds. Thus it is possible to separate and detect much more structurally
28 significant products than by conventional pyrolysis techniques, with a better chromatographic performance
29 and longer column lifetime. The most common derivatization approach in analytical pyrolysis coupled with
30 GC/MS is a trimethylation reaction, where tetramethylammonium hydroxide (TMAH) is used
31 simultaneously with pyrolysis [77], and silylation with hexamethyldisilazane (HMDS) [5].

32 Py-GC/MS, with and without derivatisation, has been used to study the chemical alterations of wood
33 components [78-80] induced by fungi [81, 82] and also by chemical and enzymatic treatments[83, 84], and
34 to investigate the degradation of archaeological wood [85-90]. Py-GC/MS produces semi-quantitative results

1 on the extent of cellulosic loss occurring in waterlogged wood artifacts such as shipwrecks, and highlights the
2 chemical modifications undergone by polysaccharides and lignin. Differences between the archaeological
3 wood of several historical periods and sound wood have been found in the relative amounts of pyrolysis
4 products, which above all show a polysaccharide degradation/depletion compared to lignin. There can be a
5 relative loss of up to 90% of polysaccharide pyrolysis products, in terms of peak areas, from sound to
6 archaeological wood

7 The loss of polysaccharides induced by degradation can be semi-quantitatively estimated by interpreting the
8 pyrograms and calculating parameters such as the holocellulose/lignin (H/L) pyrolytic coefficient, defined as
9 the ratio between the relative abundances of holocellulose (cellulose and hemicelluloses) and lignin pyrolysis
10 products[91]. H/L coefficients of different samples analyzed in the same conditions can be compared, leading
11 to a quantitative evaluation of the decay processes. H/L coefficients reported in the literature for sound wood
12 vary from around 1.0 for softwood up to 3.0 for hardwood, depending on the species. Pyrolytic H/L of
13 extensively degraded archaeological wood have been reported to be significantly lower (0.2-0.3) [88, 89].

14 Figure 3 shows the pyrogram of sound maple wood in comparison with that of waterlogged archaeological
15 maple wood, evidencing the loss of polysaccharide pyrolysis products.

16

17

18 **Figure 3. Py(HMDS)-GC/MS profiles obtained for the analysis of sound maple wood (a) and archaeological maple wood (b). C-**
19 **carbohydrates; G-guaiacyl lignin; S-syringyl lignin [72].**

20

21 The information obtained by the interpretation of pyrolysis products is not limited to the depletion of
22 carbohydrates, because the increase in specific pyrolysis products that are markers of degradation or
23 alteration can also be evaluated. A study carried out on archaeological oak (*Quercus* sp.) wood samples,
24 ranging from the 16th century AD to 6000 BP, provided the first unequivocal evidence that the demethylation
25 of syringyl units occurs very early in wood degradation [90]. The GC/MS pyrograms revealed a number of
26 methoxycatechols, directly related to syringyl units, which are characteristic building blocks of angiosperm
27 lignin. A Py-GC/MS study of a sample of waterlogged beech from the excavation of the site at San Rossore
28 (Pisa, Italy) confirmed the formation of catechols and methoxy catechols, which are derived from the
29 demethylation of both guaiacyl and syringyl lignin[87]

30 In another study [89], archaeological waterlogged wood remains from the roof of a Roman villa in
31 Herculaneum buried in AD 79 by the eruption of Vesuvius, were analyzed by pyrolysis-gas
32 chromatography/mass spectrometry (Py-GC/MS). The findings enabled the authors not only to highlight the
33 loss of polysaccharides and the demethylation undergone by lignin, but also its oxidation. The analyzed
34 samples contained a relatively high abundance of vanillin, acetovanillone, vanillic acid and coniferylaldehyde,
35 indicating that lignin monomers had also undergone oxidation reactions in the course of ageing. An O/L
36 coefficient can be taken as a pyrolytic indicator of the degree of oxidation of lignin, calculated as the sum of

1 the normalized areas of vanillin, acetovanillone, vanillic acid and coniferylaldehyde, divided by the sum of
2 the areas of all the lignin pyrolysis products. The O/L coefficient values show that the O/L for sound wood is
3 0.07 and most archaeological samples from Herculaneum showed a coefficient higher than 0.1, thus revealing
4 a significant degree of oxidation [89].

5 Polar pyrolysis products of wood, such as vanillic acid, which are significant in evaluating the extent of
6 oxidation of lignin, are not detected in GC without derivatisation. Although TMAH has been occasionally used
7 for the characterization of wood and its components [92, 93] , it is not the ideal reagent because the
8 methylation of phenolic groups makes them indistinguishable from methoxylic groups, unless isotopically
9 labelled reagents are used. Thus, the use of silylating reagents for in situ derivatisation reactions is preferred
10 in the Py-GC/MS analysis of wood [85, 94].

11

12 **3. Analysis of organic materials in classical art objects**

13 GC/MS is the most common technique for the molecular characterisation of organic materials in paintings,
14 polychrome objects and classical art in general. A plethora of studies have been reported in journals, books,
15 and conference proceedings (see for example [95-137]). In the last ten years some improvements in the
16 analytical procedures used by the scientific community for the analysis of organic materials in art samples
17 have been proposed [101, 138-147]. Particular focus has been on both understanding and removing
18 analytical interferences caused by inorganic constituents[148-150] and on developing methods for the
19 simultaneous detection of more than one class of organic materials in the same micro-sample[151-155].

20 Proteins, glycerolipids and polysaccharides are the main binders found in art samples [6]. In addition, natural
21 waxes, lacquers, and terpenoid resins have been used as additives, varnish ingredients and consolidants.
22 These materials are mixed together with pigments and fillers. They are then subjected to ageing. All this
23 results in extremely complex samples with a variety of molecules with different chemical reactivities.

24 Some organic materials cannot be chemically processed for analysis by GC/MS and require analytical
25 pyrolysis[5]. The pool of produced fragments provides a fingerprint that is characteristic of a particular
26 sample, in terms of both the fragment's nature and relative distribution. This approach means that the
27 chemical composition of a sample can be reconstructed on the basis of a detailed interpretation of the
28 chromatographic molecular profile of the thermal degradation products of the original components, and on
29 the recognition of specific molecular markers in the chromatogram or of characteristic molecular patterns,
30 which act as molecular fingerprints of the pyrolyzed material [5, 12].

31 A class of material that cannot be chemically processed for analysis by GC/MS and requires analytical
32 pyrolysis is represented by oriental lacquers, which are extracted from three species of the same tree,
33 belonging to the *Anacardiaceae* family. Their sap is composed of water (30%), glycoproteins (2%), plant gum

1 (7%), a laccase enzyme (1%), and a mixture of catechol derivatives (60-65%), which varies depending on the
2 plant of origin [156].

3 The phenolic fraction of the sap is responsible of the hardening of the lacquer, which polymerises leading to
4 the formation of C-C aromatic nucleus-side chain coupling bonds, C-O phenolic oxygen-side chain coupling
5 bonds, and C-C bonds between side chains. This results in cross-linked polymeric structures [157, 158], which
6 cannot be analysed by GC/MS, but require Py-GC/MS in order to characterize and identify the oriental
7 lacquers [124, 156, 159-168] in ancient samples of unknown composition [48, 51-60]. The low volatility of
8 acidic and alcoholic moieties of oriental lacquer pyrolysis products means they are unsuitable for gas
9 chromatographic analysis, as they cause a rather low reproducibility of the resulting pyrograms, low
10 sensitivity for specific compounds, and strong memory effects. In fact, the most promising results have been
11 achieved using thermally-assisted reactions with tetramethylammonium hydroxide (TMAH) [159, 166] and
12 hexamethyldisilazane[167] as derivatizing agents. Figure 4 shows the profiles of alkyl-catechols, which are
13 formed by thermal cleavage of C-C bonds between aromatic nuclei and side chains, obtained from the
14 pyrolysis of two lacquer samples in the presence of HMDS (Figure 4a) and TMAH (Figure 4b).

15

16 **Figure 4. a) Py (HMDS)-GC/MS: extracted ion chromatograms of the ion with m/z 179 of a sample collected from the lacquer layer**
17 **of a Chinese polychrome sculpture dating back to the 12th century. Pyrolysis temperature was 550 °C and interface temperature**
18 **was 280 °C^a. b) Py (TMAH)-GC/MS extracted ion chromatograms of the ion with m/z 151 of a sample collected from the lacquer**
19 **layer of a cabinet dating from the late 19th century. . Pyrolysis temperature was 550 °C and interface temperature was 320°C^b.**
20 **Legend to the Figure: CT2) 3-ethylcatechol; CT3) 3-propylcatechol; CT4:1) 3-butenylcatechol; CT4) 3-butylcatechol; CT5:1) 3-**
21 **pentenylcatechol; CT5) 3-pentylcatechol; CT6:1) 3-hexenylcatechol; CT6) 3-hexylcatechol; CT6 acid) 6-(2,3-**
22 **dihydroxyphenyl)hexanoic acid; CT7:1) 3-heptenylcatechol; CT7) 3-heptylcatechol; CT7 acid) 7-(2,3-dihydroxyphenyl)heptanoic**
23 **acid; CT8) 3-octylcatechol; CT8 acid) 8-(2,3-dihydroxyphenyl)octanoic acid; CT9) 3-nonylcatechol; CT9 acid) 9-(2,3-**
24 **dihydroxyphenyl)nonanoic acid; CT15:1) 3-pentadecenylcatechol; CT15) 3-pentadecylcatechol. The catechols are in the mono-TMS**
25 **form in a) and in the bis-CH₃ form in b)**

26

27 In both samples urushi, the lacquer obtained from *Rhus vernicifera*, was identified. The mixture contained in
28 the sap of *Rhus vernicifera* is called urushiol, whose principal component is 3-pentadecylcatechol [156]. The
29 lacquer was identified based on the detection of derivatised molecular biomarkers in the pyrogram, as well
30 as characteristic pyrolytic profiles of derivatised alkylcatechols and alkylphenols, aliphatic hydrocarbons, and
31 alkylbenzenes [159, 166, 167].

^a Sample was kindly provided by Catharina Blaensdorf.

^b Sample was kindly provided by Joanna Koryciarz Kitamikado. Analysis was carried out by Diego Tamburini at the workshop Recent Advances in Characterizing Asian Lacquer, 2014, held at the Centre de Recherche et de Restauration des Musées de France, under the supervision of Dr Michael Schilling.

1 However, the intrinsic non-quantitative nature of the pyrolysis technique does not always lead to the
2 unambiguous identification of the raw source of an organic material, especially in the case of mixtures. Thus,
3 the interpretation of the pyrograms is critical, especially for aged materials, and requires not only a wide
4 database of reference specimens, but also experience in interpreting the effect of the matrix. The
5 simultaneous occurrence of different organic materials, the relative abundance of one material with respect
6 to the others, the presence of inorganic materials, sample morphology, and several other factors can affect
7 the resulting pyrograms.

8 Another approach to analyse the complex mixtures of natural organic materials that can be found in art
9 samples by GC/MS is based on the wet chemical pre-treatment of the sample in order to increase the
10 volatility of the original compounds by means of hydrolysis and derivatisation. Hydrolysis conditions for these
11 materials are all very different. For example glycerolipids and waxes are quantitatively hydrolysed by an
12 alkaline solution. Proteins and polysaccharides require acidic solutions, although in very different conditions,
13 milder for polysaccharides, harsher for proteins. This means that either the sample is divided into aliquots to
14 be processed separately for various components, or the sample is subject to extractions and separations
15 steps in order to obtain different fractions for the different materials. In addition to the reliability of the
16 analytical approach chosen, the quality of the results obtained in the GC/MS analysis of art samples relies
17 both on the characterisation of the reference materials and their degradation pathways, and on the
18 development of suitable analytical models for data analysis.

19 Identifying organic materials in paint samples is generally based on three main methodologies: identification
20 in the chromatogram of specific biomarkers (chemotaxonomy), recognition of the overall chromatographic
21 profile, or quantitative analysis of significant compounds.

22 Natural terpenoid resins are identified based on the presence of molecular biomarkers in the chromatogram
23 [6]. For example butolic, aleuritic, shellolic and laccishellolic, lacsholic, laccilacsholic acids and relative
24 epimers are the markers of shellac resin, a resin of animal origin from *Coccus* species, when saponification
25 has been carried out in conditions that allow the Cannizzaro type reactions undergone by the aldehyde
26 moieties in jalaric and laccijalaric acid to be completed [169]

27 Natural waxes are identified based on the recognition of their molecular profiles [6]. For example beeswax is
28 identified based on the detection of fatty acids in the chromatogram with an even number of carbons (from
29 palmitic to dotriacontanoic acid), (ω -1)-hydroxy acids with an even number of carbons (from 15-
30 hydroxyhexadecanoic acid to 23-hydroxytetracosanoic acid), long chain linear alcohols with an even number
31 of carbons (from tetracosanol to tetratriacontanol), long chain (α,ω -1)-diols with an even number of carbons
32 (from 1,23-tetracosandiol to 1,27 octacosandiol), and long chain linear saturated hydrocarbons with the
33 prevalence of an odd number of carbons (from tricosane to tritriacontane) [170]. The volatility of some of

1 beeswax components makes it possible to identify it in a museum object also by analysing its VOCs. For
2 example beeswax was identified as the moulding material of some sculptures by analysing the VOC
3 composition (n-alkanes and n-carboxylic acids) of the showcase in which the sculpture was kept [171].

4 Proteinaceous materials can be identified based on the quantitative evaluation of the amino acidic profile
5 obtained after hydrolysis [7]. One of the main difficulties in identifying proteinaceous materials, is that with
6 the exception of animal glue containing hydroxyproline (which is an amino acid produced by hydroxylation
7 of the amino acid proline with a post translational modification), the proteins of organic paint media all
8 contain the same amino acids. Quantitative evaluations are thus necessary, however quantitative profiles
9 can be influenced by the inorganic pigments and fillers present [**Errore. Il segnalibro non è definito.** and
10 *references therein*]. Pigments give rise to strong interactions with the organic media, modifying the thermal
11 stability and tertiary structure of the proteins, forming complexes, causing crosslinking and hydrolysis of the
12 peptide chains, and favouring oxidation with ageing [172-174]. If purification procedures are not adopted,
13 inorganic media can not only interfere in the derivatisation step and damage the GC column, but can also
14 modify the quantitative profiles [[6] and *references therein*].

15 Polysaccharide media are identified on the basis of the presence / absence of sugars and uronic acids in the
16 chromatogram. Tragacanth, arabic and fruit tree gums are the most commonly used gums in classical art in
17 the Mediterranean basin and Europe, and are characterised by quite different sugar profiles. It has been
18 shown that ageing in the presence of certain pigments can modify the sugar profiles, making the gum
19 identification less straightforward [150]. In addition most of the natural organic media found in artworks
20 contain saccharides, including proteinaceous media [150]. It has also been suggested that polysaccharides
21 from plant tissues (wood, straw, paper, etc.) may be present in particulate matter both in indoor and outdoor
22 environments.

23 Four decisional schemes have thus been proposed [150] to identify the source of a plant gum (Figure 5) to
24 be used as alternatives when:

- 25 a) there are no proteinaceous materials simultaneously present and there seems to be no
26 contamination^c
- 27 b) the presence of proteinaceous materials is unknown and there seems to be no
28 contamination^c
- 29 c) proteinaceous materials are simultaneously present and their source is known, and there
30 seems to be no contamination^c

^c This is based on the evaluation of the xyl/ara ratio: when this is higher than one, contamination is hypothesised

1 d) the polychromy is on a wooden / paper support or contains straw, or the xylose/arabinose
2 ratio is higher than 1, thus the samples are clearly contaminated by sugars originating from
3 plant tissues present in the environmental particulate matter

4
5 **Figure 5.** Decisional schemes to identify a plant gum in a paint sample based on the knowledge of the simultaneous presence of
6 proteinaceous materials and contamination from sugars originating from plant tissues[150].

7
8 The identification of the origin of the saccharide material in a paint sample is even more complex when
9 considering possible sources of sugars other than polysaccharide media. One example is represented by an
10 extensive historical and scientific investigation into commercially prepared British watercolour cakes from
11 London based artists' colourmen Reeves, Rowney, Ackermann and Roberson, dating from before the 18th
12 through to the early 20th century [175]. The study revealed that although arabic gum was the main binder,
13 several other additives could be present, including smaller portions of other gums, among which the lesser
14 known gums heder, lake, ammoniac, guttae and guaiacum. Other additives, such as sugar or honey, starch
15 and other non saccharide materials were also added, in order to obtain specific rheologies of the paint. As
16 expected, the chromatograms of the saccharide fractions generated by such mixtures can be impossible to
17 interpret if the possible ingredients are not known through a systematic investigation into the historical
18 sources.

19 Glycerolipids are identified by GC/MS based on the ratio between the relative amount of palmitic and stearic
20 acid (P/S) and the ratio between the relative amount of azelaic and palmitic acid (A/P). An A/P ratio lower
21 than 0.3 suggests the presence of non-drying fats, such as egg yolk, while a ratio higher than one points to
22 the presence of a drying oil [1, 6, 11, 176] *and references therein*.

23 Azelaic acid is in fact one of the main oxidation products of polyunsaturated fatty acids, which are abundant
24 in drying oils. The P/S ratio is used to distinguish between different drying oils. This is based on the
25 assumption that as palmitic and stearic acids are saturated long chain acids, they are stable to ageing. Actually
26 using the P/S ratio to identify the source of the drying oil has several limitations. It has been recently shown
27 that evaporation of the organic medium from the paint layers takes place during ageing at a surprisingly fast
28 rate, depleting the paint layers of glycerol and fatty acids [177]. A weight loss of 15% was observed in
29 reference paint layers of linseed oil and vine black in only 12 years. When fatty acids are saponified by the
30 pigment, such as Pb²⁺ in the lead white pigment, then evaporation does not take place [177]. Thus the
31 presence in the paint layers of any material, pigment or other binder, which can form complexes or other
32 sorts of chemical compounds with the fatty acids, hinders this phenomenon. Considering that palmitic acid
33 evaporates four times more quickly than stearic acid[178], the P/S value is expected to significantly decrease

1 over time. There are thus other factors of fundamental importance in determining the final P/S value of a
2 paint sample, some of which are the direct consequence of the rapid evaporation of the free fatty acids from
3 the paint film: the film thickness at the sampling point, the presence of any other organic materials that could
4 hinder the evaporation of fatty acids as a consequence of the formation of non-volatile complexes (for
5 example protein-fatty acid complexes), the presence of pigments able to form complexes with the fatty acids
6 [179-182], the presence of overlying layers [183, 184], the cleaning treatments [185-187], and finally the
7 thermo-hygrometric conditions of the storage places throughout the history of the paint [178]. This means
8 that the P/S ratio alone is not a suitable parameter for determining the source of the oil.

9 The identification of polysaccharide, proteinaceous and lipidic binders is thus based on the quantitative
10 analysis of significant compounds, that is sugars, amino acids and long chain linear and dicarboxylic acids,
11 respectively. The reliability of such models is based on the evaluation of blanks and calibration curves. These
12 are two very important, but often neglected aspects, which in analytical chemistry are the basis for
13 quantitative measurements.

14 Environmental blanks are often impossible to determine in samples collected from cultural heritage, as in
15 the case of paintings. Laboratory blanks however can be measured and are fundamental for distinguishing
16 between the actual sample and laboratory contamination. For example, Figure 4 shows the chromatogram
17 of the saccharide fraction of a sample from the mural paintings of the Nefertari tomb in Luxor, Egypt and
18 highlights the peaks of xylose, arabinose, mannose and galactose obtained by GC/MS after extraction, acidic
19 hydrolysis, desalting, and mercaptalation followed by silylation[150]. The sample did not contain any protein
20 and no sign of environmental contamination. According to the decisional scheme in Figure 5 A, the
21 chromatographic profile suggests the presence of fruit tree gum. In fact, xylose and mannose, at a 95%
22 confidence level, fell under the detection limit of the analytical procedure [155], indicating that only
23 arabinose and galactose belonged to the sample. This led to the identification of arabic gum.

24

25 **Figure 6. GC/MS Chromatogram of the sample from the mural paintings of the Nefertari tomb, Luxor, Egypt[188] obtained by**
26 **GC/MS after extraction, acidic hydrolysis, desalting, and mercaptalation followed by silylation[150]**

27

28 Quantification in GC/MS is also often performed based on peak areas, instead of calibration curves, and this
29 may lead to erroneous evaluations of the relative amounts of the constituents of interest [189]. Even when
30 a one-point calibration method is used, the linearity of the instrument response is neither controlled nor
31 guaranteed. This was demonstrated in an evaluation of P/S ratios for the identification of the source of the
32 drying oil. A nonlinear instrument response was obtained for both palmitic and stearic acids, which was
33 attributed to incomplete sample evaporation in the GC/MS injector (Figure 7).

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Figure 7. Calibrations graphs acquired for palmitic and stearic acids in the case of empty glass liner (A) or glass wool- packed glass liner (B) (image from [189]). Quantification was obtained after alkaline hydrolysis, acidification, extraction and silylation

The non linear instrument response leads to different P/S values depending on the sample dilution. By analysing three different aliquots of the same sample (10, 20 and 30 μ L), the P/S ratios obtained were 1.7, 1.9 and 2.4, respectively. The first two values suggest the identification of linseed oil in the sample, but the third value is in agreement with the literature data for walnut oil. The authors also proved that packing the glass liner with deactivated glass wool improved the sample evaporation and ensured the linearity of the instrument response and independence of the P/S ratio from sample dilution (Figure 7).

When non-linear responses are observed, it is necessary to ensure that the areas of the analytes to be quantified fall within the portion of the calibration curve that has been experimentally measured with reference standards. For example, Figure 8 shows the score plot obtained from the principal component analysis of the amino acid profile (Ala 7.0, Gly 6.2, Val 8.3, Leu 10.0, Ile 4.7, Ser 8.4, Pro 4.6, Phe 9.3, Asp 17.6, Glu 23.8, Hyp 0.0) of a sample from a reference paint layer of egg white (Sample A) together with those of 105 reference paint samples of egg, casein and animal glue. Amino acid concentration were determined by GC/MS after extraction, desalting using a C4 loaded pipette, hydrolysis and silylation [153]. The sample clearly falls within the cluster of casein. This can be explained because the concentration of the amino acids calculated from the chromatographic areas was more than 10 times higher than the highest concentrations used for the calibration curves, and thus the quantitation was erroneous.

Figure 8. Score plot obtained from the principal component analysis of the amino acid profile (Ala 7.0, Gly 6.2, Val 8.3, Leu 10.0, Ile 4.7, Ser 8.4, Pro 4.6, Phe 9.3, Asp 17.6, Glu 23.8, Hyp 0.0) of a sample from a reference paint layer of egg (Sample A) together with those of 105 reference paint samples of egg, casein and animal glue determined by GC/MS after extraction, desalting using a C4 loaded pipette, hydrolysis and silylation [153]

The complexity of the data interpretation involved in the GC/MS analysis of samples from cultural heritage, both using pyrolysis and wet chemical pre-treatment, is very well exemplified by the analyses of a round robin sample performed by ten laboratories specialised in the field in the framework of the activities of the MaSC-Users' Group for Mass Spectrometry and Chromatography in Cultural Heritage (<http://mascgroup.org/>)[190]. The sample contained ParaloidB82, a copolymer of ethyl acrylate and methyl methacrylate (EA/MMA), sandarac, mastic, linseed oil, egg white, gum arabic, and succinic acid. The sample was analysed using FTIR and GC/MS based analytical techniques. The materials were specifically included in the round robin blind sample in order to make the data interpretation quite complex. For example, arabic gum contains a small amount of protein with a high content of hydroxyproline, which is commonly used as

1 marker for the presence of animal glue. Sandarac contains polycommunic acid, which is also abundant in
2 other compounds, such as copal resin or Baltic amber, which also contains succinic acid. This compound was
3 also added to the sample. The results of the round robin analysis can be summarised as follows: an acrylic
4 resin (EA/MMA) was identified 6 times; succinic acid 3 times, Baltic amber (hypothesized) 4 times, copal once,
5 sandarac 7 times, mastic 10 times, linseed oil 10 times, gum arabic 3 times, gum (possible) twice, egg white
6 4 times, egg 4 times. The data clearly indicate that more than one procedure is often necessary to fully
7 characterise such complex samples as those collected from cultural heritage, although this is not always
8 possible given the very small sample size.

9 **4. Analysis of organic materials in modern and contemporary art objects**

10 The investigation of materials and the diagnosis of modern and contemporary art is a relatively recent field
11 of application of analytical chemistry, to which conservation scientists have devoted increasing attention
12 over the last 10-15 years. We decided to dedicate a specific section to the topic in this chapter, due to the
13 relative lack of textbooks on the study of materials in contemporary art, compared to the applications of
14 analytical chemistry to classical art and archaeological objects, which are much more extensively described
15 in the literature. However, there are a few textbooks and publications on the investigation and analysis of
16 materials in modern art and are an excellent basis to start research in this field [8, 9, 12, 191].

17 At the turn of the 19th century a staggering array of new binders were developed and used in the production
18 of fine art paints. Modern oil paints were sold in tubes, and thus contained not only oils and pigments, but
19 also additives such as surfactants and stabilizers.

20 Oil sources have been investigated in paint tubes and samples from works of art [192-194]. Actually the
21 identification of the oil source in the case of modern oil media is even more complex, although GC/MS is still
22 the preferred technique [192, 194-198]. The range of used oils is different in modern oil paints compared to
23 classical oil paints, and includes safflower, palm, soybean and many others. The introduction of new lipid
24 materials and oleochemicals was driven by the economic sustainability of production, and the availability,
25 workability and possibility of improving their properties by means of additives and engineered treatments.
26 In some cases a specific marker for an oil can be identified in the chromatogram, permitting its identification.
27 In a recent study the detection of specific fatty acid markers such as ricinoleic and erucic acids led to the
28 assessment of castor oil and rapeseed oil among the components of the oil paints used by Lucio Fontana
29 [193]. In another work, the presence of odd-number (C7–C15) fatty acids and the observed P/S values
30 suggested the presence of animal fats and of soybean and safflower oils in the paints used by Pablo Picasso
31 [196]. Despite the difficulties in the interpretation of the fatty acid profile, GC/MS has proven to be a
32 fundamental tool in assisting the evaluation of conservation practices of modern oil paints[199, 200].

1 Alkyd resins are another class of lipid modern paint binders in contemporary art. Alkyds are an industrial
2 evolution of oil paint media.. The adoption of these oil-based industrial polymers by artists is one of the
3 milestones in the evolution of painting techniques in 20th century art. Alkyds are oil-modified polyesters
4 manufactured from poly-ols (typically, glycerol or pentaerythritol), aromatic polybasic acids (phthalic
5 anhydride and phthalic acids are the most common) and a source of fatty acids, usually a vegetable oil [201].
6 Drying and semi-drying oils, such as linseed, soybean and castor oil are used for the production of alkyd
7 resins. The lipid fraction of alkyds can be characterized by GC/MS analysis after saponification [195, 202-204],
8 however Py-GC/MS with appropriate derivatising agents is a currently used approach used for the chemical
9 characterization of these synthetic polymers, for their identification in paint samples, and to study their
10 curing processes [12, 196, 203-207]

11 Py-GC/MS analysis of alkyd paints has been performed by online thermally-assisted hydrolysis and
12 derivatization of the hydroxyl and carboxylic groups present in the resin components and fragments, with
13 the same approach successfully adopted for the chemical characterization of oil paintings [12, 205]. Fatty
14 acids derived from the lipid components and aromatic components such as phthalic anhydride and phthalic
15 acids can be observed in the pyrograms. Benzoic acid is also often observed, derived both from phthalic acid
16 or phthalic anhydride, but it can also be present in the resin as a terminal chain or length modifier. Phthalic
17 anhydride can be detected in pyrogram of an alkyd without derivatising agent; however, isophthalic acid
18 would not, leading to the possibility of incorrect identifications. In pyrolysis conditions, the reported products
19 of pentaerythrol are 3-methoxy-2,2-bis(methoxymethyl)-1-propanol and 3-methoxy-2-methoxymethyl-1-
20 propanol [12]. THM-GCMS has been successfully used to investigate alkyd paints in artworks by Lucio Fontana
21 ("Concetto Spaziale" 1961) [12], Jackson Pollock ("Yellow Islands" 1952) [206] and Pablo Picasso ("Nude
22 Woman in a Red Armchair" 1932) [196]. The results proved that Picasso experimented with alkyd resins,
23 which was unusual for the times.

24 Although many artists have used these modern paints and explored their handling and optical
25 properties, "tempera", a classic painting technique using a protein based binder, has also been rediscovered
26 in XX century. New editions of historical treatises increased the debate on technical issues and the use of
27 tempera was a key topic among those artists involved in the renewal of a classicist style and traditional
28 working methods. Consequently, numerous formulations containing proteinaceous binders were developed
29 and commercialised. Identifying modern tempera techniques is much more complex than in classical art. By
30 using GC/MS in the analysis of the lipid and proteinaceous fractions of artists' and model samples, it has
31 recently been demonstrated that the word "tempera" used by artists at the end of the 19th and beginning
32 of the 20th century is more related to the rheological properties of the paint, which is strongly influenced by
33 its minor additives (such as glycerol, soaps or tallow) more than its main constituents [208] (proteins and/or
34 lipids).

1 Since the synthesis of cellulose nitrate by Schönbein and Böttger in 1846 [209], artistic experimentation has
2 led to the introduction of synthetic resins in artistic productions: paintings, sculptures, installations and
3 restoration procedures have included synthetic materials and industrially elaborated natural materials.
4 Acrylic polymers, were initially diluted with solvents and later were used as much more practical aqueous
5 emulsions (waterborne paints), diffused as varnishes, paint binders and as material for 3D art. Similarly, vinyl
6 resins were used as adhesives and binders, and nylon was an alternative to natural fibres. The complex
7 composition of modern and contemporary paintings is thus the result of the rapid changes occurring in
8 society and culture due to industrialization during the 20th century [209-211].

9 Conservators are now for the first time facing problems related to the degradation and preservation of
10 recently introduced industrial materials. A crucial aspect of the composition of modern commercial materials,
11 affecting their stability over time and their response to conservation treatments, is the wide variety of
12 formulations, often covered by patents. Commercial formulations of synthetic materials contain several
13 components, including pigments, stabilisers, plasticisers, and other additives. These were added to the main
14 polymer in order to modify its general properties, and they can strongly contribute to several degradation
15 phenomena characteristic of plastic artefacts, including water sensitivity, brittleness, vulnerability to light,
16 deformation, surface deposits, gloss change, cracking, and shrinkage. Their unknown composition can be a
17 problem in the evaluation of the compatibility of the ingredients used during restoration with the different
18 ingredients in the original material.

19 Advanced analytical techniques based on chromatography and mass spectrometry are now playing a key role
20 in addressing these issues. Analytical pyrolysis is the preferred technique for the molecular characterization
21 of synthetic organic molecules [8, 9, 212]. Py-GC/MS leads to the chemical characterization of the synthetic
22 materials in a large range of molecular weights. The mechanisms of thermal degradation of many polymeric
23 materials used in art are described in the literature [9, 12, 55, 213, 214], and knowledge of their pyrolytic
24 markers can be exploited to identify them when they are present as paint binders or varnishes. Py-GC/MS
25 has been applied to modern paint or synthetic conservation materials using different instrumental assets
26 based on furnace, filament and Curie point pyrolysers [8, 212, 215-218].

27 Py-GC/MS identification of synthetic paint media is essential in order to fully understand the techniques of
28 contemporary art. Identifying a synthetic binder in an artwork is in fact the first step in assessing the artist's
29 technique, in addressing attribution and dating issues, evaluating the possible effects of cleaning, and in
30 establishing the best conditions for conservation [219]. FTIR spectroscopy is also used to identify the type of
31 polymer present in a sample, however when the precise identification of the monomers is needed, for
32 example to discriminate between many acrylic resins, the molecular information achieved by Py-GC/MS or
33 other mass spectrometric techniques is generally more conclusive than spectroscopic data.

1 As an example, a particular concern is the diagnosis of street art and outdoor murals [220, 221] where often
2 acrylic paints have been used, because of the complete lack of established methods and protocols for the
3 cleaning, protection and preventive conservation of these types of artworks [222-226]. As the conservation
4 treatment of outdoor acrylic paint is an emerging field, the identification of the original materials is necessary
5 in order to make informed choices regarding the conservation approach.

6 Acrylic resins are a major class of synthetic polymers used as paint binders and varnishes. The most common
7 monomers used in products sold for artistic applications are methyl methacrylate (MMA), ethyl acrylate (EA),
8 *n*-butyl- methacrylate (*n*BuMA) and ethyl-hexyl-acrylate (EHA), often used as copolymers with styrenic
9 monomers. As generally happens with macromolecules synthesized by radical addition reactions, the thermal
10 degradation molecular profile of acrylic polymers is determined by unzipping mechanism, which induces the
11 scission of the polymeric chain to form the monomer or the monomers. Normally dimers and trimers are also
12 observed. As acrylic monomers are efficiently separated and determined by GC/MS, derivatisation is not
13 required in their analysis[227, 228].

14 Figure 9 represents the chromatogram obtained in the Py-GC/MS analysis of a sample taken from the wall
15 painting Tuttomondo (1989, Pisa, Italy) by Keith Haring (1958-1990)[229]. The pyrolysis profile is
16 characterized by the presence of styrene and *n*-butylacrylate monomers as main peaks. At higher retention
17 times, *n*-butylacrylate sesquimer, dimers and trimers are detected, which are markers of a poly-*n*-
18 butylacrylate resin. Other significant pyrolysis products include the dimeric structures typical of a
19 polystyrene: 1-ethyl-2-propenyl-benzene, diphenylethylene, 1,2-diphenylpropane, and 2,5-diphenyl-1-
20 hexene. The pyrograms of the Tuttomondo paint samples also featured *n*-butylacrylate/styrene dimer. This
21 molecular profile indicates that a styrene/*n*-butylacrylate copolymer is the binder in the paint materials used
22 by Haring in Pisa [12, 213, 229].

23

24 **Figure 9. Py-GC/MS chromatogram of a paint sample from the Tuttomondo mural by Keith Haring (area painted in burgundy)**
25 **[229]**

26

27 The versatility of Py-GC/MS in studying the painting techniques in modern and contemporary artworks is
28 illustrated by a parallel case study: the characterization of paint samples from another mural by the same
29 artist, Keith Haring. *Necker Hospital's mural* created in 1987, (Figure 10) is on the exterior stairwell at the
30 Necker Children Hospital in Paris [229]. Unlike the Tuttomondo mural in Pisa, which is in an excellent state
31 of conservation, the Necker Hospital mural shows conservation problems related in particular to the black
32 paint constituting the drawing, which was applied over the other colour areas. The black areas present
33 wrinkling and paint detachments, as well as degradation phenomena not present in the other colours. Seven

1 paint samples were analysed and one of the pyrograms obtained is reported in Figure 10) with the relative
2 peak attribution.

3

4 **Figure 10. Py-GC/MS chromatogram of a paint sample from Necker Hospital's mural in Paris [229].**

5

6 The results show that in this case Haring used a different medium. The pyrolysis profiles reveal benzene and
7 acetic acids which, together with small amounts of toluene, styrene, indene and different aromatic
8 compounds, are indicative of the presence of a vinyl resin [12]. The identification of a vinyl resin by Py-GC/MS
9 requires the addition of a derivatising reagent for the thermal assistant derivatisation of acetic acid,
10 developed in the thermal degradation of vinyl resins. In this case hexamethyldisilazane was used, so that
11 acetic acid is separated in the form of trimethylsilyl ester. The pyrogram reveals several isomers of the vinyl
12 ester of versatic acid (TR range= 9.0-14.0 min.), a constituent of VeoVaTM, an internal plasticizer used in vinyl
13 paint media [230]. At higher retention times, butyl phthalate, a common plasticizer added in commercial
14 products, was also identified in all the sample. The poor conservation conditions are likely due to the
15 composition of the binding medium: a vinyl resin containing high amounts of VeoVa as an internal plasticizer.
16 VeoVa renders the paint layer more sensitive to daily variations in temperature, due to the decrease in the
17 glass transition temperature of the resin. This is particularly evident in the darkest paint areas, caused by
18 daily variations in temperature enhanced by the higher temperature reached by the dark zones due to higher
19 absorption of light, thus promoting the wrinkling, detachments and variations in the morphology of the layer
20 [229].

21 Although analytical techniques based on pyrolysis, chromatography and mass spectrometry are a powerful
22 tool in investigating the organic components of modern paint media, the complete characterisation of a
23 material is not straightforward and requires specific analytical methodologies, strategies and data analysis
24 models to be specifically developed for each analytical problem. An interesting possibility is to perform the
25 evolved gas analysis (EGA) of the volatile products released by the sample during controlled heating at a low
26 temperature desorption (100-250°C) before high temperature pyrolysis. The molecule profile produced in
27 the first and second steps are analysed separately by GC/MS in two different analytical runs. A similar
28 approach is the double shot pyrolysis [203, 219, 231], which combines the analysis of thermally desorbed
29 volatiles with the flash pyrolysis of the polymer. For example, in order to investigate the photochemical
30 degradation of commercial polyvinyl acetate, Py-GC/MS in double shot mode was used to reveal the
31 differences in the amounts of volatile components present in the specimens before and after UV ageing,
32 including the changes in amounts of the deacetylation product acetic acid and of the content plasticizers such
33 as diethyl phthalate (DEP) (Figure 11)[219]. The analysis of acrylic emulsion paints after ageing highlighted

1 the decrease in the abundance of octylphenol, which is a marker for the non-ionic surfactant octyl-phenyl-
2 polyethoxy-ethanol in the thermal desorption chromatograms.

3

4 **Figure 11. Pyrograms of Mowilith(R) 50, a polyvinyl acetate, obtained by Py-GC-MS with double shot technique: in the first step -**
5 **thermal desorption: DTBD, di-ter-buthyl dicarbonate; DEP, diethyl phthalate; * not identified compounds. Figure from [219]**

6

7 When using Py-GC/MS for characterising plastics, identifying the peaks in the pyrogram and
8 deducing the structure of the original polymer is a challenging task. In fact the same monomer can
9 be used to produce more than one plastic, and it is important to identify those peaks in the
10 pyrograms that can help in differentiating between one polymer and another. This requires the
11 development of a data analysis model to support the data interpretation. For example styrene is
12 the primary building block of a number of plastics, including polystyrene (PS), high impact styrene
13 (HIPS), styrene-butadiene-styrene (SBS), unsaturated polyester resin (UP), and acrylonitrile-
14 butadiene-styrene (ABS). In order to differentiate between these polymers using pyrolysis in the
15 presence of TMAH, a flow chart has been proposed to assist in the pyrogram interpretation [232]
16 (Figure 12).

17 **Figure 12. Flowchart for identifying styrene-containing polymers from Py-GC/MS in the presence of TMAH. Figure**
18 **adapted from[232] . ABS/PC: acrylonitrile butadiene styrene/Polycarbonate; UP: unsaturated polyester resin;**
19 **PPO/(HI)PS: poly(phenylene)oxide /(high impact) polystyrene; ASA: acrylonitrile styrene acrylate; SAN: styrene**
20 **acrylonitrile; ABS acrylonitrile butadiene styrene; SBR: styrene-butadiene rubber; SBS: styrene butadiene styrene;**
21 **MIPS: medium impact polystyrene; HIPS: high impact polystyrene; PS: polystyrene**

22

23 VOCs analysis by GC/MS can also be used in the conservation of plastics to better understand polymer
24 degradation and thus the physical damage observed in plastic artifacts and artworks. For this purpose, the
25 use of SPME sampling followed by GC/MS analysis is a non-destructive and fast tool to obtain information.
26 The affinity of the SPME fibers toward various volatiles depends on their chemical physical properties, and
27 different adsorbing phases are commercially available. SPME coated with a divinylbenzene/carboxen
28 polydimethylsiloxane (DVB/CAR/PDMS) stationary phase and thickness of 50/30 μm is particularly effective
29 in VOC trapping. It can be used to characterize the degradation state of aged paper by revealing over 50
30 compounds including acetic acid, a variety of aldehydes, 2-ethylhexanol, and furfural [233-235]. In fact, the
31 degradation state of aged paper could be based on the determination of volatile compounds produced
32 through the decomposition reactions that occur in paper upon ageing. The same approach can also be used
33 to demonstrate that the pool of VOCs emitted by plastics is strongly influenced by the polymer formulation
34 and by its decay, and can help in understanding how degradation takes place. Significant examples have been

1 described for cellulose acetate as the main constituent of various objects such as dolls, laminated documents,
2 toys and boxes. These produced a VOC pattern, which included, in addition to the expected acetic acid, also
3 phenols, phthalates and monoterpenes, ascribable to additives of a different nature [236-238]. Such research
4 has also proved that HS-SPME-GC/MS is a non-invasive technique not only useful in understanding
5 degradation phenomena, but also in identifying selected plastics at any point in their degradation, and in
6 distinguishing between different formulations.

7 The analysis of VOCs by GC/MS and the investigation of the damage caused by such VOCs on the cultural
8 heritage using GC/MS based approaches is a very powerful tool in preventive conservation. Preventive
9 conservation not only deals with climatic considerations but increasingly considers the effects of outdoor and
10 indoor air pollution in cultural institutions. Museums, archives and libraries play a special role because
11 particular climatic requirements are needed for the well-being of visitors and at the same time to protect
12 cultural assets against deterioration.

13 In this field, scientific research is aimed at assessing the complexity of the physical, chemical and biological
14 risks in situ, both in museums, galleries, churches, and in micro-environments such as showcases and micro-
15 climate frames [239, 240]. Recent research has focused on understanding the deterioration of art objects
16 which make VOCs a threat to our cultural heritage. Identifying the source of a particular pollutant can be
17 difficult, but it is now understood that modern heritage objects can act as an emissive source. The “vinegar
18 syndrome” is an example of the production of a volatile compound, acetic acid, as the effect of degradation
19 phenomena of a plastic material, cellulose acetate. In cellulose acetate, upon exposure to moisture, heat, or
20 acids, acetic acid is released (causing the characteristic vinegary smell), which has a catalytic effect on the
21 degradation process itself, and that of other materials which are kept in the vicinity. Thus, appropriate
22 storage conditions can be adopted in order to slow down the decay process, which include cold and
23 moderately dry storage [240, 241]. Similarly, the chemical compounds released from a wide range of plastic
24 objects are being investigated and how they might affect the stability of other heritage objects held in close
25 proximity to the emitting object [237, 242-244]. In general, the emission of carboxylic acids by materials used
26 for museum display cases has been observed [245].

27 Wood products, coatings, silicone-based sealants and polyvinyl acetate adhesives, usually employed in the
28 fabrication of frames or storage containers, emit aldehydes and organic acids that are potentially harmful to
29 the art objects [246-248]. Acetic and formic acid are the most abundant organic acids present in museum
30 environments. Organic acids are dangerous for monuments and buildings [249], and acetic and formic acid
31 in museum environments corrode lead, copper and some other metals and calcareous minerals [250-255].
32 However, very little is known about the possible long-term degradation impact of these gases on organic
33 materials used in works of art, although it is clear that they can have a strong effect on the degradation of
34 cellulose [256, 257]. Recently it has been shown that these volatile acids are also harmful to other organic
35 materials that constitute art objects. GC/MS based approaches have shown that paint varnishes based on

1 dammar resin and paint layers based on alkyd media are subject to accelerated degradation under exposure
2 to acetic acid [258, 259].

4 **Conclusions**

5 An overview of the literature highlights that the analytical approach for use in GC/MS analysis of organic
6 materials in cultural heritage samples is strongly dependent on the specific problematic posed by art
7 historians and conservators. The complex mixtures of molecular species present in organic materials, the
8 questions to be answered, and consequently the analytes to be searched for, determine the choice of
9 analytical approach, especially concerning sample pretreatment .

10 Research on organic materials in the cultural heritage is still an open issue, and more research into analytical
11 methodologies and data interpretation models is still necessary, based on a better understanding on the
12 degradation processes undergone by the materials. Such research needs the support of a more systematic
13 investigation into ancient technological and historical sources, in order to understand which materials were
14 originally used and how they were pre-processed. In order to shed light on the various molecular and physical
15 changes taking place in materials upon ageing, a combination of analytical techniques are being exploited
16 including spectroscopic, thermoanalytical and spectrometric techniques. Of these, GC/MS still plays a
17 fundamental role due to its unsurpassed ability to identify biomarkers and degradation products at a
18 molecular level, thereby obtaining quantitative data .

19 HPLC and HPLC/MS are increasingly being used to study of organic materials and to supplement GC/MS data
20 obtained from volatile components with information on higher molecular weight components. In addition,
21 spectroscopic techniques (such as FTIR, SEM-EDX, XRF, XRD, also using synchrotron source), spectrometric
22 (such as SIMS) and immunology-based techniques can be used to locate both organic and inorganic materials
23 in the sample cross-section.

24 The number of applications of GC/MS in conservation science and archaeometry has increased every year
25 over the two last decades, and is likely to continue to grow in the next few years thanks to improved
26 instrumentation, the reliability of the results (given the advances in the knowledge of the community in the
27 field), and GC/MS's versatility as the same instrumentation is able to give a molecular identification of several
28 classes of organic materials.

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